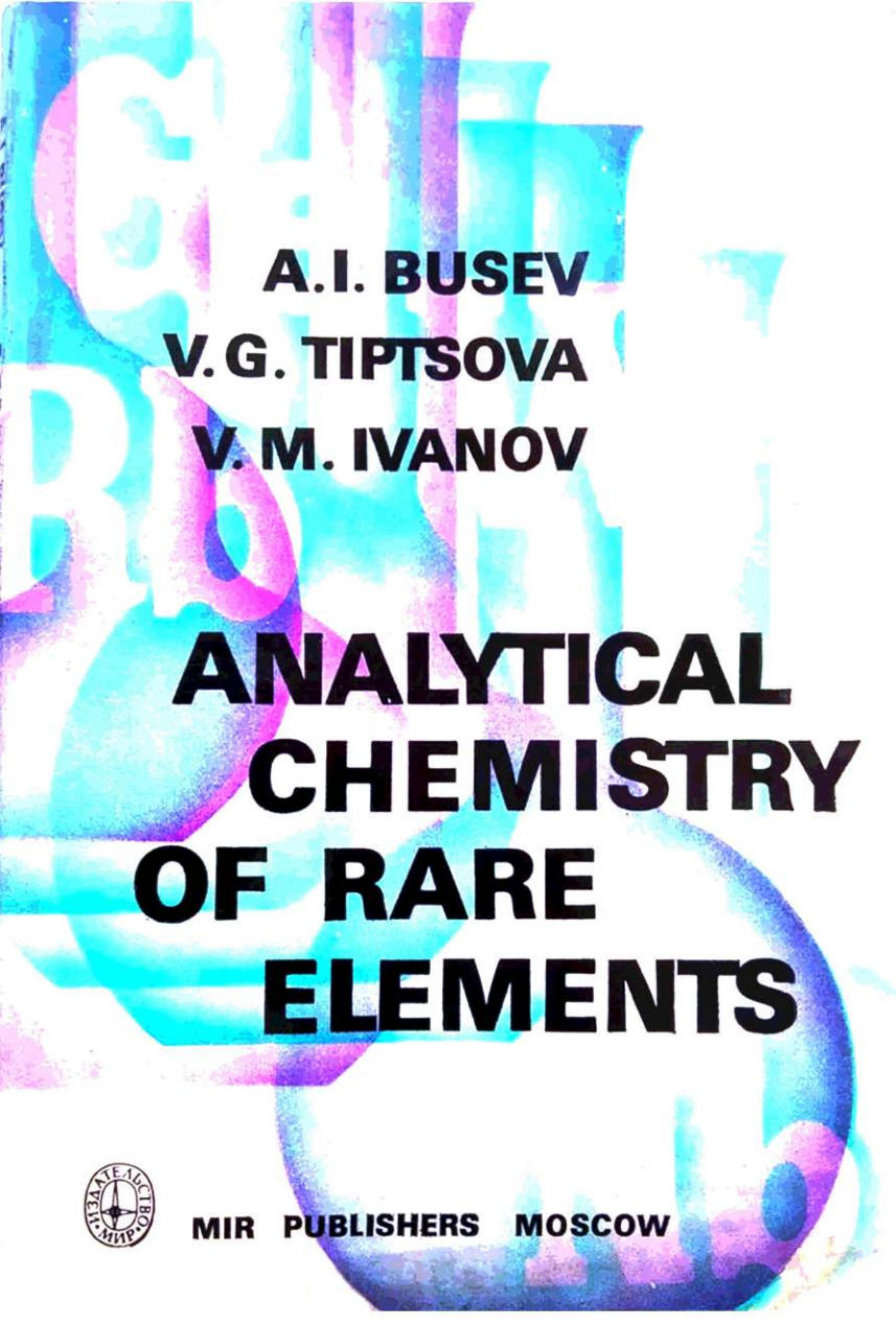

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MIR PUBLISHERS MOSCOW

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Special attention is given to the analysis of natural and technical materials containing rare elements in a wide range of concentrations.

Selective methods for isolation from composite mixtures are given for most elements.

The book is intended for research and plant laboratories in chemical, metallurgical and related industries. It will also be useful to teachers, postgraduates and students of universities and chemical institutes.

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Analytical Chemistry of Rare Elements

Translated from the Russian by Alexander Rosinkin

MIR PUBLISHERS MOSCOW

First published 1981
Revised from the 1978 Russian edition

На английском языке

TO THE READER

Mir Publishers would be grateful for your comments on the content, translation and design of this book. We would also be pleased to receive any other suggestions you may wish to make

Our address is:
Mir Publishers
2 Pervy Rizhsky Pereulok
I-110, GSP, Moscow, 129820
USSR.

Printed in the Union of Soviet Socialist Republics

IMPORTANT!

The compounds of almost all rare elements are poisons. Arsenic, mercury, and beryllium compounds, all heavy metals, organic solvents, and potassium cyanide are especially dangerous and should therefore be handled with special care.

The students must strictly follow the general safety regulations for the analytical laboratory.

Spent solutions of the rare elements and other expensive wastes should be collected and the valuable elements recovered from them. The recovery of the rare elements from wastes before their disposal is even more important from the viewpoint of the environmental protection.

PREFACE

This book is intended for chemical students engaged in the detailed study of the chemistry of the rare elements. It has been written in compliance with the curriculum of the chemical faculty of the Moscow University.

The study of this course can only be useful if the student is acquainted with the theory of photometric, polarographic, potentiometric and other analytical methods.

The Procedures in this book are always preceded by brief descriptions of the elements for which they are intended.

There are a great many methods for the analysis of the rare elements but only the simplest of them, characterized by high selectivity, rapidity and reliability, and requiring non-expensive reagents are described in this manual. The suggested methods have proved effective in industrial and research laboratories. Unfortunately, such methods have not been devised for some rare elements or for their analysis in some objects.

Except in special cases, the handbook does not describe how to prepare solutions of the reagents used in the analysis (mainly because of simplicity), but if any difficulty arises, the student can consult the book by P. P. Korostelev *Preparing Solutions for Chemical Analysis*, Nauka, Moscow, 1964, in Russian. The necessary information on the organic reagents widely used in the analytical chemistry of the rare elements can be found in the book by A. I. Lazarev *Organic Reagents in the Analysis of Metals*, Metallurgia, Moscow, 1980, 232 pages.

Each chapter is supplemented with bibliography to help the student in his independent reading. Moreover, the first chapter contains a special list of selected readings which will be of special use for the student.

The handbook does not describe the methods to analyze noble gases and the metals of the platinum group. Nor does it describe the spectral, radioactivation, flame photometric and some other methods, because there are special manuals on these subjects. Moreover, the spectral methods for the determination of the rare and common elements do not significantly differ from each other.

Many constants used in this book are cited from the comprehensive *Handbook of Analytical Chemistry* edited by Louis Meites, McGraw-Hill Book Company, 1963.

The optical methods of analysis are described in the book *Trace Analysis. Spectroscopic Methods for Elements*, edited by Winefordner, Wiley Interscience Publication, 1978.

The theoretical part of this handbook and the analytical characteristics of the rare elements are written by A. I. Busev. The methods for the determination of vanadium, niobium, tantalum, tungsten, rhenium, gallium, indium, thallium, germanium, selenium and tellurium are described by V. G. Tiptsova, and the methods for lithium, rubidium, cesium, beryllium, scandium, yttrium, lanthanum, cerium and the lanthanides, thorium, uranium, titanium, zirconium, molybdenum and bismuth are described by V. M. Ivanov.

The authors are glad to take the opportunity to express their deep gratitude to M. A. Semenova and A. N. Buseva, and also to A. A. Rosinkin, the translator of the book, for their useful cooperation and invaluable aid in preparing the manuscript for the press. The authors will also gladly accept all suggestions from their readers.

CONTENTS

Rare Elements in Modern Industry and Geochemistry

The term 'rare elements' covers a group of about 70 elements of the periodic system. Some of them are indeed rare while others occur widely in nature. By 'rare' we understand those elements which have come into common use only recently (or relatively recently) and in a certain sense are new (or relatively new) elements in industry.

In this book the following elements will be considered as rare:

metals

(1) light elements, Li, Rb, Cs and Be;
(2) lanthanides, La, Ce, Pr, Nd, Pm, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu, Sc and Y;
(3) scattered elements, Ga, In, Tl, Ge, Hf, and Re;
(4) refractory elements, Ti, Zr, Hf, V, Nb, Ta, Mo, W and Re;
(5) radioactive elements, Ra, Po, Ac, Th, Pa, U, Np, Pu, Am, Cm, and other transuranic elements;
(6) minor elements, Bi;
(7) noble elements, Pt, Ru, Os, Rh, Ir, Pd, Au and Ag;

nonmetals

(1) B, Se, Te;
(2) inert (noble) gases, He, Ne, Ar, Kr, Xe.

The composition of the lithosphere is given in Table 1. It shows that some rare elements are quite abundant in the earth's crust. For example, titanium, which is normally ascribed to the group of rare elements, stands tenth in the list of the most abundant elements of the earth's crust, and lithium is nineteenth. At the same time, the amount of some well and long known elements (mercury, arsenic, cadmium, lead, tin) in the earth's crust is small.

In geochemistry, many chemical elements are called rare because they occur in nature in small quantities. Some scattered elements (rhenium, radium, polonium and others) which do not form minerals but occur only as impurities in minerals and ores of other elements are placed in the group of 'geochemically rare' elements.

The occurrence of chemical elements in extraterrestrial objects of our galaxy and on the Earth generally depends on the stability of atomic nuclei in the depths of stars. This stability decreases sharply with increasing periodic number up to 28, and then decreases gradually. The comparatively infrequent occurrence of light elements is due to the large diameter of their nuclei, protons, neutrons, and other particles, while the low levels of the heavy metals (thori-

Table 1

Mean Chemical Composition of the Outer 10 Miles of the Lithosphere (without the ocean)*

After A. P. Vinogradov

Element	Lithosphere composition		Element	Lithosphere composition	
	atomic %	mass %		atomic %	mass %
Oxygen	58.0	47.2	Praseodymium	9×10^{-5}	7×10^{-4}
Silicon	20.0	27.6	Samarium	9×10^{-6}	7×10^{-4}
Aluminium	6.6	8.80	Thorium	7×10^{-5}	8×10^{-4}
Hydrogen	3.0	0.15	Molybdenum	7×10^{-6}	3×10^{-4}
Sodium	2.4	2.64	Dysprosium	5×10^{-5}	4.5×10^{-4}
Iron	2.0	5.10	Erbium	5×10^{-6}	4×10^{-4}
Calcium	2.0	3.6	Hafnium	5×10^{-5}	3.2×10^{-4}
Magnesium	2.0	2.10	Bromine	4×10^{-5}	1.6×10^{-4}
Potassium	1.4	2.6	Ytterbium	3×10^{-6}	3×10^{-4}
Titanium	2.5×10^{-1}	6×10^{-1}	Thallium	3×10^{-5}	3×10^{-4}
Carbon	1.5×10^{-1}	1×10^{-1}	Uranium	2×10^{-6}	3×10^{-4}
Barium	5.7×10^{-2}	5×10^{-2}	Tantalum	1.8×10^{-5}	2×10^{-4}
Phosphorus	5×10^{-2}	8×10^{-2}	Europium	1.8×10^{-5}	1.2×10^{-4}
Manganese	3.2×10^{-2}	9×10^{-2}	Selenium	1.5×10^{-5}	6×10^{-5}
Sulphur	3.0×10^{-2}	5×10^{-2}	Holmium	1.5×10^{-5}	1.3×10^{-4}
Fluorine	1.8×10^{-2}	2.7×10^{-2}	Tungsten	1×10^{-5}	1×10^{-4}
Chlorine	2.6×10^{-2}	4.5×10^{-2}	Lutetium	1×10^{-5}	1×10^{-4}
Nitrogen	2.5×10^{-2}	1×10^{-2}	Terbium	1×10^{-5}	1.5×10^{-4}
Lithium	1.9×10^{-2}	6.5×10^{-3}	Thulium	8×10^{-6}	8×10^{-5}
Strontium	1×10^{-2}	4×10^{-2}	Cadmium	7.6×10^{-6}	5×10^{-5}
Chromium	8×10^{-3}	2×10^{-2}	Antimony	5×10^{-6}	4×10^{-5}
Rubidium	7×10^{-3}	3.1×10^{-2}	Iodine	4×10^{-6}	3×10^{-5}
Vanadium	6×10^{-3}	1.5×10^{-2}	Bismuth	1.7×10^{-6}	2×10^{-5}
Zirconium	4×10^{-3}	2×10^{-2}	Silver	1.6×10^{-6}	1×10^{-5}
Copper	3.6×10^{-3}	1×10^{-2}	Indium	1.5×10^{-6}	1×10^{-5}
Nickel	3.2×10^{-3}	8×10^{-3}	Mercury	7×10^{-7}	7×10^{-6}
Zinc	1.5×10^{-3}	5×10^{-3}	Osmium	5×10^{-7}	5×10^{-6}
Cobalt	1.5×10^{-3}	3×10^{-3}	Palladium	1.6×10^{-7}	1×10^{-6}
Beryllium	1.2×10^{-3}	6×10^{-4}	Tellurium	1.3×10^{-7}	1×10^{-6}
Tin	7×10^{-4}	4×10^{-3}	Ruthenium	1×10^{-7}	5×10^{-7}
Yttrium	6×10^{-4}	2.8×10^{-3}	Platinum	5×10^{-8}	5×10^{-7}
Boron	6×10^{-4}	3×10^{-4}	Gold	5×10^{-8}	5×10^{-7}
Cerium	6×10^{-4}	4.5×10^{-3}	Rhodium	1.7×10^{-8}	1×10^{-7}
Gallium	4×10^{-4}	1.5×10^{-3}	Iridium	8.5×10^{-9}	1×10^{-7}
Neodymium	3.5×10^{-4}	2.5×10^{-3}	Rhenium	8.5×10^{-9}	1×10^{-7}
Scandium	3×10^{-4}	6×10^{-4}	Radium	9×10^{-12}	1×10^{-10}
Lanthanum	2.5×10^{-4}	1.8×10^{-3}	Protactinium	8×10^{-12}	1×10^{-10}
Germanium	2×10^{-4}	7×10^{-4}	Actinium	5×10^{-15}	6×10^{-10}
Niobium	2×10^{-4}	1×10^{-3}	Polonium	2×10^{-15}	2×10^{-14}
Lead	1.6×10^{-4}	1.6×10^{-3}	Plutonium	7×10^{-17}	1×10^{-15}
Arsenic	1.5×10^{-4}	5×10^{-4}	Radon	5×10^{-17}	7×10^{-16}
Gadolinium	1×10^{-4}	1×10^{-3}			
Cesium	9.5×10^{-5}	7×10^{-4}			

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* The figures for helium, argon, neon, krypton, xenon are not trustworthy.

um, uranium, transuranic elements) is due to alpha-decay and spontaneous fission of their nuclei.

The advances in the technology of rare elements and their increased output gradually decrease the number of elements which would normally be considered rare. Many researchers no longer regard titanium as a rare metal since it is now produced in great quantities. Moreover, titanium is one of the most abundant elements in the earth's crust. This example suggests that many elements which are now called rare will not be considered such in future.

The production of some rare metals and their compounds (zirconium, titanium, niobium, germanium, indium, gallium, lithium, cerium, and others, hydrides, borides, iodides, carbides, and many alloys) has increased greatly in the past two decades. Modern industry produces rare metals and their compounds of very high purity (ultrahigh purity) for the nuclear, semiconductor, and metallurgical industries (uranium, thorium, zirconium, etc.).

Many rare elements have valuable and unique properties.

THE ROLE OF THE ANALYTICAL CHEMISTRY OF RARE ELEMENTS

The properties and composition of substances containing rare elements (ores, minerals, alloys, etc.) are quite varied. Analytical methods are widely used to check the composition of raw materials, to control various processes, to check the finished products, and to reveal new sources of rare elements. The analytical chemistry of rare elements plays an important role in geochemistry. For example, the differentiation in rock of rare elements having similar properties such as niobium and tantalum, zirconium and hafnium, tungsten and molybdenum, sulphur and selenium, rubidium and thallium, aluminium and gallium, nickel and cobalt, radium and cadmium, etc., is essential before accurate geochemical conclusions can be hoped for.

Traces of some rare elements (molybdenum, vanadium, etc.) are important in biochemical processes.

The nuclear, semiconductor and metallurgical industries require high purity nuclear fuel, construction materials, and semiconductor substances. For example, pure zirconium is one of the best construction materials for nuclear reactors but even very small admixtures of hafnium make it unfit for the purpose. The semiconductor properties, for example, of germanium and silicon, show only in the purest samples. Germanium can contain no more than one atom of another element per ten billion germanium atoms. Even greater purity is required for silicon.

High purity materials are required in the electronics industry in the manufacture of oscilloscopes, computers, radar apparatus, etc). Titanium of very high purity is required for the manufacture of cathode-ray tubes and other evacuated apparatus. Thermo- and photoelectric cathodes and cathode-luminophores are produced from titanium, nickel, iron, tungsten, molybdenum, tantalum and niobium of very high purity.

These few examples clearly illustrate the great importance of analytical methods able to show up the smallest impurities. It is impossible to obtain high purity materials unless production processes are provided with analytical controls at each important stage

QUANTITATIVE METHODS IN THE ANALYTICAL CHEMISTRY OF RARE ELEMENTS

The reagents used in the analysis of rare elements are classified as group, selective, and specific reagents.

Group reagents give a similar reaction for many ions and are therefore used to isolate groups of elements from a composite mixture. Metal ions (cations) are often classified according to the action of group reagents.

Selective reagents give similar reactions for only a few ions. For example, hydrogen peroxide (in a sulphuric acid solution) forms coloured soluble compounds only with the ion of titanium (IV) and with vanadate and molybdate.

Specific reagents react only with one ion. There are no specific reagents for the ions of rare elements. But if special conditions are provided, group reagents can be made more selective. To that end, the interfering ions are bound in stable complexes. For example, the ferric ion interferes with the detection by hydrogen peroxide of tetravalent titanium (an orange compound is formed) because it colours the solution yellow. If moderate quantities of phosphoric acid are added to the solution, the ferric ion can be turned into colourless complexes which will no longer interfere. There are also other methods to make reagents more selective.

Rare elements contained in a system as simple substances or their compounds are determined by different methods, for example, by measuring the mass, volume, density, absorption and transmission of light (infra-red, visible, ultra-violet, X-rays), light scattering, etc. The most important quantitative methods are classified in Table 2.

Methods based on the linear dependence of the element concentration on the measured physical value are of great practical importance. These include the gravimetric, titrimetric, spectral, some spectrophotometric methods, and others. In many of these methods, the dependence is linear only for a limited range of concentration. Take, for example, spectral methods of determinations where the linear dependence of the element concentration on the intensity of the analytical spectral lines is limited. For many photometric methods, the dependence between the concentration of the sought substance and the absorption of the solution is directly proportional (the Bouguer Lambert-Beer law). The quantity of radioactive iso-

Table 2

Classification of the Main Quantitative Methods

Measured variable	Method	Measurable mass*
Mass	Gravimetric (electro-gravimetric included)	Macro- and micro-quantities
	Mass-spectral	Micro- and ultra-micro-quantities
Volume	Titrimetric	Macro- and micro-quantities
	Gas-volumetric	Ditto
	Determination by precipitate volume	Macro-, micro-, and ultra-micro-quantities
Density	Densimetric	Macro-quantities
Absorption of I-R radiation	I-R spectroscopy	Ditto
	Spectral	Semi-micro- and micro-quantities
Absorption and emission of visible, U-V, and X-rays. Light diffusion	Nuclear absorption spectroscopy. Flame photometry.	
	X-ray spectral methods	Macro- and semi-micro-quantities
	Photometric (colorimetric, spectrophotometric, turbidimetric, nephelometric)	Semi-micro- and micro-quantities
	Luminescence and fluorescence methods	Micro-quantities
Refractive index	Refractometric	Macro-quantities
Polarization plane rotation	Polarimetric	Ditto
	Spectropolarimetric	Ditto
Diffusion current in reduction or oxidation on electrodes	Polarographic	Semi-micro, and micro-quantities
Amount of electricity used in electrode reaction	Coulometric	Micro- and ultra-micro-quantities
Electrode potential	Potentiometric	Macro- and micro-quantities
Electrical conductivity	Conductometric	Ditto
Electric strength	Ditto	Macro-quantities
Radioactivity	Radioactivation	Micro- and ultra-micro-quantities

---

* The following quantitative ranges are accepted:

Method	Macro-method	Micro-method	Ultra-micro-method
Mass, g	10^{-2}	10^{-4}	10^{-6}

topes formed by irradiation with a current of neutrons in radioactivation methods is proportional to the number of pulses per second.

The quantities which are dealt with in semi-microchemical analysis are ten times smaller than in macroanalysis, and ten times larger than in microanalysis. But there exists no commonly accepted classification of analytical methods by size of sample or content of the desired element.

The most important methods in the analysis of rare elements are the gravimetric, mass-spectral, titrimetric, spectral, X-ray spectral, photometric, polarographic and radioactivation methods. But others are also used wherever necessary.

Gravimetric methods are based on measuring mass. They make use of the law of mass conservation in chemical reactions. Using appropriate reactions, the desired chemical element is reduced, or converted into a compound of known composition with the desired properties. It contains the sought element in the same proportion as it is contained in the original sample. Since the composition of the compound is known, it is easy to calculate the content of the element in the sample. All gravimetric determinations must meet some special requirements: the composition of the weighing form should correspond to the chemical formula, the weighing form should be stable to washing, drying, weighing, etc. Gravimetric methods are used for the analysis of rare elements when high accuracy is required, but they take a lot of time. They are commonly used to determine beryllium in ores, zirconium in its concentrates and alloys, thorium in tungsten and other objects, niobium and tantalum in some materials, molybdenum in alloys and concentrates, tungsten in ferrotungsten, rhenium in tungsten alloys, etc.

Titrimetric methods usually employ oxidation-reduction reactions, precipitation reactions and the formation of complex compounds. Complexometric methods are of particularly great importance.

More trustworthy results are obtained with methods based on stoichiometric reactions which proceed practically to the end at sufficiently high velocities.

Indicators are used to establish the point of equivalence. If suitable chemical indicators are not available, the point of equivalence is located by various instruments. The concentration of the sought element sharply decreases and the concentration of the reagent sharply increases as the point of equivalence is approached. At the same time, the electrode potential, the conductivity of the solution, and the diffusion current or absorption sharply change as well. These changes can be measured instrumentally and used to detect the point of equivalence during titration. Sometimes the changes in radioactivity, freezing point, density, refractive index, surface tension, or viscosity are also used. The most important instrumental methods for determining the point of equivalence are potentiometric and amperometric. The amperometric method is used to locate the point of equivalence in precipitation reactions, in complexation, and in oxidation-reduction reactions. The method is used for the determination of small quantities of substances in dilute solutions (0.01-0.0001 mole/litre).

The conductometric and high-frequency titration methods are not important in the analytical chemistry of rare elements.

Titrimetric methods are highly selective compared with many gravimetric methods, and they take less time, but the results are less accurate. Sometimes, to increase the accuracy of determination, the volumes of solutions are not measured, but the solutions are weighed instead.

We shall list here the most commonly used titrimetric methods: the ferriperiodate method for the determination of lithium in silicate ores; the arsenate method for the determination of beryllium in minerals, concentrates, and alloys; the determination of titanium in ferrotitanium and titanium-nickel alloys; the determination of germanium in industrial concentrates; the determination of vanadium in alloys; the determination of molybdenum in alloys and concentrates; the determination of selenium and tellurium in ore and metallurgical products; the potentiometric determination of rhenium in alloys, etc. The complexometric determination of gallium, indium, thallium, scandium, thorium, zirconium and some other elements is also widely used.

Sometimes, the quantity of the substance sought is determined by the volume of the precipitate. This method is very important in ultra-micro-analysis, for example, of transuranic elements, when the precipitate is scarce and is difficult to isolate and weigh. The volume of the precipitate is measured through a microscope. If the volume and the density of the precipitate are known, its mass can be calculated.

The most popular electrochemical method is polarography with a mercury-dropping electrode or with a platinum wire micro-electrode. The method is used in theoretical research as well as for practical and rapid analysis. The polarographic method is used to determine indium in polymetallic ores and in the products of its conversion, titanium and germanium in various materials, and niobium in tantalum and in tantalum-containing materials. The method is also used to determine molybdenum, selenium and tellurium. Oscillographic polarography is used to determine, for example, niobium in its alloys with tantalum and ytterbium in the presence of erbium.

The coulometric method is very sensitive and accurate. It is successfully used to determine uranium and some other elements.

Photometric methods are based on the measurement of light absorption in solutions in the visible or UV region of the spectrum (colorimetry, spectrophotometry) or in suspensions (turbidimetry) or of light scattering in suspensions (nephelometry). Measuring the absorption of a solution on a spectrophotometer is usually the concluding stage of the determination. Before the determination begins, the sought component is usually separated from the accompanying elements by precipitation, distillation, extraction, or electrolysis. The analyst usually chooses the most selective method suitable for a particular case, the one involving the least number of stages so that the risk of contamination (introduced with the reagents) is minimized. This is especially important in the determination of very small quantities of elements.

Spectrophotometric methods are used to determine traces of elements in various industrial materials, e.g. in semiconductors, metals and their alloys. Photometric methods are used to determine small quantities of many rare elements, such as beryllium in tungsten and its alloys; gallium, indium, thallium, rare earths, and germanium in various objects; titanium in rock, ores, alloys, tungsten and zirconium; thorium in rock, in zirconium and other materials; zirconium in different materials, vanadium in ore, minerals, alloys, steels, and zirconium; niobium in rock and minerals; tantalum in zirconium, hafnium and niobium; bismuth in molybdenum; molybdenum in titanium alloys, in steel and mineral raw materials; selenium and tellurium in ores and minerals; rhenium in molybdenum products and alloys with tantalum or tungsten. In order to determine large quantities of rare elements to a high degree of accuracy, differential spectrophotometry is used. Titanium, tantalum and rhenium are successfully determined by this method.

X-ray spectroscopy is highly selective but of comparatively low sensitivity (quantities over 0.1 per cent only are detectable). The method is used to determine elements having similar chemical properties, such as niobium and tantalum, zirconium and hafnium, or rare earth elements.

Ordinary spectral analysis is based on the capacity of atoms to emit certain wavelengths in conditions of constant excitation. The arrangement of lines in the spectrum indicates the presence of a sought element in the given material, while the intensity of the lines is indicative of its concentration.

The spectral method is used for determining lithium, beryllium, scandium and rare earth elements, gallium, indium, thallium, germanium, zirconium, hafnium, niobium and tantalum in rock, concentration products, and alloys.

Flame photometry is used to determine lithium, rubidium, cesium, strontium in rock and minerals, lanthanum, europium, ytterbium and yttrium in rare earth oxides; indium, gallium and thallium in concentrates and intermediates.

In the nuclear-absorption method (absorption flame photometry) the solution is sprayed in a flame and the absorption of the radiation from a standard source by the atoms of the sought element is measured. The method can be used to determine elements which are present in the flame as free atoms. The sensitivity of this method is higher than that of ordinary flame photometry. Moreover, the nuclear-absorption method can be used to determine elements which cannot be determined by ordinary flame photometry (e.g. selenium, tellurium, bismuth). The method has been widely used since 1955.

Methods based on measuring the radioactivity of elements with natural radioactivity (radium, radon, uranium, thorium, potassium, rubidium, samarium etc.) can be used for the determination of these elements or the products of their radioactive decay in a state of equilibrium with the original elements (after their separation). The method is effectively used for the determination of thorium in ores, minerals, rock and soils. Artificial radioactive isotopes of various elements (labelled atoms) are used to control the separation of substances by precipitation, extraction, adsorption, electrolysis, and other methods, as well as for the determination of the solubility of salts, the completeness of precipitation, for the study of adsorption, co-precipitation and extraction, and for the determination of the stability of complex compounds. Dilution with radioactive isotopes is also used. This method can determine 0.001-0.3 per cent of lithium in rock, 0.002-0.02 per cent of rubidium in granite, diabase and sea water.

Impurities in various materials can be detected by the formation of radioactive isotopes during their bombardment mainly with neutrons (radioactivation method). This method is not susceptible to contamination by extraneous elements. The method can be used to determine, to an accuracy of less than 10 per cent, the elements for which artificial radioisotopes can be prepared.

The radioactivation method is used to determine impurities in chemical compounds, metals, and alloys, to control the purity of materials used in nuclear reactors, to determine lithium and rubidium in rock, beryllium in mineral raw materials and the products of hydrometallurgy and to determine rare earth elements. The sensitivity of radioactivation analysis increases with the intensity of the activating current of neutrons. When the intensity of irradiation is 5×10^{11} neutrons per square centimeter per second, 1×10^{-4} μg of manganese, rhenium, irridium, samarium, europium, holmium, and lutetium can be determined.

As a rule, the sensitivity of activation analysis is better than that of spectrophotometric, spectrographic, amperometric or chemical methods based on the use of coloured reactions. Compare the sensitivity of determination of indium by various methods:

Method	Limit of detection of indium, μg/ml
Radioactivation:	
neutron current 10^{13} sq.cm $\times$ s^{-1}	5×10^{-6}
neutron current 10^{11} sq.cm $\times$ s^{-1}	1×10^{-4}
Spectral analysis (excitation in a spark with a copper electrode)	1
Flame photometry	1
Most sensitive chemical reactions (with 8-quinolinol)	0.2
Amperometric titration	100

Many reagents are not sufficiently selective, and therefore methods of separation based on different properties of compounds of rare elements are of great importance in the analytical chemistry of these elements. Individual elements of groups are separated by these methods, in which the elements are transferred into another phase by precipitation, distillation, or extraction. The isolation of an element (or a group of similar elements) by precipitation as sparingly soluble compounds is one of the most popular techniques. Precipitation of many accompanying ions can be precluded by converting them into stable complex ions.

Sometimes, when an element is separated by precipitation, it can trap other substances in the precipitate and hold them firmly. This is known as conjugated precipitation or co-precipitation. It interferes with the quantitative separation of elements. The dissolution of the washed precipitate with subsequent precipitation does not always give pure precipitate. But this method is still used to isolate traces of elements. An effective method for the separation of traces of some elements by co-precipitation with organic substances has been developed.

Electrolysis can also be used for the selective isolation from solution of a desired element in the free form or as an oxide. Small quantities of some metals are separated by internal electrolysis.

When elements are separated by solvent extraction, an aqueous solution of the sought element is shaken with a suitable solvent immiscible with water. If one of the substances is well soluble in the organic solvent, it passes into the organic phase, but part of it still remains in the aqueous solution. Repeated extraction ensures more complete separation. This method is used to separate ferric ions from the ions of aluminium, bismuth, calcium, cadmium, chromium, cobalt, lead, manganese, nickel, osmium, palladium, titanium, uranium (extraction with ether from hydrochloric acid solution). Extraction is a rapid method of separation and an effective method of concentrating small quantities of the desired elements.

Distillation is often used as a separation technique. For example, fluorine is distilled as hydrogen fluoride or fluocilicic acid, and germanium as its tetrachloride.

One of the most effective separation methods is chromatography: adsorption, distribution, ion-exchange, and precipitation chromatographies.

Solution adsorption chromatography is based on different adsorbing abilities of substances. Solvents should be adsorbed much more slowly than the other components of the mixture. The separating power of the adsorbent will then be utilized most effectively.

Distribution chromatography is based on the different distribution coefficients of the substances which are to be distributed between two immiscible phases one of which (the stationary phase) is the sorbent with pores, while the other phase (mobile) is the moving solution. The sorbent, retaining the liquid phase, is a hydrophilic substance of the silica gel type (with large pores to decrease the adsorption effect) or starch. Water, methyl alcohol, or nitromethane are used as the stationary phase. Distribution chromatography is used, for example, to separate niobium and tantalum from titanium.

Paper chromatography, a variant of distribution chromatography, in which paper pulp or sheets of paper are used, has become very popular. The efficiency of separation depends on the difference in the rate of movement of the components of the mixture and that of the solvent. Paper chromatography is used, for example, for the separation of rare earths.

Ion-exchange chromatography is based on the different ability of ions to exchange for mobile sorbent ions. Synthetic organic ion-exchange materials (cation- and anion-exchangers) are usually used, while alumina, silica gel and others are not so popular. Ion-exchange chromatography can be used to separate zirconium from hafnium and other elements, rhenium from molybdenum, titanium from molybdenum, thorium from rare earths, etc. Separation on strongly basic anion-exchange materials has been developed. For example, indium can be successfully separated from aluminium, iron and arsenic by passing a hydrochloric acid solution through a column packed with a strongly basic anion-exchanger.

* * *

Further advances in the analytical chemistry of rare elements depend to a great extent on the successful development of the theoretical principles of analytical methods. Chemical reactions of rare elements should be studied systematically by modern methods of analytical chemistry.

It is necessary to mention the importance of the development of phase inorganic analysis, one of the least developed branches of analytical chemistry. It is very important in mineralogy, the metallurgical industry, the science of metals, the silicate industry, and in other fields where quantitative information on certain forms of compounds in natural and industrial materials is required.

IMPORTANT LITERATURE ON THE ANALYTICAL CHEMISTRY OF RARE ELEMENTS

The analytical chemistry of rare elements is developing rapidly. Each issue of any magazine or journal on analytical chemistry contains material devoted to the analytical chemistry of rare elements. Numerous collections of papers, transactions, etc., containing valuable material on the analytical chemistry of rare elements are being published.

The most important journals dealing with analytical chemistry are as follows: "Zhurnal analiticheskoi khimii" and "Zavodskaya laboratorya" (USSR), "Analytical Chemistry", "The Analyst", "Zeitschrift für analytische Chemie", "Analytica Chimica Acta", "Talanta", "Analytical Letters", etc.

Valuable information on rare elements is contained in the fundamental handbook on inorganic chemistry by Gmelin (Gmelins Handbuch der anorganischen Chemie, 8 Aufl., published from 1924), in monographs on the analytical chemistry of rare elements published by the Academy of Sciences of the USSR since 1953, and a multivolume reference book by W. Fresenius and G. Jander (*Handbuch der analytischen Chemie*, Teil II, *Qualitative Nachweisverfahren*; Teil III. *Quantitative Bestimmungs- und Trennungsmethoden*, Springer-Verlag) and also a manual *Treatise on Analytical Chemistry*. Part II. *Analytical Chemistry of the Elements*, ed. by I. M. Kolthoff, P. J. Elving, with the assistance of E. B. Sandal, New York.

The bibliography of books in the Russian language 1941-1952 contains 8495 references concerning all aspects of the theory and practice of analytical chemistry, the chemistry of rare elements included. The bibliography has been systematized by A. I. Busev in his reference book "Analytical Chemistry in the Russian Language, 1941—1952", published in 1956 by the Academy of Sciences of the USSR. For quick reference the book is supplied with a subject index.

The journals "Analytical Chemistry" and "Zavodskaya Laboratorya" (in Russian) and special monographs contain yearly reviews of the literature and systematized references.

There are bibliographic indices on polarography, microchemical methods of analysis, luminescence analysis, etc., which also contain information on the analytical chemistry of rare elements.

Given below is a brief list of the most important reference books, manuals and other publications on the analytical chemistry of rare elements.

Morachevskii, Yu. V., Tserkovnitskaya, I. A. *Fundamentals of Analytical Chemistry of Rare Elements*", Leningrad, University press, 1964, 183 pages.

This is a textbook for university students. It is a review of the most important chemical properties and chemical reactions of rare elements which underly chemical methods. The book contains instructions on how to work out schemes for analysis. It describes natural compounds and uses of rare elements.

Songina, O. A., *Rare metals*, 3rd ed. Moscow, Metallurgiya, 1964, 568 pages.

The book contains brief characteristics of analytical chemistry of rare elements.

Patrovskii, V. *Analytical Chemistry of Rare Elements.* Translated from the Czech, Gosgeoltekhizdat, Moscow, 1960, 176 pages.

The book describes the techniques of taking samples and preparing them for analysis, the methods of detecting rare metals, methods of their concentration and determination in mineral raw materials and some products by titrimetric, gravimetric, photometric and other methods.

"Methods of Determining and Analyzing Rare Elements" (Institute of Geochemistry and Analytical Chemistry named after V. I. Vernadskii), Academy of Sciences of the USSR Press, 1961, 668 pages.

This is a practical manual for the determination and analysis of rare elements. The book describes the methods verified in analytical research and industrial laboratories. Review articles describe the modern state of analytical chemistry of most rare elements. The experience in analytical chemistry in this country and elsewhere is summarized. The book alludes to many sources. Detailed descriptions of time-tested physical, physico-chemical and chemical methods of analysis of raw materials, intermediate products, and pure metals are given for each element.

Busev, A. I. *Analytical Chemistry of Bismuth*, Moscow, Academy of Sciences of the USSR Press, 1953, 382 pages.

Busev, A. I. *Analytical Chemistry of Indium*, Moscow, Academy of Sciences of the USSR Press, 1958, 243 pages.

Busev, A. I. *Analytical Chemistry of Molybdenum*, Moscow, Academy of Sciences of the USSR Press, 1962, 302 pages.

Riabchikov, D. I., Golbraikh, E. K. *Analytical Chemistry of Thorium*, Moscow, Academy of Sciences of the USSR Press, 1960, 296 pages.

Korenman, I. M. *Analytical Chemistry of Thallium*, Moscow, Academy of Sciences of the USSR Press, 1960, 172 pages.

Avtokratova, T. D., *Analytical Chemistry of Ruthenium*, Moscow, Academy of Sciences of the USSR Press, 1962, 264 pages.

Palei, P. N., Udaltsova, N. I., Savvin, S. B., Nemodruk, A. A. et al. *Analytical Chemistry of Uranium*, Moscow, Academy of Sciences of the USSR Press, 1962, 431 pages.

Nemodruk, A. A., Karalova, Z. K. *Analytical Chemistry of Boron*, Moscow, Nauka, 1964, 283 pages.

Elinson, S. V., Petrov, K. I. *Analytical Chemistry of Zirconium and Hafnium*, Moscow, Nauka, 1965, 240 pages.

Miliukova, M. S., Gusev, N. I., Sentiurina, I. G. Skliarenko, I. S. *Analytical Chemistry of Plutonium*, Moscow, Nauka, 1965, 454 pages.

Novoselova, A. V., Batsanova, L. R. *Analytical Chemistry of Beryllium*, Moscow, Nauka, 1966, 223 pages.

Riabchikov, D. I., Riabukhin, V. A. *Analytical Chemistry of Rare Earths and Yttrium*, Moscow, Nauka, 1966, 380 pages.

Lavrukhina, A. K., Pozdniakova, A. A. *Analytical Chemistry of Technetium, Prometium, Astatine and Francium*, Moscow, Nauka, 1966, 307 pages.

Gibalo, I. M. *Analytical Chemistry of Niobium and Tantalum*, Moscow, Nauka, 1967, 352 pages.

Palshin, E. S., Myasoedov, B. F., Davydov, A. V. *Analytical Chemistry of Protactinium*, Moscow, Nauka, 1968, 240 pages.

Dymov, A. M., Savostin, A. P. *Analytical Chemistry of Gallium*, Moscow, Nauka, 1968, 256 pages.

Nazarenko, I. I., Ermakov, A. N. *Analytical Chemistry of Selenium and Tellurium*, Moscow, Nauka, 1971, 251 pages.

Ginzburg, S. I., et al., *Analytical Chemistry of Platinum Metals*, Moscow, Nauka, 1972, 616 pages.

Busev, A. I., Ivanov, V. M. *Analytical Chemistry of Gold*, Moscow, Nauka, 1973, 264 pages.

Nazarenko, V. A. *Analytical Chemistry of Germanium*, Moscow, Nauka, 1973, 264 pages.

Borisova, L. V., Ermakov, A. N., *Analytical Chemistry of Rhenium*, Moscow, Nauka, 1974, 319 pages.

Poluektov, N. S., Meshkova, S. B., Poluektova, E. N. *Analytical Chemistry of Lithium*, Moscow, Nauka, 1975, 204 pages.

Plushchev, V. E., Stepin, B. D. *Analytical Chemistry of Rubidium and Cesium*, Moscow, Nauka, 1975, 224 pages.

Pyatnitskii, I. V., Sukhan, V. V. *Analytical Chemistry of Silver*, Moscow, Nauka, 1975, 264 pages.

Busev, A. I., Ivanov, V. M., Sokolova, T. A. *Analytical Chemistry of Tungsten*, Moscow, Nauka, 1976, 240 pages.

The above listed monographs describe gravimetric, titrimetric, photometric, spectral and other methods of detecting and determining the elements, and also methods of isolating them. The books contain many references, which are exhaustive for some elements.

Markov, V. K., et al. *Uranium and Methods of Its Determination*. 2nd ed., Moscow, Atomizdat, 1964, 503 pages.

Described are gravimetric, titrimetric, photometric, luminescence, electrochemical and radiochemical methods for the determination of uranium.

Schoeller, W. R., Powell, A. R. *The Analysis of Minerals and Ores of the Rare Elements*. Third Edition. Ch. Griffin and Co., London, 1955, 408 pages.

Described are chemical and some other methods of analysis of ores and minerals of 22 rare elements, and of the lanthanides in platinum group metals. The properties and the methods of preparing analytically important compounds of rare elements, their identification, isolation and determination are described. Schemes for ultimate analysis of ore and minerals are given. Each chapter begins with brief information on the important minerals of rare elements.

Hillebrand, W. F., Lundell, G. E. F. *Applied Inorganic Analysis with Special Reference to the Analysis of Metals, Minerals and Rocks*. Second Edition. Revised by G. E. F. Lundell, H. A. Bright, J. I. Hoffman, J. Wiley and Sons, New York, Chapman and Hall, London, 1953, 1034 pages.

The most important methods to isolate and determine rare and common elements are described. Considered are the methods of decomposition of the sample, separation of the desired elements from the accompanying ones, and the methods for their determination (gravimetric, titrimetric, photometric, etc.). The conditions for determining each element in the presence of all others are discussed. The book contains bibliography.

Charlot, G. *Lés méthodes de la Chimie analytique. Analyse quantitative minérale.* Quatrième edition, Masson et C^{ie} Editeurs, 1961.

The book describes the methods of determining almost all elements. It is supplemented with a bibliographic index.

Standard Methods of the Chemical Analysis, vol. I. *The Elements.* 6th ed. Toronto-London-New York, 1962.

Methods for the analysis of rare and other elements are described.

Analysis of Mineral Raw Materials. 3rd ed. Ed. Yu. N. Knipovich and Yu. V. Morachevskii, Moscow, Goskhimizdat, 1959, 1055 pages.

Methods of sampling rock and minerals are described. Brief characteristics of natural compounds of each element are given. Described are the methods to decompose ores of rare elements, to separate the elements, to determine separate components, and methods of ultimate analysis. Bibliography is given.

Fainberg, S. Yu., Filippova, N. A. *Analysis of Non-ferrous Metal Ore.* 3rd ed., Moscow, Metallurgizdat, 1963, 871 pages.

Described are the methods of isolation of rare elements such as bismuth, molybdenum, tungsten, selenium, tellurium, thallium, indium, gallium, germanium and rhenium in various materials, analysis of polymetallic ores, concentrates, and some other materials.

Nazarenko, V. A., Poluektov, N. S. *Semi-micro-chemical Analysis of Minerals and Ores*, Moscow, Goskhimizdat, 1950, 191 pages.

The book describes techniques of quantitative semi-micro-analysis of rare and common elements in ores and minerals. Instructions how to manage field laboratories are given.

Zheleznova, E. I., Sochevanov, V. G., Titov, V. I. *Determination of Radioactive Elements in Mineral Raw Materials.* 2nd ed., Moscow, Gosgeoltekhizdat, 1961.

Described are methods of determining uranium, thorium, radium and ionium in rock, ores, minerals, waters by chemical-analytical methods, by measuring radioactivity, and by the spectral method.

Methods of Chemical Analysis of Mineral Raw Materials. (National research institute of mineral raw materials of the Ministry of geology and preservation of sources), Gosgeoltekhizdat (issues 1-7), Nedra (issues 8, 10-12).

Issue 1, 1955 (Analytical methods for tungsten, vanadium, molybdenum, titanium, zirconium), 78 pages.

Issue 2, 1956 (Polarographic methods for molybdenum, antimony, indium and thallium), 100 pages.

Issue 3, 1957 (Analytical methods for beryllium, lithium, niobium, tantalum, and titanium), 92 pages.

Issue 4, 1958. (Analytical methods for beryllium, gallium, hafnium, germanium, indium, lithium, rare earths, selenium, tellurium, thallium, and zirconium), 60 pages.

Issue 5, 1959. (Analytical methods for beryllium, gallium, indium, molybdenum, niobium, strontium, rare earths, rhenium, tantalum and zirconium), 73 pages.

Issue 6, 1960. (Analytical methods for rare earths), 40 pages.

Issue 7, 1963. (Analytical methods for beryllium, germanium, rhenium, scandium, and tantalum), 72 pages.

Issue 8, 1965. (Methods for the determination of boron, beryllium, vanadium, bismuth, tungsten, gallium, hafnium, germanium, indium, molybdenum, niobium, tantalum, rare earths, rhenium, mercury, selenium, tellurium, antimony, thallium, titanium, cerium, and zirconium), 287 pages.

Issue 10, 1966. (Polarographic methods for the determination of bismuth, molybdenum, rhenium, mercury, selenium, and tellurium), 112 pages.

Issue 11, 1968. (Methods for the determination of beryllium, gold, molybdenum and tungsten, of niobium and tantalum, of selenium, silver, thallium, tellurium), 63 pages.

Issue 12, 1970. (Phase analysis of ores, of beryllium, tungsten, molybdenum, tin, antimony, niobium, and tantalum), 64 pages.

Publications of the State Research Institute of Rare and Minor Metals: (1) Transactions of the State Research Institute of Rare and Minor Metals, 1931-1956, vol. 2. Analytical methods. Moscow, Metallurgizdat, 1959, (2) Transactions of the State Research-Project Institute of Rare-metal Industry, 1959. vol. 3. Methods of analysis of materials used in rare-metal industry. Moscow, Metallurgizdat, 1961. (3) vol. 10. Analytical methods. Moscow, Metallurgizdat, 1963. (4) Analytical methods. Moscow, Metallurgizdat, 1964. (5) vol. 71. Methods of analytical control in industry of rare metals and semiconductor materials. Moscow, 1976.

Mukhina, Z. S., et al. *Methods of Analysis of Metals and Alloys*, Moscow, Oborongiz, 1959.

Described are the methods for analysis of steels, cast iron, refractive alloys, iron alloys, slags, aluminium alloys, magnesium and copper. Given are the methods for the determination of many alloying elements in these materials.

Samsonov, G. V., et al. *Analysis of Refractory Compounds*, Moscow, Metallurgizdat, 1962, 256 pages.

Given are detailed descriptions of methods for chemical analysis of all known refractory compounds (carbides, nitrides, borides, silicides, phosphides) of transition elements.

Yakovlev, P. Ya., Fedorov, A. A., Buyanov, N. V. *Analysis of Metallurgical Materials.* (Determination of microimpurities), Moscow, Metallurgizdat, 1961, 316 pages.

Described are the methods for determining bismuth, cerium, niobium, vanadium, and titanium.

Mukhina, Z. S., Nikitina, E. N. *Accelerated Methods for Analysis of Titanium and Its Alloys.* Moscow, Oboronizdat, 1961, 124 pages.

Described are the methods for determining molybdenum, titanium,

niobium, zirconium, beryllium, cerium, vanadium, tungsten, rhenium, bismuth in titanium and its alloys.

Lyalikov, Yu. S., et al. *Analytical Chemistry of Semiconductors*, Kishinev, Shtiintsa, 1975.

A review of methods to control purity of elements and complex semiconductors, methods of concentration and determination of impurities.

Methods of Analysis of High Purity Substances. Ed. I. P. Alimarin. Moscow, Nauka, 1965, 528 pages.

Described are the methods for the determination of traces of rare and other elements in silicon, germanium, gallium, indium, thallium, arsenic, antimony, phosphorus, aluminium, lead, bismuth, zinc, cadmium, sulphur, selenium, tellurium, iodine, boron, graphite, reagents, and other materials.

Umland, F., Janssen, A., Thierig, D., Wunsch, G. *Theorie und praktische Anwendung von Komplexbildner*. Akademische Verlagsgeselschaft. Frankfurt am Mein, 1971, 759 pages.

Zolotov, Yu. A., Kuzmin, N. M. *Extraction Concentration*, Moscow, Khimiya, 1971, 271 pages.

Group concentration of impurities (rare elements included) in analysis of various materials.

Morrison, G. H., Freiser, H. *Solvent Extraction in Analytical Chemistry*. J. Wiley and Sons, New York, Chapman and Hall, London, 1957, 269 pages.

(*Chemical Analysis. A Series of Monographs on Analytical Chemistry and Its Applications*, vol. 25).

Described are the extraction methods of separation of rare and common elements, fundamentals of the theory of extraction, apparatus and general methods.

Samuelson, O. *Ion Exchange Separations in Analytical Chemistry*. Almqvist and Wiksell, Stockholm Göteborg Uppsala, J. Wiley and Sons, New York, London, 474 pages.

Described are the examples of separation of some rare elements. A detailed bibliography is supplemented.

Schwarzenbach, G., Flaschka, H. *Die Komplexometrishe Titration*. F. Enke Verlag, Stuttgart, 1965.

Complexometric determination of rare and common elements.

Přibil, R. *Analytical Application of EDTA and Related Compounds*. Pergamon Press, Oxford, New York, Toronto, Braunchweig, 1972, 368 pages.

(*International Series of Monographs in Analytical Chemistry*, vol. 52).

Gravimetric, titrimetric, and photometric determination of rare and common elements with masking by complexones.

Dyatlova, N. M., Temkina, V. Ya., Kolpakova, I. D. *Complexones*, Moscow, Khimiya, 1970, 417 pages.

The book gives brief information of complexones and their use in analytical chemistry of some rare elements.

Babko A. K., and Pilipenko, A. T. *Photometric Analysis*, Moscow, Khimiya, 1969, 386 pages*.

Described are some photometric methods for determining rare elements.

Sandell E. B. *Colorimetric Determination of Traces of Metals*, 3rd ed., N.Y., 1959.

Described are the methods for photometric determination of some rare elements.

Chemical Analysis. A Series of Monographs on Analytical Chemistry and Its Applications. Vol. 8: *Colorimetric Determination of Nonmetals.* Ed. by D. F. Boltz; Interscience Publishers, 1958, New York-London.

Described are the important photometric methods of determination of selenium and tellurium, boron, and other elements.

Savvin, S. B., *Organic Reagents of the Arsenazo III group*, Moscow, Atomizdat, 1971, 349 pages.

Described is the use of arsenazo III and its various structural analogues for photometric determination of thorium, uranium, zirconium, hafnium, scandium, rare earths, plutonium, neptunium, protactinium, niobium, molybdenum, vanadium, palladium.

Bozhevolnov, E. A. *Luminescence Analysis of Inorganic Substances.* Moscow, Khimia, 1966, 415 pages.

Theory and apparatus of luminescence analysis. Identification and determination of rare and common elements.

Luminescence analysis. *Physics and Techniques of Spectral Analysis.* Ed. M. A. Konstantinova-Shlezinger. Moscow, Phyzmatgiz, 1961, 399 pages.

Luminescence determination of many rare elements, apparatus and instructions how to manage them.

Shcherbov, D. P. *Fluorimetry in Chemical Analysis of Mineral Raw Materials. Concise manual*, Moscow, Nedra, 1965, 260 pages.

Described are the methods of fluorimetric determination of beryllium, gallium, indium, thallium, rhenium, zirconium, selenium, in mineral raw materials, fluorescence methods for identification and determination of vanadium, tungsten, germanium, yttrium, lithium, molybdenum, niobium, scandium, tantalum, tellurium, titanium, thorium, uranium, zirconium, and rare earths.

Songina, O. A. *Amperometric (Polarimetric) Titration*, 2nd ed., Moscow, Khimiya, 1967, 287 pages.

Described are the methods of amperometric determination of rare and common elements, theory and apparatus for amperometric titration.

Kryukova, T. A., Sinyakova, S. I., Arefyeva, T. V., *Polarographic Analysis*, Moscow, Goskhimizdat, 1959, 772 pages.

A review of polarographic methods for determining many rare elements.

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* **Translated into English by Mir Publishers in 1973.**

Poluektov, N. S. *A Flame Photometry.* 2nd ed., Moscow, Khimiya, 1967, 307 pages.

Described are the apparatus and methods for determination of alkali, alkaline earth and some other elements by intensity of their emission in flame.

Slavin, W. *Atomic Absorption Spectroscopy*, 1968. Interscience Publishers, J. Wiley and Sons, New York, London, Sydney 1968, 307 pages.

Given are the methods to determine more than 60 elements by the nuclear-absorption method. Fundamentals of the nuclear-absorption spectrophotometry are described.

Rusanov, A. K. *Spectral Analysis of Ore and Minerals*, Moscow, Gosgeolizdat, 1948, 259 pages.

Described are the apparatus and methods for spectral analysis. The book gives practical instruction for the determination of over 50 elements in ore. The book is supplemented with tables of spectral lines and the atlas of arc-spectra of elements.

Bowen, H. J. M., Gibbons, D. *Radioactivation Analysis.* Oxford at the Clarendon Press, 1963, 295 pages.

Methods of radiochemical isolation of rare and common elements. Fundamentals of radioactivation analysis.

Lithium

Lithium, Li, has the positive valency of 1. The standard electrode potential in an aqueous medium at 25°C for $Li = Li^+ + e^-$ is -3.045 V (with reference to the standard hydrogen electrode). The low potential is probably due to strong hydration of the lithium ion in aqueous solution. It is impossible to isolate lithium by electrolysis of its aqueous solutions.

By its properties, lithium is similar to magnesium and the alkaline-earth elements, but it sharply differs from sodium, potassium and other alkali metals. For example, LiOH is a much weaker base (pK = 13.7) than the hydroxides of the other alkali metals.

Lithium phosphate $(Li_3PO)_4$, carbonate (Li_2CO_3), fluoride (LiF) and oxalate ($Li_2C_2O_4$) are comparatively sparingly soluble in water*. Lithium carbonate and lithium phosphate are soluble in the presence of ammonium salts.

In contrast to chlorides of the other alkaline metals, the chloride of lithium is soluble in anhydrous organic solvents (ethyl alcohol, *n*-propyl alcohol, isoamyl alcohol, acetone, pyridine, a mixture of equal volumes of ethyl and diethyl ethers). Lithium nitrate is soluble in ethyl alcohol, diethyl ether (like calcium nitrate).

Organic solvents are used to separate the lithium ion from the ions of sodium and potassium. The Li, Na and K ions can be separated quantitatively by cation-exchange chromatography [1, 2].

Lithium is precipitated as Li_3PO_4 by disodium phosphate:

$$3Li^+ + HPO_4^{2-} \rightleftharpoons Li_3PO_4 + H^+$$

White crystalline Li_3PO_4 is soluble in acids and the liberated H^+ should therefore be neutralized by adding ammonia. Lithium is detected by formation of Li_3PO_4. This reaction underlies the gravimetric and photometric methods for the determination of lithium. The weighing form of lithium is Li_2SO_4. It is obtained by evaporation of LiCl solution or LiF in H_2SO_4 [3, 4]. Ferric potassium periodate, $K_2Fe(IO_6)$, precipitates quantitatively the lithium ion as $LiKFe(IO_6)$.

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* The solubility of lithium salts, in grams, per 100 grams of water:

Temperature, °C	0	18	20	25	35	50	75	100
Li_3PO_4	0.022	—	0.030	—	—	—	—	—
Li_2CO_3	1.53	—	—	1.27	—	1.01	0.85	0.72
LiF	0.120	0.27	—	0.133	0.135	—	—	—

The formation of this compound underlies the identification of lithium and its gravimetric, titrimetric and photometric determination [5]. The titrimetric ferriperiodate method is used to determine lithium in silicate minerals and ore which contain it in quantities from hundredths fraction to a few per cent [6]. After lithium has been isolated as ferriperiodate, the determination ends iodimetrically. If the procedure is correct, the method ensures satisfactory results.

Zinc uranyl acetate precipitates greenish-yellow crystals of $LiZn(UO_2)_3(CH_3COO)_9 \cdot 6H_2O$. This compound is used to detect and determine (gravimetrically) lithium.

Quinazolinazo is used for the photometric determination of lithium in the presence of large quantities of the ions of Rb, Cs, Na, Ba, Al, Fe, Ca, Sr and Mg [7].

Thorin reacts with the Li ion in a 2 per cent NaOH solution (pH 13.5) to give an orange compound [8]. The reagent reacts with the Li ion in the molar ratio of 1 : 1 [9]. The instability constant of the complex is $(2.4 \pm 0.3) \times 10^{-3}$. The molar extinction coefficient is 1.07×10^7 at 470 nm. Solutions of thorin and its compounds with lithium [9] have close absorption maxima (at 470 nm and 458 nm respectively) [10]. The greatest difference of absorption of thorin and its compound with lithium in aqueous solution is at pH 13.5 [9]. The maximum absorption of lithium compounds with thorin in 70 per cent acetone is at 480-490 nm and the absorption of solutions increases [10]. The coloured compound is formed in this reaction in 30 minutes. Thorin is used for the detection and photometric determination of lithium [10, 11].

Dipivaloyl methane, $(CH_3)_3CCOCH_2COC(CH_3)_3$, reacts quantitatively with the Li ion in an alkaline medium to form an inner complex soluble in organic solvents but comparatively sparingly soluble in water [12]. If an ether solution of the reagent is used, lithium can be separated from the accompanying alkaline metal ions by extraction. If a sodium ion is present in large quantities, a small correction should be introduced. The potassium ion does not interfere with the determination.

Lithium 8-hydroxyquinolinate fluoresces (green) in weakly alkaline solutions of 95 per cent ethyl alcohol [13]. The limit of detection is 5 μg of Li in 25 ml. Mg, Ca and Zn ions interfere, and Na and K ions do not interfere with the determination of lithium. The selectivity of the fluorimetric determination of lithium with 5,7-dibromo-8-hydroxyquinoline is slightly higher [14].

Lithium salts give characteristic crimson colour to a flame (the spectral line is at 670.0 nm). Volatile strontium salts give the same colour. The flame-photometric [15, 16] and spectrographic methods ensure more reliable results. The chemical methods are only auxiliary. The polarographic determination of lithium is also possible [17, 18]. The review of the methods for detecting and determining lithium is given in the literature [19, 20].

CHROMATOGRAPHIC SEPARATION OF LITHIUM FROM POTASSIUM AND SODIUM

Cations of lithium, potassium and sodium are sorbed by the cation-exchanger СДВ-3 in the H^+ form; the lithium ion is eluted with 0.12 *N* hydrochloric acid in 80 per cent methyl alcohol, next washed out with 0.24 *N* hydrochloric acid in 80 per cent methyl alcohol is the sodium ion and the last is eluted the potassium ion (with 0.6 *N* aqueous solution of hydrochloric acid). If aqueous solutions of hydrochloric acid are used, the zones of the ions overlap and they are not separated quantitatively. In order to wash out all lithium ions, 660 ml of 0.12 *N* hydrochloric acid in 80 per cent methyl alcohol are sufficient. The sodium ion begins its desorption when another 120 ml of 0.12 *N* hydrochloric acid in 80 per cent methyl alcohol are added. To wash out the sodium ion, 1450 ml of 0.24 *N* hydrochloric acid in 80 per cent methanol are required. In these conditions the ions of lithium, potassium and sodium are separated quantitatively.

Methyl alcohol is poison, and its aliquot should be taken by a syringe.

Reagents

Cation exchanger СДВ-3 in the H^+ form; the granule size, from 0.10 to 0.25 mm.
Hydrochloric acid, 0.12 *N* and 0.24 *N* solutions in 80 per cent methyl alcohol, 2 *N* and 0.6 *N* aqueous solutions.

Procedure

Pack a chromatographic column, 170 mm high and 15 mm in diameter, with 10 g of cation-exchange resin СДВ-3 in the H^+ form. Wash the column with 50 ml of a 0.12 *N* hydrochloric acid in 80 per cent methyl alcohol solution seeing to it that the liquid layer over the ion-exchanger is not less than 1 cm. Adjust the rate of the solution outflow in the range of 5-6 ml/min.

Place a solution containing the ions of lithium (not more than 30 mg), sodium (not more than 100 mg) and potassium (not more than 200 mg) in a 50-ml volumetric flask and add a 0.12 *N* hydrochloric acid in 80 per cent methyl alcohol to the mark. Transfer 10 ml of the obtained solution to the chromatographic column. Wash the column with a 0.12 *N* hydrochloric acid in a 80 per cent methanol and collect the eluate in a 500-ml volumetric flask. Stir the solution in the flask and determine lithium photometrically.

Wash the column with 50 ml of a 2 *N* hydrochloric acid and then with water to neutral reaction to methyl orange. Discard the eluate containing sodium and potassium ions.

GRAVIMETRIC DETERMINATION OF LITHIUM IN SILICATE ROCK

A sample is first treated with hydrofluoric acid, then calcium oxide is added. The alkali metal ions remain in the solution while the ions of the other metals precipitate. The precipitate is separated on a filter and washed, while the filtrate is evaporated with hydrochloric acid. The residue is calcined and the chlorides of the alkali metals are weighed. Lithium chloride is separated from the chlorides of the other metals by dissolving in anhydrous acetone (100 g of acetone dissolve 3.94 g of LiCl at 25°C). The chlorides of sodium and potassium are practically insoluble in acetone. The solution of LiCl in acetone is evaporated, the residue calcined and weighed (the weighing form is Li_2SO_4).

Reagents

Hydrofluoric acid, concentrated.
Calcium oxide, calcined. Calcine $CaCO_3$ free from alkali metals immediately before the procedure in a platinum crucible over a burner.
Phenolphthalein, 1 per cent solution in ethyl alcohol.
Calcium hydroxide, 0.05 per cent solution prepared for the test.
Ammonium carbonate, saturated (at room temperature) solution.
Ammonium oxalate, saturated solution.
Hydrochloric acid, density 1.19 g/cu.cm.
Acetone, anhydrous, kept over calcium chloride and distilled at 56-57°C.
Sulphuric acid, density 1.84 g/cu.cm.

Procedure

Isolation of the Alkali Metal Chlorides. Grind thoroughly a sample of silicate rock weighing 0.5 g, wetten with water in a platinum dish, add 5-10 ml of hydrofluoric acid, mix by a platinum rod and heat on a water bath until the silicate sample is all decomposed. Evaporate the solution to dryness on a sand bath, add 30-40 ml of hot water and 5-8 drops of phenolphthalein to the dry residue. Stir the mixture and add calcium oxide in small portions until a persistent pink colour develops. (Add each new portion of calcium oxide only after the previous one has been dissolved.) Add 0.4-0.5 g of calcium oxide in excess, cover the dish with a watch glass, place on a water bath and keep for about two hours with periodically stirring the contents and keeping the volume constant by adding water.

Add filter-paper pulp, mix, and separate the precipitate on a white ribbon filter seeing to it that the filtrate is clear. Wash the precipitate on the filter with a hot solution of calcium hydroxide 7-8 times. Combine the filtrate and the washings, heat, and add 3-4 ml of ammonium carbonate solution to precipitate the calcium ion. Boil the mixture for five minutes, pass the solution through a blue ribbon filter into a platinum dish, evaporate to dryness on a sand bath and calcine the residue to remove ammonium salts. Dissolve the residue in 1-3 ml of hot water, add 0.5-1 ml of ammonium oxalate and keep for an hour on a water bath at 50-60 °C. Separate the precipitate on a blue ribbon filter, wash with hot water, combine the filtrate and the washings, and evaporate them in a platinum dish to dryness. Treat the dry residue with a few drops of hydrochloric acid, evaporate to dryness, and fuse carefully. Repeat the acid treatment with subsequent evaporation 2 or 3 times. Weigh the residue (chlorides of alkaline metals).

Notes. 1. Correctness of the determination of the alkali metal chlorides depends on the accuracy of treatment of the silicate solution with calcium oxide.
2. A blank test should be performed simultaneously.

Separation of Lithium Chloride from Chlorides of Sodium and Potassium. Grind the calcined chlorides of the alkali metals using a glass rod or a pestle, add 25 ml of anhydrous acetone, mix, allow to settle, and decant the solution through a blue ribbon filter. Collect the filtrate in a platinum dish. Repeat the acetone treatment with subsequent decantation two or three times to ensure complete separation of lithium chloride.

Combine the filtrates, remove acetone by evaporation on a warm water bath, calcine the residue carefully, add a few drops of sulphuric acid, evaporate, calcine the residue (Li_2SO_4) to fuse it, and weigh.

PHOTOMETRIC DETERMINATION OF LITHIUM IN ORES AND MINERALS BY FERRIPERIODATE METHOD

The sample is fused with alkalis, lithium is then separated from the interfering ions by calcining with oxalic acid: soluble carbonates of the alkali metals and insoluble carbonates as well as oxides of other elements accompanying lithium are formed.

The determination of lithium is completed by the ferriperiodate method. The lithium ion is precipitated in the presence of the ferric and periodate ions in the form of $LiKFe(IO_6)$. Lithium is determined in the precipitate indirectly, by determining iron by the thiocyanate method.

The ferriperiodate method is used to determine lithium in the presence of the other alkali metals, but large quantities of sodium exaggerate the results. Lithium should therefore be separated from the other alkali metals by a mixture of concentrated hydrochloric acid and ethyl alcohol: lithium precipitates as LiCl (the solubility of LiCl strongly decreases in the presence of alcohol).

The error of lithium determination by this method is ±10%.

Reagents

Lithium sulphate, standard solution. 1 ml is equivalent to 20 μg of lithium.
Potassium hydroxide, crystalline and 1 *N* solution.
Oxalic acid, ground.
Ammonium carbonate, 5% solution.
Hydrochloric acid, density 1.19 g/cu.cm 1 *N* solution, and solution diluted 1 : 1.

Ethyl alcohol, 96%.

Potassium periodate, dissolve 2.3 g of KIO_4 in 50 ml of 0.5 *N* potassium hydroxide solution, add 12 ml of 0.1 *N* ferric chloride solution in 0.2 *N* hydrochloric acid solution with stirring and dilute with 2 *N* potassium hydroxide solution to 100 ml.

Potassium thiocyanate, 20% and 2% solutions.

Washing solution, a mixture of one part of concentrated hydrochloric acid with two parts of 96% ethyl alcohol.

Constructing a Calibration Curve

Place 1, 2, 3, 4, and 5 ml of standard lithium sulphate solution into five 20-25 ml beakers and evaporate the solutions on a sand bath to 0.1-0.2 ml. Add 1 ml of 1 *N* potassium hydroxide solution to the residues, heat to boiling, and add 2 ml of hot (90°C) potassium periodate solution. Heat the solutions for another five minutes, cool, and separate the precipitates on small blue ribbon filters with suction. Wash the precipitates four times with 0.5-0.7 ml portions of potassium hydroxide solution and dissolve with 10 ml of 1 *N* hydrochloric acid. Collect the filtrates in 25-ml volumetric flasks and add water to the mark.

Using a pipette, transfer 2.0-ml portions of the obtained solutions into 10-ml graduated test tubes, add 5 ml of water and 3 ml of 20 per cent potassium thiocyanate solution into each test tube, dilute with a 2 per cent potassium thiocyanate solution to the mark, and mix.

Measure the absorption of the obtained solutions on an absorptiometer using water as a reference solution. Construct the calibration curve using the data obtained.

Procedure

Grind thoroughly a sample weighing 25-30 mg (containing 0.05-3.5 per cent of Li) and fuse in a small silver crucible with 100-150 mg of potassium hydroxide. Add 6-10 drops of water, transfer the solution together with the precipitate into a porcelain crucible having the capacity of 3 ml, add 0.5-0.6 g of oxalic acid, evaporate carefully the solution and calcine the residue over a micro-burner until all oxalic acid is decomposed.

Wet the residue with ammonium carbonate solution, transfer the solution into a calibrated centrifuge test tube, add water to 2 ml, and centrifuge. Take 1.0 ml of the centrifugate by a dry pipette, transfer it into a 3-ml porcelain crucible, evaporate to dryness, wet the residue with 2-3 drops of hydrochloric acid (density 1.19 g/cu.cm), evaporate and calcine slightly. Now add 0.2 ml of the same hydrochloric acid and 0.5 ml of ethyl alcohol, allow the mixture to stand for five minutes with periodically stirring, and pass through a small filter (blue ribbon) into another 3-ml porcelain crucible. Wash the residue in the porcelain crucible and the filter with a mixture of ethyl alcohol and hydrochloric acid. Evaporate the filtrate to dryness, calcine the precipitate slightly, and dissolve in 1-2 drops of water. Add 1 ml of potassium hydroxide solution to the crucible, heat almost to boiling, and add 2 ml of potassium periodate solution (also heated to boiling). Heat the solution for a further five minutes and cool. Separate the precipitate on a small filter (blue ribbon) with suction. Wash four times with 0.75-ml portions of potassium hydroxide solution and dissolve in 10 ml of 1 N hydrochloric acid. Collect the solution in a 25-ml volumetric flask and add water to the mark.

Pipette 5.0 ml of the obtained solution into a 10-ml graduated test tube, add 3 ml of a 20 per cent potassium thiocyanate solution, a 2 per cent solution of potassium thiocyanate to 10 ml, mix, and measure the absorption of the solution on an absorptiometer as for the construction of the calibration curve.

Determine the lithium content of the aliquot from the calibration curve. Using the result, determine the lithium content of the sample remembering that the Li/Fe ratio in the ferriperiodate is 0.124.

Notes. 1. The following aliquots should be taken (depending on the lithium content of the sample):

Lithium content, %	0.05-0.3	0.3-1.0	1.0-3.5
Sample weight, mg	50	25	25
Aliquot, ml	5.0	3.0	1.0-2.0

2. The method is applicable to the analysis of silicate rock. When phosphate materials are analysed, the sample should be fused with potassium hydroxide, then dissolved in 8-10 drops of water, hydrochloric acid (1 : 1) added to a strongly acid reaction, and finally 0.5 ml of a 5 per cent zirconium oxychloride solution should be added. The mixture is evaporated to dryness and calcined slightly. The residue is wetted with 3-5 drops of water, oxalic acid is then added and the procedure completed as in the analysis of silicate rock.

PHOTOMETRIC DETERMINATION OF LITHIUM WITH QUINAZOLINAZO

Quinazolinazo, 2-(4″,5″-dimethylimidazole-2″-azo-2′-phenyl)-8-hydroxy-4,5,7-trimethylquinazolin, reacts with the ions of Li, Cu, Pd, Te, Ag, Pb, Co, Mg, and Zn to give coloured compounds. In the presence of dimethyl formamide, the reagent in an alkaline medium is selective toward lithium ion. Solutions of its compounds with lithium have the maximum absorption at 480 nm; the absorption should be measured at 530 nm. Lithium and quinazolinazo react in the ratio of 1 : 1, the molar extinction coefficient is 1.28×10^4. The optimum ratio of water to dimethyl formamide is 1 : 4.5, the absorption is maximum and constant with the concentration of KOH of 0.007-0.1 N for 15 minutes. Fifty-fold quantities of Ca, Sr, and Mg, hundred-fold quantities of Na, Ba, Al and Fe, and 200-fold quantities of Pb and Cs do not interfere with the determination of lithium. The reagent is used for determining 0.0004-0.06 per cent of lithium in albite ore and in brakish water from natural sources at Borzhomi.

Reagents

Lithium chloride, standard solution. 1 ml is equivalent to 4 μg of lithium.
Quinazolinazo, 0.004 M solution in chloroform.
Potassium hydroxide, 0.2 N solution.
Dimethyl formamide.

Hydrofluoric acid, 40 per cent solution.
Hydrochloric acid, density 1.17 g/cu.cm.
Ammonia, 2 *N* solution.
Acetone.

Constructing a Calibration Curve

Place 0, 0.2, 0.4, 0.6, 0.8 and 1.0 ml of the standard lithium chloride solution into graduated test tubes. Add water to each tube to 1 ml, add 4.5 ml of dimethyl formamide, 0.1 ml of quinazolinazo and 0.15 ml of potassium hydroxide solution. Stir the solutions and measure their absorption at 530 nm using a blank solution as the standard. Construct the calibration curve using the data obtained.

Procedure

Determining Lithium in Albite Ore. Add 10 ml of hydrofluoric acid to a sample of ore weighing 0.5 g, evaporate to dryness, treat the residue two times with hydrochloric acid, and evaporate the solution on a sand bath to obtain a damp salt. Dissolve the residue in water, transfer the solution to a 10-100 ml volumetric flask and add water to the mark.

Take an aliquot of the solution, filter, and evaporate to dryness on a water bath. Treat the dry residue three times with acetone, discard the used acetone, transfer the residue into a beaker, treat with ammonia to pH 5-6, separate the iron hydroxide precipitate on a filter, collect the filtrate in a 25-ml volumetric flask and add water to the mark. Transfer an aliquot containing 0.3-3 μg of lithium (the volume not greater than 1 ml) into a calibrated test tube and follow as for the construction of the calibration curve.

Determining Lithium in Water from the "Borzhomi" Spring. Evaporate 25 ml of the Borzhomi water, treat the residue with acetone, three times discard the acetone, transfer the residue into a volumetric flask of suitable capacity, and add water to the mark. Determine lithium in an aliquot (not greater than 1 ml) as for the construction of the calibration curve.

FLUORIMETRIC DETERMINATION OF LITHIUM WITH 5,7-DIBROMO-8-QUINOLINOL

5,7-Dibromo-8-quinolinol reacts with the lithium ion to give a compound whose solutions absorb maximum at 345 and 385 nm. When irradiated with the ultra-violet light of a mercury lamp, the compound fluoresces with a green light, the maximum of the absorption being at 530 nm. The components react in the molar ratio of 1 : 1, the apparent constant of the complex formation is 3.6×10^5. The limit of detection of lithium is 0.1 μg/ml. The optimum conditions are: ethanol concentration 92.5-93.5 per cent, pH 9.0-9.5. The compound is formed during 510 minutes, the intensity of fluorescence is constant for 1-2 hours.

Amounts to 1.5. mg of Rb, Cs, K, Na and to 1 μg of Ca, Sc, Ba, Mg and Al do not interfere with the determination of 1-100 μg of lithium. The ferric ion strongly interferes.

Reagents

Lithium chloride, standard solution. 1 ml is equivalent to 1000 µg of lithium
5,7-dibromo-8-quinolinol, 2×10^{-3} *M* solution in ethanol.
Ammonia, 5 *M* solution.
Ethyl alcohol.

Constructing a Calibration Curve

Place from 0 to 0.1 ml of the standard lithium chloride solution (containing from 0 to 100 µg of lithium) into dry test tubes, dilute with water to 0.1 ml, add 1 ml of the reagent solution, 0.05 ml of ammonia solution and dilute with alcohol to 4 ml. Measure the intensity of fluorescence in ten minutes at 530 nm. Construct the calibration curve using the data obtained.

Procedure

Take an aliquot of the solution containing 100 µg (or less) of lithium and determine lithium as instructed for the construction of the calibration curve.

FLAME-PHOTOMETRIC DETERMINATION OF LITHIUM IN MINERALS

Lithium is determined by the red resonance line at 670.8 nm. Strontium and other alkaline earths interfere with the determination. To remove the interfering effect of the alkaline earths and phosphates, 0.1 mole of aluminium nitrate and 0.7 g-equiv/litre of sulphuric acid are added to solutions. Minerals are decomposed by alkali fusion or by heating with acids.

Determination of Lithium in Minerals with Their Decomposition by Alkali Fusion

Lithium is determined graphically. The method is convenient for rapid analysis of minerals and ore containing from 0.1 to 10 per cent of lithium oxide. If the backgrounds are known, to 0.002 per cent of Li_2O can be determined. Aluminium, phosphorus, silicon (as oxides) and the alkaline earth metals do not interfere with the determination provided their quantities do not exceed 2.5 mg/ml

Reagents

Lithium sulphate, standard solution. 1 ml is equivalent to 2 mg of Li_2O.
Potassium hydroxide, crystalline, and 15 per cent solution.

Procedure

Dehydrate a sample of potassium hydroxide weighing 3 g in a silver crucible, cool the melt, place about 0.5 g of the sample atop the melt, and fuse for 15 minutes over a burner, or in a muffle at 700°C. Cool the melt and leach with 50-60 ml of water. Boil the solution together with the precipitate for 15 minutes with stirring. Cool, transfer the solution together with the precipitate into a 100-ml volumetric flask and add water to the mark. Pass the liquid through a dry filter, discarding the first portions of the filtrate. Observe the filtrate against an acetylene flame (through a 0.1 mm slit) and compare its colour with those of a series of standards containing to 200 μg/ml of Li_2O in a 3 per cent potassium hydroxide solution (concentration interval of Li_2O in the series of standard solutions is 20 μg/ml).

The concentration of the sample solution is 5 mg/ml, and its lithium oxide content (x) is therefore

$$\%\,x = a \cdot 100/(1000 \times 5) = 0.02a$$

where a is the found concentration of lithium oxide in the sample solution, μg/ml.

Notes. 1. Iron crucibles can be used to fuse the sample with alkali, but from 3 to 5 per cent of lithium can thus be lost.

2. If the mineral in question contains much lithium and phosphates, the size of the sample should be about 0.2 g, or the sample is decomposed by heating with acid.

Determining Lithium in Minerals with Decomposition by Acids

The method is recommended for the analysis of silicate rocks. Lithium is determined graphically. A photometer supplied with a set of optical filters can be used. Perchloric acid can be used instead of sulphuric acid. The residue after the removal of the acid should be treated with hydrochloric acid. The concentration of hydrochloric acid in the solution used for photometry should not exceed 0.02 *M*.

Reagents

Lithium sulphate, standard solution. 1 ml is equivalent to 2.5 mg of lithium.
Aluminium sulphate, $Al_2(SO_4)_3 \cdot 18H_2O$; 1 ml is equivalent to 13.5 mg of aluminium.
Sulphuric acid, density 1.84 g/cu.cm and 7 *N* solution.
Hydrofluoric acid, 48 per cent solution.

Constructing a Calibration Curve

Place from 1 to 7 ml of standard lithium sulphate solution (gradient, 1 ml) into 250-ml volumetric flasks, add 5 ml of aluminium sulphate solution, 25 ml of 7 *N* sulphuric acid, and water to the mark. Perform photometry at 670.8 nm. Construct the calibration curve using the data obtained.

Procedure

Calcine a sample weighing 0.5 g in a platinum dish at 1000°C for 30 minutes. Cool, add 1-2 ml of sulphuric acid, density 1.84 g/cu cm, and then, carefully, drop by drop, add hydrofluoric acid, waiting each time until the vigorous reaction stops. If the

Reagents

Lithium chloride, standard solution. 1 ml is equivalent to 1000 μg of lithium
5,7-dibromo-8-quinolinol, 2×10^{-3} *M* solution in ethanol.
Ammonia, 5 *M* solution.
Ethyl alcohol.

Constructing a Calibration Curve

Place from 0 to 0.1 ml of the standard lithium chloride solution (containing from 0 to 100 μg of lithium) into dry test tubes, dilute with water to 0.1 ml, add 1 ml of the reagent solution, 0.05 ml of ammonia solution and dilute with alcohol to 4 ml. Measure the intensity of fluorescence in ten minutes at 530 nm. Construct the calibration curve using the data obtained.

Procedure

Take an aliquot of the solution containing 100 μg (or less) of lithium and determine lithium as instructed for the construction of the calibration curve.

FLAME-PHOTOMETRIC DETERMINATION OF LITHIUM IN MINERALS

Lithium is determined by the red resonance line at 670.8 nm. Strontium and other alkaline earths interfere with the determination. To remove the interfering effect of the alkaline earths and phosphates, 0.1 mole of aluminium nitrate and 0.7 g-equiv/litre of sulphuric acid are added to solutions. Minerals are decomposed by alkali fusion or by heating with acids.

Determination of Lithium in Minerals with Their Decomposition by Alkali Fusion

Lithium is determined graphically. The method is convenient for rapid analysis of minerals and ore containing from 0.1 to 10 per cent of lithium oxide. If the backgrounds are known, to 0.002 per cent of Li_2O can be determined. Aluminium, phosphorus, silicon (as oxides) and the alkaline earth metals do not interfere with the determination provided their quantities do not exceed 2.5 mg/ml

Reagents

Lithium sulphate, standard solution. 1 ml is equivalent to 2 mg of Li_2O.
Potassium hydroxide, crystalline, and 15 per cent solution.

Procedure

Dehydrate a sample of potassium hydroxide weighing 3 g in a silver crucible, cool the melt, place about 0.5 g of the sample atop the melt, and fuse for 15 minutes over a burner, or in a muffle at 700°C. Cool the melt and leach with 50-60 ml of water. Boil the solution together with the precipitate for 15 minutes with stirring. Cool, transfer the solution together with the precipitate into a 100-ml volumetric flask and add water to the mark. Pass the liquid through a dry filter, discarding the first portions of the filtrate. Observe the filtrate against an acetylene flame (through a 0.1 mm slit) and compare its colour with those of a series of standards containing to 200 μg/ml of Li_2O in a 3 per cent potassium hydroxide solution (concentration interval of Li_2O in the series of standard solutions is 20 μg/ml).

The concentration of the sample solution is 5 mg/ml, and its lithium oxide content (x) is therefore

$$\% x = a \cdot 100/(1000 \times 5) = 0.02a$$

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Notes. 1. Iron crucibles can be used to fuse the sample with alkali, but from 3 to 5 per cent of lithium can thus be lost.

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Determining Lithium in Minerals with Decomposition by Acids

The method is recommended for the analysis of silicate rocks. Lithium is determined graphically. A photometer supplied with a set of optical filters can be used. Perchloric acid can be used instead of sulphuric acid. The residue after the removal of the acid should be treated with hydrochloric acid. The concentration of hydrochloric acid in the solution used for photometry should not exceed 0.02 M.

Reagents

Lithium sulphate, standard solution, 1 ml is equivalent to 2.5 mg of lithium.
Aluminium sulphate, $Al_2(SO_4)_3 \cdot 18H_2O$; 1 ml is equivalent to 13.5 mg of aluminium.
Sulphuric acid, density 1.84 g/cu.cm and 7 N solution.
Hydrofluoric acid, 48 per cent solution.

Constructing a Calibration Curve

Place from 1 to 7 ml of standard lithium sulphate solution (gradient, 1 ml) into 250-ml volumetric flasks, add 5 ml of aluminium sulphate solution, 25 ml of 7 N sulphuric acid, and water to the mark. Perform photometry at 670.8 nm. Construct the calibration curve using the data obtained.

Procedure

Calcine a sample weighing 0.5 g in a platinum dish at 1000°C for 30 minutes. Cool, add 1-2 ml of sulphuric acid, density 1.84 g/cu cm, and then, carefully, drop by drop, add hydrofluoric acid, waiting each time until the vigorous reaction stops. If the addition of another drop of hydrofluoric acid does not provoke a vigorous reaction, add another 5 ml of the acid and evaporate almost to dryness. Add 5 ml of sulphuric acid to the residue and heat on an electric hotplate until the acid fumes start evolving. Cool, wash the residue with water into a 250-ml beaker, add water to about 100 ml, heat to boiling and boil to prepare a clear solution. Pass the solution through a filter into a 250-ml volumetric flask, wash the residue on the filter several times with water, ignite the filter with the precipitate and calcine the ash in a platinum crucible to red heat. Wet the residue with hydrofluoric acid, evaporate to dryness, add 1-2 drops of sulphuric acid, density 1.84 g/cu.cm, and evaporate to dryness on a sand bath.

Dissolve the residue with heating in 10 ml of water, pass the solution through a filter into the same 250-ml volumetric flask, add water to the mark, and measure the absorption on a photometer at 670.8 nm.

Note. The selectivity of lithium determination depends on the instrument used. The selectivity coefficients which are important for the determination of lithium by various instruments are given below. The selectivity coefficient is the ratio of the mass of the accompanying ion to the mass of the sought ion, responsible for the error of determination of less than 5 per cent.

Selectivity Coefficients for Determination of Lithium in the Presence of Potassium, Sodium and Calcium

Apparatus	Selectivity coefficients for determination of lithium in the presence of		
	K	Na	Ca
Photometer with **interference optical filters**	2000-7800	640-5200	100-1000
Spectrophotometer on the basis of monochromator УМ-2	150 000	77 000	1 600
Beckmann spectrophotometer	3300	4500	—

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Rubidium and Cesium

Rubidium, Rb, and cesium, Cs, have the positive valency of 1. Standard electrode potentials in an aqueous medium at 25°C (with reference to the standard hydrogen electrode) are as follows:

$$\mathrm{Rb} \rightleftharpoons \mathrm{Rb}^+ + e^- \qquad -2.925\ \mathrm{V}$$

$$\mathrm{Cs} \rightleftharpoons \mathrm{Cs}^+ + e^- \qquad -2.923\ \mathrm{V}$$

Rubidium and cesium metals are extraordinarily strong reductants. The ions of these metals can only be reduced in solution by electrolysis.

Their hydroxides, RbOH and CsOH, are readily soluble in water and are strong bases.

The possibilities of chemical methods for the determination of Rb and Cs ions in their mutual presence and in the presence of the other alkali metal ions are limited. The ions of Rb and Cs form comparatively few sparingly soluble compounds, they do not form stable complex compounds (only double salts are known), nor do they give oxidation-reduction reactions.

The ions of rubidium and cesium are colourless and are similar to the potassium ion with respect to their chemical properties. They are all precipitated with perchloric acid, platinic-hydrochloric acid, sodium hexanitrocobaltate (III), hexanitrodiphenylamine, and other reagents. The solubility of rubidium compounds is intermediate between the corresponding compounds of potassium and cesium. There are reagents that can detect cesium in the presence of rubidium and potassium. Some salts of rubidium and cesium are well shaped crystals for which they can be detected microcrystalloscopically.

The difficulties which arise in separation of potassium, rubidium, and cesium are due to the great similarity of properties of their compounds. The most effective separation of rubidium and cesium is effected by various chromatographic methods. Organic and inorganic cation-exchangers (e.g. zirconium phosphate, ammonium molybdate) are used for their separation. The ions of Fr, Cs and Rb are separated [1] on a cation-exchanger КУ-1; the ions of Li, Na, K, Rb and Cs can also be separated by cation-exchangers [2, 3].

Precipitates of chloroplatinates of potassium, rubidium and cesium, $M_2[PtCl_6]$ are yellow or orange. Chloroplatinates of rubidium and cesium are less soluble than potassium chloroplatinate. A saturated solution of potassium chloroplatinate is used to detect the ions of rubidium and cesium in the presence of potassium ions.

Rubidium and cesium form triiodides MI_3. They dissociate according to the equation

$$MI_3 \rightleftharpoons MI + I_2$$

The triiodide CsI_3 is much more stable than RbI_3. This makes it possible to determine rubidium and cesium titrimetrically.

Potassium tetraiodobismuthite precipitates the cesium ion from aqueous solutions and from solutions in concentrated acetic acid as $Cs_3Bi_2I_9$. The formation of this compound underlies gravimetric, titrimetric and photometric determinations of cesium. The ions of rubidium (not more than three-fold quantities), lithium, sodium, potassium, magnesium, calcium and aluminium do not interfere with the determination.

Rubidium and cesium ions are precipitated by solutions of halide complexes of tin (IV) in the form of the compounds M_2SnX_6 (where X is Cl, Br or I). These complexes are used for separation of rubidium and cesium from potassium. The ions of rubidium and cesium form characteristic crystals with halides of other elements (chlorides of gold and palladium, chlorides of gold and silver). Hexachlorotellurous acid, H_2TeCl_6, precipitates the cesium ion from solutions of 11-12 *N* hydrochloric acid. Large quantities of potassium ion do not interfere with the determination [4].

Silicotungstic acid precipitates only the cesium ion from a 6 *N* solution of hydrochloric acid in the form of $Cs_4[Si(W_3O_{10})_4]\cdot xH_2O$ [5]. The same salt of rubidium is more soluble. It is possible to separate 0.01-0.02 g of CsCl from 0.02-0.03 g of RbCl. NH_4^+ interferes with the determination. The ions of lithium and the alkaline earth metals do not interfere.

Silicomolybdic acid reacts with Rb, Cs, NH_4, K and Tl^I under certain conditions to form crystals. This phenomenon is used for their microcrystalloscopic detection.

Ammonium silicomolybdate practically quantitatively coprecipitates the Cs ion from H_2SO_4 solutions [6]. This reaction is used to isolate Cs from solutions of potassium salts whose ion is not precipitated. Rubidium phosphomolybdate and cesium phosphomolybdate are less soluble than potassium phosphomolybdate. Rubidium and cesium are often isolated in the form of these compounds.

If a cesium salt is added to $Cd_2[Fe(CN)_6]$ solution in 5 per cent potassium iodide, white precipitate of $Cs_2Cd[Fe(CN)_6]$ is formed [7, 8]. From 0.02 to 0.2 mg of cesium can be detected in the form of this compound in 10 ml of the final solution. Ten-fold quantities of NH_4^+ and Rb, and also heavy metal ions, which form precipitates with the $[Fe(CN)_6]^{4-}$ ion, interfere, and the ions of Li, Na and 100-fold quantities of the potassium ion do not interfere with the determination.

Silver-sodium hexanitrobismuthite, $Na_2AgBi(NO_2)_6$, precipitates quantitatively rubidium and cesium ions. The yellow crystalline precipitates of variable composition are characterized by low solubility. The reagent is used to separate rubidium and cesium from potassium.

Rubidium and cesium can be isolated from dilute aqueous solutions by precipitation with potassium hexanitrocobaltate (cobalt potassium nitrite). To that end, $Na_3[Co(NO_2)_6]$ is added to the solution at a temperature below 10°C. Hexanitrocobaltates of rubidium and cesium are less soluble than potassium hexanitrocobaltate (III). From 1 to 10 mg of rubidium and cesium can be isolated from 10 litres of solution by this method, which is used to determine rubidium in sea water.

Sodium tetraphenylborate, $[B(C_6H_5)_4]Na$, precipitates quantitatively K, Rb and Cs ions under certain conditions. This reagent is used for gravimetric and titrimetric determination of these elements [9, 10].

Sodium triphenylcyanoborate, $[(C_6H_5)_3B(CN)]Na$, almost quantitatively precipitates the Cs^+ ion [11]. When a filtered 3 per cent solution of the reagent is added to a 0.005 *M* solution of Cs_2SO_4, a comparatively coarse white precipitate is immediately separated. The solubility product of $[(C_6H_5)_3B(CN)]Cs$ is 3×10^{-6}, i.e. about 100 times higher than that of $[B(C_6H_5)_4]Cs$. The reagent does not precipitate the Rb ion from 1.4×10^{-2} *M* solution of Rb_2SO_4, but the ion of Rb is coprecipitated with $(C_6H_5)_3B(CN)Cs$. The potassium ion is not precipitated from a 5 per cent solution of KNO_3. The ions of Ca, Sr, Ba, Mg, Ni, Co, Mn^{II}, Zn, $Fe^{II, III}$, Cd, Pb, Cu^{II}, U^{VI}, Al, Ce^{III}, Cr^{III} or Bi are not precipitated. The ions of Tl^I, Ag, Cu^I are precipitated. The precipitate $[(C_6H_5)_3B(CN)]Cs$ is easily soluble in acetone and its mixture with water (1 : 1). It is practically insoluble in benzene, and comparatively sparingly soluble in dioxane. Sodium triphenylcyanoborate is used for the detection and gravimetric determination of cesium, but the results are always low. The determination of cesium can be ended by argentometric or thallometric titration.

The sodium salt of hexanitrodiphenylamine (dipicrylamine) gives characteristic precipitates with the ions of potassium rubidium, cesium and thallium (I). The ions of Na, Li, Mg and of the alkaline earth metals are not precipitated. The ions of Al, Fe^{III}, Cr^{III}, Ni, Co, Bi and Hg give amorphous precipitates. The reagent is used for the detection and photometric determination of rubidium and cesium.

The cesium ion is coprecipitated isomorphically with sparingly soluble dipicrylaminates of NH_4^+, K, Rb and Tl^I [12]. Dipicrylaminates of thallium and ammonium can be used as carrying agents for the isolation of traces of cesium (12 μg) from very dilute solutions. Cesium dipicrylaminate is extractable with nitrobenzene from alkaline solutions [13]. This makes it possible to isolate small quantities of radioactive cesium from many long-lived fission products and from large quantity of uranium. Large quantity of the sodium ion in solution decreases the extractability of cesium.

Hexanitrohydrazobenzene in the form of its monosodium salt (a saturated solution in water) precipitates the ions of Rb, Cs and K. It is used for the photometric determination of these elements [14]. Filtered precipitates are dissolved in acetone and the absorption of the obtained solutions is measured. From 10 to 130 μg of Rb or Cs can be determined. Small quantities of Na and comparatively large quantities of Li, Ca, Sr, Ba and Mg ions do not interfere with the determination.

Picric and picrolonic acids (alcoholic solutions) are used for the microcrystalloscopic detection of the rubidium and cesium ions. But the sodium, ammonium and potassium ions form similar crystals.

Dilituric acid (5-nitrobarbituric acid), 2,4-dinitrophenol, 2,4,6-trinitro-*m*-cresol, 2,4,6-trinitroresorcinol, and dinitrobenzofuroxane are used for the microcrystalloscopic or the detection of the rubidium and cesium ions by the spot test. All these reagents have low selectivity. Ions of many elements interfere with the determination.

Tartaric acid or sodium hydrotartrate precipitate white crystals of $RbHC_4H_4O_6$ or $CsHC_4H_4O_6$ from neutral solutions of rubidium or cesium salts. They are readily soluble in mineral acids but sparingly soluble in water or acetic acid. The ions of K and NH_4^+ are precipitated in a similar way. Hydrotartrates of all these elements readily form supersaturated solutions.

Rubidium and cesium ions are reduced on a mercury dropping electrode in aqueous solutions at very low potentials. Rubidium and cesium cannot be determined polarographically in aqueous solutions. The half-wave potential of the cesium ion in a 80 per cent isopropyl alcohol against the back-ground of a 0.1 *M* solution of lithium hydroxide is —2.03 V; for rubidium ion it is —1.97 V (at 20-30°C), with reference to the saturated calomel electrode [15]. Hence the elements can be determined polarographically in these conditions. When both are present in solution, their sum is determined.

Rubidium salts colour a flame red-violet. But potassium salts give the same colour to flame and the difference cannot be detected with an unaided eye. The spectra of rubidium and cesium have characteristic lines at 421.6 and 420.2 nm. Cesium salts colour flame violet-blue, and the spectrum has characteristic lines at 459.3 nm and 455.5 nm. The flame-photometric [16] and spectral methods of determination of rubidium and cesium are the most reliable and widely used for the analysis of various materials.

The flame-photometric method can be used to determine rubidium and cesium in the presence of the other alkali and alkaline earth metals. The method has been successfully used for the determination of small quantities of cesium in various rocks [17, 18]. There are no reliable chemical methods for the detection and determination of rubidium in the presence of the other alkali metals. The chemical methods of determination of cesium are only of secondary importance.

Rubidium and cesium are determined by the neutron-activation method in rocks, minerals, and extraterrestrial objects [19].

The monograph [20] is dedicated to the analytical chemistry of rubidium and cesium. 2-Tenoyltrifluoroacetone selectively extracts cesium ion [21].

SELECTIVE EXTRACTION OF CESIUM WITH 2-TENOYLTRIFLUOROACETONE

Cesium and other alkali metals can be extracted with solutions of 2-tenoyltrifluoroacetone in nitromethane or nitrobenzene, the pH of the aqueous phase being 8.7-9.0. At pH higher than 9 the reagent is decomposed. In the presence of EDTA, cesium (alkali metals) can be separated from many ions which form stable complexonates and remain in the aqueous phase. Chlorides, sulphates, and nitrates contained in the concentration less than 1 *M* do not interfere with the separation of cesium. Cesium is extracted from an organic phase with acids. In optimum conditions, the alkali elements are extracted in the following quantities (parenthesized are quantities of the elements taken for the determination): lithium, 94.4 per cent (13.6 mg); sodium 44.8 per cent (112 mg); potassium, 82.1 per cent (10.8 mg); rubidium, 92.2 per cent (6.2 mg), cesium, 99.5 per cent (7.4 mg). The method is recommended for the separation of cesium from the products of uranium fission to prepare highly active preparations of ^{137}Cs and to separate cesium from nuclear fuel production effluents before their disposal.

Reagents

Lithium hydroxide, 1 *N* solution.
Sodium carbonate, 2 *N* solution.
2-Tenoyltrifluoroacetone, 0.5 *M* solution in nitromethane or nitrobenzene.

Procedure

Add 5 ml of lithium hydroxide solution to the solution of the sample, dilute with sodium carbonate solution to make a total of 10 ml and extract with an equal volume of the extracting agent for three minutes. The equilibrium pH of the aqueous phase should be 8.7-9.0.

Note. If extraneous (not alkali) ions are present, EDTA should be added in the quantity sufficient to mask the accompanying ions before adding the extracting agent. The organic phase is then separated by centrifuging.

GRAVIMETRIC DETERMINATION OF RUBIDIUM IN SCINTILLATORS WITH SODIUM TETRAPHENYLBORATE

Sodium tetraphenylborate precipitates rubidium at pH 3-6 as sparingly soluble $[B(C_6H_5)_4]Rb$. The precipitate is stable to temperatures below 240°C. As a rule it is dried to constant weight at a temperature of 105-130°C. The factor for conversion into rubidium is 0.2112. The ions of lithium, sodium, magnesium, calcium, barium, cadmium, copper, divalent manganese, lead, cobalt, nickel, zinc, iron, chromium (III), aluminium, arsenic (III), antimony (III), tin (IV), titanium, and uranium (VI) do not interfere with the determination in the presence of EDTA. The ions of ammonium, mercury (I), thallium (I), thorium, potassium and cesium interfere. If an ammonium ion is present, rubidium is precipitated in an alkaline solution by formaldehyde with heating.

The proposed method for the determination of rubidium in scintillating materials provides for the separation of thallium by ion-exchange chromatography and the removal of the ammonium ion by alkali.

Reagents

Nitric acid, density 1.4 g/cu.cm.
Hydrochloric acid, density 1.17 g/cu.cm.
Sodium bromate, 0.001 *M* solution in 2 *M* hydrochloric acid.
Anion-exchange resin AG1X8 in the Cl-form.
Acetic acid, 0.1 *M* solution.
Bromcresol purple, 0.01% solution in ethyl alcohol.
Sodium hydroxide, 0.1 *M* solution.
Sodium tetraphenylborate, 0.1 *M* solution.
Rubidium tetraphenylborate, saturated aqueous solution.

Procedure

Dissolve a sample of crystals containing from 1 to 10 mg of rubidium in 100 ml of hot water, add nitric acid in the quantity sufficient to convert sodium iodide into sodium nitrate and to liberate iodine, and heat the solution to remove iodine. Evaporate to dryness, add 1-2 ml of hydrochloric acid and evaporate to dryness again. Dissolve the residue in 75 ml of sodium bromate solution in hydro-chloric acid and pass through the anion-exchange column. Wash the column with sodium bromate solution in hydrochloric acid, collect the eluate and evaporate to dryness.

Dissolve the residue in 90 ml of water, add three drops of acetic acid, three drops of an indicator solution and a solution of sodium hydroxide (pH 6.5). Now add 8 ml of sodium tetraphenyl borate, drop by drop, with constant stirring. Allow the mixture to stand for 30 minutes, separate the precipitate by filtration into a glass crucible with a porous bottom, wash with a saturated solution of rubidium tetraphenylborate (with a portion not exceeding 50 ml), then with about 1 ml of water, and dry at 110°C to constant weight. Calculate the rubidium content using the conversion factor.

TITRIMETRIC DETERMINATION OF CESIUM IN POLLUCITE

The method is based on the ability of cadmium hexacyanoferrate, $Cd[CdFe(CN)_6]$ to exchange quantitatively its cadmium ion found in the outer sphere of the complex for the cesium ion with the formation of a less soluble salt

$$Cd[CdFe(CN)_6] + 2Cs^{\cdot} \rightleftharpoons Cs_2[CdFe(CN)_6] + Cd^{\cdot\cdot}$$

The quantity of the cadmium ion which passes into solution is equivalent to that of the cesium ion. The determination ends by the titration of the cadmium ion with $K_4[Fe(CN)_6]$ solution. Cadmium can also be precipitated with hydrogen sulphide; the precipitate should then be washed and dissolved in hydrochloric acid with subsequent determination of cadmium by complexometric titration.

The method can be used for the determination of cesium in pollucite, cesium aluminium silicate, $H_2Cs_4Al_4(SiO_3)_9$. The ions of rubidium, 4-fold quantities of potassium, the ions of copper, zinc, iron and other elements which form sparingly soluble ferrocyanides, interfere with the determination. The ions of Na, Mg, Ca and Al do not interfere.

The ion-exchange reaction should be carried out in a neutral medium or in sulphuric acid solution, with passing the solution through powdered cadmium hexacyanoferrate (II).

Reagents

Hydrofluoric acid, concentrated.
Sulphuric acid, diluted 1 : 3.
Cadmium hexacyanoferrate (II), crystalline. Place 300 ml of a solution containing 40.69 g of cadmium sulphate and 48 ml of hydrochloric acid, density 1.19 g/cu.cm, into a 2-litre beaker, add 300 ml of a solution containing 38.50 g of sodium hexacyanoferrate (II), in small portions and with constant stirring by a mechanical agitator. Dilute the mixture with water to make 1 litre, mix thoroughly and allow to stand overnight. Separate the precipitate on a Büchner funnel with a blue ribbon filter, wash with distilled water to remove the $SO_4^{=}$ ion and dry in air. Keep the preparation in a bottle with a ground-in stopper. The preparation is not hygroscopic and does not change its properties on standing.
Ammonium sulphate, 50% solution.
Hydrochloric acid, density 1.19 g/cu.cm.
Potassium hexacyanoferrate (III), $K_3[Fe(CN)_6]$, 1% solution.
Potassium hexacyanoferrate (II), $K_4[Fe(CN)_6] \cdot 3H_2O$, 0.05 *M* solution.
Diphenylamine, 1% solution in concentrated sulphuric acid.
Zinc sulphate, 0.075 *M* solution.

Procedure

Isolation of Cesium from Pollucite. Grind finely a sample of pollucite weighing 0.2-0.3 g and dry to constant weight at a temperature of 105-110°C. Place the powder into a platinum dish and treat, with heating on a sand bath, with four 5-ml portions of hydrofluoric acid.

Add 3 ml of sulphuric acid, and evaporate until fumes of sulphuric acid appear. Cool the residue, dissolve in 10 ml of water, separate the insoluble residue on a blue ribbon filter and wash with water. The overall volume of the filtrate and the washings should be 50 ml.

Place 10 g of cadmium hexacyanoferrate (II) into a glass crucible with a porous bottom No. 3 or No. 4 inserted into a Büchner flask, wet with a small quantity of water and gently press it on the filter bottom with slight suction. Heat the solution to 60-70°C and pass through a bed of cadmium hexacyanoferrate (II) on the filter at a rate of one drop in 4-5 seconds, adjusting the rate by a water-jet ejector. Wash with 3-4 portions of hot water (5-6 ml in each portion). Add the washings to the filtrate to make the total volume of 70-80 ml.

Titration of Cadmium. Place the solution into a 300-ml Erlenmeyer flask, add 10 ml of ammonium sulphate solution, 10 ml of hydrochloric acid, and finally add from a burette, with energetically stirring, about 20 ml of $K_4[Fe(CN)_6]$ solution. Allow the solution with the precipitate of $5Cd_2[Fe(CN)_6] \cdot (NH_4)_4[Fe(CN)_6]$ to stand for 5-10 minutes, add 0.5 ml of $K_3[Fe(CN)_6]$ solution, 3-4 drops of diphenylamine, and titrate excess ion of $[Fe(CN_6)]^{4-}$ with zinc sulphate solution until lilac colour develops. Now add 4-5 drops of the reagent in excess, and add, from a burette, the solution of $K_4[Fe(CN)_6]$ until the lilac colour changes to greenish, which turns lilac again from the addition of one drop of zinc sulphate solution.

Determine the ratio of the volumes of potassium hexacyanoferrate (II) and zinc sulphate solution in the same conditions. Determine the concentration of potassium hexacyanoferrate solution against a standard solution of cadmium sulphate.

Calculation. Calculate the percentage of cesium from the following formula:

$$\%Cs = (V_1 - V_2 f)\, TF \times 100/g$$

where V_1 is the volume of 0.05 M solution of $K_4[Fe(CN)_6]$ spent for titration, ml; V_2 is the volume of 0.075 M solution of zinc sulphate spent for titration, ml; f is the factor for conversion of 1 ml of zinc sulphate solution into 1 ml of $K_4[Fe(CN)_6]$ solution (1 ml of 0.075 M solution of $ZnSO_4$ is equivalent to 1 ml of 0.05 M solution of $K_4[Fe(CN)_6]$, f is 1 in this case); T is the titre of $K_4[Fe(CN)_6]$ solution with respect to cadmium, g/ml; F is the factor for conversion of cadmium into cesium, equal to 2.365; and g is the weight of the sample, g.

FLAME-PHOTOMETRIC DETERMINATION OF RUBIDIUM AND CESIUM

Rubidium and cesium are determined by the emission method in a low-temperature flame (a mixture of illuminating gas and air). Rubidium and cesium are determined by the lines at 780.0 or 794.8 nm and 852.1 nm respectively.

The selectivity coefficients for the determination of rubidium and cesium are given below.

Element	Wavelength, nm	Selectivity coefficients for determination of rubidium and cesium in the presence of the following elements							
		Li	Na	K	Rb	Cs	Ca	Sr	Ba
Rb	794.8	9350	5800	260	—	700	2800	700	78
Cs	852.1	5300	1280	465	200	—	2000	1070	40

The proposed method can be used to determine 10^{-3}% (or greater) of rubidium and cesium by the increment method against a scattered light background. Cesium and rubidium increments are introduced separately to rule out their mutual effect; moreover, the background at the base of the analytical lines is measured and taken into consideration during calculations.

Reagents

Rubidium chloride, standard solution. 1 ml is equivalent to 100 μg of rubidium.
Cesium chloride, standard solution. 1 ml is equivalent to 100 μg of cesium.
Hydrofluoric acid, 48 per cent solution.
Sulphuric acid, diluted 1 : 1.

Procedure

Grind a sample weighing 1 g, place it in a platinum dish, add 10 ml of hydrofluoric acid and 2 ml of sulphuric acid, and heat to decompose the sample and to remove the acids. Treat the dry residue with 15 ml of water, heat to boiling, cool and transfer into a 25-ml volumetric flask. Add water to the mark, pass the solution through a dry filter, and place 4 ml of the filtrate into one beaker and 3-ml portions into four other beakers. Add 4 ml of water into the original beaker, 2.4 ml and 1.8 ml of water and 0.6 ml and 1.2 ml of rubidium chloride solution into the other two beakers respectively. Add 0.3 ml and 0.6 ml of cesium chloride solution and 2.7 ml and 2.4 ml of water into the remaining two beakers respectively.

Measure the absorption of the sample solutions at 794.8 nm for rubidium and at 852.1 nm for cesium and compare the results with the readings obtained with the solutions containing the increments of rubidium and cesium. Determine the content of these elements graphically or by calculations.

Note. If samples contain 0.1-0.15% of rubidium or cesium, dilute the sample solutions from 2 to 5 times.

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Beryllium

Beryllium, Be, has the positive valency of 2. The standard electrode potentials in aqueous solutions at 25°C are as follows (with reference to the standard hydrogen electrode):

$$\begin{aligned} \mathrm{Be} &\rightleftharpoons \mathrm{Be^{2+}} + 2e^- && -1.847\ \mathrm{V} \\ \mathrm{Be} + 2\mathrm{H_2O} &\rightleftharpoons \mathrm{Be(OH)_2} + 2\mathrm{H^+} + 2e^- && -1.820\ \mathrm{V} \\ 2\mathrm{Be} + 3\mathrm{H_2O} &\rightleftharpoons \mathrm{Be_2O_3^{2-}} + 6\mathrm{H^+} + 4e^- && -1.387\ \mathrm{V} \\ \mathrm{Be} + 2\mathrm{H_2O} &\rightleftharpoons \mathrm{BeO_2^{2-}} + 4\mathrm{H^+} + 2e^- && -0.909\ \mathrm{V} \end{aligned}$$

Acid solutions contain the ion Be^{2+}; weak acid solutions contain the ions $BeOH^+$, Be_2OH^{3+}, Be_2O^{2+} and others. Colourless ions BeO_2^{2-}, $Be_2O_3^{2-}$ and others are formed in alkali solutions (see Fig. 1).

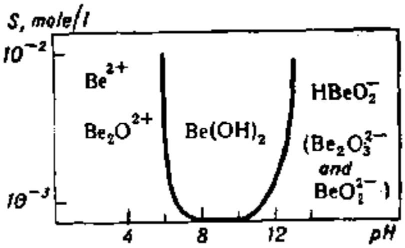


Fig. 1. Dependence of solubility of $Be(OH)_2$ on pH

Beryllium hydroxide has amphoteric properties. It begins precipitating from 0.01 *M* solutions of beryllium salts at pH of about 6 and redissolves at pH of about 13.5.

The beryllium ion is very much like that of aluminium. The separation of beryllium and aluminium was a very difficult problem in analytical chemistry for a long time. The problem has become much simpler after the introduction of EDTA into practical analysis. This reagent forms a stable complex compound with aluminium while its compound with beryllium is unstable. EDTA is used to mask the Al ion and also the ions of many other elements during the quantitative determination of beryllium. Beryllium hydroxide is precipitated quantitatively with ammonia at pH 8.5 from solutions containing excess EDTA [1]. The ions of di-, ter-, and tetravalent elements form stable complexes and remain in solution. EDTA does not mask Ti^{IV}, Sn^{IV} or Cr^{III} ions. Washed precipitate of beryllium hydroxide is calcined and weighed as BeO.

When excess NaF is added, beryllium hydroxide, $Be(OH)_2$, converts into a low dissociated fluoride, and NaOH is formed in equivalent quantity:

$$BeSO_4 + 2NaOH \xrightarrow{pH\ 8.5} Be(OH)_2 + Na_2SO_4$$
$$Be(OH)_2 + 2NaF \longrightarrow BeF_2 + 2NaOH$$

The liberated NaOH is titrated potentiometrically with H_2SO_4 solution. The ions of Al, Zr, U, Th and of the lanthanides interfere with the determination. The described reactions are not stoichiometric and the method is therefore empirical. But if the conditions are strictly observed, the method gives satisfactory results. The solution of H_2SO_4 is standardized against beryllium metal.

Beryllium metal readily dissolves in acids or alkalis:

$$Be + 2KOH \rightleftharpoons K_2BeO_2 + H_2$$

Beryllium is determined by measuring the volume of the liberated hydrogen or by measuring the increase in the pressure inside a known closed volume. The method is used to determine metallic beryllium in slags and precipitates. Aluminium metal interferes with the determination. If the sample contains a carbide or nitride of beryllium (Be_2C, Be_3N_2) an appropriate correction should be introduced.

Beryllium is precipitated quantitatively [2] at pH 5.5 as the crystalline phosphate $BeNH_4PO_4$ from solutions containing EDTA. The ions of Mg, Ca, Fe, Al, Cu, Ni and others remain in solution. The separated and washed precipitate is calcined and weighed as $Be_2P_2O_7$. The gravimetric phosphate method is used for the determination of beryllium in concentrates of any composition [3].

Beryllium is precipitated quantitatively as a crystalline beryllium ammonium arsenate, $BeNH_4AsO_4$, of constant composition from acetate solutions at pH 5.2 in the presence of EDTA. Beryllium is determined by iodimetric titration of the arsenate in the medium of hydrochloric acid (1 : 3) [4].

Beryllium forms various complex compounds with inorganic and organic ligands. The citrate and tartrate complexes are quite stable. Freshly precipitated beryllium hydroxide dissolves in solutions of carbonates of the alkali metals and is reprecipitated by boiling (in contrast to aluminium hydroxide).

The beryllium ion forms fluoride complexes

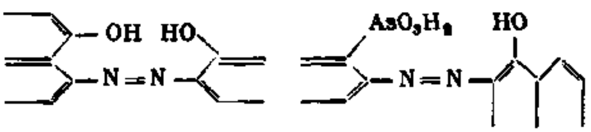
$$BeF_2 \rightleftharpoons Be^{2+} + 2F^- \qquad pK \approx 2$$
$$BeF_4^{2-} \rightleftharpoons BeF_3^- + F^- \qquad pK_1 = 2;\ pK_2 = 3.6;$$
$$pK_3 = 5;\ pK_4 = 4.3-5.9$$

The carbonate complex of beryllium is precipitated by the ion $[Co(NH_3)_6]^{3+}$ as $[Co(NH_3)_6][Be_2(CO_3)_2(OH)_3(H_2O)_2]\cdot 3H_2O$. This compound is used for the gravimetric determination of beryllium [5, 6].

Beryllium reacts with salicylic and sulphosalicylic acid to form stable complex compounds. These reagents are used for the titrimetric determination of beryllium [7-9].

Uramyl-N,N-diacetic acid reacts with the beryllium ion to form two compounds. One of them, a neutral complexonate BeL, has the stability constant $\log K = 10.36$. The reagent is used for the amperometric titration of beryllium in the presence of the ions of Al, Ca, Mg, $Fe^{II,III}$, Mn^{II}, Ni, Co, Zn and Cu [10, 11].

Various hydroxyl-containing organic substances are used as reagents for the beryllium ion. They are used under certain conditions for the detection and photometric determination of beryllium. The examples are H-resorcinol and arsenazo I, containing the following atom groupings:



Arsenazo I reacts with the beryllium ion at pH 6-6.5 (urotropin) to form a red-violet compound [12], while own colour of the reagent is pink. The limit of detection is 0.02 μg of Be in 1 ml, the dilution being 1 : 5 × 10^7. The ions of Mg, Zn, Mn and of the alkali metals do not interfere with the determination. Alluminium ion can be masked by tartrate or EDTA, the ions of Fe^{III}, rare earth elements and of copper, by oxalates; and the ion of U^{VI}, by hydrogen peroxide. Arsenazo I is used for the detection and photometric determination of beryllium.

Thorin reacts with beryllium ions in the molar ratio of 3 : 2 [13]. $BeOH^+$ and the pentanegatively charged reagent ion enter the reaction. The optimum pH is 12.5. The complex formation constant is $(4.5 \pm 0.4) \times 10^{18}$.

A violet-blue 0.02 per cent aqueous solution of beryllon II turns pale blue in the presence of the beryllium ion and at pH 12-13 [14]. The selectivity of the reagent slightly increases in the presence of EDTA. But ferric ions, which are not masked by other substances, interfere with the determination. The reagent is used for the detection [14] and photometric determination of beryllium [15].

Compared with beryllon II, its analogue beryllon IV is more selective since it can be used to determine beryllium photometrically at pH 5-7. The ions of Al, Fe^{III}, Mn, Cu and Ni do not interfere with the determination. The reagent is used for the determination of 0.01-0.9 per cent of beryllium in aluminium alloys [16, 17].

p-Nitrobenzeneazoorcinol reacts with the beryllium ion (probably $BeOH^+$) in a medium of a 0.5 *N* solution of NaOH in the molar ratio of 1 : 1 [18]. The absorption maximum of the formed beryllium compound is at 490-500 nm, and of the reagent solutions in 0.5 *N* NaOH, at 450-460 nm. The colour develops quickly and persists for at least 48 hours. The molar extinction coefficient is 3.14×10^4 (at 500 nm).

The complex formation constant is $(2.87 \pm 0.06) \times 10^{-3}$. The reagent is used for the detection [19] and photometric determination of beryllium [20-22].

At pH 13, morin reacts with the beryllium ion to form a compound fluorescing in the ultraviolet light (green fluorescence). Morin is highly sensitive and can be used to determine small quantities of beryllium in ores and silicate rock without its separation from the accompanying elements, whose ions are masked [23-25]. The intensity of fluorescence is proportional to the beryllium concentration. It depends also on the concentration of morin, the pH of the solution, and slowly decreases on standing. The standard solution and the solution of the sample should be prepared simultaneously. Ascorbic acid, citrate ion and EDTA provide the conditions for the determination of microgram quantities of beryllium in the presence of the ions of Al, Ca, Mg, Mn, Mo, Cd and Zn (to 5 mg of each ion), Fe (to 0.35 mg), Ti (0.2 mg), and Cr (0.03 mg). The reagent is used for the fluorimetric determination of beryllium in mineral raw materials provided the metal is contained in quantities greater than 10^{-5}% [26].

Aluminon reacts with the beryllium ion to form a red compound which is used for the photometric determination of this element [27-31].

8-Hydroxyquinoline does not precipitate the beryllium ion from acetic acid buffer solution with pH 5.7. The reagent is used to separate beryllium from other elements whose ions precipitate in these conditions (Al, Fe, Mo, W, U, Cu, Ni, Co, Zn, Cd, Hg, and Bi).

Some β-diketones form a sparingly soluble compound with the beryllium ion. 2,2-Dimethylhexanedione-3,5 precipitates quantitatively the beryllium ion at pH 7-8. It is used for the gravimetric [32, 33] and titrimetric [34] determination of beryllium.

Acetylacetone forms a stable compound with the beryllium ion. Beryllium acetylacetonate can be easily extracted with chloroform in the presence of EDTA in a weak alkaline medium (pH 9). The ions of Al, Cr, Co, Fe, Ni, Mn, Zn, Cd, Pb, Cu, Ca and Mg are not extracted in these conditions, and beryllium can be separated from aluminium and other elements [35, 36]. Satisfactory results can be obtained with separation of 4-24 mg of BeO from 24-4 mg of Al_2O_3.

Spectral and radioactivation methods are used for the determination of beryllium. The review of the methods is given in the literature [37].

SELECTIVE EXTRACTION AND EXTRACTION-PHOTOMETRIC DETERMINATION OF BERYLLIUM WITH ACETYLACETONE

Acetylacetone reacts with the beryllium ion at pH 6-10 to form a compound soluble in chloroform and having the absorption maximum at 295 nm, the molar absorption coefficient of 3.16×10^4, and the molar ratio of the reacting components of 1 : 1. The reaction becomes selective for beryllium in the presence of EDTA. The method can be used to separate and determine beryllium spectrophotometrically in quantities greater than 0.25 μg to an accuracy of ±5 per cent in the presence of 1 mg of UO_2^{II}, Pb, Ag, Cr, Mn, Fe^{III}, Co, Cu, Na, K, Ca, Sr, Ba, Mo, Zn, Al, fluorides, phosphates, acetates, great quantities of sulphates, nitrates, chlorides and perchlorates. The citrate ion interferes with the determination.

Reagents

EDTA, 10 per cent solution.
Sodium hydroxide, 0.1 *N* solution.
Acetylacetone, 5 per cent and 1 per cent solutions.
Chloroform.
Nitric acid, 16 *M* and 0.1 *N* solutions.
Perchloric acid, 60 per cent solution.

Procedure

Add nitric acid to 50 ml of a solution containing not more than 10 μg of beryllium to adjust the pH to 0.5-1.0, and 2 ml of EDTA solution and 0.1 *N* sodium hydroxide solution to adjust the pH to 7-8 (to bromothymol blue indicator). Next add 5 ml of a 5 per cent solution of acetylacetone and adjust the pH to 7-8. Extract beryllium in five minutes with three 10-ml portions of chloroform, and collect the extracts in a platinum dish. Add 15 ml of water, 2.0 ml of 16 *M* nitric acid and 2.0 ml of perchloric acid, evaporate chloroform on a water bath, and then evaporate the acid mixture to dryness on a hotplate. Treat the dry residue with 2.0 ml of a mixture of nitric and perchloric acids and evaporate to dryness again.

If beryllium will be determined spectrophotometrically, add 15 ml of a 0.1 *N* nitric acid to the dry residue and transfer the mixture into a separating funnel. Add 1 ml of EDTA solution and neutralize with sodium hydroxide solution to pH 7. Add 2 ml of a 1 per cent solution of acetylacetone and neutralize to pH 7. Allow the mixture to stand for 5 minutes and extract with three 8-ml portions of chloroform. Collect the extracts in a 25-ml volumetric flask and add chloroform to the mark. Transfer the extract into a separating funnel and wash two times with 50-ml portions of sodium hydroxide solution with shaking for 30-60 seconds. Pass the extract through a dry paper filter into a cell with the layer thickness of 1 cm and measure the absorption at 295 nm using chloroform as a reference solution.

Construct the calibration curve for beryllium concentrations from 0.5 to 10 μg by carrying the solutions through all stages as for the spectrophotometric determination of beryllium.

GRAVIMETRIC DETERMINATION OF SMALL QUANTITIES OF BERYLLIUM IN ORE AND ITS PRODUCTS WITH 2,2-DIMETHYLHEXANEDIONE-3,5

2,2-Dimethylhexanedione-3,5 reacts with the beryllium ion at pH 7-8 to form a sparingly soluble crystalline compound of the composition $[CH_3COCHCOC(CH_3)_3]_2Be$. The precipitate is easy to wash and dry to constant weight at 45-55°C. At temperatures above 70-75°C, it sublimes.

EDTA can be used to determine from 0.1 to 3 per cent of beryllium in ore. Al (600 mg), Fe^{III} (200 mg), Ca (30 mg), rare earth elements (20 mg), U^{VI} (30 mg), Ti^{IV} (20 mg) do not interfere with the determination of 1-2 mg of beryllium in the presence of EDTA. Sulphate, chloride, nitrate, fluoride and acetate ions (20-fold quantities), carbonate ion (30-fold quantity) and phosphate ion (100-fold quantity) do not interfere with the determination. Sn^{II} interferes since it cannot be masked with EDTA in conditions under which beryllium precipitates. But tin accompanies beryllium only in rare cases.

The method has the following advantages over the complexone-phosphate method: (1) compounds of definite composition are obtained by a single precipitation, which markedly shortens the procedure; (2) the precipitate has a distinct crystalline structure, it is easy to wash and dry to constant weight at low temperature.

The factor for conversion to beryllium is 0.03096.

Reagents

Potassium hydrofluoride, KHF_2, crystalline.
Sulphuric acid, diluted 1 : 1.
Hydrochloric acid, diluted 1 : 1.
EDTA, 5 per cent solution.
Ammonia, solution diluted 1 : 1.
2,2-Dimethylhexanedione-3,5, saturated solution prepared 2-3 days before the analysis (to attain the ketone-enol equilibrium in the solution).

Procedure

Fuse a sample weighing 0.25-1.0 g (containing from 0.05 to 0.5 per cent of beryllium) with a five-fold quantity of potassium hydrofluoride in a platinum dish in a muffle furnace at 800-900°C. Add 15 ml of sulphuric acid and evaporate the solution until heavy fume stops evolving.

Transfer the dish contents into a 400-ml beaker, add 10 ml of hydrochloric acid and water to make 100 ml, and heat to dissolve the salts. Whenever necessary, pass the solution through a white ribbon filter and cool to room temperature. If the sample contains tin (II), precipitate it from the hot acid solution with hydrogen sulphide. Add 35-40 ml of EDTA solution, neutralize with ammonia to pH 7-8 to the universal indicator paper and add 2,2-dimethylhexanedione-3,5 (20-30 ml of solution per 1 mg of beryllium). Stir the solution by a jet of water (15-20 ml).

When the reagent is added the solution becomes cloudy, but the precipitate coagulates into loose flocks in 2-3 hours and the solution clarifies. Separate the precipitate on a glass crucible with a porous bottom No. 4 dried to constant weight, wash several times with cold water, and dry to constant temperature at 45-55°C. Using the conversion factor, find the quantity of beryllium contained in the sample.

TITRIMETRIC DETERMINATION OF BERYLLIUM WITH 2,2-DIMETHYLHEXANEDIONE-3,5

Dissolve the precipitate obtained by the above procedure in hydrochloric acid and determine the liberated diketone bromatometrically (in the presence of methyl red). The accuracy of the method is close to that of the gravimetric determination: the error for 0.87-2.60 mg of beryllium does not exceed 0.6 per cent. The method can be used for the determination of 4-10 per cent of beryllium in alloys.

Reagents

Hydrochloric acid, diluted 1 : 1.
Bromide-bromate mixture, 0.1 *M* solution.
Methyl red, 0.1 per cent solution.
The other reagents are the same as in the previous procedure.

Procedure

Separate beryllium diketone (obtained by the previous procedure) on a dense filter, wash several times with water, and transfer (with water) into an Erlenmeyer flask. Add 50 ml of hydrochloric acid, close the flask with a stopper, and allow to stand for 15-20 minutes to dissolve the precipitate. Add water to 150 ml, and 3 drops of methyl red solution, and titrate with a 0.1 *M* solution of the bromide-bromate mixture until the indicator colour vanishes.

1 ml of a 0.1 *M* solution of the bromide-bromate mixture is equivalent to 0.2253 mg of Be or 0.6253 mg of BeO.

GRAVIMETRIC DETERMINATION OF BERYLLIUM IN ALLOYS USING HEXAMMINE COBALTICHLORIDE

The method is based on the formation of a sparingly soluble compound of the carbonate complex of beryllium and hexammine cobalt-ichloride. Ions forming stable ethylene diamine tetraacetates do not interfere with the determination. Nb, Ta, Ti and Sn, which form stable tartrate complexes, do not interfere either if tartaric acid is present. Fluoride ions forming stable fluoride complexes with beryllium ions, and great amounts of U^{VI} ion, precipitating with beryllium in the form of carbonate complexes, interfere with the determination.

The method can be used to determine beryllium in its concentrates, intermediates and alloys, provided the beryllium content of the sample is not less than 1 mg. The error of the determination is ±0.5-2 per cent.

Reagents

Ammonia, 25 per cent solution.
Hydrochloric acid, density 1.19 g/cu.cm and diluted 1:1
Nitric acid, density 1.4 g/cu.cm.
Ammonium chloride, crystalline.
EDTA, saturated solution.
Tartaric acid, 10 per cent solution.
Ammonium carbonate, saturated in the cold solution.
Hexammine cobaltichloride, $[Co(NH_3)_6]Cl_3$. Dissolve 11 g of $CoCl_2 \cdot 6H_2O$ in the minimum possible quantity of water, add 23 ml of a 25 per cent ammonia solution, 7.4 g of ammonium chloride and 1 g of thoroughly ground active carbon. Cool the mixture on ice, add 4 ml of a 30 per cent hydrogen peroxide solution in small portions, cool to room temperature and then heat for 5 minutes on a water bath. Acidify with hydrochloric acid (1 : 1), cool, separate the precipitate on a filter, and dissolve it on the filter with hot water. Heat the solution to 80°C, add hydrochloric acid, density 1.19 g/cu.cm, to a strong acid reaction and cool the solution; separate the precipitate of $[Co(NH_3)_6]Cl_3$ on a filter, wash with ethyl alcohol and dry in air. Prepare a saturated solution of $[Co(NH_3)_6]Cl_3$, and then dilute to prepare a 0.2 per cent solution.
Washing solution, 100 ml of 60 per cent ethyl alcohol containing 1 ml of a 2 per cent solution of hexammine cobaltichloride.
Ethyl ether.
Ethyl alcohol, 96 per cent solution.

Procedure

Dissolve a sample of alloy containing not less than 2 mg of beryllium in 10 ml of hydrochloric acid (1 : 1) with slightly heating, add 3-5 drops of nitric acid and evaporate to dryness. Treat the residue with hydrochloric acid (1 : 1) and evaporate to dryness again. Repeat the dehydration of silicic acid once again.

Separate the precipitate on a filter, evaporate the filtrate almost to dryness and add 1 g of ammonium chloride, 10-15 ml of EDTA solution, 5 ml of tartaric acid, and heat. Add ammonium carbonate solution to the clear solution until the precipitate, which first falls out, is completely dissolved.

Add 1-2 ml of a saturated solution of hexammine cobaltichloride without stirring and then 2-5 drops of ethyl alcohol. Allow the mixture to stand for 2-3 minutes and then slightly shake the beaker without mixing the liquid layers. Add excess reagent solution until an orange-yellow colour develops at the interphase. Now stir the solution and add water to adjust the concentration of the salts to 2-3 per cent. Allow the solution and the precipitate to stand for 90-120 minutes, then filter through a crucible with a porous bottom No. 3 or No. 4 dried in a vacuum desiccator to constant weight. Transfer the precipitate quantitatively into the crucible using 0.2 per cent solution of hexammine cobaltichloride. Rinse the beaker and the crucible two or three times with 3-4 ml portions of the washing solution, then three times with 96 per cent ethyl alcohol (3-ml portions), and two or three times with ethyl ether.

Transfer the crucible containing the precipitate into a vacuum desiccator, start a water-jet ejector, and run it for 25-30 minutes. Carefully admit air into the desiccator through a tap. Weigh the crucible containing the precipitate.

The factor for convertion of $[Co(NH_3)_6][Be_2(CO_3)_2(OH)_3(H_2O)_2]\cdot 3H_2O$ to beryllium is 0.0410, and to beryllium oxide, 0.1138.

TITRIMETRIC DETERMINATION OF BERYLLIUM WITH SALICYLIC OR SULPHOSALICYLIC ACID

Beryllium reacts with salicylic and sulphosalicylic acid to form several stable complex compounds. These dissociate slower than the beryllium compounds with quinalizarin, aluminon, acid alizarin blue BB, acid chrome blue K, chromoxane pure blue BLD (alberon), etc. Said reagents can be used as indicators for beryllium. The expenditure of titrant, a salt of salicylic or sulphosalicylic acid at pH 9-10, is 3 moles per mole of beryllium sulphate. Sulphosalicylic acid is more suitable for the purpose because it is readily soluble in water. Acid chrome blue K should preferably be used as an indicator (the limit of detection is 0.1 μg of Be per ml). Chromoxane pure blue BLD is also recommended (the detection limit is 0.025 μg/ml).

The pH should be adjusted to the required level with an ammonia-chloride buffer solution having the pH of 9-10 or glycolic and veronal buffer solutions with the pH of 9.5-10. Ammonia acetate buffer solution may not be used since a sparingly soluble beryllium hydroxyacetate precipitates and the colour does not sharply change at the point of equivalence.

Mg, Ca, Sr, Ba, Zn, Cd, Mn^{II}, Ni, Co and Hg^{II} do not interfere with the determination of beryllium in the presence of EDTA. The sample can also contain a 80-fold quantity of aluminium, not more than 10 mg of Fe^{III} (ferric hydroxide precipitates with larger quantities of iron) and 40-fold quantity of copper.

Reagents

Sulphosalicylic acid, 0.1 *M* solution.
Chromoxane pure blue, BLD (alberon), 0.1 per cent solution.
Ammonia-chloride buffer solution (pH 9-10); dilute 20 g of NH_4Cl and 100 ml of 25 per cent ammonia solution with water to make 1 litre.
EDTA, 0.1 *M* solution.

Procedure

Place a solution containing from 4 to 15 mg of beryllium in a 50-ml measuring flask and add water to the mark. Using a pipette, transfer 15.0 ml of the solution into a 100-150 ml Erlenmeyer flask, add water to make 50 ml, add 1 ml of EDTA solution to bind traces of calcium, magnesium, etc., 6 drops of alberon and 10 ml of the ammonia-chloride buffer. Heat the mixture to 70-80°C and titrate with sulphosalicylic acid until the red-violet colour changes to pure yellow. 1 ml of sulphosalicylic acid is equivalent to 0.300 mg of beryllium.

To titrate 1.0-5.0 mg of beryllium in the presence of aluminium, copper or ferric iron, add 10 per cent of EDTA solution in excess, adjust the pH to 6, heat to 60-70°C, add 6 drops of alberon, and buffer solution, and titrate with sulphosalicylic acid. If copper is present, titrate the solution until the blue-violet colour changes to pure green.

TITRIMETRIC ARSENATE METHOD OF DETERMINATION OF BERYLLIUM IN MINERALS AND CONCENTRATES

The method is based on the precipitation of the beryllium ion in the form of beryllium-ammonium arsenate in a medium of an acetate buffer solution at pH 5.2 with subsequent iodometric determination of the arsenate ion:

$$BeCl_2 + NH_4Cl + Na_3AsO_3 \rightleftharpoons BeNH_4AsO_4 + 3NaCl$$

$$3BeNH_4AsO_4 + 6KI + 6HCl \rightleftharpoons 3I_2 + 2BeCl_2 + (NH_4)_3AsO_3 + 2K_3AsO_3 + 3H_2O$$

$$I_2 + 2Na_2S_2O_3 \rightleftharpoons Na_2S_4O_6 + 2NaI$$

A single precipitation of beryllium as $BeNH_4AsO_4$ in the presence of EDTA ensures almost complete separation of beryllium from the aluminium ion (Be : Al = 1 : 8), copper ion (1 : 50), nickel ion (1 : 8) and iron ion (1 : 16). In order to retain the titanium ion in solution, hydrogen peroxide is added. The method is used to determine large quantities (over 2 per cent) of beryllium in beryllium concentrates, intermediates, and alloys.

The error of the determination is ±1.5 per cent; the analysis continues from 6 to 8 hours.

Reagents

Potassium hydrofluoride, KHF_2, crystalline.
Sulphuric acid, diluted 1 : 1.
Hydrogen peroxide, 3 per cent solution.
EDTA, saturated solution.
Ammonium nitrate, crystalline.
Sodium arsenate, crystalline.
Ammonia, solution diluted 1 : 1.
Ammonium acetate, 15 per cent solution.
Silver nitrate, 1 per cent solution.
Hydrochloric acid, diluted 1 : 1 and 1 : 3.
Potassium iodide, crystalline.

Sodium thiosulphate, 0.1 *N* solution.

Starch, 0.5 per cent solution prepared for the analysis.

Washing solution: a mixture of 3 per cent ammonium acetate and 3 per cent ammonium nitrate solutions.

Procedure

Grind thoroughly a sample weighing 0.5 g, place it in a platinum dish, add 4-5 g of potassium hydrofluoride and heat until the sample solidifies. Now heat the sample in a muffle furnace, first to dark-red heat and then at 700-800°C to prepare a clear melt. Cool the material and add 15 ml of sulphuric acid. Heat the solution on a sand bath until the fumes of sulphuric acid stop evolving; fuse the residue over a burner at a temperature of 500°C to prepare a clear melt. Cool it and leach with hot water in a 300-ml beaker; dilute the solution with water to make 70-80 ml, add 10 ml of hydrochloric acid, diluted 1 : 1, and heat to dissolve the solid.

Add 2 ml of hydrogen peroxide to the solution, then add 7 ml of EDTA, 10 g of ammonium nitrate, 5 g of sodium arsenate and stir to dissolve the salt. Add ammonia solution until a persistent turbidity develops and then add, with constant stirring, 20 ml of ammonium acetate solution. Boil the solution together with the precipitate for 2-3 minutes over a low flame of a burner and keep on a boiling water bath for 1-2 hours. Cool the mixture, separate the precipitate on a blue ribbon filter, wash the precipitate several times with the washing liquid to the negative reaction for the arsenate ion (with $AgNO_3$ in a neutral medium, the chocolate-brown silver arsenate is absent). Dissolve the precipitate on the filter with hot hydrochloric acid (1 : 3), collect the filtrate in a 300-ml Erlenmeyer flask, wash the filter with the same hydrochloric acid, and add the washings to the filtrate in the flask (the total volume of the dissolved beryllium-ammonium arsenate and the washings should be about 150 ml).

Cool the obtained solution, add 5 g of potassium iodide, close the flask with a stopper and place in the dark for five minutes. Titrate the liberated iodine with sodium thiosulphate until the solution turns pale yellow. Add a few drops of starch solution and continue the titration with sodium thiosulphate until the solution becomes colourless.

1 ml of a 0.1 *N* solution of sodium thiosulphate is equivalent to 0.45 mg of beryllium or 1.25 mg of beryllium oxide.

AMPEROMETRIC TITRATION OF BERYLLIUM WITH URAMYL-N,N-DIACETIC ACID

The beryllium ion reacts with uramyl-N,N-diacetic acid (aminobarbituric-N,N-diacetic acid) to form two compounds, viz., an acid complexonate BeHL, with $\log K = 3.44$, and a neutral complexonate with $\log K = 10.36$ ($\mu = 0.1$, 20°C). Neutral complexonate is predominantly formed at pH 5-6. The current of reagent oxidation at $E = 0.6\text{-}0.8$ V is observed at this acidity at a graphite electrode impregnated in paraffin. The interfering effect of Al, Ca, Mg, $Fe^{II,III}$, Mn^{II}, Ni, Co, Zn, and Cu is removed by EDTA which does not generate oxidation current at $E = 0.6\text{-}0.8$ V. A 200-fold quantity of Fe^{II}, 100-fold quantities of Al, Mg, Fe^{III}, Zn and Cu, a 4-fold quantity of Co, two-fold quantities of Mn^{II} and Ni, and an equal quantity of Ca (by mass) do not interfere with the determination of 0.40 mg of beryllium. The error of the determination of 1.0-64.2 mg of Be is 0.1-2.9 mg respectively. The method is used in the analysis of Be—Al—Mg—Zn alloys containing 0.8-1.7 per cent of beryllium.

Reagents

Hydrochloric acid, diluted 1 : 3.
EDTA, 5 per cent solution.
Uramyl-N,N-diacetic acid, 0.1 *M* standard solution
Acetate buffer solution, pH 5-6.

Procedure

Dissolve a sample weighing 50-100 mg in the minimum possible quantity of hydrochloric acid with heating on a sand bath, transfer the solution into a 25-ml volumetric flask and add water to the mark. Transfer an aliquot containing 1.0-1.5 mg of beryllium into a titration cell, add EDTA in the quantity sufficient to bind all the components of the melt, add the buffer solution, and titrate with uramyl-N,N-diacetic acid at 0.6-0.8 V.

PHOTOMETRIC DETERMINATION OF BERYLLIUM WITH ALUMINON

Aluminon (the ammonium salt of aurin tricarboxylic acid) reacts with the beryllium ion to form a red complex compound with the absorption maximum at 530 nm. The coloured compound is best of all obtained at pH 4.6-5.4; the molar absorption coefficient is 9.2×10^3. If the concentration of beryllium is 2-50 μg in 50 ml of solution, it is necessary to add 2 ml of a 0.4 per cent solution of aluminon. The following elements do not interfere with the determination of beryllium in the presence of 100 mg of EDTA: Cu, Ni, Co, W (1000 μg of each element); Pb (5000 μg), Mn, Mo (500 μg each), Cr^{III}, Cd (200 μg each), Bi (100 μg), Al, Fe^{III}, Ti, Zr, Sb (50 μg each). Niobium can be masked with tartaric acid.

Determining Beryllium in Niobium Alloys

Reagents

Beryllium chloride, standard solution. 1 ml is equivalent to 5 μg of beryllium.
EDTA, 5 per cent solution.
Aluminon, 0.4 per cent solution. Dissolve 1 g of aluminon in 50-70 ml of water, add 2 g of benzoic acid dissolved preliminarily in 25 ml of ethyl alcohol, and

finally 100 ml of acetate buffer solution having the pH of 5.1-5.3. Filter the solution into a 250-ml volumetric flask and add water to the mark. Keep in the dark. The reagent can be used for 7-10 days.

Acetate buffer solution, pH 5.1-5.3. Dilute 34 ml of acetic acid, density 1.05 g/cu.cm, with water to make 100 ml, add 32 ml of a 25 per cent solution of ammonia and add water to make 1 litre.

Potassium pyrosulphate, crystalline.

Ammonia, solution diluted 1 : 3.

Tartaric acid, 10 per cent solution.

Constructing a Calibration Curve

Place 2-ml portions of aluminon solution into 50-ml volumetric flasks, add beryllium chloride standard solution containing 5, 10, 15, 20 and 25 μg of beryllium, 2 ml of EDTA, and 10 ml of the acetate buffer solution into each flask and dilute the solutions with water to the mark. Measure the absorption of the solutions against a blank solution using a green optical filter. Construct the calibration curve using the data obtained.

Procedure

Place a sample weighing 0.1 g in a platinum or a quarts crucible and heat in a muffle furnace to 700-800°C. Fuse the obtained oxides with 1.5-2.0 g of potassium pyrosulphate to obtain a clear melt. Cool the material and leach with 10 ml of tartaric acid in a 100-150 ml beaker. Using a glass rod, remove the crucible carefully, rinse it with 10-15 ml of hot water, add ammonia solution to the beaker contents to adjust the pH to 6 to a universal test paper. Filter the solution into a 100-ml volumetric flask and add water to the mark.

Place 2 ml of aluminon solution and 2 ml of EDTA solution into a 50-ml volumetric flask and then add an aliquot of the alloy solution (5-25 μg Be). Add 10 ml of the acetate buffer solution to the flask, dilute its contents with water to the mark, and measure the absorption of the solution as in constructing the calibration curve.

Find the beryllium content of the aliquot using the calibration curve.

Determining Beryllium in Carbonates of Calcium, Strontium, and Barium Used in Electronic Engineering

The ions of the alkaline earth elements do not react with aluminon and do not therefore interfere with the photometric determination of beryllium. The aluminium ion, which is almost always present in carbonates of the alkaline earth metals, can be masked by EDTA, which is added before the addition of aluminon.

Reagents

Beryllium chloride, standard solution. 1 ml is equivalent to 2 μg of beryllium.

Hydrochloric acid, diluted 1 : 1.

The other reagents are specified in the previous section.

Constructing a Calibration Curve

Place 1, 2, 3, 4 and 5 ml of beryllium chloride standard solution into 5 separate 50-ml volumetric flasks, add 1 ml of aluminon solution and 1 ml of EDTA solution into each flask, then add 10 ml of acetate buffer solution and water to make 25 ml. Heat the solutions to 70-80°C on a sand bath, cool, add water to the mark and stir. Measure the absorption of the solutions by an all-purpose photometer or an absorptiometer at 530 nm against a blank solution. Construct the calibration curve using the data obtained.

Procedure

Place a carbonate sample weighing 0.05-0.1 g into a 50-ml beaker and treat carefully with small portions of hydrochloric acid until CO_2 stops evolving. Evaporate the solution to dryness on a sand bath, dissolve the residue in water, transfer the solution into a 100-ml volumetric flask and add water to the mark. Using a pipette, transfer 0.5 ml of the solution into a 50-ml volumetric flask and carry through all operations as for the construction of the calibration curve.

Determine the beryllium content from the calibration curve.

Determining Beryllium in Bronze

Reagents

Beryllium chloride, standard solution. 1 ml is equivalent to 10 μg of beryllium.
Reagent solution. Place 100 ml of a buffer solution (pH 4.4), which is a mixture of 75 ml of 0.1 *N* solution of CH_3COOH and 25 ml of a 0.1 *N* ammonia solution, into a 250-ml volumetric flask and add 1.25 g of EDTA and 0.1055 g of aurintricarboxylic acid or 0.1182 g of aluminon. When the reagents have been dissolved, add the same buffer to the mark. Keep in a stoppered bottle in the dark. The solution can be used for over two months.
Nitric acid, diluted 1 : 5.
The other reagents are the same as in "Determining Beryllium in Niobium Alloys".

Constructing a Calibration Curve

Place 1, 2, 3, 4, 5 and 6 ml of the standard solution of beryllium chloride into 100-ml volumetric flasks, add water to make 6 ml, add 6 ml of the reagent solution into each flask. Heat the mixture for 5 minutes on a boiling water bath or allow it to stand for 30 minutes at room temperature, then cool, and measure the absorption in a cell with a layer thickness of 1 cm at 520 nm. Prepare a reference solution by mixing equal volumes of the reagent solution and a solution containing the copper ion in the quantity equivalent to the copper content of the aliquot. Construct the calibration curve using the data obtained.

Procedure

Dissolve a sample of bronze weighing 0.10 g in a small amount of nitric acid, transfer the solution into a 100-ml volumetric flask and add water to the mark. Transfer 10 ml of the obtained solution into a 100-ml volumetric flask, add ammonia solution until slight turbidity develops which resolves from the addition of a drop of nitric acid, and add water to the mark. Dilute an aliquot containing

20-50 μg of Be with water to make 6 ml and proceed as in constructing the calibration curve. Determine the beryllium content of the aliquot from the calibration curve.

PHOTOMETRIC DETERMINATION OF BERYLLIUM IN ALUMINIUM ALLOYS WITH BERYLLON IV

Beryllon IV, benzene-2-arsonic [acid-(1-azo-2)-1-hydroxynaphthalene-6-iminodiacetic-3-sulphonic acid, reacts with the beryllium ion to form a crimson compound. The sensitivity of the reagent is 0.02 μg/ml. The compound is formed during five minutes and is stable for about 5 days. The optimum pH is 5-7. The method is used for the determination of 0.01-0.9 per cent of beryllium in aluminium alloys. The interfering effect of aluminium, iron, manganese, copper and nickel can be removed by EDTA.

Reagents

Beryllium sulphate, standard solution. 1 ml is equivalent to 2 μg of beryllium.
Hydrochloric acid, diluted 1 : 1.
Nitric acid, density 1.4 g/cu.cm.
EDTA, 10 per cent solution.
Urotropin, 25 per cent solution.
Beryllon IV, 0.1 per cent solution.

Constructing a Calibration Curve

Place 2, 4, 6, 8, 10 and 12 μg of beryllium in the form of the standard solution into 100-ml volumetric flasks. Add 2 ml of EDTA solution, 10 ml of beryllon IV and 30 ml of urotropin solution into each flask and dilute with water to the mark. Allow the solutions to stand for ten minutes and measure their absorption at 530 nm in a cell with a layer thickness of 1 cm using a blank solution as reference. Construct the calibration curve using the data obtained.

Procedure

Dissolve a sample of an alloy weighing 1 g in 40 ml of hydrochloric acid, first in the cold and then with heating. Add 5-6 drops of nitric acid to ensure complete dissolution. Cool the solution, transfer it into a 250-ml volumetric flask and add water to the mark. Transfer an aliquot containing 3-11 μg of beryllium into a 100-ml volumetric flask and proceed as for the construction of the calibration curve. Determine the beryllium content of the aliquot from the calibration curve.

Note. Add EDTA in the quantity of 1 ml per each millilitre of the aliquot.

FLUORIMETRIC DETERMINATION OF BERYLLIUM IN MINERAL RAW MATERIALS WITH MORIN

Morin reacts with the beryllium ion to form a compound giving green fluorescence when illuminated with ultraviolet light. The reagent is used for the fluorimetric determination of beryllium in mineral raw materials after its separation by either of the following techniques: precipitation of the accompanying ions with sodium hydroxide or sodium sulphide, coprecipitation of beryllium with titanium phosphate, extraction of beryllium acetylacetonate with carbon tetrachloride. The latter method can be used to separate beryllium from iron, aluminium, chromium, copper and vanadium in the presence of EDTA at pH 6-8. 800 mg of iron and 50 mg of titanium do not interfere with the separation of 0.2-2 μg of beryllium and with the determination of beryllium in quantities exceeding 10^{-5} per cent.

Reagents

Beryllium sulphate, standard solution. 1 ml is equivalent to 1 μg of beryllium.
Sulphuric acid, density 1.84 g/cu.cm, diluted 1 : 1 and 1 : 19.
Masking solution. Dissolve subsequently 1 g of potassium (or sodium) metabisulphite, 2.5 g of citric acid, 2.5 g of ascorbic acid and 5 g of EDTA in 80-90 ml of water, and then dilute the solution with water to 100 ml. Prepare the solution immediately before use.
Sodium hydroxide, 10 per cent and 5 per cent solutions.
Alizarine blue, 0.05 per cent solution in ethyl alcohol.
Buffer solution (pH 13). Dissolve 28.6 g of boric acid, 96.0 g of sodium hydroxide in water and dilute to 1 litre.
Morin, 0.02 per cent solution in ethyl alcohol; dilute with ten volumes of alcohols before use.
Nitric acid, density 1.4 g/cu.cm.
Hydrofluoric acid, 40 per cent solution.
Fusing mixture. Heat crystalline sodium tetraborate in a dish to prepare a foaming mass. Cool it and grind. Mix the powder with anhydrous sodium carbonate in the ratio 1 : 3. Keep in a closed bottle.
Potassium hydrofluoride, crystalline.
Hydrochloric acid, density 1.17-1.19 g/cu.cm.
EDTA, 15 per cent solution.
Acetylacetone.
Phenol red, 0.1 per cent solution in ethyl alcohol.
Ammonia, diluted 1 : 1.
Carbon tetrachloride.
Washing liquid. A 0.1 per cent solution of EDTA, pH about 7.
Perchloric acid, 57 per cent solution.

Constructing a Calibration Curve

Place 0.1-1.0 ml (gradient, 0.1 ml) portions of the standard solution of beryllium sulphate in separating funnels and add sulphuric acid (1 : 19) to make 2 ml in each funnel. Then add 2 ml of the masking solution, neutralize with a 10 per cent sodium hydroxide solution until Congo red paper begins reddening. Add 5 drops of alizarine blue and neutralize with a 5 per cent sodium hydroxide solution until the colour of the solution changes from yellow-brown to green-blue. Add 1 ml of a buffer solution, 1 ml of morin solution, add water to make 10 ml (or 12 ml if the aliquot is 5 ml), allow to stand for 5 minutes and measure the intensity of fluorescence. Construct the calibration curve using the data obtained.

Procedure

Place a sample in a platinum dish, add 1 ml of nitric acid and 1 ml of sulphuric acid, density 1.84 g/cu.cm, 5-10 ml of hydrofluoric acid, heat, and evaporate to dryness. Depending on the composition of the sample, decompose it by one of the methods described below, with subsequent extraction.

Fusion with a Mixture of Sodium Carbonate and Sodium Tetraborate. Add 3-6 g of the fusing mixture to the dry residue, and heat to 1000°C until a clear liquid melt is formed (10-15 minutes). Cool and leach with 10 ml of sulphuric acid (1 : 1). Add 3-4 four volumes of water, filter into a 25-250 ml volumetric flask and add water to the mark.

Fusion with Potassium Hydrofluoride. Add 5-8 g of potassium hydrofluoride to the residue in the dish, heat on a hotplate until the liquid solidifies, transfer into a muffle furnace heated to a temperature of 850-900°C and heat to prepare a clear melt. Cool it, add 8-10 ml of sulphuric acid, density 1.84 g/cu.cm, and heat on a hotplate to decompose the residue completely. Evaporate the mixture until the fumes of sulphuric acid stop evolving, heat the residue at 600-650°C to obtain a clear melt, and cool it. Leach with hot water containing 5-10 ml of hydrochloric acid, heat to dissolve the salts, filter into a 25-250 ml volumetric flask, and add water to the mark.

Extraction of Beryllium Acetylacetonate. Place an aliquot of the solution into a separating funnel, add 10-15 ml of EDTA solution, 0.25 ml of acetylacetone and mix. Add three drops of phenol red solution, ammonia to pH 6-8 (until red colour develops) and 10 ml of carbon tetrachloride. The extraction continues for 30 seconds. Transfer the organic layer into another separating funnel and add 2-3 drops of acetylacetone to the aqueous layer. Neutralize with ammonia to pH 6-8 and extract again with 10 ml of carbon tetrachloride. Wash the extracts with 20 ml of the washing liquid for one minute, transfer the organic layer into a 50-ml beaker, add 3 ml of nitric and 3 ml of perchloric acids, heat gently on a hotplate to remove carbon tetrachloride, rinse the beaker with water and evaporate to obtain moist salts. Dissolve the residue in 2-3 ml of water and determine beryllium as for the construction of the calibration curve.

Find the beryllium content of the sample from the calibration curve.

Notes. 1. The following conditions are recommended (depending on the anticipated beryllium content):

Anticipated beryllium content, %	Weight of sample, g	Dilution, ml	Aliquot, ml
0.00002-0.0002	1.0	50	20
0.00005-0.001	0.5	50	10
0.0001-0.002	0.25	50	10
0.0002-0.004	0.1	25	5
0.0005-0.01	0.1	50	5
0.001-0.02	0.1	200	5
0.002-0.05	0.1	250	5

2. If the solution contains much magnesium, molybdenum (to 10 mg), aluminium, calcium and manganese (to 25 mg), a masking solution (2.5 ml) should be added.

DIFFERENTIAL PHOTOMETRIC DETERMINATION OF BERYLLIUM WITH *p*-NITROBENZENEAZOORCINOL

The reagent reacts with beryllium in an alkaline medium to give a red compound whose solutions have the maximum absorption at 510 nm. Cu, Zn and Co interfere with the determination of small quantities of beryllium since they form coloured precipitates with the reagent, large quantity of magnesium also interferes with the determination. These ions can be masked by EDTA. The differential method can be used to determine 1-2 mg of beryllium in 100 ml of solution with a relative error of ±0.1 per cent in the presence of a 2.5-fold quantity of U^{VI}, a ten-fold quantity of Al and a 50-fold quantity of F^-.

Reagents

Beryllium sulphate, standard solution. 1 ml is equivalent to 0.1 mg of beryllium.
p-Nitrobenzeneazoorcinol, 0.025 per cent solution. Dissolve 0.125 g of the reagent in 300 ml of water and 25 ml of 2 *N* in solution of NaOH. Stir for 4-6 hours until the reagent is fully dissolved and add water to 500 ml.
Sodium hydroxide, 2 *N* solution.
Buffer solution, pH 12.7. Dissolve 178 g of sodium citrate, 92 g of sodium tetraborate and 143 g of sodium hydroxide in 600 ml of water and dilute to one litre.

Constructing a Calibration Curve

Place 10, 11, 12, 13, 14, 15 and 16 ml of the standard solution of beryllium sulphate in 100-ml volumetric flasks. Add 20 ml of the reagent solution, sodium hydroxide to adjust the pH to 5-6, 10 ml of the buffer solution, and water to the mark. Allow the mixtures to stand for ten minutes and then measure their absorption at 510 nm in cells with the layer thickness of 1 cm using a solution prepared by the same procedure but containing 1 mg of beryllium in 100 ml as a reference solution. Construct the calibration curve using the data obtained.

Procedure

Place an aliquot containing 1.1-1.6 mg of Be in a 100-ml volumetric flask and proceed as described for the construction of the calibration curve. Measure the absorption in the specified conditions using a solution containing 1 mg of Be and prepared by the procedure described for the construction of the calibration curve as a reference solution. Determine the beryllium content from the calibration curve.

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Scandium

Scandium, Sc, has the positive valency of 3. The standard electrode potentials in an aqueous medium at 25°C are as follows (with reference to the standard hydrogen electrode potential):

$$Sc \rightleftharpoons Sc^{3+} + 3e^- \qquad -2.077\ V$$

$$Sc + 3H_2O \rightleftharpoons Sc(OH)_3 + 3H^+ + 3e^- \qquad -1.787\ V$$

The ion Sc^{3+} is colourless. Its properties are more like those of Al^{3+} than of Y^{3+} or of the lanthanides.

Like aluminium hydroxide, the hydroxide of scandium has amphoteric properties in an aqueous solution and can dissociate like an acid and a base.

The acid dissociation of the hydrated ion of scandium can be expressed by the following expression:

$$[Sc(H_2O)_6]^{3+} + H_2O \rightleftharpoons [Sc(H_2O)_5OH]^{2+} + H_3O^+$$

The dissociation constant at 20°C is 1.17×10^{-5}.

The proton dissociation is complicated by the formation of dimers (and probably of higher polymers):

$$2[Sc(H_2O)_5OH]^{2+} \rightleftharpoons [Sc(H_2O)_5OH]_2^{4+}$$

The constant of dimerization is $(13.8\text{-}2.17) \times 10^3$.

The degree of polymerization increases with the concentration of the ion OH^-.

The constants of acid dissociation and dimerization strongly depend on temperature and on the ionic strength of the solution.

Freshly precipitated $Sc(OH)_3$ is readily soluble in dilute acids with the formation of scandium salts, and much worse in concentrated alkali and ammonia solutions, solutions of NH_4Cl and NH_4NO_3, with the formation of the scandate ion and complex ammonia ion $[Sc(NH_3)_6]^{3+}$ respectively.

The scandium ion begins precipitating from chloride solutions (0.005 *M*) or sulphate solutions (0.0025 *M*) at pH 4.8-4.9 in the form of basic salts. The precipitation stops at pH 5.45 and 5.10 respectively. The composition of the precipitates approximately corresponds to the formulas $Sc(OH)_2Cl \cdot xH_2O$ and $Sc(OH)SO_4 \cdot xH_2O$. Basic chloride or sulphate of scandium pass into the hydroxide if NaOH is added in the quantity equivalent to that of scandium [1].

Ammonium carbonate or carbonates of the alkali metals precipitate the basic carbonate $Sc(OH)CO_3 \cdot H_2O$ from scandium salt solutions in the form of a bulky white amorphous precipitate. The precipitate is moderately soluble in cold solutions of $(NH_4)_2CO_3$ and Na_2CO_3; the solubility sharply increases with heating and double salts are formed. The compounds $NH_4Sc(CO_3)_2 \cdot 2H_2O$, $2Sc_2(CO_3)_3 \times \times (NH_4)_2CO_3 \cdot 6H_2O$ and $Sc_2(CO_3)_3 \cdot 4Na_2CO_3 \cdot 6H_2O$ can be isolated in the crystalline form. These are soluble in concentrated solutions of $(NH_4)_2CO_3$ and Na_2CO_3. The double carbonates are hydrolyzed when dissolved in water.

Scandium oxide, Sc_2O_3, is a fine white crystalline powder. It is very difficultly soluble in cold dilute acids, better soluble with heating, and readily soluble in concentrated acids. Scandium oxide is obtained by calcining scandium hydroxide, carbonate, nitrate or oxalate.

Scandium salts are hydrolyzed in aqueous solutions better than the salts of the lanthanides, but worse than similar aluminium salts.

Scandium forms complex compounds in which it has the coordination number of 6. Double salts of scandium (fluorides, oxalates, carbonates) and its complex compounds with various organic ligands are known. The tendency to form complexes is more marked in scandium than in the lanthanides or aluminium. In this respect scandium is closer to zirconium, and to thorium in particular. An aqueous solution of scandium sulphate, $Sc_2(SO_4)_3$, is the medium in which a scandium salt of a complex acid, $Sc[Sc(SO_4)_3]$, exists.

There are no sufficiently selective reagents for the detection or determination of scandium, because its properties are intermediate between those of aluminium and the yttrium subgroup elements. Moreover, scandium is similar in many respects to other tri- and tetravalent elements, such as iron or thorium. Scandium is therefore usually separated by precipitation as basic scandium-ammonium tartrate with subsequent extraction by ether as the thiocyanide complex.

Scandium chloride is 10^3-10^4 times more soluble in concentrated hydrochloric acid (in the presence of ethyl ether) than chlorides of yttrium, lanthanides or aluminium. Scandium can therefore be separated quantitatively from these elements. When $AlCl_3$, YCl_3 and the chlorides of lanthanides are precipitated from an aqueous-ether solution, the crystalline precipitate does not coprecipitate $ScCl_3$. Scandium chloride is extractable with tributyl phosphate. Scandium can be separated from the lanthanides by a one-step extraction from 5-8 *M* solutions of hydrochloric acid.

When ferric iron is extracted from 6 *N* hydrochloric acid with ethyl ether, the scandium ion practically quantitatively remains in the aqueous phase.

The solubility of ScF_3 in water and mineral acids is close to that of ThF_4. But scandium fluoride is readily soluble in solutions of KF, NaF, NH_4F with the formation of the hexafluoscandates, K_3ScF_6, Na_3ScF_6 and $(NH_4)_3ScF_6$. The fluorides of thorium and lanthanides are insoluble in excess solutions of fluorides of the alkali metals. But various factors interfere with the separation of scandium from the lanthanides.

Scandium thiocyanide obtained by adding ammonium thiocyanide to $ScCl_3$ solution can be extracted by ether. The distribution coefficient in optimum conditions (20-30 g of NH_4SCN per 100 ml of 0.5-1 *M* solutions of hydrochloric acid in the absence of SO_4^{2-} and PO_4^{3-} ions) is 16-17.4. From 94.1 to 94.6 per cent of scandium pass into the organic phase in these conditions. The method can be used to separate scandium ions from those of the lanthanides Zr, Hf, Th, Fe^{II}, Mn, Be, Mg, Ti and U.

Scandium nitrate is well extractable by ether from solutions saturated with $LiNO_3$. The distribution coefficient of $Sc(NO_3)_3$ in the ether extraction from a 1 *N* solution of HNO_3 saturated with $LiNO_3$ at 35°C is 4.97. To 83.3 per cent of scandium nitrate are extracted in these conditions. Scandium nitrate is poorly extracted in the absence of $LiNO_3$.

Scandium nitrate is well extracted by tributyl phosphate from nitric acid solutions. The distribution coefficient in extraction from 15.6 *N* solution of HNO_3 is over 1000. Scandium can therefore be separated from the lanthanides.

Sodium pyrophosphate precipitates $Sc_4(P_2O_7)_3$. It is practically insoluble in mineral acids and only slightly soluble in hot sulphuric acid. Scandium pyrophosphate very slowly dissolves with heating in the presence of a great excess of sodium pyrophosphate, while the pyrophosphates of heavy metals are readily soluble in these conditions. Scandium pyrophosphate is only soluble in the presence of sodium fluoride and in ammonia solution of ammonium carbonate, and it reprecipitates when acetic acid or ammonia is added.

Oxalic acid or ammonium oxalate precipitates scandium from solutions of its salts in the form of a white crystalline mass readily soluble in excess ammonium oxalate. It is impossible to precipitate scandium quantitatively as the oxalate $Sc_2(C_2O_4)_3$. The solubility of the salt is 156 mg in one litre of water at 25°C. It is much more soluble than the oxalates of the lanthanides.

Ammonium tartrate reacts with the scandium in the presence of excess ammonia to form ammonium-scandium tartrate, whose approximate formula is $NH_4OOCCH(OH)CH(OH)COOSc(OH)_2 \cdot nH_2O$. The completeness of precipitation depends on the pH of the solution. The minimum solubility of the ammonium-scandium tartrate is at pH 7 (0.25 mg of Sc_2O_3 per litre). The solubility increases with acidity or alkalinity of the medium. The solubility of ammonium-scandium tartrate markedly differs from that of similar compounds of Zr, Hf, Th, Mn, Fe^{III}, Al, Ti and the elements of the cerium subgroup. Ammonium tartrate is used for separation of scandium.

Inositolhexaphosphoric acid, $C_6H_6O_6[P(OH)_2OP(OH)_2]_3$, reacts with the scandium ion to form a very sparingly soluble compound

$C_6H_6O_6[P(O_3Sc)OP(O_3Sc)]_3$; its white flakes are insoluble even in concentrated hydrochloric acid, HNO_3, a mixture of HCl and HNO_3 or H_2O_2. The reagent precipitates also the ions of Ti, Zr, Hf and Th The precipitates are insoluble in acids. Unlike scandium and thorium compounds, the compounds of zirconium and hafnium are readily soluble in oxalic acid, the titanium compound is soluble in the presence of fluorides of the alkali metals. A salt of thorium with inositolhexaphosphoric acid is readily soluble in the presence of nitrilotriacetic acid. Inositolhexaphosphoric acid is used for the detection and determination of scandium.

Benzene seleninic acid precipitates the scandium ions quantitatively and it is therefore used for the gravimetric determination of scandium [2, 3].

Mandelic acid, $C_6H_5CH(OH)COOH$, precipitates the scandium ion quantitatively from solutions at pH 1.8-3.2 [4]. The composition of the precipitate corresponds to the formula $H_3[Sc(C_8H_6O_3)_3]\cdot nH_2O$. It is soluble in ammonia with the formation of $(NH_4)_3[Sc(C_8H_6O_3)_3]$. Mandelic acid is used to separate scandium from the lanthanides and small quantities of thorium. The precipitate usually contains admixtures of mandelic acid and it is therefore calcined to Sc_2O_3 at 800°C.

8-Quinolinol precipitates a lemon-yellow compound $Sc(C_9H_6ON)_3\cdot$ $\cdot C_9H_7ON$ from an aqueous solution of $Sc(ClO_4)_3$ at pH 7.5. To precipitate the scandium ion, excess 8-quinolinol is first added, and then a buffer mixture (ammonium acetate and ammonia). The filtered and washed precipitate is dried at 100-110°C and weighed. All ions precipitated by 8-hydroxyquinoline interfere with the determination of scandium. The compound of scandium with 8-quinolinol is soluble in benzene, chloroform and other organic solvents.

Scandium reacts with the I^- ion and diantipyrylmethane to form a complex compound extractable by chloroform. This makes it possible to separate scandium from the accompanying elements [5].

Alizarine, morin, and aurintricarboxylic acid react with the Sc^{3+} ion as with Al^{3+}.

Quinalizarine reacts with the Sc ion and also with the ions of Be, Mg and lanthanides, to form blue compounds. Scandium quinalizarinate differs from the corresponding compounds of beryllium, and magnesium in that it can be separated quantitatively from the aqueous phase with ethyl acetate or isoamyl alcohol. Quinalizarine is used for the detection of scandium.

Schiff base reacts with the scandium ion in a neutral or a weak acetic acid solution to form a yellow solution or a bright yellow precipitate [6]. In order to detect the scandium ion, it is not recommended to use a commercial reagent, since it is only sparingly soluble. Instead, it is recommended to prepare the reagent by adding salicylic aldehyde and then *o*-aminophenylarsonic acid to the sample solution. The limit of detection is 1 μg of Sc in 1 ml of solution (limit dilution 1 : 10^6). The ions of Al, Y, lanthanides, In, and Tl^I, and also the ions of divalent elements do not interfere with the determination of scandium. The gallium ion forms a yellow precipitate. The ions of Ti, Zr, Nb, Th, U^{IV}, Hf, Sn^{IV}, Ta, Sb, Bi, Fe^{III}, V^{V}, and Pd^{II} interfere.

Arsenazo III is used for the photometric determination of 0.001-0.1 per cent of scandium in alumosilicates, coal ash, and cassiterites after its isolation and concentration [7].

Derivatives of 2,3,7-trihydroxy-6-fluorone react with the scandium ion to form coloured compounds. The most sensitive derivative is 9-propyl-2,3,7-trihydroxy-6-fluorone [8]. This reagent forms a red compound with scandium at pH 3-7. The red precipitate is formed at a relatively high concentration of the scandium ion. Gelatine stabilizes colloidal solutions of this compound. Weak acid solutions of the reagent are yellow with yellowish-green fluorescence. The optimum pH at which the coloured scandium compound is formed is 5.6. The absorption of the reagent solution increases at pH 6. Its maximum absorption is at 480 nm, while of the scandium compound, at 510 nm. The reagent reacts with the scandium ion in the ratio of 1 : 1.

Sulphonazo [9], chlorophosphonazo III [10, 11], xylene orange [12, 13], arsenazo I [14] and 2,4-sulphochlorophenol P [15] react with the scandium ion to give coloured compounds and are therefore used for its photometric determination.

Scandium can be determined quantitatively by the emission spectral and X-ray spectral analysis.

SELECTIVE EXTRACTION AND COMPLEXOMETRIC TITRATION OF SCANDIUM

The scandium ion reacts in a moderately acid medium with diantipyrylmethane in the presence of the iodide ion to form a mixed complex, which is readily soluble in chloroform and dichloroethane. In these conditions, the lanthanides and also Fe, Cr, Mn, Mg, Ba, Ca, Co, Ni, and As do not form compounds soluble in chloroform or dichloroethane and do not interfere with the determination of scandium. The ions of Hf^{IV} and Zr^{IV} react like scandium but they can be easily masked with EDTA. Satisfactory results have been obtained with liberation of 8 mg of scandium from a solution containing 1 g of Al, Cr, Co, Mn, Fe, Y, La, Be, Ni or Mg, 0.1 g of Ce, Ba, Ti and lanthanides, and 0.2 g of Hf or Zr Cd, In, Hg, Bi and Sb form stable iodide complex anions and interfere.

Scandium is re-extracted by ammonia solution of EDTA and the procedure ends complexometrically.

Reagents

Potassium iodide, crystalline.
Ascorbic acid, crystalline.
Chloroform.
Diantipyrylmethane.

EDTA, 0.2 *M* and 0.025 *M* solutions.
Zinc sulphate, 0.025 *M* solution.
Ammonia, 25 per cent solution.
Indicator mixture (eriochrome black ET00 and sodium chloride, 1 : 100).
Buffer solution, pH 10. Mix ammonia with NH_4Cl solution.

Procedure

Isolation of Scandium by Extraction. Transfer quantitatively the solution containing 2-30 mg of Sc (0.75-1.25 *N* with respect to HCl) into a 60-ml separating funnel, and add 2 g of potassium iodide, 0.2 g of ascorbic acid (to preclude oxidation of the iodide ion), 15 ml of chloroform and 2.5 g of diantipyrylmethane. The total volume of the aqueous phase should be 15-30 ml. Shake the mixture on a mechanical shaker for 15-20 minutes, allow the phases to separate and transfer the chloroform layer into another separating funnel. Repeat the extraction in the first funnel with 15 ml of chloroform and 1-2.5 g of diantipyrylmethane. Wash the aqueous phase of the second extraction with 10 ml of chloroform, join the chloroform extracts and pass them through a dry paper filter into a separating funnel.

Note. If the solution contains not more than 50 mg of zirconium or hafnium, add 3-4 ml of a 0.2 *M* EDTA solution to mask them. Shake the mixture for a short time and extract scandium.

Complexometric Determination of Scandium. Add 40 ml of a 0.025 *M* solution of EDTA to the chloroform extract in the separating funnel. Then add 3 ml of ammonia solution and shake for 15-20 minutes. Separate the chloroform layer and wash with water. Add the washings to the filtrate, then add 15 ml of the buffer solution with pH 10, and the indicator mixture (on the tip of the spatula), and titrate excess EDTA with zinc sulphate until the blue solution turns vine-red.

1 ml of a 0.0250 *M* solution of EDTA is equivalent to 1.124 mg of scandium.

GRAVIMETRIC DETERMINATION OF SCANDIUM IN THE PRESENCE OF ZIRCONIUM WITH BENZENESELENINIC ACID

Benzeneseleninic acid and its ammonium salt precipitate scandium from neutral and weak acid solutions in the form of a white crystalline compound readily soluble in mineral acids. When dried at 105-120°C, its composition is $(C_6H_5SeO_2)_3Sc$. The scandium content is 7.38 per cent. The conversion factor for scandium is 0.0738. Ammonia destroys the compound to form scandium hydroxide. When heated to 600°C, it is fully converted into scandium oxide.

Zirconium forms a similar compound with benzeneseleninic acid but in a more acid medium. During the determination, zirconium is first precipitated; scandium is then precipitated from the filtrate.

The method ensures satisfactory results with the Sc : Zr ratio of 1 : 10 and less. The limit of detection is 5 μg/ml of Sc.

Reagents

Benzeneseleninic acid, 20 per cent and 0.5 per cent solutions.
Hydrochloric acid, 1 *N* solution.
Ammonia, solution diluted 1 : 1.
Methyl orange, indicator solution.

Procedure

Determination of Scandium in Solution of Pure Salt. Dilute the solution containing 0.1-3 mg of scandium with water to make 50 ml in a 100-ml beaker, heat on a water bath, and add a drop of methyl orange. Neutralize the solution with ammonia until the indicator colour changes. Add 5 ml of a 20 per cent solution of ammonium benzeneseleninate to the hot solution and cool to room temperature. Separate the precipitate in a glass microcrucible with a porous bottom No. 4, wash with 10-15 ml of double-distilled water and with the same quantity of ethyl alcohol, dry at 105°C for 20 minutes and weigh.

Determination of Scandium in the Presence of Zirconium. Add hydrochloric acid to the solution containing 0.1-3 mg of scandium and not more than 10-fold quantity of zirconium to make 50 ml and heat. To precipitate zirconium, add 5 ml of a 20 per cent solution of ammonium benzeneseleninate, then cool, separate the precipitate on a blue ribbon filter, and wash thoroughly with a 0.5 per cent solution of ammonium benzeneseleninate. Evaporate the filtrate containing scandium on a water bath to 50 ml and determine scandium as described above.

PHOTOMETRIC DETERMINATION OF SCANDIUM WITH SULPHONAZO IN THE PRESENCE OF RARE EARTHS

Sulphonazo, or bis[-3 (8-amino-1-hydroxy-3,6-disulpho-2-naphthylazo)]-4-hydroxyphenyl sulphone, is a highly sensitive and selective reagent for the scandium ion. Its violet-pink solutions turn violet or blue-violet when scandium salts are added. The new colour persists for many hours. The absorption of the solutions obeys the Bouguer-Lambert-Beer law for the concentrations of scandium in the range of 5-80 μg in 25 ml of solution. The absorption maximum is at 610-620 nm. The reaction should be carried out at pH 4.0-5.0 (urotropine buffer solution). If the acetate buffer solution is used (pH 5.0-5.5) the formation of the complex is slightly slowed down but the selectivity of the reagent increases.

The limit of determination is 0.004 μg of scandium in 1 ml.

The ions of the alkaline, alkaline earth metals, lanthanides, Mn, Tl, Be, Cr^{III}, Cd, Pb, Ge, Mo, and Re do not interfere with the determination. The ions of Fe^{III}, Ti, Zr and of some other elements, which are hydrolized in the conditions of the determination, should be removed. The ions of V^{V}, Co, and Ga which form intensely coloured compounds with sulphonazo, and also the ion of Au^{III}, which decolourizes the reagent, interfere. The ions of In, Cu, U^{VI}, Ni, Al, Zn and also phosphate, citrate, and tartrate ions should be absent.

The method is applicable to the determination of scandium in silicate rock and coal ash after isolation of scandium by the tartrate method.

Reagents

Scandium salt, standard solution. 1 ml is equivalent to 10 μg of Sc.

Sulphonazo, 0.03 per cent solution.

Buffer mixture. Dissolve 8.2 g of sodium acetate in water, add 100 g of urotropine, mix, and filter if necessary. Acidify with hydrochloric acid to adjust the pH to 5.0-5.2 and add water to 1 litre.

Constructing a Calibration Curve

Place 1, 2, 3, 4 and 5 ml of the standard solution of scandium salt into 25-ml volumetric flasks and add 3 ml of sulphonazo and 5 ml of buffer mixture in each flask. Add water to the mark and allow the solutions to stand for 10-15 minutes. Measure the absorption of the solutions using a blank solution as the standard. Construct the calibration curve using the data obtained.

Procedure

Add the requisite reagents into the solution as for the construction of the calibration curve, measure the absorption of the solution, and determine the scandium content from the calibration curve.

PHOTOMETRIC DETERMINATION OF SCANDIUM IN WOLFRAMITE WITH CHLOROPHOSPHONAZO III

Chlorophosphonazo III, {2,7-bis[(4-chloro-2-phosphinic acid phenyl-azo)-1,8-dihydroxynaphthalene-3,6-disulphonic acid]} reacts with the scandium ion to form a specifically coloured compound. If the concentration of scandium is high, a precipitate falls out. The colour develops almost instantaneously and persists for 24 hours. The absorption maximum is at 640 and 690 nm. The optimum range of pH is from 2 to 4.

The limit of scandium determination is 0.1-0.2 μg in 1 ml.

The reagent reacts with the ions of Th, Zr, Ti, Nb, Ta, U and lanthanides. The interfering effect of Ti, Zr, Fe and Al can be considerably reduced by adding tartaric acid. The fluoride, oxalate, ethylenediaminetetraacetate and phosphate ions interfere with the determination. The nitrate and sulphate ions, as well as a 20 000-fold quantity of the tartrate ion (pH 2-2.5) can be present in solution.

The method can be used for the determination of scandium in wolframite after decomposition of the sample by fusion with sodium carbonate, treatment of the residue with sulphuric acid and extraction of scandium as its thiocyanide with ethyl ether. The elements which can be completely or partly extracted with ether do not interfere with subsequent determination.

Reagents

Sodium carbonate, crystalline and 1 per cent solution.
Sulphuric acid, density 1.84 g/cu.cm.
Formaldehyde.
Ammonia, 25 per cent solution.
Hydrochloric acid, 0.1 and 1 *N* solutions, and diluted 1 : 1.
Ammonium thiocyanide, crystalline.
Ascorbic acid, crystalline.
Ethyl ether.
Nitric acid, density 1.4 g/cu.cm.
Acetate buffer, pH 2.5.
Tartaric acid, 10 per cent solution (neutralized with sodium hydroxide to pH 2.5).
Chlorophosphonazo III, 0.05 per cent solution.
Scandium chloride, standard solution. 1 ml is equivalent to 5 μg of scandium.

Constructing a Calibration Curve

Place the standard solution of scandium into 25-ml volumetric flasks in quantities equivalent to 5, 10, 15, 20 and 25 μg of Sc. Add 5 ml of tartaric acid, 1 ml of chlorophosphonazo III and 5 ml of the acetate buffer into each flask. Add water to the mark, mix, and measure the absorption of each solution against a reference solution containing the same reagents except the scandium salt. Construct the calibration curve using the data obtained.

Procedure

Grind thoroughly a sample weighing 0.005-0.10 g and containing from 150 to 300 μg of scandium. Fuse the sample in a platinum or nickel crucible with 1 g of sodium carbonate and leach with hot water in a 100-ml beaker. Decant the solution onto a blue ribbon filter, wash the precipitate twice with small portions of sodium carbonate, transfer back into the beaker by a jet of hot water from a washing bottle and evaporate to dryness on a sand bath. Treat the dry residue with 3-5 ml of sulphuric acid, heat on a sand bath, cool, add with stirring 10 ml of water and 3-5 drops of formaldehyde to reduce manganese, and heat the solution to remove excess formaldehyde. The solution becomes colourless.

Add water to 25-30 ml, filter, and add ammonia to the filtrate until the faint odour is felt. Separate the hydroxides on a white ribbon filter and dissolve in hot hydrochloric acid (1:1) with subsequent washing the filter with 1 *N* hydrochloric acid. Evaporate the hydrochloric acid solution on a sand bath almost to dryness, dissolve the residue in 5 ml of 0.1 *N* hydrochloric acid, transfer into a 25-30 ml separating funnel, add 3 g of ammonium thiocyanide and a few grains of ascorbic acid (to reduce ferric iron), and shake with 10 ml of ethyl ether. Repeat the extraction procedure two times, each time adding 1 ml of 1 *N* hydrochloric acid. Join the ether extracts, acidify with 2 ml of 1 *N* hydrochloric acid and evaporate to dryness on a water bath in a 100-ml beaker.

Treat carefully the dry residue with 1 ml of nitric acid, cover with a watch glass and heat on a water bath to destroy the orange-red decomposition products of thiocyanic acid. Evaporate the solution almost to dryness, dissolve the residue in 5 ml of 0.1 *N* hydrochloric acid, transfer the solution into a 50-ml volumetric flask, add water to the mark and stir. Using a pipette, transfer a 2-4 ml aliquot of the solution into a 25-ml volumetric flask, and add the reagents as described for the construction of the calibration curve.

Determine the scandium content of the solution from the calibration curve.

PHOTOMETRIC DETERMINATION OF SCANDIUM IN MAGNESIUM ALLOYS USING XYLENOL ORANGE

Xylenol orange reacts with the scandium ion in an acid medium (pH 1.5-5) to form a red-violet soluble compound. Own colour of the reagent in an acid medium is yellow. At pH higher than 5.5 the colour changes to red-violet. The full colour develops in ten minutes after mixing the solution, and persists for two days. The absorption of the solution obeys the Bouguer-Lambert-Beer law in a wide range of scandium concentrations.

The limit of determination is 0.1 μg of scandium in 1 ml.

The determination is carried out at pH 1.5. The ions of the alkaline earth elements, La, Pr, Nd, Sm, Ce^{III}, Y, Zn, Cd, Al, Mn, and Fe^{II} do not interfere with the determination, while Zr, Th, In, Ga and Bi, which form coloured compounds with the reagent, interfere. The ions of tervalent iron and tetravalent cesium are first reduced by ascorbic acid.

The method is used to determine scandium in magnesium metal and magnesium alloys without separation of their components.

Reagents

Scandium nitrate, standard solution, 1 ml is equivalent to 10 μg of scandium.
Xylenol orange, 0.05 per cent solution.
Buffer solution, pH 1.5. Mix 263 ml of 0.2 *N* hydrochloric acid with 500 ml of 0.2 *N* potassium chloride solution.
Sodium acetate, 50 per cent solution.
Ascorbic acid, 2 per cent solution prepared for the test.
Hydrochloric acid, diluted 1 : 1.

Constructing a Calibration Curve

Place the standard solution of a scandium salt into five 50-ml volumetric flasks in quantities equivalent to 10, 20, 30, 40 and 50 μg of scandium. Add 5 ml of the buffer solution, 5 ml of xylene orange solution, and water to the mark.

In 20 minutes, measure the absorption of the solutions on an absorptiometer with a green filter using a blank solution as the standard. Construct the calibration curve using the data obtained.

Procedure

Dissolve a sample of alloy weighing 1 g (containing from 0.002 to 0.005 per cent of scandium) in 10-20 ml of hydrochloric acid in a 100-ml beaker. Evaporate the solution to 10 ml, transfer the residue quantitatively into a 50-ml volumetric flask, rinse the flask walls with small portions of water, add 5 ml of ascorbic acid solution, sodium acetate solution until congo paper turns lilac, 5 ml of the buffer solution and 5 ml of xylene orange solution. Finally, add water to the mark. Allow the solution to stand for 20 minutes and measure its absorption as for the construction of the calibration curve. Determine the scandium content from the calibration curve.

Note. If the scandium content is over 0.005 per cent, decrease the size of he sample. Determine scandium in an aliquot containing 20-40 μg of scandium.

PHOTOMETRIC DETERMINATION OF SCANDIUM WITH ARSENAZO I

Arsenazo I reacts with the scandium ion in a weak acid medium to form a soluble compound with the absorption maximum at 570 nm (as measured against the reagent solution) and the molar extinction coefficient of 1.7×10^4. The optimum pH is 6.1-6.3 (acetate buffer solution), the reagent concentration, 2-5 ml of 0.1 per cent solution in 50 ml of solution. The selectivity of the reaction is low. The ions of Al, Cr^{III}, Cu, Fe^{III}, lanthanides, Th, Ti, U, Zr, F^-, and PO_4^{3-} interfere with the determination. In order to increase selectivity, scandium is extracted by tenoyltrifluoroacetone in xylene from a solution with the pH 1.5, separating scandium from Mg, Ca, lanthanides, Zr, Co, Fe^{II}, As^{III}, Mn, Pb, Y, Zn, SO_4^{2-}, F^-, PO_4^{3-}. Mo^{VI}, Ti, Cu, Al, Fe^{III} can be separated from scandium by extraction with 8-hydroxyquinoline in chloroform. U^{VI} can be separated from scandium by the anion-exchange process in a medium of 8 *M* HCl, and Th^{IV} in a medium of 8 *M* HNO_3. Scandium can be determined with arsenazo I in the presence of thorium in a solution with the pH 1.7. The summary quantity of thorium and scandium can be determined at pH 6.1.

Reagents

Scandium chloride, standard solution, 1 ml is equivalent to 10 μg of scandium.
Arsenazo I, 0.1 per cent solution.
Acetate buffer solution, pH 6.1. Mix 10 ml of 1 *M* solution of CH_3COOH with 320 ml of 1 *M* solution of CH_3COONa.
Tenoyltrifluoroacetone (*TTA*), 0.5 *M* solution in xylene.
8-Hydroxyquinoline, 5 per cent solution. Dissolve 5.0 g of 8-hydroxyquinoline in 10 ml of glacial acetic acid and add water to make 100 ml.

Hydrochloric acid, density 1.17 g/cu.cm, 8 *M*, 6 *M*, 2 *M*, 0.5 *M*, 0.1 *M*, and 0.03 *M* solutions.
Ammonia, 0.1 *M* solution.
Xylene.
Perchloric acid, 70 per cent solution.
Nitric acid, density 1.4 g/cu.cm and 8 *M* solution.
Ammonium acetate, 3.5 *M* solution.
Chloroform.
Dowex I ion-exchange resin in Cl- and NO_3-forms.

Constructing a Calibration Curve

Place 1, 2, 3, 4 and 5 ml of $ScCl_3$ standard solution into 25-ml volumetric flasks, add 1.0 ml of 0.1 *M* HCl solution, 2 ml of arsenazo I solution, 2.5 ml of the acetate buffer and 1.0 ml of ammonia solution into each flask and then add water to the mark. The pH of the solution should be 6.1-6.3. Measure the absorption of the solutions at 570 nm in a cell with a path length of 1 cm, using a blank solution as the standard. Construct the calibration curve using the data obtained.

Procedure

Determining Scandium after Extraction by Tenoyltrifluoroacetone (TTA). Evaporate a solution containing 10-50 μg of scandium to dryness, dissolve the residue in 0.9 ml of 0.5 *M* hydrochloric acid, add 4 ml of water, and transfer into a 60-ml separating funnel. Wash the beaker with two 5-ml portions of water. The solution pH should be 1.3-1.7. Add 10 ml of TTA and shake for 5 minutes. Add 10 ml of TTA solution to the aqueous phase and shake again for 5 minutes. Join the extracts and add 10 ml of 0.03 *M* hydrochloric acid. Shake for ten seconds, discard the aqueous phase, add 20 ml of 2 *M* hydrochloric acid solution into the funnel and shake for 5 minutes. Transfer the aqueous phase into another separating funnel, shake with 10 ml of xylene for 10 seconds, transfer the aqueous phase into a beaker and evaporate to dryness. Add 1 ml of perchloric acid and 2 ml of HNO_3, density 1.4 g/cu.cm, to the residue and evaporate to dryness. Rinse the beaker walls with the minimum of water and evaporate the solution to dryness. Dissolve the residue in 1.0 ml of a 0.1 *M* solution of HCl and procede as for the construction of the calibration curve.

Determining Scandium after Extraction of 8-Hydroxyquinolinates. Add 1.0 ml of 8-quinolinol solution, 1.0 ml of ammonium acetate solution and 3 ml of water to 10 ml of the solution containing 10-50 μg of scandium (the pH 2-3). The pH of the mixture should be 4.5-4.7. Now add 20 ml of chloroform and shake for one minute. Separate the phases and add 0.3 ml of 8-quinolinol solution and 20 ml of chloroform to the aqueous phase and shake for one minute. Separate the phases, and add another 0.3-ml portion of 8-quinolinol and 20 ml of chloroform to the aqueous phase. Shake again for one minute, wash the aqueous phase with 20 ml of chloroform for ten seconds, transfer into a beaker, and evaporate to dryness. Add 3 ml of hydrochloric acid, density 1.17 g/cu.cm, 1 ml of HNO_3 solution, density 1.4 g/cu.cm, to the residue in the beaker, cover it with a watch glass and heat to dissolve the residue. Evaporate the solution to dryness, dissolve the residue in 1.0 ml of a 0.1 *M* solution of hydrochloric acid and proceed as described for the construction of the calibration curve.

Determining Scandium in the Presence of Uranium (VI). Evaporate the solution containing from 10 to 50 μg of scandium in a beaker to dryness. Dissolve the residue in 10 ml of 8 *M* hydrochloric acid and pass the solution through a column packed with a strongly basic anion-exchange resin Dowex I in the Cl-form at a rate of 2 ml/min. Rinse the beaker and the column four times with 10-ml portions of 8 *M* hydrochloric acid, collect the eluate in a 100-ml beaker and evaporate to dryness. Add 1.0 ml of 0.1 *M* hydrochloric acid to the residue and proceed as for the construction of the calibration curve.

Note. In a medium of 12 *M* hydrochloric acid, scandium can be separated from Mo^{VI}, W^{VI}, Fe^{III}, Ru^{VI}, Os^{IV}, Co, Ir^{IV}, Pd^{II}, Pt^{IV}, Cu, Au^{III}, Zn, Cd, Hg^{II}, Ga, In, Tl^{III}, Ge^{IV}, $Sn^{II, IV}$, As^{III}, $Sb^{III, V}$, Bi^{III}.

Determining Scandium in the Presence of Thorium. Evaporate the solution containing 10-50 μg of scandium to dryness. Dissolve the residue in a beaker in 10 ml of 8 *M* nitric acid and pass through a column packed with Dowex I anion-exchanger in the NO_3-form at a rate of 2 ml/min. Wash the column with four 10-ml portions of 8 *M* nitric acid, evaporate the eluate in a beaker to dryness. Add 1 ml of 6 *M* hydrochloric acid to the residue, evaporate to dryness, dissolve the residue in 1.0 ml of 0.1 *M* hydrochloric acid and determine scandium as for the construction of the calibration curve.

Note. Other organic reagents can probably be used to remove the interfering effect of the accompanying ions for the photometric determination of scandium.

EXTRACTION-PHOTOMETRIC DETERMINATION OF SCANDIUM IN PREPARATIONS OF RARE EARTH ELEMENTS WITH 2,4-SULPHOCHLOROPHENOL P

2,4-Sulphochlorophenol P reacts with the scandium ion to form a red soluble compound. The solutions absorb maximum at 530 nm; the reagent absorbs maximum at 505 nm. The compound is extracted quantitatively in the presence of diphenylguanidine with *n*-butyl alcohol, the pH of the aqueous medium being 2.5-3.0. The following elements do not interfere with the determination of 2 μg of scandium: 25 mg of La, 20 mg of Yb, and Y, 15 mg of Mg, 12.5 mg of Ca, 1 mg of Fe^{II}, 10 μg of Al and 1 μg of U^{VI}, Ti and Th. The method is suitable for the determination of over 0.01 per cent of scandium in rare earth preparations after separation of thorium by extraction of its compounds with thorin I and diphenylguanidine using a mixture of chloroform and butyl alcohol (1:1). The method can also be used for rapid purification of rare earth preparations from scandium, thorium, zirconium and divalent iron by extraction of their compounds with 2,4-sulphochlorophenol P and diphenylguanidine at pH 3.0 of the aqueous phase.

Reagents

Scandium chloride, standard solution. 1 ml is equivalent to 1.0 μg of scandium.
2,4-Sulphochlorophenol P, 0.05 per cent solution.
Diphenylguanidine, 1 *N* solution. Dissolve 130 g of diphenylguanidine base in 500 ml of 1 *N* HCl with heating. Cool the solution, filter and adjust the pH to about 2.5.
n-Butyl alcohol.
Mixture of chloroform and n-butyl alcohol (1 : 1).
Thorin I, 0.1 per cent solution.
Ascorbic acid, 0.25 per cent solution.
Hydrochloric acid, 1 *N* solution.

Constructing a Calibration Curve

Place the standard solution of scandium chloride in quantities equivalent to 0.5, 1.0, 1.5, 2.0, 2.5, 3.0, 3.5, 4.0, 4.5 and 5.0 μg of scandium into ten 50-ml beakers. Add 1 ml of ascorbic acid into each beaker. Allow the solutions to stand for five minutes and then add 5 ml of 2,4-sulphochlorophenol P and, using a potentiometer, adjust the pH to 2.5-2.9. Transfer the solutions into 100-ml separating funnels, add water to make 50 ml, add 3 ml of diphenylguanidine solution and stir. Allow the solutions to stand for two minutes and add 25 ml of butyl alcohol with energetically shaking for a minute. Separate the phases, add 25 ml of water and 1.5 ml of diphenylguanidine solution to the organic phase and shake for a few seconds. Transfer the organic phase into a cell with a light path of 1 cm and measure the absorption at 530-535 nm using the reagent extract as the standard. Construct the calibration curve using the data obtained.

Procedure

Dissolve a sample of rare earths weighing about 20 mg in 2.5 ml of hydrochloric acid, add 5 ml of thorin I, 2 ml of 2,4-sulphochlorophenol P, transfer the mixture into a separating funnel, add water to make 35 ml and 3 ml of diphenylguanidine solution. Extract with 25 ml of a mixture of chloroform and butyl alcohol. Withdraw the lower layer, add the same reagents (except 2,4-sulphochlorophenol P) to the upper layer, and extract again with 25 ml of the same extracting agent.

Repeat the extraction procedure, transfer the aqueous phase into a 100-ml beaker, and proceed as for the construction of the calibration curve.

Note. The recommended size of samples of rare earth oxides is 20.0 and 5.0 mg, the scandium content being 0.01 and 0.04 per cent respectively.

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Yttrium

Yttrium, Y, has the positive valency of 3 in its compounds. When in solution form, yttrium is a stable colourless ion Y^{3+} which is difficult to separate chemically from the ions of scandium (III) and rare earth elements [1]. The reactions of the Y^{3+} ion resemble in many respects those of Sc^{3+}.

A sparingly soluble yttrium hydroxide, $Y(OH)_3$, turns into the oxide Y_2O_3 on calcining.

The standard electrode potentials in an aqueous medium at 25°C are as follows (with reference to the standard hydrogen electrode):

$$Y \rightleftharpoons Y^{3+} + 3e^- \qquad -2.372\ V$$

$$2Y + 3H_2O \rightleftharpoons Y_2O_3 + 6H^+ + 6e^- \qquad -1.676\ V$$

Hydrofluoric acid precipitates the white fluoride YF_3.

Oxalic acid reacts with the yttrium ion to give a white precipitate soluble in excess oxalate.

Erio violet B (4-aminobenzene-azo-chromotropic acid), whose own colour is red, colours violet the solution containing the Y^{3+} ion.

Yttrium is determined photometrically with boropyrocatechol complex [2], arsenazo M [3], quinalizarine [4] and some other reagents.

Since yttrium has no specific reactions, it is detected by spectral, and mainly by X-ray spectral analysis.

PHOTOMETRIC DETERMINATION OF YTTRIUM WITH BOROPYROCATECHOL COMPLEX IN THE PRESENCE OF SOME RARE EARTH ELEMENTS

Pyrocatechol violet reacts with the yttrium ion in an alkaline medium to give a blue complex compound. The presence of ions of other elements interferes with the reaction. It is reasonable to use a red pyrocatechol complex with boric acid instead of pyrocatechol violet proper. The yttrium ion reacts with the boropyrocatechol complex (BPCC) in the molar ratio of 1:1. The absorption of the solutions obeys the Bouguer-Lambert-Beer law in the range of concentrations from 1×10^{-5} to 4×10^{-5} g-ion/l (0.9-4.5 μg/ml). The absorption maximum is at 590 nm, the molar extinction coefficients are 1.85×10^4 (at 590 nm) and 1.90×10^4 (at 607 nm). The ions of cerium (III) and lanthanum (III) also react with BPCC, but the stability of the formed complexes is lower. The effect of lanthanum can be removed by adding boric acid to the concentration of 0.05 *M*, while the effect of cerium, by adding hydrogen peroxide which oxidizes Ce^{III} to Ce^{IV}. In these conditions, 77 per cent of yttrium is bound in a complex with BPCC. Equal quantities of Pr, Nd, a two-fold quantity of La, and 0.5-fold quantities of Ce and Sm do not interfere with the determination.

Reagents

Yttrium chloride, standard solution. 1 ml is equivalent to 20 μg of yttrium.
Acetate-ammonia buffer solution, pH 8.7. Dilute 26 ml of acetic acid, density 1.05 g/cu.cm, with water to 200 ml, add 32 ml of 25 per cent ammonia solution, and dilute with water to 2 litres.
Pyrocatechol violet, 0.1 per cent solution.
Boric acid, 4 per cent solution.
Hydrogen peroxide, 3 per cent solution.

Constructing a Calibration Curve

Place 1 ml of pyrocatechol violet solution and 2 ml of boric acid into 25-ml volumetric flasks. Shake the contents and add 1, 2, 3, 4 and 5 ml of the standard solution of yttrium chloride. Next add 10 ml of the acetate-ammonia buffer into each flask, mix the solutions, add 3-4 drops of hydrogen peroxide and dilute with the acetate-ammonia solution to 25 ml. Allow the solutions to stand for 10-15 minutes and measure their absorption at 590-610 nm on an absorptiometer against a blank solution as the standard. Construct the calibration curve using the data obtained.

Procedure

Add the requisite reagents to the solution as instructed above and measure the absorption of the solution. Determine the yttrium content from the calibration curve.

PHOTOMETRIC DETERMINATION OF YTTRIUM WITH ARSENAZO M IN THE PRESENCE OF SCANDIUM

Yttrium and arsenazo form a compound with two absorption maxima: at 595 and 645 nm (excess arsenazo M) or at 605 and 652 nm (excess yttrium ion). The components react in the molar ratio 1:1, the equilibrium constant of the complexing reaction is 0.55, the molar extinction coefficient at 645 nm is 6.75×10^4. The optimum pH of the solution is 3.25-3.45. The ions of iron (II), aluminium, copper, zinc, lead, manganese (II), and cobalt do not interfere with the determination of yttrium. Lanthanides, bismuth, zirconium hafnium, thorium and scandium interfere.

The proposed method for the determination of yttrium in the presence of scandium is based on masking scandium with NaH_2PO_4. The presence of a ten-fold quantity of scandium does not interfere with the determination of yttrium in this case.

Reagents

Yttrium chloride, standard solution. 1 ml is equivalent to 10 μg of yttrium.
Arsenazo M, 0.1 per cent solution.
Sodium phosphate, monosubstituted, 0.1 *M* solution.
Acetate buffer solution, pH 3.35 ± 0.1

Constructing a Calibration Curve

Place 1, 2, 3, 4 and 5 ml of the standard solution of the yttrium salt into 50-ml volumetric flasks, add 2 ml of arsenazo M, 5 ml of the buffer solution and 2 ml of NaH_2PO_4 into each flask, and dilute with water to the mark. Measure the absorption of the solutions at 645 nm against a blank solution as the standard. Construct the calibration curve using the data obtained.

Procedure

Add all reagents specified for the construction of the calibration curve to the sample solution containing 10-50 μg of yttrium, then add water to 50 ml and measure the absorption of the solution at 645 nm. Determine the yttrium content from the calibration curve.

Note. If the yttrium concentration in the solution exceeds 8×10^{-6} g-ion/l, add 1 ml of 0.05 per cent gelatin solution (prepared immediately before the test) to prevent precipitation of scandium phosphate by sodium phosphate.

EXTRACTION-PHOTOMETRIC DETERMINATION OF YTTRIUM IN STEEL WITH QUINALIZARINE

Yttrium can be quantitatively extracted with tributyl phosphate from 12 *M* HNO_3 solutions. Many components of steel, including ten-fold quantities of Mo, W and Nb, do not interfere with the extraction. The extraction of Ce^{III} is insignificant, but Ce^{IV} is extracted completely. Fe^{III} is extractable to 30-35 per cent. Yttrium can be determined without re-extraction in an organic phase with quinalizarine. The method can be used to determine. 0.004-0.1 per cent of yttrium. The analysis continues 50-60 minutes, including the time of taking sample and its dissolution. The error of the determination is 1-7 per cent.

Reagents

Yttrium nitrate, standard solution. 1 ml is equivalent to 4 μg of yttrium. The solution is prepared with 12 *M* HNO_3.
Nitric acid, diluted 1 : 1 and 12 *M* solution.
Tributyl phosphate.
Tartaric acid, crystalline.
Sodium hydroxide, 3 *M* solution.
Acetate buffer solution, pH 5.8.
Quinalizarine, 10^{-3} *M* solution in acetone.

Constructing a Calibration Curve

Place 1, 2, 3, 4 and 5 ml of yttrium nitrate into five 25-ml separating funnels, add 12 *M* HNO_3 to make 5 ml, and add 5 ml of tributyl phosphate. Shake for three minutes, transfer the organic layer into graduated test tubes, and 5 ml of the buffer solution, 2 ml of quinalizarine and shake for a minute. Transfer the organic layer into cells with the light path of 1 cm and measure the absorption of the solutions on an absorptiometer with an optical filter (540 nm) against a blank solution as the standard. Construct the calibration curve using the data obtained.

Procedure

Dissolve a sample of steel weighing 0.5-1 g in a 50-ml beaker in 15 ml of HNO_3 (1 : 1) and evaporate to 3-5 ml. Transfer the solution into a 100-ml volumetric flask and add 12 *M* HNO_3 to the mark. Take an aliquot containing 6-15 μg of yttrium, place it in a separating funnel, add 5 ml of tributyl phosphate and extract for three minutes. Add 0.5-1.2 g of tartaric acid to the organic phase, then add sodium hydroxide to adjust the medium to the alkaline side, and extract for one minute. Procede further as for the construction of the calibration curve. Determine the yttrium content from the calibration curve.

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Lanthanum and Lanthanides

Lanthanum and the lanthanides La, Ce, Pr, Nd, Pm, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu are the elements with very similar properties and hence are difficult to separate from one another. The lanthanides, together with lanthanium, scandium and yttrium from a group of rare earth metals. As a rule, lanthanum and all lanthanides have the positive valency of 3. Cerium forms also compounds in which its valency is 4. Oxides of tetravalent praseodymium and terbium, and salts of divalent samarium, europium and ytterbium are also known.

The standard electrode potentials in an aqueous medium at 25°C are as follows (with reference to the standard hydrogen electrode):

$La \rightleftharpoons La^{3+} + 3e^-$	−2.522 V
$2La + 3H_2O \rightleftharpoons La_2O_3 + 6H^+ + 6e^-$	−1.856 V
$Ce \rightleftharpoons Ce^{3+} + 3e^-$	−2.483 V
$Ce^{3+} + 2H_2O \rightleftharpoons Ce(OH)_2^{2+} + 2H^+ + e^-$	+1.731 V
$Pr \rightleftharpoons Pr^{3+} + 3e^-$	−2.462 V
$2Pr + 3H_2O \rightleftharpoons Pr_2O_3 + 6H^+ + 6e^-$	−1.829 V
$Pr_2O_3 + H_2O \rightleftharpoons 2PrO_2 + 2H^+ + 2e^-$	+0.863 V
$Pr(OH)_3 \rightleftharpoons PrO_2 + H_2O + H^- + e^-$	+1.431 V
$Nd \rightleftharpoons Nd^{3+} + 3e^-$	−2.431 V
$2Nd + 3H_2O \rightleftharpoons Nd_2O_3 + 6H^+ + 6e^-$	−1.811 V
$Pm \rightleftharpoons Pm^{3+} + 3e^-$	−2.423 V
$Sm \rightleftharpoons Sm^{3+} + 3e^-$	−3.121 V
$Sm^{2+} \rightleftharpoons Sm^{3+} + e^-$	−1.000 V
$Eu \rightleftharpoons Eu^{2+} + 2e^-$	−3.395 V
$Eu + 3H_2O \rightleftharpoons Eu(OH)_3 + 3H^+ + 3e^-$	−2.002 V
$Eu^{2+} \rightleftharpoons Eu^{3+} + e^-$	−0.429 V
$Gd \rightleftharpoons Gd^{3+} + 3e^-$	−2.397 V
$Gd + 3H_2O \rightleftharpoons Gd(OH)_3 + 3H^+ + 3e^-$	−1.994 V
$Tb \rightleftharpoons Tb^{3+} + 3e^-$	−2.391 V
$Tb + 3H_2O \rightleftharpoons Tb(OH)_3 + 3H^+ + 3e^-$	−1.999 V
$Dy \rightleftharpoons Dy^{3+} + 3e^-$	−2.353 V
$Dy + 3H_2O \rightleftharpoons Dy(OH)_3 + 3H^+ + 3e^-$	−1.956 V
$Ho \rightleftharpoons Ho^{3+} + 3e^-$	−2.319 V

$Ho + 3H_2O \rightleftharpoons Ho(OH)_3 + 3H^+ + 3e^-$	-1.937 V
$Er \rightleftharpoons Er^{3+} + 3e^-$	-2.296 V
$Tm \rightleftharpoons Tm^{3+} + 3e^-$	-2.278 V
$Tm + 3H_2O \rightleftharpoons Tm(OH)_3 + 3H^+ + 3e^-$	-1.913 V
$Yb^{2+} \rightleftharpoons Yb^{3+} + e^-$	-1.205 V
$Lu \rightleftharpoons Lu^{3+} + 3e^-$	-2.255 V
$2Lu + 3H_2O \rightleftharpoons Lu_2O_3 + 6H_2O + 6e^-$	-1.892 V

Metallic lanthanium and the lanthanides are strong reductants. When in solution form, lanthanum and the lanthanides are stable ions, Ln^{3+}. None of the elements, except cerium, can exist in solution as Ln^{4+}. The cerium ion Ce^{4+} has strong oxidizing properties in an acid medium. The ion Eu^{2+}, and especially Yb^{2+} and Sm^{2+}, reduce the hydrogen ion to H_2 (in aqueous solutions).

Solutions containing the ions La^{3+}, Ce^{3+}, Gd^{3+}, Yb^{3+}, Lu^{3+} and Tb^{3+} (and also Y^{3+} and Sc^{3+}) are colourless. Solutions containing Pr^{3+} are green, Nd^{3+} violet pink, and Er^{3+} pink.

The ions of tervalent lanthanides (except lanthanum and lutetium) have absorption spectra with very distinct bands to the U-V, visible, and I-R regions of the spectrum [1]. These bands are characteristic of each ion and their wavelengths are the same for the solid state and aqueous solutions. The absorption spectra can be used for the determination of lanthanide mixtures provided spectrophotometers of high resolving power are available. The molar extinction coefficients are small but milligram quantities of many lanthanides can still be detected. Separate spectrophotometric determination of praseodymium, neodymium, holmium, erbium and thulium is possible in the presence of the other lanthanides. Ordinary spectrophotometers are used for the purpose [2].

Emission spectral, X-ray spectral, and some other physical methods are used for the detection and determination of separate lanthanides if their quantities in mixtures of the lanthanides exceed 0.01 per cent. The emission spectra of the lanthanides have many lines.

The ions of lanthanum and the lanthanides (and also yttrium and scandium) give similar reactions in their tervalent state and are therefore difficult to distinguish chemically from one another in solution.

If cerium is in its tetravalent state it can relatively easily be determined by chemical means in the presence of the other lanthanides. Praseodymium can be detected in the presence of the other lanthanides by its ability to form oxides in which its valency state is also 4. Europium can be separated and determined by reducing in solution to its divalent state. The ions Yb^{2+} and Sm^{2+} are very unstable in solution and chemical means of their analysis are practically absent.

Lanthanides can be successfully separated chromatographically (ion-exchange with complex-forming substances, paper chromatography). Extraction methods are also used. After separation of the lanthanides by distribution chromatography on paper or ion-exchange resins, each of them can be determined photometrically.

Lanthanum hydroxide and the hydroxides of the lanthanides Ln $(OH)_3$ are practically insoluble in water and show only basic character. The basic properties of the hydroxides gradually decrease from lanthanum to lutetium. The hydroxides are soluble in acids, insoluble in excess ammonia solution or solutions of caustic alkalis. Hydroxides (or basic salts) of the lanthanides precipitate at pH of about 6.8-8.5. Hydroxides of separate elements are precipitated at the following pH:

Element...	La	Ce	Pr and Nd	Sm	Gd	Dy	Yb	Lu
pH...	7.3-8.4	7.1-7.4	7.0-7.4	6.8	6.2	7.0	6.2-7.1	6.0

Calcining lanthanum hydroxide, $La(OH)_3$, gives a white oxide La_2O_3. Traces of lanthanides colour it grey. When cerium hydroxide, $Ce(OH)_3$ is calcined in air, it turns into CeO_2. Calcining of praseodymium oxalate or nitrate (or terbium oxalate or nitrate) gives their oxides of variable composition. Part of praseodymium or terbium is in its tetravalent and part in tervalent state in these oxides. The formation of these oxides is used to detect praseodymium in the presence of the other lanthanides.

Fluorides, phosphates, carbonates of lanthanum and the lanthanides are sparingly soluble in water. The fluorides are sparingly soluble in acids as well. The lanthanides of the cerium group form relatively sparingly soluble double sulphates with sulphates of the alkali metals. The chlorides and nitrates are soluble in water.

The ions of lanthanum and the lanthanides are not precipitated by ammonia from solutions containing organic oxyacids (tartaric, citric, malic acid, etc.) because complex compounds are formed. Oxalic acid precipitates lanthanum and the lanthanides from weak acid solutions and is therefore used for their isolation. Oxalates of the alkali metals, or ammonium oxalate, may not be used since the precipitated oxalates will partly dissolve due to the formation of soluble complexes. The curd-like precipitates of oxalates turn into crystals when heated to 60°C. The ions of Zr, Th, Bi, Sb^{III} are precipitated together with the lanthanides. The composition of a white crystalline precipitate of lanthanum oxalate is described by the formula $La_2(C_2O_4)_3 \cdot 10H_2O$.

Dihydroxytartaric acid precipitates the ions of all lanthanides from weak acid or neutral solutions [3]. Curd-like precipitates are first formed which then turn into crystals. The composition of the precipitate is approximately described by the formula $4La_2O_3 \cdot 5C_4H_4O_8 \cdot 24H_2O$. The reagent is used to detect lanthanum, yttrium, gadolinium, erbium, etc. The ions of Be, Mg, Sr, Ba, Hg^{II}, Al, In, Tl^{I}, Ti^{IV}, V^{V}, Bi^{III}, U^{VI}, Mn^{II}, Re^{VII}, Fe^{II}, Fe^{III} and Cd are not precipitated.

Alizarine, quinalizarine, morin and other organic reagents react with the ion La^{3+} and the lanthanide ions to give coloured compounds. The reagents selectivity is low. The ions of Al, Sc, Mg and of many other elements react similarly.

Xylenol orange is used for the differential spectrophotometric determination of large quantities of the lanthanides in their mutual presence at pH 5.6 (570 nm) [4]. The method is as accurate as gravimetric.

8-Quinolinol precipitates quantitatively the ion Ce^{3+} from ammoniacal solutions containing tartrate [5] in the form of $Ce(C_9H_6ON)_3$ (yellow crystals). The precipitate is not formed in a weak acetic acid solution and this is used for the separation of Ce^{III} from Th (the latter is precipitated). The reagent is used for the gravimetric and titrimetric determination of cerium.

8-Quinolinol, 5,7-dichloro-8-quinolinol and other 5,7-dihalide-8-quinolinols react with the lanthanides to give sparingly soluble compounds used for quantitative analysis. Compounds with 8-quinolinol are not extractable with organic solvents. Compounds with 5,7-dichloro-8-quinolinol can be extracted with chloroform.

9-(*o*-Hydroxyphenyl)-2,3,7-trihydroxyfluorone (salicylfluorone) reacts with the ions of the lanthanides at pH about 6.7 [6]. The absorption maximum of colloidal solutions of the lanthanide compounds is at 530 nm. Gelatin is used to stabilize them. Salicylfluorone is used for the photometric determination of the sum of lanthanides after their separation. The ions of calcium and magnesium are masked by sulphosalicylic acid. Thorium, zirconium, uranium iron (II and III), and tetravalent titanium form coloured compounds.

Arsenazo I is a group reagent for the lanthanide ions [7]. The aqueous solution of the reagent is pink. It reacts with the lanthanide ions in a natural medium (pH 7.2, urotropin) to form red-violet compounds which are detected in solutions diluted $1 : 3 \times 10^6$. Large quantities of the ions of ammonia, Li, K, Na, Ag, Ca, Sr, Ba, Mg, Zn, Cd, Hg^{II}, Sn^{IV}, Pb, V^{V}, Mo, Co and Ni, as well as the chloride ion, do not interfere with the determination. Phosphate, pyrophosphate, fluoride and tungstate ions interfere because they mask the lanthanide ions. The lanthanides can also be detected in the presence of the ions of Cu and Al after the addition of salicylates, and the ion of U^{VI}, after the addition of H_2O_2. Moderate quantities of the ions of Ti^{IV}, Zr, Th and Fe^{III} can be precipitated with stannic acid which is formed during hydrolysis of $SnCl_4$. Arsenazo I is used for the photometric determination of the sum of lanthanides [8-10].

Carboxylic oxyacids (tartaric, citric, and others) react with the ions of tervalent lanthanides to form soluble anion complexes. These are used for separation of the lanthanides by ion-exchange chromatography.

Aminopolycarboxylic acids (iminodiacetic, nitrilotriacetic, ethylenediaminetetraacetic acid) react with the ions of tervalent lanthanides to form complex compounds of various stability which are used for chromatographic and other methods of separation. The stability of complex compounds with EDTA [11] increases with decreasing radius of a lanthanide ion (ionic strength, 0.1; temperature, 20°C):

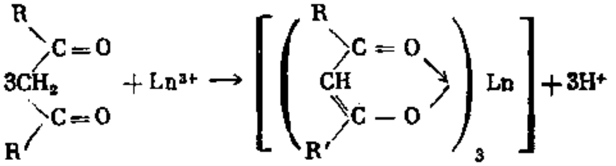
Ion	La	Ce	Pr	Nd	Sm	Eu	Gd	Tb
pK	14.72	15.39	15.75	16.06	16.55	16.69	16.70	17.25

Ion	Dy	Ho	Er	Tm	Yb	Lu
pK	17.57	17.67	17.98	18.59	16.68	19.06

The sum of the lanthanides is determined by complexometric methods [12, 13].

The ions of the lanthanides are precipitated from solutions containing excess pyrocatechol by adding ethylenediamine, pyridine, quinoline [14]. In the case with ethylenediamine (En), the composition of the precipitate is described by the formula $En_3[Ln(C_6H_4O_2)_3]_2$. The precipitates are insoluble in excess ammonia (in contrast to the corresponding precipitates of many heavy metals). La, Y, Gd and Er can be detected by this method, their concentrations being 100, 5, 10 and 100 µg/ml, respectively. The ions of Cu, Be, Mg, Ba, Hg^{II}, Ti^{IV}, Zr, Pb, V^{V}, As^{III}, Sb^{III}, Nb, Ta, Bi, Mo^{VI}, W, U^{VI}, Se^{IV}, Te^{IV}, Mn^{II}, Re^{VII}, Ni, Pd, and Pt^{IV}, and also BO_2^- are not precipitated. The ions of Al, Ga, In, Sn^{IV}, Th, Zn, Cd, Cr^{III}, Fe^{III} and Co react with ethylenediamine or piperidine to form precipitates soluble in ammonia.

β-Diketones react with the ions of tervalent lanthanides as follows:



The compounds in which $R=R'=CH_3$ (acetylacetonates), $R=R'=C_6H_5$ (dibenzoylmethanates) and $R=CF_3$, $R'=C_4H_3S$ (tenoyltrifluoroacetonates) are studied best of all. These are usually obtained by adding the corresponding β-diketone to an acidified solution of a lanthanide salt with a thoroughly controlled increase in the pH (basic compounds are otherwise formed). The liberated compounds are crystalline substances readily soluble in organic solvents.

All mentioned reagents are group reagents. They react with the ions of tervalent lanthanides in about the same manner. But comparatively selective analytical methods have been developed for tetravalent cerium and divalent europium. The lanthanides can be selectively separated from many elements by extraction with *n*-butyric acid [15-17].

The compounds of tervalent cerium are easily oxidized in an alkaline medium to yellow compounds of tetravalent cerium. This differs them from the compounds of lanthanum and of the lanthanides. Thus, under special conditions, cerium (III) has reducing properties. For example, it reduces phosphomolybdic acid to molybdenum blue. The Ce^{IV} ion has strong oxidizing properties in acid solutions. The Ce^{IV}/Ce^{III} potential depends on the nature of the acid:

Solution	9 *M* $HClO_4$	1 *M* $HClO_4$	1 *M* HNO_3	1 *M* H_2SO_4	1 *M* HCl
Ce^{IV}/Ce^{III} potential, V	1.90	1.70	1.64	1.44	1.28

The cerium (IV) ion oxidizes, in acid solutions, the ions of Fe^{II}, $[Fe(CN)_6]^{4-}$, and also H_2S, SO_2, NH_3, $H_2C_2O_4$, H_2O_2. The oxidation of benzidine, *N*-phenylanthranilic acid gives intensely coloured products. The oxidizing properties of the Ce^{IV} ion rapidly decrease with increasing pH of the solution while the reducing properties of the Ce^{III} ion increase accordingly.

The cerium (IV) ion can be selectively titrated by solutions of hydroquinone [18, 19].

The reactions of cerium in its tetravalent state are the same as those of Th, Zr, Ti and U^{IV} ions. Its properties are markedly different from those of the lanthanides in their tervalent state.

The Ce^{4+} ion is stable in strong acid solutions. When the acidity decreases, the solution is hydrolyzed to liberate basic salts. Cerium (IV) forms yellow cations $Ce(OH)^{3+}$ and orange cations $Ce(OH)_2^{2+}$.

An ammonium solution of silver nitrate oxidizes (with heating) salts of cerium (III) to cerium hydroxide (IV). The finely dispersed silver formed colours black the bulky precipitate. This method is used to discover the Ce^{III} ion in the presence of the ions of the other lanthanides. The ions of Mn^{II}, Fe^{II} and Co^{II} interfere with the determination.

Ammonium persulphate oxidizes colourless salts of tervalent cerium to yellow salts of cerium (IV) with heating in a sulphuric acid solution in the presence of Ag^{I}.

Sodium bismuthate oxidizes the tervalent cerium ion in acid solutions.

Cerium hydroxide, $Ce(OH)_4$, is pale yellow and is precipitated at pH higher than 0.8. When ammonia solution KOH, or salts of weak acids and strong bases are added to solutions of cerium salts, a yellow amorphous substance $Ce(OH)_4$ precipitates. When calcined, it converts into CeO_2. Calcined CeO_2 is very sparingly soluble in hydrochloric acid but readily soluble in hot concentrated H_2SO_4.

To separate cerium from the lanthanides, the solution pH is adjusted to 1.5-6.0 and cerium is oxidized to its tetravalent state with precipitation of $Ce(OH)_4$.

Potassium hydroxide, or ammonia, precipitate a red-brown peroxidic compound from solutions of salts of tetravalent and tervalent cerium in the presence of hydrogen peroxide. The peroxidic compound is stable in neutral and alkaline media.

Cerium (IV) phosphate is a sparingly soluble compound. It is used for the gravimetric determination of cerium (IV).

The ion of tetravalent cerium is precipitated quantitatively from nitric acid solutions by potassium iodate. This method is used to separate cerium from the lanthanides. The composition of the precipitate depends on the precipitation conditions.

Cerium (IV) forms soluble complex compounds with tartrate, citrate, oxalate, chloride, sulphate, nitrate and perchlorate ions.

Precipitated cerium (IV) oxalate is dissolved in excess $H_2C_2O_4$. The formed oxalate complexes are usually destroyed with precipitation of $Ce_2(C_2O_4)_3$ due to reduction of cerium (IV) to its tervalent state.

Molybdoceric heteropolyacid is used for the photometric determination of cerium in solutions of pure salts.

Dibenzoylmethane, $C_6H_5COCH_2COC_6H_5$, (in methyl alcohol) precipitates a ruby-red crystalline substance, $(C_{15}H_{11}O_2)_4Ce$, from methanol solutions of cerium (IV) salt if the pH of the solution is adjusted to 8 by NH_3 solution in methyl alcohol [20]. The ion of cerium (IV) precipitates quantitatively in these conditions. The ion of tervalent cerium is not precipitated but oxidized with atmospheric oxygen to the Ce^{IV} ion after which it also forms the precipitate $(C_{15}H_{11}O_2)_4Ce$. The other lanthanides in their tervalent state are precipitated with $H_2C_2O_4$ solution in methyl alcohol from the filtrate after separation of red crystalline $(C_{15}H_{11}O_2)_4Ce$. Dibenzoylmethane precipitates also the thorium (IV) ion at pH 4-5 in the form of $(C_{15}H_{11}O_2)_4Th$ [20] and is used for the separation of thorium from cerium (III), lanthanum and the lanthanides.

Europium can be determined by redox methods. To determine europium in mixtures of lanthanide compounds, the solution of their chlorides is passed through a Jones reductor charged with zinc metal. The europium (III) ion is reduced to the ion of europium (II). The solution discharged from the reductor is collected in a receptacle containing excess $FeCl_3$. The ferrous ion which is formed in equivalent quantity, is titrated with potassium bichromate after the addition of H_3PO_4. Samarium and ytterbium, as well as the other lanthanides, do not interfere with the determination since they are not reduced with zinc.

All lanthanides, except europium and ytterbium, have very similar reduction half-wave potentials and they cannot therefore be identified in mixtures [21]. Only europium and ytterbium, and also cerium, after the conversion into its tetravalent state, can be determined by the polarographic method.

Europium can be determined in the presence of samarium while dysprosium, in the presence of holmium, by the radioactivation method [22]. The irradiation is effected with neutrons from a radium-beryllium source. The presence of the other lanthanides (except lutetium) causes an error of less than 1 per cent if the elements are contained in quantities equal to or smaller than those of europium and dysprosium. An equal quantity of lutetium causes an error of 5 per cent.

Eu^{III} can be determined fluorimetrically against the background of most lanthanides [23].

A review of the methods for the determination of the lanthanides is given in the literature [24, 25].

SELECTIVE CONCENTRATION AND SEPARATION OF LANTHANIDES

The lanthanides can be extracted quantitatively at pH 4.0-5.5 by solutions of *n*-butyric acid in chloroform. The lanthanides can be separated from Fe, Al, Ti, Zr, Nb, Ta, Sn, W, Mo, Th, Sc, U, Ca, Sr, Ba, and Mg by extraction from solutions containing sulphosalicylic acid. The lanthanides can be separated from Th, Sc, U, Ca, Sr, Ba and Mg in the absence of sulphosalicylic acid if the pH is maintained at 2.0-2.3 in the presence of Th, Sc, U and 4.0-4.5 in the presence of Ca, Sr, Ba and Mg. The method can be used to concentrate $n \times 10^{-2}$-$n \times 10^{-3}$ per cent of the lanthanides and determine them in mineral raw materials of variable composition. The determination ends complexometrically, gravimetrically or photometrically.

Reagents

Ammonium nitrate, saturated solution.
Sulphosalicylic acid, crystalline.
Ammonia, 25 per cent solution and diluted 1 : 4.
n-Butyric acid.
Chloroform.
Washing solution. Saturated solution of ammonium nitrate containing 10 per cent of sulphosalicylic acid, 1-2 drops of 30 per cent hydrogen peroxide in 100 ml of solution with pH adjusted to 4.0-5.5.
Nitric acid, density 1.4 g/cu.cm.
Hydrogen peroxide, 30 per cent solution.

Procedure

Place 3-5 ml of the test solution in hydrochloric acid in a separating funnel and add 20 ml of ammonium nitrate solution, 1 g of sulphosalicylic acid, 25 per cent ammonia solution to dissolve the precipitate of the acid (and 1 ml in excess), 10 ml of *n*-butyric acid and 10 ml of chloroform. Cool the mixture to room temperature and shake for a minute. Separate the organic layer, wash three times with the washing solution, then add 2 ml of HNO_3 to the organic layer, shake for 30 seconds, add 10 ml of water and mix again. Transfer the aqueous layer to a beaker and evaporate to dryness. Add 5-10 ml of ammonium nitrate solution to the dry residue, transfer into a 50-ml separating funnel, add a few crystals of sulphosalicylic acid, 1-2 drops of ammonia (1 : 4) to adjust the pH to 2.0-2.3 and 5 ml of *n*-butyric acid. Extract for a minute, transfer the aqueous layer into another separating funnel, wash the organic layer with 5 ml of ammonium nitrate solution and add the washings to the aqueous solution in the second separating funnel. Add 2 ml of a 25 per cent ammonia solution and 10-15 ml of *n*-butyric acid to the joint solution and extract the lanthanides. Add 3-5 ml of chloroform and 2 ml of HNO_3 to the extract, re-extract the lanthanides, and evaporate the aqueous layer to dryness. Treat the dry residue with HNO_3 and 30 per cent hydrogen peroxide with heating, evaporate to dryness, and determine the lanthanides in the dissolved residue.

COMPLEXOMETRIC DETERMINATION OF SUM OF LANTHANIDES IN PHOSPHORUS-CONTAINING MATERIALS

The lanthanides, calcium, and iron are separated from phosphorus, silicon and aluminium by fusing the sample with sodium-potassium carbonate. The lanthanides are precipitated from the solution together with calcium by ammonia, and then separated as oxalates. The oxalates are decomposed by heating with nitric acid and the sum of the lanthanides is determined by titration with EDTA in the presence of xylenol orange. The crimson solution abruptly turns yellow at the point of equivalence at pH 5.2-5.4. The yellow colour is characteristic of the solutions of unbound xylenol orange. The method gives good results if the sum of the lanthanides exceeds 0.1 per cent. Smaller quantities of the lanthanides are determined photometrically.

The error of the complexometric determination is 1-2 per cent.

Reagents

Sodium-potassium carbonate, crystalline.
Hydrogen peroxide, 30 per cent solution.
Sodium carbonate, 10 per cent solution.
Oxalic acid, 1 and 10 per cent solution.
Nitric acid, density 1.4 g/cu.cm.
Ammonia, 1 per cent and 2 *N* solutions.
EDTA, 0.01 *M* solution. The solution should be better standardized against the sum of rare earth elements after their separation from the sample.
Ascorbic acid, 1 per cent solution.
Acetic acid-ammonia buffer solution, pH 5.2-5.4. Dilute 32 ml of acetic acid, density 1.05 g/cu.cm with water to 200 ml, add 34 ml of 25 per cent ammonia solution and dilute with water to 500 ml.
Xylenol orange, 0 5 per cent solution.

Procedure

Separation of the Sum of the Lanthanides. Calcine a sample weighing 0.5-1 g in a porcelain crucible, mix with a 15-fold quantity of potassium-sodium carbonate and transfer into a platinum crucible using potassium-sodium carbonate. Place the crucible into a muffle furnace heated to 600-700°C, raise the temperature gradually to 950°C and keep for 40-50 minutes. Transfer the crucible quickly into a cup filled with water, cool, and place in a 500-ml beaker. Fill the crucible with water from the cup and add water to 200-250 ml. Heat the beaker on a sand bath and boil for 30-40 minutes, adding from time to time several drops of hydrogen peroxide to accelerate leaching of the melt.

Pass the hot solution through a blue ribbon filter, rinse the beaker and the crucible with a hot solution of sodium carbonate and, using the same solution, rinse the precipitate on the filter 4 or 5 times. Remove the crucible from the beaker and rinse with a hot 10 per cent solution of oxalic acid. Transfer the precipitate into the same beaker with small portions of hot water and a hot 10 per cent oxalic acid solution. Add 100 ml of a 10 per cent oxalic acid solution into the beaker, heat the mixture to the boil with stirring, boil for 2-3 minutes, and allow to stand overnight.

Separate the precipitate on a blue ribbon filter, wash with a 1 per cent oxalic acid solution, dry slightly the precipitate and the filter, transfer them into a porcelain crucible, incinerate the filter, and calcine the precipitate for 30-40 minutes. Wetten the residue with water, add 10-15 ml of nitric acid and 1 ml of hydrogen peroxide, transfer into a 200-ml beaker, evaporate on a sand bath to 5 ml, dilute with water to 70-80 ml, heat to water vapour, and add, with stirring, 2 N solution of ammonia until a strong odour is felt.

Heat the solution together with the precipitate for 5-10 minutes, cool, and separate the precipitate on a blue ribbon filter. Rinse the precipitate with 1 per cent ammonia solution. Next wash off the precipitate with 20-30 ml of 10 per cent oxalic acid into a 100-ml beaker, heat the mixture to boiling and allow to stand on a water bath for two hours. Separate the precipitate on a blue ribbon filter and wash with 1 per cent oxalic acid to collect the precipitate in the filter cone. Wash the filter and remove the oxalate precipitate into the precipitation beaker using 10 ml of nitric acid. Wash the filter again. Evaporate the solution on a sand bath (in the presence of 1 ml of hydrogen peroxide) to 1 ml and wash off the residue with hot water into a 250-300 ml Erlenmeyer flask.

Complexometric Titration of the Sum of the Lanthanides. Add 2-3 drops of ascorbic acid solution, 20 ml of acetate-ammonia buffer, and 3-5 drops of xylenol orange to the solution containing not less than 1 mg of the sum of lanthanides, and dilute with water to 100 ml. Titrate with EDTA solution from a microburette until the crimson colour changes to pure yellow.

TITRIMETRIC DETERMINATION OF CERIUM IN CAST IRON WITH HYDROQUINONE

The method is based on the titration of Ce^{IV} with hydroquinone solution in the presence of ferroin as an indicator. Ce^{IV} can be also reduced with ferrous sulphate solution ($E^0 = +0.76$ V), ascorbic acid ($E^0 = +0.43$ V), and stannous chloride ($E^0 = +0.2$ V) solutions. Hydroquinone ($E^0 = +0.68$ V) is more convenient because it reduces tetravalent cerium in an acid solution at room temperature instantaneously and quantitatively. Solutions of hydroquinone in 1-3 per cent sulphuric acid are stable in storage.

Oxidizers such as bromine, iodine, chlorine, and also the bromate, chromate, and vanadate ions interfere with the determination of cerium. When cerium is determined in cast iron, it is first separated in the form of the fluoride CeF_3 at pH 2-5 ($L_{CeF_3} \approx 10^{-15}$). Before precipitating CeF_3, the iron is reduced with ascorbic acid. The fluoride precipitate is separated on a filter, washed and after incineration of the filter, the residue is treated with sulphuric acid to remove the fluoride ion completely. Cerium is oxidized to its tetravalent state with ammonium persulphate and titrated with hydroquinone solution. Lanthanum, neodymium and praseodymium do not interfere with the determination. The method can be used for a comparatively quick (5-6 hours) and reliable determination of cerium in concentrations from 0.05 to 0.1 per cent.

Reagents

Hydrochloric acid, diluted 1 : 1.
Ascorbic acid, crystalline.
Ammonia, concentrated solution, density 0.91 g/cu.cm, and 25 per cent solution.
Sodium fluoride, crystalline.
Sulphuric acid, density 1.84 g/cu.cm, and diluted 1 : 4.
Ammonium persulphate, 25 per cent solution.
Hydroquinone, 0.005 *N* solution in 1 per cent sulphuric acid.
Ferroin. Mix equal volumes of 0.05 *M* solutions of *o*-phenanthroline and ferrous sulphate.

Procedure

Place a sample of cast iron weighing 1-3 g (the cerium content of the sample should be 2-3 mg) in a 250-ml Erlenmeyer flask, add 25-30 ml of hydrochloric acid and heat the mixture on a sand bath to dissolve the sample completely, avoiding vigorous reaction. Separate graphite on a filter and collect the filtrate in a 100-ml Erlenmeyer flask. Wash the filter with water. (The volume of the filtrate and the washings should not exceed 50 ml). Add 0.5 g of ascorbic acid to the cooled solution and then, drop by drop, add 25 per cent ammonia solution until precipitation begins. Then add 0.5 g of sodium fluoride, close the flask with a rubber stopper and shake on a mechanical shaker for an hour. Separate the precipitated fluorides on a blue ribbon filter and wash 4-5 times with hot water. Transfer the filter and the precipitate into a platinum crucible, incinerate the filter and slightly calcine the precipitate in a muffle furnace at 300-400°C.

Add 15 ml of sulphuric acid (1:4) to the calcined precipitate, evaporate to dryness, and calcine the residue until dense white fumes stop evolving. Dissolve the residue in water acidified with sulphuric acid, transfer into a 250-ml Erlenmeyer flask, add water to 150 ml, acidify with 5 ml of sulphuric acid, density 1.84 g/cu.cm, add 10-25 ml of ammonium persulphate solution and boil for 5-7 minutes on a gause with an asbestos centre to completely destroy excess persulphate. Cool the solution, add a drop of ferroin solution and titrate with hydroquinone solution until the solution turns pink.

SELECTIVE TITRIMETRIC DETERMINATION OF CERIUM (IV) WITH HYDROQUINONE

The method is based on the reaction of salts of tetravalent cerium with manganous sulphate, reduction of the formed hydrate $MnO_2 \cdot xH_2O$ with manganous salts in pyrophosphate medium, and titration of the pyrophosphate complex of Mn^{III}, which is formed in the quantity equivalent to that of Ce^{IV}, with hydroquinone solution in the presence of diphenylamine:

$$2Ce^{IV} + Mn^{II} + 3H_2O = 2Ce^{III} + MnO(OH)_2 + 4H^+$$

$$MnO(OH)_2 + [Mn(H_2P_2O_7)_2]^{2-} + 4H_2P_2O_7^{2-} + 4H^+ = 2[Mn(H_2P_2O_7)_3]^{3-} + 3H_2O$$

$$[Mn(H_2P_2O_7)_3]^{3-} + C_6H_4(OH)_2 = 2[Mn(H_2P_2O_7)_2]^{2-} + C_6H_4O_2 + 2H_2P_2O_7^{2-} + 2H^+$$

The method can be used to determine from 39 to 158 mg of cerium in the presence of 730 mg of $Cr_2O_7^{2-}$ with an error of 0.6 per cent.

Reagents

Hydroquinone, 0.1 *N* solution in 3 per cent sulphuric acid.
Sulphuric acid, 4 *N* solution.
Potassium sulphate, saturated solution.
Manganous sulphate, 0.1 *N* and 0.5 *M* solutions.
Sodium pyrophosphate, disubstituted, saturated solution.
Diphenylamine, 1 per cent solution in concentrated H_2SO_4.

Procedure

Add sulphuric acid to a solution containing 30-200 mg of cerium to adjust the acid concentration to 0.2-0.4 *N*. Next add 20 ml of potassium sulphate (the total volume of the solution should not exceed 40 ml), heat to boiling and add 20 ml of a 0.1 *N* manganous sulphate solution. Heat the solution until it clears, separate the precipitate on a blue ribbon filter and wash with water. Place the filter with the precipitate in a titration flask and dissolve the precipitate in a mixture of 60 ml of saturated solution of sodium pyrophosphate, 10 ml of 0.5 *M* manganese sulphate solution and 40 ml of a 4 *N* sulphuric acid solution. Titrate the red-violet solution with hydroquinone until its colour turns pale pink, add two drops of diphenylamine solution and continue titrating until the solution turns pure yellow.

1 ml of 0.1 *N* solution of hydroquinone is equivalent to 14.013 mg of cerium.

PHOTOMETRIC DETERMINATION OF THE SUM OF THE LANTHANIDES IN MONAZITES

Rare earth elements react with arsenazo I to give violet compounds with absorption maximum at 540-560 nm. The characteristics of the compounds of arsenazo I with some lanthanides are given below:

Element	Y	La	Ce	Nd	Pr
$\varepsilon \times 10^{-4}$ at					
580 nm	2.25	2.35	2.40	2.50	2.45
600 nm	1.35	1.35	1.40	1.50	1.45
$K \times 10^{10}$	2.7	4.1	3.1	3.3	3.1

Coloured compounds begin forming at pH 2.5-3.0, their absorption increases with pH to 6.5; the absorption is practically constant at pH from 7.0 to 9.0. The molar ratio of the components is 1 : 1.

The following elements also form coloured compounds with arsenazo I in the conditions of the determination: Sc, U^{VI}, Cu, Al, Th, V^{IV}, Zr, Ga, In, Pd and Fe^{III}. To separate them from the lanthanides, the latter are precipitated with thorium as oxalates in an acid medium. Precipitation can be effected with oxalic acid from a hot solution or with acetonedioxalic acid at pH 0.5-2 from homogeneous solutions.

If thorium is present in solution, it is first determined photometrically with arsenazo I at pH 1.6-1.8 (the lanthanides do not interfere at this acidity). Next the sum of thorium and the lanthanides is determined with the same reagent at pH 6-7. The lanthanides are determined by deduction.

Reagents

Sulphuric acid, diluted 1 : 2.
Hydrogen peroxide, 3 per cent solution.
Ammonia solution, diluted 1 : 4.
Oxalic acid, 1 and 10 per cent solutions.
Nitric acid, density 1.4 g/cu.cm and 0.1 *M* solution.
Arsenazo I, 0.05 per cent solution.
Borate buffer solution, pH 7.5. Dissolve 10.53 g of boric acid and 2.84 g of sodium tetraborate in water and dilute to 1 litre.
Cerous chloride, standard solution. 1 ml of the solution is equivalent to 20 μg of cerium.
Hydrochloric acid, diluted 1 : 2.
Methyl orange, 1 per cent solution.

Constructing a Calibration Curve

Place 1, 2, 3, 4 and 5 ml of the standard solution of cerous chloride into five 50-ml volumetric flasks, add 3 ml of arsenazo I solution, 10 ml of the borate buffer into each flask and finally add water to the mark. Measure the absorption of the solutions on a universal photometer or an absorptiometer using a solution containing 3 ml of arsenazo I and 10 ml of the buffer in 50 ml as the standard. Construct a calibration curve using the data obtained.

Procedure

Place a sample of monazite weighing 0.1-0.3 g into a 100-ml beaker and heat with 10-15 ml of sulphuric acid on a sand bath for 90-120 minutes with periodical stirring. Evaporate the solution to 2-3 ml, add 10-15 ml of hydrogen peroxide solution, mix, add 20-25 ml of water and pass through a white ribbon filter into a 150-200 ml beaker. Add three drops of methyl orange to the filtrate and neutralize with ammonia solution with stirring. Next add 2 ml of hydrochloric acid (excess acid increases the solubility of rare earth oxalates), heat the solution almost to boiling, add 15 ml of a 10 per cent solution of oxalic acid, keep at the boiling point for 20-30 minutes and allow the mixture to stand overnight.

Separate the precipitate on a blue ribbon filter, wash with 1 per cent oxalic acid and allow the solution to drip from the filter. Now puncture the filter and wash off the oxalates into a 100-ml beaker using nitric acid, density 1.4 g/cu.cm. Heat to dissolve the precipitate, evaporate to 1-2 ml, add water to 25 ml and transfer into a 100-ml volumetric flask.

Using a pipette, transfer an aliquot containing 20-100 μg of the lanthanides into a 50-ml volumetric flask, add 3 ml of arsenazo I solution, 10 ml of the borate buffer solution and dilute with water to the mark. Measure the absorption of the solution at 540-580 nm (D_1).

Pipette another aliquot of the same size into another 50-ml volumetric flask, add 3 ml of arsenazo I solution, 5 ml of 0.1 *M* nitric acid, and dilute with water to the mark. Measure the absorption of the solution in the same conditions (D_2).

The difference in the absorptions, $D = D_1 - D_2$, is the absorption of solution of arsenazo I compounds with the lanthanides.

Determine the lanthanides in the aliquot using the calibration curve.

FLUORIMETRIC DETERMINATION OF EUROPIUM COMPOUNDS IN THE PRESENCE OF OTHER LANTHANIDES

The ion of tervalent europium reacts with phenanthroline and atophan (2-phenylquinoline-4-carboxylic acid) to form a sparingly soluble complex which emits bright fluorescence when irradiated with a mercury lamp. The fluorescence curve has three maxima, at 579, 583 and 612 nm. The maximum fluorescence is at 612 nm. The model СВД-120А mercury lamp, and a УФС-1 monochromator are used for the irradiation. The optimum conditions for the determination are as follows: pH 6-7 (urotropine), the concentration of urotropine is 200 mg, of phenanthroline 7 mg, of atophan 2.5 mg in 5 ml of solution; to stabilize the colloid, 0.1-0.2 ml of 1 per cent gelatin solution is added; the intensity of fluorescence is measured in 20-30 minutes after the solution is prepared.

Only the samarium (III) fluoresces, while the other lanthanides either increase (La, Gd, Tb, Lu, Y) or decrease (Ce, Pr, Nd, Ho, Er, Tm, Dy) the fluorescence of the reagent compound with europium. The increment method is therefore used for the determination of europium.

The method is suitable for the determination of europium in various lanthanides (parenthesized are the limits of detection of europium, as calculated with reference to 200 μg of lanthanide oxide): Gd (0.0005), La, Y, Tb (0.001), Yb (0.015), Sm, Tm, Lu (0.02), Ce, Ho, Er (0.05), Pr (0.08) and Nd (0.1). It is not recommended to take quantities exceeding 200 μg of the oxides because of the limited solubility of triple complexes with phenanthroline and atophan. The method can be used to determine 0.093 per cent of Eu in minerals with mixed lanthanide composition, 0.07 per cent of Eu in monazite, 0.85 per cent of Eu in a mixture of lanthanide oxides and 0.115 per cent of Eu in loparite.

Reagents

*Europium chloride, **standard solution.*** 1 ml is equivalent to 0.001-0.2 μg of Eu_2O_3 (depending on the properties of the sample).

Urotropine, 40 per cent solution.

Gelatin, 1 per cent solution.

Atophan, 0.5 per cent solution, pH 8. Add 22 ml of 0.1 *N* solution of KOH to 0.5 g of atophan. Heat the mixture to dissolve the solid, cool, and dilute with water to 100 ml.

Phenanthroline, 1 per cent solution, pH 5. Add 20 ml of 0.1 *N* solution of HCl to 1 g of phenanthroline and dilute with water to 100 ml.

Procedure

Calcine a sample of lanthanide oxides to remove CO_2 and water, dissolve the sample in a small quantity of hydrochloric acid and dilute with water to adjust the oxide concentration to 1 mg/ml. Place accurately measured volumes of the solution (containing 100-200 μg of lanthanides) into three test tubes, add different volumes of the standard solution of europium chloride into two of them, one additive being approximately equivalent to the europium content of the sample. Add 0.5 ml of urotropine solution, 0.1-0.2 ml of gelatin solution, 0.5 ml of atophan and 0.7 ml of phenanthroline solution into all test tubes with stirring. Dilute with water to 5 ml and allow to stand for 20-30 minutes. Measure the fluorescence intensity at 612 nm.

Determine the europium content of the aliquot (x) from the equation:

$$x = cI_x/(I_{(x+c)} - I_x)$$

where c is the increment weight, in μg; I_x and I_{x+c} is the intensity of fluorescence of solutions of the sample and of the sample plus the increment.

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Thorium

Thorium, Th, has the positive valency of 4. Compounds of thorium in its lower valency states are unstable in aqueous solutions. The ion of Th^{IV} is colourless. The standard electrode potential in an aqueous medium at 25°C with reference to the standard hydrogen electrode in the reaction $Th \rightleftharpoons Th^{4+} + 4e^-$ is -1.899 V.

The reactions of Th^{4+} resemble greatly those of Zr^{4+} and Ti^{4+}. Thorium hydroxide is white. It begins precipitating from thorium salt solutions at pH 3 (0.01 *M*). Thorium is precipitated quantitatively at pH 6. The solubility product of thorium hydroxide is about 10^{-50}.

Potassium fluoride and hydrofluoric acid precipitate a bulky jelly-like substance, $ThF_4 \cdot xH_2O$, which is sparingly soluble in water, in excess HF (in contrast to Zr, Ti, Be, Al, Ta and Nb but Ce^{IV} and U^{IV} also form sparingly soluble fluorides) and in dilute HNO_3. The solubility product of thorium fluoride is about 10^{-27} (ionic strength, 0.5).

Ammonium carbonate precipitates a white substance from thorium salt solution. The precipitate is soluble in excess precipitant because $(NH_4)_6[Th(CO_3)_5]$ is formed. When hydrogen peroxide is added, a peroxidic compound of thorium precipitates from the solution of this complex. Thallium salts of the carbonate complex of thorium precipitate as small prisms (crystals) suitable for microcrystalloscopic detection of thorium [1]. The phosphate $Th_3(PO_4)_4$ precipitates at pH 2.7. Sodium hypophosphate, $Na_2H_2P_2O_6$, precipitates white amorphous $ThP_2O_6 \cdot xH_2O$ from strong acid (HCl) solutions. The precipitate is practically insoluble in caustic alkalis and in concentrated hydrochloric acid [2]. Zr^{IV} and Ti^{IV} react similarly but the lanthanides do not interfere with the isolation of thorium.

Thorium pyrophosphate, ThP_2O_7, and thorium hexacyanoferrate (II), $Th[Fe(CN)_6]$ are sparingly soluble in dilute acids.

Precipitation with sodium selenite, Na_2SeO_3, can be used to separate Th from Be [3]. The precipitate of thorium selenite is calcined to ThO_2.

Potassium iodate reacts with the thorium ion even in a strong nitric acid medium to give a sparingly soluble white compound [4] used for the isolation and titrimetric determination of thorium [5].

Oxalic acid precipitates white crystals of $Th(C_2O_4)_2 \cdot 6H_2O$

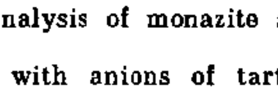
from thorium salt solutions. The substance is practically insoluble in excess precipitant. The addition of ammonium oxalate to a dilute hydrochloric or nitric acid solution also gives a precipitate. When boiled with ammonia (in the presence of excess oxalate ion) the precipitate is dissolved and re-precipitated on subsequent acidification with hydrochloric acid. The complex ion, $[Th(C_2O_4)_4]^{4-}$, is formed in the presence of excess ammonium oxalate or an alkali metal. When acidified, the ion is decomposed because the concentration of the oxalate ion $C_2O_4^{2-}$ decreases due to the formation of slightly dissociated $H_2C_2O_4$. Precipitation of thorium oxalate from dilute nitric acid solutions is used for the isolation of thorium and also cerium and other lanthanides, for example, in the analysis of minerals [6, 7]. Other dicarboxylic acids (succinic, adipic, phthalic) also precipitate Th^{IV} from weak acid solutions.

Benzoic, *o*-chlorobenzoic, *m*-nitrobenzoic, *o*- and *p*-aminobenzoic acids precipitate Th^{IV} and Zr^{IV}. These acids are used to isolate thorium from the lanthanides in the analysis of monazite sand, and also to separate Th from U.

Thorium forms complex compounds with anions of tartaric, citric and other organic oxyacids.

EDTA reacts with the thorium ion in the molar ratio of 1 : 1. It is used for the titrimetric determination of thorium [5, 7].

N-benzoylphenylhydroxylamine precipitates quantitatively the thorium ion at pH 2 in the form of white crystals. The precipitate is stable to 220°C. The reagent is used for the gravimetric determination of thorium and its separation from the lanthanides (pH 4.5) and uranium (in the presence of ammonium carbonate at pH 7-8.5). The compound of thorium with N-benzoylphenylhydroxylamine is readily extracted with organic solvents such as benzene, chloroform, isoamyl alcohol, etc. The separation of thorium from the lanthanides is based on its extraction with isoamyl alcohol at pH 4.5. This reagent can also be used to separate thorium from cerium which is precipitated and extracted only at pH 6.5-7.5.

Azo compounds, containing the group  react with the thorium ion to form coloured compounds [8].

Thorin, *o*-(2-hydroxy-3,6-disulpho-1-naphthylazo)-benzenearsonic acid, is often used in practice. Its aqueous solution is orange. When acidified, the reagent solution turns pale yellow. If a thorium salt solution is added to the yellow solution of the reagent in 0.5 *M* hydrochloric acid (pH 0.7), red colour develops. If the concentration of the salt increases, a red precipitate falls out. The absorption maximum of the reagent solution in 0.5 *M* hydrochloric acid is at 480 nm, and of the thorium compound with the reagent in 0.5 *M* hydrochloric acid is at 510 nm. The thorium ion reacts with the reagent in the molar ratio of 1 : 2, the optimum pH being 1.7.

The reaction equation is

$$Th^{4+} + 2H_3R^{2-} \rightleftharpoons Th(H_3R)_2$$

where R is the thorin anion.

The constant of the complexation reaction is $(7.9 \pm 0.9) \cdot 10^9$ [9].

Thorin is used for the detection and photometric determination of thorium in dilute hydrochloric acid medium. The ions of U^{IV}, Fe^{III}, Ti^{IV}, Zr, Sn^{IV}, large quantity of SO_4^{2-} interfere and the ions of the lanthanides, of Al, and U^{VI} [10] do not interfere with the determination of thorin. Anion-exchange resin AB-17, impregnated in thorin solution, can be used for separation of microgram quantities of thorium from gram quantities of lanthanides, aluminium and iron [11]. The method can be used for determining thorium in oxides and lanthanide salts in quantities over 1×10^{-4} per cent. Other anion-exchangers (ЭДЭ-10, ЭДЭ-10П, АН-2Ф, АВ-16) are not suitable for the purpose.

Arsenazo III reacts with the thorium ion even in 4-10 *N* hydrochloric acid at which the ions of most other elements do not react with this reagent [12, 13]. Only Zr, Ti^{IV} and U^{IV} ions interfere with the photometric determination of thorium. The reagent is used for the determination of thorium in zirconium [13-17]. Very small quantities of thorium are determined by the extraction-photometric method [18]. The absorption of the solutions is measured at 665 nm.

Arsenazo I [19-21] and arsenazo II [22, 23] are also used for the photometric determination of thorium. Arsenazo I (the solution of the reagent in the presence of thorium is pink) reacts with the thorium ion (1 : 1) in a weak acid medium to form a blue-violet complex compound. The absorption maximum of the complex solutions is at 580 nm, the optimum pH being 1.3-3.0. The compound is formed immediately after mixing the components and remains stable in scattered light for a month. The instability constant of the complex is 1.6×10^{-16}. The limit of determination is 0.7 μg of thorium in one millilitre. The maximum intensity of colour is at the concentration of arsenazo I of 2-3 mg in 50 ml of solution. The ions of U^{IV}, Pu^{IV}, Ti^{IV}, Fe^{III}, Zr and Al react with arsenazo I like thorium. The ions of the lanthanides do not interfere with the determination of thorium at pH 1.9 even if contained in 1300-fold quantities. This makes it possible to separate traces of thorium in the form of oxalate from the interfering ions using lanthanide oxalates as co-precipitators.

Thorium can be determined in the presence of Zr and Ti if tartaric and ascorbic acids are used to mask zirconium and titanium respectively; 50 mg of tartaric acid mask a 35-fold quantity of zirconium, while 50 mg of ascorbic acid in 50 ml of solution make it possible to determine thorium in the presence of a ten-fold quantity of Ti. Great (over hundred-fold) amounts of Ce^{IV} interfere with the determination, since they oxidize ascorbic acid. The fluoride, sulphate, phosphate and other ions which form precipitates or complex compounds with the thorium ion, also interfere.

1-(2-Pyridylazo)resorcinol reacts with the thorium ion to form coloured compound. It is used for the photometric determination of thorium.

Alizarin (solution in ethyl alcohol) colours thorium containing solutions violet. It is used for the detection of thorium [24].

8-Quinolinol precipitates quantitatively Th^{IV} even from dilute acetic acid solutions (pH 3.7-4.0) [25, 26]; this provides the conditions for the separation of thorium from Ce^{III} (the hydroxyquinolinates of Ce^{III} begin precipitating at pH 4.4). A yellow substance $Th(C_9H_6OH)_4$ precipitates at room temperature while at temperatures over 70°C, an orange compound with the formula $Th(C_9H_6OH)_4 \cdot C_9H_7ON$ precipitates.

Morin causes yellow-green fluorescence in a 1 *N* hydrochloric acid solution in the presence of the thorium ion. The fluorescence vanishes at higher acid concentrations. Unlike thorium, zirconium fluoresces even in a 10 *N* hydrochloric acid solution.

Quertcetin reacts with the thorium ion in a water-ethanol medium to form a yellow compound. It is used for the photometric determination of thorium.

Xylenol orange reacts with Th^{4+} (molar ratio 1 : 1) at pH 2.7-3.3 to form a compound with the absorption maximum at 570 nm [27]. The stability constant of the complex is 6.7×10^{59} (the ionic strength 10^{-3}). The reagent is used as a complexometric indicator for titration of the thorium ion [28] and for the photometric determination of thorium [27].

A review of the methods for the determination of thorium is given in the literature [29-33].

ISOLATION OF THORIUM FROM MONAZITES

Monazite is decomposed by fusion with sodium peroxide. Thorium and a sum of the lanthanides are precipitated as oxalates. After decomposition of the oxalates by heating with nitric acid, thorium is determined photometrically with arsenazo I, quertcetine, or 1-(2-pyridylazo)resorcinol.

Reagents

Sodium peroxide, crystalline.
Hydrochloric acid, 2 *N* solution.
Oxalic acid, 1 and 10 per cent solutions.
Nitric acid, diluted 1 : 1.

Procedure

Place a sample of monazite weighing 50-100 mg and containing 250-500 μg of thorium in a porcelain crucible over sodium peroxide (about 0.5 g) and cover with another portion of sodium peroxide

(0.5 g). Place the crucible into a larger crucible and heat over a burner raising the temperature gradually until a uniform melt is obtained. Keep the mixture liquid for about 10 minutes, then cool and place the crucible in a 100-ml beaker. Add 20-25 ml of water acidified with a few drops of hydrochloric acid. After leaching, remove the crucible from the beaker, rinse with water, and then with hydrochloric acid, and add the washings to the solutions. Acidify the solution with hydrochloric acid to pH 1, add 5 ml of hydrochloric acid and pass the solution into another beaker, having the capacity of 250 ml, through a blue ribbon filter. Heat the filtrate until water vapour begins evolving, add 10 ml of a hot 10 per cent solution of oxalic acid, heat for another 1-2 minutes and allow to stand overnight.

Separate the precipitate of thorium oxalate and lanthanide oxides on a blue ribbon filter, wash with a 1 per cent solution of oxalic acid, puncture the filter and wash off the precipitate with nitric acid into a 100-150 ml beaker. Heat the beaker contents to completely dissolve the oxalates, evaporate to 5 ml, transfer into a 50-ml volumetric flask, add water to the mark, and mix.

Determine thorium photometrically in an aliquot.

Note. If the thorium content of monazite is less than 0.1 per cent, decompose the sample with sulphuric acid. If the monazite sample contains thorium in the quantity exceeding 0.5 per cent, increase the volume of the solution or take a smaller aliquot for the photometric determination of thorium.

IODATE-COMPLEXOMETRIC DETERMINATION OF THORIUM

Potassium iodate precipitates the thorium ion in a nitric acid medium as a sparingly soluble compound, whose formula depends on the conditions of precipitation [31-33]. The ions of zirconium, titanium, uranium (IV), and cerium (IV) interfere with the determination. The ions of titanium and zirconium can be masked with oxalic acid; the uranium (IV) ion is oxidized to uranyl ion; cerium (IV) is reduced to cerium (III) with hydrogen peroxide. Other lanthanides do not interfere with the precipitation of thorium. When thorium is determined by the combined iodate-complexometric method, the thorium iodate may have any composition, because thorium is determined complexometrically and not by the iodate bound with it. To that end, the thorium iodate precipitate is dissolved in a definite quantity of standard solution of EDTA and its excess is titrated with a standard solution of copper sulphate in the presence of 1-(2-pyridylazo)-2-naphthol as an indicator. The greenish colour of the solution sharply changes at the end point of the titration into red-violet from a single excess drop of copper sulphate.

The error of the determination of 4-20 mg of thorium does not exceed 3-4 per cent.

Reagents

Nitric acid, density 1.4 g/cu.cm.
Potassium iodate, 0.5 per cent solution in 1 *M* nitric acid and 15 per cent solution of nitric acid diluted 1 : 1.
EDTA, 0.01 *M* solution.
Copper sulphate, 0.01 *M* solution.
1-(2-Pyridylazo)-2-naphthol, 0.1 per cent solution in ethanol.
Ammonia, 1 *M* solution.

Procedure

Take 10 ml of solution containing 4-20 mg of thorium and add 6-7 ml of nitric acid. Dilute with water to 25 ml, add 5 ml of a 15 per cent potassium iodate solution and heat on a sand bath to complete coagulation of the precipitate. Separate the precipitate on a blue ribbon filter, wash 3-4 times with a 0.5 per cent potassium iodate solution and transfer on the filter into the original precipitation beaker. Add 15 ml of EDTA solution, and adjust the pH of the solution to 3-4 with ammonia solution to paper indicator. Heat the mixture on a sand bath to complete dissolution of the precipitate (10-15 minutes at 80-90°C). Separate the paper pulp, wash several times with water, collect the filtrate and the washings in a 100-ml Erlenmeyer flask, add 3-4 drops of a solution of 1-(2-pyridylazo)-2-naphthol and titrate excess EDTA with copper sulphate solution until the yellow-green solution turns red-violet.

1 ml of 0.0100 *M* solution of EDTA is equivalent to 2.32 mg of thorium.

Note. The pH of the solution should be maintained during the titration at the level not below 3 since otherwise the solution will turn red-violet from the very first drop of copper sulphate because the copper compound with 1-(2-pyridylazo)-2-naphthol is more stable at pH 3 than copper complexonate.

COMPLEXOMETRIC DETERMINATION OF THORIUM IN MONAZITE SAND

Monazite contains thorium, lanthanides, calcium, phosphate. It often associates in rock with zircon, $ZrO_2 \cdot SiO_2$, and ilmenite, $FeTiO_3$.

The sample is decomposed by concentrated sulphuric acid

$$2LnPO_4 + 3H_2SO_4 = Ln_2(SO_4)_3 + 2H_3PO_4$$

$$Th_3(PO_4)_4 + 6H_2SO_4 = 3Th(SO_4)_2 + 4H_3PO_4$$

where Ln are the lanthanide ions.

After dissolution of the sample, thorium is separated together with the lanthanides (in the form of oxalates) from zirconium, titanium, iron and the phosphate ion. The oxalate precipitate is dissolved in concentrated nitric acid, and thorium is precipitated as the iodate with its subsequent separation from the lanthanides. Thorium is finally determined complexometrically.

Reagents

Sulphuric acid, density 1.84 g/cu.cm and 1 per cent solution.
Oxalic acid, 10 per cent and 1 per cent solution.
The other reagents are the same as in the previous section.

Procedure

Grind thoroughly a sample of monazite weighing 50-80 mg and decompose with sulphuric acid, density 1.84 g/cu.cm, with heating. Cover the crucible with a watch glass and heat on a sand bath to complete dissolution of the sample. Remove the glass, evaporate the crucible contents to dampness, cool, and dissolve the residue in water. Separate the precipitate on a filter and wash with a 1 per cent sulphuric acid solution. Join the filtrate and the washings, heat almost to boiling, add 30-40 ml of a hot 10 per cent solution of oxalic acid, heat, and allow to stand overnight.

Separate the precipitate of oxalates and wash with 1 per cent oxalic acid solution. Dissolve the precipitate in 5-10 ml of nitric acid, wash the filter with water and proceed further as for the determination of thorium by the iodate-complexometric method in solutions of pure salts.

PHOTOMETRIC DETERMINATION OF THORIUM IN MONAZITES WITH ARSENAZO II

Arsenazo II reacts with the thorium ion in an acid solution in the molar ratio of 1 : 1 to form a blue-violet compound. The maximum absorption of the compound solutions is at 560 nm. The colour develops practically instantaneously and persists for a considerable period of time. The absorption of the complex solutions changes inconsiderably within the acidity range from 0.01 to 0.6 *N* HCl. The Bouguer-Lambert-Beer law holds for the thorium concentrations from 10 μg/25 ml and above. Sulphates mask thorium by 5-6 per cent, their content being 1-5 mg/ml, at the acidity of 0.2 *N* (HCl), and the reagent concentration of 10^{-4} *M*. But the error can be eliminated if equal quantities of sulphate are added to all solutions. The effect of the phosphate ion is lower in the determination of thorium in a medium of 0.1-0.4 *N* hydrochloric acid. The fluoride ion, which masks thorium, is practically removed during the decomposition of monazite by fusion with pyrosulphate.

Zirconium and titanium interfere with the determination but since their content of monazites does not exceed 0.02 per cent, their presence can be ignored. Cations hydrolyzing at pH higher than 2 (cations of the alkali, alkaline earth metals, lanthanides, and also of Al, Cu, Fe^{II}, even when contained in 1000-fold quantities) do not interfere with the determination of thorium.

The method can be used to determine thorium (0.5-7 per cent) in monazites, the procedure containing only 25-30 minutes, and the error being 3-5 per cent. If the thorium content is smaller, it should be separated from the other elements by double fluoride or fluoride-oxalate precipitation. Arsenazo II should be used for the analysis of monazites containing 20-30 per cent of the lanthanides.

Reagents

Thorium nitrate, standard solution. 1 ml is equivalent to 20 μg of thorium.
Arsenazo II, 0.1 per cent solution.
Potassium pyrosulphate, crystalline, 2 per cent solution in hyrochloric acid (1 : 5).
Sodium phosphate, monosubstituted, $NaH_2PO_4 \cdot 2H_2O$, 0.5 per cent solution.
Hydrochloric acid, diluted 1 : 1.
Ascorbic acid, crystalline.

Constructing a Calibration Curve

Place 1, 2, 3, 4 and 5 ml of the standard thorium nitrate solution into five 25-ml volumetric flasks, add 2.5 ml of potassium pyrosulphate solution, 2.0 ml of NaH_2PO_4 solution and 5 ml of arsenazo II into each flask. Next add water to the mark, stir, allow to stand for 5 minutes, and measure the absorption of the solutions at 560 nm using a blank solution as the standard. Construct the calibration curve using the data obtained.

Procedure

Place a sample of monazite weighing 10-200 mg and containing 0.5 per cent (and over) of thorium into a quartz test tube or a porcelain crucible and fuse with 2 g of potassium pyrosulphate for a few minutes, first over a low flame of a soldering lamp and then to the dark-red heat. Cool the melt, dissolve in 40 ml of hydrochloric acid (the solution should be almost clear and free from heavy particles, which is indicative of incomplete decomposition of the sample). Transfer the solution into a 100-ml volumetric flask, add water to the mark, and pass a part of the solution through a filter into a dry flask.

Using a pipette, transfer a 2.5 ml aliquot (containing 25-100 μg of Th) into a 25-ml volumetric flask, add 10-20 mg of ascorbic acid (if iron is contained in the monazite sample), 2.0 ml of NaH_2PO_4, 5.0 ml of arsenazo II solution, dilute with water to the mark, stir, allow to stand for 5 minutes, and measure the absorption of the solution in conditions specified for the construction of the calibration curve, using a solution of 5.0 ml of arsenazo II and 2.5 ml of potassium pyrosulphate solution in the total volume of 25 ml as the standard.

Note. If the thorium content of the monazite sample exceeds 10-15 per cent, the aliquot size should be diminished accordingly and potassium pyrosulphate solution added in quantity to make the total volume of 2.5 ml.

PHOTOMETRIC DETERMINATION OF THORIUM WITH ARSENAZO III

Arsenazo III reacts with the thorium ion to form an inner complex compound whose stability is higher than that of the thorium complexes with arsenazo I and II. Thorium can therefore be determined by the proposed method in strong acid solutions without preliminary separation of the sulphate, phosphate, fluoride, oxalate and other anions. The reagent is very sensitive. The table which follows below gives some characteristics of thorium compounds with arsenazo III.

Some Characteristics of Thorium Compounds with Arsenazo III

Th to arsenazo ratio in complex	pH 3.0-1.5		Concentration 3.5 *M* of HCl or HNO_3	
	Maximum absorption, nm	Molar extinction coefficient, $\varepsilon \times 10^{-4}$	Maximum absorption, nm	Molar extinction coefficient, $\varepsilon \times 10^{-4}$
1 : 1	620	3.23	612	4.15
	670	2.45	665	6.53
1 : 2	565	4.70	not found	
1 : 3	no complex found		615	9.40
			665	12.70
1 : 4	ditto		570	6.41

The following conditions are optimum for the determination of thorium: the concentration of nitric or hydrochloric acid is 3.5-6 *M*, the molar ratio of arsenazo III to thorium is 7.5 : 1. To prevent oxidation of the reagent, 1 g of carbamide is added to nitric acid solutions per mole of the acid. A complex with the molar ratio of 1 : 3 is formed in these conditions. Its absorption maximum is at 665 nm, the molar absorption coefficient being 1.27×10^5.

The reagent can be used to determine thorium in zirconium, niobium-containing materials, etc.

Reagents

Thorium nitrate, standard solution. 1 ml is equivalent to 5 μg of thorium.
Arsenazo III, 0.05 per cent solution.
Hydrochloric acid, density 1.18 g/cu.cm.
Oxalic acid, 0.5 per cent solution.

Constructing a Calibration Curve

Place 1, 2, 3, 4 and 5 ml of the thorium nitrate standard solution into five 25-ml volumetric flasks, add 1 ml of arsenazo III solution and 8 ml of hydrochloric acid into each flask. Dilute the solutions with water to the mark, stir, and measure the absorption on an absorptiometer or a universal photometer using a blank solution as the standard. Construct the calibration curve using the data obtained.

Procedure

Add all the reagents as for the construction of the calibration curve to the solution of the sample and measure the absorption of the resulting solution. Determine the thorium content from the calibration curve. If titanium or zirconium is present in quantities not exceeding 100 μg and 1 mg respectively, add 1 ml of oxalic acid before adding water.

EXTRACTION-PHOTOMETRIC DETERMINATION OF MICROGRAM QUANTITIES OF THORIUM WITH ARSENAZO III

When minute quantities of thorium are determined its compound with arsenazo III is extracted with isoamyl alcohol in the presence of diphenylguanidine chloride and monochloroacetic acid. The method combines the determination of thorium with its concentration by extraction, and can be used for the determination of thorium in dilutions to $1 : 5 \times 10^8$ (0.002 μg/ml).

Reagents

Thorium nitrate, standard solution. 1 ml is equivalent to 1 μg of thorium.
Arsenazo III. 0.025 per cent solution.
Diphenylguanidine chloride, 20 per cent solution.
Isoamyl alcohol.
Monochloroacetic acid, crystalline.
Nitric acid, 0.1 *N* solution.

Constructing a Calibration Curve

Place 1, 2, 3, 4 and 5 ml of the thorium nitrate standard solution into five 25-30 ml separating funnels, add 1 ml of arsenazo III, 4.0 ml of nitric acid, 1 g of monochloroacetic acid, 10 ml of diphenylguanidine chloride solution and 10.0 ml of isoamyl alcohol into each separating funnel. Shake the mixture for two minutes, allow to stand for a while, separate the organic phase, pass it through a paper filter into a dry cell, and measure its absorption against a blank solution at 665 nm. Construct the calibration curve using the data obtained.

Procedure

Add all the reagents as for the construction of the calibration curve to the dissolved sample and measure the absorption of the resulting solution. Determine the thorium content from the calibration curve.

PHOTOMETRIC DETERMINATION OF MICROQUANTITIES OF THORIUM IN ROCK WITH ARSENAZO III

The method can be used to determine 1×10^{-5}-1×10^{-4} per cent of thorium in rock. The sought element is separated from the accompanying ions by precipitation as the fluoride in the presence of calcium salts with subsequent treatment on a cation-exchange resin КУ-2. Thorium is sorbed from 3-4 *M* solutions of HCl by the ion-exchange resin while the accompanying ions (calcium, magnesium, lanthanides, co-precipitated admixtures of iron, manganese, aluminium and titanium) pass into the filtrate. Zirconium, which is sorbed together with thorium, is eluted with 0.1 *N* solution of oxalic acid.

Reagents

Thorium salt, standard solution. 1 ml is equivalent to 1 μg of thorium.
Hydrochloric acid, density 1.18 g/cu.cm. and 3.5 *M* solution.
Arsenazo III, 0.1 per cent solution.
Hydrofluoric acid, 40 per cent solution.
Calcium chloride. 1 ml is equivalent to 100 mg of calcium.
Perchloric acid, 42 per cent solution.
Cation-exchange resin КУ-2 in the NH_4 form; granule size, 0.1-0.25 mm.
Oxalic acid, 0.1 *N* solution.
Ammonium oxalate, saturated solution.

Constructing a Calibration Curve

Place 0.5, 1.0, 1.5, 2.0, 2.5 and 3.0 μg of thorium into 25-ml volumetric flasks, add 15 ml of ammonium oxalate solution, 9 ml of hydrochloric acid, density 1.18 g/cu.cm, 0.5 ml of arsenazo III solution and water to the mark. Measure the absorption of each solution in a cell with a light path of 50 mm against a blank solution. Construct the calibration curve using the data obtained.

Procedure

Wetten a sample of rock containing from 0.5 to 2.5 μg of thorium with water in a platinum dish, add 10-30 ml of hydrofluoric acid (for a sample of 0.5-5.0 g), heat on a sand bath and evaporate to a damp salt. Add 1 ml of calcium chloride solution, then 5-20 ml of hydrofluoric acid, evaporate to 2-3 ml and add 10-50 ml of hot water. Mix the contents, decant over a blue ribbon filter and wash the precipitate two times with 5-10 ml of hot water. Wash off the fluorides into the original platinum dish, add 4-6 ml of hydrochloric acid, density 1.18 g/cu.cm, and evaporate on a sand bath to dryness. Treat the dry residue with 2 ml of perchloric acid and 1 ml of hydrochloric acid, density 1.18 g/cu.cm and heat on a sand bath to remove $HClO_4$ vapour. Wet the residue with 2-4 ml of hydrochloric acid, density 1.18 g/cu.cm, 2-6 ml of water, and evaporate to dryness again. Dissolve the dry residue in 3.5 *M* hydrochloric acid (see Note 1). Pass the solution through a cation-exchange column at a rate of 0.7 or 0.8 ml/min, wash the beaker and the column with 10 ml of 3.5 *M* hydrochloric acid, and then with 6 ml of oxalic acid solution. Eluate thorium with 15 ml of ammonium oxalate solution at a rate of 5-6 drops per minute collecting the eluate in a 25-ml volumetric flask. Add 9 ml of hydrochloric acid, density 1.18 g/cu.cm, 0.5 ml of arsenazo III solution, water to the mark, and measure the absorption of the resulting solution as for the construction of the calibration curve. Determine the thorium content from the calibration curve.

Notes. 1. If thorium is determined in a sample weighing 3-5 g and containing much calcium, magnesium, and aluminium, dissolve the dry residue in 100-150 ml of hot hydrochloric acid (1 : 2) and add a concentrated solution of ammonia until a strong odour is felt. Separate the precipitated hydroxides on a white ribbon filter, wash 4-5 times with NH_3 solution (1 : 5), dissolve the hydroxides in 50-150 ml of hot 3.5 *M* hydrochloric acid solution and collect the solution in the beaker where the hydroxides were precipitated. Add ascorbic acid to the hot solution to reduce tervalent iron, cool the solution and pass it through the cation-exchanger at a rate of 1 ml/min, wash the column with 20 ml of 3.5 *M* hydrochloric acid solution and then with 15 ml of oxalic acid. Eluate thorium into a platinum dish with 50 ml of ammonium oxalate. Evaporate the solution to dryness and heat the residue to complete removal of ammonium oxalate. Calcine the dish contents in a muffle furnace at a temperature of 600-700°C for 3-5 minutes, dissolve the residue in 9 ml of hydrochloric acid, density 1.18 g/cu.cm, transfer into a 25-ml volumetric flask, rinse the dish with 15 ml of ammonium oxalate solution, add 0.5 ml of arsenazo III solution and finally water to the mark. Measure the absorption of the resultant solution as described above.

2. When thorium is determined in a sample weighing 0.2-1 g, the dimensions of the column should be the following: the inner diameter 0.5-0.6 cm, height 24-25 cm; if the sample weighs 2-5 g, the dimensions should be 1 cm and 30 cm respectively.

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Uranium

Uranium, U, has the positive valency from 3 to 6 in its compounds. The compounds of hexa- and tetravalent uranium are of greater importance.

The standard electrode potentials in an aqueous medium at 25°C for uranium are as follows (with reference to the standard hydrogen electrode).

$U \rightleftharpoons U^{3+} + 3e^-$	-1.798 V
$U^{3+} \rightleftharpoons U^{4+} + e^-$	-0.607 V
$U^{3+} + H_2O \rightleftharpoons UOH^{3+} + H^+ + e^-$	-0.538 V
$U^{3+} + 4H_2O \rightleftharpoons U(OH)_4 + 4H^+ + e^-$	-0.019 V
$UO_2^+ \rightleftharpoons UO_2^{2+} + e^-$	-0.052 V
$UOH^{3+} + H_2O \rightleftharpoons UO_2^{2+} + 3H^+ + 2e^-$	-0.299 V
$U^{4+} + 2H_2O \rightleftharpoons UO_2^{2+} + 4H^+ + 2e^-$	-0.333 V

The reactions of the U^{3+} ion resemble those of Fe^{3+}. The U^{III} ion is pinkish-purple. The compounds of uranium (III) in solutions are readily oxidized with oxygen of the air to compounds of uranium (IV). The compound $U(OH)_3$ is brown. It reduces the hydrogen ion in solutions. The U^{III} ion is prepared by the reduction of the U^{VI} ion with very energetic reductants, e.g. by amalgamated zinc.

The cation U^{4+} is green. The ion $U(OH)^{3+}$ is formed in a weak acid solution and slowly polymerizes. The equilibrium constant of the reaction $U^{4+} + H_2O \rightleftharpoons U(OH)^{3+} + H^+$, pK is 1.5 (ionic strength 0.5) and 0.7 (zero ionic strength). The compounds of tetravalent uranium are stable in air. The compound $U(OH)_4$ is green. Sparingly soluble complexes of uranium (IV) are similar to the corresponding compounds of thorium (IV). The tetrafluoride, oxalate and phosphate of tetravalent uranium are sparingly soluble in dilute mineral acids. The ion U^{IV} is precipitated with cupferron from weak acid solutions.

Xylenol orange reacts with the tetravalent uranium ion at pH 1.2-1.6 in the molar ratio of 1 : 1 to form compounds with the absorption maximum at 550 nm [1]. The stability constant of the complex is 1.4×10^{69} (ionic strength, 0.1). The reagent can be used to determine photometrically 2-70 μg of U^{IV}. Even a 2500-fold quantity of the uranium (VI) ion does not interfere with the determination.

Tetravalent uranium forms coloured compounds with arsenazo III.

EDTA reacts with the ions of tetravalent and hexavalent uranium in the molar ratio of 1 : 1. It is used for titrimetric determination of uranium.

The compounds of pentavalent uranium are unstable and disproportionate with the formation of compounds of tetra- and hexavalent uranium:

$$2UO_2^+ + 4H^+ \rightleftharpoons UO_2^{2+} + U^{4+} + 2H_2O$$

Uranium (V) forms anions in an alkaline solution.

The compounds of hexavalent uranium (salts of uranyl and uranates) are most stable. The chloride, UCl_6, forms the uranyl ion UO_2^{2+} when dissolved in water:

$$UCl_6 + 2H_2O \rightleftharpoons UO_2^{2+} + 4H^+ + 6Cl^-$$

The uranyl ion is yellow and stable in acid solutions. At pH 2-3, various condensed basic ions are formed. The reactions of uranium (VI) resemble those of the W^{VI} and Mo^{VI} ions.

The hydroxide $UO_2(OH)_2$ is formed at pH greater than 3.8. It is practically quantitatively precipitated at pH 5.3 (the hydroxide can remain in the colloidal state at pH to 7) and is characterized by pronounced amphoteric properties readily forming the uranate ion UO_4^{2-} and polyuranate ion $U_2O_7^{2-}$, $U_3O_{10}^{2-}$, etc. when the pH is further increased (like polytungstate and polymolybdate ions). When a solution of a uranyl salt is neutralized, a yellow uranate of the alkali metals, e.g. Na_2UO_4, $Na_2U_2O_7$, etc. is precipitated.

Uranyl salts give yellow fluorescence in the solid state and in the alloys with borax or fluoride. This phenomenon is used for a high-accuracy detection and semiquantitative determination of uranium. Fluorescence vanishes in an aqueous solution but develops to the full extent in concentrated sulphuric acid and syrupy H_3PO_4.

Uranyl sulphide, UO_2S, is a brown substance soluble in dilute mineral acids.

Potassium ferrocyanide reacts with the uranyl ion in acetic acid or neutral medium to give red-brown precipitate of variable composition. The reagent is used for the detection of the uranyl ion, and also for its photometric determination.

Sodium phosphate precipitates the uranyl ion as pale yellow $UO_2HPO_4 \cdot 4H_2O$. $NH_4UO_2PO_4 \cdot 6H_2O$ is formed in the presence of ammonia salts.

Selenious acid precipitates quantitatively [2] the uranyl ion as UO_2SeO_3 from a 50 per cent alchoholic solution at pH 4-5. The precipitate is soluble in concentrated hydrochloric acid. Uranium can be determined iodimetrically by titration with H_2SeO_3 after dissolution of the precipitate [2].

The uranium (VI) ion forms unstable oxalate complexes and stable tartrate and citrate complexes. The stability of the fluoride and carbonate complexes is low and they are decomposed at pH below 7 and below 12 respectively.

A yellow peroxide hydrate $UO_4 \cdot 2H_2O$ is precipitated in a neutral concentrated solution of U^{VI} salts by the action of hydrogen peroxide. The hydrate is soluble in ammonium carbonate solution with the development of yellow colour. The solutions in alkali carbonates are orange-yellow.

Thiocyanides react with the U^{VI} ion to form a bright yellow compound.

8-Hydroxyquinoline reacts with UO_2^{2+} to form a brown precipitate, $UO_2(C_9H_6ON)_2 \cdot C_9H_7ON$. The reagent is used for the detection and gravimetric and photometric determination of the uranium (VI) ion.

Ferron reacts with the uranium (VI) ion at pH 5 (urotropine buffer solution) to form a heavy brown compound [3]. The limit of detection of U is 10 μg/ml (finite dilution, $1:10^5$). The reagent reacts with uranium in the molar ratio of 2 : 1. The absorption maximum of uranium compounds is at 360 nm. The reagent is not very selective. The ions of Fe^{III} and Al and of many other elements, as well as the acetate anion, interfere with the determination.

Pearls of uranium with borax obtained in the oxidizing flame are yellow and emit green fluorescence; the pearls obtained in the reducing flame are green; fluoride pearls (NaF) give intense fluorescence.

Cupferron does not precipitate the uranium (VI) ion and it can therefore be separated from the ions of vanadium (V), iron (III) and titanium (IV). After separation of the cupferronates of these metals, UO_2^{2+} can be reduced in the filtrate and the U^{IV} ion precipitated with cupferron.

The ion of U^{VI} can be separated from the ions of Fe^{III}, Ti^{IV}, Bi, Mg, Sr, Cd, Zn, Pb and Mn as readily soluble carbonate complexes. The ion of U^{VI} remains in solution together with the ions of V^{V}, Mo, Al and Th.

To separate uranium (VI) from other elements, $UO_2(NO_3)_2 \cdot 2H_2O$ is extracted with ethyl ether or ethyl acetate, or with amines from sulphuric acid or phosphoric acid solution, with tributyl phosphate, $(C_4H_9)_3PO_4$, trialkyl oxyphosphides, R_3PO, etc. Uranium is extracted in the form of complexes with the SCN^- ion, in the form of compounds with acetyl acetone, 8-quinolinol, cupferron, diethyl dithiocarbamate, xanthogenate, etc.

Uranium is separated from other elements by ion-exchange and distribution chromatography. Both cation- and anion-exchangers are used.

When various materials are analyzed, uranium is precipitated as sparingly soluble ammonium diuranate, $(NH_4)_2U_2O_7$, hydrate peroxide $UO_4 \cdot 2H_2O$, uranium cupferronate $(C_6H_5N_2O_2)_4U$, ammonium uranyl cupferronate $NH_4[UO_2(C_6H_5N_2O_2)_3]$, uranyl 8-hydroxyquinolinate $UO_2(C_9H_6ON)_2 \cdot C_9H_6NOH$, uranyltricarbonate hexaaminocobalt nitrite $[UO_2(CO_3)_3(H_2O)_3][Co(NH_3)_6NO_2]_2$, ammonium uranyl phosphate $NH_4UO_2PO_4 \cdot 3H_2O$, uranium phosphate (IV), $U(HPO_4)_2 \cdot 4H_2O$, uranium (IV) fluoride $UF_4 \cdot 2.5H_2O$, etc.

Valuable titrimetric methods for the determination of small and large quantities of uranium are based on the oxidation-reduction and complex-formation reactions.

Uranium (VI) is titrated with a solution of $CrCl_2$ or $TiCl_3$ in an atmosphere of carbon dioxide, the end point being detected potentiometrically or by indicators.

The methods involving oxidation of the ion U^{IV} to U^{VI} are most popular. Many modifications of these methods have been developed [4, 5]. The U^{VI} ion is first reduced electrochemically to U^{IV} by oxalic acid in the light, by metallic cadmium or bismuth, by amalgamated zinc, cadmium or bismuth, by sodium dithionite, $Na_2S_2O_4$, sodium rongalite $NaHSO_2 \cdot CH_2O \cdot 2H_2O$. The U^{IV} ion is then titrated with a solution of $KMnO_4$, $K_2Cr_2O_7$, NH_4VO_3, $Ce(SO_4)_2$, $Fe_2(SO_4)_3$ and others. Sometimes, the obtained U^{IV} ion is oxidized with excess salt of tervalent iron:

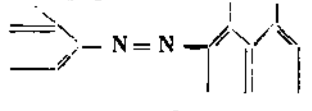
$$U^{4+} + 2Fe^{3+} + 2H_2O \rightleftharpoons UO_2^{2+} + 2Fe^{2+} + 4H$$

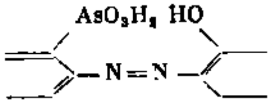
The ferrous ion formed by this reaction in equivalent quantity is titrated with an oxidizer solution. The substances, that can be reduced or oxidized, interfere with the determination of uranium by redox methods.

The complexometric method of determination of uranium (VI) after its reduction to uranium (IV) is of great importance. Titration is carried out at pH 1.7 with EDTA in the presence of arsenazo I [6-9].

Many photometric methods for the determination of uranium with inorganic, and mainly organic reagents are known.

Highly sensitive and sufficiently selective reagents for uranium are those containing the following atom groupings:





These are, for example, arsenazo I, arsenazo III, [10-15], thorin, 4-(2-thiazolylazo)resorcinol [16, 17]. The first two reagents react with the ions of U^{VI} and U^{IV} to give intensely coloured compounds. Thorin reacts with U^{IV}, 4-(2-thiazolylazo)resorcinol reacts with the U^{VI} ion. Among the other reagents for the photometric determination of uranium are chlorophosphonazo I and chlorophosphonazo III [18] (containing the groups $-PO_3H$ and $-OH$), pyridylazo compounds, such as 1-(2-pyridylazo)-2-naphthol and 1-(2-pyridylazo)resorcinol, solochromic azo-compounds (containing two OH-groups in the orthoposition to the azo-group), and hydroxyflavonic dyes (flavonol, morin, quertcetin). Alizarin S, bromopyrogallol red, sulphosalicylic acid, 8-quinolinol, chromotropic acid and other hydroxyl-containing reagents, sodium diethyldithiocarbamate, thioglycolic acid, and ascorbic acid are also used.

Polarographic, coulometric, luminescence, radiometric methods are used for the determination of uranium. The literature contains a review of the methods used for the detection and determination of uranium [6, 19].

VANADATOMETRIC DETERMINATION OF URANIUM

The method is based on titration of tetravalent uranium with ammonium vanadate in the presence of N-phenylanthranilic acid as an indicator:

$$U(SO_4)_2 + 2NH_4VO_3 + 2H_2SO_4 = UO_2SO_4 + 2VOSO_4 + 2H_2O + (NH_4)_2SO_4$$

Uranium (IV) rapidly oxidizes in a 6 N solution of sulphuric acid (and in its stronger concentrations). A direct titration with a dilute (0.001 N) solution of the vanadate is therefore feasible. Phosphoric acid is added to the solution before titration to accelerate the oxidation of N-phenylanthranilic acid with vanadate.

Amperometric titration of U^{IV} contained in quantities exceeding 2.5 μg/ml by NH_4VO_3 solution (with a dropping mercury electrode) is also possible.

Uranium (VI) is reduced to U^{IV} in a reductor filled with electrolytically reduced cadmium in 3 N sulphuric acid. The amount of the U^{III} ion which is formed in this reaction is insignificant. The ions of Fe^{III}, Ti^{IV}, Mo^{VI}, V^{V} and Sn^{IV}, which are reduced together with uranium, interfere with its determination. Uranium is determined in pure solutions after its separation.

Reagents

Sulphuric acid, density 1.84 g/cu.cm 0.1, 1 and 6 N solutions.
Cadmium metal, electrolytic.
Ammonium vanadate, 0.02 N solution.
Phosphoric acid, a density 1.6 g/cu.cm.
N-phenylanthranilic acid, 0.4 per cent solution in 0.4 per cent solution of sodium carbonate.

Procedure

Dilute the solution of uranyl sulphate with water to the mark in a 50-ml volumetric flask. Dilute a 15-ml aliquot containing 5-20 mg of uranium with an equal volume of 6 N sulphuric acid. Wash a cadmium reductor with 1 N sulphuric acid and pass the solution 3 or 4 times through the apparatus at a rate of 1 or 2 drops per second. Wash the reductor twice with 20 ml of 1 N sulphuric acid and twice with 10 ml of 0.2 N sulphuric acid.

The cadmium packing should be covered with liquid during the washing procedure, since penetration of air will interfere with complete reduction of uranium.

Collect the solution containing uranium (IV) in a 250-ml Erlenmeyer flask, add sulphuric acid, density 1.84 g/cu.cm, to adjust its concentration to 10-12 *N* (40-45 ml) and add 5 ml of phosphoric acid and 5-6 drops of N-phenylanthranilic acid. Cool the solution, and titrate slowly with ammonium vanadate until the yellow colour of the solution changes to persistent cherry red from a single drop of the vanadate solution.

Repeat the reduction and titration of U^{IV} until the results become reproduceable. 1 ml of 0.0200 *N* ammonium vanadate solution is equivalent to 2.3807 mg of uranium.

COMPLEXOMETRIC DETERMINATION OF URANIUM IN ALUMINIUM ALLOYS

EDTA reacts with the uranium (IV) ion in a molar ratio of 1 : 1 to form a complex compound with the stability constant of $4.2 \times \times 10^{25}$. The solution is titrated at pH 1.7 ± 0.1 in the presence of arsenazo I as an indicator. The uranyl ion is reduced by formamidine sulphuric acid. At the end point of titration, the blue solution turns pink. The ions of potassium, sodium, lithium, silver, barium, calcium, strontium, magnesium, sulphate, chloride, nitrate, acetone, or limited quantities of aluminium and ferrous iron do not interfere with the determination of uranium. If vanadium is present, ammonium sulphate is added. The ions of thorium zirconium, scandium, indium and titanium interfere and should therefore be removed.

The method is used for the determination of uranium in its alloys with magnesium, aluminium, iron, silicon, in technical salts (nitrates, sulphates, chlorides, acetates, oxalates, etc.), in oxides, and industrial solutions.

Reagents

Hydrochloric acid, density 1.9 g/cu.cm.
Sulphuric acid, diluted 1 : 1.
Potassium peroxydisulphate, crystalline.
Thymol blue, 0.1 per cent solution.
Ammonia solution, diluted 1 : 1.
Formamidine sulphinic acid, 0.66 per cent solution in 0.25 *N* sulphuric acid. Prepare before use.
Arsenazo I, 0.1 per cent solution.
EDTA, 0.025-0.05 *M* solution.

Procedure

Place a sample weighing 0.5-1 g in a beaker and treat with 20-30 ml of hydrochloric acid. When the vigorous reaction stops, add 5 ml of hydrochloric acid, 4 ml of sulphuric acid, and heat to fumes of sulphuric acid. Cool the solution, add 30-40 ml of water and heat to dissolve the salts. If some solid remains undissolved, filter it and wash with water. Collect the filtrate and the washings in a 100-ml volumetric flask. Calcine the filter with the residue in a platinum crucible, fuse with 0.5-1 g of potassium peroxydisulphate, cool the melt and dissolve in water. Add the solution to the main solution in the volumetric flask and dilute with water to the mark.

Transfer an aliquot of the solution containing 15-50 mg of uranium into a 300-350 ml volumetric flask, add 2-3 drops of thymol blue and ammonia until the solution becomes orange yellow (pH 2.5-2.7). Add 30 ml of formamidine sulphinic acid, heat to boiling, and boil for 6-8 minutes to complete reduction of uranium. Add 175 ml of water: the pH of the resultant solution should be 1.7 ± 0.1. Add 1 ml of arsenazo I and titrate with EDTA until the blue solution becomes pure pink.

1 ml of 0.05 *M* EDTA solution is equivalent to 11.904 mg of U.

EXTRACTION-PHOTOMETRIC DETERMINATION OF URANIUM (VI) WITH ARSENAZO III

Arsenazo III reacts with the uranyl ion in an acid medium to form green soluble complex compound with the absorption maximum at 655 nm. The limit of detection of U^{VI} is 0.01-0.02 μg, the molar extinction coefficient being 7.55×10^4. The optimum pH range is 1.7-2.5. The ions of Th, Zr, Al, Cr^{III} and the lanthanides interfere with the determination. The sulphate, fluoride, and phosphate ions do not interfere.

The coloured compound is extractable by butyl alcohol in the presence of diphenylguanidium chloride and EDTA. In these conditions, EDTA masks many cations. The chloride, nitrate, and fluoride ions (when contained to 1 mg) do not interfere with the determination. The sulphate and phosphate ions are precipitated by diphenylguanidium chloride and floated. The precipitate is filtered from the extracts. The effects of thorium is removed by adding fluoride (5 mg KF per 5 ml of solution).

Reagents

Uranyl nitrate, standard solution. 1 ml is equivalent to 5 μg of uranium.
Hydrochloric acid, 0.05 *N* solution.
EDTA, 5 per cent solution.
Arsenazo III, 0.05 per cent solution.
Diphenylguanidinium chloride, 20 per cent solution. Mix about 105 g of diphenylguanidine base with 80 ml of 6 *N* hydrochloric acid, dilute the mixture with water to 500 ml, separate the undissolved residue and acidify the filtrate with a few drops of concentrated hydrochloric acid to pH 3-4.
Butyl alcohol.

Constructing a Calibration Curve

Place 1, 2, 3, 4 and 5 ml of the standard solution of uranyl nitrate into five 25-ml test tubes, heat them on a boiling water bath, evaporate to dryness with bubbling air through a capillary tube, and dissolve the dry residue in 2.0 ml of hydrochloric acid. Add 2.5 ml of EDTA solution, 1.0 ml of arsenazo III, 0.5 ml of diphenylguanidium chloride and 5.0 ml of butyl alcohol into each test tube. Shake energetically the test tubes for about 30 seconds and after the phases have separated, measure the absorption of the solution on an absorptiometer at 655 nm against a blank solution. Construct the calibration curve using the data obtained.

Note. The extraction can first be done with a 20 per cent solution of tributyl phosphate in chloroform using ammonium nitrate as a salting out agent and EDTA to bind the interfering elements in the aqueous phase, with subsequent re-extraction of uranium with arsenazo III and its determination by measuring the absorption of the aqueous phase.

Procedure

Dissolve the sample as for the preparation of the standard series. Determine the uranium content from the calibration curve.

PHOTOMETRIC DETERMINATION OF URANIUM IN ORE WITH 4-(2-THIAZOLYLAZO)RESORCINOL

4-(2-Thiazolylazo)resorcinol (TAR) reacts with the uranyl ion to form two sparingly soluble compounds. One of them, a protonated complex UO_2RH^+, is formed at pH below 3. At pH higher above 3.5, it transfers into another complex, UO_2R. The absorption maximum of the latter is at 540-545 nm. The compound is well soluble in organic solvents miscible with water, such as methyl alcohol, ethyl alcohol, acetone, dioxane, dimethylformamide. The complex is sufficiently stable; $\log K = 11.35$; the molar extinction coefficient is 3.30×10^4. The complex is formed quantitatively at pH 5.0-8.0. The optimum value of pH can be adjusted by an acetate, acetate-ammonia, borate and triethanolamine buffer solution. The solutions obey the Bouguer-Lambert-Beer law in a wide range of uranium concentrations. The solutions are stable for long periods of time. The following elements do not interfere with the determination of uranium in the presence of a masking mixture consisting of cyclohexanediamine tetraacetic acid (CHTA), sulphosalicylic acid and sodium fluoride (in mg/ml): Al 0.111, Mn^{II} 0.130, Cd 1.168, Bi 0.105, Fe^{III} 0.326, Be 0.053, In 0.186, Ga 0.049, Th 0.154, La 0.300, Y^{III} 0.063, Dy 0.107, Yb 0.099, Pr 0.220, Zr 0.114, V^{IV} 0.010, Hg^{II} 0.104, Cu 0.194, Co 0.024, Ni 0.057, Zn 0.735, Cr^{VI} 0.027, Ce^{IV} 0.018, Mo^{VI} 2.70 and W^{VI} 0.488.

Reagents

Uranyl, nitrate, standard solution. 1 ml is equivalent to 20 μg of uranium.
Sulphuric acid, 98 per cent solution.
Ammonia, solutions diluted 1 : 1 and 1 : 3.
Hydrofluoric acid, 40 per cent solution.

Nitric acid, diluted 1 : 1.

Masking mixture. Suspend 25 g of CHTA, 2.5 g of sodium fluoride, and 65 g of 5-sulphosalicylic acid in water, neutralize with ammonia (1 : 1) to pH 7-8 and add water to 1 litre. If necessary, filter the solution. The reagent is stable in storage.

Phenolphthalein, 1 per cent solution in ethyl alcohol.

Triethanolamine buffer solution, pH 7.5-8.0. Dissolve 74.5 g of triethanolamine in 250-300 ml of water, neutralize with nitric or perchloric acid to pH 7.5-8.0, and dilute with water to 500 ml. The solution is colourless or pale yellow. Keep in a dark-yellow bottle.

4-(2-Thiazolylazo)resorcinol, 4×10^{-4} M (about 90 mg) solution in dimethyl formamide.

Constructing a Calibration Curve

Place 1, 2, 3, 4, 5 and 6 ml of the uranyl nitrate standard solution into six 50-ml volumetric flasks, add 10 ml of the masking mixture, 5 ml of TAR solution, 5 ml of triethanolamine buffer and dilute with water to the mark. Measure the absorption of the solutions on an absorptiometer or a spectrophotometer at 560 nm against blank solution. Construct the calibration curve using the data obtained.

Procedure

Place a sample of ore weighing 30-250 mg and containing 30-120 μg of uranium in a platinum crucible, add 1 ml of hydrofluoric acid, heat gently on a sand bath to evaporate to about 0.2 ml, add 3-5 drops of sulphuric acid and heat until sulphuric acid fumes stop evolving. Repeat the treatment with HF and H_2SO_4 two or three times. Add to the residue 1 ml of nitric acid, 3-5 ml of hot water, and pass the solution through a blue ribbon filter into a 50-ml volumetric flask. Add 10 ml of a masking mixture, 5-8 drops of phenolphthalein and ammonia solution (1 : 3) until pale pink colour develops. Continue the procedure as for the construction of the calibration curve. Determine the uranium content from the calibration curve.

Notes. 1. If the sample weighs over 0.25 g, add 15-20 ml of the masking agent to remove the interfering effect of extraneous ions. Accordingly, use larger amounts of the reagents to dissolve the sample.

2. To ensure correct results, measure the absorption at 560 nm.

PHOTOMETRIC DETERMINATION OF URANIUM (VI) WITH ARSENAZO III

Arsenazo III reacts with the uranyl ion to form several complex compounds (depending on the acidity of the solution). The determination of uranium is more selective in a strong acid medium. A green soluble compound is formed in 5.0-7.5 M HNO_3 or HCl. Nitric acid solutions treated with carbamide should preferably be used to create a strong acid medium. The reagent proper is sparingly soluble in hydrochloric acid. The absorption maximum of the complex compound solutions is at 655 nm, the molar extinction coefficient is 6.0×10^4, the molar ratio of the components, 1 : 1, K_{stab} =

$= 1 \times 10^4$.* 5000-fold quantities of Fe, Al, Pb, Zn, Cd, Mg, Mn^{II}, Co, Ba, Sr, Ni, In, Ga and La, hundred-fold quantities of Ca, Cu, Be, and Hg, 500-fold quantities of Bi, Sb, Sc, Cr, and Mo, 100-200-fold quantities of W^{VI}, Sn^{IV}, and Ce^{III}, and a 25-fold quantity of Ti do not interfere with the determination of uranium. The ions of Th, Zr, Hf and Pu strongly interfere. The method has been tested in the determination of uranium in artificial solutions.

The selectivity of the method can significantly be increased by extracting uranium from solutions with pH 1.0, containing NH_4NO_3 and EDTA, by tributyl phosphate solution in toluene or benzene. Uranium is re-extracted from the organic phase by arsenazo III solution with subsequent photometric determination. The ions specified above, as well as the ions of Th, Zr, Hf and Pu do not interfere. The method can be used for the determination of 1×10^{-4}—1.5×10^{-2} per cent of uranium in soil, rock and minerals, samples weighing from 0.1 to 1 g.

Reagents

Uranyl nitrate, *standard solution*. 1 ml is equivalent to 10 μg of uranium.
Nitric acid, density 1.4 g/cu.cm. Add 1 g of carbamide per each 100 ml of the acid, mix the solution and syphon the liquid.
Arsenazo III, 0.25 per cent solution.
Ammonium nitrate, crystalline.
EDTA, crystalline.
Ammonia, 25 per cent solution.
Tributyl phosphate, 20 per cent solution in toluene or benzene.
Washing solution. Dissolve 650 g of NH_4NO_3 and 5 g of EDTA in 400 ml of water, adjust the pH to about 2.0, add water to 1 litre, and filter.

Constructing a Calibration Curve

Place 0.2, 0.4, 0.6, 0.8 and 1 ml of the uranium standard solution into 10-ml graduated test tubes, add 2.5 ml of nitric acid, 0.6 ml of arsenazo III, add water almost to 5 ml and cool to room temperature. Measure the absorption of the solutions at 656 nm against a blank solution, the light path being 1 cm. Construct the calibration curve using the data obtained.

Procedure

Place a solution of the sample (rock, soil, mineral) containing 2-10 μg of uranium into a separating funnel, add 25 g of NH_4HO_3, 0.25 g of EDTA, dissolve the solid, add NH_3 to adjust the pH to 1 (to the universal indicator), and extract for 3 minutes with 25 ml of tributyl phosphate. After phase separation, shake the organic phase four times with 7.5-8.0 ml portions of the washing solution. Add to the extract 1.5 ml of water, 0.6 ml of arsenazo III solution, 3 drops of ammonia solution and shake for three minutes. Transfer the aqueous phase into a test tube or a cylinder with a ground-in stopper, add 0.4 ml of water to the remaining organic phase and

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* According to Joshi, M.K. [2] a M_4L_2 complex is formed. Its stability constant is 6.5×10^9, the molar extinction coefficient being 8.8×10^8.

shake for three minutes again. Join the aqueous phases, add 2.5 ml of HNO_3, mix, and pass through a blue ribbon filter into a cell. Allow the solution to stand for 5 minutes and measure its absorption. Determine the uranium content from the calibration curve.

PHOTOMETRIC DETERMINATION OF URANIUM IN ZIRCONIUM ALLOYS USING CHLOROPHOSPHONAZO III

The uranyl ion reacts with chlorophosphonazo III to form a green compound with the absorption maximum at 670 nm and the molar extinction coefficient of 7.36×10^4. The absorption of the solutions is maximum and constant in a medium of 4-0.5 *N* hydrochloric acid. A 50-fold quantity of oxalic acid, a 100-fold quantity of fluorides and a 5000-fold quantity of phosphates do not interfere with the determination of uranium. The ions of Th, Zr, Hf, Ce^{IV}, Fe^{III} and Ti interfere. Zirconium and hafnium can be masked by ammonium fluoride, titanium by hydrogen peroxide, and cerium (IV) can be reduced to cerium (III) and iron (III) to iron (II).

Reagents

Uranyl nitrate, standard solution. 1 ml is equivalent to 50 μg of uranium.
Hydrochloric acid, diluted 1 : 1.
Ammonium fluoride, crystalline, and 0.1 *M* solution.
Sodium silicate, 0.1 *M* solution.
Chlorophosphonazo III, 0.001 *M* solution.
Buffer solution. Dissolve 10 g of sodium monochloroacetate and 20 g of monochloroacetic acid in water and dilute to 1 litre.

Constructing a Calibration Curve

Place 1, 2, 3, 4 and 5 ml of the uranium standard solution into five 100-ml volumetric flasks, add 5 ml of the buffer solution, 2.5 ml of sodium silicate solution, 12.5 ml of 0.1 *M* ammonium fluoride solution and 2 ml of chlorophosphonazo III into each flask. Now add water to the mark and measure the absorption of the solutions at 670 nm in a cell with a light path of 1 cm against a blank solution. Construct the calibration curve using the data obtained.

Procedure

Dissolve 100 mg of the alloy in a platinum dish in 10 ml of hydrochloric acid and 0.5 g of ammonium fluoride with heating on a water bath. When the solid is all dissolved, add 20 ml of sodium silicate solution, transfer the liquid into a 250-ml volumetric flask, rinse the dish with hydrochloric acid and add the washings to the main solution. Add water to the mark, and determine uranium in an aliquot using the calibration curve.

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Titanium

Titanium, Ti, has the positive valency of 4, 3 and 2. The compounds of titanium (IV) are the most stable. The compounds of tervalent titanium are easily oxidized by the oxygen of air. The compounds of divalent titanium disproportionate in water with liberation of titanium metal and formation of Ti^{III} compounds.

The standard electrode potentials in an aqueous medium at 25°C (with reference to the standard hydrogen electrode) are as follows:

$Ti \rightleftharpoons Ti^{2+} + 2e^-$	-1.630 V
$Ti + H_2O \rightleftharpoons TiO + 2H^+ + 2e^-$	-1.306 V
$Ti + 6F^- \rightleftharpoons TiF_6^{2-} + 4e^-$	-1.19 V
$Ti^{2+} \rightleftharpoons Ti^{3+} + e^-$	-0.368 V
$Ti^{2+} + H_2O \rightleftharpoons TiO^{2+} + 2H^+ + 2e^-$	-0.135 V
$Ti^{3+} + H_2O \rightleftharpoons TiO^{2+} + 2H^+ + e^-$	-0.100 V

When in solution form, the Ti^{3+} ion is violet. The Ti^{4+}, TiO^{2+}, and $[TiHal_6]^{2-}$ ions and various polymeric ions are colourless.

A rather stable complex ion $[TiO(SO_4)_2]^{2-}$ is formed in solutions of titanium (IV) sulphate and also in solutions acidified with sulphuric acid. Some analytical reactions for tetravalent titanium do not therefore occur. To mask the tetravalent titanium ion, oxalic, tartaric, and citric acids, which form low-dissociated complexes with titanium, are used.

The reactions of the Ti^{III} ion are similar to those of the ions of Fe^{III} and Al. The *ion of tervalent titanium is hydrolyzed and* oxidized with atmospheric oxygen to Ti^{IV}. Solutions of tervalent titanium salts are used as reductants in an inert gas atmosphere (titanometry). They reduce the ions of Fe^{III}, NO_3^-, ClO_3^-, ClO_4^- on heating.

KOH solution precipitates the dark-violet hydroxide, $Ti(OH)_3$, at pH higher than 3; $pL_{Ti(ON)_3} = 35$. When acted upon by atmospheric oxygen, $Ti(OH)_3$ turns into titanic acid. $Ti(OH)_3$ does not precipitate in the presence of sodium-potassium tartrate but an intense blue colour develops, and if the concentration is not high, the colour is green and unstable (gradually vanishing). When sodium acetate is added to solutions of Ti^{III} salts, dark green colour develops, and grey-blue precipitate falls out on heating. When concentrated solutions of KSCN or NH_4SCN are added to solutions of tervalent titanium salts an intense violet colour develops.

The colourless cation Ti^{4+} is stable only in strong acid solutions. TiO^{2+} and other ions prevail in solutions with decreased acidity.

Basic sparingly soluble salts begin forming at pH 1.9. At pH 4 the hydrolysis is practically complete. When dilute acid solutions of Ti^{IV} salts are boiled, a white titanic acid precipitates

$$Ti^{IV} + 3H_2O \rightleftharpoons H_2TiO_3 + 4H^+$$

EDTA reacts with the Ti^{IV} ion to form an unstable compound [1] which hydrolyzes at high pH. A more stable compound is obtained in the presence of hydrogen peroxide [2, 3]. The formed peroxytitanyl ion $[OTi(H_2O_2)]^{2+}$ reacts with EDTA in the molar ratio of 1 : 1 to give the compound $Na_2[OTi\,(H_2O_2)Y]$. The reagent is used for the titrimetric determination of titanium [4-8].

The ions of titanium (IV) are reduced to Ti^{III} in an acid solution by metallic zinc, cadmium, or tin. The ions SO_3^{2-} and S^{2-} do not reduce the Ti^{IV} ion.

Ammonia solution precipitates a white hydroxide $Ti(OH)_4$ from solutions of tetravalent titanium salts. The precipitate is practically insoluble in excess precipitant, sparingly soluble in hydroxides of the alkali metals. $Ti(OH)_4$ is liberated also by dilution with water of strongly alkaline solutions of titanates. When boiled, $Ti(OH)_4$ quickly ages and its solubility decreases.

Potassium fluoride precipitates TiF_4 which converts into a relatively sparingly soluble complex compound K_2TiF_6 in the presence of excess precipitant.

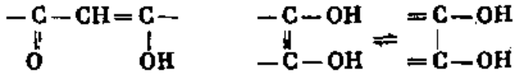
Hydrofluoric acid, HF, reacts with Ti^{IV} to form the acid H_2TiF_6. When solutions of Ti^{IV} salts are evaporated with HF and concentrated H_2SO_4, a non-volatile precipitate TiF_4 remains. When calcined and treated with H_2SO_4, TiF_4 gives TiO_2.

The ferrocyanide ion reacts with the Ti^{IV} ion to form a dark orange precipitate.

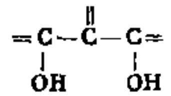
Acid phosphate and arsenate of sodium react with the Ti^{IV} ion to form white sparingly soluble in acetic acids precipitates (Al and Fe^{3+} form similar precipitates). Precipitation does not occur in the presence of hydrogen peroxide (as distinct from Zr).

When hydrogen peroxide is added to acid solutions of Ti^{IV} salts, the solution turns yellow or orange due to the formation of peroxytitanic acid. The colour vanishes on alkalization because a colourless complex is formed. When potassium fluoride crystals are added to the coloured solution of peroxidic compound of titanium, the colourless anion TiF_6^{2-} is formed. Hydrogen peroxide is used for the determination of titanium in ilmenite concentrates by the differential method [9].

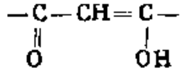
The ions of tetravalent titanium form coloured compounds in weak acid solutions [10-12] with aliphatic and aromatic oxy-compounds containing the following atom groupings



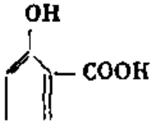
$$-\underset{\underset{O}{\|}}{C}-CH=\underset{\underset{OH}{|}}{C}- \qquad \begin{array}{c}-C-OH\\ \| \\ -C-OH\end{array} \rightleftharpoons \begin{array}{c}=C-OH\\ | \\ =C-OH\end{array}$$



$=\underset{\underset{OH}{|}}{C}-\overset{\|}{\underset{\underset{OH}{|}}{C}}-C=$



$-\underset{\underset{O}{\|}}{C}-CH=\underset{\underset{OH}{|}}{C}-$



Yellow or yellow-orange soluble compounds are formed by Ti^{IV} (in weak acid solutions) with *o*-diphenols, *o*-phenolcarboxylic acids, oxy-γ-pyrones, flavones, aliphatic 1,3-diketones, and endioles. Peri-diphenols (1,8-dihydroxynaphthalene, chromotropic acid) form soluble red-violet compounds at pH 3.3-4.7 which convert into stable orange compounds in a sodium acetate medium (pH 3.8-5.5).

Chromotropic acid (1,8-dihydroxynaphthalene-3,6-disulphonic acid) reacts with the TiO^{2+} ion to form a red-brown soluble compound in a weak acid solution [13], an orange-red compound in sodium acetate solution, and a red-violet compound in concentrated sulphuric acid solution [14]. Chromotropic acid is also used for the detection and photometric determination of titanium [15, 16].

2,7-Dichlorochromotropic acid [17] reacts with the titanium (IV) ion like chromotropic acid. The acid is used for the photometric determination of microgram quantities of titanium in uranium [18], steels [19], aluminium alloys containing vanadium [20], beryllium metal [21], in rock and ore [22]. Small quantities of titanium are determined by the extraction-photometric method [19]. The ion of titanium (IV) reacts with 2,7-dichlorochromotropic acid at pH 2.0 in the molar ratio of 1 : 3. The formed compound absorbs maximum at 490-500 nm. At pH 4.5, the reaction proceeds in the molar ratio of 1 : 4, and the maximum absorption of the solution is at 470 nm [23].

Titanium (IV) reacts with pyrocatechol to form several compounds, depending on the pH of the medium and on the amount of the reagent excess [24, 25]. If the excess of pyrocatechol is great, the complex $[Ti(C_6H_4O_2)_3]^{2-}$ is formed. Diantipyrylmethane increases the stability of the titanium (IV) complex with pyrocatechol in acid solutions [26]. A sparingly soluble compound is formed by diantipyrylmethane, titanium (IV), and pyrocatechol taken in the ratio of 1 : 1 : 2. This compound is extracted with chloroform or dichloroethane from 1-2 *N* HCl medium. The absorption maximum of the extracts is at 330 nm. When the acidity of the aqueous phase decreases, the absorption maximum of the extracts shifts to the region of longer wavelengths. When titanium is determined photometrically [27] in the form of its compound with pyrocatechol and diantipyrylmethane, the extraction is effected with dichloroethane from a 1 *N* hydrochloric acid. Iron (III) is reduced by ascorbic acid. V^V and Mo^{VI}, $W^{(VI)}$ strongly interfere, and V^{IV} does not interfere with the determination. The limit of detection is 6 μg of Ti in 25 ml of the extract, the absorption being measured at 320 nm and 10 μg of Ti in 25 ml of the extract at 420 nm.

Titanium (IV) reacts with phenols and polyphenols in a medium of concentrated sulphuric acid to form coloured compounds: orange-yellow with thymol and red with salicylic acid.

Tichromin [N-methyl-N,N-bis (methylenochromotropic acid)amine] [28, 29] is used for the photometric determination of titanium in alumina, slags, aluminium alloys, highly mineralized water from hot springs.

9-Methyl-2,3,7-trihydroxy-6-fluorone reacts with the Ti^{IV} ion in the molar ratio of 2 : 1 to form [30] a pink complex with the maximum absorption at 520 nm. The molar extinction coefficient is 6.04×10^4. The Bouguer-Lambert-Beer law holds true for titanium concentrations in the range of 0.025-0.6 μg/ml. The optimum pH is 1.7-2.1.

9 (2′,4′-Disulphophenyl)-2,3,7-trihydroxy-6-fluorone (disulphophenylfluorone) reacts with titanium ions [31] at pH 6 in the molar ratio of 2 : 1. Coloured solutions have the absorption maximum at 570 nm, the absorption being directly dependent on the titanium compound concentration. The limit of detection of titanium is 0.01 μg/ml. The reagent is used for the determination of titanium in germanium and silicon in quantities over 5×10^{-6} per cent.

Ascorbic acid reacts with the titanium (IV) ion in weak acid solutions (pH 3.5-6) to form yellow or orange soluble compounds. Ascorbic acid is less sensitive as a reagent for titanium than polyphenols but more selective. It is used for the photometric determination of titanium [32-34].

Cupferron precipitates a yellow salt, and 8-hydroxyquinoline a yellow-orange salt from acid solutions containing the titanium ion.

Both reagents are used for the separation of titanium ions from the ions of other elements, especially from the aluminium ion. Titanium cupferronate is extracted quantitatively with chloroform. Titanium is thus separated from aluminium.

Diantipyrylmethane reacts with titanium (IV) in hydrochloric acid solutions to form coloured compounds. This reagent is one of the most selective and highly sensitive reagents for titanium. It is used for the determination of titanium in vanadium and in vanadium oxychloride, in niobium, molybdenum, aluminium and magnesium alloys, steel, refractory nickel and iron alloys [35-39]. Large quantities of titanium are determined by the differential method [40].

Titanium (IV) reacts with the SCN^- ion and diantipyrylmethane in a 2 *N* HCl medium to form an intensely coloured precipitate which can be easily extracted with chloroform or dichloroethane [41]. The probable formula of the compound is $[TiDiant(SCN)_4]$. The absorption maximum of the extract is at 420 nm, the molar extinction coefficient is 6.00×10^4. The extraction-photometric determination of titanium in steels [42] is based on the formation of this compound.

N-Benzoyl-N-phenylhydroxylamine reacts with titanium (IV) in the molar ratio of 1 : 1 in a 60 per cent ethanol solution [43] containing 1.06×10^{-2} mole/litre of tartaric acid at pH 1.8 ± 0.1. The Bouguer-Lambert-Beer law holds for coloured solutions in the range of concentrations from 3 to 160 μg of Ti in 10 ml of solution at 340 nm, 370 and 400 nm, the deviation being not more than 2 per cent. Fe^{III}, V^{IV} and Mo^{VI} interfere with the determination of titanium. Titanium can be determined [43] in the presence of the ions of Nb, Ta, Zr, and W. N-Benzoyl-N-phenylhydroxylamine is used for the gravimetric determination of Ti^{IV} in the presence of Al [44] and for separation and determination of Nb, Ta and Ti [45].

3-Hydroxy-1-(*p*-chlorophenyl)-3-phenyltriazine reacts with TiO^{2+} to form an orange heat-resistant precipitate. This reagent [46] can be used to separate Ti^{IV} ion from Al, Be, Mg, Th, etc.

The review of the methods used for the analysis of titanium is given in the literature [47].

COMPLEXOMETRIC DETERMINATION OF TITANIUM IN ALLOYS

EDTA reacts with Ti^{IV} in the presence of hydrogen peroxide to form a compound stable at pH below 2 (p*K* about 20.4).

Titanium is determined indirectly by titrating excess EDTA with Fe^{III} salt in the presence of salicylic acid or with a bismuth salt solution in the presence of xylenol orange. In the latter case, a preferable one, the optimum acidity is 0.3 *N* HCl. If the concentration of HCl is higher than 0.5 *N*, the negative error increases. At the acidity lower than 0.2 *N* HCl, niobium interferes since it also forms a stable compound with EDTA and hydrogen peroxide. The method can be used for the determination of titanium in its alloys with uranium, zirconium, molybdenum, tungsten and niobium. Mg, Mn, Zn, La, Ce^{III}, Al and W (to 50 mg), Ta (to 70 mg), Mo (to 100 mg), Cu (to 5 mg), Nb (to 60 mg) and U (to 200 mg) do not interfere with the determination. Fe^{III} and Zr^{IV} form stable complexonates in an acid medium and therefore interfere. During the determination of Ti^{IV} in the presence of Fe^{III} and Zr^{IV}, the sum of these elements is first titrated in the absence of hydrogen peroxide, then hydrogen peroxide is added, and the sum of Ti, Fe and Zr is titrated.

Reagents

EDTA, 0.01 *M* solution.
Bismuth nitrate, 0.01 *M* solution.
Hydrogen peroxide, 30 per cent solution.
Xylenol orange, 0.5 per cent solution.
Sulphuric acid, density 1.84 g/cu.cm and 1 *N* solution.
Ammonium sulphate, crystalline.
Hydrochloric acid, density 1.17-1.19 g/cu.cm.
Nitric acid, density 1.4 g/cu.cm.

Procedure

Determining Titanium in Niobium Alloys. Place a sample weighing 0.1-0.2 g in a 100-ml refractory glass beaker. Add 2-3 ml of sulphuric acid, density 1.84 g/cu.cm, 1-2 g of ammonium sulphate, and heat to dissolve the sample. Evaporate the solution on a sand bath to 0.5-1 ml. Add 3-5 ml of hydrogen peroxide to the residue and dissolve it in 1 *N* hydrochloric acid. Transfer the solution into a 100-ml volumetric flask and add 1 *N* sulphuric acid to the mark. Using a pipette, transfer a 20-ml aliquot (1-5 mg of Ti) into a 300-ml Erlenmeyer flask, add 10 ml of 1 *N* sulphuric acid, add water to 100 ml, 3-5 drops of hydrogen peroxide, and 15 ml of 0.01 *M* solution of EDTA. Stir the solution, keep for 15 minutes, add 3-4 drops of xylenol orange, and titrate excess EDTA with $Bi(NO_3)_3$ until the yellow solution becomes orange-red.

1 ml of 0.01 *M* EDTA solution is equivalent to 0.479 mg of titanium.

Determining Titanium in Ti-Nb-Mo, Ti-Nb-W, Ti-U, Ti-U-Mo, Ti-U-Al, Ti-U-W *and* Ti-Nb-Al *Alloys.*

Place a sample of an alloy containing 5-25 mg of Ti in a 100-ml refractory beaker, dissolve it in a mixture of 8-10 ml of hydrochloric and 1-2 ml of nitric acid with heating on a sand bath. Add 3 ml of sulphuric acid, density 1.84 g/cu.cm, to the obtained solution and evaporate to heavy fumes of H_2SO_4. Dissolve the residue in water, transfer the solution into a 100-ml volumetric flask, and add water to the mark. Using a pipette, transfer a 20.0 ml aliquot into a 300-ml Erlenmeyer flask, add 30 ml of 1 *N* sulphuric acid, dilute the solution with water to 100 ml and proceed further as for the determination of titanium in niobium alloys.

PHOTOMETRIC DETERMINATION OF TITANIUM IN ALLOYS USING CHROMOTROPIC ACID

Chromotropic acid (1,8-dihydroxynaphthalene-3,6-disulphonic acid) reacts with Ti^{IV} to form two compounds, viz., a red compound with the molar ratio of the components of 2 : 1 (the absorption maximum at 470 nm, the molar extinction coefficient, 1.20×10^4) which is formed at pH 1-4; and a yellow compound with the molar ratio of the components of 3 : 1 (the absorption maximum at 423 nm, the molar extinction coefficient, 1.84×10^4) which is formed at pH 3-7. The red complex is more stable and it is therefore more often used for the photometric determination of titanium. The absorption is measured at 520 nm where the difference of the absorption of the red and the yellow complex is greater.

The absorption of the solutions is proportional to the titanium concentration in the range from 5 to 200 μg in 50 ml. U^{VI} and Fe^{III} form a brown and a green compound respectively with chromotropic acid and therefore interfere with the determination of titanium.

Fe^{III} and U^{VI} are first reduced with sulphite or hydrosulphite of sodium to Fe^{II} and U^{IV} and titanium (IV) is then determined. The nitrite, nitrate, fluoride, and oxalate ions also interfere and they should be removed by evaporation with sulphuric acid. The ion of V^{V}, small quantities of tartrate, chloride, sulphate and molybdate ions do not interfere.

The method can be used for the determination of titanium in various objects, for example, in alloyed steels. Chromotropic acid is quickly oxidized and its solutions should therefore be prepared immediately before the analysis. Its pH should also be strictly controlled.

Reagents

Titanyl sulphate, standard solution in 1 *N* sulphuric acid. 1 ml is equivalent to 10 μg of titanium.
Ammonia, 1 *N* solution.
Chromotropic acid, 2.5 per cent solution. Mix 2.5 g of chromotropic acid with 0.15 g of sodium sulphite, and add water to 100 ml. The solution is stable for 2-3 days.
Monochloroacetic acid, 5 per cent solution.
Hydrochloric acid, diluted 1 : 1.
Cupferron, 0.6 and 6 per cent solutions.
Potassium pyrosulphate, crystalline.
Ammonium thiocyanate, 5 per cent solution.
Sodium sulphite (or hydrosulphite), crystalline.
Oxalic acid, 5 per cent solution.

Constructing a Calibration Curve

Place 1, 2, 3, 4 and 5 ml of the titanyl sulphate standard solution into five 50-ml volumetric flasks, add 0, 1, 2, 3 and 4 ml of ammonia solution respectively, and mix. Now add 2 ml of chromotropic acid and 10 ml of monochloroacetic acid into each flask and dilute the solutions with water to 50 ml. Stir the solutions and measure their absorption at 520 nm on an absorptiometer against a blank solution. Construct the calibration curve using the data obtained.

Procedure

Treat a sample of steel weighing 0.5-1.0 g (containing from 0.1 to 1.0 per cent of titanium) with 30 ml of hydrochloric acid with heating until hydrogen bubbling stops. Dilute the solution with water to 200 ml, cool to 5-10°C, add 6 per cent cupferron solution to precipitate vanadium, titanium, and part of iron (control completeness of precipitation), and allow the mixture to stand at the same temperature for 90-120 minutes with frequently stirring. Separate the precipitate on a white ribbon filter, wash with 50-100 ml of 0.6 per cent cupferron solution, transfer into a quartz or a platinum crucible, incinerate carefully, and calcine. Fuse the residue with 3-4 g of potassium pyrosulphate by raising the temperature gradually. Transfer the crucible with the homogeneous melt into a 200-ml beaker, add 30 ml of water, then 1-2 drops of ammonium thiocyanate solution and a few crystals of sodium sulphite (or hydrosulphite) to decolourize the solution. Add 30 ml of oxalic acid solution, dilute with water to the mark in a 200-ml volumetric flask, and stir the liquid.

Using a pipette, transfer 5 ml of the solution into a 50-ml volumetric flask and repeat the procedure as for the construction of the calibration curve. Determine the titanium content of the aliquot from the calibration curve.

PHOTOMETRIC DETERMINATION OF TITANIUM IN ALUMINIUM ALLOYS USING 2,7-DICHLOROCHROMOTROPIC ACID

Solutions of 2,7-dichlorochromotropic acid are oxidized in the light 400 times slower than solutions of chromotropic acid. 2,7-Dichlorochromotropic acid reacts with the Ti^{IV} ion in an acid medium (at pH higher than 0.2) to form a crimson complex compound (the optimum pH range 1.5-2.5). At pH 2, the reagent for Ti^{IV} is 14 times more sensitive than H_2O_2. The solutions absorb maximum at 490 nm, the molar extinction coefficient being 1.12×10^4 at pH 2 and 80×10^3 at pH 1. The absorption is proportional to the Ti concentration in the range of 0.1-5 μg/ml.

Ag, Al, Ba, Be, Bi, Ca, Co, Cr^{III}, Fe^{II}, Ga, Hg, In, Mg, Mn, Ni, Pb, Pt^{IV}, Sb^{III}, Se^{VI}, Sn, Sr, Te^{IV}, Th, Tl^{III}, the lanthanides, Zn and Zr do not interfere with the determination of titanium. Only Fe^{III}, Cr^{VI}, V^{V}, Mo and W interfere at pH 1. The ions of Mo and W can be masked with phosphate, the other ions being reduced by ascorbic acid, which can be present in a hundred-fold excess. The ethylenediamine tetraacetate anion, the fluoride ion (hundred-fold quantities of the tartrate and phosphate ions) interfere with the determination of titanium.

The reagent is used for the photometric determination of titanium in steels, uranium, aluminium alloys containing vanadium, and in water.

Reagents

Aluminium metal, pure.

Titanyl sulphate, standard solution. 1 ml is equivalent to 2 μg of titanium. Prepare the solution in 0.1 *N* sulphuric acid.

2,7-Dichlorochromotropic acid (disodium salt), 0.5 per cent solution.

Sulphuric acid, diluted 1 : 3.

Hydrochloric acid, 1 *N* solution and diluted 1 : 1.

Reductant for Fe^{III} *and* V^V. Mix equal volumes of 5 per cent solutions of hydroxylamine hydrochloride and ascorbic acid.

Sodium acetate, 50 per cent solution.

Constructing a Calibration Curve

Dissolve a sample of aluminium weighing 1 g in a flask in a mixture of 20 ml of sulphuric acid and 2 ml of hydrochloric acid (1 : 1), add water to 50 ml, filter into a 100-ml volumetric flask (for the determination of over 0.005 per cent of titanium) or into a 250-ml flask (for the determination of 0.4 per cent of titanium) and add water to the mark. Place 10 or 5 ml (for 0.005 or 0.4 per cent of titanium respectively) of the solution into five 100-ml volumetric flasks, add 1, 2, 3, 4 and 5 ml of the titanyl sulphate standard solution, 5 ml of the reductant solution into each flask and neutralize with sodium acetate to Congo test paper (the paper colours violet). Now add 10 ml of 1 *N* hydrochloric acid. 5 ml of 2,7-dichlorochromotropic acid into each flask and water to the mark. Measure the absorption of the solutions at 490 nm in cells with a light path of 5 cm, against a blank solution. Construct the calibration curve using the data obtained.

Procedure

Dissolve a sample of aluminium weighing 1 g and containing from 0.005 to 0.4 per cent of titanium in an Erlenmeyer flask in a mixture of 20 ml of sulphuric acid and 2 ml of hydrochloric acid (1 : 1). Dilute the solution with water to make 30 ml and pass into a 100-ml (for thousandth fractions of per cent of titanium) or into a 250-ml (for tenth fractions of per cent of titanium) volumetric flask through a white ribbon filter. Wash thoroughly the dissolution flask and the filter with hot water, cool the solution in the volumetric flask, add water to the mark and stir. Transfer a 10 or 5-ml aliquot (for the thousandth or tenth fractions of per cent of titanium respectively) into a 100-ml volumetric flask, add a small quantity of water and proceed as for the construction of the calibration curve.

EXTRACTION-PHOTOMETRIC DETERMINATION OF TITANIUM IN STEELS WITH 2,7-DICHLOROCHROMOTROPIC ACID

Very small concentrations of titanium (0.01-1 μg/ml) are determined by the extraction-photometric method. Diphenylguanidine reacts with sulpho groups of 2,7-dichlorochromotropic acid to form a low-dissociated compound which is readily extracted with *n*-butyl or isoamyl alcohol. Even lower concentrations (0.001-0.01 μg/ml) are determined by precipitating titanium compounds with 2,7-dichlorochromotropic acid by α-anthracene sulphonate of diphenylguanidinium. The precipitate is separated and dissolved in *n*-butyl alcohol. Mo and W are extracted together with titanium. Cr^{III}, Ni, Cu, V^{IV} are not extracted. The ions of Fe^{III}, V^{V} and Cr^{VI} are reduced with ascorbic acid. The method is used for the determination of titanium in composite steels.

Reagents

Titanium salt, standard solution. 1 ml is equivalent to 5 μg of titanium.
Sulphuric acid, diluted 1 : 8.
Nitric acid, density 1.4 g/cu.cm.
Sodium hexametaphosphate, 1 per cent solution (can stand for a week).
Ascorbic acid, 2 per cent solution.
2,7-Dichlorochromotropic acid, 1 per cent solution.
Diphenylguanidine hydrochloride, 20 per cent solution.
n-Butyl alcohol.

Constructing a Calibration Curve

Place 1, 2, 3, 4 and 5 ml of the titanium salt standard solution into five 50-ml separating funnels, add 5 ml of sodium hexametaphosphate, 10 ml of ascorbic acid and 2 ml of 2,7-dichlorochromotropic acid into each funnel. Stir the solutions, allow to stand for five minutes, and add 4 ml of diphenylguanidine hydrochloride, drop after drop. Stir the solutions, add 10 ml of *n*-butyl alcohol to each funnel and extract for two minutes. Measure the absorption of the extracts at 490 nm against a blank solution. Construct the calibration curve using the data obtained.

Procedure

Dissolve 0.25 g of steel (containing 0.02-0.1 per cent of titanium) in a 100-ml refractory glass beaker in 20 ml of sulphuric acid with heating on a sand bath. Add 1 ml of nitric acid, boil to remove nitrogen oxides, transfer the solution into a 50-ml volumetric flask, add water to the mark, and mix. Proceed further as for the construction of the calibration curve using a 5-ml aliquot of the solution. Determine the titanium content of the sample from the calibration curve.

Notes. 1. If hexametaphosphate is added to the blank solution, titanium can be determined in the presence of many cations. Hexametaphosphate masks tungsten (VI) which forms a coloured compound with 2,7-chlorochromotropic acid in the conditions of the determination.

2. Extraction should preferably be done from sulphuric rather than from hydrochloric acid solution.

PHOTOMETRIC DETERMINATION OF TITANIUM WITH DIANTIPYRYLMETHANE

Diantipyrylmethane reacts with the titanium ion in an acid medium to form a yellow soluble compound with the absorption maximum at 380 nm. Variations of acidity within the range from 0.5 to 4 *N* (HCl) do not affect the absorption of the solutions. The limit of detection of titanium is 0.01 μg/ml, the molar extinction coefficient being 1.80×10^4. The colour develops during 45 minutes and persists for a few months. The absorption of the solution is proportional to the titanium concentration within a wide range of concentrations.

Mg, Al, Zn, Cd, Mn, Cu, Zr, the lanthanides, Mo, Nb, Ta or V^{IV} do not interfere with the determination of titanium. The ions of Fe^{III} and V^{V} are reduced with hydroxylamine.

The method can be used for the determination of titanium in light, ferrous, and non-ferrous alloys.

Determining Titanium in Nickel Alloys in the Presence of Vanadium

Reagents

Titanium salt, standard solution. 1 ml is equivalent to 5 μg of titanium.

Diantipyrylmethane, 1 per cent solution. Dissolve 10 g of diantipyrylmethane in 300-400 ml of water acidified with 15 ml of sulphuric acid, density 1.84 g/cu.cm, and add water to 1 litre.

Sodium acetate, 50 per cent solution.

Mixture of concentrated nitric and hydrochloric acids (1 : 3).
Sulphuric acid, diluted 1 : 1.
Hydroxylamine, 10 per cent solution.
Hydrochloric acid, diluted 1 : 1.

Constructing a Calibration Curve

Place 1, 2, 3, 4 and 5 ml of the titanium salt standard solution into five 25-ml volumetric flasks, add 6 ml of diantipyrylmethane solution and 2.5 ml of hydrochloric acid into each flask, and add water to the mark. Measure the absorption of the solutions at 380 nm against water and construct the calibration curve using the data obtained.

Procedure

Dissolve a sample of alloy weighing 0.25 g (containing 0.01-0.1 per cent of titanium) in 15 ml of the acid mixture, add 15 ml of sulphuric acid and evaporate to dense white fumes. Cool the residue, add 30 ml of water, mix to dissolve the solid, transfer the solution into a 50-ml volumetric flask and add water to the mark. Pipette an aliquot of the solution containing 5-25 μg of titanium, add sodium acetate solution until Congo test paper colours red, and then add, drop by drop, hydrochloric acid until the mixture turns lilac. Add 2.5 ml of hydroxylamine solution, allow the mixture to stand for five minutes, and add 2.5 ml of hydrochloric acid and 6 ml of diantipyrylmethane.

Prepare a blank solution of the alloy by the same procedure but omitting diantipyrylmethane.

Measure the absorption of the solution in 45-50 minutes against the blank solution. Determine the titanium content in an aliquot using the calibration curve.

Determining Titanium in the Presence of Iron and Aluminium

The ion of Fe^{III} is precipitated by diantipyrylmethane in the presence of halides or thiocyanides. The formed compound is extracted with chloroform, and iron can thus be separated from titanium. Titanium is determined photometrically in the aqueous phase using diantipyrylmethane. If the titanium content is very small, the determination can be completed by the extraction-photometric method, with extraction of the titanium compound with diantipyrylmethane by chloroform after separation of iron.

Reagents

Titanium salt, standard solution. 1 ml is equivalent to 5 μg of titanium.
Diantipyrylmethane, 5 per cent solution.
Hydrochloric acid, density 1.17-1.19 g/cu.cm.
Chloroform, pure.
Sulphuric acid, diluted 1 : 1.
Mixture of concentrated nitric and hydrochloric acids (1 : 3).

Constructing a Calibration Curve

Place 1, 2, 3, 4 and 5 ml of the titanium salt standard solution into five 25-m volumetric flasks, add 5 ml of diantipyrylmethane solution and 5 ml of hydrochloric acid into each flask. Add water to the mark and measure the absorption of the solutions at 380 nm against water. Construct the calibration curve using the data obtained.

Procedure

Dissolve a sample containing 100-200 μg of titanium in 10 ml of sulphuric acid with heating on a sand bath, evaporate to 1-2 ml, and dissolve the residue in water. Add water to 15 ml, add 15 ml of hydrochloric acid, 10 ml of diantipyrylmethane solution and 10 ml of chloroform. Extract the iron compound for 5-6 minutes, separate the organic phase, add chloroform and 10 ml of diantipyrylmethane solution to the aqueous phase and repeat the extraction.

Transfer the aqueous phase into a 50-ml volumetric flask and add water to the mark. Using a pipette, transfer 10 ml of the obtained solution to a 25-ml volumetric flask, add 5 ml of diantipyrylmethane solution and dilute with water to the mark. Measure the absorption of the resulting solution. Determine the titanium content from the calibration curve.

EXTRACTION-PHOTOMETRIC DETERMINATION OF TITANIUM WITH THIOCYANATE AND DIANTIPYRYLMETHANE

A sparingly soluble complex of titanium (IV) with diantipyrylmethane and thiocyanate is extracted with pure chloroform from 2-4 *M* hydrochloric acid. The absorption is measured at 420 nm. The molar extinction coefficient at this wavelength is about $6.0 \times \times 10^4$. The interfering effect of tervalent iron, divalent copper, and other elements is removed by sodium thiosulphate which is added before extraction.

The limit of detection is 2 μg of titanium in 25 ml of the chloroform extract. The absorption of the extract is proportional to the titanium concentration in the range of 2-20 μg in 25 ml of the chloroform extract.

Fe^{II}, Ta, Cr, Al, Mn, Zn, Cd, Sn, Sb, Zr, EDTA, fluorides, phosphates, and small quantities of Ni and V do not interfere with the determination of titanium. The ions of Co, W, Mo and Nb interfere.

The error of determination of titanium in steels containing the metal from 0.03 to 0.6 per cent does not exceed ± 5 per cent.

Reagents

Sulphuric acid, diluted 1 : 5.
Hydrochloric acid, density 1.19 g/cu.cm and diluted 1 : 5.
Nitric acid, density 1.40 g/cu.cm.
Ammonium thiocyanate, 20 per cent solution.
Sodium thiosulphate, 20 per cent solution.

Diantipyrylmethane, 5 per cent solution in 2 *N* hydrochloric acid.
Chloroform, pure. Shake chloroform in a separating funnel with concentrated sulphuric acid, and wash with water and then with KOH solution.
Titanium salt, standard solution. 1 ml is equivalent to 10 μg of titanium.

Constructing a Calibration Curve

Dissolve a sample of chromium-nickel steel weighing 1 g free from titanium (for example, a standard sample of steel No. 125) as in the Procedure. Dilute the obtained solution with water in a 100-ml volumetric flask, place 5-ml portions into separating funnels, add the standard solution of titanium salt in quantities equivalent to 2.4 to 24 μg of Ti and proceed further as instructed in the Procedure. Construct the calibration curve using the data obtained.

Procedure

Dissolve a sample of steel weighing 0.1 g in 30 ml of sulphuric acid (1 : 5) with heating. Oxidize the carbides with nitric acid with heating. As soon as the solid has dissolved, add water to 40-50 ml, boil to remove nitrogen oxides, cool, transfer into a 100-ml volumetric flask and add water to the mark.

If the sample contains titanium from 0.1 to 0.5 per cent, transfer 5 ml of this solution into a separating funnel, add 5 ml of ammonium thiocyanate and then, gradually, sodium thiosulphate until the colour due to ferric thiocyanate vanishes. Add 5 ml of diantipyrylmethane solution and 2 ml of concentrated hydrochloric acid. Extract the titanium compound with two 10-ml portions of chloroform. Pass the extracts through a dry filter into a 25-ml volumetric flask and add chloroform to the mark.

Measure the absorption of the extract at 420 nm on an absorptiometer with a blue optical filter or on a spectrophotometer СФ-4 in a cell with a light path of 20 mm against the extract of the reagents. Determine the titanium content from the calibration curve.

PHOTOMETRIC DETERMINATION OF TITANIUM WITH TICHROMIN IN ALUMINIUM ALLOYS

Tichromin, [N-methyl-N, N-bis(methylenechromotropic acid) amine], reacts with the ion of Ti^{IV} at pH 1.0 to form a yellow compound. When the solution is acidified to 3 *M* HCl, its colour changes to red-brown and persists for a few days. The absorption maximum of the solutions is at 470 nm, the molar ratio of Ti to HR is 1 : 2, the molar extinction coefficient is 1.03×10^4, the equilibrium constant of the reaction is 1.34×10^8. 10 000-fold quantities of Al, Fe^{2+}, Zn, Mg, Ca, Ga, In, Tl, rare earths, a 5000-fold quantity of Th, 2000-fold quantities of oxalates, tartrates, EDTA, citrates and phosphates, 1000-fold quantities of Cu and Ni, a 500-fold quantity of Cr^{III}, 150-fold quantities of Co, V^{IV}, a 100-fold quantity of fluorides, and a 4-fold quantity of Mo do not interfere with the determination of titanium. The interfering effect of Cr^{VI}, V^{V} and Fe^{III} is removed by ascorbic acid.

The method can be used for the determination of 1.2×10^{-3} per cent of titanium in alumina, 4.4×10^{-3} per cent of titanium in slags, from 1.1×10^{-3} to 1.5×10^{-2} per cent of titanium in aluminium alloys and 0.1-15 mg/l of titanium in highly mineralized waters of hot springs.

Reagents

Titanyl sulphate, standard solution in 1 N hydrochloric acid. 1 ml is equivalent to 5 μg of titanium.
Hydrochloric acid, diluted 1 : 1 and 1 *N* solution.
Sulphuric acid, diluted 1 : 1.
Ascorbic acid, 2 per cent solution.
Tichromin, 1 per cent solution.

Constructing a Calibration Curve

Place from 0.5 to 8 ml (the gradient, 0.5 ml) of the titanyl sulphate standard solution into 100-ml volumetric flasks and add 5 ml of ascorbic acid into each flask. Allow the solution to stand for 2-3 minutes and add 5 ml of tichromin solution. Add 1 *N* hydrochloric acid to the mark and measure the absorption of the solutions at 470 nm on an absorptiometer in a cell with a light path of 5 cm or on a spectrophotometer in a cell with a light path of 1 cm against a blank solution. Construct the calibration curve using the data obtained.

Procedure

Dissolve a sample of alloy weighing about 2 g in a mixture of 30-35 ml of hydrochloric acid (1 : 1) and 5 ml of sulphuric acid (1 : 1). When the vigorous reaction stops, heat the beaker on a sand bath to completely dissolve the alloy. Rinse the glass cover and the beaker walls with hot water and heat again for 5-7 minutes. Now cool the solution, filter it into a 100-ml volumetric flask, and add water to the mark. If the expected content of titanium is $n \times 10^{-3}$ per cent, take a 25-ml aliquot, and if $n \times 10^{-2}$ per cent, take 10 ml and continue as for the construction of the calibration curve. Determine the titanium content from the calibration curve.

DIFFERENTIAL DETERMINATION OF TITANIUM IN NIOBIUM ALLOYS WITH DIANTIPYRYLMETHANE

The method can detect 50 and less per cent of titanium in niobium alloys with a relative error of ± 0.5 per cent. Al, Mg, Cd, Zn, Fe^{II}, V^{IV}, Nb, Ta, Mo, W, Mn, Ce, Zr and the lanthanides do not interfere with the determination of titanium.

Reagents

Titanium salt, two standard solutions. 1 ml is equivalent to 0.2 mg and 0.1 mg of titanium respectively. The solutions contain 3 per cent of tartaric acid.
Diantipyrylmethane, 2 per cent solution. Dissolve 20 g of the reagent in 300-400 ml of water containing 60 ml of H_2SO_4 (1 : 1), add about 2 g of ascorbic acid and dilute with water to 1 litre.
Tartaric acid, 15 per cent solution.
Potassium pyrosulphate.
Hydrochloric acid, diluted 1 : 1.

Constructing a Calibration Curve

Place 10 ml of the standard solution of titanium salt (the titanium concentration 0.2 mg/ml) into five 50-ml volumetric flasks and add 1, 2, 3, 4 and 5 ml of the other standard solution of titanium (the concentration 0.1 mg/ml) into the flasks respectively. Add 10 ml of tartaric acid solution into each flask and keep them on a boiling water bath for five minutes. Add 15 ml of diantipyrylmethane solution and 10 ml of hydrochloric acid to the hot solutions, cool to room temperature and add water to the mark. Measure the absorption of the solutions at 480 nm in cells with a light path of 1 cm against a solution prepared by a similar procedure and containing 2.0 mg of titanium in 50 ml. Construct the calibration curve using the data obtained.

Procedure

Fuse a sample of the alloy weighing 0.1 g with 3-5 g of potassium pyrosulphate (add a few drops of concentrated sulphuric acid if necessary). Dissolve the melt in 20 ml of tartaric acid, cool, transfer into a 100-ml volumetric flask and add water to the mark. Take an aliquot containing 2.0-2.5 mg of titanium and continue the analysis as for the construction of the calibration curve. Determine the titanium content from the calibration curve.

DIFFERENTIAL DETERMINATION OF TITANIUM IN ILMENITE CONCENTRATES WITH HYDROGEN PEROXIDE

The method can be used to determine to 62 per cent of TiO_2 with a relative error of ± 0.5 per cent. The interfering effect of tervalent iron can be removed by phosphoric acid.

Reagents

Titanium salt, standard solution. 1 ml is equivalent to 1.2 mg of titanium. Treat a sample of TiO_2 calcined at 900 °C and weighing 0.5000 g with 12.5 g of $(NH_4)_2SO_4$ and 27.5 ml of concentrated sulphuric acid in an Erlenmeyer flask and heat to dissolve the solid. Cool the solution, transfer into a 250-ml volumetric flask, and add water to the mark.

Hydrogen peroxide, 6 per cent solution.

Potassium pyrosulphate.

Sulphuric acid, 20 per cent solution.

Phosphoric acid, concentrated.

Constructing a Calibration Curve

Place 10, 11, 12, 13, 14 and 15 ml of the standard solution of the titanium salt into 100-ml volumetric flasks, add 20 ml of phosphoric acid, 50 ml of sulphuric acid, and 5 ml of hydrogen peroxide into each flask and then add sulphuric acid to the mark. Measure the absorption of the solutions at 390 nm in cells with a light path of 1 cm using a solution containing 12 mg of titanium in 100 ml as the standard. Construct the calibration curve using the data obtained.

Procedure

Fuse a sample of concentrate weighing 0.3 g in a platinum crucible with 5 g of potassium pyrosulphate at 800-900°C to prepare a clear melt. Dissolve it in 50 ml of sulphuric acid containing 1 ml of hydrogen peroxide solution. Cool the solution, transfer into a 100-ml volumetric flask, and add sulphuric acid to the mark. Take an aliquot containing 12-18 mg of titanium and continue with the analysis as for the costruction of the calibration curve. Determine the titanium content from the calibration curve.

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Zirconium and Hafnium

Zirconium, Zr, and hafnium, Hf, have the positive valency of 4 in their compounds. Halides of zirconium and hafnium in which these elements are di- and tervalent (positive) are known. These compounds are not important for analytical chemistry. There are no methods based on the changing valency of hafnium and zirconium.

The chemical properties of zirconium and hafnium are quite similar. There are no reagents by which the zirconium ion could be effectively separated from the hafnium ion. The ions of these elements interact with inorganic and organic reagents almost under the same conditions and their products only slightly differ from each other by their properties. Physical methods, such as roentgenospectral, optical spectral and radioactivation methods ensure reliable identification and determination of hafnium in the presence of zirconium. Photometry and some organic reagents also give positive results. The photometric method is effective in the separate determination of zirconium and hafnium.

Aqueous salts of zirconium and hafnium easily hydrolyze. Solutions of zirconium salts can contain simultaneously the colourless ions Zr^{4+} and ZrO^{2+} and various polymerized ions. The polymerization degree increases with the concentration of zirconium salt and depends on the acidity of the solution. If hydrofluoric acid is added, the polymerization of the zirconium ions decreases.

The conditions under which various zirconium ions can exist in solutions are not defined. Solutions with the acidity over 2 *N* ($HClO_4$) contain the simple ion Zr^{4+}. If the pH is 0.7 and below, the $Zr(OH)^{3+}$ ion is predominantly present in solution. At pH higher than 0.7, the $Zr(OH)_2^{2+}$ ion is present.

The Zr^{4+} ion reacts with many reagents much faster than the oxycation ZrO^{2+} and various isopolyoxy cations. In order to ensure the presence of zirconium in solution mainly in the form of Zr^{4+}, at least a ten-fold quantity of aluminium salt should be added as a coprecipitant. Zirconium and aluminium are precipitated by ammonia and the precipitate is dissolved in dilute hydrochloric acid [1]. This method increases the sensitivity and reproducibility of the photometric determination of zirconium with arsenazo I.

The dioxides ZrO_2 and HfO_2 are insoluble in water. The corresponding hydrates are prepared by the hydrolysis of the aqueous solutions of the salts. The meta-acids $ZrO(OH)_2$ or H_2ZrO_3 are formed in this reaction. If alkali solutions are added to the solutions of the salts, the ortho-acids, $Zr(OH)_4$ or H_4ZrO_4, are formed. These are always contaminated with basic salts of zirconium. The dioxides ZrO_2 and HfO_2 can be converted into the soluble state by fusion with alkali or potassium hydrosulphate. The fusion of ZrO_2 and HfO_2 with alkali gives zirconates and hafnates. They are hydrolyzed in water. The fusion of ZrO_2 and HfO_2 with SiO_2 or TiO_2 gives silicates or titanates of zirconium and hafnium. Zirconium dioxide, ZrO_2, melts at a temperature not below 2700°C, while hafnium dioxide, HfO_2, melts at 2990°C.

The products of hydrolysis of zirconium salts can exist in colloidal solutions.

Carbonates of ammonium or the alkali metals precipitate white basic salts of zirconium and hafnium. The precipitate dissolves in excess ammonium carbonate and is re-precipitated by boiling the solution.

If the pH of the solution containing the zirconium and hafnium ions is gradually increased (by adding alkali), mainly the basic salt of zirconium is first precipitated and then the basic salt of hafnium. At pH about 2, a 0.01 *M* solution of zirconyl chloride precipitates a white basic salt of zirconium.

Hydroxides of zirconium and hafnium show their amphoteric character, while their acid and basic properties are not manifest. These compounds are dissolved in strong acids, their solubility decreasing with time (due to ageing).

Hydrogen sulphide does not precipitate the zirconium and hafnium ions from aqueous solutions.

Zirconium and hafnium form many compounds sparingly soluble in dilute acids (phosphates, arsenates, selenites, iodates, arylarsonates, etc.) and complex compounds. Halide, sulphate, oxalate, tartrate, citrate, EDTA and other complexes are known. The information on the composition and the stability constants of many of them is controversial

The halide complexes have the formula M_2ZrHal_6. The fluoride complex ions of zirconium and hafnium, ZrF_6^{2-} and HfF_6^{2-} are very stable and the corresponding solid compounds are soluble in water.

The addition of the alkali metal fluorides to solutions of various coloured compounds of zirconium and hafnium with organic reagents, gives colourless soluble fluozirconate and fluohafnate with liberation of the organic reagent. The colour of the solution changes in this process. The fluorides of the alkali metals are used to mask zirconium.

Hydrofluoric acid and the fluorides of the alkali metals precipitate bulky white ZrF_4 and HfF_4 from concentrated solutions of zirconium and hafnium salts. The precipitates easily dissolve in excess precipitant. Hydrofluoric acid is used for the separation of the lanthanides and thorium from zirconium and hafnium (the latter two remain in solution).

The sulphate complexes $[ZrO(SO_4)_2]^{2-}$, $[Zr(SO_4)_4]^{4-}$ and others are relatively stable.

Ammonium phosphate, $(NH_4)_2HPO_4$, precipitates quantitatively the ions of zirconium and hafnium from strong acid solution containing 10 per cent (v/v) of hydrochloric or sulphuric acid. The composition of the precipitate depends on the conditions of precipitation. The precipitates are difficult to filter, and the separation of zirconium and hafnium from the other elements is not always satisfactory. If the ions of Ti, Nb and Ta are present, zirconium is precipitated in the presence of hydrogen peroxide. The ion of Sn^{IV} interferes.

Disubstituted ammonium arsenate precipitates quantitatively the ion of zirconium from a 2.5 *N* solution of HCl or 3.75 *N* solution of HNO_3. If the ions of Th, Ce, and Ti are present, zirconium arsenate should be re-precipitated. The precipitate is calcined to ZrO_2.

Selenious acid precipitates quantitatively the zirconium ion from hydrochloric acid solutions in the form of basic selenite. The filtered and washed precipitate is calcined to ZrO_2. Selenious acid separates zirconium from aluminium, some lanthanides, and from small amounts of iron. If hydrogen peroxide is added to the solution,, zirconium can also be separated from small quantities of titanium. Thorium and phosphorus are admixed with the precipitate. Zirconium selenite, $Zr(SeO_3)_2$, can be prepared under special conditions.

Potassium iodate precipitates the double salt $2Zr(IO_3)_4 \cdot KIO_3 \times \times 8H_2O$ from nitric acid solutions. Conditions can be provided under which the compound characterized by a more or less stable composition, corresponding to the above formula, can be precipitated. The ions of Th and Ce are precipitated by potassium iodate in the same conditions as zirconium. Potassium iodate can separate zirconium from aluminium. During titrimetric determination, the filtered and washed precipitate is dissolved in hydrochloric acid, KI is added, and the liberated iodine titrated with thiosulphate solution.

Potassium ferrocyanide precipitates the zirconium ion, the composition of the precipitate being inconstant.

Ammonium oxalate precipitates white zirconium oxalate soluble in excess precipitant and in strong acids (in contrast to the oxalates of cerium and thorium). The ion SO_4^{2-} forms $[ZrO(SO_4)_2]^{2-}$ and therefore interferes with the precipitation of zirconium oxalate.

Arylarsonic acids are highly selective precipitants of Zr^{4+} from dilute mineral acid solutions. Phenylarsonic acid, $C_6H_5AsO_3H_2$, is most frequently used. The precipitating properties of *p*-hydroxyphenylarsonic acid, *m*-nitrophenylarsonic, *p*-dimethylamino-azophenylarsonic and other arsonic acids have also been studied. The precipitates are white. Phenylarsonic acid precipitates quantitatively [2] the ions of zirconium and hafnium from hydrochloric acid solution diluted 1 : 9. The acid is used for the separation of Zr and Hf from the ions of many elements: Fe, Al, lanthanides, Th, etc.

p-Hydroxyphenylarsonic acid [3] is used for the determination of zirconium in the presence of the ions of Fe, Al, Zn, Co, Ni, Be, Cr, Mn, Ca, Mg, Be, Tl, Ce^{III}, Th, V, U, etc. Zirconium is precipitated from a 2.5-3.0 N solutions of hydrochloric or sulphuric acid. Hydrogen peroxide is added to the solution in the presence of the Ti ion. The ions of Ce^{IV} and Sn^{IV} interfere with the determination.

The ions of zirconium and hafnium are precipitated quantitatively with mandelic, phthalic, fumaric and other organic acids and their derivatives. Mandelic acid, $C_6H_5CH(OH)COOH$, is used to separate zirconium from Ti, Fe, Al, Cr, V, Mo, the rare earths and other elements. If the zirconium content is small (about 10 mg), the precipitated $[C_6H_5CH(OH)COO]_4Zr$ is weighed straight after the separation, but if the zirconium content is high (over 25 mg), the precipitate should be first calcined [4, 5] to zirconium dioxide, ZrO_2.

Thiodiglycolic acid, $HOOCCH_2SCH_2COOH$, precipitates quantitatively [6] the zirconium ion from a 0.2-0.4 N solution of HCl or HNO_3. The composition of the crystalline precipitate corresponds approximately to the formula $(OOCCH_2SCH_2COO)ZrO$. The precipitate is calcined to ZrO_2. The ions of Co, Ni, Zn, Mg, Cd, Mn, Al, Pb, Ti, Be, the rare earths, and a small quantity of the Th ion do not interfere with the determination.

Thiomalic acid, $HOOCCHSHCH_2COOH$, is a highly selective precipitant [7] of zirconium from dilute hydrochloric and nitric acid solutions. The ions of Bi only interfere. When the solution is boiled, the reagent precipitates a substance with the composition corresponding approximately to the formula $(OOCCHSHCH_2COO)ZrO$.

Cupferron precipitates quantitatively the ions of zirconium and hafnium from sulphuric acid solution. It is used for the separation of zirconium from some elements.

N-Benzoylphenylhydroxylamine, $C_6H_5CON(OH)C_6H_5$, precipitates quantitatively the zirconium ion from acid solutions [8, 9]. The complex precipitated from sulphuric acid solution with the concentration lower than 0.5 N has the constant composition [2] $(C_{13}H_{10}O_2N)_4Zr$ and meets the requirements for the weighing form after drying at 110°C. The factor for the conversion into zirconium is 0.0970. The precipitate from hydrochloric acid solution (5 per cent), has no constant composition. It is calcined to ZrO_2. The reagent is highly sensitive and can be used to detect 1 μg of Zr in 1 ml, and to determine 0.2 mg of Zr. The ions of Th and lanthanides, do not interfere with the determination. The ions of Sn^{IV}, V^{V}, Ce^{IV} and Ti^{IV} interfere. The Zr ion is not precipitated in the presence of fluorides of the alkali metals.

Various oxy compounds react with the zirconium ion to form coloured compounds; they are used for the detection of Zr and for its photometric determination. The oxy compounds include hydroxyanthraquinones (alizarine, quinalizarine, purpurine, rufigallic acid, etc.), hydroxy-derivatives of flavone (quercetin, morin, and others), carminic acid, hematoxyline, xylenol orange, pyrocatechol violet, and many others [10].

The hydroxy-derivatives of flavone are used for the luminescent determination of zirconium.

Xylenol orange is a highly selective reagent for the zirconium and hafnium ions in strongly acid solutions (0.8-1.0 N $HClO_4$). The reagent is used for the photometric determination of small quantities of zirconium [11]. Conditions can be provided under which separate determination of zirconium and hafnium in their mutual presence can be effected [12]. The reagent is used also for the photometric determination of microquantities of zirconium in niobium metal. Coloured compounds of zirconium are formed in 0.4 N sulphuric acid in the presence of hydrogen peroxide which is added in the minimum quantity to keep niobium in solution form. Xylenol orange is also used as a complexometric indicator. Its analogue methyl thymol blue behaves similarly.

Pyrocatechol violet is used for the photometric determination of zirconium [13-15].

Arsenazo I reacts with the Zr ion [1] in a 0.08-0.1 N hydrochloric acid solution to form a violet compound (the reagent itself is pink in these conditions). The optimum pH is 1.5-1.8. Only Hf and Ti, and also the fluoride and phosphate ions and oxy acids interfere with the determination. Small quantities of gelatin solution preclude the precipitation of a coloured zirconium compound. Arsenazo I is used for the photometric determination of zirconium in aluminium and magnesium alloys, as well as in ores.

Arsenazo III is used for the photometric determination of zirconium [16-20].

Inositol hexaphosphoric acid (phytic acid) precipitates a white substance from zirconium salt solutions. It is used for the gravimetric determination of zirconium.

Datiscine is used for the fluorimetric determination of zirconium.

Complexometric methods are very important for the analytical chemistry of zirconium. There are several direct and indirect methods for determining zirconium [21, 22].

To determine 3-5 per cent of zirconium in niobium alloys [21, 23, 24] excess standard solution of EDTA is added to the solution of the alloy, the pH is adjusted to 2, and excess reagent is titrated with bismuth nitrate amperometrically with a dropping-mercury electrode (the potential being −0.3 V against a saturated calomel electrode). One milligram of zirconium can be titrated in the presence of 50 mg of niobium.

Tri-n-octylamine (0.1 M solution) extracts quantitatively zirconium from 9-12 N solutions of hydrochloric acid [25]. To determine zirconium, a xylenol orange solution in alcohol and acetic acid are added to the obtained extract. The absorption of the resultant solution is measured at 550 nm (absorption maximum). Zirconium and xylenol orange react in these conditions in the molar ratio of 1 : 1

The molar extinction coefficient is 5.30×10^4 (at 550 nm). The method can be used for the determination of zirconium in the presence of 10 000-fold quantities of the ions of the alkali and alkaline-earth metals, and the lanthanides, which are not extractable from aqueous solutions, and also of aluminium, of 100-fold quantities of many other extractable ions, such as those of Mn, Sn^{II}, Bi, Cd, Pb, Cr, Hg^{II}, Tl^{III}, Au^{III}, Pd, Se^{IV}, Zn, Th, La, In.

Zirconium and hafnium are extracted selectively by diantipyrylmethane [26], heptylphosphoric tetraethyldiamide [11] and 2-tenoyltrifluoroacetone [27].

Hafnium and zirconium are determined indirectly by the chemical methods. For example, zirconium and hafnium are precipitated by *p*-bromomandelic acid, $BrC_6H_4CH(OH)COOH$, from a strong hydrochloric acid solution in the presence of sulphuric acid at a temperature of 85-95°C. The precipitates, $(C_8H_6O_3Br)_4Zr$ and $(C_8H_6O_3Br)_4Hf$, are dried at 120-130°C and weighed. The precipitates are then calcined to ZrO_2 and HfO_2 and weighed again. The obtained data are used for the calculation of zirconium and hafnium contents in the mixture [28]. If hafnium is admixed with zirconium in the quantity exceeding 10 per cent, the absolute error is ± 0.5 per cent. The determination procedure continues for 5-6 hours.

Zirconium and hafnium are separated by ion-exchange chromatography and extraction.

Hafnium is determined in zirconium by the spectral and radioactivation methods.

The review of the methods for the determination of zirconium and hafnium is given in the literature [29, 30].

SELECTIVE EXTRACTION OF ZIRCONIUM AND HAFNIUM

Diantipyrylmethane (DAM) and its alkyl homologues extract selectively zirconium and hafnium from 6 *N* solutions of nitric acid in the presence of nitrates. The method is used for the separation of zirconium and hafnium from the rare earths, Sc, Th, U, Ti, Mo, Fe, Pb, Co, Ni, Hg, Ga, and In. The separated zirconium and hafnium can be determined by any suitable method.

Reagents

Nitric acid, density 1.4 g/cu.cm and 2 *N* solution.
Diantipyrylmethane, 7 per cent solution in chloroform.

Procedure

Add nitric acid, density 1.4 g/cu.cm to the test solution containing 3-30 mg of zirconium (hafnium) to adjust the acid concentration to 6 *N* (the volume of the solution should be 15-30 ml), then add 15 ml of the reagent and shake in a separating funnel for 5-10 minutes. Keep the solution for 2-3 minutes, pass the extract through a dry ashless filter into another separating funnel, add 10 ml of the reagent to the aqueous phase, extract again in the same conditions, and add the organic layer filtrate to the first extract. Add 10 ml of 2 *N* nitric acid to the extracts, shake for 15-20 minutes, and dilute with water to 40-50 ml. Shake again for 10-15 minutes and determine zirconium (hafnium) in the aqueous phase.

Note. To re-extract zirconium (hafnium), a standard solution of EDTA can be added together with HNO_3, and excess EDTA titrated by bismuth nitrate in the presence of xylenol orange.

SELECTIVE EXTRACTION OF ZIRCONIUM BY HEPTYLPHOSPHORIC TETRAETHYLDIAMIDE

Heptylphosphoric tetraethyldiamide solution in benzene extracts quantitatively zirconium from a 8 *M* solution of HCl. 5000-fold quantities of Sc, Th, Y, Nd, a 4000-fold quantity of In and a 300-fold quantity of Fe^{II} do not interfere.

Reagents

Hydrochloric acid, density 1.17-1.19 g/cu.cm.
Heptylphosphoric acid tetraethyldiamide, 0.02 *M* solution in benzene.

Procedure

Add hydrochloric acid to the solution of the sample to adjust the acid concentration in the final solution to 9 *M* and extract zirconium for 2 minutes with the extracting agent.

Note. Zirconium can be determined in the organic phase photometrically with xylenol orange.

SELECTIVE EXTRACTION OF ZIRCONIUM WITH 2-TENOYLTRIFLUOROACETONE

Zirconium is extracted quantitatively with a 0.5 *M* solution of 2-tenoyltrifluoroacetone in xylene from a 1.3-12.5 *N* solution of nitric acid or 1.7-6.9 *N* solution of hydrochloric acid. When zirconium is extracted from 2 *M* HCl or HNO_3, the reagent can separate zirconium selectively from the alkali, alkaline-earth metals, tervalent lanthanides, Sn^{II}, Ni, Co, Cr^{III}, UO_2^{2+}, Th, Fe^{II}, Al, Bi and Nb. To separate from Nb^{95}, a 0.9 per cent solution of H_2O_2 or a 1.25 *M* solution of $NH_2OH \cdot HCl$ should be added to the aqueous phase before the extraction. In the presence of Fe^{III} zirconium is extracted from 6 *M* HCl. The same extracting agent is used for the separation of zirconium from Pa^{233}, but 2 *M* HNO_3 and 1 per cent of H_2O_2 are added to the test solution, and the organic phase is washed three times with a 31.2 per cent solution of hydrogen peroxide. Zirconium can be re-extracted from the organic phase with a mixture of a 0.25 M solution of nitric acid and 0.25 M hydrofluoric acid, and also with 8 M HNO_3 or concentrated hydrochloric acid with preliminary dilution of the extract to the concentration of 2-tenoyltrifluoroacetone of 0.05 M.

The method can be used for the separation of microquantities of zirconium and for rapid determination of Zr^{95} in mixtures with Nb^{95} and other fragments.

Reagents

Nitric acid, density 1.4 g/cu.cm.
Hydrochloric acid, density 1.17-1.19 g/cu.cm.
2-Tenoyltrifluoroacetone, 0.5 M solution in xylene.

Procedure

Add nitric (hydrochloric) acid to the solution of the sample to adjust the acid concentration to 2 M, then add 10 ml of the extracting agent solution and shake for 10 minutes. Separate the organic layer, add another 10 ml of the extracting agent to the aqueous phase and extract for another ten minutes. Combine the extracts, wash them with 2 M nitric (hydrochloric) acid and determine zirconium.

COMPLEXOMETRIC DETERMINATION OF ZIRCONIUM

EDTA reacts with the zirconium ion in a strongly acid medium (2 N HCl) to form a complex compound with a molar ratio of the components of 1 : 1. The titration is carried out in the presence of *p*-sulphobenzeneazopyrocatechol, eriochrome black T or other indicators. If *p*-sulphobenzeneazopyrocatechol is used, the determination can be carried out in a medium of 1.5-2.2 N hydrochloric acid. At the end point of titration, the crimson-pink colour sharply changes to yellow. The method can be used to determine 0.5-40 mg of zirconium in a 10-ml volume. If the zirconium content is higher, the solution should be diluted accordingly.

Equal quantities of the ions of Fe^{II}, Th, Ti, Sn^{IV}, Mo, Nb, Al, Bi, Sb, Ni, Ge and also of the alkali and alkaline-earth elements and the lanthanides do not interfere with the determination.

The oxidants which decompose the indicator, for example tervalent iron, should preliminarily be reduced with hydroxylamine. Ta and W precipitate in the form of acids which adsorb the zirconium compound with the indicator, and therefore interfere with the determination. 10-20 mg of sulphates, 10 mg of tartaric acid can be present in the solution. Oxalate, fluoride and phosphate ions interfere with the determination.

The method can be used for the analysis of various materials such as ores, concentrates, intermediates, alloys containing over 0.2 per cent of zirconium.

The zirconium ion reacts with eriochrome black T in a medium of 1.5-2 N hydrochloric acid to form a blue-violet compound which is less stable than zirconium complexonate. The titration can be effected with a 0.01 M solution of EDTA, which increases the sensitivity of the determination. But if the titration is carried out in a 2 N hydrochloric acid solution, the ratio between the quantity of zirconium taken for the determination and the quantity of EDTA spent for its titration, is not strictly stoichiometric. The EDTA solution is therefore standardized against the zirconium salt solution. The advantage of eriochrome black T over the other complexometric indicators is that it can determine zirconium in the presence of large amounts (about 200 mg) of sulphate. It is very important, because sulphuric acid is mostly used to decompose zirconium-containing materials. Divalent tin does not interfere. Its presence decreases the error of zirconium determination in the presence of 100 mg of copper, vanadium, molybdenum, or iron (due to reduction of these elements). The ions of Mg, Ca, Ba, Zn, Sn^{II} (to 500 mg), Mn, UO_2^{2+}, Ti^{IV}, Ni (to 200 mg), Al (to 100 mg), Cr^{III} (to 75 mg), Bi, La (to 50 mg), Nb (to 30 mg) and Th (to 4 mg) do not interfere.

Hafnium, which is titrated together with zirconium, and also fluoride, phosphate, oxalate and tartrate ions which form low dissociated compounds with zirconium, interfere with the determination of zirconium.

The method can be used for the determination of 1-100 mg of zirconium in its salts and various zirconium-containing materials in volumes not exceeding 100 ml. The error of the determination is about 1 per cent.

Reagents

Hydrochloric acid, density 1.19 g/cu.cm and 2 N solution.
EDTA, 0.01 M and 0.05 M solutions.
p-Sulphobenzeneazopyrocatechol, 0.02 per cent solution.
Eriochrome black T, a mixture with NaCl (1 : 50).

Procedure

Determining Zirconium with p-Sulphobenzeneazopyrocatechol. Dilute a solution containing 40-80 mg of zirconium as chloride or perchlorate with hydrochloric acid to 50 ml and mix. Using a pipette, transfer 15 ml of the solution into a 100-150 ml Erlenmeyer flask, heat to boiling, add 5 drops of the indicator solution and titrate with a 0.05 M solution of EDTA until the crimson-pink solution turns yellow.

1 ml of a 0.0500 M solution of EDTA is equivalent to 4.56 mg of zirconium.

Determining Zirconium with Eriochrome Black T. Dilute a solution containing 15-30 mg of zirconium as chloride, nitrate or sulphate with 2 N hydrochloric acid in a volumetric flask to 50 ml and mix.

Transfer 15 ml of the solution into a 100-ml Erlenmeyer flask, heat to boiling, add the indicator on the tip of the spatula, and titrate with a 0.01 *M* solution of EDTA until the blue-violet solution turns pink.

1 ml of a 0.0100 *M* solution of EDTA is equivalent to 0.9122 mg of zirconium.

COMPLEXOMETRIC DETERMINATION OF ZIRCONIUM IN ZIRCON AND EUDIALITE

Zirconium ores containing much silicon are fused with Na_2CO_3 or a mixture of Na_2CO_3 and $Na_2B_4O_7$. The following processes occur:

$$ZrSiO_4 + 2Na_2CO_3 = Na_2ZrO_3 + Na_2SiO_3 + 2CO_2$$

$$ZrSiO_4 + 3Na_2CO_3 + Na_2B_4O_7 = Na_2ZrO_3 + Na_2SiO_3 + 4NaBO_2 + 3CO_2$$

The melt is leached with concentrated hydrochloric acid to preclude hydrolysis of zirconium and to coagulate silicic acid.

Reagents

Mixture of sodium carbonate and sodium tetraborate (1 : 1). Keep the mixture in a tightly closed bottle. For other reagents see the previous section.

Procedure

Fuse a sample of zircon or eudialite containing 5-10 mg of zirconium with a ten-fold quantity of the flux in a platinum crucible. To that end, first melt about 1/3 of the flux in the crucible, add the sample, and finally add the remaining flux. Heat the mixture over a burner, first gently and then to red heat, and finally in a muffle furnace to 900-1000°C for 15-30 minutes. Add hydrochloric acid, density 1.19 g/cu.cm, cover the crucible with a watch glass and heat on a water bath. When the carbon dioxide evolution stops, remove the glass and evaporate the solution to dryness. Repeat the hydrochloric acid treatment and evaporation two times more, and heat the residue in a drying cabinet for 15-30 minutes at a temperature of 100-110°C. Wet the residue with hydrochloric acid, density 1.19 g/cu.cm, stir with a glass rod, cover the crucible with a watch glass, keep on a water bath for 5 minutes, add water to 2/3 crucible capacity, stir, and heat again on a water bath to dissolve the salts.

Separate the precipitate $SiO_2 \cdot xH_2O$ on a filter, wash with 2 *N* hydrochloric acid, collect the filtrate and the washings in a 25-ml volumetric flask and add water to the mark. The acidity of the solution should be 2 *M* HCl. Add a small portion of eriochrome black T to the solution, boil for 7-10 minutes until a persistent blue-violet colour develops, and titrate with a 0.01 *M* solution of EDTA until the solution turns violet-pink. Now heat the solution again and if the blue-violet colour is restored, continue the titration with EDTA until the violet-pink colour persists.

EXTRACTION-PHOTOMETRIC DETERMINATION OF ZIRCONIUM WITH XYLENOL ORANGE

Zirconium reacts with xylenol orange in an acid medium in a mixture of organic solvents consisting of benzene, and ethyl alcohol, and containing heptylphosphoric tetraethyldiamide. The formed compound is stable. The colour of maximum intensity develops with a ten-fold excess of the reagent. The optimum concentration of hydrochloric acid is 0.8-1.0 *M*.

Reagents

Zirconium salt, standard solution. 1 ml is equivalent to 20 μg of zirconium.
Hydrochloric acid, density 1.17-1.19 g/cu.cm.
Xylenol orange, 0.2 per cent solution in ethyl alcohol.
Heptylphosphoric tetraethyldiamide, 0.02 *M* solution in benzene.
Benzene.

Constructing a Calibration Curve

Place 0.2, 0.4, 0.6, 0.8 and 1.0 ml of the standard solution of zirconium salt into separate 25-ml volumetric flasks, add 2 ml of hydrochloric acid, 3 ml of heptylphosphoric tetraethyldiamide, 5 ml of benzene and 2.5 ml of xylenol orange into each flask and add ethyl alcohol to the mark. Measure the optical density of the obtained solutions at 535 nm against a blank solution. Construct the calibration curve using the data obtained.

Procedure

Take an aliquot of the extract of the zirconium compound with heptylphosphoric tetraethyldiamide (see page 158) containing 10-15 μg of zirconium and determine zirconium as for the construction of the calibration curve. Find the zirconium content from the calibration curve.

PHOTOMETRIC DETERMINATION OF ZIRCONIUM WITH ARSENAZO III

Arsenazo III is a highly sensitive and selective reagent for the photometric determination of zirconium. The reagent is red in an acid medium, but when the zirconium salt is added, it quickly turns blue or blue-violet, depending on the ratio of the reagent and the zirconium ion. The colour intensity is stable in the acidity range from 1 to 3 *N* HCl, but changes rapidly with time. To stabilize the colour, gelatin is added. The absorption obeys the Bourguer-Lambert-Beer law in the range of zirconium concentrations from 5 to 30 μg in 50 ml of the solution. The results are reproducible if zirconium is converted into a stable ionic form (zirconyl ion) by boiling with a 2 *N* solution of hydrochloric acid. The reproducibility of the results can be increased if the reaction is carried out in a medium of 6-8 *M* HCl containing 20 per cent (v/v) of acetone.

Microquantities of zirconium can be determined in the presence of over 100 mg of Al, to 20 mg of Sn, to 10 mg of Be, Ni, Ti, to 5 mg of Cr, lanthanides and Nb, to 50 mg of the tartrate, and to 100 mg of the sulphate ion. If divalent tin is added, zirconium can be determined in the presence of 15 mg of Fe and 5 mg of Cu. Uranium and thorium, which react with the reagent in an acid medium to form coloured complex compounds, and also fluoride, phosphate and oxalate ions, which react with the zirconium ion to form stable complex compounds and thus destroy the coloured compound of zirconium with arsenazo III, interfere with the determination of zirconium.

The method is used for the determination of zirconium in ores and side products (tailings, slurries, fractions rich in titanium, iron, aluminium and tin).

Reagents

Zirconium oxychloride, $ZrOCl_2$, *standard solution* in 2 *N* hydrochloric acid. 1 ml is equivalent to 5 μg of zirconium.
Hydrochloric acid, 2 *N* solution.
Arsenazo III, 0.05 per cent solution.
Gelatin, 1 per cent solution.
Mixture of sodium carbonate and sodium tetraborate, 3 : 2.

Constructing a Calibration Curve

Place 1, 2, 3, 4 and 5 ml of the zirconium oxychloride standard solution into five 50 ml volumetric flasks, and dilute with hydrochloric acid to 10 ml. Heat the solutions to boiling on a sand bath, cool, add 3 ml of gelatin solution and 2 ml of arsenazo III solution into each flask and add hydrochloric acid to the mark. Measure the absorption of the obtained solutions at 655 nm against a blank solution. Construct the calibration curve using the data obtained.

Procedure

Place a sample weighing 0.1-0.2 g and containing 0.1-0.5 per cent of zirconium, in a platinum dish containing 5 g of a mixture of sodium carbonate and sodium tetraborate. Mix the components, and fuse in a muffle furnace for 7-10 minutes at a temperature of 900°C. Distribute the molten mass in the dish (by rotating it) so that it sets in a thin layer on the dish walls, add water and heat on a sand bath. Transfer the solution and the precipitate into a 300-ml beaker, dilute with water to 100-150 ml, and heat to coagulate the precipitate. Separate the precipitate on a filter, wash with hot water and dissolve on the filter with hydrochloric acid. Collect the filtrate in a 50-ml volumetric flask (if the sample weighs 0.2 g and contains 0.1 per cent of zirconium) or in a 100-ml volumetric flask (if the sample weighs 0.1 g and contains 0.5 per cent of zirconium), and add hydrochloric acid to the mark. Transfer an aliquot of the solution containing about 10-15 μg of zirconium into a 50-ml volumetric flask and continue the analysis as for the construction of the calibration curve. Find the zirconium content from the calibration curve.

PHOTOMETRIC DETERMINATION OF ZIRCONIUM IN PHOSPHORITES WITH PYROCATECHOL VIOLET

Pyrocatechol violet reacts with the zirconium ion to form a blue compound with the maximum absorption at 625 nm. The aqueous solution of the compound is yellow with maximum absorption at 450 nm. The compound is formed in a medium of hydrochloric, nitric and sulphuric acids. The optimum pH for the determination is 5-5.5. The colour of the solution develops in 30 minutes and persists for 2-3 hours. The absorption of the solution obeys the Bouguer-Lambert-Beer law in the range of zirconium concentrations from 0 to 100 μg in 50 ml of solution. The zirconium compound with the reagent is stable in the presence of EDTA, which can therefore be used to mask the accompanying ions. Al (5 mg), Fe^{II} (15 mg), Fe^{III} (less than 2 mg), Ti (3 mg), Th (1 mg), Be, U, Bi, V, Mo, W and Co (not over 5 mg each) Cu and Ni (not over 0.5 mg) do not interfere with the determination of microquantities of zirconium.

The method is used for the determination of hundredth fractions of per cent of zirconium in uranium, its alloys, in ores (phosphorites, monazites) and other materials with an error of ± 10%.

Reagents

Zirconium salt, standard solution. 1 ml is equivalent to 10 μg of zirconium.

Nitric acid, diluted 1 : 3.

Potassium hydrofluoride, crystalline.

Sulphuric acid, density 1.84 g/cu.cm.

Hydrochloric acid, density 1.19 g/cu.cm and diluted 1 : 2.

EDTA, 0.05 *M* solution.

Ammonia, solution 1 : 1.

Methyl red, 0.001 per cent solution in alcohol.

Pyrocatechol violet, 0.04 per cent solution.

Acetate buffer solution, pH 5.2-5.4. Mix 32 ml of acetic acid, density 1.05 g/cu.cm, with 34 ml of 25 per cent ammonia solution and dilute with water to 1 litre.

Constructing a Calibration Curve

Place 1, 2, 3, 4 and 5 ml of the zirconium salt standard solution in five 50-ml beakers, add 5 ml of hydrochloric acid, density 1.19 g/cu.cm, into each beaker, and evaporate on a sand bath to 1-1.5 ml.

Mix EDTA separately and neutralize with ammonia in the presence of 1-2 drops of methyl red and then with hydrochloric acid (1 : 2) until pale pink colour develops. Transfer the solutions into 50-ml volumetric flasks, add 4 ml of pyrocatechol violet, add the buffer solution to the mark, and mix. In 30 minutes measure the absorption of the solutions at 625 nm against a blank solution and construct the calibration curve.

Procedure

Grind thoroughly a sample weighing 0.05-0.2 g, treat it with 10 ml of nitric acid in a 100-ml beaker, cover with a watch glass and heat on a sand bath for 15-20 minutes. Separate the precipitate containing all zirconium ($ZrSiO_4$) on a blue ribbon filter, wash *thoroughly* with hot water, transfer the filter with the residue into a platinum dish, dry slightly, incinerate the filter and calcine for 15-20 minutes. Cool the residue, add 0.5-1.5 g of potassium hydrofluoride and fuse in a muffle furnace at 900°C to obtain a clear melt. Cool, add 10 ml of sulphuric acid, evaporate on a sand bath to heavy fumes of H_2SO_4, cool the residue and dissolve in a small quantity of water. Transfer the solution quantitatively into a 50-ml flask and add water to the mark.

Transfer an aliquot containing 15-45 μg of zirconium into a 50-ml beaker and continue the analysis as for the construction of the calibration curve. Determine the zirconium content from the calibration curve.

PHOTOMETRIC DETERMINATION OF HAFNIUM IN THE PRESENCE OF ZIRCONIUM WITH XYLENOL ORANGE OR METHYLTHYMOL BLUE

Xylenol orange and its analogue methylthymol blue react with the zirconium and hafnium ions to form coloured compounds which are used for the photometric determination of these elements. Unlike the hafnium ion, the zirconium ion can be masked under certain conditions by hydrogen peroxide in the presence of a sulphate ion. This makes it possible to determine hafnium photometrically in the presence of zirconium. Hafnium compounds with both reagents are formed practically instantaneously when the solutions are poured together. A three-fold molar excess is recommended for xylenol orange

Properties of Zirconium and Hafnium Compounds with Xylenol Orange and Methylthymol Blue

Properties	Xylenol orange		Methylthymol blue	
	Zr	Hf	Zr	Hf
Maximum absorption, nm	535	530	580 (600)	570 (590)
Optimum acidity	0.5-1.0 *N* $HClO_4$	0.2-0.4 *N* $HClO_4$	0.3-1.2 *N* $HClO_4$	pH 3
Complex formation constant (1 : 1)	4.0×10^7 (0.8 *N* $HClO_4$)	3.2×10^6 (0.3 *N* $HClO_4$)	1.0×10^5 (1.0 *N* $HClO_4$)	—
Molar extinction coefficient, $\varepsilon \times 10^{-4}$	2.42 (0.8 *N* $HClO_4$)	1.57 (0.2 *N* $HClO_4$)	2.17 (1.0 *N* $HClO_4$)	1.87 (pH 3)
Sensitivity, μg/sq.cm ($D = 0.001$)	0.004	0.011	0.004	0.010
Colour	Red	Red	Red (1 : 1) Violet (2 : 1)	Red (1 : 1) Violet (2 : 1)
Masking substance	EDTA, F^-, citrate ion, H_2O_2, PO_4^{3-}	EDTA, F^-, citrate ion, PO_4^{3-}	EDTA, F^-, citrate ion, H_2O_2, PO_4^{3-}	EDTA, F^-, citrate ion, PO_4^{3-}

and a two-fold molar excess for methylthymol blue. The colour intensity does not change for three days. The Bourguer-Lambert-Beer law holds for hafnium concentrations in the range from 0 to 0.65 μ mole in 25 ml (xylenol orange) and 0.1-0.5 μ mole in 25 ml (methylthymol blue).

The ions of Bi, Fe^{III}, Sn^{IV}, Th, Nb, Mo, V^{IV} and Ti react similarly with the reagents. Ce oxidizes the reagents. Se^{IV}, Te^{IV}, Pt^{IV}, Ge, Ta and W, as well as some other elements do not form coloured compounds with the reagents. All of them except niobium, are masked with EDTA. The table above describes the properties of Zr and Hf compounds with the reagents.

EDTA, the phosphate, citrate, and the fluoride ion and over a two-fold molar quantity of the sulphate ion interfere with the determination of hafnium. The perchlorate, chloride and nitrate ions, and also hydrogen peroxide (5 ml of 30 per cent H_2O_2 per 0.5 μ mole of hafnium) do not interfere.

The method should preferably be used after separation of zirconium and hafnium from most accompanying ions.

Reagents

Zirconium perchlorate, standard solution in 0.2 *N* perchloric acid. 1 ml is equivalent to 10 μg of zirconium.
Hafnium perchlorate, standard solution in 0.2 *N* perchloric acid. 1 ml is equivalent to 10 μg of hafnium.
Sodium sulphate, 10^{-3} *M* solution.
Hydrogen peroxide, 30 per cent solution.
Xylenol orange, 10^{-3} *M* solution.
Perchloric acid, 5 *N solution.*

Constructing a Calibration Curve

Place 1, 2, 3, 4 and 5 ml of the standard solution of hafnium (zirconium) perchlorate in five 25-ml volumetric flasks, add 1.5 ml of perchloric acid, 2 ml of xylenol orange into each flask, and add water to the mark. Stir the solutions and measure their absorption at 535 nm against a blank solution. Construct the calibration curve using the data obtained.

Procedure

Place the solution containing 5-40 μg of hafnium and not more than 25 μg of zirconium into a 25-ml volumetric flask and add the reagents as for the construction of the calibration curve. Measure the absortion of the solutions (*D*).

Place the same aliquot into another 25-ml volumetric flask, add 1.5 ml of perchloric acid, 5 ml of hydrogen peroxide, 1 ml of sodium sulphate solution, 2 ml of xylenol orange, and water to the mark. Measure the absorption of the resultant solution (D_1) and determine the hafnium content from the calibration curve.

The difference in the absorptions $D_2 = D - D_1$ corresponds to the absorption of the solution of the zirconium compound with the reagent. Determine the zirconium content from the calibration curve constructed with pure solutions of zirconium perchlorate.

PHOTOMETRIC DETERMINATION OF ZIRCONIUM IN HAFNIUM WITH ARSENAZO III

The optimum medium for the formation of the coloured compounds of zirconium and hafnium with arsenazo III is 1 *N* HCl. If the concentration of HCl is 4 *N*, the absorption of the solutions of hafnium compounds sharply decreases, while for zirconium compounds it remains practically unchanged. The method is based on the measurement of the absorption of the solutions of the zirconium compound with arsenazo III, formed in a medium of 4 *N* HCl. Th, U^{IV}, and Ti^{IV} interfere with the determination. Iron (III) is reduced with ascorbic acid. When 0.5-1 per cent of zirconium is determined in hafnium, the error is 20 and 10 per cent respectively.

Reagents

Zirconium salt, standard solution in 4 *N* hydrochloric acid. 1 ml is equivalent to 2 μg of zirconium.
Hafnium salt, standard solution in 4 *N* hydrochloric acid. 1 ml is equivalent to 4 μg of hafnium.
Hydrofluoric acid, concentrated.
Sulphuric acid, concentrated.
Hydrochloric acid, 4 *N* solution.
Arsenazo III, 0.05 per cent solution prepared for the test. Dissolve 0.05 g of the reagent in 80-90 ml of water, add 5 ml of 6 *N* hydrochloric acid, and add water to 100 ml.

Constructing a Calibration Curve

Place 1, 2, 3 and 4 ml of the zirconium salt solution into four 50 ml volumetric flasks, add 12-10.5 ml of hafnium salt solution (the sum of zirconium and hafnium in each flask should be 50 μg), 25-35 ml of hydrochloric acid, heat to boiling and cool. Add 2 ml of arsenazo III into each flask and 4 *N* hydrochloric acid to the mark. Allow the solutions to stand for 30 minutes and measure their absorption at 655 nm. Construct the calibration curve using the data obtained.

Procedure

Place 10-20 mg of hafnium metal in a platinum dish, add 50 ml of water and 1 ml of hydrofluoric acid, cover the dish with a lid and allow to stand to complete dissolution. Add 1 ml of sulphuric acid to the solution, evaporate the mixture to dense white fumes of SO_3, rinse the wall of the dish with 2-3 ml of water and evaporate to dryness. Dissolve the residue in 4 *N* hydrochloric acid, transfer in a 500-ml volumetric flask and add 4 *N* hydrochloric acid to the mark. Transfer an aliquot containing not more than 50 μg of hafnium into a 50-ml volumetric flask, and proceed as for the construction of the calibration curve. Determine the zirconium content from the calibration curve.

Note. If the sample contains molybdenum, dissolve it, evaporate with sulphuric acid, and then dissolve in 10-15 ml of water. Transfer the solution into a centrifuge tube and precipitate hafnium with ammonia. Separate the precipitate by centrifuging, wash with water containing ammonia, dissolve in 4 *N* hydrochloric acid, transfer in a volumetric flask and continue as described above.

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Vanadium

Vanadium, V, in its compounds has the positive valency of 2 to 5. The cations V^{2+}, V^{3+} and VO^{2+} are oxidized in solution to vanadates. The compounds of pentavalent vanadium are most stable in solutions. The compounds of V^{IV} in acid solutions are also stable.

The standard electrode potentials in aqueous solutions at 25°C are as follows (with reference to the standard hydrogen electrode):

$V \rightleftharpoons V^{2+} + 2e^-$	−1.175 V
$V^{2+} \rightleftharpoons V^{3+} + e^-$	−0.255 V
$VO^+ \rightleftharpoons VO^{2+} + e^-$	−0.044 V
$V^{3+} + H_2O \rightleftharpoons VO^{2+} + 2H^+ + e^-$	0.337 V
$VO^{2+} + H_2O \rightleftharpoons VO_2^+ + 2H^+ + e^-$	1.004 V
$VO^+ + 3H_2O \rightleftharpoons VO_4^{3-} + 6H^+ + 2e^-$	1.256 V
$VO^{2+} + 3H_2O \rightleftharpoons H_3VO_4^- + 4H^+ + e^-$	1.314 V

Figure 2 shows the most important forms in which vanadium exists in its various valency states and the corresponding standard redox potentials.

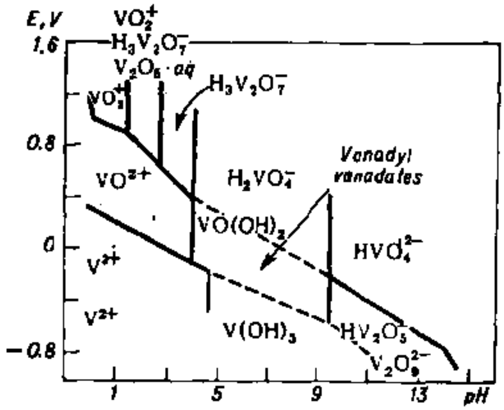

Fig. 2. Dependence of redox potentials and valency of Vanadium on pH. Vanadium concentration in the original solution, 10^{-3} *M*

The reduction of pentavalent vanadium and oxidation of vanadium in its lower valencies underlie many variants of the titrimetric determination of this element.

The redox potential at 25°C of the system

$$VO_2^+ + 2H^+ + e^- \rightleftharpoons VO^{2+} + H_2O$$

$$E = 1.01 + 0.06 \log \frac{[VO_2^+][H^+]^2}{[VO^{2+}]}$$

changes within a wide range along with the acidity: for 9 N $HClO_4$ or 8 N H_2SO_4 E^0 is 1.30 V. The potential becomes very low in an alkaline medium ($E^0 = -0.74$ V at pH 14). The ion of pentavalent vanadium in strongly acid media (for example in 6 N H_2SO_4) has strong oxidizing properties. Vanadate solutions are used for the titrimetric determination of many reductants. When the acid concentration decreases, the oxidizing properties of pentavalent vanadium weaken. If the medium is weakly acid, the vanadate ion fails to oxidize many reductants.

Vanadyl salts (VO^{2+}) are oxidized in moderately acid solutions with strong oxidants. For example, they are oxidized quantitatively with potassium permanganate solution in a medium of about 5 per cent sulphuric acid or with a potassium bromate in dilute hydrochloric acid solutions containing ammonium salts. If the pH increases, the oxidability of V^{IV} increases and it can be oxidized even by atmospheric oxygen in an alkaline medium.

Consider the reaction of vanadium and iron compounds:

$$V^V + Fe^{II} \rightleftharpoons V^{IV} + Fe^{III}$$

In an acid medium the process occurs from left to right and is practically quantitative. The reaction proceeds from right to left in an alkaline medium [1], i.e. Fe^{III} oxidizes V^{IV} to V^V. The ferrous ion is formed in this process, and it can easily be detected with dimethylglyoxime and *o*-phenanthroline.

The actual redox potential of the system

$$VO^{2+} + 2H^+ + e^- \rightleftharpoons V^{3+} + H_2O$$

in a 1 N sulphuric acid solution is 0.34 V.

The V^{3+} ion (VOH^{2+}) is oxidized by atmospheric oxygen to VO^{2+}. In neutral or alkaline solutions, V^{III} is quickly oxidized to V^V.

The actual potential of the system

$$V^{3+} + e^- \rightleftharpoons V^{2+}$$

is found in the range from -0.21 to -0.25 V [2].

Salts of divalent vanadium are prepared by reducing the compounds of penta- and tetravalent vanadium with zinc metal or amalgamated zinc in an acid solution. Salts of V^{II} are strong reductants, they are used for the potentiometric titration of some substances. In acid solutions, they reduce the NO_3^- ion to NH_4^+, ClO_3^- and ClO_4^- to Cl^-, Cu^{2+} to Cu^0, Bi^{3+} to Bi^0; the hydrogen ion is slowly reduced with the ion of divalent vanadium to H_2. Salts of divalent vanadium are easily oxidized by atmospheric oxygen. The reducing properties of the divalent vanadium ion are stronger in alkaline solutions than in acid solutions. The compound $V(OH)_2$ reacts with water to liberate H_2. The oxidation-reduction potential of the system

$$V^{2+} + 2e^- \rightleftharpoons V$$

is -1.5 ± 0.3 V. But due to passivation, water remains inactive toward vanadium metal. Vanadium is dissolved in nitric, 8 *M* hydrochloric or hydrofluoric acid.

The V^{2+} ion is pale violet. The ions V^{3+} and VOH^{2+} are green, they react almost like the ions Fe^{3+}, Al^{3+}, and Ti^{3+}. They readily form the complex ions $[VF_5]^{2-}$, $[V(CN)_6]^{3-}$ and oxalate complexes. Alums of the composition $K_2SO_4 \cdot V_2(SO_4)_3 \cdot 24H_2O$ are known.

Thiocyanates react with the tervalent vanadium ion in a dilute acid solution to form a yellow compound with the absorption maximum at 400 nm. The pK of the ions $V(SCN)^{2+}$ is 1.7-2.0 ($\mu = 2.6$). The formation of other thiocyanate complexes of V^{III} is reported. The ion of tervalent vanadium is determined spectrophotometrically as a thiocyanate complex in a medium of 60 per cent acetone [3].

Hydroxides of the alkali metals precipitate green $V(OH)_3$ at pH 4-5. The compound is quickly oxidized and turns brown. The hydroxide $V(OH)_3$ has basic properties. Salts of V^{III} reduce the ions Ag^+, Cu^{2+} and Hg^{2+}.

The ion of tetravalent vanadium VO^{2+} colours aqueous solutions blue and the colour remains noticeable at vanadium concentration of 0.1 mg/ml. The compounds of tetravalent vanadium are not oxidized by atmospheric oxygen in an acid solutions and are stable. In alkaline solutions they are easily oxidized to vanadates.

Salts of tetravalent vanadium are obtained by reduction of vanadates with hydroxylamine, ascorbic acid, etc., with boiling. The chloride of tetravalent vanadium is formed during evaporation of vanadate solutions with hydrochloric acid.

Ammonium sulphide precipitates the vanadyl ion VO^{2+} as the oxysulphide VOS.

At pH about 4, a 0.01 *M* solution of tetravalent vanadium salt precipitates a greyish-brown $VO(OH)_2$ with $-pL_{VO(OH)_2} = 22.1$ (see Fig. 3). The precipitate is appreciably soluble in caustic alkalies with the formation of polyions of tetravalent vanadium $HV_2O_5^-$ or $V_4O_9^{2-}$. The compounds are first brownish-red and then red. The pK of the reaction

$$2VO(OH)_2 \rightleftharpoons HV_2O_5^- + H_2O + H^+$$

is 10.5. Thus, the hydroxide of vanadyl, $VO(OH)_2$ has amphoteric properties.

Sodium phosphate reacts with tetravalent vanadium to give a blue-green precipitate. Potassium cyanide reacts with it to give a pale green precipitate. Both precipitates are soluble in excess precipitant to form green solutions.

Vanadium (IV) forms strongly dissociated fluoride complexes and very strongly dissociated thiocyanide complexes. Quite stable oxalate and tartrate complexes also exist:

$$\mathrm{VOF^+ \rightleftharpoons VO^{2+} + F^-} \qquad pK = 3.2$$

$$\mathrm{VO(SCN)^+ \rightleftharpoons VO^{2+} + SCN^-} \qquad pK = 0.9\ (\mu = 2.6)$$

$$\mathrm{VO(C_2O_4)_2^{2-} \rightleftharpoons VO^{2+} + 2C_2O_4^{2-}} \qquad pK = 12.0$$

$$\mathrm{VO(OH)C_2O_4^- \rightleftharpoons VOOH^+ + C_2O_4^{2-}} \qquad pK = 6.5$$

$$\mathrm{VOTart \rightleftharpoons VOTart^- + H^+} \qquad pK = 2.8$$

Vanadium (IV) is oxidized quantitatively with $\mathrm{Ce^{IV}}$ salt [4].

The ion of vanadium (IV) forms thiocyanate blue complexes (VOSCN and others) [2, 5], the colour intensity being 4-5 higher than that of the vanadyl salt solution of the same molar concentration. When vanadium is determined photometrically, a thiocyanate complex of tetravalent vanadium is formed in an aqueous-acetone medium whose absorption is measured at 750 nm [5].

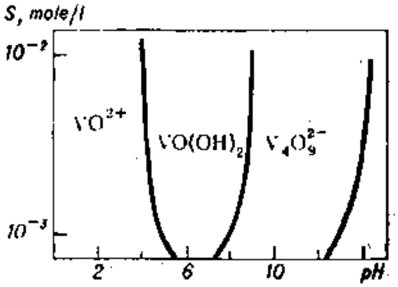

Fig. 3. Dependence of the solubility of $VO(OH)_2$ on pH

The ion of tetravalent vanadium reacts with hydroxyl-containing and some other organic reagents [6] but these reactions are not sufficiently well studied. Pyrocatechol reacts with the tetravalent vanadium ion to form a blue complex compound used for the photometric determination of vanadium. The hydroxyl-containing azo compound, acid chrome blue K reacts with the ion of tetravalent vanadium to form a violet compound. The reagent is used for the photometric determination of vanadium. β-Hydroxynaphthylethylamine and β-hydroxynaphthylaldoxime precipitate vanadium (IV) quantitatively in the form of crystalline substances with the formulas $\mathrm{VO[OC_{10}H_6CHNC_2H_5]}$ and $\mathrm{VO[OC_{10}H_6CHNOH]_2}$, which are yellow-green and grey-green respectively [7]. The precipitates meet the requirements for the weighing form and can be used for the gravimetric determination of vanadium in ferrovanadium. The ions of Fe do not interfere with the determination; the ions of $\mathrm{Cu^{II}}$ and $\mathrm{Ti^{IV}}$ interfere.

EDTA reacts with the ion of tetravalent vanadium in weakly acid solutions and is used for its titrimetric determination [8].

Formaldoxime is a highly sensitive reagent for the ion of tetravalent vanadium and is used for its photometric determination [9]. The reagent forms a yellow soluble compound with the ion of tetravalent vanadium.

The ion of pentavalent vanadium, VO_4^{3-}, prevails in alkaline solutions. The metavanadate ion exists in acid solutions:

$$VO_4^{3-} + H^+ \rightleftharpoons VO_3^- + OH^-$$

Polymetavanadate ions ($V_2O_7^{4-}$, $V_3O_9^{3-}$, $V_4O_{11}^{2-}$, $V_{10}O_{28}^{6-}$ and others) are formed along with the metavanadate ions. At pH below 3, there exist also a yellow cation VO_2^+ and a small quantity of VO^{3+} (Fig. 4). The reactions of VO_4^{-3} resemble some reactions of the PO_4^{3-} and AsO_4^{3-}, as well as of the Mo^{VI}, W^{VI} and Cr^{VI} ions. The salts of orthovanadic (H_3VO_4) and meta-vanadic acid (HVO_3) are usually colourless or coloured only slightly. The salts of polyvanadic acids are yellow or orange.

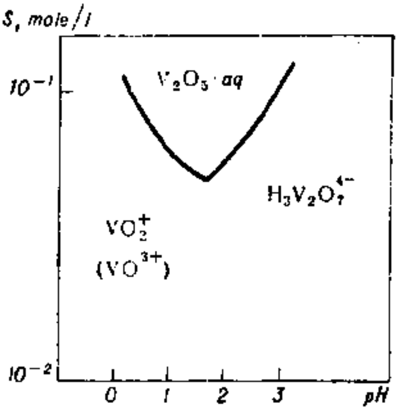

Fig. 4. Dependence of the solubility of vanadium pentoxide hydrate, $V_2O_5 \cdot aq$, on pH

Vanadium pentoxide, V_2O_5, is a solid non-volatile red substance melting at 658°C. The pentoxide is formed by calcining a vanadium compound with cupferron and meets the requirements for the weighing form. It is readily soluble in alkali solutions, worse in acid, and only slightly soluble in ammonia solutions. Vanadium pentoxide has a strong acid character but acid solutions contain the cations VO^{3+} and VO_2^+.

Vanadates of most metals are sparingly soluble in water, except the vanadates of potassium and sodium. The solubility of ammonium metavanadate, NH_4VO_3, decreases when a large quantity of ammonium chloride is added, and a white crystalline substance,

NH_4VO_3, precipitates. Lead acetate precipitates a yellow vanadate (of variable composition) soluble in HNO_3. A colourless solution of metavanadate turns orange when acidified with acetic acid. If silver nitrate is added to this solution (after heating), an orange crystalline substance silver pyrovanadate ($Ag_4V_2O_7$), slowly precipitates.

Ammonia does not precipitate the pentavalent vanadium ion. But if sufficient quantities of aluminium, iron or titanium salts are present in solution, ammonia can precipitate quantitatively the ion of V^V at pH 6-7, probably in the form of vanadates, together with hydroxides of the named elements [10]. This reaction is used in the chemical analysis to separate small quantities of vanadium.

When ammonium sulphide is added to the vanadate solution, the solution turns brick-red due to the formation of the VS_4^{3-} ion. When the resultant solution is acidified with sulphuric acid, brown V_2S_5 precipitates (not quantitatively). The V_2S_5 precipitate is sparingly soluble in very dilute acids, soluble in alkali and sulphide solution to form orange-red sulpho salts.

Hydrogen sulphide does not precipitate vanadium sulphide from acid solutions, but reduces the V^V ion to the V^{IV} ion. Vanadium is separated from the metals of the hydrogen sulphide group by precipitating them from acid solution in the presence of tartaric acid (to preclude co-precipitation of the vanadium ion with sulphides of other metals).

Phosphovanadates and phosphovanadotungstates are yellow substances soluble in organic solvents. The formation of yellow phosphovanadotungstic acid upon adding phosphoric acid and sodium tungstate to an acid solution of vanadate is the basis of various photometric methods for the determination of vanadium [11-13].

Hydrogen peroxide reacts in an acid solution with the ion V^V to form red-brown peroxidic compounds. If hydrogen peroxide is taken in great excess, the colour intensity decreases and yellow solutions are formed. Hydrogen peroxide reduces pentavalent vanadium to its tetravalent state in a medium of concentrated sulphuric acid. The peroxidic compounds of vanadium are not extractable with ethyl ether (in contrast to the peroxidic compounds of hexavalent chromium). Hydrogen peroxide is used for the photometric determination of vanadium in sulphuric or nitric acid solution [14, 15].

The ions of pentavalent vanadium are readily reduced to V^{IV} ions by SO_2 and Mohr's salt, in acid solutions.

Many titrimetric methods for the determination of vanadium in ores, steel, cast iron and other materials have been developed. These are based on the oxidation of the ferrous ion with the V^V ion in acid solutions [16]. N-Phenylanthranilic acid is used to locate the point of equivalence. The methods in which the point of equivalence is detected potentiometrically or amperometrically (by the current of oxidation of the ferrous ion at the rotating platinum anode) are widely used in analytical chemistry.

The ion of pentavalent vanadium oxidizes some organic substances in acid solution to form intensely coloured products. For example, benzidine is oxidized to benzidine blue and aniline to aniline black. Diphenylamine is oxidized in concentrated sulphuric acid to a blue compound. *p*-Phenylenediamine reacts with the ion of pentavalent vanadium in dilute hydrochloric acid solutions (with boiling) to form a red compound. A yellow compound is formed in a neutral solution. The reaction of pentavalent vanadium with diantipyryl-3,4-dimethoxyphenylmethane is very sensitive [17].

3,3-Diaminobenzidine is oxidized by the vanadate ion in a solution of phosphoric acid to form red-brown substances. The reagent is used for the determination of small quantities of vanadium [18]. The absorption of the solution is measured at 470 nm. The method is highly selective and takes short time. The ions of Fe^{III}, Cr^{III}, Ti^{IV}, Nb^{V}, Ta^{V}, Sn^{IV}, Mo^{VI}, Zr^{IV}, Cu^{II}, W^{VI} and Mn^{II} do not interfere with the determination.

Pyrocatechol reduces V^{V} to V^{IV} and forms a blue compound which is used for the photometric determination of vanadium [19]. Tribromopyrogallol is used for the extraction-photometric determination of vanadium [20].

Diphenylcarbazide reacts with the vanadate ion in dilute H_2SO_4 to form an orange-brown compound. It is a highly sensitive reagent for vanadium. The ions CrO_4^{2-}, MoO_4^{2-}, Fe^{3+} and Hg^{2+} interfere with the determination. The ions Fe^{3+} and MoO_4^{2-} can be masked by NaF, and the ion Hg^{2+} by chlorides.

Cupferron precipitates quantitatively the ion of vanadium (V) from solutions in 1 per cent hydrochloric acid. It is used for the separation of V^{V} from Cr^{III}, Al^{III}, phosphate ion, etc. [21]. The red precipitate is calcined to V_2O_5 and weighed.

N-Benzoylphenylhydroxylamine (alcoholic solution) precipitates a brown substance from a dilute vanadate solution in sulphuric acid [22]. The precipitate is easily extractable with chloroform. The orange-yellow extract absorbs maximum at 450 nm; its molar extinction coefficient is 3.7×10^3. When the reagent is added to hydrochloric acid solutions containing the ion of pentavalent vanadium, the solution turns purple or a precipitate falls out. The purple extract absorbs maximum at 530 nm and its molar extinction coefficient is 4.5×10^3. The chloroform extracts of the reagent are stable if the concentration of HCl in the aqueous phase is 5-9 mole/l. In these conditions, the ion of tetravalent vanadium does not form coloured compounds. N-Benzoylphenylhydroxylamine is a highly selective reagent for the V^{V} ion. It is used for the photometric determination of vanadium in steels and ores.

Hydroxamic acids (e.g. benzohydroxamic acid) react with the pentavalent vanadium ion to form coloured and extractable compounds which are used for the photometric determination of vanadium [23].

Xylenol orange reacts with pentavalent vanadium in a weak acid solution to form coloured compounds which are used for the photometric determination of vanadium [24]. The reagent is highly selective in the presence of 1,2-diaminocyclohexanetetraacetic acid and can be used to detect traces of vanadium.

8-Quinolinol reacts with the vanadate ion to form two differently coloured compounds whose nature is obscure. The chloroform extraction of a red vanadium compound with 8-quinolinol at pH 4 is used for the separation of vanadium from Cr^{VI} (but not from Fe^{III}, Mo^{VI}, W^{VI}) [25].

Tannic acid precipitates quantitatively the pentavalent vanadium ion from almost a neutral solution in the presence of ammonium chloride or ammonium acetate. A massive blue-black substance precipitates. Tannic acid is used for the separation of small quantities of vanadium.

The reaction of vanadium with sulphonitrazo is very sensitive and it is used for the photometric determination of vanadium in steels [26]. Azo-compound of the heterocyclic series, 1-(2-pyrydylazo) resorcinol, reacts with V^V in the presence of hydroxylamine to form three-component compounds suitable for the photometric determination of vanadium [27, 28].

Vanadium compounds catalyze oxidation of some organic substances, for example, of *p*-phenetidine by potassium chlorate (phenol acts as an activator). Some methods have been developed [29] for the catalytic (kinetic) determination of small quantities of vanadium. The catalytic properties of vanadium are probably explained by its ability of passing from one of its valency states into another.

Titrimetric methods based on the oxidation-reduction reactions are mostly used for the determination of comparatively large quantities of vanadium. The gravimetric methods are not frequently used. Small quantities of vanadium are determined photometrically (as peroxidic compounds or as phosphovanadotungstate). Polarographic methods are not widely used in analytical practice. The spectral method is usually used to determine vanadium in alloys.

The review of the methods for the determination of vanadium is given in the literature [30].

TITRIMETRIC DETERMINATION OF VANADIUM IN ORES WITH MOHR'S SALT

The method is based on the titration of the pentavalent vanadium ion in a medium of a 5 *N* solution of sulphuric acid using a standard solution of Mohr's salt in the presence of excess phosphoric acid which binds the Fe^{3+} ion in a colourless complex. The end point of titration is detected by the internal indicator, phenylanthranilic acid, or potentiometrically, using a platinum spiral or plate as an indicator electrode.

The V^{VI} ion is oxidized to V^V ion in acid solutions in the cold by a dilute solution of potassium permanganate which is added drop after drop with stirring intensely until the solution develops a stable pink colour. Excess oxidant is removed by heating with hydrochloric acid (or NaCl), by the action of sodium nitrite (excess is decomposed by carbamide) at room temperature, or by oxalic acid.

Ore is dissolved in a mixture of sulphuric and phosphoric acids with heating.

Reagents

Acid mixture. Add carefully 150 ml of H_2SO_4, density 1.84 g/cu.cm, to 300 ml of water, cool the solution, and add 150 ml of H_3PO_4, density 1.70 g/cu.cm.
Potassium permanganate, 3 per cent solution.
Hydrochloric acid, diluted 1 : 2.
Sulphuric acid, diluted 1 : 1.
N-Phenylanthranilic acid. Dissolve 0.2 g of the acid and 0.2 g of Na_2CO_3 in 100 ml of water with heating.
Mohr's salt. Dissolve 1.08 g of the salt in a 5 per cent solution of sulphuric acid and add the same acid to make 1 litre. Standardize the solution against a solution containing 0.135 g of $K_2Cr_2O_7$ in 1 litre.

Procedure

Place an ore sample weighing 1 g in a 250-300 ml flask and dissolve in 20-30 ml of the acid mixture with heating and periodically stirring. Cool the solution to room temperature and add potassium permanganate solution, drop after drop, until stable pink colour develops and persists for 5 minutes. Now add 3-5 drops of hydrochloric acid and boil until the solution becomes colourless. Cool the solution, add 15 ml of sulphuric acid and 5-6 drops of N-phenylanthranilic acid. Add water to 100 ml and mix thoroughly. Titrate with Mohr's salt solution until the dark cherry-red colour changes to pale green.

COMPLEXOMETRIC DETERMINATION OF VANADIUM

The method is based on the formation of a stable (in a weak acid medium) complex compound of V^{IV} with EDTA ($\log K = 18.77$). The complex is blue. N-Benzoylphenylhydroxylamine is used as an indicator for titration. At pH 3, it forms a red complex with the vanadyl ion. The complex is soluble in 50 per cent ethanol. The red solution turns blue at the end point of titration. The ion of pentavalent vanadium is reduced to the tetravalent vanadium ion by sodium sulphite in a sulphuric acid medium. The ions of Ti, Mn and Mo (10 mg and less) do not interfere with the determination. The ferric ion should be separated by precipitation with ammonia in the presence of hydrogen peroxide.

The method is used to determine from 3 to 40 mg of vanadium.

Reagents

Sodium sulphite, crystalline.
Acetate buffer solution, pH 3.
N-Benzoylphenylhydroxylamine, 2 per cent solution in 95 per cent alcohol.
EDTA, 0.01 *M* solution.
Ethanol, 96 per cent solution.

Procedure

Add solid sodium sulphite to an acid solution of vanadate and boil to remove SO_2. Adjust the pH of the solution to 3 and add the acetate buffer and alcohol until its concentration is 50 per cent. Titrate the solution with EDTA until the red solution turns blue.

1 ml of a 0.01 *M* solution of EDTA is equivalent to 0.5095 mg of vanadium.

AMPEROMETRIC DETERMINATION OF VANADIUM (IV)

The method is based on the titration of the tetravalent vanadium ion by a cerium (IV) sulphate solution. The end point of titration is detected by the current of reduction of excess Ce^{4+} ion (a platinum rotating electrode) at the potential of +0.5 V (with reference to a saturated calomel electrode).

The method can be used to determine vanadium in ferrochrome.

Reagents

Sulphuric acid, diluted 1 : 4.
Nitric acid, density 1.4 g/cu.cm.
Cerium sulphate (IV), 0.004 *N* solution.
Mohr's salt, about 0.02 *N* solution.

Procedure

Dissolve a sample of ferrochrome weighing 0.5-1.0 g in 30-40 ml of sulphuric acid with heating, add a small quantity of nitric acid and boil to remove nitrogen oxides. Transfer the solution into a 100-ml volumetric flask, and add water to the mark. Transfer an aliquot (25 ml) of the solution into an electrolyzer, immerse the electrodes, and adjust the potential to +0.9 V. The absence of the diffusion current shows that the solution does not contain the ferrous ion. If so, add a small quantity of Mohr's salt solution, drop by drop. Now titrate with a solution of $Ce(SO_4)_2$. When all Fe^{2+} ion is titrated, the galvanometer will read zero. Now adjust the potential to +0.5 V and titrate with $Ce(SO_4)_2$ solution until diffusion current appears.

PHOTOMETRIC DETERMINATION OF VANADIUM AS PHOSPHOVANADOTUNGSTIC ACID

In the presence of sufficient excess of the tungstate ion ($V_2O_5:WO_3 = 1:100$) and phosphate ion, vanadium forms phosphovanadotungstic acid which is reduced to the blue form at the acidity of 0.2-

0.75 *N* (phosphotungstic acid is not reduced at this acidity). The absorption maximum of the reduced heteropolyacid is at 510-550 nm. Phosphovanadotungstic acid reacts best when boiled. It should be reduced at room temperature.

The method can be used for the analysis of steel and alloys. The vanadate ion can be separated from the interfering ions (with own colour), such as Ni^{2+}, Co^{2+}, and Cu^{2+}, by precipitating with iron hydroxide. The interfering chromium (III) is oxidized to $Cr_2O_7^{2-}$ by $(NH_4)_2S_2O_8$ in the presence of $AgNO_3$ (catalyst). Mg, Ca, Sr, Ba, Zn, Cd, Hg^{II}, Al, Pb, As and Th do not interfere.

The method can be used to determine decimal fractions of a microgram of vanadium in 1 ml of solution.

Determining Vanadium in Solutions

Reagents

Sodium tungstate, 5 per cent solution.
Phosphoric acid, density 1.7 g/cu.cm.
Stannous chloride, 0.5 per cent solution. Dissolve 50 g of $SnCl_2 \cdot 2H_2O$ in 250 ml of concentrated hydrochloric acid and add water to make 500 ml. Dilute the obtained solution with 20 volumes of water.
Ammonium vanadate, standard solution. 1 ml is equivalent to 0.2 mg of vanadium.

Constructing a Calibration Curve

Place 1, 2, 3, 4 and 5 ml of the vanadate standard solution into five 50-ml volumetric flasks and heat to boiling. Add 4 ml of sodium tungstate, 3 ml of phosphoric acid, and 5 ml of water into each flask and heat to 90-95 °C again (use a thermometer). Allow the solutions to stand for two minutes, cool to room temperature, add 2 ml of stannous chloride solution and water to the mark. Measure the absorption of the solutions on an absorptiometer or a photometer with a green optical filter. Construct the calibration curve using the data obtained.

Procedure

Add the reagents as for the construction of the calibration curve and measure the absorption of the resultant solution. Determine the vanadium content from the calibration curve.

Determining Vanadium in Ores

Reagents

Sodium peroxide, solid.
Sulphuric acid, diluted 1 : 1.
Hydrochloric acid, diluted 1 : 2.
Nitric acid, diluted 1 : 2.
For the other reagents see the previous section.

Constructing a Calibration Curve

Construct the calibration curve using various portions of the standard sample (as in the procedure). If there is an ore with the composition similar to that of the ore in question, except that vanadium is absent, construct the calibration curve by adding a definite quantity of the standard solution of NH_4VO_3 to the solution after leaching.

Procedure

Place a sample of an ore weighing 0.4 g in an iron crucible, add 4 g of Na_2O_2, and mix by a glass rod. Heat the crucible gradually in a muffle furnace or over a burner to dark-red heat (500-600°C). When the contents liquefy take hold of the crucible by the tongs and stir the liquid by rotating the crucible. Continue heating for another five minutes. Avoid over-heating to preclude the formation of a sparingly soluble alloy. Cool to 30-40°C, wash the melt from the crucible by a jet of warm water into a 100-150 ml beaker. Add 12 ml of sulphuric acid, 4 ml of hydrochloric acid, and 4 ml of nitric acid to the obtained solution. Heat the solution and evaporate to 50 ml. Separate the residue on a filter, wash the filter several times with hot water. Cool the filtrate to room temperature, add 5 ml of phosphoric acid: the solution must become colourless. If phosphoric acid is added to the warm solution, it turns yellow. The colour is stable and this makes the determination impossible.

Add 20 ml of sodium tungstate to the colourless solution and heat to 90-95°C. Allow the solution to stand for 5 minutes, cool to room temperature and add 2 ml of stannous chloride. Transfer the solution into a 100-ml volumetric flask and add water to the mark. Measure the absorption of the solution with a green optical filter. Determine the vanadium content from the calibration curve.

PHOTOMETRIC DETERMINATION OF VANADIUM WITH HYDROGEN PEROXIDE

The method is based on the formation of an orange-red complex of the vanadium (V) ion with hydrogen peroxide in a sulphuric acid medium. The constant of the formation reaction $K = 1.2 \times 10^{-5}$. The complex solution absorbs maximum at 450 nm. The optimum concentration of H_2O_2 is 0.03 per cent and of sulphuric acid 0.6-6 N. If the concentration of hydrogen peroxide is higher than 0.09 per cent, the red-brown solution turns yellow. The ion of Ti^{IV}, considerable quantities of Fe^{III} and Mo^{VI} ions interfere with the determination. The interfering effect of Ti^{IV} and Fe^{III} ions can be removed by adding F^- and PO_4^{3-} ions. Reductants, e.g. I^- and Br^-, interfere with the determination.

The method is used for the determination of vanadium in cast iron and steel.

Reagents

Hydrogen peroxide, 3 per cent solution.
Potassium permanganate, 0.01 N solution
Oxalic acid, 2.5 per cent solution.

Phosphoric acid, density, 1.7 g/cu.cm.
Hydrochloric acid, density 1.19 g/cu.cm
Nitric acid, density 1.4 g/cu.cm.
Sulphuric acid, diluted 1 : 4.
Ammonium vanadate, standard solution. 1 ml is equivalent to 0.01 mg of vanadium. Dissolve 0.1286 g of NH_4VO_3 in 1 litre of water and dilute with ten volumes of water.

Constructing a Calibration Curve

Place 1, 2, 3, 4 and 5 ml of the standard vanadate solution into five 100-ml volumetric flasks, dilute with water to 50 ml, add 3 ml of phosphoric acid, potassium permanganate solution until a pale pink colour develops, and allow the solutions to stand for 1-2 minutes. Then add 3-4 drops of oxalic acid and keep the solutions for three minutes. Add 2 ml of hydrogen peroxide into each flask and then water to the mark. Measure the absorption of the solutions on an absorptiometer with a green optical filter. Construct the calibration curve using the data obtained

Procedure

Dissolve a sample of steel weighing 0.5 g in a mixture of 30 ml of hydrochloric and 10 ml of nitric acid or in 50 ml of sulphuric acid containing nitric acid. If the sample contains tungsten, add 3 ml of phosphoric acid. Evaporate the obtained solution with 10 ml of sulphuric acid to white fumes of SO_3. Dissolve the salts in 50 ml of water, separate silicic acid on a filter, collect the filtrate in a 250-ml volumetric flask, cool, add water to the mark, and stir. Transfer 50-ml portions into two 100-ml volumetric flasks, add 3 ml of phosphoric acid (if it was not used to dissolve the sample) and proceed as for the construction of the calibration curve but do not add hydrogen peroxide into one flask. Measure the absorption of the solution against a solution containing hydrogen peroxide. Use a green optical filter. Determine the vanadium content from the calibration curve.

PHOTOMETRIC DETERMINATION OF VANADIUM WITH PYROCATECHOL

The method is based on the ability of vanadium to react with pyrocatechol in an alkaline medium with the formation of a blue complex containing tetravalent vanadium. The interfering effect of the ions of Fe, Co, Ni, Cr, Mo, W and Cu is removed by ascorbic acid, the citrate and cyanate ions and EDTA. Zn, Cd, Zr, Th, Sn, Pb, As, La, Ce, U (less than 20 per cent), Sb (less than 10 per cent), Ga (less than 10 per cent) and other elements do not interfere with the determination. The interfering effect of the Nb, Bi, Ti and other ions which form yellow complexes is completely removed if the absorption is measured at 800 nm.

The method is highly selective and can be used to determine less than 1 per cent of vanadium in various materials.

Reagents

Perchloric acid, concentrated.
Pyrocatechol. Dissolve 35 g of the reagent in 300 ml of water, add 50 ml of citric acid, 2 g of ascorbic acid, 60 ml of ammonia solution, density 0.92 g/cu.cm and dilute with water to 500 ml. Keep the solution under toluene to prevent its oxidation by atmospheric oxygen.
Ascorbic acid, crystalline.
Citric acid. Dissolve 500 g of the reagent in 1 litre of water.
Potassium cyanide and EDTA solution. Dissolve 25 g of KCN and 12.5 g of EDTA in 250 ml of concentrated ammonia solution.
Sodium vanadate, standard solution. 1 ml is equivalent to 0.5 mg of vanadium. Fuse 0.8925 g of chemically pure V_2O_5 with 6 g of Na_2CO_3 in a platinum crucible, dissolve the melt in 100 ml of water, transfer the solution quantitatively into a 1-litre volumetric flask and add water to the mark.

Constructing a Calibration Curve

Place 0.2, 0.4, 0.6, 0.8 and 1.0 ml of the standard solution of the vanadate into five 100-ml volumetric flasks, add 5 ml of potassium cyanide and EDTA solution into each flask, and boil for 1-2 minutes. Cool the solutions and add water to 100 ml. Transfer an aliquot (5 ml) into a 25-ml volumetric flask, add pyrocatechol to the mark and in 20 minutes measure the absorption at 800 nm (light path, 3 cm). Construct the calibration curve using the data obtained.

Procedure

Add a few millilitres of $HClO_4$ to the solution of the decomposed sample (0.1-0.5 mg of V) and evaporate the solution. Transfer quantitatively the residue with 35 ml of water into a 100-ml volumetric flask. Add 5 ml of potassium cyanide and EDTA solution, boil for 1-2 minutes, cool and add water to the mark. Filter out $KClO_4$, transfer 5 ml of the clear filtrate into a 25-ml volumetric flask, and proceed as for the construction of the calibration curve. Determine the vanadium content from the calibration curve.

EXTRACTION-PHOTOMETRIC DETERMINATION OF VANADIUM WITH BENZHYDROXAMIC ACID

The method is based on the reaction between the V^V ion and benzhydroxamic acid with the formation of a blue complex in a strongly acid medium and of a red complex in a weakly acid medium. The complex formed at pH 1.2-5.5 is extracted with 1-hexanol. The absorption of the solutions is proportional to the concentration of vanadium in the range of 0.4-8 μg/ml. Ta, Cr, Cu, Zn, Cd, F^-, SCN^-, the citrate and tartrate ions do not interfere with the determination. Oxidants or reductants should be absent. The ions of Ti, Zr, Mn, Fe^{III}, Th, Al, Sn, Mo^{VI} and W^{VI} interfere. The interfering effect of the elements forming colourless complexes with the reagent can be removed by adding excess quantities of the latter.

Reagents

Potassium benzhydroxamate, 0.3 per cent solution, pH 5.
Sulphuric acid, diluted 1 : 5.
Hexanol-1.
Ammonium vanadate, standard solution. 1 ml is equivalent to 0.05 μg of vanadium.

Constructing a Calibration Curve

Place 1, 2, 3, 4 and 5 ml of the standard vanadate solution into five separating funnels, add 10 ml of potassium benzhydroxamate solution into each funnel and dilute with water to 30 ml. Adjust the pH of the solutions to 2 by adding sulphuric acid and extract the vanadium complex with 20 ml of hexanol-1. Measure the absorption of the extracts at 450 nm using hexanol as a reference solution. Construct the calibration curve using the data obtained.

Procedure

To determine vanadium proceed as for the construction of the calibration curve

PHOTOMETRIC DETERMINATION OF VANADIUM WITH DIANTIPYRYL-3,4-DIMETHOXYPHENYLMETHANE

The method is based on the ability of V^V to oxidize diantipyryl-3,4-dimethoxyphenylmethane with the formation of a coloured compound absorbing maximum at 475 nm. The molar extinction coefficient is 9.2×10^4. The sensitivity of the method is 0.03 μg/ml. The Bouguer-Lambert-Beer law holds for the range of vanadium concentrations of 0.25-2.5 μg/ml. The ions of Fe, Cu, Al, Ti, Ni, Co, W, Mo, Nb, Cr^{III}, Mg, Zn, Ta, Be, Se, Cl^-, PO_4^{3-}, $C_2O_4^{2-}$ *do* not form coloured compounds. The following elements have own colour and interfere when present in the following quantities: Fe^{III}, over 500 mg/litre, Cr over 1000 mg/litre, Co over 30 mg/litre and Cu over 2500 mg/litre.

Reagents

Vanadium, standard solution. 1 ml is equivalent to 20 μg of vanadium.
Diantipyryl-3,4-dimethoxyphenylmethane, 1 per cent solution in ethyl alcohol.
Phosphoric acid, diluted 1 : 1.
Hydrochloric acid, density 1.19 g/cu.cm.
Potassium permanganate, 10 per cent solution.
Oxalic acid, saturated solution.

Constructing a Calibration Curve

Place 10-160 μg of vanadium (gradient, 20 μg) into 100-ml volumetric flasks, add 25 ml of hydrochloric acid, 1 ml of a 1 per cent solution of the reagent into each flask, and dilute with phosphoric acid to the mark. Keep the solutions for 15 minutes and measure their absorption in a cell with a light path of 5 *cm* on an absorptiometer with a blue optical filter against a blank solution. Construct the calibration curve using the data obtained.

Procedure

Add a few drops of potassium permanganate to the test solution in a 100-ml volumetric flask to oxidize vanadium, and in five minutes decompose excess potassium permanganate with oxalic acid. Then add the same reagents and in the same order as for the construction of the calibration curve.

EXTRACTION-PHOTOMETRIC DETERMINATION OF VANADIUM WITH TRIBROMOPYROGALLOL

The method is based on the formation of a blue complex of vanadium (V) or (VI) with tribromopyrogallol (TBP). The complex can be extracted with a mixture of chloroform and isoamyl alcohol (1:2) in the presence of diphenylguanidine (DPG). The absorption maximum of the extract is at 600-650 nm. The complex is formed at the ratio of V:TBP:DPG of 1 : 2 : 1. The ions of Ni, Mn, Cu, Co, Cr, and Al, and (in the presence of thioglycolic acid) also Fe^{III} and Mo do not interfere with the determination of vanadium. Tungsten can be masked by tartrate and zirconium by fluoride.

Reagents

Vanadium salt, standard solution. 1 ml is equivalent to 5 μg of vanadium
Acetate buffer solution, pH 3.5.
Diphenylguanidinium chloride, 2 per cent solution.
Mixture of chloroform and isoamyl alcohol (1 : 2) containing 0.35 per cent of tribromopyrogallol.
Ascorbic acid, 20 per cent solution.
Ammonia, aqueous solution diluted 1 : 10.
Sulphuric acid, diluted 1 : 4.
Ammonium tartrate, 10 per cent solution.

Constructing a Calibration Curve

Place 5, 10, 15, 20 and 25 μg of vanadium into five separating funnels, add acetate buffer solution, 0.5 ml of diphenylguanidinium solution to 10 ml, and extract with 10 ml of the extracting agent. Measure the absorption of the extract against a blank solution. Construct the calibration curve using the data obtained.

Procedure

Add 0.2 ml of ascorbic acid to the test solution containing to 40 mg of Fe, 5 mg of Zr and 3.5 mg of W, neutralize the solution carefully with ammonia until the solution turns violet, and add sulphuric acid to discolour the solution. Allow the solution to stand for 5 minutes, then add 0.2 ml of ammonium tartrate, 0.5 ml of diphenylguanidinium chloride, 2 ml of the buffer solution and dilute with water to 10-15 ml. Extract the solution by 10 ml of the extracting agent. Measure the absorption of the extract against a blank solution. Determine the vanadium content from the calibration curve.

PHOTOMETRIC DETERMINATION OF VANADIUM IN STEELS WITH SULPHONITRAZO

The method is based on the reaction of V^{IV} in acid solutions (pH 2.3 ± 0.3) with sulphonitrazo, [2-(2-hydroxy-5-nitro-3-sulphobenzene)-1-naphthol-3,8-disulphonic acid] with the formation of a coloured complex, the component ratio being 1 : 1. The molar extinction coefficient at 582 nm is 2.1×10^4. The colour of the complex is not affected by many masking agents in relatively large quantities: 1 g of ascorbic acid, 300 mg of H_3PO_4, 700 mg of thioglycolic acid, 200 mg of tartaric acid, 2 g of thiocarbamide, 500 mg of $NaBF_4$, 200 mg of pyrocatechol-3,5-disulphonic acid. The reagent is practically selective for vanadium in the presence of the above masking substances.

Reagents

Vanadium salt, standard solution. 1 ml is equivalent to 5 µg of vanadium.
Nitric acid, density 1.4 g/cu.cm.
Hydrochloric acid, density 1.19 g/cu.cm.
Tartaric acid, 10 per cent solution.
Ascorbic acid, 10 per cent solution.
Phosphoric acid., 10 per cent solution.
Thioglycolic acid, 5 per cent solution.
Sodium fluoroborate, 5 per cent solution.
Thiocarbamide, 10 per cent solution.
Pyrocatechol-3,5-disulphonic acid, 4 per cent solution.
Sulphonitrazo, 0.2 per cent solution.

Constructing a Calibration Curve

Place 0.4, 0.8, 0.12, 0.16, and 2.0 ml or 1, 2, 3, 4 and 5 ml of the vanadium solution into 50-ml volumetric flasks, add 2.5 ml of the reagent solution, adjust the pH to 2.3 ± 0.3, add water to the mark and stir. Allow the solutions to stand for ten minutes and measure their absorption at 582 nm against a blank solution in cells with the layer thickness of 5 cm (for 0.4-10 µg of vanadium) or 1 cm (for 2-25 µg of vanadium). Construct the calibration curve using the data obtained.

Procedure

Dissolve a sample of steel weighing 0.1 g in 15 ml of a mixture of hydrochloric and nitric acids (3 : 1) with moderate heating and evaporate the solution to a syrup consistency. Add 40 ml of hot water to the syrup, heat to boiling, pass through a dense filter into a 100-ml volumetric flask, add 10 ml of tartaric acid, water to the mark, and mix. Transfer an aliquot containing 0.4-0.25 µg of vanadium into a 50-ml volumetric flask, add 10 ml of ascorbic acid, 2 ml of thiocarbamide solution, 2 ml of phosphoric acid, 10 ml of $NaBF_4$ solution, 1 ml of thioglycolic acid (in the presence of molybdenum), 5 ml of pyrocatechol-3,5-disulphonic acid (in the presence of titanium), and mix. Allow the solution to stand for five minutes, add 2.5 ml of the reagent and proceed as for the construction of the calibration curve. Determine the vanadium content from the calibration curve.

PHOTOMETRIC DETERMINATION OF VANADIUM IN URANIUM ALLOYS USING HYDROXYLAMINE AND 1-(2-PYRIDYLAZO)RESORCINOL

The method is based on the formation of a three-component complex of pentavalent vanadium with hydroxylamine and 1-(2-pyridylazo)resorcinol (1 : 1 : 1) in a medium of 0.4 *N* sulphuric acid. The molar extinction coefficient of the complex is 3.0×10^4, the absorption maximum being at 550 nm. Re, Th, U, Mo, Mn, Zr, etc. do not interfere with the determination. Cu, Fe and W interfere. The Bouguer-Lambert-Beer law holds for the vanadium concentrations in the range of 1-8 μg/ml.

Reagents

Vanadium salt, standard solution. 1 ml is equivalent to 0.1 mg of vanadium.
1-(2-Pyridylazo)resorcinol, 0.1 per cent solution.
Nitric acid, density 1.4 g/cu.cm.
Hydrochloric acid, density 1.19 g/cu.cm.
Sulphuric acid, density 1.84 g/cu.cm, and 1 *N* solution.
Ammonium tartrate, 2 per cent solution.
Hydroxylamine hydrochloride, 10 per cent solution.
Ammonia, diluted 1 : 10.
Phenolphthalein, 1 per cent solution in ethyl alcohol.
Acetate buffer, pH 4.0-4.3.

Constructing a Calibration Curve

Place 0.05-0.4 mg (gradient, 0.05 mg) of vanadium into 50-ml volumetric flasks, add 1 ml of ammonium tartrate solution into each flask and neutralize with ammonia to phenolphthalein. Add 10 ml of the buffer and 1 ml of hydroxylamine solution, heat the mixture for two minutes on a water bath, add 1 ml of 1-(2-pyridylazo)resorcinol and allow the solutions to stand for 15-20 minutes. Cool in water, add 20 ml of 1 *N* sulphuric acid and water to the mark. Measure the absorption of the solutions in 90 minutes on an absorptiometer in cells with a light path of 5 cm against a blank solution. Construct the calibration curve using the data obtained.

Procedure

Place a sample of the alloy weighing 0.1 g in a 100-ml refractory beaker, add 10 ml of the mixture of hydrochloric and nitric acids (3 : 1), and heat on a water bath to dissolve the sample. Cool the solution, add 3 ml of sulphuric acid, density 1.84 g/cu.cm, and evaporate the liquid to dense fumes of SO_3. Wash carefully the walls of the beaker with water, transfer the contents into a 50-ml volumetric flask, and add water to the mark. Transfer an aliquot into a 50-ml volumetric flask, add 1 ml of ammonium tartrate solution and continue with the analysis as for the construction of the calibration curve. Determine the vanadium content of the aliquot from the calibration curve.

KINETIC DETERMINATION OF VANADIUM

The method is based on the acceleration of oxidation of 1,5-diphenyl-3-aminopyrazoline with potassium bromate by the action of pentavalent vanadium. The catalytic action of vanadium (V) is intensified in the presence of 8-hydroxyquinoline. One product of oxidation is formed. Its absorption maximum is at 530 nm. The sensitivity of the determination is 5×10^{-5} μg of vanadium in 1 ml, the optimum concentration of $KBrO_3$ being 0.05 *M*, (at pH 4.0). The vanadium content is determined from the calibration curve

Reagents

Vanadium salt, standard solution. 1 ml is equivalent to 0.1 μg of vanadium.

Acetate buffer solution, pH 4.0, purified by extraction with 5,7-dibromo-8-quinolinol solution in chloroform.

1,5-Diphenyl-3-aminopyrazoline, 0.1 per cent solution in acetone prepared for the analysis.

Potassium bromate, analytical purity, recrystallized, 0.05 per cent solution.

8-Quinolinol, analytical purity, purified by sublimation; 0.01 *M* solution in acetone.

Water distilled, deionized on a cation exchanger (КУ-2).

Constructing a Calibration Curve

Add 5 ml of the buffer solution to the standard solutions containing 0.02-0.2 μg of vanadium (gradient 0.02 μg) and place the solution in one branch of a mixing vessel. Place 1 ml of 1,5-diphenyl-3-aminopyrazoline into another branch, and 1 ml of potassium bromate and 1 ml of 8-quinolinol and water to 10 ml into the third branch. Place the mixing vessel in a thermostat and keep there for 30 minutes at 25 ± 0.1 °C. Now mix the solution, start a stop-watch and measure the absorption of the solution on a ФЭК-Н-57 absorptiometer in a cell with a light path of 2 cm using an optical filter No. 5. Take the first measurement one minute after mixing the components and continue with the measurements for ten minutes at one minute interval. Construct the calibration curve using the data obtained.

Procedure

Add 5 ml of the buffer to the test solution containing 0.03-0.15 μg of vanadium and proceed further as for the construction of the calibration curve. Determine the vanadium content using the calibration curve.

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Niobium and Tantalum

The compounds in which niobium, Nb, and tantalum, Ta, have the positive valency of 5 and also some compounds of tervalent niobium are important for analytical chemistry.

Niobates (V) have no marked oxidizing properties and are reduced only by energetic reductants (e.g. by zinc metal in acid solutions). This distinguishes niobates from vanadates which are energetic oxidants in acid solutions.

Titrimetric methods for the determination of niobium have been developed. These are based on the reduction of niobium to its tervalent state in acid solutions by zinc, cadmium or aluminium with subsequent titration by a standard solution of an oxidant [1]. The greatest difficulties arise during quantitative reduction of Nb^V in the presence of tantalum and other elements, and titrimetric methods are not therefore widely used in practical analysis.

Compounds of tantalum (V) are not reduced in aqueous solutions.

The properties of niobium and tantalum are very much alike and are similar to those of titanium, zirconium and tungsten. All these elements often occur in natural materials.

The analysis of complicate minerals of tantalum and niobium containing titanium, zirconium and tungsten takes much time and requires high skill on the part of the analyst. The reliability of the results is low. There are no reliable or simple methods for the isolation of small quantities of niobium and tantalum in the analysis of rock, pure metals and alloys, or methods for the determination of niobium and tantalum contained in quantities of about 10^{-5} per cent in titanium, zirconium, tungsten, and other metals. The most reliable results can only be obtained by the extraction and chromatographic methods of separation. The difficulties which arise in the analytical chemistry of niobium and tantalum are due to the tendency of the niobium and tantalum compounds, and also of titanium, zirconium and tungsten, to form colloidal solutions, hydrolysis, and to form polynuclear compounds.

Complex-formation reactions of niobium and tantalum have been studied insufficiently well. Only molar ratios in which the ions of niobium and tantalum react with organic reagents have been established in some cases and very little attention has been given to the study of the formation of heteroligand (mixed) complex compounds. There are no trustworthy values of stability constants for complex compounds of niobium and tantalum or the constants for the reactions of their formation.

As a rule solutions of oxalate, tartrate, fluoride, peroxidic compounds of niobium and tantalum, and also solutions of niobates and tantalates are used in the chemical analysis of these elements. Some methods for preparing these solutions will be described below. Oxalic acid and ammonium oxalate are used to keep niobium and tantalum in solution form. Water-soluble oxalate complex compounds of niobium and tantalum are stable in the presence of excess oxalate ion. The composition of the complex ions probably depends on the conditions under which they are formed. Oxalate-niobates of the alkali metals, $M_3[NbO(C_2O_4)_3][M—Na^+, K^+, NH_4^+]$, have been isolated in the solid state.

Some α-hydroxycarboxylic acids (tartaric, citric, lactic-trihydroxyglutaric) react with the ions of niobium (V) and tantalum (V) to form complex compounds.

Niobates and tantalates are stable in solution in the presence of excess KOH; they tend to polymerization with the formation of various polyanions.

When potassium niobate or potassium tantalate solution is acidified with dilute sulphuric acid, white amorphous niobic or tantalic acids precipitate. They are dissolved in warm concentrated sulphuric acid. After cooling and dilution with water, niobic acid remains in solution while tantalic acid precipitates. But it is impossible to separate niobium and tantalum quantitatively by this method.

When niobic and tantalic acids are calcined, high-melting white pentoxides, Nb_2O_5 and Ta_2O_5, are formed. When heated, Nb_2O_5 turns yellow. The pentoxides Nb_2O_5 and Ta_2O_5 meet many requirements for the weighing form. But as a rule, they are contaminated with oxides of other metals. Therefore, after weighing the pentoxides of niobium and tantalum, their impurities are determined and the corrections introduced. The pentoxides Nb_2O_5 and Ta_2O_5 are also obtained by calcining niobium and tantalum compounds with pyrogallol, tannic acid, etc.

Niobium (V) in concentrated hydrochloric acid is probably present as $H[Nb(OH)_2Cl_4]$ [2]. The absorption maximum of the solutions is at 281 nm [3]. The apparent molar extinction coefficient is $9.0 \times \times 10^3$. The Bouguer-Lambert-Beer law holds for the range of Nb_2O_5 concentrations from 0.9 to 10 μg/ml. Significant quantities of the Fe ions, and also the ions of Mo, U, and Ti, and (to a lesser degree) the ions of Ta interfere with the determination of niobium. Zr, W, rare earths, tartaric acid and small quantities of the sulphate ion almost do not affect the results of the determination.

Differential spectrophotometric determination of large quantity of niobium in its alloys (containing 3-30 per cent of tantalum), and also small quantities of titanium and iron [4] is possible. The accuracy of the differential spectrophotometric determination is not worse than that of the gravimetric method, the error being 0.03 per cent, while the procedure is 4-5 times shorter.

The ion of Nb^V reacts with thiocyanic acid (at high acid concentration) to form a yellow complex compound, $H[NbO(SCN)_4]$ [5]. Alkaloids precipitate specifically coloured substance from aqueous solutions of the complex compound. The compound can be extracted by alcohols, ethers, aldehydes, and ketones. The niobium content is determined by the absorption of the ether extract of the compound. Methods based on the measurement of the absorption of water-acetone solutions of the thiocyanate complex of niobium have been proposed [6, 7].

Tantalum forms a colourless complex $H_2[TaO(SCN)_5]$, extractable by organic solvents and precipitated by alkaloids (in contrast to niobium, the compounds are colourless). The reaction of formation of the thiocyanate complex is employed in various modifications of the method for the detection and photometric determination of niobium in the presence of tantalum and some other elements [8-11]. The thiocyanate method is used for the determination of small quantities of niobium in ores containing titanium, tungsten, molybdenum and chromium.

The solubility of potassium fluotantalate and potassium oxyfluoniobate (K_2TaF_7 and K_2NbOF_5) in hydrofluoric acid is different which makes fractional crystallization of niobium and tantalum (Mariniak method) possible. The theoretical fundamentals of this separation are described in the literature [12]. At the present time, more advanced methods for separation of niobium and tantalum are used.

Selenious acid quantitatively precipitates niobium and tantalum ions from tartaric acid solution containing hydrochloric acid and heated to boiling. Selenious acid is used to separate these elements from titanium and also to separate niobium from zirconium [13, 14].

Hypophosphorous acid precipitates quantitatively tantalum as hypophosphite from oxalic acid solutions. The niobium ion is not precipitated in these conditions and the elements can therefore be separated [15]. Hypophosphorous acid is used for the determination of tantalum in steels and minerals.

The formation of phosphomolybdoniobic heteropoly-acid by the Nb^V ion is used for the photometric determination of niobium.

Hydrogen peroxide reacts with the Nb^V ion in sulphuric and phosphoric acid media to form yellow peracids. The formation of peracids underlies various modifications of the photometric determination of niobium [16-18].

Phenylarsonic acid [19] and its derivatives are valuable reagents for mutual isolation of large and small quantities of niobium and tantalum and their separation from some elements. Phenylarsonic acid precipitates quantitatively the tantalum ion from oxalate solutions at $pH \leqslant 5.8$ (the acidity is adjusted by adding sulphuric acid [20]). The niobium ion is precipitated at pH above 4.8. As a rule, the tantalum ion is precipitated at pH below 3.0 (or from a 5 per cent sulphuric acid solution). Next the niobium ion is precipitated from the filtrate at pH 5.0 (by ammonium acetate and phenylarsonic acid). If the filtrate contains much oxalate, the niobium ion is precipitated with cupferron. If the niobium oxide to tantalum oxide ratio is greater than 2, it is necessary to re-precipitate the tantalum compound, the results being not always satisfactory. Phenylarsonic acid is used to separate tantalum from Fe^{III}, Cr^{III}, Al^{III}, R.E., Ce^{IV}, Be^{II}, U^{VI}, Th^{IV}, Ca, Mg, Sn^{II}, Cu^{II}, Cd, Bi^{III}, Hg^{II}, Zn, Mn, Ni, Co^{II}, As^{III}, Sb^{III}, W^{VI} and Mo^{VI} by precipitation at pH 2-3 from solutions containing excess EDTA. The reagent is used for the gravimetric determination of niobium and tantalum [6].

Cupferron quantitatively precipitates Nb, Ta, and also Ti, Zr, Fe^{III}, V and Sn from a 10 per cent solution of sulphuric acid. The ions of Al^{III}, Cr^{VI}, U^{VI}, Be^{II}, Mn^{II}, Ni^{II}, Co^{II}, Zn^{II}, P, and B remain in solution. The reagent is used [21] for the separation of niobium from tantalum and other elements in tartrate solutions containing ammonium acetate (pH 4.5-5.0) in the presence of EDTA. The niobium ion is precipitated with cupferron using tin as a precipitating agent. Re-precipitation is required in the presence of hundred-fold quantities of tervalent iron and other tervalent metals. To separate niobium from tungsten, the niobium ion is precipitated with cupferron from dilute acid solutions in the presence of oxalic or tartaric acid [22, 23].

N-Benzoyl-N-phenylhydroxylamine [24-26] precipitates niobium from tartaric acid solutions at pH 3.5-6.5. It is used for the separation of niobium from tantalum. Tantalum is precipitated from filtrate at pH below 1.5. Compounds of niobium with N-benzoyl-N-phenylhydroxylamine are extracted with chloroform from tartaric acid solutions at pH 4-6. One portion of chloroform can extract 98-100 per cent of niobium compounds [27]. The tantalum ion remains in the aqueous phase in these conditions.

Benzhydroxamic acid is used to determine niobium photometrically in steels [28].

Niobium and tantalum react with various hydroxyl-containing organic reagents, such as pyrogallol, tannic acid, pyrocatechol, derivatives of 2,3,7-trihydroxy-6-fluorone, 4-(2-pyridylazo)resorcinol, arsenazo I and others.

Pyrogallol precipitates the ions of niobium and tantalum from hydrochloric acid solutions. The ions of Ti and Zr remain in solution [29]. Precipitation does not occur in the presence of tartaric or citric acid. The tantalum ion reacts with pyrogallol in an oxalic acid solution containing a mineral acid to form a yellow-orange compound soluble in water. The niobium ion does not form coloured compounds in these conditions [30]. Conversely, the niobium ion forms an orange compound [30] in a weak alkaline medium, while the tantalum ion does not form coloured compounds. These properties of niobium and tantalum are used in various modifications of photometric determination of niobium and tantalum in their mutual presence [30-47].

Tannic acid precipitates tantalum and then niobium from oxalic acid solutions at various pH [38, 39]. The precipitate of tantalum is yellow, and of niobium, red. Complete precipitation of tantalum is accompanied by partial precipitation of niobium. If fractional precipitation is repeated several times, it is possible to separate tantalum and niobium quantitatively. The titanium ion (over 2 per cent of tantalum concentration) interferes with the separation of niobium and tantalum. Tannic acid is also used for the combined isolation of niobium and tantalum from hydrochloric acid solutions and their separation from many elements. Various masking substances are used for the precipitation of niobium and tantalum. For example, the niobium (V) ion is precipitated quantitatively by tannic acid from a 5 per cent solution of hydrochloric acid in the presence of ascorbic acid. The titanium ion remains in solution [22].

Tannic acid quantitatively precipitates [40] the ions of niobium, tantalum, and also titanium from oxalate-tartrate solutions at pH 4.5 in the presence of EDTA. The tungsten ion (when its content is less than 2 per cent of the sample), and also the ions of many other elements remain in solution. The reagent is used for the determination of total niobium, tantalum and titanium in various minerals. To separate niobium and tantalum from titanium, their fluorides are dissolved in hydrochloric acid solution of tannic acid to prepare a relatively stable clear solution. When boric acid is added, the compounds of niobium and tantalum with tannic acid precipitate, while the titanium ion remains in solution [41]. The method is used for the analysis of various minerals.

The ions of niobium and tantalum react with EDTA and pyrocatechol solutions at pH 2.5 to form red and yellow triple complexes respectively [42]. The niobium ion (or tantalum ion) reacts with EDTA in the molar ratio of 1:1. Conditions can be created under which only niobium or only tantalum will form a coloured compound.

A method has been developed for the determination of niobium and tantalum in a mixture of their oxides with the ratio from 1:5 to 5:1.

To determine niobium in the presence of tantalum, a hydrosulphate melt of the oxides is dissolved in tartaric acid, then EDTA and excess pyrocatechol are added, the pH of the solution is adjusted to 2.5, the solution is heated to boiling and the absorption measured at 470 nm. Niobium is determined from a calibration curve. Tantalum does not form coloured compounds in tartaric acid solutions. To determine tantalum in the presence of niobium, a hydrosulphate melt of their oxides is transferred into a concentrated solution of ammonium oxalate; EDTA, and a great excess of pyrocatechol are added. Finally, crystalline ammonium oxalate is added, the pH of the solution adjusted to 2.5 and the absorption of the yellow solution is measured. Niobium does not form coloured compounds in these conditions.

Pyrocatechol is used also for the extraction separation with subsequent photometric determination of niobium, tantalum and titanium [43]. Complexes of titanium and tantalum with pyrocatechol are extracted with *n*-butanol from oxalate solutions at pH 3, while the niobium ion remains in the aqueous phase. The method can be used for quantitative separation of titanium and tantalum from niobium.

Derivatives of 2,3,7-trihydroxy-6-fluorone substituted at position 9, e.g. dimethylfluorone, react with the ions of niobium, titanium and tantalum. Under certain conditions (controlled acidity of the medium, etc.), the reaction can be sufficiently selective for each element. For example, only the niobium ion reacts with substituted trihydroxyfluorones in solutions of mineral acids (sulphuric, hydrochloric, phosphoric). The tantalum ion almost does not react in these conditions. The reaction, if any, is very slow [44, 45].

Arsenazo I reacts with the tantalum ion in a strongly acid solution (mostly hydrochloric acid) containing tartrates or citrates to form a violet compound soluble in water [46]. The compound is stable at temperatures to 100°C. A titanium complex with arsenazo I is destroyed completely in these conditions and titanium does not therefore interfere with the photometric determination of tantalum. The niobium ion also forms a coloured compound in these conditions and therefore interferes. Fluoride and oxalate ions prevent the formation of coloured compounds. The photometric method can be used to determine tantalum in titanium alloys in quantities from 1 to 15 per cent without preliminary separation.

A peroxidic compound of niobium reacts with methylthymol blue [47, 48], 4-(2-pyridylazo)resorcinol [47, 49], nitrilotriacetic acid, N-hydroxyethylethylenediamine-N,N′,N′-triacetic acid and diethylenetriamine-N,N,N′,N″,N″-pentaacetic acid [50, 51] to form mixed complex compounds containing H_2O_2 and the organic reagent. A heteroligand compound of niobium with 4-(2-pyridylazo)resorcinol and tartrate is used for the determination of niobium in ores and minerals [52].

The peroxidic compound of niobium reacts with nitriloacetic or N-hydroxyethylethylenediamine-N,N′, N′-triacetic acid [50] in the molar ratio of 1:1. Niobium can also be determined complexometrically [50].

Like the peroxidic compound of niobium, the peroxidic compound of tantalum reacts with various complexones to form mixed complex compounds [51].

4-(2-Pyridylazo)resorcinol reacts with the tantalum ion in the presence of oxalates, fluorides, citrates or hydrogen peroxide at pH 4-5.5 to form coloured complex compounds [49, 53-55]. The components react in the molar ratio of 1:1. A tantalum complex with 4-(2-pyridylazo)resorcinol and the oxalate ion is most suitable for the photometric determination of tantalum in alloys on the basis of zirconium, molybdenum, tungsten and uranium. The absorption of the solution does not depend on the concentration of the oxalate ion in a wide range. The absorption maximum is at 535 nm (at 410 nm for the reagent). The molar extinction coefficient is 1.70×10^4. The sensitivity of determination of Ta is 0.2 μg/ml. The method is used for the determination of tantalum in alloys in quantities over 0.1 per cent.

Niobium complexes with hydrogen peroxide, oxalate, tartrate, or fluoride ions [56, 57] react with xylenol orange at pH 2-3 to form coloured compounds. The absorption maximum of the solutions is at 570 nm (at 445 nm, for the reagent). The molar extinction coefficient is about 1.4×10^4. A photometric method for the determination of niobium with xylenol orange in the presence of ammonium oxalate in alloys on the basis of uranium, molybdenum and tungsten has been developed. The sensitivity of the method is 0.1 μg of niobium in 1 ml. The mean quadratic error for the niobium content of 10 per cent in the alloys is ±0.2 per cent.

Lumogallion reacts with the tartrate complex of Nb^V in a 0.5-2 *N* sulphuric acid to form a compound with the absorption maximum at 510 nm [58]. Tantalum does not form coloured compounds with lumogallion, nor does it interfere with the photometric determination of niobium. The effect of the Zr, Fe and Ti ions is removed by adding a small quantity of EDTA. The reagent was used for the determination of niobium in loparite concentrate [59].

8-Quinolinol quantitatively precipitates the niobium ion at pH 6 from a tartaric acid solution [60]. It is used for the separation of niobium from tantalum and other elements.

The fluoride complex of tantalum is extracted with benzene from acid solutions in the presence of methyl violet [61], rhodamine 6G [62], butylrhodamine B [62], brilliant green [63] and other organic compounds capable of giving cations in acid solutions. The extraction is effected from solutions containing HF. The tantalum content is determined photometrically. Small amounts of niobium, and also titanium, zirconium and hafnium do not interfere with the determination.

Methyl violet is used for the extraction-photometric determination of tantalum in ores [61], and also in zirconium, hafnium and niobium metals [64, 65]. The extraction and chromatographic methods of separation of niobium, tantalum and titanium are very important since there are no sufficiently selective reagents for the determination of these elements. The extraction methods ensure more complete separation of niobium and tantalum in a shorter time compared with the methods based on precipitation reactions. But special requirements for glassware (hydrofluoric acid destroys glass and special plastic vessels should therefore be used instead) impose limitations on the use of these methods.

Sulphochlorophenol S [66-68] is a sensitive and selective reagent for niobium. It is used for the photometric determination of niobium in the presence of Zr, Hf, Ti, Fe^{III}, chlorides, sulphates, phosphates, tartrates and citrates. Sulphonitrophenol M offers even greater advantages [69-71].

Ketones [72, 73], amines [74, 75], a mixture of *n*-butylphosphoric acids (solution in di-*n*-butyl ether) [76], tributyl phosphate [77, 78] and diisobutylcarbinol [79, 80] are used for the separation by extraction of niobium and tantalum in the form of chloride and fluoride complexes, and also for the separation of niobium and tantalum. Ketones extract tantalum complexes at much lower concentration of HF than niobium complexes. Extractability of the fluoride complexes of niobium and tantalum by diisopropyl ketone from sulphuric acid, nitric acid, hydrochloric acid, or perchloric acid solutions is different, the extractability of the tantalum complex being much better [72]. This difference makes it possible to separate quantitatively tantalum from niobium.

The niobium ion is well extracted from a 11 *M* solution of HCl by an 8 per cent solution of tribenzylamine in chloroform or methylene chloride. The tantalum ion is extracted insignificantly [75] and niobium can therefore be quickly and quantitatively separated from tantalum. Methyldioctylamine and other aliphatic or aromatic amines with a long chain of carbon atoms, dissolved in organic solvents, can be used instead of tribenzylamine.

Cyclohexanone extracts tantalum, as its fluoride complex, from hydrofluoric and sulphuric acid solutions and does not extract the niobium and titanium ions [37]. The tantalum ion is then re-extracted with ammonium oxalate solution containing boric acid and is determined photometrically with pyrogallol (in an oxalate-sulphuric acid solution). The method can be used to determine hundredth and thousandth fractions of per cent of tantalum in ores, loparite concentrates and other materials. Cyclohexanone is used for the separation of tantalum from zirconium by triple extraction of the fluoride complex of tantalum from a 2-4 *M* solution of sulphuric acid [81]. This is one of the best methods to separate tantalum and zirconium.

Niobium, tantalum and also titanium can be separated quantitatively by various chromatographic techniques [82-88]. A mixture of methyl isobutyl ketone and HF is used as the solvent for the separation of niobium and tantalum by paper chromatography [82].

Niobium and tantalum are detected by 8-quinolinol. The limit of detection is 20 μg of each element. The method has been used for the detection of niobium and tantalum in steels.

The niobium (V) ion, in contrast to the tantalum ion, is reduced on a mercury electrode in solutions of mineral acids, and also in solutions containing organic addends, to give catalytic waves.

The polarographic determination of niobium and titanium in solutions containing both metals (Nb:Ti = 1:20) against a background of pyrophosphoric acid [89], and of niobium in tantalum pentoxide against a background of phosphoric acid [90] is the method which offers advantages.

The determination of niobium and tantalum by isotopic dilution does not require complete separation of these elements. It is only sufficient to separate part of niobium or tantalum as pure metals. The radioactivation method is used for the determination of tantalum in alloys containing niobium, titanium, zirconium, in ores and also for the determination of niobium in alloys.

X-ray spectral method is used for the rapid determination of more than 0.1 per cent of niobium and tantalum in ores, minerals, and alloys.

Emission spectral methods of the determination of niobium and tantalum have practical importance but their sensitivity is low. Emission analysis is used for the determination of niobium and tantalum in industrial raw materials and intermediates [91].

The literature contains reviews of the methods for the determination of tantalum and niobium [92-94].

GRAVIMETRIC DETERMINATION OF NIOBIUM AND TANTALUM IN STEELS WITH PHENYLARSONIC ACID IN THE ABSENCE OF TUNGSTEN

The method is based on the quantitative isolation of niobium and tantalum from a dilute hydrochloric acid solution by hydrolysis with subsequent precipitation with phenylarsonic acid. Pentoxides of the metals are the weighing form.

Reagents

Hydrochloric acid, density 1.18 g/cu.cm, diluted 1 : 1, and 1 per cent solution.
Nitric acid, density 1.4 g/cu.cm.
Phenylarsonic acid, 3 per cent solution.
Ammonium nitrate, 2 per cent solution.
Sulphuric acid, density 1.84 g/cu.cm and diluted 1 : 1.
Hydrofluoric acid, concentrated.
Potassium pyrosulphate, crystalline.

Procedure

Dissolve a sample of steel weighing 1-2 g in 30 ml of concentrated hydrochloric acid and 10 ml of nitric acid in a 300-ml beaker. Evaporate the solution to dryness and calcine the residue slightly. Add 10 ml of concentrated hydrochloric acid to the residue, and heat. Dilute the solution with the precipitate with hot water to 200 ml and heat to 90°C. Now add 40 ml of phenylarsonic acid solution (to precipitate Nb and Ta) and allow the mixture to stand overnight. Separate the precipitate of niobic, tantalic and silicic acids on a blue ribbon filter and wash with a hot 1 per cent hydrochloric acid, and then with ammonium nitrate solution.

Place the washed precipitate on the filter into a platinum dish, char the filter carefully and calcine at 1000°C (use the hood!). To remove the silicic acid, treat the calcined precipitate with 6 ml of concentrated sulphuric acid and a few drops of hydrofluoric acid.

To preclude the loss of tantalum, see to it that sulphuric acid be in excess during the removal of silicic acid. Evaporate the dish contents to remove sulphuric acid fumes. Calcine the residue slightly in a muffle furnace at 800°C and fuse with potassium pyrosulphate. Leach the melt with water and transfer into a 300-ml beaker. Add hot water to 200 ml, add 8 ml of concentrated hydrochloric acid and heat for an hour at 90°C. The greater part of niobium and tantalum is isolated by hydrolysis (white flocks). To ensure complete precipitation, add 40 ml of phenylarsonic acid solution, heat the mixture for another 30 minutes and allow to stand overnight. Separate the precipitate on a white ribbon filter, wash with a hot 1 per cent hydrochloric acid solution, then two times with water, and calcine in a porcelain crucible at 1000°C (use the hood!). Weigh Nb_2O_5 and Ta_2O_5.

Notes. 1. If tungsten is present, it is precipitated together with niobium and tantalum.

2. If titanium is present in the steel, it is contained in the precipitate of the pentoxides of niobium and tantalum as titanium oxide. The weighed precipitate is fused with potassium pyrosulphate, leached with 20 ml of sulphuric acid (1 : 4), the solution is transferred into a 50-100-ml volumetric flask, and titanium is determined photometrically. The found number of grams of titanium dioxide is subtracted from the mass of the pentoxides of niobium and tantalum

GRAVIMETRIC DETERMINATION OF NIOBIUM WITH CUPFERRON IN THE PRESENCE OF TUNGSTEN

The method is based on the precipitation of the niobium ion with cupferron in a weak acid medium in the presence of oxalic (tartaric) acid which masks the tungsten ion. When niobium is determined in objects containing tungsten, iron, titanium, vanadium and other elements precipitated by cupferron, it is necessary first to isolate niobium with tannic acid in the presence of ascorbic acid (considerable quantities of the tungsten ion are co-precipitated), and niobium should then be separated from tungsten in oxalic acid solution. Satisfactory results are obtained with the determination of 12-15 per cent of Nb in alloys containing 36-70 per cent of tungsten.

Reagents

Tannic acid, 1 per cent solution prepared for the test.
Ascorbic acid.
Hydrochloric acid, density 1.19 g/cu.cm, diluted 1 : 2 and 1 : 1, and 4 per cent solution.
Nitric acid, density 1.4 g/cu.cm.
Sulphuric acid, diluted 1 : 1.
Hydrofluoric acid, 40 per cent solution.
Ammonium chloride, crystalline.
Potassium pyrosulphate, crystalline.
Oxalic acid 4 per cent solution.
Cupferron, 3 per cent solution.
Washing solution. 1 litre contains 20 ml of 3 per cent cupferron and 1 ml of hydrochloric acid, density 1.19 g/cu.cm.

Procedure

Dissolve a sample of steel weighing 0.5 g in 100 ml of hydrochloric acid (1:1) in a 300-ml beaker. Add 5 ml of nitric acid and boil to evaporate almost to dryness. Add 30 ml of hydrochloric acid (1:2) to the residue and boil to remove nitrogen oxides (if the volume of the solution diminishes by 1/3, add 10-20 ml of water). Dilute the solution with water to 180-190 ml, disregarding the black precipitate which may appear in some cases, add 1-2 g of ammonium chloride, 0.1-0.2 g of ascorbic acid and heat to boiling. Add, drop by drop, 10 ml of tannic acid solution, to the hot solution with constant stirring and heat almost to the boiling point for 2-3 hours to ensure complete coagulation of the precipitate.

Add a small quantity of filter paper pulp, cool the solution (it can be allowed to stand overnight), separate the precipitate on a white ribbon filter, 7-9 cm in diameter, and wash 6-8 times with a cold 4 per cent hydrochloric acid. Place the filter with the precipitate in a platinum crucible, char, and calcine the precipitate in a muffle furnace at 500-600°C until all organic matter is burnt out. Wet the residue with water, add 2-3 ml of sulphuric acid, 2-3 ml of hydrofluoric acid, and place the crucible on a sand bath. Heat to dissolve the precipitate and to fumes of sulphuric acid. Allow the fumes to evolve for ten minutes, then cool the crucible, add 1-2 ml of water to the residue and evaporate again until two or three drops remain in the crucible (not to dryness). Cool the crucible, add 10 ml of hydrochloric acid (1:1) and heat to dissolve the solid. Transfer the solution into a 100-ml beaker (rinse the crucible several times with cold water), and add 0.05-0.1 g of ascorbic acid and water to make 80-90 ml. Heat the contents to boiling and re-precipitate niobium with tannic acid following the above instruction.

Incinerate the precipitate in a platinum dish, fuse the residue with 1-2 g of potassium pyrosulphate, add 10-20 ml of oxalic acid and heat to dissolve the solid. Transfer the solution into a 250-300 ml beaker, rinse the dish walls with cold water, add water to 150-200 ml, add 5 drops of hydrochloric acid, density 1.19 g/cu.cm, and precipitate niobium with 20-25 ml of cupferron solution adding it drop by drop with stirring. Add a small quantity of filter paper pulp and mix thoroughly to ensure complete coagulation of the precipitate. Separate the precipitate on a white ribbon filter, 7-9 cm in diameter and wash it 6-8 times with the washing solution. Place the filter with the precipitate into a platinum dish, incinerate and calcine the residue at 500-600°C. Fuse the residue with 1-2 g of potassium pyrosulphate over a low flame of the burner. Add 20-30 ml of oxalic acid, heat the mixture, add 20-30 ml of water and continue heating to complete dissolution of the melt. Transfer the solution into a beaker, add 5 drops of hydrochloric acid, density 1.19 g/cu.cm, and re-precipitate as instructed above.

Place the filter with the precipitate in a weighed platinum or porcelain crucible, incinerate and calcine the residue for 15-20 minutes in a muffle furnace at 1000°C, cool in a desiccator and weigh Nb_2O_5. The conversion factor for Nb is 0.6990.

SEPARATION OF TANTALUM AND NIOBIUM WITH N-BENZOYL-N-PHENYLHYDROXYLAMINE

Niobium (V) is precipitated from a tartaric acid solution at pH 3.5-6.5 with N-benzoyl-N-phenylhydroxylamine as $(C_{13}H_{10}NO_2)_3 \cdot NbO$, then tantalum is precipitated from the filtrate (after separation of the niobium precipitate) by acidifying the solution by sulphuric acid (to pH 1). Satisfactory separation is attained with the Nb_2O_5 to Ta_2O_5 ratio from 1:16 to 100:1. Niobium can be separated from mixtures containing hundred-fold quantities of Ta_2O_5 (with respect to Nb_2O_5) by re-precipitation of the niobium compound with N-benzoyl-N-phenylhydroxylamine. When the ions of Fe, U, Th, Cr, Al, lanthanides, Cu, Cd, Bi, Pb, Hg, Zn, Mn, Ni, Co, As, Sn, Sb, Ba, Sr, Ca, Mg, and P are present, the precipitation is carried out after adding 2-3-fold excess (with respect to the theoretically required amount of EDTA).

Reagents

N-Benzoyl-N-phenylhydroxylamine, 10 per cent solution in ethyl alcohol.
Tartaric acid, crystalline.
Ammonium acetate, 20 per cent solution.
Sulphuric acid, density 1.84 g/cu.cm.
Washing solution. Dissolve 0.1 g of the reagent in 100 ml of boiling water.

Procedure

Add ammonium acetate solution to a solution containing 5 per cent of tartaric acid to adjust the pH to 3.5-6.5 (if Ta is contained in large quantities, adjust the pH to 6), add water to 350 ml, heat to boiling and precipitate niobium by adding the reagent solution, drop after drop. Separate the precipitate by filtration, wash with diluted solution of the reagent, calcine, and weigh as Nb_2O_5. Acidify the filtrate with sulphuric acid to adjust the pH to 1.0, heat for 45 minutes on a boiling water bath, separate the precipitate on a paper filter, wash with diluted solution of the reagent, calcine to Ta_2O_5, and weigh.

TITRIMETRIC DETERMINATION OF NIOBIUM IN ITS CARBIDE

Nb^V is reduced to Nb^{III} in hydrochloric and sulphuric acid media (15-20 ml of concentrated sulphuric acid and 30-40 ml of concentrated hydrochloric acid are added per each 100 ml of solution) by cadmium or aluminium metals with additional reduction in a cadmium reductor. The olive-green solution of the reduced niobium is added to the solution of ferriammonium sulphate. Divalent iron which is formed in equivalent quantity, is titrated with $K_2Cr_2O_7$ solution in the presence of phenylanthranilic acid. The method can be used for the determination of niobium in its carbide.

Reagents

Nitric acid, density 1.4 g/cu.cm.
Hydrochloric acid, density 1.19 g/cu.cm.
Sulphuric acid, density 1.84 g/cu.cm and diluted 1 : 20.
Hydrofluoric acid, 40 per cent solution.
Potassium bichromate, 0.1 *N* solution standardized against niobium compound.
Phenylanthranilic acid, 0.1 per cent solution.
Ferriammonium sulphate, 0.1 *N* solution.
Cadmium metal.

Procedure

Dissolve a sample of carbide weighing 0.1 g in a platinum dish in a mixture of 15-20 ml of nitric and 5-10 ml of hydrofluoric acids. When the solid is all dissolved, add 10 ml of sulphuric acid and evaporate to fumes of H_2SO_4. Transfer the residue into an Erlenmeyer flask, rinse the dish with 15-20 ml of water. Add 15-20 ml of sulphuric acid, 30-40 ml of hydrochloric acid and water to 100 ml. Add, in small portions, 2-2.5 g of cadmium metal and heat slightly to dissolve the metal (the solution turns green). Cool the solution and pass it through a cadmium reductor with the charge bed not lower than 30 cm. Wash the reductor preliminarily 2-3 times with sulphuric acid (1:20). Pass the solution slowly, drop after drop, into a receptacle containing 20-25 ml of ferriammonium sulphate solution. Pass CO_2 through the receptacle. Wash the reductor 2-3 times with 25 ml of sulphuric acid (1:20) and 2-3 times with water saturated with CO_2. Titrate the formed ferrous ion with potassium bichromate in the presence of several drops of phenylanthranilic acid.

PHOTOMETRIC DETERMINATION OF NIOBIUM IN STEELS CONTAINING TUNGSTEN (THIOCYANATE METHOD)

The method is based on the hydrolytic isolation of niobium in the presence of tannic acid and stannous chloride which is added to reduce ferric ion and to stabilize thiocyanic acid in hydrochloric acid solutions. Stannous chloride does not affect the reaction of formation of the thiocyanate compound of niobium. The precipitate (containing also co-precipitated tungsten) is calcined and the residue fused with potassium pyrosulphate. The melt is dissolved in tartaric acid and niobium is determined in tartaric acid solution by the thiocyanate photometric method in a water-acetone medium. The oxalate and fluoride ions, and also large quantities of the sulphate ion interfere with the determination. The thiocyanate method can be used for the determination of niobium in steels and other materials.

Reagents

Hydrochloric acid, density 1.19 g/cu.cm and diluted 1 : 9.
Nitric acid, density, 1.4 g/cu.cm.
Sulphuric acid, diluted 1 : 1.
Aluminium shavings.
Tannic acid, 0.5 and 10 per cent solutions in sulphuric acid, diluted 1 : 100.
Stannous chloride, 20 per cent solution in hydrochloric acid, density 1.19 g/cu.cm.
Potassium pyrosulphate, crystalline.
Potassium thiocyanate, 30 per cent solution.
Acetone, pure.
Tartaric acid, 20 per cent solution.
Niobium compound, standard solution. 1 ml is equivalent to 0.1 mg of niobium. Fuse 0.05 g of spectrally pure Nb_2O_5 with 2 g of $K_2S_2O_7$, dissolve the melt in 30 ml of 20 per cent tartaric acid and dilute with water to 500 ml in a volumetric flask.

Preparing a Standard Scale

Place 0.1, 0.2, 0.3, 0.4 and 0.5 ml of standard solution of a pentavalent niobium compound in five colorimetric tubes. Add 5 ml of hydrochloric acid, density 1.19 g/cu.cm, 1 ml of stannous chloride solution, 2 ml of water and 5 ml of acetone into each tube. Mix the solutions and cool to 15 °C. Add 5 ml of potassium thiocyanate into each solution.

Procedure

Place a sample of steel weighing 0.5 g in a 100-ml beaker and dissolve in 30 ml of hydrochloric acid, density 1.19 g/cu.cm and 10 ml of nitric acid. Add 10 ml of sulphuric acid and evaporate to white fumes. Cool the residue, add carefully water, and evaporate to 2-3 ml. Transfer quantitatively the beaker content into a 250-ml beaker with 100 ml of hot hydrochloric acid (1:9). Heat the solution to boiling, add 0.1-0.5 g of aluminium chips, and continue boiling to complete dissolution (the ions of Fe^{III} and Ti^{IV} are reduced and the solution turns violet, the colour being characteristic of tervalent titanium ion).

Add 10 ml of a 10 per cent solution of tannic acid and 2 ml of stannous chloride solution, boil for ten minutes and allow to stand for ten hours. Separate the precipitate containing niobium on a filter and wash with a cold 0.5 per cent solution of tannic acid. Incinerate the filter with the precipitate in a porcelain (quartz) crucible and calcine at 900°C. Fuse the residue with 2 g of $K_2S_2O_7$, leach the melt with 50 ml of tartaric acid with heating, transfer the solution into a 250-ml volumetric flask and add water to the mark. Mix the solution.

Add 5 ml of hydrochloric acid, density 1.19 g/cu.cm, 1 ml of stannous chloride solution, 2 ml of water and 5 ml of acetone to the aliquot (1-2 ml) of the solution and mix. Cool to 15°C and add 5 ml of potassium thiocyanate. Allow the solution to stand for five minutes and compare its colour with that of the solutions in the standard series to find the niobium content.

PHOTOMETRIC DETERMINATION OF SMALL QUANTITIES OF NIOBIUM IN ORES CONTAINING TITANIUM, TUNGSTEN, MOLYBDENUM AND CHROMIUM BY THE THIOCYANATE METHOD

To isolate niobium and to separate it from chromium, tungsten, molybdenum, tin, titanium, zirconium, and iron, it is co-precipitated with $MnO_2 \cdot nH_2O$. Niobium is transferred into solution by fusing with sodium hydrosulphate and leaching the melt with tartaric acid. The determination of niobium in solution ends photometrically by the thiocyanate method in an acetone medium.

Reagents

Sodium hydroxide, crystalline, and 2 per cent solution.
Sulphuric acid, diluted 2 : 250 and 1 : 2.
Hydrogen peroxide, 30 per cent solution.
Manganese sulphate, 1 *N* solution.
Ammonium persulphate, or potassium persulphate, crystalline.
Sodium hydrosulphate, crystalline.
Tartaric acid, 15 per cent solution.

Procedure

Fuse a sample of ore weighing 0.1-2 g with 5-10 g of sodium hydroxide in a nickel or an iron crucible. Leach the melt with water, boil the solution with the precipitate for 2-3 minutes, separate the precipitate on a filter and wash 3-5 times with sodium hydroxide solution. The filtrate contains the ions of Cr, W, Mo, Sn, Si, Al and the precipitate contains Nb, Ta, Ti and Fe. Unfold the filter with the precipitate on the edge of the beaker and wash the precipitate into it with a small quantity of water. Wash the filter several times with sulphuric acid (2:250) containing a few drops of hydrogen peroxide, and discard. Add 6-8 ml of sulphuric acid (1:2) to the solution in the beaker and boil to destroy hydrogen peroxide. Add 1 ml of manganese sulphate solution to the cooled solution, add 2 g of potassium (or ammonium) persulphate, and water to make 200 ml. Heat the solution on an electric hotplate, boil for 7-10 minutes, allow to stand for a while, and separate the precipitate on a large dense filter. Wash the filter with sulphuric acid (2:250). The filtrate contains the ions of Mo, Ti, Cr, Zr and Fe. Niobium is separated quantitatively with manganese dioxide.

To separate quantitatively the interfering elements, re-precipitate the manganese dioxide. To that end, wash the precipitate from the filter into the same beaker, wash the filter with sulphuric acid (2:250) containing a few drops of hydrogen peroxide, and then with water to remove the hydrogen peroxide completely. The solution and the precipitate, whose volume is 200 ml, should contain 6-8 ml of sulphuric acid (1:2). Boil the solution to destroy hydrogen peroxide, cool, and repeat the precipitation of manganese dioxide as instructed above. Separate the precipitate on the same filter and wash with dilute sulphuric acid.

Fuse the precipitate of manganese dioxide and co-precipitated niobium with 1.5-3 g of $NaHSO_4$, dissolve the melt in tartaric acid and dilute the solution to 25-50 ml. The final concentration of tartaric acid should be 7.5 per cent. Determine niobium photometrically using thiocyanate (see the previous procedure).

PHOTOMETRIC DETERMINATION OF NIOBIUM IN ALLOYS WITH ZIRCONIUM AND TITANIUM USING 4-(2-PYRIDYLAZO)RESORCINOL

4-(2-Pyridylazo)resorcinol reacts with the Nb^V ion in the presence of hydrogen peroxide at pH 5 to form a red soluble complex compound (the molar ratio 1:1). The absorption maximum of the solution is at 590 nm. The molar extinction coefficient is 3.20×10^4 at 540 nm. The Bouguer-Lambert-Beer law holds for the niobium concentrations in the range from 2 to 60 μg in 50 ml. If EDTA is used as a masking agent, the method can be used for the determination of niobium in the presence of the titanium ion (equal to or less than 5 mg) and Zr (equal to or less than 10 mg). But EDTA decreases the absorption of the coloured solution of niobium. Therefore, if niobium is determined in the presence of the Zr and Ti ions, the corresponding quantities of EDTA should be added to the solutions in the standard series.

Reagents

Niobium compound, standard solution. 1 ml is equivalent to 5 μg of niobium. Fuse spectrally pure Nb_2O_5 with potassium pyrosulphate, and dissolve the melt in a volumetric flask.
Sulphuric acid, density 1.84 g/cu.cm and 1 *N* solution.
Potassium sulphate, crystalline.
Hydrogen peroxide, 30 per cent solution.
Potassium pyrosulphate, 2 per cent solution and crystals.
EDTA, 0.025 *M* solution.
Acetate buffer solution, pH 5.
4-(2-Pyridylazo)resorcinol, 0.1 per cent solution.

Constructing a Calibration Curve

Place 1, 2, 3, 4 and 5 ml of the niobium standard solution into five 50-volumetric flasks, add 5 ml of potassium pyrosulphate solution, 0.5 ml of EDTA, and 0.25 ml of hydrogen peroxide into each flask. Add the acetate buffer solution to make 45 ml. Add 0.5 ml of 4-(2-pyridylazo)resorcinol solution and dilute with the acetate buffer solution to the mark. Allow the solutions to stand for 30 minutes and measure their absorption on an absorptiometer with an optical filter transmitting maximum at 536 nm against a blank solution. Construct the calibration curve using the data obtained.

Procedure

Place a sample of an alloy weighing 0.1-0.2 g into a 100-ml refractory glass beaker, add 1-2 g of potassium sulphate and 1-2 ml of sulphuric acid, density 1.84 g/cu.cm, and heat to dissolve the solid. Evaporate almost to dryness, add 0.5-1.0 ml of hydrogen peroxide, and 20 ml of 1 N sulphuric acid to the residue, transfer the solution into a 50- or a 100-ml volumetric flask, and add water to the mark. Transfer an aliquot (containing $\leqslant 10$ mg of Zr or $\leqslant 5$ mg of Ti and 5-10 μg of Nb) into a 50-ml volumetric flask and proceed as for the preparation of the standard solutions. Measure the absorption of the solution and determine the niobium content from the calibration curve.

PHOTOMETRIC DETERMINATION OF TANTALUM WITH PYROGALLOL

Pyrogallol reacts with Ta^{V} in a medium of 4 N HCl and 0.0175 M $H_2C_2O_4$ to form a soluble complex compound. The molar extinction coefficient of the complex solution is 4.8×10^3 at 325 nm. The Bouguer-Lambert-Beer law holds for tantalum concentrations to 40 μg/ml. Mo^{VI}, W^{VI}, U^{VI}, and Sn^{IV} interfere with the determination. The effect of Nb, Ti, Zr, Cr, V^{V}, Bi and Cu is insignificant and can be compensated by adding these ions into the blank solution. The fluoride ion and platinum interfere with the determination of tantalum. Do not use platinum dishes to fuse the sample.

Reagents

Tantalum pentoxide, standard solution. 1 ml is equivalent to 0.2 mg of tantalum. Fuse 0.2000 g of spectrally pure tantalum pentoxide with 10 g of $K_2S_2O_7$ in a quartz crucible, leach the melt with 50 ml of a solution containing 50 g of ammonium oxalate in 1 litre, and heat on a water bath. Cool the solution, transfer it into a 1 litre volumetric flask and dilute with water to the mark.

Pyrogallol. Dissolve 200 g of pyrogallol in 100 ml of hydrochloric acid, density 1.19 g/cu.cm, add 10 ml of 2 M stannous chloride solution and dilute with water to 1 litre. The solution can be used within a month.

Diluting solution. 1 litre contains 12.5 g of ammonium oxalate and 50 g of potassium pyrosulphate. The solution can stand for two weeks.

Hydrochloric acid, 8 N solution.

Constructing a Calibration Curve

Place 1, 2, 3, 4 and 5 ml of the tantalum pentoxide standard solution into five 50-ml volumetric flasks, add 25 ml of hydrochloric acid, 10 ml of pyrogallol solution into each flask, and add the diluting solution to the mark. Measure the absorption of each solution on the СФ-4 spectrophotometer, at 325 nm and construct the calibration curve using the data obtained.

Procedure

Add to the solution all the reagents as for the construction of the calibration curve and measure the absorption of the resultant solution. Determine the tantalum content from the calibration curve.

PHOTOMETRIC DETERMINATION OF TANTALUM IN TITANIUM TETRACHLORIDE WITH PYROGALLOL

Tantalum is separated from the greater part of titanium by precipitation with tannic acid after preliminary reduction of titanium to its tervalent state. After dissolution of the precipitate, tantalum is extracted by cyclohexanone and separated from the co-precipitated titanium. The tantalum determination is concluded photometrically using pyrogallol.

Reagents

Tannic acid, 10 per cent solution in hydrochloric acid 1 : 9.
Cadmium, metal.
Tin, metal.
Potassium pyrosulphate, crystalline.
Mixture of acids, 0.4 *M* HF and 2 *M* H_2SO_4.
Cyclohexanone.
Ammonium sulphate, crystalline.
Hydrofluoric acid, 0.1 *N* solution.
Ammonium oxalate, 4 per cent solution containing boric acid.
Hydrochloric acid, diluted 1 : 3.

Procedure

Add 2-5 ml of titanium tetrachloride solution to 80 ml of hydrochloric acid and heat until the solution becomes clear. Add tin (a collecting agent), 3 g of cadmium metal and heat until a persistent violet colour develops. Add 10 ml of tannic acid solution, boil, and allow to stand for an hour. Separate the precipitate, incinerate the filter, and fuse the precipitate with potassium pyrosulphate. Dissolve the melt in 25 ml of the acid mixture with heating. Transfer the solution into a separating funnel, add 8 ml of cyclohexanone, 2 g of ammonium sulphate and shake the mixture energetically for a minute. After settling, transfer the lower layer into another separating funnel and extract tantalum again with 8 ml of cyclohexanone. Repeat the extraction procedure. Wash the joint extracts with hydrofluoric acid solution and shake with a small quantity of cyclohexanone which should be added to the main bulk of the extract. Repeat the re-extraction three times, each time taking 7 ml of 4 per cent ammonium oxalate solution containing boric acid. Dilute the re-extracts with water to 25 ml.

To determine tantalum by the pyrogallol method, evaporate an aliquot of the solution with sulphuric acid in the presence of hydrogen peroxide to destroy organic matter. Dissolve the vitreous residue in a 4 per cent ammonium oxalate solution, transfer the solution into a 50-ml volumetric flask, add 25 ml of an 8 *N* hydrochloric acid solution, 10 ml of pyrogallol, and ammonium oxalate to the mark. Measure the absorption of the resultant solution and determine the tantalum content from the calibration curve (see the previous procedure).

EXTRACTION-PHOTOMETRIC DETERMINATION OF TANTALUM IN COMMERCIAL NIOBIUM USING METHYL VIOLET

The method consists in measuring the absorption of a benzene extract of methyl violet fluotantalate. The optimum concentration of HF is 0.25-0.5 *N*. The ions of Zr, Hf and Nb are not extracted.

from the solution. The colour of the extract is stabilized by acetone during extraction of the associate with toluene, the molar extinction coefficient of the associate being 7.5×10^4. The method can be used for the determination of 10-50 per cent of Ta_2O_5 in tantalite and tantalmicrolite concentrates [53].

Reagents

Tantalum salt, standard solution. 1 ml is equivalent to 50 μg of tantalum.
Hydrofluoric acid, 40 per cent solution.
Methyl violet, 0.2 per cent solution.
Benzene.
Washing solution, 0.2-0.3 *N* hydrofluoric acid containing 0.2 g of methyl violet in 100 ml.

Constructing a Calibration Curve

Place 40-45 ml of water and 1.5 ml of hydrofluoric acid into 50 ml paraffin-coated volumetric flasks. Now add 0.5, 1.0, 1.5 and 2.0 ml of the standard solution of tantalum salt into the flasks respectively and dilute with water to the mark. Transfer 5 ml of each solution into separating funnels, add 4 ml of water, 10 ml of benzene and 1 ml of methyl violet solution. Shake carefully 3-4 times. After the phases have separated withdraw the aqueous phase, wash the benzene layer with 5 ml of the washing solution, place in tubes and centrifuge for 1-2 minutes. Transfer the clear solution into a cell (a light path, 1 cm) and measure the absorption at 570 nm using a green-orange optical filter. Construct the calibration curve using the data obtained.

Procedure

Dissolve 10 mg of niobium metal in hydrofluoric acid adding nitric acid dropwise and heating the vessel on a water bath. Evaporate the solution carefully on a hotplate to dryness, treat the residue with 2-3 ml of hydrofluoric acid and evaporate to dryness again without overheating the residue. Dissolve the residue in 1.5 ml of hydrofluoric acid and 5-6 ml of water. Transfer the solution into a 50-ml paraffin-coated volumetric flask and add water to the mark. Transfer an aliquot (5 ml) into a separating funnel and proceed as for the construction of the calibration curve. Determine the tantalum content from the calibration curve.

PHOTOMETRIC DETERMINATION OF TANTALUM IN ORES WITH DIMETHYLFLUORONE

Dimethylfluorone reacts with the pentavalent tantalum ion to give a red precipitate. If the tantalum concentration is low (less than 50 μg in 10 ml) the precipitate remains in the colloidal state, especially so if gelatin is present. In a weak acid medium, in the presence of oxalic acid, the corresponding reaction of niobium is sharply inhibited. The titanium ion is masked by hydrogen peroxide. The absorption of the coloured solution obeys the Bouguer-Lambert-Beer law in the range of Ta concentrations from 5 to 50 μg in 10 ml. The following quantities of the accompanying elements (in μg in

10 ml of solution) do not interfere with the determination in these conditions: Nb 400, Ti 100, Zr 500, W 150, Mo 100, Sb^{V} 500, Sb^{III} 3, Sn^{IV} 5, Ge 3, Fe 1000. If the tantalum contents of the ore is low, the metal should be first separated from the main bulk of the interfering elements.

Reagents

Hydrofluoric acid, concentrated.
Sulphuric acid, diluted 1 : 1 and 6 per cent solution.
Potassium pyrosulphate, crystalline.
Hydrogen peroxide, 3 per cent solution.
Potassium metahydrosulphite, crystalline.
Tannic acid, 2 per cent solution.
Gelatine, 1 per cent solution.
Washing solution, 0.6 per cent sulphuric acid containing 0.2 per cent of tannic acid.
Acid mixture. Dilute 16 ml of 40 per cent hydrofluoric acid with water to 200 ml and add slowly, with cooling, 100 ml of sulphuric acid, density 1.84 g/cu.cm.
Isobutyl alcohol.
Acetone.
Ammonium sulphate, saturated solution.
Washing solution for extracts. Place 5 ml of a mixture of hydrofluoric and sulphuric acid, 5 ml of a saturated ammonium sulphate solution, 5 ml of acetone, and 5 ml of isobutanol in a separating funnel and shake. Separate the lower layer and use for washing.
Boric acid, 5 per cent solution.
Oxalic acid, 4 per cent solution.
Potassium hydroxide, 1 *N* solution.
α-Dinitrophenol, indicator solution.
Hydrochloric acid, 2 *N* solution.
Diluting solution, 1 per cent of potassium pyrosulphate, 2 per cent of boric acid, 0.2 per cent of oxalic acid and 0.1 *N* of hydrochloric acid.
Dimethylfluorone. Grind 50 mg of the reagent with 0.5 ml of 6 *N* hydrochloric acid, add 50 ml of 96 per cent alcohol, and heat the mixture to 60 °C. Filter the solution into a 100-ml volumetric flask, wash the filter with alcohol and add the alcohol to the mark.
Tantalum standard solution. Dissolve 20 mg of tantalum sheet in a mixture of 5 ml of 40 per cent hydrofluoric and 2 ml of nitric acid, density 1.42 g/cu.cm. Evaporate the solution to dryness; add 4 g of boric acid and 5 ml of water. Evaporate to dryness and fuse with 4 g of potassium pyrosulphate in a muffle furnace at 700 °C to prepare a clear melt. Dissolve the melt in 100 ml of a 4 per cent solution of oxalic acid with heating, cool, and dilute with the same acid in a 200-ml volumetric flask to the mark. 1 ml is equivalent to 0.1 mg of Ta.
Evaporate 2.5 ml of the solution to dryness on a water bath, calcine the dry residue over a burner and treat with 2 ml of hydrofluoric acid containing 20 ml of 5 per cent boric acid. Evaporate the solution to dryness, transfer the residue into a muffle furnace and fuse with 0.5 g of potassium pyrosulphate. Dissolve the melt with heating in 2.5 ml of a 4 per cent solution of oxalic acid, transfer with water into a 50-ml volumetric flask and neutralize with 1 *N* potassium hydroxide solution to α-dinitrophenol until a pale yellow colour develops. Add 2.5 ml of 2 *N* hydrochloric acid and water to the mark. 1 ml is equivalent to 5 μg of Ta.

Constructing a Calibration Curve

Place a standard solution containing 5, 10, 15, 20 and 25 μg of tantalum into colorimetric tubes, add 0.4 ml of dimethylfluorone, and mix. Heat on a boiling water bath for 3 minutes and keep there until the water in the bath cools (30 minutes). Allow the solution to stand for 90 minutes at room temperature until it develops colour. Add 0.5 ml of hydrogen peroxide, shake the solution, allow to stand for 15 minutes and measure the absorption of the solution on a photometer or an absorptiometer at 530 nm. Construct the calibration curve using the data obtained.

Procedure

Place a sample of ore weighing 1-3 g (depending on the tantalum concentration) in a platinum dish and treat with 15 ml of concentrated hydrofluoric acid with heating on a water bath. Add 5 ml of sulphuric acid (1:1) and transfer the dish on a sand bath. When the fumes of sulphuric acid stop evolving, fuse the residue with 5-7 g of potassium pyrosulphate in a muffle furnace. Transfer the clear melt into a beaker with 50 ml of 6 per cent sulphuric acid, adding it into the dish and heating on a hotplate. Add 5 ml of 3 per cent hydrogen peroxide and heat.

Separate the insoluble residue on a filter, wash with 50 ml of water (the total volume of the filtrate and the washings should be 100 ml, the concentrations of sulphuric acid being 3 per cent). Heat the solution on a hotplate and destroy hydrogen peroxide, by carefully adding potassium metahydrosulphite until the yellow colour of the peroxidic compound of titanium vanishes. If titanium is absent, add 2 g of potassium metahydrosulphite.

If the ore is rich in titanium, dissolve the melt in 100 ml of 6 per cent sulphuric acid.

Heat the solution to boiling, add 20 ml of a hot tannic acid solution, 2 ml of a gelatin solution and allow the mixture to stand for at least six hours. Separate the precipitate on a double paper filter and wash with the washing solution. Place the filter with the precipitate in a platinum dish, incinerate and calcine in a muffle furnace. Dissolve the residue in 2 ml of hydrofluoric acid and evaporate the solution to dryness on a water bath. Dissolve the dry fluorides in 2 ml of the acid mixture, transfer the solution into a 50-ml separating funnel, add 5 ml of isobutanol, 5 ml of acetone (first rinse the dish with this acetone) and 2 ml of a saturated solution of ammonium sulphate. Shake the mixture for a minute and allow to stand for five minutes to separate the phases. Leave the upper layer in the separating funnel, transfer the lower layer into another separating funnel, add 2.5 ml of acetone and 2.5 ml of isobutanol, and repeat the extraction. Decant the upper layer into the first separating funnel. Rinse the second funnel with 1 ml of the solution for washing the extract, transfer the liquid into the first funnel containing the extracts, and shake for 0.5 minute. Discard the lower layer, wash the upper layer with 1 ml of the washing solution, shake the washed extract with 5 ml of boric acid and transfer the funnel contents into a platinum dish. Rinse the funnel with three 5-ml portions of boric acid and add the washings to the solution in the platinum dish.

Place the platinum dish on a water bath, evaporate the solution to dryness, avoiding splashing. Place the dish with the residue on a sand bath, remove part of sulphuric acid, and fuse the residue with 0.5 g of potassium pyrosulphate at 600-700°C for 30-40 minutes. Dissolve the clear melt in 2.5 ml of oxalic acid solution with heating on a hotplate. Add water in small portions since oxalic acid quickly crystallizes. Transfer the solution from the dish into a 50-ml volumetric flask, wash the dish several times with water, transfer the washings to the flask, seeing to it that the total volume of the liquid is about 10 ml below the mark. Add two drops of α-dinitrophenol solution and potassium hydroxide solution from a burette drop by drop, until the solution turns slightly yellow. Add 2.5 ml of hydrochloric acid and water to the mark.

Transfer an aliquot (2-10 ml) into a test tube, add the diluting solution to 10 ml, 1 ml of gelatin solution, and mix. Further proceed as for the construction of the calibration curve.

Determine the tantalum content from the calibration curve.

PHOTOMETRIC DETERMINATION OF NIOBIUM WITH SULPHOCHLOROPHENOL S

The method is based on the formation of a complex compound of pentavalent niobium with sulphochlorophenol S. The solution of the compound is blue and has the absorption maximum at 650 nm. The colour develops on heating in acid solution for five minutes and persists for a day. The Bouguer-Lambert-Beer law holds for the niobium concentrations in the range of 5-40 μg in 50 ml. The interfering effect of Zr and Hf is removed by adding complexing agents (EDTA, KF, and others). The effect of ferric ion is removed by ascorbic acid. Titanium (with the Nb:Ti ratio of 1:100), about equal quantities of Ta, chlorides, sulphates, phosphates, tartrates, and citrates do not interfere with the determination. Oxalates interfere.

Reagents

Niobium (V), *standard solution*. 1 ml is equivalent to 5 μg of niobium.
EDTA, 5 per cent solution.
Ascorbic acid, crystalline.
Hydroxylamine hydrochloride, 10 per cent solution.
Sulphochlorophenol S, 0.1 per cent solution.
Hydrochloric acid, density 1.19 g/cu.cm.

Constructing a Calibration Curve

Place 1, 2, 3, 4 and 5 ml of standard solution of Nb^V into 25-ml volumetric flasks, add as much hydrochloric acid as required to adjust the concentration to 1 *N*, add 1 ml of the reagent solution into each flask and finally add water to the mark. Heat the solution on a water bath at 60-80 °C for 20-30 minutes. Cool the solutions and measure their absorption on an absorptiometer or spectrophotometer СФ-4 at 650 nm using cells with the light path of 50 mm. Construct the calibration curve using the data obtained.

Procedure

Place a solution containing not more than 25 μg of Nb^V in a 25-ml volumetric flask and add 1 ml of hydroxylamine solution. If Fe^{3+} is present, add 20-50 mg of ascorbic acid and heat the solution slightly. Add 1 ml of EDTA and hydrochloric acid to adjust the acid concentration to 1 *N*. Proceed with the analysis as for the construction of the calibration curve. Determine the niobium content from the calibration curve.

EXTRACTION-PHOTOMETRIC DETERMINATION OF NIOBIUM IN ALLOYED STEELS USING BENZHYDROXAMIC ACID

Niobium reacts with benzhydroxamic acid in a hydrochloric acid solution to form a coloured complex compound extractable with chloroform. The molar extinction coefficient of the solution is 7.7×10^3. The Bouguer-Lambert-Beer law holds for the niobium concentrations in the range from 2 to 40 μg. Microgram quantities of niobium can be determined in the presence of 1000-fold quantities of Zn, Fe, Co, Ni, Mn, 500-fold quantities of Cr, Mo, Zr, a 100-fold quantities of W, a 10-fold quantity of Ta and a 2-fold quantity of Ti.

Reagents

Niobium, standard solution. 1 ml is equivalent to 20 μg of niobium. Dissolve spectrally pure Nb_2O_5 in a mixture of 0.5 g of $(NH_4)_2SO_4$ and 1 ml of H_2SO_4 with heating. Cool the solution, transfer it into a 100-ml volumetric flask and add hydrochloric acid, density 1.19 g/cu.cm to the mark.
Benzhydroxamic acid, 1.5 per cent solution in hydrochloric acid, density 1.19 g/cu.cm.
Hydrochloric acid, density 1.19 g/cu.cm.
Chloroform.
Ammonium sulphate, crystalline.
Sulphuric acid, density 1.84 g/cu.cm.

Constructing a Calibration Curve

Place 0.25, 0.50, 0.75, 1.00, 1.25, 1.50, 1.75 and 2 ml of the niobium solution into separating funnels, add 5 ml of benzhydroxamic acid into each funnel and hydrochloric acid to make 10 ml. Extract with 10 ml of chloroform for three minutes. Measure the absorption of the solutions at 380 nm against a blank solution. Construct the calibration curve using the data obtained.

Procedure

Dissolve a sample of alloy weighing 0.2 g in a mixture of 0.5 g of ammonium sulphate and 1 ml of sulphuric acid with heating. Cool the solution and transfer into a 100-ml volumetric flask. Add hydrochloric acid to the mark. Add 5 ml of the reagent to an aliquot of the solution containing less than 40 μg of niobium, then add hydrochloric acid to 10 ml and continue as for the construction of the calibration curve. Determine the niobium content from the calibration curve.

EXTRACTION-PHOTOMETRIC DETERMINATION OF NIOBIUM IN ROCK WITH NITROPHENYLFLUORONE

The method is based on the formation of a coloured *o*-nitrophenylfluorone complex of niobium extractable with chloroform from hydrochloric acid water-ethanol medium. This is preceded by precipitation of niobium with $Fe(OH)_3$ to separate the interfering tungsten, and by extraction of Nb with a chloroform solution of tribenzylamine from an 11 *N* solution of hydrochloric acid.

Reagents

Niobium, standard solution. 1 ml is equivalent to 5 μg of Nb.
Hydrofluoric acid, 40 per cent solution.
Sulphuric acid, density 1.84 g/cu.cm.
Ferric chloride; Fe concentration 40 mg/ml.
Sodium hydroxide, 20 and 1 per cent solutions.
Hydrochloric acid, density 1.19 g/cu.cm, diluted 1 : 4 and 12.3 *N* solution prepared by saturating at 0 °C 11 *N* solution with HCl gas.
Hydrogen peroxide.
Tribenzylamine, 8 per cent solution chloroform
Thioglycolic acid, 8 per cent solution.
Sodium fluoride, 1 per cent solution.
o-Nitrophenylfluorone, 1×10^{-3} *M* alcoholic solution (0.03 *N* HCl).
Aluminium chloride; Al concentration 50 mg/ml.
Chloroform.

Constructing a Calibration Curve

Place 0.4, 0.8, 0.12, 0.16 and 2 ml of the niobium standard solution into separate 35-50 ml separating funnels, add 5 ml of the reagent solution and 7.5 ml of chloroform into each funnel. Shake for two minutes, separate the extracts, pass them through a dry paper filter, and measure the absorption at 530 nm against a blank solution. Construct the calibration curve using the data obtained.

Procedure

Decompose a sample weighing 0.1-1 g in a platinum dish with sulphuric and hydrofluoric acid, and evaporate excess acid to obtain a moist residue. Wet the residue with 3 ml of concentrated sulphuric or hydrochloric acid and dissolve with heating in 200 ml of water. If the sample is poor of iron, add 1 ml of $FeCl_3$ (or another quantity, to make the total iron content of 40-50 mg). Heat to boiling, precipitate with a 20 per cent solution of NaOH and boil for 2-3 minutes. Separate the hydroxides on a filter (not dense, paper filter), wash 4-5 times with a 1 per cent NaOH solution, wash the precipitate into a 100-ml beaker with small (total of 10 ml) portions of hot hydrochloric acid (1:4) containing H_2O_2, and add an equal volume of concentrated hydrochloric acid. Boil to decompose H_2O_2. Evaporate the solution to 10 ml. Cool, add 40 ml of 12.3 *N* hydrochloric acid, extract niobium with 20 ml of tribenzylamine solution in chloroform, shaking for five minutes. Wash the extracts two times with 10-ml portions of 11 *N* HCl for 1 minute.

Add 7 ml of 1 *N* hydrochloric acid and 2 ml of thioglycolic acid to the washed extract, shake for 2 minutes, then add 2 ml of NaF and 5 ml of *o*-nitrophenylfluorone. Shake for two minutes and discard the organic phase. Add 0.5 ml of $AlCl_3$ to the aqueous phase to destroy the Nb^V complex and further proceed as for the construction of the calibration curve.

Determine the niobium content from the calibration curve.

PHOTOMETRIC DETERMINATION OF TANTALUM IN STEELS WITH 4-(2-PYRIDYLAZO)RESORCINOL

The method is based on the interaction of Ta with 4-(2-pyridylazo)-resorcinol at pH 5.4 in the presence of the citrate ion with the formation of a red complex absorbing maximum at 540 nm, the molar extinction coefficient being 2.5×10^4. If EDTA is present, up to 1 (and more) mg of Fe, Ni, Cr, 0.5 mg of W, 0.2 mg of Nb, Ti, 0.05 mg of Zr and 0.02 mg of Cu do not interfere with the determination. Uranium interferes. The determination ends comparimetrically.

Reagents

Potassium pyrosulphate, crystalline.
Sulphuric acid, concentrated.
Sodium citrate, 20 and 3.2 per cent solutions.
Sodium hydroxide, 0.1 *M* solution.
Sodium hydrosulphate, 0.1 *M* solution.
EDTA, 0.05 *M* solution.
Acetate buffer solution, pH 5.4.
4-(2-Pyridylazo)resorcinol, 0.1 per cent solution.
Steel, standard sample, containing tantalum in quantities close to those anticipated in the sample.

Procedure

For the determination of tantalum in steel, fuse a sample weighing 100 mg and a standard sample in quartz beakers with 10 g of potassium pyrosulphate and a few millilitres of sulphuric acid to prepare a uniform melt. Dissolve the melt in 40 ml of a hot 20 per cent solution of sodium citrate (pH 5) and 20 ml of water with boiling for 5-6 minutes. Cool the solutions, adjust their pH to 2.8 using NaOH or $NaHSO_4$ solution, boil for five minutes, and add water to 200 ml in a volumetric flask. Add to 3 ml of 3.2 per cent solution of sodium citrate, 2 ml of 0.05 *M* EDTA solution, 40 ml of acetate buffer, 2 ml of the reagent solution to aliquots of the solutions of the test and standard samples (80 μg of Ta) and add water to 50 ml. Allow the solutions to stand for 50-60 minutes, and measure their absorption at 540 nm on a model ФЭК-Н-57 absorptiometer (light path of 2 cm).

Calculate the tantalum content by the formula

$$x = cD_1/D_2$$

where D_1 and D_2 are the absorptions of the sample and of the standard, respectively; and c is the tantalum content of the standard sample.

PHOTOMETRIC DETERMINATION OF NIOBIUM IN ORES AND MINERALS WITH 4-(2-PYRIDYLAZO)RESORCINOL

Niobium in 1 *M* solutions of hydrochloric acid and in the presence of tartrate, reacts with 4-(2-pyridylazo)resorcinol (PAR) to form heteroligand compounds with the Nb to PAR ratio of 1:2 and with two absorption maxima, at 405 and 540 nm. When the absorption of the solutions is measured against PAR, the first maximum, due to the own absorption of PAR is masked and the absorption is therefore measured at 540 nm. Tartrate, rather than tartaric acid should be used as the third component, because in the latter case the colour of the complex develops only with heating. The solutions obey the Bouguer-Lambert-Beer law in the range of Nb concentrations from 2 to 50 μg in 25 ml. A 400-fold quantity of phosphorus, a 10-fold quantity of Ta, 1000-fold quantities of Ti, Fe, Al, Mo and a 200-fold quantity of Zr do not interfere with the determination of 10 μg of niobium. The variation coefficient is 2-3 per cent. The method can be used for the determination of 0.01-0.4 per cent of niobium in ores and standards of the minerals columbite and loparite.

Reagents

Niobium, standard solution. 1 ml is equivalent to 10 μg of niobium.
Ammonium tartrate, 4 and 25 per cent solutions.
Hydrochloric acid, 4 *M* solution.
EDTA, 5 per cent solution.
4-(2-Pyridylazo)resorcinol (PAR), 0.1 per cent solution.
Hydrofluoric acid, 40 per cent solution.
Sulphuric acid, density 1.84 g/cu.cm.
Sodium pyrosulphate, crystalline.

Constructing a Calibration Curve

Place 1, 2, 3, 4 and 5 ml of niobium standard solution into five 25-ml volumetric flasks, add 4 per cent solution of ammonium tartrate to 5 ml in each flask, then add 6 ml of hydrochloric acid, 0.5-3 ml of EDTA solution (depending on the Zr, Fe and other ions contents of the sample) and 1 ml of PAR solution. Add water to the mark, allow the solutions to stand for an hour and measure their absorption at 540 nm (the light path being 3-5 cm) against a blank solution. Construct the calibration curve using the data obtained.

Procedure

Treat a sample of ore weighing 0.3-0.5 g and containing 0.5-1 mg of niobium, with hydrofluoric and sulphuric acid in a platinum dish, evaporate the solution to white dense fumes of sulphuric acid (to 1.5 m residual volume), add 1 g of sodium pyrosulphate and fuse in a muffle furnace at 700°C to obtain a clear melt. Cool and dissolve in 10 ml of a hot 25 per cent solution of ammonium tartrate, transfer quantitatively into a 100-ml volumetric flask and add water to the mark. Transfer an aliquot (5-10 ml) into a 25-ml volumetric flask and proceed as for the construction of the calibration curve. Determine the niobium content from the calibration curve.

PHOTOMETRIC DETERMINATION OF NIOBIUM IN MINERAL RAW MATERIALS WITH SULPHONITROPHENOL M

Sulphonitrophenol M, a bis-azo-derivative of chromotropic acid, reacts with niobium in 0.5-6 *M* solutions of hydrochloric acid to form a blue compound with the absorption maximum at 620 nm (the reagent's absorption maximum is at 540 nm) and the molar extinction coefficient of 5.3×10^4. The optimum concentration of HCl is 3 *N*, the absorption being maximum and constant in 30-40 minutes at room temperature and in 10 minutes when heated to 60-80°C. 100 mg of EDTA and tartaric acid, 100-200-fold quantities of Ti, Mo, a 4000-fold quantity of uranium, and a 8000-fold quantity of W do not interfere with the determination. When the analysis is carried out in a 2 *N* hydrochloric acid in the presence of EDTA, a 200-fold quantity of Zr does not interfere. If the reaction is carried out in sulphuric acid, the sensitivity slightly decreases, but the selectivity to Ti, Zr, Mo, and Ta increases. A 1000-fold quantity of Al, 500-fold quantities of Ca, Fe, Ti and Zr, a 25-fold quantity of Ta and a 10-fold quantity of Mo do not interfere with the determination of 0.5 per cent of niobium. The method can be used for the determination of 0.005-20 per cent of Nb_2O_5 in loparite, hatchettolite, and in pegmatites containing tantalum, niobium and tin. The analysis of 15-20 samples takes two working days. The coefficient of variation is $\leqslant 9.8$ per cent.

Reagents

Niobium, standard solution. 1 ml contains 20 μg of Nb_2O_5. Prepare the solution as follows. Fuse 10 mg of Nb_2O_5 in a quartz crucible at 800-1000 °C with 0.5 g of $K_2S_2O_7$, cool the melt, add a few drops of sulphuric acid, density 1.84 g/cu.cm and fuse again. Repeat the acid treatment and fusion 3-4 times. Cool the solution and dissolve in sulphuric acid (1 : 3), cool again, transfer into a 100-ml volumetric flask and add sulphuric acid (1 : 3) to the mark. On the day of the analysis, dilute the solution with sulphuric acid (1 : 3); 1 ml of the solution is equivalent to 100 μg of Nb_2O_5.

Sulphuric acid, density 1.84 g/cu.cm and diluted 1 : 3.

Sulphonitrophenol M, 0.1 per cent solution.

Ammonium sulphate, 10 per cent solution.

EDTA, 10 per cent solution.

Potassium pyrosulphate, crystalline.

Hydrofluoric acid, 40 per cent solution.

Constructing a Calibration Curve

Place 0.5, 1.0, 1.5, 2.0, 2.5, 3.0, 3.5 and 4 ml of the Nb_2O_5 standard solution into separate 50-ml volumetric flasks, add sulphuric acid (1 : 3) to 6 ml in each flask, add 20 ml of water, 1.5 ml of sulphonitrophenol M, 2 ml of ammonium sulphate solution, add water almost to the mark and heat for 20-30 minutes at 60-70 °C. Cool and add 1 ml of EDTA solution, and water to the mark. Allow the solutions to stand for 15 minutes and measure their absorption at 656 nm (the light path, 1 cm) on a model ФЭК-Н-57 absorptiometer using optical filter No. 8. Construct the calibration curve using the data obtained.

Procedure

Place a sample weighing 0.01-1 g (containing 20-0.005 per cent of Nb_2O_5 respectively) into a quartz dish containing a small quantity of potassium pyrosulphate and cover with another portion of the pyrosulphate. Heat, first on a hotplate covered with asbestos, then transfer into a muffle furnace and fuse at 800-1000°C. The amount of potassium pyrosulphate required for fusion depends on the size of the sample but should not exceed 5 g in any case. Cool the melt, add a few drops of sulphuric acid, density 1.84 g/cu.cm and fuse again. Repeat the operation 3-4 times. Cool the melt, transfer it quantitatively in a platinum dish, add HF and H_2SO_4 density 1.84 g/cu.cm, and heat to dense fumes of sulphuric acid. Dissolve the residue in sulphuric acid (1:3) with heating, cool, transfer into a 50-ml volumetric flask, and dilute with sulphuric acid (1:3) to the mark. Transfer an aliquot (2-5 ml) into a 50-ml volumetric flask and proceed as for the construction of the calibration curve. Determine the niobium content of the aliquot from the calibration curve.

EXTRACTION-PHOTOMETRIC DETERMINATION OF TANTALUM WITH BRILLIANT GREEN

Tantalum reacts with brilliant green in the presence of the fluoride ion (fluorotantalate) to form an ionic association extractable with benzene. The component ratio in the association is 1:1, the optimum pH is 0-0.25 (2.2-3.5 N H_2SO_4), the absorption maximum of the benzene extract is at 640 nm, the molar extinction coefficient is 1.2×10^5. Ti, Nb, W and V do not interfere with the determination of tantalum. B and NO_3^- interfere. The chloride ion should preferably be absent. The solutions obey the Bouguer-Lambert Law provided the Ta_2O_5 content in 5 ml of the extract is equal to or less than 25 μg.

Reagents

Tantalum salt, standard solution. 1 ml is equivalent to 10 μg of Ta_2O_5. Solution in 4 per cent ammonium oxalate and 2.7 N sulphuric acid.
Ammonium oxalate, 4 per cent solution in 2.7 N sulphuric acid.
Hydrofluoric acid, 5 per cent solution.
Sulphuric acid, 2.7 N solution.
Brilliant green, 0.5 per cent solution.
Benzene.

Constructing a Calibration Curve

Place 0.5, 1.0, 1.5, 2.0 and 2.5 ml of the standard solution of tantalum into five separate quartz test tubes, add ammonium oxalate to 3 ml in each test tube, add 1 ml of hydrofluoric acid, 1 ml of brilliant green solution and 5 ml of benzene. Close the test tubes with polyethylene stoppers and shake for 30 seconds. Separate the organic phase, centrifuge it, and measure the absorption at 640 nm (the light path, 0.5 cm) against a blank solution. Construct the calibration curve using the data obtained.

Procedure

Place an aliquot of a solution containing 10-20 μg of tantalum pentoxide in a quartz test tube and proceed as for the construction of the calibration curve. Determine the tantalum content from the calibration curve.

POLAROGRAPHIC DETERMINATION OF NIOBIUM IN TANTALUM PENTOXIDE

The polarographic determination of Nb is carried out in a 20 *M* solution of phosphoric acid using an A.C. polarograph. The peak potential of Nb^V is —0.85 V with reference to bottom mercury.

Reagents

Niobium, standard solution, 1 ml is equivalent to 0.1 mg of niobium. Prepare by dissolving niobium metal in HF.
Phosphoric acid, concentrated.
Hydrofluoric acid, 40 per cent solution.
Nitric acid, 1.4 g/cu.cm.

Procedure

Dissolve a sample weighing 0.1-0.5 g in HF containing nitric acid in a platinum dish with heating and evaporate the solution to the minimum volume. Add 9 ml of phosphoric acid and heat for 40 minutes to remove completely HF, HNO_3 and H_2O. Add 1 ml of water to the cooled residue and examine the solution on a polarograph at —0.5 to —1.1 V. Determine the niobium content from the calibration curve constructed for the Nb concentrations in the range from 0.1 to 0.5 mg/ml.

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Molybdenum

Molybdenum, Mo, in its compounds has the positive valency of 2, 3, 4, 5 and 6. The compounds of hexa-, penta-, and tervalent molybdenum are more important.

The standard electrode potentials in an aqueous medium at 25°C are as follows (with reference to the standard hydrogen electrode potential):

$$\mathrm{Mo} \rightleftharpoons \mathrm{Mo^{3+}} + 3e^- \qquad -0.200\ \mathrm{V}$$

$$\mathrm{Mo} + 4\mathrm{H_2O} \rightleftharpoons \mathrm{MoO_4^{2-}} + 8\mathrm{H^+} + 6e^- \qquad +0.154\ \mathrm{V}$$

$$\mathrm{MoO_2} + 2\mathrm{H_2O} \rightleftharpoons \mathrm{MoO_4^{2-}} + 4\mathrm{H^+} + 2e^- \qquad +0.606\ \mathrm{V}$$

$$[\mathrm{Mo(CN)_8}]^{4-} \rightleftharpoons [\mathrm{Mo(CN)_8}]^{3-} + e^- \qquad +0.73\ \mathrm{V}$$

The compounds of hexavalent molybdenum are most stable in solution. In hydrochloric acid solution (4 *N* HCl), the compounds of pentavalent molybdenum are quite stable in the air. The oxidability in air of the pentavalent molybdenum compounds increases with decreasing acidity of solution. The molybdenum (V) ion readily oxidizes in alkaline solutions.

The molybdenum ion (IV) is stabilized in the form of a very stable cyanide complex $[\mathrm{Mo(CN)_8}]^{4-}$.

The compounds of tervalent molybdenum are quite stable to atmospheric oxygen in strongly acid solution (9 *N* HCl) because brick-red complex ions $[\mathrm{MoCl_6}]^{3-}$, $[\mathrm{MoCl_5}]^{2-}$ and others are formed. A green hydrated ion $\mathrm{Mo^{3+}}$ exists in a medium of 2.5-4 *N* HCl in equilibrium with the halide complex ion of $\mathrm{Mo^{III}}$ (the equilibrium between these ions sets slowly). The $\mathrm{Mo^{3+}}$ is very easily oxidizable. The ions of molybdenum (III) are much easier oxidized in sulphuric acid than in hydrochloric acid medium. Only green ions of molybdenum (III) exist in sulphuric acid medium. They react with the ions $\mathrm{C_2O_4^{2-}}$ or $\mathrm{SCN^-}$ to form complex ions, e.g. yellow complex $[\mathrm{Mo(SCN)_6}]^{3-}$.

The compounds of divalent molybdenum are unstable in solutions.

When the ions of $\mathrm{Mo^{VI}}$ are reduced in a weak hydrochloric acid solution (less than 2 *N*), bright blue colloidal solutions or precipitates are formed. Molybdenum is partly in its pentavalent state and partly in hexavalent state, in these compounds. The ion of hexavalent molybdenum is reduced to green $[\mathrm{MoOCl_5}]^{2-}$ in a medium of relatively concentrated hydrochloric acid (e.g. 8 *N* HCl). When reduced in dilute hydrochloric acid (2 *N*), yellow-brown to intensely brown ions of pentavalent molybdenum are formed. In an alkaline medium, the reduction of the ion of Mo^{VI} is very slow and incomplete. Silver and mercury metals reduce Mo^{VI} ions to the ions of Mo^{V} and Mo^{III} in strong acid solutions (depending on the concentration of HCl, see Fig. 5). Zinc reduces the ions of Mo^{VI} to the ions of Mo^{III} in a dilute acid medium. Solutions of salts of chromium (II) reduce the ions of hexavalent molybdenum in hydrochloric and

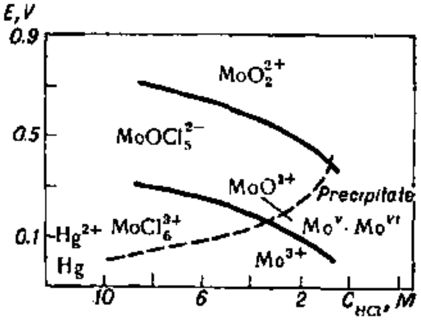


Fig. 5. Dependence of the potentials of the systems Mo^{VI}/Mo^{V}, Mo^{V}/Mo^{III} and Hg^{II}/Hg on the concentration of hydrochloric acid

sulphuric acids first to pentavalent and then to tervalent molybdenum [1]. This reaction underlies the potentiometric methods of titration of the molybdenum ions with a tungsten indicator electrode. Under special conditions, the tervalent molybdenum ion reduces the hexavalent molybdenum ion to the ion of pentavalent molybdenum:

$$2Mo^{VI} + Mo^{III} \rightleftharpoons 3Mo^{V}$$

The solutions of molybdenum (III) salts are used for the potentiometer titration of hexavalent molybdenum ions in the presence of ions of other elements [2, 3].

In weak acid solutions, reducing agents (Zn, Sn^{II}, Fe^{II}, and others) reduce molybdates to molybdenum blue [4] which contains Mo^{V} and Mo^{VI}. Alkaline solutions (pH ⩾ 7) contain the ions MoO_4^{2-}, and weak acid solutions contain the ion $Mo_7O_{24}^{6-}$. Other polymerized anions of hexavalent molybdenum can also be formed:

$$MoO_4^{2-} + H^+ \rightleftharpoons HMoO_4^- \qquad pK \approx 4.08$$

$$7MoO_4^{2-} + 8H^+ \rightleftharpoons Mo_7O_{24}^{6-} + 4H_2O \qquad pK \approx 57.7$$

$$Mo_7O_{24}^{6-} + H^+ \rightleftharpoons HMo_7O_{24}^{5-} \qquad pK \approx 4.33$$

$$HMo_7O_{24}^{5-} + H^+ \rightleftharpoons H_2Mo_7O_{24}^{4-} \qquad pK \approx 3.7$$

When alkalized, the polymolybdate ion converts into MoO_4^{2-}. Hydrolysis of the ion MoO_4^{2-} is described in the literature [5].

Acid solutions can also contain various polymerized cations of hexavalent molybdenum.

Molybdic acid in the form H_2MoO_4 is colourless. The crystal hydrate $H_2MoO_4 \cdot H_2O$ is yellow. Molybdic acid precipitates on acidification of concentrated molybdate solutions. When the acid is further added, the precipitate dissolves (unlike tungstic acid). Molybdic and paramolybdic acids are easily soluble in alkalis.

Molybdenum (VI) forms complex compounds with chloride, fluoride, oxalate, tartrate, and citrate ions. Many complex compounds of molybdenum with ortho-diphenols and organic substances containing sulph-hydryl groups are known.

Molybdates of most metals ($PbMoO_4$, Hg_2MoO_4, Ag_2MoO_4, $CaMoO_4$ and others) are sparingly soluble in water. Molybdates of the alkali metals are only soluble. Silver nitrate or silver acetate precipitates the ion MoO_4^{2-} from dilute acetic acid solution in the form of white precipitates ($pL_{Ag_2MoO_4} = 10.5$). The precipitate does not form in the presence of excess hydrogen peroxide.

Benzidine reacts with the ions MoO_4^{2-}, WO_4^{2-} and SO_4^{2-} to form sparingly soluble white crystalline salts.

Hydrogen sulphide partly reduces the ion MoO_4^{2-} in acid solution to colour the solution blue and to precipitate a brown substance, $MoS_2 + MoS_3$.

Ammonium sulphide reacts with MoO_4^{2-} to form a red-brown solution of a sulphosalt ($MoSO_4^{2-}$). When acidified to pH 6-7, the solution precipitates a black sulphide MoS_3. The precipitate is sparingly soluble in dilute hydrochloric acid, and soluble in ammonium sulphide solution.

Hydrogen peroxide colours the solid ammonium molybdate, wetted preliminarily with dilute ammonia solution, pink or red. The colour is due to the formation of peroxymolybdate [6]. Ti^{IV} and V^{V} interfere.

KSCN reacts with the ion of Mo^{V} in hydrochloric acid solution to form a carmine-red compound extractable with ether and other organic solvents [7, 8]. If ammonia is added to the solution, the colour vanishes, and re-appears on acidification. Molybdenum is detected and determined in various materials photometrically as thiocyanate complexes. Large quantities of molybdenum are determined by the differential method [9].

Molybdic acid reacts under certain conditions with phosphoric, arsenic, vanadic, silicic, germanic, and other acids to form heteropolyacids. Ammonium phosphate precipitates yellow ammonium phosphomolybdate from nitric acid solutions. The precipitate is sparingly soluble in nitric acid, and is soluble in alkalis with decomposition.

Phosphomolybdate is easily reduced in an acid solution, for example with $SnCl_2$, to form bright molybdic blue.

Germanic, phosphoric, arsenic and silicic acids are detected and determined photometrically in the form of molybdic heteropolyacids.

When reduced, molybdate reacts with 2,2-dipyridyl to form bright red solutions [10], which is utilized for the highly sensitive detection of molybdenum. The sensitivity is impaired by the ion WO_4^{2-} because tungstic blue is formed. Fe^{II}, Fe^{III}, SeO_3^{2-}, TeO_3^{2-} and TeO_4^{2-} interfere.

α-Benzoinoxime precipitates Mo^{VI}, and also W^{VI} and V^{V} from strong acid solutions. The precipitate formed by molybdenum is insoluble in a 20 per cent solution of sulphuric acid [8, 11, 12]. The reagent is used for the detection and quantitative separation of molybdenum from many elements. If the addition of a 2 per cent solution of the reagent does not form turbidity or cloudiness, it indicates that the ions MoO_4^{2-} (and WO_4^{2-}) are absent.

EDTA reacts with the ions of Mo^{VI} and Mo^{V} to form compounds [13-15] with the molar ratio of the components 1:2. The compound of EDTA with Mo^{VI} strongly dissociates in solution and can only exist in a weak acid medium. The compound with Mo^{V} is more stable. It can exist in both acid and weak alkaline media (pH 0.3-10) and is used for complexometric determination of molybdenum [14, 16, 17].

o-Diphenols (pyrocatechol, Tiron, stilbazo), derivatives of 2,3,7-trihydroxy-6-fluorone and others react with Mo^{VI} ions in neutral and weak acid solutions to form coloured compounds (sometimes, sparingly soluble). Tiron reacts with the molybdate ions to form two yellow compounds: one compound with the molar ratio of the components 1:1 at pH 3.5-4.5 (the absorption maximum at 322 nm) and the other compound with the molar ratio of 1:2 at pH 6-8 (the absorption maximum at 390 nm). The molar extinction coefficient of the second compound, in the presence of a 500-fold quantity of the reagent, is 6.5×10^3. The colour of the solution develops instantaneously and persists for a long period [18-20]. The reagent reacts with Mo^{V} to form coloured soluble compounds with the absorption maximum at 332 nm and the molar extinction coefficient 4.2×10^3 [20]. The reagent is used for the photometric determination of molybdenum [8, 21, 22] as well as for its detection.

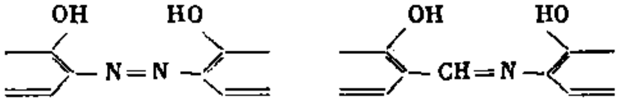
Stilbazo reacts with the ions of Mo^{VI} and Mo^{V} at pH 2 to form bright violet compounds. The reagent is used for the photometric determination of molybdenum [23].

8-Quinolinol reacts with Mo^{V} to form two compounds [24]. At room temperature and pH about 3, it forms a greenish yellow precipitate of $H_2Mo_4O_{11} \cdot (C_9H_7ON)_7 \cdot 11H_2O$. When the solution is boiled (at pH 3.8-4.4), a black fine precipitate, $Mo_2O_3(C_9H_6ON)_4 \cdot H_2O$ falls out. The reagent is used for the photometric determination of molybdenum in a medium of 50 per cent acetone. Solutions of $Mo_2O_3(C_9H_6ON)_4 \cdot H_2O$ in chloroform have two absorption maxima, at 397.5 nm ($\varepsilon = 1.65 \times 10^4$) and at 550 nm ($\varepsilon = 9.5 \times 10^3$). A solution of $H_2Mo_4O_{11} \cdot (C_9H_7ON)_7 \cdot 11H_2O$ has one absorption maximum, at 395 nm ($\varepsilon = 1.82 \times 10^4$).

The reagent is used for the extraction-photometric determination of molybdenum in steels, alloys of zirconium, beryllium, and in oxides of thorium and uranium [25].

8-Quinolinol-5-sulphonic acid reacts with Mo^V at pH 3-4.5 to form a soluble and very stable red compound with the absorption maximum at 540 nm (molar extinction coefficient, 5.2×10^3). The reagent is suitable for the photometric determination of molybdenum in the presence of tungsten and other elements [26].

Azo- and azomethine compounds containing the atom groupings



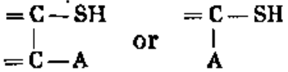
react with the molybdenum (VI) ion to give specifically coloured compounds. These reagents can be used to detect and determine photometrically molybdenum [27]. For example, lumogallion 2,2′,4′-trihydroxy-5-chloro(1-azo-1′)-benzene-3-sulphonic acid reacts with the molybdate ion in the molar ratio of 1:1 to form a brightly coloured stable chelate compound [28]. The molar extinction coefficient of solutions of the compound at 510 nm is $(1.13 \pm 0.19) \times 10^4$. The limit of molybdenum detection is 0.05 μg/ml [28]. The reagent is used for the photometric determination of traces of molybdenum. Ca, Mg, Co, Zn, Cd, Ni, Mn^{II}, Cr^{III} and Ce^{IV} do not interfere with the determination.

The reaction of molybdenum with magnezon IREA in a medium of isoamyl acetate is very selective [29].

Phenylhydrazine, $C_6H_5NHNH_2$, reacts with molybdate in acetic acid solutions to form a bright red compound, probably due to oxidation of the reagent to diazonium salt which reacts with excess phenylhydrazine to form an azo compound [30]. The reagent is used for the detection and photometric determination of molybdenum. Strong oxidants or strong reductants should be absent from the solution. The ion WO_4^{2-} interferes with the determination if its concentration exceeds 1 per cent.

Sulphur-containing organic substances of various classes react with Mo^{VI} and Mo^V to form coloured compounds.

Sulphur-containing organic compounds having the following groupings



$$\begin{array}{l}=C-SH\\ \;\;|\\ =C-A\end{array} \quad \text{or} \quad \begin{array}{c}=C-SH\\ |\\ A\end{array}$$

where A is COOH, SH or OH

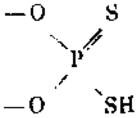
are, as a rule, valuable analytical reagents for Mo^{VI} and Mo^V. These groups can be found in compounds of the aromatic or aliphatic series [31].

Thioglycolic acid, $HSCH_2COOH$, reacts with Mo^{VI} (at pH 3-6) and with Mo^V (at pH about 2, in hydrochloric acid) in the molar ratio of 1:2 to form specifically coloured compounds [32-34]. At pH less than 3, the reagent reduces Mo^{VI} to Mo^V and forms the coloured compound $Mo_2O_3(SCH_2COOH)_4$. Solutions of the reagent compound with Mo^{VI} at pH 4 absorb maximum at 365 nm (molar extinction coefficient, 4.4×10^3); the compound of Mo^V at pH 0.6 and 1.5 has the absorption maximum at 352 nm (molar extinction coefficient, 2.4×10^3).

Thiomalic (mercaptosuccinic) acid, $HOOC{-}CH_2{-}CH(SH){-}COOH$, 2,3-dimercaptopropionic acid $CH_2(SH)CH(SH)COOH$ [35-37], and also sodium 2,3-dimercaptopropanesulphonate, $CH_2(SH)CH(SH)CH_2SO_3Na$, [38] and sodium *p*-(mercaptoacetamide) benzenesulphonate, $HSCH_2CONH{-}C_6H_4{-}SO_3Na$, [39] react with the molybdenum ions (VI and V) like thioglycolic acid. All these reagents are used for the detection and photometric determination of molybdenum in the presence of other elements. *p*-Phenetidide-1-mercaptopropionic acid is used for the determination of molybdenum in steels against the background of other elements [40]. Anion complexes of pentavalent and hexavalent molybdenum with thioglycolic and thiomalic acids are extracted in the form of diphenylguanidinium salts by some organic solvents, best of all by a mixture of isoamyl alcohol and chloroform. One complex anion of Mo^V with thioglycolic acid or thiomalic acid attaches one cation of diphenylguanidinium (two cations in the case with Mo^{VI}) [41]. The extraction-photometric method for the determination of molybdenum in the form of diphenylguanidinium salt of the Mo^V compound with thioglycolic acid has been developed.

Toluene-3,4-dithiol reacts with Mo^{VI} (and also W^{VI}) to form sparingly soluble specifically coloured compounds which are however soluble in some organic solvents. The reagent is used for the detection and photometric determination of molybdenum [42, 43].

Dialkyl- and diaryldithiophosphoric acids containing the atom grouping



react in an acid medium with the Mo^{VI} ion to form intensely coloured compounds of unknown composition [32]. The reagents are used for the detection of Mo^{VI} in the presence of the ions of tungsten and other elements [44, 45]. Molybdenum (V) does not form coloured compounds with these reagents.

Various xanthogenates, $ROC(S)SNa$, and dithiocarbamates, $R_2NC(S)SNa$, react with the Mo^{VI} ion in acid solutions to form intensely coloured compounds extractable with organic solvents [8]. The reagents are used for the detection and photometric and titrimetric determination of molybdenum.

The polarographic method can be used for the determination of molybdenum in its low concentrations. Molybdenum gives a catalytic wave against the background of 1 *M* $HClO_4$ + 0.75 *M* H_2SO_4 at $E_{1/2} = -0.18$ V. The wave height is proportional to the Mo concentration in the range from 0.2 to 2 μg/ml. Molybdenum is first separated as the citrate complex from the accompanying elements by ion-exchange chromatography (КУ-2 resin in the hydrogen form). The polarographic method is used to determine molybdenum in ores and other materials.

Small quantities of molybdenum are concentrated by co-precipitation with tannic acid and methyl violet [46, 47].

The literature [8, 48] contains review of the methods for the detection and determination of molybdenum.

ISOLATION OF TRACES OF MOLYBDENUM BY CO-PRECIPITATION

The molybdenum ions, together with the ions of tungsten and some other accompanying elements, are separated with the precipitate formed by tannic acid and methyl violet. The precipitate is incinerated, the molybdenum ion dissolved and then re-precipitated together with methyl violet thiocyanate from a 0.2 *M* solution of hydrochloric acid, the concentration of tartaric acid in the solution being about 0.05 *M*. During the second co-precipitation only 10-20 per cent of the tungsten ion are precipitated with the molybdenum ion. Small quantities of the ions of Sn, Sb, and Bi are also co-precipitated with the molybdenum. The co-precipitation method can isolate from 95 to 100 per cent of molybdenum with the dilution of $1:10^9$.

After separation, molybdenum is determined photometrically.

Reagents

Sodium hydrocarbonate, crystalline.
Sodium carbonate, 1 per cent solution.
Hydrochloric acid, 6 *N* solution.
Tannic acid, 2 per cent solution.
Methyl violet, 2 per cent solution.
Methyl orange, 0.1 per cent solution.
Sulphuric acid, diluted 1 : 1.
Sodium hydroxide, 1 *N* solution.
Tartaric acid, crystalline.
Ammonium thiocyanate, crystalline.
Washing solution I. Add 10 ml of 6 *N* hydrochloric acid, 1 mg of 2 per cent tannic acid solution and 5 ml of 2 per cent methyl violet solution to 1 litre of water.
Washing solution II. Add 10 ml of 6 *N* hydrochloric acid, 5 g of ammonium thiocyanate, 5 g of tartaric acid and 5 ml of 2 per cent methyl violet solution to 1 litre of water.

Procedure

Decomposition of Rock (*Granite*). Grind finely a sample of granite weighing 1-2 g and fuse it with a five-fold quantity of sodium bicarbonate in a muffle furnace or over the flame of a torch. Leach the melt with 200-250 ml of hot water, separate the residue on a filter, wash with 50-100 ml of sodium carbonate solution, and neutralize the solution with hydrochloric acid (to methyl orange). Add 10 ml of the acid in excess. If silicic acid precipitates in the course of the analysis, separate it on a filter, incinerate the filter with the precipitate, and fuse the residue with sodium bicarbonate.

Co-precipitation with Methyl Violet Tannate. Add 7.5 ml of tannic acid to the test solution, and then add 15 ml of methyl violet, drop by drop, with stirring. Separate the precipitate in 30 minutes on a filter wetted with the washing solution I. Pass the washings through the filter once again. Wash the precipitate 3-4 times with the washing solution I, transfer it on the filter into a crucible, wet with a few drops of sulphuric acid, char the filter under an infra-red lamp and incinerate in a muffle furnace at a temperature not above 500°C.

Co-Precipitation with Methyl Violet Thiocyanate. Wet the residue after incineration in a crucible with 3-5 drops of sodium hydroxide solution, add 2-3 ml of water, heat on a water bath for 20-30 minutes, transfer the solution into a 500-ml beaker, and rinse the crucible with 250 ml of water. Add a solution of 7 g of tartaric acid in 30 ml of water and of 5 g of ammonium thiocyanate in 10 ml of water, and then add 10 ml of hydrochloric acid. If turbidity develops, filter the solution. Add 25 ml of methyl violet slowly, drop after drop with stirring, and separate the precipitate in 30-40 minutes on a filter wetted with the washing solution II. Wash the precipitate 3-4 times with the same solution, transfer into a crucible and incinerate. Dissolve the residue in sodium hydroxide solution and determine molybdenum photometrically (e.g. as thiocyanate).

GRAVIMETRIC DETERMINATION OF MOLYBDENUM WITH α-BENZOINOXIME

α-Benzoinoxime (cupron) precipitates quantitatively the ion of Mo^{VI} from acetic acid solution containing acetates, and also from solutions containing 5 per cent (v/v) of acetic, phosphoric, nitric, hydrochloric or sulphuric acid. Precipitation is effected in the presence of bromine water to preclude reduction of the Mo^{VI} ion to Mo^{V} ion which is not precipitated with the reagent. To prevent precipitation of excess reagent, 20 per cent of acetone are added to the solution. The precipitate is dried at 105°C and weighed as $MoO_2(C_{14}H_{12}O_2N)_2$.

The ions of Ag, Pb, Hg^{II}, Bi, Cu^{II}, Cd, As^{V}, Sb^{III}, Sn^{II}, Al, Fe^{II}, Fe^{III}, Ti, Zr, Cr^{III}, V^{IV}, Ce, U, Ni, Co, Mn, Zn do not interfere with the determination. Te, Se, Re, Ru, Rh, Ir, Os, and Pt probably do not interfere. The ions of Nb, Si, Pd, W and Ta interfere. They contaminate the precipitate and should be separated. The effect of the ions of V^{V} and Cr^{VI} can be removed by reducing them with sulphurous acid or Mohr's salt. Tartaric and hydrofluoric acids interfere with complete precipitation of molybdenum.

The method can be used for the determination of molybdenum in steels free from tungsten.

α-Benzoinoxime is one of the best reagents for the separation of molybdenum from the accompanying elements.

Reagents

Mohr's salt, 5 per cent solution in 5 per cent sulphuric acid.
α-Benzoinoxime. 0.05 *M* solution in a mixture of acetone and water (1 : 1).
Mixture of acetone and water, 1 : 1.
Sulphuric acid, density 1.84 g/cu.cm and 1 per cent solution.

Procedure

Add 1-1.5 ml of sulphuric acid, density 1.84 g/cu.cm, to the solution containing 8-20 mg of Mo^{VI}, dilute with water to 25 ml and add excess solution of Mohr's salt to reduce Cr^{VI} and V^{V}. Add 10 ml of α-benzoinoxime solution, drop by drop with stirring, and allow the solution to stand for ten minutes. Decant the supernatant layer through a filtering crucible with a porous bottom No. 2 or No. 3 dried to constant weight, wash the precipitate by decantation with 5 ml of 1 per cent sulphuric acid and transfer with water onto the filter. See to it that the precipitate on the filter is covered with liquid. Wash the crucible walls and the precipitate with two 5-ml portions of a mixture of acetone and water, dry at 105°C to constant weight, and weigh as $MoO_2(C_{14}H_{12}O_2N)_2$.

Note. The precipitate can be calcined in a porcelain crucible in a muffle furnace at 500-550 °C and weighed as MoO_3.

COMPLEXOMETRIC DETERMINATION OF MOLYBDENUM

EDTA reacts with the Mo^{V} ion to form a stable complex compound, the component ratio being 1:2. The formation constant is $(1.75 \pm 0.52) \times 10^{11}$. Mo^{VI} is reduced to Mo^{V} by hydrazine in a sulphuric acid medium in the presence of excess EDTA which is titrated with a standard solution of a zinc salt to eriochrome black *T*. An aliquot should not contain more than 20 mg of molybdenum because the solutions of molybdenum complexonate are intensely coloured and interfere with the location of the equivalence point.

The ions of manganese, alkali and alkaline-earth elements do not interfere with the determination. The ions of Ti, Nb, Ta, W, Th, Al, Ce^{III}, La and U^{IV} do not interfere in the presence of tartaric acid and potassium fluoride which are added after reduction of Mo^{VI}. The determination is possible in the presence of the chloride, sulphate, nitrate, phosphate, acetate, tartrate, and citrate ions.

The method can be used for the determination of over 0.5 mg of molybdenum, the error being ±0.2 mg.

The method is applicable to the analysis of alloys containing bismuth, cadmium, cobalt, zinc, nickel, copper, mercury, vanadium chromium and lead. All accompanying elements are first titrated in one portion of the solution without reducing Mo^{VI}. The total amount of molybdenum (after its reduction) and the accompanying elements are titrated in the other portion.

Reagents

EDTA, 0.01 *M* solution.
Zinc sulphate, 0.01 *M* solution.
Hydrazine sulphate, crystalline.
Sulphuric acid, 6 *N* solution and diluted 1 : 1.
Ammonia, 25 per cent solution.
Chloride-ammonia buffer solution, pH 10. Dissolve 54 g of ammonium chloride in water, add 350 ml of a 25 per cent solution of ammonia and dilute with water to 1 litre.
Eriochrome black T. A mixture with sodium chloride, 1 : 150.
Tartaric acid, crystalline.
Sodium fluoride, crystalline.
Methyl red. Dissolve 0.2 g of the indicator in 60 ml of ethyl alcohol and add 40 ml of water.
Zinc sulphate, 0.005 *M* solution.

Procedure

Determining Molybdenum in Solutions. Place a solution containing 25-50 mg of molybdenum in the form of molybdate into a 50-ml volumetric flask and add water to the mark. Mix the solution and, using a pipette, transfer 10.0 ml into an Erlenmeyer flask (refractory glass, capacity 300-ml). Add 10 ml of EDTA solution, 3 g of hydrazine sulphate, 10 ml of a 6 *N* sulphuric acid solution, water to 100 ml, heat, and boil for five minutes. Cool the solution, add 5 ml of ammonia solution, 20 ml of the chloride-ammonia buffer solution and eriochrome black T, on the tip of a spatula (20-30 mg). Titrate with zinc sulphate solution until the blue solution turns lilac.

1 ml of a 0.0100 *M* solution of EDTA is equivalent to 1.92 mg of molybdenum.

Determining Molybdenum in Alloys. Place a sample of an alloy containing 10-50 mg of molybdenum in a 50-ml refractory-glass beaker and dissolve in 10 ml of sulphuric acid (1:1) with heating on a sand bath. Transfer the solution quantitatively into a 50-ml volumetric flask, add water to the mark and mix. Using a pipette transfer 10 ml of the solution into a 300-ml Erlenmeyer flask, add 20 ml of EDTA solution and heat on a hotplate to 70-80°C. Cool the solution, add 2 g of tartaric acid, 5 ml of ammonia solution and 20 ml of the chloride-ammonia buffer solution and mix. Add 20-30 mg (at the tip of the spatula) of eriochrome black T and titrate with zinc sulphate until the blue solution turns lilac. Record the volume (V_1) of the EDTA solution spent for titration of the alloy components (Bi, Cd, Co, Ni, Zn, V^{VI}, Cr^{III} and Pb).

Using a pipette, transfer 10 ml of the alloy solution into another 300-ml Erlenmeyer flask, add 20 ml of EDTA solution, 5 ml of a 6 *N* sulphuric acid, 3 g of hydrazine sulphate, 2 g of tartaric acid, dilute the mixture with 60-70 ml of water, heat, and boil for five minutes. Cool the solution, add 5 ml of ammonia solution, 20 ml of the chloride-ammonia buffer solution, eriochrome black T (at the tip of a spatula) and titrate excess EDTA with zinc sulphate until the blue solution turns lilac. Record the volume (V_2) of the EDTA solution spent for titration of molybdenum and the other components of the alloy.

The difference $V_2 - V_1$ is the volume of the EDTA solution reacted with the molybdenum.

Note. The quantities of the reagents are indicated for the determination of molybdenum in alloys containing from 8 to 40 per cent of molybdenum in a sample weighing 0.025-0.05 g. If the molybdenum content is lower, the metal should preliminarily be separated because the specified amount of EDTA is insufficient to bind all components of the alloy. Small quantities of molybdenum can be determined complexometrically with titration of excess EDTA by zirconium sulphate in 0.3 *N* sulphuric acid in the presence of xylenol orange.

EXTRACTION-PHOTOMETRIC DETERMINATION OF MOLYBDENUM IN STEEL BY THIOCYANATE METHOD

Thiocyanates react with Mo^V in an acid solution to form coloured compounds whose composition depends on the thiocyanate concentration. The Mo^{VI} ion is reduced to Mo^V with stannous chloride, potassium iodide, ascorbic acid or thiocarbamide in the presence of divalent copper salts and other reductants. Depending on the thiocyanate concentration, compounds with the molar ratio of Mo to SCN from 1:1 to 1:6 can be formed. The colour is more intense in the compounds with the Mo to SCN ratio of 1:5 (the molar extinction coefficient 1.50×10^4) and 1:6 (the molar extinction coefficient 1.26×10^4). The thiocyanate complexes of Mo^V are extractable with diethyl ether and other extracting agents.

The ions of Al, Co, U, Ta, Na, K, Si, Ca, Mg, Ti, V, Cr, Mn, Ni, Zn, As, Ag, Sn, Sb and Hg do not interfere with the determination. The ions of Fe^{III} and Cu^{II} intensify the colour probably due to the formation of multinuclei thiocyanate complexes containing molybdenum and iron (or copper) in the molar ratio of 1:1. The interfering effect of tungsten is removed by tartaric acid which prevents the formation of its thiocyanate complex.

Reagents

Sodium molybdate (*ammonium molybdate*), *standard solution*. 1 ml is equivalent to 0.1 mg of molybdenum.

Sulphuric acid, diluted 1 : 4 and 1 : 1.

Hydrogen peroxide, 30 per cent solution.

Tartaric (*citric*) *acid*, crystalline.

Sodium hydroxide, 10 per cent solution.

Potassium thiocyanate, 5 per cent solution.

Stannous chloride, 35 per cent solution. Dissolve 350 g of $SnCl_2 \cdot 2H_2O$ in 300 ml of hydrochloric acid, density 1.19 g/cu.cm, with heating; dilute the clear solution with 800 ml of water and add a few pieces of tin metal.

Diethyl ether.

Ferric sulphate, 8 per cent solution in 1 *N* sulphuric acid.

Constructing a Calibration Curve

Place 3-ml portions of ferric sulphate solution into five 50-ml separating funnels, add 0.5, 1.0, 1.5, 2.0 and 2.5 ml of the sodium molybdate standard solution into each funnel respectively, then add 5 ml of sulphuric acid (1 : 1) and 5 ml of potassium thiocyanate into each funnel, and shake energetically for 2-3 minutes. Add 5 ml of stannous chloride solution and shake energetically again for 1-2 minutes. The solutions gradually develop amber or reddish-brown colour. Add 10-12 ml of ethyl ether to the coloured solutions, extract the molybdenum compound for 2-3 minutes, transfer the ether layer into dry 25-ml volumetric flasks and repeat the extraction. Dilute the extracts with the ether to 25 ml and measure their absorption on an absorptiometer using cells with covers to preclude ether evaporation. Construct the calibration curve using the data obtained.

Procedure

Place a sample of steel weighing 0.05-0.25 g (containing 0.05-0.1 per cent of molybdenum) in a 100-ml beaker, add 10 ml of sulphuric acid (1:4) and heat to 60-70°C. Add 2 ml of hydrogen peroxide to the solution, boil for a few minutes to oxidize carbides, pass through a paper filter to remove carbon, wash the insoluble precipitate with water and discard. Reduce the volume of the filtrate and the washings to 10-15 ml by evaporation in a beaker. If carbon or alloyed steel, or steel containing tungsten is analysed, do not filter off the precipitate. Add 0.5 g of tartaric acid if the steel contains tungsten. Neutralize the solution with sodium hydroxide to pH 8-9 (to a universal indicator), add 5 ml of sulphuric acid (1:1) and transfer the solution into a 50-ml separating funnel. Add 5 ml of potassium thiocyanate solution, and proceed as for the construction of the calibration curve. Determine the molybdenum content of the sample from the calibration curve.

EXTRACTION-PHOTOMETRIC DETERMINATION OF MOLYBDENUM IN STEEL WITH *p*-PHENETIDIDE-1-MERCAPTOPROPIONIC ACID

p-Phenetidide-1-mercaptopropionic acid reacts with the Mo^{V} and Mo^{VI} ions to form yellow compounds insoluble in water but soluble in organic solvents. The compound of Mo^{V} with the reagent is formed in the pH range of 0.7-6. The absorption of the extracts is maximum at the pH of the aqueous phase of 1.6-3.8 (molybdenum concentration, 2×10^{-4} mole/litre, the reagent concentration, 2×10^{-2} mole/litre). The Mo^{VI} ion reacts with *p*-phenetidide-1-mercaptopropionic acid at pH 0-6; the maximum absorption of the extracts is at pH 0.5-4 (the molybdenum concentration, 2×10^{4} mole/litre, the reagent concentration, 2×10^{-2} mole/litre). Excess reagent does not reduce the molybdenum (VI) ion at acidity of 0.3 *M* HCl. Gradual oxidation of the molybdenum (V) compound begins at pH of about 4.

A mixture of isoamyl alcohol and benzene (1:1) is the recommended extracting agent. The maximum absorption of the extract is at 355-360 nm, the molar extinction coefficient is 2.7×10^{3} for the

Mo^V compounds and 4.6×10^3 for the Mo^{VI} compounds. The molar ratio of the molybdenum to the reagent is 1:2, irrespective of the valency of molybdenum. The absorption of the extracts is proportional to the molybdenum concentrations in the range from 10 to 200 μg in 5 ml of the solvent.

The ions of Fe^{III}, Cr, Ti, Co, Ni, Zn, Al and also W (hundred-fold quantity) do not interfere with the determination. The Cu ions interfere.

Reagents

Sodium paramolybdate, standard solution. 1 ml is equivalent to 25 μg of molybdenum.

p-Phenetidide-1-mercaptopropionic acid, 1 per cent solution in a mixture of isoamyl alcohol and benzene (1 : 1).

Hydrochloric acid, 1 : 1.

Nitric acid, density 1.4 g/cu.cm.

Constructing a Calibration Curve

Place 1, 2, 3, 4, 5, 6, 7 and 8 ml of the sodium paramolybdate standard solution into 50-ml separating funnels, and add 0.5 ml of hydrochloric acid and water to 10 ml. Now add 5 ml of the reagent, shake for 30 minutes, decant the organic phase into dry cells and measure the absorption at 360 nm on a spectrophotometer or an absorptiometer against a blank solution. Construct the calibration curve using the data obtained.

Procedure

Place a sample of steel weighing 0.1 g in a 50-ml beaker, add 5-6 ml of hydrochloric acid, and heat moderately on a sand bath. If steel does not dissolve completely, add 1-2 ml of nitric acid. Evaporate the solution to dryness, dissolve the residue in 5 ml of hydrochloric acid, transfer the solution into a 500-ml volumetric flask and add water to the mark. Transfer from 1 to 10 ml of the obtained solution into a 50-ml separating funnel, add water to 10 ml, hydrochloric acid to adjust its concentration in the solution to 0.3 *N* and proceed as for the construction of the calibration curve. Determine the molybdenum content from the calibration curve.

EXTRACTION-PHOTOMETRIC DETERMINATION OF MOLYBDENUM WITH 8-QUINOLINOL

Molybdenum is extractable quantitatively and selectively by chloroform (in the form of its compound with 8-quinolinol) from sulphuric acid solutions with the pH 0.85. The absorption maximum of the chloroform extract is at 385 nm. The method can therefore be used both for the separation and for the spectrophotometric determination of molybdenum. 5 g of U, 4 g of Th, 3 g of Mg, 2 g of Al, Be, Fe, Zr, 1 g of Zn, 90 mg of Cr, 46 mg of Ni, 45 mg of Cu, 10 mg of Ti, 8.5 mg of Mn, 1 mg of Co, 0.5 mg of $Sb^{III,V}$, Pb, V, $As^{III,V}$, 0.05 mg of Bi, 0.025 mg of Cu, 0.005 mg of Cd and Ag do not interfere with the determination of 50-200 μg of molybdenum. W, Nb and Ta, in amounts exceeding 100 μg, and halides interfere. Niobium and tantalum are masked by sodium fluoride or precipitated as hydroxides.

The method can be used for the determination of $\geqslant 5 \times 10^{-3}$ per cent of molybdenum in steels, zirconium and beryllium alloys, and in the oxides of thorium and uranium.

Reagents

Sodium molybdate, *standard solution*. 1 ml is equivalent to 10 μg of molybdenum.
Sulphuric acid, 2 *N* solution and solution with pH 0.85.
8-Quinolinol, 4 per cent solution acidified with sulphuric acid to pH 0.85.
Ammonium chloride, 4 per cent solution acidified with sulphuric acid to p*H* 0.85.
Chloroform.

Constructing a Calibration Curve

Place 1, 2, 3, 4, and 5 ml of the sodium molybdate standard solution into separating funnels, acidify with 2 *N* sulphuric acid to pH 0.85, dilute the solutions with sulphuric acid; with pH 0.85, to 60 ml and add 25 ml of 8-quinolinol. Add 20 ml of chloroform and extract molybdenum for two minutes. Transfer the organic phase into another separating funnel, containing 50 ml of 4 per cent ammonium chloride solution and shake again for two minutes. Pass the organic layer through a paper filter and measure the absorption at 385 nm in a cell with the light path of 4 cm against chloroform. Construct the calibration curve using the data obtained.

Note. If the anticipated molybdenum content is 50-400 μg, the absorption should be measured in a cell with the light path of 1 cm.

Determination of Molybdenum in Thorium Oxide

Reagents

Perchloric acid, 70 per cent solution.
Sodium fluoride, crystalline.
Boric acid, crystalline.
Ammonium chloride, 20 per cent solution acidified with sulphuric acid to pH 0.85.
8-Quinolinol, 4 per cent solution acidified with sulphuric acid to pH 0.85.
Potassium persulphate, crystalline.
Sulphuric acid, pH 0.85.

Procedure

Treat a sample of thorium oxide weighing about 4 g with 20 ml of perchloric acid and 50 mg of sodium fluoride with heating. Add 50 ml of water, 0.5 g of boric acid and 5 ml of ammonium chloride to the solution. The pH of the resulting solution should be 0.85 (neutralize free acid with dilute ammonia solution). Add 25 ml of 8-quinolinol solution and extract with 20 ml of chloroform. Evaporate the extract to dryness, fuse the residue with 3 g of potassium persulphate, dissolve in sulphuric acid and determine molybdenum as for the construction of the calibration curve.

Note. Other objects should be dissolved by a suitable method avoiding the use of nitrates, chlorides or fluorides. If these are still used, take measures to remove them after dissolution of the object.

PHOTOMETRIC DETERMINATION OF MOLYBDENUM WITH MAGNEZON IN ISOAMYL ACETATE EXTRACT

The method is based on the selective extraction of molybdenum with isoamyl acetate from hydrochloric acid solutions and its determination in the organic phase using magnezon IREA. The optimum acidity of the solution during the extraction is 9 *M* HCl. One-step extraction separates 93.7 per cent of 0.01-5 mg of Mo. $Re^{IV,VII}$, V^{IV} are not extracted in these conditions. The other elements are extracted in the following quantities (in per cent): W^{VI}, 40.0; V^{V}, 95.0; Sb^{V}, 99.1; Sn^{IV}, 53.5; Ti^{IV}, 16.6; Nb^{V}, 24.6; Cr^{VI}, 98.0; Fe^{III}, 85.9. The colour of the Mo^{VI} compound with magnezon IREA develops in the course of five minutes and persists for a few days. The absorption maximum of the solutions is at 560 nm, the molar extinction coefficient, 6.7×10^3. The allowable limit ratios of the interfering ions to molybdenum are: F^{III}, 5; W, 15; V^{V}, 2; Cr^{VI}, Nb^{V}, 10; Sb^{V}, 1000; Sn^{IV}, 200; Ge^{IV}, 500; Ga, 16; and Tl^{III}, 50. The method is used to determine 6.5-10 g of Mo in one litre of liquid fractions in hydrometallurgy.

Reagents

Sodium molybdate, standard solution. 1 ml is equivalent to 400 μg of molybdenum.
Hydrochloric acid, density 1.17-1.19 g/cu.cm.
Isoamyl acetate, saturated with 9 *M* hydrochloric acid.
Magnezon IREA, 10^{-3} *M* solution in ethanol.
Sodium hydroxide, 2 per cent solution.
Isoamyl acetate, + *ethanol* (1 : 1).

Constructing a Calibration Curve

Place 0.1, 0.2, 0.3, 0.4 and 0.5 ml of the standard solution of molybdenum in five 25-ml separating funnels, add 3.5 ml of hydrochloric acid, water to 4 ml into each funnel and extract with 4 ml of isoamyl acetate for a minute. Transfer the organic layer into dry test tubes fitted with ground-in stoppers, and take 0.5 ml from each test tube. Add 1.0 ml of magnezon IREA and dilute with a mixture of isoamyl acetate and ethanol to 5 ml. In five minutes measure the absorption of the solutions at 560 nm in a cell with a light path of 0.5 cm against a blank extract. Construct the calibration curve using the data obtained.

Procedure

Determining Molybdenum in Liquid Fractions of Hydrometallurgical Production. Place 10 ml of the test solution into a 250-ml volumetric flask, and add sodium hydroxide solution to the mark. Transfer an aliquot containing to 200 μg of molybdenum into a separating funnel and proceed as for the construction of the calibration curve.

PHOTOMETRIC DETERMINATION OF MOLYBDENUM AND TUNGSTEN WITH PYROCATECHOL IN ONE SAMPLE

Molybdenum (VI) reacts with pyrocatechol to form orange-yellow soluble compounds. The compound which forms most completely at pH about 6 absorbs maximum at 400 nm; the molar ratio of molybdenum to pyrocatechol is 1:2, the molar extinction coefficient is 5.56×10^3, the stability constant, 3.3×10^6.

In these conditions tungsten (VI) also reacts with pyrocatechol to form a yellow soluble compound with the absorption maximum at 300-305 nm; the molar extinction coefficient, 5.9×10^3, the stability constant 5.2×10^6, and the molar ratio of tungsten to pyrocatechol, 1:2.

A hundred-fold excess of pyrocatechol (pH 5-6) is required to completely bind molybdenum and tungsten in a complex compound. Both elements (in their hexavalent state) react with EDTA to form colourless compounds, but the complexonate of Mo^{VI} is more stable.

The proposed method is based on masking molybdenum (VI) complexonate and on determining tungsten as the pyrocatecholate after introducing a correction for the absorption of molybdenum pyrocatecholate. The correction can be found by determining molybdenum (V) photometrically in the form of its complexonate in another aliquot of the solution. The method can be used for the determination of molybdenum and tungsten in binary mixtures and alloys, the tungsten to molybdenum ratio being from 5:1 to 1:10.

Reagents

Sodium molybdate, standard solution. 1 ml is equivalent to 1.0 mg of molybdenum.

Sodium tungstate, standard solution. 1 ml is equivalent to 0.4 mg of tungsten.

Pyrocatechol, 0.45 *M* solution. Dissolve 3 g of $Na_2S_2O_5$ in 100 ml of a 0.4 per cent solution of sodium hydroxide, then dissolve 10 g of sublimed pyrocatechol and dilute with water to 200 ml.

EDTA, 5 per cent solution.

Sulphuric acid, diluted 1 : 1.

Ammonia, 25 per cent solution.

Hydrazine sulphate, solution. 1 ml contains 100 mg of hydrazine sulphate.

Sodium acetate, 1 *M* solution.

Ammonia-acetate buffer, pH 5.3-5.5. Dilute 63.9 ml of 97 per cent acetic acid with water, mix with 64.7 ml of 25 per cent ammonia solution, and add water to 1 litre.

Constructing Calibration Curves for Molybdenum (VI) and Tungsten (VI)

Place 1, 2, 3, 4 and 5 ml of the corresponding standard solution into separate 25-ml volumetric flasks, add 2 ml of pyrocatechol solution, 5 ml of the buffer solution, 5 ml of EDTA solution and dilute with water to the mark. Allow the solutions to stand for ten minutes and measure their absorption on a spectrophotometer or an absorptiometer against a blank solution. Construct the calibration curves using the data obtained.

Constructing a Calibration Curve for Molybdenum (V)

Place 1, 2, 3, 4 and 5 ml of the standard solution of sodium molybdate into five 50-ml beakers, dilute with water to 5 ml, add 2 ml of EDTA solution and 0.5 ml of hydrochloric acid, heat on a sand bath, then add 2 ml of hydrazine sulphate solution and boil for five minutes. Cool the solutions quickly, transfer into 25-ml volumetric flasks, add 2.5 ml of sodium acetate solution, adjust the pH to 4-5 (to a universal indicator paper) using ammonia, and dilute with the buffer solution to the mark. Measure the absorption of the solutions at wavelengths selected for the construction of calibration curves for tungsten.

Procedure

Dilute a solution containing from 2 to 10 mg of tungsten and from 5 to 25 mg of molybdenum with water to 25 ml, in a volumetric flask. Determine molybdenum as the molybdenum (V) complexonate in a 5.0-ml aliquot (absorption D_1). Use another aliquot of the same size to prepare pyrocatecholates of molybdenum (VI) and tungsten (VI) (absorption D). Using the calibration curve for molybdenum pyrocatecholate, determine the absorption corresponding to the molybdenum content of the aliquot found for the molybdenum (V) complexonate (absorption D_2). The difference $D - D_2$ is the absorption of tungsten pyrocatecholate whose content is found from the calibration curve.

Note. The correctness of determination of molybdenum and tungsten depends on the constancy of pH in solutions of molybdenum complexonate and the pyrocatecholates of molybdenum and tungsten. The ammonia-acetate buffer solution should therefore be prepared from 2 *M* solutions of acetic acid and ammonia.

DIFFERENTIAL PHOTOMETRIC DETERMINATION OF MOLYBDENUM IN ALLOYS AND CONCENTRATES BY THE THIOCYANATE METHOD

The method can be used to determine 4-45 per cent of Mo in the presence of nickel and cobalt with a relative error of ±1 per cent. The effect of chromium (III) is removed by adding it to the reference solution.

Reagents

Molybdenum, standard solution. 1 ml is equivalent to 0.1 mg of molybdenum.
Phosphoric acid, concentrated.
Acid mixture. Mix 1450 ml of water with 400 ml of concentrated sulphuric and 100 ml of concentrated hydrochloric acids.
Copper sulphate, 1 per cent solution.
Thiocarbamide, 5 per cent solution.
Ammonium thiocyanate, 50 per cent solution.
Tartaric acid, 25 per cent solution.
Hydrochloric acid, diluted 1 : 1.
Nitric acid, concentrated.
Sulphuric acid, concentrated.

Constructing a Calibration Curve

Place 4, 5, 6, 7, 8, 9, 10, 11, 12, 13, 14 and 15 ml of the standard solution of molybdenum into separate 100-ml volumetric flasks, add 25 ml of the acid mixture, 1 ml of copper sulphate solution, 15 ml of thiocarbamide solution, and 2 ml of potassium thiocyanate solution into each flask and then add water to the mark. Allow the solutions to stand for an hour and measure their absorption at 490-510 nm in a cell with a light path of 1 cm against a blank solution containing 1 mg of Mo. Construct the calibration curve using the data obtained.

Procedure

Determining Molybdenum in Alloys. Dissolve a sample of alloy weighing 0.2 g in a mixture of 10 ml of hydrochloric acid (1:1), 10 ml of nitric acid, and 5 ml of phosphoric acid. Evaporate the solution two times with 5 ml of sulphuric acid to dense fumes of SO_3. Dissolve the residue in 30-40 ml of hot water and filter. Collect the filtrate into a 100-ml volumetric flask and add water to the mark. Transfer an aliquot (20.0 ml) into a 100-ml volumetric flask and proceed as for the construction of the calibration curve.

Determining Molybdenum in Concentrates. Dissolve a sample of concentrate weighing 0.2 g by fusing it first with alkali or by acid decomposition. Transfer the solution into a 100-ml volumetric flask and add water to the mark. Transfer an aliquot containing 0.5-1.5 mg of molybdenum into a 100-ml volumetric flask, add 2.5 ml of tartaric acid, and proceed as for the construction of the calibration curve.

Determine the molybdenum content from the calibration curve.

EXTRACTION-PHOTOMETRIC DETERMINATION OF MOLYBDENUM WITH TOLUENE-3,4-DITHIOL IN NIOBIUM AND ITS ALLOYS

Toluene-3,4-dithiol (dithiol) reacts with Mo^{VI} in solutions of 4.6-12 M HCl (3-7 M H_2SO_4) to reduce it to Mo^V and to form a green compound soluble in amyl acetate and other organic solvents. Amyl acetate extracts have two absorption maxima, at 430-440 and 670-690 nm. The absorption maximum of petroleum ether and carbon tetrachloride extracts is at 680 nm. Tungsten reacts in the same conditions but with heating. To remove the effect of tungsten, citric acid is added to the solution. Ten-fold quantities of Al, Fe, Cr, Co, Ni and V do not interfere with the determination of 1×10^{-2} per cent of Mo. Large amounts of copper interfere. The reagent is suitable for the determination of molybdenum in rock, minerals, tungsten ores, soils, water, steels, medicines, plant and animal materials, metals and their oxides.

Reagents

Molybdenum, standard solution. Dissolve 0.3684 g of ammonium molybdate, $(NH_4)_6Mo_7O_{24} \cdot 4H_2O$, in water and dilute to 1 litre. 1 ml of the solution contains 0.2 mg of Mo. Dilute 25 ml of this solution with water to 1 litre. 1 ml of the final solution contains 5 μg of Mo.

Dithiol, 0.5 per cent solution. Dissolve 1 g of dithiol in 100 ml of a 4 per cent solution of sodium hydroxide with heating to 35 °C. Add 2 ml of thioglycolic acid and dilute with water to 200 ml.

Niobium, standard solution. 1 ml contains 10 mg of niobium. Place 1 g of high purity niobium into a 100-ml conical flask, dissolve in 5 g of a hot mixture of potassium hydrosulphate and 20 ml of sulphuric acid, density 1.84 g/cu.cm, and cool. Transfer the solution into a 100-ml volumetric flask and add sulphuric acid (1 : 2) to the mark.

Hydrochloric acid, diluted 1 : 2.

Hydrofluoric acid, 40 per cent solution.

Hydroxylamine chloride, 10 per cent solution.
Carbon tetrachloride.
Potassium hydrosulphate, crystalline.
Sulphuric acid, density 1.84 g/cu.cm and diluted 1 : 2.

Constructing a Calibration Curve

Place 15 ml of the standard solution of niobium into 100-ml Erlenmeyer flasks, and add 0.6, 1.2, 1.6, 2.4, and 3.0 ml of the standard solution of molybdenum. Evaporate the solutions to fumes of sulphuric acid, and cool. Add 15 ml of hydrochloric acid, 0.5 ml of hydrofluoric acid, 0.5 ml of hydroxylamine chloride into each flask, and cool. Transfer the solutions into 100-ml separating funnels with the minimum of water, add 10 ml of dithiol solution, mix thoroughly by shaking for 15 minutes, add 20 ml of carbon tetrachloride, and shake for another two minutes. Transfer the organic layer into 50-ml volumetric flasks and repeat the extraction two times using 10-ml portions of carbon tetrachloride and shaking the funnels for one minute. Transfer the extracts into the original flasks and add carbon tetrachloride to the mark. Measure the absorption of the extracts at 680 nm in a cell with a light path of 4 cm. Construct the calibration curve using the data obtained.

Procedure

Place a sample weighing 0.5 g and containing 2×10^{-3} to 2×10^{-2} per cent of Mo into a dry 100-ml Erlenmeyer flask, dissolve, with heating, in a mixture of 5 g of potassium hydrosulphate and 10 ml of sulphuric acid, density 1.84 g/cu.cm, and cool. Transfer the solution into a 50-ml volumetric flask with sulphuric acid (1:2) and add the acid to the mark. Transfer 15 ml of the resultant solution into a 100-ml Erlenmeyer flask, evaporate to sulphuric acid fumes, cool, add 15 ml of hydrochloric acid, and proceed as for the construction of the calibration curve. Determine the molybdenum content of an aliquot from the calibration curve.

Note. The method can be used for the determination of 2×10^{-3} to 2×10^{-2} per cent of Mo in tantalum. The standard solution of tantalum containing 10 mg/ml of the metal should then be used instead of the niobium standard solution.

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Tungsten

Tungsten, W, in its compounds has the positive valency of 2, 3, 4, 5, and 6. The compounds of penta- and hexavalent tungsten are the most important ones.

The standard electrode potentials in an aqueous medium at 25°C with reference to the standard hydrogen electrode) are as follows:

$$W + 2H_2O \rightleftharpoons WO_2 + 4H^+ + 4e^- \qquad -0.119\ \mathrm{V}$$

$$2WO_2 + H_2O \rightleftharpoons W_2O_5 + 2H^+ + 2e^- \qquad -0.031\ \mathrm{V}$$

$$W_2O_5 + H_2O \rightleftharpoons 2WO_3 + 2H^+ + 2e^- \qquad -0.029\ \mathrm{V}$$

$$W + 4H_2O \rightleftharpoons WO_4^{2-} + 8H^+ + 6e^- \qquad +0.049\ \mathrm{V}$$

$$[W(CN)_8]^{4} \rightleftharpoons [W(CN)_8]^{3-} + e^- \qquad +0.457\ \mathrm{V}$$

Stannous chloride reduces tungstates to tungsten blue which is stable in an acid solution (unlike molybdenum blue). The formation of molybdenum blue underlies many methods for detecting the WO_4^{2-} ion.

Energetic reductants (Zn + HCl, amalgamated zinc) reduce W^{VI} in concentrated hydrochloric acid solutions to brown ions of W^{III} which are unstable in air. If the solution is moderately acid (HCl) tungsten blue is formed under these conditions.

Mercury metal also reduces W^{VI} to W^{V}. Divalent iron ($FeSO_4$) does not reduce the ions WO_4^{2-}. The titrimetric method for the determination of tungsten is based on the reduction of W^{VI} to W^{V} by divalent chromium salts [1, 2].

The red ion of tervalent tungsten WCl_5^{2-} has a strong reducing action. It converts into yellow or yellowish-green ion $W_2Cl_9^{3-}$. Tervalent tungsten in solution is oxidized by atmospheric oxygen, and can be determined titrimetrically [3].

Divalent tungsten compounds are unstable in solution.

Tungsten metal is inactive. Hydrochloric acid does not act on it. Concentrated nitric acid acts on compact tungsten slowly.

Hot concentrated phosphoric acid, as well as hydrofluoric acid, dissolve tungsten to form complexes. Molten alkalies react with tungsten metal, especially in the presence of oxidants.

Acidified solutions of the alkali metal tungstates precipitate tungstic acid which is insoluble in excess HNO_3, $HClO_4$ and H_2SO_4 (as distinct from molybdic acid). Tungstic acid precipitate is soluble in 9-12 *N* hydrochloric acid. A cold solution precipitates a white amorphous substance, $H_2WO_4 \cdot nH_2O$. If the solution is heated, the precipitate is yellow and less hydrated. Tungstic acid tends to form colloidal solutions. To preclude peptization, its precipitate is washed with an electrolyte solution. Tungstic acid completely converts into an insoluble form only by evaporation of acid solutions to dryness.

Tungstic acid can be isolated from solutions of samples fused with hydroxides or carbonates of the alkali metals by acidifying with hydrochloric acid. The acid is precipitated together with silicic acid (acid hydrolysis). When evaporated with hydrochloric acid, the acid modifications are less hydrated and less soluble. Tungsten is thus separated from many elements.

Tungstic acid can be dissolved in excess standard solution of NaOH with subsequent titration of unreacted alkali by a standard solution of the acid. The method is used for the determination of tungsten in steel [4].

Tungstic acid forms various polytungstic acids (similar to polymolybdic and polyvanadic acids) in acid solutions, the modifications being dependent on the acid concentration and the pH of solutions. They easily disintegrate in an alkaline medium to form the tungstate ion WO_4^{2-}. Tungstic acid is readily soluble in ammonia solution and in solutions of the alkali metal hydroxides with the formation of tungstates:

$$\left.\begin{array}{l} H_3WO_5^- \rightleftharpoons H_2WO_5^{2-} + H^+ \\ H_2WO_5^{2-} \rightleftharpoons HWO_5^{3-} + H^+ \\ HWO_5^{3-} \rightleftharpoons WO_5^{4-} + H^+ \end{array}\right\} \mathrm{p}K = 6\text{-}8$$

The tungstates of silver, mercury (I), lead and the alkaline earths are sparingly soluble in water (e.g. $\mathrm{p}L_{Ag_2WO_4} = 9.3$).

The chloride, fluoride, oxalate, tartrate and citrate ions react with W^{VI} to form various complexes.

Hydrogen sulphide does not precipitate sulphides from solutions containing the ion WO_4^{2-}. Ammonium sulphide reacts with the WO_4^{2-} ion to form the yellow-orange thio salt WS_4^{2-}. When the solution is acidified, a light brown precipitate WS_3 is formed. The thio salt is completely destroyed at $pH < 4$.

Ortho-phosphoric acid reacts with the ion W^{VI} to form a heteropolyacid. The thiocyanate ion forms coloured complex compounds with pentavalent tungsten. The thiocyanates are used for the photometric determination of tungsten [5-7].

Nitrogenous organic bases and some triphenylmethane dyes precipitate tungstic acid ions and are used for the quantitative separation of W^{VI} from solution. The precipitates are usually characterized by unstable composition. They are calcined to WO_3. Alkaloids (quinine, cinchonine), benzidine, 1-naphthylamine, nitron, vanilidenebenzidine, β-naphthoquinoline [8], sulphamide-2,4-diaminoazobenzene (red streptocide), dimethylaminoantipyrine (amidopyrine), rhodamine B, etc. are used to precipitate tungstic acids.

Amidopyrine is of great practical value for the isolation of tungstic acid [9]. Hydrochloric acid is first added to a dilute solution of sodium tungstate, and then amidopyrine is added. The reagent is successfully used for the determination of tungsten in ferrotungsten.

Rhodamine B precipitates tungstic acid from acidified solutions [10, 11]. The precipitation is the most complete from 0.10-0.15 *M* HCl solutions. The precipitate is not formed in neutral media. The solubility product of this precipitate is 2×10^{-18} (in a 0.12 *M* HCl medium). The reagent is used for the detection of W in minerals and alloys, and also for its gravimetric determination.

The numerous derivatives of 2,3,7-trihydroxy-6-fluorone [12] react with the tungstate ion in a weak acid medium (pH 2.0-3.5) to form red compounds. (The molar ratio of the reactants is 1:1.) If the tungstate ion concentration is high enough, these compounds precipitate. The coloured solutions remain clear in the presence of gelatine. To prevent precipitation of tungstic acid, citric acid is added to the tungstate solution before acidification. Ethyl alcohol is also added to prevent precipitation of the reagent.

Photometric methods have been proposed which are based on the formation of intensely coloured three-component compounds of tungsten with magnezon CS, and hydrogen peroxide [13], with 3,5-dinitropyrocatechol and brilliant green [14], and with sulphonitrophenol *M* and hydrogen peroxide [15, 16].

The best reagents for the photometric determination of tungsten are probably 9-(2′-hydroxyphenyl)trihydroxyfluorone, 9-(9′-anthracenyl)-2,3,7-trihydroxyfluorone and salicylfluorone [17-21].

8-Quinolinol precipitates the tungsten (VI) ion and is used for the determination of tungsten.

The most important photometric methods for the determination of tungsten are based on the ability of W^V to form, under certain conditions, stable coloured complexes with toluene-3,4-dithiol [22].

The oxidation-reduction reactions underlie various titrimetric methods for the determination of tungsten.

The polarographic method is effective in the determination of tungsten in the presence of large quantities of niobium and tantalum [23].

The literature contains a review of the methods for the determination of tungsten [2, 24].

GRAVIMETRIC DETERMINATION OF TUNGSTEN IN FERROTUNGSTEN

The method is based on the precipitation of tungsten by β-naphthoquinoline at pH 1-6. Ni, Zn, Mn, Al, Ti, Pb, Be, Zr, V, Cr and a small quantity of Fe do not interfere with the determination. If the iron content is high, the precipitate is treated with ammonia, and tungsten is precipitated again by β-naphthoquinoline. If molybdenum is present, tungsten is precipitated in a more acid medium.

The method can be used for the analysis of pig iron, steel, alloys, slags, and ores.

Reagents

β-Naphthoquinoline, 2 per cent solution. Dissolve 2 g of the reagent in 100 ml of water and acidify with a few drops of concentrated sulphuric acid.
Oxalic acid, saturated solution.
Hydrogen peroxide, 30 per cent solution.
Sulphuric acid, diluted 1 : 1.
Hydrochloric acid, 2 per cent solution.
Ammonia, 10 and 2.5 per cent solutions.
Ammonium nitrate, 2 per cent solution.
Potassium ferrocyanide, crystalline.

Procedure

Place a sample of ferrotungsten weighing 0.25-0.50 g in a 500-ml beaker and dissolve, with heating on a hotplate (covered with an asbestos sheet), in 30 ml of oxalic acid and 5 ml of hydrogen peroxide. Evaporate the solution carefully to a small volume and add 15 ml of sulphuric acid, drop by drop, to the cooled residue. Heat the beaker contents to fumes of sulphuric acid and continue heating for 3 minutes. Cool the solution, add 400 ml of cold water and heat gradually to dissolve the salt. Add 30 ml of β-naphthoquinoline and allow the mixture to stand for 1-2 hours (or overnight) at room temperature.

Separate the precipitate on a blue ribbon filter and wash with hydrochloric acid to the negative reaction to the iron ion ($K_4[Fe(CN)_6]$ crystal test). Unfold the filter, place it into the precipitation beaker, and treat with 50 ml of a 10 per cent ammonia solution. When the precipitate has dissolved, disintegrate the filter by a glass rod. Heat the beaker contents on a water bath for 20-30 minutes, separate the paper pulp on a filter, and wash it with a 2.5 per cent ammonia solution several times.

Cool and acidify the filtrate with hydrochloric acid to pH 3-4. Add 20 ml of β-naphthoquinoline solution, separate the precipitate, wash it on the filter two times with hydrochloric acid and two times with NH_4NO_3, place in a porcelain crucible, dry slightly on a hotplate covered with an asbestos sheet, and incinerate carefully in a muffle furnace, first with gentle heating (to preclude tungsten sublimation) and then at 600-650°C. Cool the residue and weigh.

The conversion factor to tungsten is 0.7931.

POTENTIOMETRIC DETERMINATION OF TUNGSTEN WITH CHROMOUS SALTS IN SCHEELITE CONCENTRATE

The method is based on the reduction of W^{VI} to W^{V} with salts of divalent chromium in an acid medium.

$$WO_2Cl_5^- + 2H^+ + 2Cl^- + e^- \rightleftharpoons WOCl_5^{2-} + H_2O$$

The equivalence point is detected potentiometrically. When the reduction process is over, the platinum electrode potential sharply changes. The potential at the platinum electrode is established immediately after adding each new portion of the chromous salt. The titration is carried out in concentrated hydrochloric acid (100 or 150 ml of the acid are taken per 5 or 10 ml of 0.1 *M* sodium tungstate solution respectively). Two sharp changes in the potential are observed in the presence of Fe^{III}, Cu^{II}, Cr^{VI} and Mo^{VI}. The first jump corresponds to the termination of the reduction of the above named elements, and the second jump corresponds to complete reduction of W^{VI}, and also of Mo^{V} to Mo^{III}. W^{VI} and the other elements are therefore first reduced by a solution of a chromous salt and then tungsten (V) is titrated with a solution of potassium dichromate. Citric, tartaric, oxalic and formic acids do not produce any effect on the titration.

Reagents

Hydrochloric acid, density 1.19 g/cu.cm.
Chromous sulphate, 0.1 *N* solution. Dissolve 29.421 g of pure dry $K_2Cr_2O_7$ in 500 ml of water in a 2-litre flask and acidify the solution with 27.8 ml of 36 *N* sulphuric acid. Add slowly (with stirring) 75 ml of a 30 per cent solution of hydrogen peroxide to reduce $Cr_2O_7^{2-}$ to Cr^{3+}. Heat the solution to boiling, cool to room temperature, transfer into a 2-litre volumetric flask and add water to the mark. Fill a bottle 2/3 full with amalgamated zinc and connect with a titration burette and a Kipp generator. Rinse the bottle containing amalgamated zinc with two small portions of the solution and then transfer the whole solution into it. The reduction of Cr^{3+} to Cr^{2+} is completed in 24 hours. The liberated hydrogen should pass through a Kipp generator. Determine the titre of $CrSO_4$ solution using a standard solution of copper sulphate, $CuSO_4 \cdot 5H_2O$. To that end, add 3 ml of concentrated hydrochloric acid to 2 ml of a 0.1 *M* solution of $CuSO_4$ and titrate potentiometrically with a platinum indicator electrode. The $CrSO_4$ solution, when kept in a bottle over amalgamated zinc in a hydrogen atmosphere, can be stored for a few weeks.
Sodium hydroxide, 20 per cent solution.
Oxalic acid, saturated solution.
Potassium bichromate, 0.1 *N* solution.

Procedure

Grind thoroughly a sample of scheelite concentrate weighing 0.25 g, place it in a small porcelain dish and treat with 4-5 ml of hydrochloric acid with heating. Evaporate excess acid and wet an almost dry residue with 3 ml of sodium hydroxide solution. Add 10 ml of oxalic acid to the obtained solution and transfer the dish contents with water into a beaker containing 100 ml of hydrochloric acid. Cover the beaker with a rubber plug provided with holes to pass carbon dioxide inlet and outlet tubes, a burette, a salt bridge, and the platinum indicator electrode. Pass carbon dioxide from a Kipp generator for 30 minutes into the solution to remove oxygen from it. Titrate the solution with chromous sulphate without discontinuing the carbon dioxide current and with stirring (by a magnetic stirrer) until the potential jumps to indicate the reduction of hexavalent tungsten. Now titrate pentavalent tungsten with potassium dichromate solution.

BICHROMATOMETRIC DETERMINATION OF TUNGSTEN

The method is based on the reduction of W^{VI} to W^{III} in concentrated hydrochloric acid with granulated zinc in the presence of ammonium chloride. To ensure complete reduction, the solution is passed through a reductor filled with lead. The solution containing the W^{III} ions is added to the solution of a ferric salt. The Fe^{2+} ion which is formed in an equivalent quantity is titrated with potassium bichromate in the presence of diphenylaminosulphonic acid as an indicator.

Reagents

Ferriammonium sulphate. Dissolve 10 g of $Fe(NH_4)(SO_4)_2 \cdot 12H_2O$ in 20 ml of concentrated hydrochloric acid and add 80 ml of water.
Potassium bichromate, 0.01 *N* and 0.05 *N* solutions.
Diphenylaminosulphonic acid, 0.005 *M* solution.
Lead, granules. Place lead in an 18-cm high reductor (dia. 2 cm), wash with a solution containing 15 g of NH_4Cl in 150 ml of hot hydrochloric acid (2 : 1), and then fill with hydrochloric acid (1 : 1).
Hydrochloric acid, density 1.19 g/cu.cm and diluted 1 : 1.
Ammonium chloride, crystalline.

Procedure

Add water to a solution containing from 5 to 50 mg of tungsten to make 25 ml, add 5-8 g of ammonium chloride and heat to dissolve the salt. Add 25 ml of hydrochloric acid, density 1.19 g/cu.cm, and boil. Add 10 g of lead, cover the flask with a watch glass and boil for two minutes. Transfer the hot solution into the reductor and wash the flask with three 8-ml portions of concentrated hydrochloric acid. Pass the solution through the reductor at a rate of 20 ml/min. Collect the outflowing solution in a flask containing excess hydrochloric acid solution of ferriammonium sulphate. Wash the reductor with 10 ml of hydrochloric acid (1:1), with two 15-ml portions of water, and then with 15 ml of hydrochloric acid again. Add two drops of an indicator and titrate the warm solution with a 0.05 *N* solution of potassium bichromate until violet colour develops and persists for 15 seconds.

Deduce a correction for the indicator from the amount of the potassium bichromate solution spent for titration. (Determine the correction by titrating a blank solution.)

ACIDIMETRIC DETERMINATION OF TUNGSTEN IN STEEL

Tungstic acid is separated by acid hydrolysis, dissolved in sodium hydroxide solution, and excess sodium hydroxide is titrated by a standard acid solution.

Reagents

Hydrochloric acid, diluted 1 : 1 and 5 : 95.
Nitric acid, density 1.4 g/cu.cm.
Potassium nitrate, 1 per cent solution.

Silver nitrate, 1 per cent solution.
Standard alkali solution. Add 1.8 litre of boiled water and 0.5 g of $BaCl_2 \cdot 2H_2O$ to 16 ml of concentrated solution of sodium hydroxide (200 g/l). Keep the solution in a 2-litre bottle provided with a calcium chloride tube. Standardize the solution against accurately weighed $H_2C_2O_4 \cdot 2H_2O$.
Standard acid solution. Dilute 65 ml of nitric acid, density 1.4 g/cu.cm, with water to make 2 litres. Standardize the acid against the standard solution of sodium hydroxide using phenolphthalein as an indicator.
Phenolphthalein, 0.1 per cent solution in ethyl alcohol.

Procedure

Dissolve a sample of steel weighing 0.5-1 g in hot hydrochloric acid (1:1) in a beaker, and add hot nitric acid. Boil the solution, add 60 ml of hot water, 5 ml of hydrochloric acid (1:1) and boil for another 5 minutes. Separate the precipitated tungstic acid on a double filter (blue ribbon), wash with hot hydrochloric acid (5:95) and with water to negative reaction to the chloride ion (test with $AgNO_3$). Rinse the beaker with potassium nitrate solution, place the filter together with the precipitate into the beaker, and add 60 ml of hot water. Shake to disintegrate the filter, add 2 drops of phenolphthalein and dissolve tungstic acid in excess standard solution of alkali. Titrate excess alkali with nitric acid until the solution is colourless. Carry out a blank test with the filter.

Calculate the tungsten content using the results of the titration.

PHOTOMETRIC DETERMINATION OF TUNGSTEN BY THE THIOCYANATE METHOD

The thiocyanate ions react with W^{V} to form a green-yellow complex compound. The molar extinction coefficient of the complex solution is 1.76×10^4 at 398 nm.

W^{VI} is reduced to W^{V} by titanium (III) chloride. The violet colour of the reductant excess does not practically affect the accuracy of measurement of the absorption provided a blue filter is used. Molybdenum (VI) does not interfere with the determination because it is reduced to Mo^{III} to form a slightly coloured complex compound with the thiocyanate ion. Cr, V, Se and Te interfere. The effect of As and Sb is removed by hypophosphite. Ti, Nb, Ta, Cu and the platinum family elements, as well as F and P, do not interfere.

The method can be used to determine 1.5-0.003 per cent of tungsten in mineral materials in the presence of arsenic ($\leqslant$10 per cent), antimony ($\leqslant$3 per cent), molybdenum ($\leqslant$0.5 per cent), chromium ($\leqslant$ 0.3 per cent), vanadium, selenium and tellurium ($\leqslant$ 0.1 per cent).

Reagents

Tungsten, standard solution. 1 ml is equivalent to 0.1 mg of W.
Potassium thiocyanate, 25 per cent solution.
Sodium hydroxide, 2 per cent solution.

Titanium (III) chloride, 0.1 *N* solution. Add 9 volumes of hydrochloric acid (1 : 1) to one volume of 15 per cent solution of $TiCl_3$ and use immediately.
Hydrochloric acid, density 1.19 g/cu.cm.

Constructing a Calibration Curve

Place 1, 2, 3, 4 and 5 ml of the standard solution of tungstate into 50-ml volumetric flasks, and dilute with sodium hydroxide solution to 10 ml. Now add 2 ml of potassium thiocyanate solution, 12 ml of hydrochloric acid and 0.2 ml of titanium (III) chloride into each flask. In five minutes add water to the mark and measure the absorption of the solutions on an absorptiometer with a blue filter. Construct the calibration curve using the data obtained.

Procedure

Determine the tungsten content of the solution as instructed for preparing the standard scale.

EXTRACTION-PHOTOMETRIC DETERMINATION OF TUNGSTEN WITH TOLUENE-3,4-DITHIOL

Toluene-3,4-dithiol reacts with W^V ions to form blue compounds extractable with butyl, amyl or isoamyl acetate. The molar extinction coefficient of the extract is 2.00×10^4 at 640 nm. Titanium metal is usually used as the reductant and toluene-3,4-dithiol is substituted by its zinc complex.

Lead and molybdenum ions when contained in quantities exceeding 1 mg and 10-20 μg respectively, interfere with the determination. Bismuth, antimony and tin ions do not interfere. If the molybdenum content exceeds several times that of tungsten, both elements should be first separated and then determined. Their determination is based on the reaction in which the ions of Mo^V (in contrast to W^V ions) react with dithiol to form a green complex, with the absorption maximum at 690 nm. This makes it possible to determine 0.4 mg of tungsten. After separation of molybdenum with dithiol, and isoamyl acetate, tungsten is determined in the aqueous phase.

Reagents

Hydrochloric acid, density 1.19 g/cu.cm.
Toluene-3,4-dithiol, zinc salt, suspended in alcohol.
Grind 0.2 g of zinc dithiol with the minimum quantity of alcohol in a porcelain mortar and add ethyl alcohol to 50 ml. Shake the suspension before use.
Titanium, metal chips.
Isoamyl acetate.
Sodium tungstate, standard solution. 1 ml is equivalent to 2 μg of tungsten.
Sulphuric acid, density 1.84 g/cu.cm and diluted 1 : 1.
Hydrofluoric acid, 40 per cent solution.
Hydrogen peroxide, 30 per cent solution.
Sodium carbonate or potassium pyrosulphate.
Ammonia, solution, density 0.9 g/cu.cm.
α-Benzoinoxime, 2 per cent solution in ethyl alcohol.
Chloroform.
Acid mixture, consisting of 2-3 ml of distilled nitric acid, 5 drops of sulphuric acid, density 1.84 g/cu.cm, and 5 drops of concentrated perchloric acid.

Preparing a Standard Series

Place standard tungstate solution containing 1, 2, 3, 4 and 5 μg of tungsten into five separate test tubes and dilute with water to 3 ml. Add 7 ml of hydrochloric acid and 100-200 mg of titanium metal into each test tube. Heat the solutions until a slight violet colour develops. Transfer the solutions into tubes fitted with glass stoppers, and add zinc-dithiol suspension until a slight turbidity develops. Close the test tubes with their stoppers (not tightly!) and place in a beaker with boiling water for 20 minutes. Transfer the solutions into separating funnels, cool to room temperature, and extract with 2 ml of isoamyl acetate for 90-120 seconds. Transfer the extracts into test tubes (with ground-in stoppers) containing 10 ml of distilled hydrochloric acid. The scale can be used for 10-12 days provided it is kept in a refrigerator.

Procedure

Wetten a sample of silicate rock weighing 0.5-1.0 g in a platinum dish with a small quantity of water. Add 1-2 ml of sulphuric acid (1:1) and 8-10 ml of hydrofluoric acid. Heat the dish on a hotplate periodically stirring its contents by a platinum rod. Repeat the treatment with hydrofluoric acid two times. Evaporate the dish contents to fumes of sulphuric acid. Cool the residue, add hot water, and evaporate again to a small volume. Add hydrogen peroxide, drop by drop, until the solution clarifies, dilute with hot water, and boil until bubbling discontinues. Pass the solution through a paper filter into a 50-ml or 100-ml volumetric flask. If the residue is large, incinerate the filter with the residue in a platinum crucible, fuse the residue with sodium carbonate or potassium pyrosulphate, dissolve and add the solution to the main filtrate.

Neutralize a 10-15 ml aliquot with ammonia solution until the hydroxides precipitate. Dissolve the precipitate with 1-2 drops of sulphuric acid (1:1), transfer the solution into a separating funnel, add the same acid to the concentration of 2-4 per cent (v/v) and add 2 ml of α-benzoinoxime solution, stirring the mixture after adding each new reagent. Allow the solution to stand for 5-10 minutes, and extract with three 5-ml portions of chloroform shaking the column for one minute. Collect the extracts in a beaker and distil chloroform. Add the acid mixture to the dry residue and cover the beaker with a watch glass. Heat the beaker to fumes of sulphuric acid, keep for 15-20 minutes, remove the watch glass, evaporate to dryness, and calcine the residue. Add 3 ml of water and 10 drops of concentrated ammonia solution to the colourless residue, boil the solution till the ammonia odour is not felt, add 7 ml of concentrated hydrochloric acid and proceed as for the preparation of the standard scale solutions. Compare the colour of the solution with the standards in the scale and determine the tungsten content of the sample.

Note. In the analysis of polymetallic ores, extract tungsten (and molybdenum) by chloroform in the form of α-benzoinoxime complex from sulphuric acid solution.

PHOTOMETRIC DETERMINATION OF SMALL QUANTITIES OF TUNGSTEN IN MOLYBDENUM AND ITS COMPOUNDS BY THE THIOCYANATE METHOD

The method is based on the reduction of Mo^{VI} in sulphuric acid medium by hydrazine with subsequent binding of Mo^{V} with EDTA and extraction of W^{VI} in the form of 8-hydroxyquinolinate by chloroform. The extraction of Mo^{V} is insignificant in these conditions. After removal of chloroform and decomposition of 8-hydroxyquinolinate of tungsten, the metal is determined by the thiocyanate method using titanium trichloride as the reductant. The effect of small quantities of molybdenum is removed in this case.

Reagents

Sulphuric acid, diluted 1 : 1 and 8 *N* solution.
Hydrochloric acid, density 1.19 g/cu.cm and diluted 1 : 1.
Nitric acid, density 1.40 g/cu.cm.
Ammonia, 25 per cent solution.
Aqua regia.
EDTA, 10 per cent solution.
Hydrazine chloride, 20 per cent solution.
Mixture of butyl alcohol and chloroform (1 : 2).
8-Quinolinol, 1 per cent solution. Dissolve 1 g of the preparation in 100 ml of the mixture of butyl alcohol and chloroform (1 : 2).
Potassium thiocyanate or ammonium thiocyanate, 50 per cent solution.
Titanium (III) chloride, 1.5 per cent solution. (Dilute a 15 per cent solution.)
Tungstate, standard solution. 1 ml is equivalent to 0.01 mg of tungsten. Dissolve 0.126 g of WO_3 in a few millilitres of a 10 per cent solution of sodium hydroxide and dilute with water to 1 litre: 1 ml contains 0.1 mg of tungsten. Dilute this solution to prepare a solution whose 1 ml is equivalent to 0.01 mg of W.

Preparing a Standard Scale

Place different portions of a standard solution of tungstate containing 10, 15, 20, 25, 30, 35, 40, 45 and 50 μg of tungsten, or 2, 4, 6, 8, 10, 12, 14, 16, 18 and 20 μg into separate 25-ml volumetric flasks. Add 12 ml of hydrochloric acid (1 : 1), dilute with water to about 22 ml and cool. Stir the solutions and add 1 ml of potassium (or ammonium) thiocyanate and then, drop by drop with stirring, titanium chloride solution until the brown colour vanishes. Add five drops of the solution in excess.

Procedure

Dissolve a sample of molybdenum or its concentrate weighing 0.1-0.2 g in 10-15 ml of aqua regia and 5 ml of sulphuric acid (1:1). Evaporate the solution to fumes of sulphuric acid, wet the residue with water and evaporate to fumes of sulphuric acid again. Add 5 ml of water to the residue, heat to dissolve it, neutralize the solution with ammonia solution to neutral or weakly acid reaction and transfer into a 100-ml volumetric flask. Take an aliquot containing not more than 50 μg of tungsten, add 5 ml of an 8 *N* solution of sulphuric acid, 10-20 ml (depending on the molybdenum content) of EDTA solution, water to 30 ml, and heat to boiling. Add 10 ml of hydrazine chloride solution and boil for 2-3 minutes. Cool quickly the solution, neutralize it with ammonia solution to dissolve the precipitate, and transfer into a 100-150 ml separating funnel.

Adjust the pH of the solution to 2-3 (not higher), add 10 ml of 8-quinolinol solution and shake the mixture for 1-2 minutes. Allow the mixture to settle, withdraw the lower (organic) layer into another separating funnel and repeat the extraction two times more, each time adding 5 ml of a mixture of butyl alcohol with chloroform. Wash the extracts with water (5-10 ml), transfer the organic layer into a 50-ml beaker and evaporate on a water or a sand bath and heat the residue with a mixture of concentrated sulphuric and nitric acids to obtain a white dry residue. Add 12 ml of hydrochloric acid (1:1), heat to dissolve the residue, and transfer the solution into a 25-ml volumetric flask with water to make 22 ml, and proceed further as for the preparing a standard scale. Allow the solution to stand sor 30 minutes and compare its colour with those in the standard feries.

Note. If ammonium molybdate is analyzed, dissolve its sample weighing 0.2 g in 5-10 ml of 1 N sulphuric acid, add 20 ml of EDTA and proceed as in the Procedure.

PHOTOMETRIC DETERMINATION OF TUNGSTEN AS TRIPLE COMPLEX WITH HYDROGEN PEROXIDE AND MAGNEZON CS

The method is based on the reaction of tungsten (VI) in an acid medium in the presence of hydrogen peroxide with the formation of a triple complex, tungsten-(VI)-H_2O_2-magnezon CS, with the maximum absorption at 580 nm and the molar extinction coefficient of 2×10^4. The selectivity of the method is improved by adding masking substances, viz. EDTA, HF, and H_2O_2. 50-fold quantities of iron, thorium, bismuth, titanium, do not interfere with the determination in these conditions. Nb, Ta and Mo interfere.

Reagents

Tungsten (VI), standard solution. Dissolve $Na_2WO_4 \cdot 2H_2O$ in a 1 per cent solution of sodium hydroxide to prepare a solution with the tungsten concentration of 1 mg/ml. Dilute the solution to decrease the tungsten concentration to 20 μg/ml.
Hydrogen peroxide, 0.01 M solution.
Hydrochloric acid, 6 M solution.
Magnezon CS, 0.02 per cent water-acetone solution (1 : 1).

Constructing a Calibration Curve

Place 20, 40, 60, 80 and 100 μg of tungsten into 25-ml volumetric flasks, add 0.5 ml of 0.01 M hydrogen peroxide, 4 ml of 6 M hydrochloric acid (the final acidity should be 1 M HCl), 5 ml of 0.02 per cent solution of magnezon CS and water to the mark. Allow the solutions to stand for two hours and measure their absorption on a spectrophotometer at 580 nm in a cell with a light path of 2 cm against a blank solution.

Procedure

Place a sample of the solution containing from 30 to 90 μg of W in a 25-ml volumetric flask, add all the reagents and in the same quantities as for the construction of the calibration curve and measure the absorption at 580 nm ($l = 2$ cm). Find the tungsten content of the aliquot from the calibration curve.

EXTRACTION-PHOTOMETRIC DETERMINATION OF TUNGSTEN WITH 3,5-DINITROPYROCATECHOL AND BRILLIANT GREEN IN POTASSIUM HYDROXIDE

The complex WO_4^{2-} with 3,5-dinitropyrocatechol reacts with brilliant green to form an ionic association with the component ratio of 1:2:2, which is floated at the interface between water and petroleum ether. When chloroform is added to the ether, the floated precipitate of the association completely dissolves. The molar extinction coefficient of the association in chloroform is 1.32×10^5 at 646 nm. The Bouguer-Lambert-Beer law holds for the range of W concentrations from 0 to 6 μg in 1 ml. The method is used to determine tungsten in potassium hydroxide.

Reagents

Sodium tungstate, standard solution. 1 ml is equivalent to 10 μg of tungsten.
3,5-Dinitropyrocatechol. 0.01 *M* solution in ethyl alcohol.
Brilliant green, 0.01 *M* solution in 25 per cent alcohol-water mixture.
Petroleum ether.
Chloroform.
Sulphuric acid, diluted 1 : 1 and 0.1 *N* solution.

Constructing a Calibration Curve

Place 1, 2, 3, 4 and 5 ml of the standard solution of sodium tungstate in separating funnels, adjust the pH of the solution to 0.1 *N* H_2SO_4, add 0.8 ml of dinitropyrocatechol solution, 2 ml of brilliant green solution, and allow the solution to stand for 30 minutes. Shake the solution with 5 ml of petroleum ether and separate the lower layer. Wash the ether layer with the floated precipitate of the association with 0.1 *N* sulphuric acid using two 5-ml portions, each time shaking for 10-15 seconds. Place the extract in a 25-ml volumetric flask, rinse the separating funnel several times with chloroform and add the washings to the flask contents. Add chloroform to the mark and measure the absorption of the solution at 646 nm against a blank extract. Construct the calibration curve using the data obtained.

Procedure

Dissolve 10 g of KOH in 20 ml of water, neutralize the solution with sulphuric acid (1:1) and adjust the acidity to 0.1 *N* (sulphuric acid). Transfer the solution into a separating funnel and proceed as for the construction of the calibration curve. Determine the tungsten content from the calibration curve.

PHOTOMETRIC DETERMINATION OF TUNGSTEN WITH SULPHONITROPHENOL M IN STEEL AND NICKEL ALLOYS

Sulphonitrophenol M reacts with W^{VI} in the presence of H_2O_2 in 0.1-0.5 *N* hydrochloric acid solution to form a compound with the absorption maxima at 580 and 630 nm. The molar ratio of the components in the complex is 1:1, the molar extinction coefficient, 3.5×10^4 (630 nm). With the recommended wavelength of 650 nm, the molar extinction coefficient is 3.1×10^4. The colour develops in the course of one hour, after which the absorption of the solution stays invariable for a long time. The optimum quantities of the reagent and hydrogen peroxide are 20-25-fold with respect to tungsten. The solutions obey the Bouguer Lambert-Beer law within the range of tungsten concentrations from 10 to 60 μg in 25 ml. If no masking substances are used, Mo, Fe^{III}, Cu^{II} and oxalates interfere with the determination in 0.1 *N* solutions of hydrochloric acid. 6.0 mg of EDTA, 0.2 mg of tartaric acid, 0.25 mg of fluoride ion and also the parenthesized quantities (multiple masses) of the following elements do not interfere with the determination: Na (10^4), K (5×10^3), Mn (500), Zn and NH_4^+ (100), Re (80), Pb (20), Co and Ni (12), Al, Ta (10), La (4) and Nb (0.4). 20-fold quantities of Ti and Zr do not interfere in the presence of EDTA. The components of steel and nickel alloys do not interfere with the determination of $\leqslant$ 5-6 per cent of Mo in the presence of hexametaphosphate. The method is used for the determination of 1.5-6.3 per cent of W in nickel alloys, the relative error of determination being 1-3 per cent.

Reagents

Tungsten, standard solution. 1 ml is equivalent to 10 μg of tungsten. Prepare a 1 per cent NaOH solution.

Background solution. Dissolve 0.1 g of alloy with the composition similar to that of the alloy in question and dilute with water to 100 ml.

Acetate buffer solution, pH 4.5. Mix equal volumes of 1 *M* solutions of CH_3COOH and CH_3COONa.

Hydrogen peroxide, 0.1 per cent solution.

Sodium hexametaphosphate, 8 per cent solution.

Hydrochloric acid, density 1.19 g/cu.cm.

Sulphonitrophenol M, 0.02 per cent solution in a mixture (1 : 4) of acetone and water.

Constructing a Calibration Curve

Place 1, 2, 3, 4 and 5 ml of the standard solution of tungsten in 25-ml volumetric flasks containing 1 ml of the background solution. Add 2.5 ml of the buffer solution, 1 ml of hydrogen peroxide, 0.1 ml of sodium hexametaphosphate and dilute with water to 15 ml. Add 2 ml of hydrochloric acid, 5 ml of sulphonitrophenol M and water to the mark. Allow the solutions to stand for an hour and measure the absorption at 630-650 nm ($l = 3$ cm) against a blank solution. Construct the calibration curve using the data obtained.

Procedure

Dissolve a sample of the alloy weighing 0.1 g by a suitable method, transfer the solution quantitatively into a 100-ml volumetric flask and add water to the mark. Transfer an aliquot (1 ml) into a 25-ml volumetric flask, add 2.5 ml of the acetate buffer solution, and proceed as for the construction of the calibration curve. Determine the tungsten content from the calibration curve.

PHOTOMETRIC DETERMINATION OF TUNGSTEN IN ZIRCONIUM WITH SALICYLFLUORONE

Salicylfluorone reacts with W^{VI} to form a red compound. The solution of the reagent in a 7 per cent aqueous solution of ethyl alcohol has the absorption maximum at 468 nm. The absorption maxima of the compound with W^{VI} are at 475 and 560 nm, the molar extinction coefficient being 2.55×10^4 and the optimum pH, 0.5-3. The component ratio in the complex is 1:1, the constant of formation, 5.5×10^{-5}. The reagent is used for the photometric determination of tungsten in steel, vanadium, V_2O_5, ammonium vanadate, caustic alkalies, steel, aluminium, zirconium and its salts. The maximum sensitivity is 1×10^{-6} per cent of W. To remove the interfering effect of the accompanying ions, tungsten is first extracted as the benzhydroxamate by a mixture (1:1) of isobutyl alcohol and chloroform. 100 μg of Sn, Ti, Zr, Th, Bi, and In, 20 μg of Nb, 40 μg of Ta, 10 μg of Mo and 500 μg of Sb do not interfere with the determination of 2-9 μg of W. Ge and Ga interfere. When $\geqslant 1 \times 10^{-4}$ per cent of W is determined (the variation coefficient 1) in zirconium and its salts, tungsten is extracted as the benzhydroxamate from solutions containing EDTA. But only 77 per cent of the total tungsten are extracted and the quantity found from the calibration curve should therefore be multiplied by the factor of 1.3 to find the true tungsten content of the aliquot. When tungsten is determined in the presence of EDTA as the masking agent, 1.5×10^5-fold quantity of zirconium does not interfere.

Reagents

Acid mixture (1 : 3), consists of hydrochloric acid, density 1.19 g/cu.cm and nitric acid, density 1.4 g/cu.cm.
Hydrochloric acid, density 1.19 g/cu.cm, 1, 2, and 4 *M* solutions.
EDTA, crystals and 0.05 per cent solution.
Potassium benzhydroxamate, 4 per cent solution.
Mixture of isobutanol and chloroform (1 : 1).
Ascorbic acid, crystalline.
Sodium carbonate, 2 per cent solution.
Potassium chlorate, saturated solution.
Sodium citrate, 0.01 *M* solution.
Thioglycolic acid, 10 per cent solution.
Buffer solution, pH 2.51. Mix 9 ml of 0.01 *M* solution of glycol with 48.1 ml of 0.1 *M* hydrochloric acid.
Ammonium fluoride, 1 per cent solution.
Salicylfluorone, 1 per cent alcohol solution in 0.03 *M* hydrochloric acid.
Tungsten, standard solution. 1 ml is equivalent to 2 μg of tungsten.

Constructing a Calibration Curve

Place 1, 2, 3, 4 and 5 ml of the standard solution of tungsten into 25-ml volumetric flasks, add 0.2 ml of 1 *M* hydrochloric acid, 0.2 ml of sodium citrate solution, 1 ml of EDTA solution, 0.5 ml of thioglycolic acid, 10 ml of buffer solution, 1 ml of ammonium fluoride solution and 1 ml of salicylfluorone solution into each flask. Mix thoroughly after adding each new component. Add the buffer solution to the mark, allow the solutions to stand for two hours and measure their absorption at 530 nm in a cell with the light path of 5 cm against a blank solution. Construct the calibration curve using the data obtained.

Procedure

Dissolve 0.5-1 g of zirconium in a mixture of acids, evaporate to dryness on a water bath, treat the residue with hydrochloric acid, density 1.19 g/cu.cm, and evaporate to dryness again. Dissolve the residue in 25 ml of 2 *M* hydrochloric acid. Add 2 g of EDTA to the solution and boil for 15 minutes. Cool the solution, add 32 ml of hydrochloric acid, density 1.19 g/cu.cm, 5 ml of potassium benzhydroxamate solution and dilute with water to 100 ml. Extract the solution two times with two 10-ml portions of chloroform mixture with isobutanol for two minutes each time and allow the mixture to settle for at least 5 minutes after each extraction. Join the extracts, wash them with 10 ml of 4 *M* hydrochloric acid in a separating funnel (adding a small quantity of ascorbic acid) and evaporate to dryness in a platinum dish. Add 1 ml of Na_2CO_3 solution, 0.2 ml of potassium chlorate solution to the dry residue, evaporate the mixture, dry slightly, and fuse it quickly in a muffle furnace at 800-900°C. Dissolve the melt in a small portion of water, transfer the solution into a 25-ml volumetric flask and proceed as for the construction of the calibration curve. Multiply the quantity of tungsten found in the calibration graph by the factor 1.3 to determine the true tungsten content in the sample.

POLAROGRAPHIC DETERMINATION OF TUNGSTEN IN NIOBIUM, TANTALUM AND THEIR COMPOUNDS

The method is based on polarography of W^{VI} in 18 *M* solution of phosphoric acid, using an A.C. polarograph with a dropping mercury electrode. The peak potential of W is 0.75 V against the bottom mercury.

Reagents

Tungsten, standard solution. 1 ml is equivalent to 0.1 mg of tungsten. Prepare the solution by dissolving tungsten metal.
Phosphoric acid, concentrated.
Hydrofluoric acid, 40 per cent solution.
Nitric acid, density 1.4 g/cu.cm.

Procedure

Dissolve the metal or its oxide (0.1-0.3 g) in HF containing HNO_3 in a platinum dish with heating. Evaporate the solution to the minimum volume, and 25 ml of phosphoric acid and heat for 40 minutes to remove completely HF, NO_2 and H_2O. Cool the solution, dilute it with water, transfer in a 50-ml volumetric flask, and add water to the mark. Transfer an aliquot into a polarographic cell and carry out A.C. polarography in the range from −0.6 to −1 V. Determine the tungsten content from the calibration curve, constructed for the range of tungsten concentrations from 0.02 to 0.1 mg/ml against the background of the base.

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Rhenium

Rhenium, Re, has the positive valency of 3, 4, 5, 6 and 7. The compounds of heptavalent rhenium (perrhenates) and of tetravalent rhenium are of the greatest importance in analytical chemistry. The valency of rhenium in many of its compounds formed by the reaction of potassium perrhenate with analytical reagents is not yet known.

The chemical properties of rhenium are similar to those of molybdenum. The compounds of hepta- and tetravalent rhenium are, in some respects, similar to the corresponding compounds of manganese.

The standard electrode potentials in an aqueous medium at 25°C are as follows (with reference to the standard hydrogen electrode):

$$Re^{3+}+2H_2O \rightleftharpoons ReO_2+4H^++e^- \qquad +0.157\ V$$

$$Re \rightleftharpoons Re^{3+}+3e^- \qquad +0.300\ V$$

$$Re^{3+}+4H_2O \rightleftharpoons ReO_4^-+8H^++4e^- \qquad +0.422\ V$$

$$ReO_2+2H_2O \rightleftharpoons ReO_4^-+4H^++3e^- \qquad +0.510\ V$$

$$Re^{3+}+4H_2O \rightleftharpoons ReO_4^{2-}+8H^++3e^- \qquad +0.795\ V$$

Rhenium metal is insoluble in hydrochloric, hydrofluoric and dilute sulphuric acids. It is easily soluble in nitric acid with oxidation to $HReO_4$. When fused with caustic alkali, it forms brown-green ions of the rhenate ReO_4^{2-} (similar to MnO_4^{2-}) which are disproportioned immediately in an aqueous solution with the formation of colourless ions of perrhenate ReO_4^- and black ReO_2:

$$3ReO_4^{2-}+2H_2O=2ReO_4^-+ReO_2+4OH^-$$

Rhenium oxide, ReO_2, is stable and resembles MnO_2. But unlike MnO_2 it dissolves in concentrated hydrochloric acid to form the chloride complex of rhenium (IV), chlororrhenate, $H_2[ReCl_6]$.

Rhenium (V) compounds are slowly disproportioned in solution to form compounds of Re^{VII} and Re^{IV}. Oxalate and tartrate complexes are known for rhenium (V).

The oxidizing properties of perrhenates are much weaker than those of permanganates. Reduction reactions are characteristic of ReO_4^-. Relatively weak reductants (SO_2, N_2H_4) probably reduce rhenium (VII) to its hexavalent state to give yellow colour to the solutions. More energetic reductants ($SnCl_2$, Zn) reduce the ReO_4^- ions to a greater extent in a hydrochloric acid medium and the solutions first turn brown and then green. A black turbidity ($ReO_2 \cdot nH_2O$) can finally develop or the solution can become colourless.

Liquid amalgams of zinc, cadmium, lead and bismuth reduce the perrhenate ion in sulphuric acid or hydrochloric acid solutions to the ions of rhenium in its various states [1].

Amalgamated bismuth reduces heptavalent rhenium to its pentavalent state in a medium of 3.5-9 M H_2SO_4 and to the valency state close to 4 in solutions containing over 2 mole/l of hydrochloric acid [1].

In titrimetric determination [1, 2], the ion of heptavalent rhenium is reduced in ten minutes to the ion of Re^V in a medium of 18 N sulphuric acid by 2-3 per cent amalgamated bismuth in carbon dioxide atmosphere. The amalgam is then separated and the Re^V ion is titrated with $K_2Cr_2O_7$ solution in the presence of N-phenylanthranilic acid or $Ce(SO_4)_2$ solution. Satisfactory results are obtained with the determination of 4-11 mg of Re. It is recommended that excess $Fe_2(SO_4)_3$ be added to the sulphuric acid solution containing the ion of Re (V), with subsequent titration of the formed ferrous ion with $Ce(SO_4)_2$ solution.

The perrhenate ion is reduced quantitatively [3-5] to Re^{IV} ion by $CrSO_4$ solution in a medium of 4-12 N sulphuric acid at 60-70°C or in a medium of 8 N hydrochloric acid.

Solutions of chromous salts are used for potentiometric titration of heptavalent rhenium.

Mercurous salts (nitrate or perchlorate) reduce [6] the ReO_4^- ion in hydrochloric acid to the ion of tetravalent rhenium. Reduction does not occur in a 0.5-1 N sulphuric acid in the presence of the thiocyanate ion. It begins only in 5 N H_2SO_4. The molybdate ion is reduced in these conditions and the formed molybdenum-thiocyanate complex is extracted with ethyl ether. This reaction is used for the separation of molybdenum from rhenium.

The reduction of ReO_4^- ion with stannous chloride in the presence of potassium thiocyanide gives a yellow compound extractable with ethyl ether (like MoO_4^{2-}). The valency of rhenium in this compound is not determined. The formation of the thiocyanate compound of rhenium underlies various photometric methods for the determination of this element. The thiocyanate method is used for the determination of 0.0001-0.01 per cent of Re in ores, molybdenite and concentrates [7]. The material in question is sintered with CaO and $KMnO_4$ or fused with CaO and Na_2O_2. Rhenium is then separated from the interfering elements by extraction with methyl ethyl ketone from a 5 N solution of NaOH. The thiocyanate compound of rhenium is extracted by n-butyl alcohol. The sensitivity of the method is 2 μg of Re in 20 ml of n-butanol. The thiocyanate method is used also for the determination of rhenium in molybdenum and tungsten-containing alloys [8-10] and in molybdenite [6, 11].

Hydrogen sulphide precipitates the heptasulphide Re_2S_7 from strong hydrochloric acid solutions of Re^{VII} salts (4 *N* HCl), especially with heating. Sulphides of rhenium in its lower valency states are also precipitated by this reaction. The precipitate is black. It is readily soluble in HNO_3 with the formation of $HReO_4$. Hydrogen sulphide precipitates rhenium sulphide from an alkaline solution very slowly and only on standing. The sulphide precipitate is sparingly soluble in solutions of ammonium polysulphide. Pure Re_2S_7 is formed by reacting perrhenate solution with excess sodium sulphide or ammonium sulphide, great excess of ammonium sulphate (20-25 g) and hydrochloric acid (to adjust its concentration to 6 *N*) with subsequent heating to boiling [12]. The precipitate of Re_2S_7 is washed, dried, and weighed. The method gives satisfactory results.

Perrhenic acid, $HReO_4$, is strong. The ion ReO_4^- is colourless. Perrhenates of thallium (I), silver, cesium, rubidium and potassium are sparingly soluble in water. The solubility of $KReO_4$ is 0.95 g/l. Perrhenates of sodium and ammonium (lihe perchlorates) are relatively well soluble. The anions ReO_4^- form sparingly soluble compounds with large organic cations (tetraphenylarsonium, nitron, 2,2′,2″-tripyridyl, methylene blue, methyl violet, rhodamine 6G, butyl rhodamine B, and others). The obtained compounds are soluble in various organic solvents. This is used for the separation, gravimetric and especially photometric determination of rhenium.

Tetraphenylarsonium chloride precipitates quantitatively the ion ReO_4^- at pH 8-9. The formed precipitate is extractable with chloroform [13, 14]. The molybdate ion is not precipitated in these conditions and remains in the aqueous phase when the chloroform extract is shaken with 6 *N* HCl, the ReO_4^- ion passes into the aqueous phase. A coloured thiocyanide complex of rhenium is formed in the aqueous phase (without separating the chloroform layer) by successive addition of NaSCN and $SnCl_2 \cdot 2H_2O$ solutions. Isoamyl alcohol is then added, the thiocyanide complex is extracted, and its absorption measured at 430 nm. Good results are attained with the determination of 0.01-0.1 mg of Re in solution containing 0.07 g of molybdenum. The procedure continues for two hours.

From 0.1 to 10 per cent of Re can be determined in alloys containing molybdenum and tungsten. The method consists in extraction of tetraphenylarsonium perrhenate from a citrate-containing solution (pH 8-9) by chloroform with subsequent measurement of the absorption at 255 nm against chloroform as the standard [15]. The ions of tin, permanganate, perchlorate, bromide and fluoride interfere. Tetraphenylarsonium chloride is also used for the gravimetric determination of rhenium.

In the presence of methylene blue, the perrhenate ion is extracted by ethyl acetate. In the presence of methyl violet, the ion is extracted by ethyl acetate from neutral or ammonia solution and by chloroform or ethyl acetate from sulphuric acid solutions [16]. In the extraction-photometric method, the perrhenate compound with methyl violet is extracted from neutral solutions by ethyl acetate [16], benzene or toluene [17].

Antipyrine dyes are very sensitive and are used for the extraction-photometric determination of rhenium in ores [18, 19].

Rhodamine 6G reacts with the perrhenate ion in a medium of 0.5-1.5 *N* sulphuric acid to form a compound extractable with benzene. The extract gives an orange fluorescence [20]. The fluorescence spectrum is a structureless band with the maximum at 550-560 nm. When the rhenium compound is extracted from the aqueous solution (10-25 ml) with 6 ml of benzene, from 1 to 30 μg of Re can be determined. Relatively large quantities of the Hg^{II} ions interfere with the determination since they also form an extractable and fluorescing compound. The intensity of fluorescence of the rhenium compound decreases in the presence of ions of gold (III), chromate, permanganate and tungstate. The ions of antimony and uranium, in quantity of 5-10 mg, intensify fluorescence of 5 μg of Re by 30-40 per cent. The ion of Mo (25-30 mg) does not interfere. Gallium, indium, and thallium react with rhodamine 6G in the presence of the halide ions to form fluorescing complexes extractable with benzene. The halide ions should therefore be absent from the solution during the determination of rhenium.

Butyl rhodamine B reacts with the perrhenic acid ion in a medium of 5 *N* sulphuric acid or 3 *M* phosphoric acid to give a coloured compound extractable with benzene [21]. The absorption of the obtained extract is measured and the rhenium content is determined. The method can be used for the determination of rhenium in ores. The sample is sintered with MgO and $KMnO_4$. Vanadium, tungsten and mercury (interfering elements) remain in the insoluble precipitate and have no effect on the results of the determination. The sensitivity of the method (sample weighing 2 g) is 0.002 per cent.

Dimethyl glyoxime, α-furildioxime and other oximes react with the reduced (by $SnCl_2$) perrhenate to form a red compound of indefinite composition. The coloured compound formed by α-furildioxime is extractable with cyclohexanone. The oximes are used for the detection and photometric determination of rhenium [22, 23].

Thiocarbamide reacts with the compound of rhenium of lower valency to form a coloured compound [24, 25]. The compound is formed when thiocarbamide and then $SnCl_2 \cdot 2H_2O$ solution in hydrochloric acid are added to the solution of perrhenic acid in hydrochloric acid. Thiocarbamide is used for the photometric determination of rhenium [24, 26].

8-Mercaptoquinoline (thiooxine) reacts with the perrhenate ion to form various coloured compounds [27] (depending on the acidity). The valency of rhenium and the composition of the formed compounds are not yet established. A very stable compound of rhenium with the reagent (formed in 5-12 *N* HCl) is used for the extraction-photometric determination of small quantities of rhenium. The reagent is used for the extraction-photometric determination of 0.05-7 per cent of rhenium in titanium alloys [28].

Diphenyl carbazide reacts with the ion of perrhenic acid in a medium of 8 *N* HCl to form a coloured compound extractable with choloroform [29]. The absorption of the extract is measured at 540 nm. The following ions do not interfere with photometric determination: Cd, Ag, Bi, Zn, Mn, Al, Fe, Au^{I}, Cr^{III}, W, Ti, Co, Ni, Zr and Nb. Cu, Se, V, and Mo, as well as oxidants interfere. Diphenyl carbazide can be used to determine rhenium in some alloys without its preliminary separation. The sensitivity of determination is 0.1 μg of Re in 1 ml.

When 2,4-diphenyl thiosemicarbazide is added to a warm (80°C) solution of potassium perrhenate in about 6 *N* HCl or 14-16 *N* H_2SO_4, an intense red colour develops [30]. The formed coloured compound is easy to extract with chloroform. The absorption maximum of the extract is at 510 nm. The intensity of the colour of the aqueous solution or of the chloroform extract persists for several hours without appreciable changes. The nature of the compound is obscure. The compounds of tetravalent rhenium (K_2ReCl_6) do not form coloured compounds with the reagent. The photometric methods employin 2,4-diphenyl thiosemicarbazide can be used to determine less tha 50 μg of Re in 10 ml of solution. Moderate quantity of the molybdat ion does not interfere with the determination under special conditions.

Thioglycolic acid reacts with Re^{VII} in an acid medium to reduce rhenium to its lower valency with subsequent formation of a pink complex suitable for the photometric determination of rhenium. As a rule, stannous chloride is used as the reductant [31, 32]. An ionic association is formed in the presence of diantipyrylmethane. It is soluble in a mixture of isoamyl alcohol and chloroform.

Rhenium compounds show catalytic properties. Traces of rhenium catalyze the reduction of tellurate with stannous chloride.

$$Na_2TeO_4 + 3SnCl_2 + 8HCl = Te\downarrow + 3SnCl_4 + 2NaCl + 4H_2O$$

The reaction does not practically proceed in the absence of rhenium compounds in the solution. Black tellurium which is liberated in this reaction remains in solution in the presence of a protective colloid. The proposed photometric method can determine from 0.1 to 0.001 μg of rhenium in 1.5 ml of solution [33, 34]. The absorption of the obtained colloidal solutions depends on the concentration of the reactants, the duration of the reaction, and the presence of other electrolytes. All these factors are important for the determination of rhenium. If the molybdate ion is present in relatively large quantities, it catalyzes the above reaction and should therefore be separated. Rhenium is separated from the greater part of molybdenum by sintering the sample with calcium oxide and calcium nitrate at 700-800°C with subsequent treatment with water. Almost all rhenium passes into solution while molybdenum remains in the precipitate as $CaMoO_4$. The remaining molybdenum is then separated from rhenium by chloroform extraction in the form of 8-hydroxyquinolinate. The method can be used to determine ten thousandth fractions of a per cent of rhenium in molybdenite [34] and rock [33, 35].

The ion of rhenium (VII) can be determined polarographically. Its reduction on a dropping-mercury electrode is a complicated process [36]. Good results are attained [37] with polarography of the perrhenate ion against the background of a 4 *N* solution of HCl or 4 *N* $HClO_4$ in the presence of 0.005 per cent of gelatin and against the background of a 5 *N* solution of sulphuric acid.

When rhenium is determined in various materials it should, in most cases, be first concentrated either by distillation from acid solutions, or by extraction with various organic solvents, or else by precipitation with hydrogen sulphide in an acid medium in the presence of the salts of copper, osmium, mercury and arsenic. The molybdenum (VI) ion is precipitated with ferric hydroxide at pH 5-7.5.

Good results are attained with thioacetamide which is used for concentration of rhenium as the sulphide. When sulphuric acid solutions of potassium perrhenate containing thioacetamide are heated, a black substance, whose composition is close to Re_2S_7, is precipitated [38]. The precipitate is easy to separate by filtration. When contained in the concentrations over 10 mg/l, rhenium can be precipitated quantitatively from 2-6 *N* solutions of sulphuric acid. Smaller quantities of rhenium are separated by coprecipitation with sulphides of copper and mercury from a 3 *N* solution of sulphuric acid. It is possible to precipitate 5 μg of Re from 500 ml of solution (as sulphate) in the presence of 100 mg of copper.

The methods of separation of rhenium and molybdenum are of great importance. Methods based on volatility of Re_2O_7 in HCl current, on the precipitation of molybdenum with α-benzoin oxime and other organic reagents, on the extraction of molybdenum compounds (e.g. with ethyl xanthogenate or thiocyanide), or rhenium compounds, are available. Many modifications of chromatographic separation of rhenium and molybdenum have been suggested. All these methods take much time, are complicated, and the results are not always satisfactory. Sintering with CaO is used to separate the major part of molybdenum during decomposition of molybdenum minerals. Sparingly soluble calcium molybdate is formed in this reaction. Subsequent leaching partly dissolves it together with perrhenate. Rhenium can be determined directly in the obtained solution by the thiocyanide method without separating small amounts of molybdenum, the concentration of HCl being 5 *N* (the thiocyanide complex of molybdenum is unstable at higher acid concentration).

The literature contains the review of the analytical methods for rhenium [39, 40].

GRAVIMETRIC DETERMINATION OF RHENIUM AS TETRAPHENYLARSONIUM PERRHENATE

Tetraphenylarsonium chloride precipitates quantitatively the ion ReO_4^- within a wide range of acidities (from 5 *M* HCl to 6 *M* NH_3). The ions Hg^{2+}, Bi^{3+}, Pb^{2+}, Ag^+, Sn^{II}, VO^{2+}, and also MnO_4^-, ClO_4^-, IO_4^-, I^-, Br^-, F^-, and SCN^- interfere with the determination. Vanadates and tungstates do not interfere. Molybdates do not interfere if rhenium is precipitated from ammonia solutions or if 0.6 *M* tartaric acid is present.

Reagents

Tetraphenylarsonium chloride, 1 per cent solution.
Sodium chloride, crystalline.

Procedure

Add sodium chloride to 5-25 ml of a hot solution of perrhenate (containing 0.5-100 mg of Re) to adjust the salt concentration to 0.5 *N*. Add the reagent with stirring until the precipitation process stops. Stir the mixture, cool, and allow to stand for a few hours. Separate the precipitate on a glass filter No. 3, wash several times with ice-cold water, dry at 110°C and weigh as $(C_6H_5)_4AsReO_4$. The conversion factor for ReO_4 is 0.3952.

POTENTIOMETRIC DETERMINATION OF RHENIUM IN ALLOYS

The method is based on the reduction of the perrhenate ion Re^{IV} by a standard solution of a chromous salt:

$$ReO_4^- + 4H^+ + 3e^- \rightarrow ReO_2 + 2H_2O$$

The titration of Re^{VII} is carried out in a hot (60-70°C) solution of sulphuric acid (4 *N*) in the presence of a small quantity of potassium iodide as a catalyst. The equivalence point is detected with a platinum electrode (the reference electrode is a saturated calomel half-cell). Equal quantity of molybdenum does not interfere with the determination. The ions Fe^{3+}, Ti^{4+}, Cr^{3+}, V, Ni^{2+}, Co^{2+}, Nb and Cu^{2+}, which interfere with the determination, can be easily separated by precipitation with ammonia or alkali.

The method can be used to determine over 0.5 per cent of Re in alloys with a relative error of 1-3 per cent.

Reagents

Chromous sulphate, 0.1 *N* solution. See Sec. Potentiometric Determination of Tungsten with Chromous Salts in Scheelite Concentrate (page 243).
Hydrochloric acid, density 1.19 g/cu.cm.
Nitric acid, density 1.4 g/cu.cm.

Sulphuric acid, density 1.84 g/cu.cm.
Ammonia, solution, density 0.9 g/cu.cm.
Sodium hydroxide, 5 per cent solution.
Potassium iodide, crystalline.

Procedure

Dissolve with heating, a sample of an alloy weighing 0.5 g in a mixture of 5 ml of hydrochloric and 5 ml of nitric acids. Evaporate the solution on a water bath to 2-3 ml, add a small amount of water, 2 ml of sulphuric acid and evaporate again, first on a water bath and then on a hotplate (gentle heating) to fumes of sulphuric acid. Dissolve the residue in 50 ml of water with heating, precipitate the hydroxides with ammonia (for Re alloys with Fe, Cr, V, Ti, and Nb) or sodium hydroxide solution (for Re alloys with Co, Ni and Cu). Evaporate the filtrate to a small volume, neutralize with sulphuric acid to litmus, add sulphuric acid to 5-6 *N* concentration (7 ml of the acid per each 50 ml of the final volume of the solution) and dilute with water in a 50-ml volumetric flask.

Transfer an aliquot (5, 10, or 20 ml, depending on the Re concentration) into a sealed cell for potentiometric titration and pass a nitrogen current through it. Heat the solution to 80°C, add 1 mg of potassium iodide into the cell and titrate with chromium sulphate solution, first adding it in 1-ml portions, and as the point of equivalence is approached, decrease the portion to 0.1 ml. Continue the titration in the presence of the molybdenum ion to the second jump of the potential. The amount of the solution spent for titration of Re is equivalent to the difference in volumes of $CrSO_4$ between the second and the first jump of the potentials. 1 ml of a 0.100 *N* solution of $CrSO_4$ is equivalent to 6.210 mg of Re.

PHOTOMETRIC DETERMINATION OF RHENIUM BY THE THIOCYANIDE METHOD IN MOLYBDENUM AND TUNGSTEN ALLOYS

The method is based on the measurement of the absorption of yellow-orange solutions of the thiocyanide complex of rhenium whose formula is probably $K_2[ReO_2(SCN)_4]$. Rhenium (VII) is reduced with stannous chloride in a hydrochloric acid medium. The absorption maximum of the solutions is at 420 nm. V, Ga, Ge, In, Ir, Co, Ni, Os, Ru, Pb, Tl, Cr, V, and Ce in quantities less than 2 mg do not interfere with the determination. Mo^{VI} and W^{VI} interfere. They are separated chromatographically, the method being based on sorption of the anions of phosphomolybdic and phosphotungstic heteropolyacids from a medium of 2 *M* phosphoric acid by the anion-exchange resin ЭДЭ-10 in the PO_4^{3-} form. Rhenium (VII) is not sorbed in this process.

Reagents

$KReO_4$, standard solution. 1 ml is equivalent to 10 μg of Re.
Potassium thiocyanide, 20 per cent solution.
Stannous chloride, 35 per cent solution. Dissolve 350 g of $SnCl_2 \cdot 2H_2O$ in 200 ml of hydrochloric acid (1 : 1), cool the solution and dilute with boiled water to 1 litre.
Hydrochloric acid, density 1.19 g/cu.cm.
Acid mixture, concentrated nitric and hydrochloric acids (1 : 3).
Ammonia, concentrated solution.
Phosphoric acid, concentrated and 2 *M* solution.
Hydrogen peroxide, 30 per cent solution.

Constructing a Calibration Curve

Place 1, 2, 3, 4 and 5 ml of standard solution of rhenium into 25-ml volumetric flasks, add 10 ml of hydrochloric acid, 4 ml of 2 *M* phosphoric acid into each flask, and dilute the solutions with water to 20 ml. Cool the solutions in a stream of cold water and add 2 ml of potassium thiocyanide solution and 1 ml of stannous chloride solution into the flasks. Mix the solutions thoroughly after adding each new reagent. Add water to the mark and measure the absorption of each solution on an absorptiometer, model ФЭК-М, using a blue optical filter. Construct the calibration curve using the data obtained.

Procedure

Dissolve a sample of alloy weighing 1 g in 30 ml of the acid mixture and evaporate on a water bath two times: first after adding 10-15 ml of hydrochloric acid and then after adding water. Dissolve the dry residue in 10-15 ml of ammonia solution and add concentrated phosphoric acid to an acid reaction. To ensure complete dissolution of tungsten, add 30 per cent hydrogen peroxide solution and boil to destroy its excess. Transfer the solution into a 200-ml volumetric flask and add water to the mark.

Pass 5 ml of the obtained solution through a chromatographic column (20 cm long, 6 cm in dia.) filled with anion-exchange resin ЭДЭ-10 in the PO_4^{3-} form. Next wash the column with a 2 *M* solution of phosphoric acid. Collect 40 ml of the eluate issuing at a rate of one drop every 15 seconds. Place the eluate containing rhenium into a 50- or 100-ml volumetric flask and add 2 *M* H_3PO_4 to the mark.

Take 5 ml of the solution for the photometric determination of rhenium and proceed as for the construction of the calibration curve.

Determine the rhenium content from the calibration curve.

PHOTOMETRIC DETERMINATION OF RHENIUM IN MOLYBDENITE BY THE THIOCYANIDE METHOD

The colour of the molybdenum thiocyanide complex in a 5 *M* solution of hydrochloric acid is unstable (as distinct from the colour of the rhenium thiocyanide complex). In ten minutes the absorption of the molybdenum complex solution decreases sharply to a degree at which molybdenum contained in the quantity of less than

100 μg in 25 ml of solution does not practically have any effect on the determination of 4-175 μg of Re. To increase the sensitivity of determination, $FeCl_3$ should be added to the solution.

Reagents

$KReO_4$, standard solution. 1 ml is equivalent to 20 μg of Re.
Potassium permanganate, crystalline.
Calcium oxide, prepare immediately before the test.
Hydrochloric acid, density 1.19 g/cu.cm.
Ferric chloride, 6 per cent solution.
Potassium thiocyanide, 20 per cent solution.
Stannous chloride, $SnCl_2$ $2H_2O$, 35 per cent solution (see the previous section).

Constructing a Calibration Curve

Place 1, 2, 3, 4 and 5 ml of $KReO_4$ standard solution into separate 25-ml volumetric flasks, add 10 ml of hydrochloric acid, 0.5 ml of $FeCl_3$ and 2 ml of KSCN solution into each flask. Cool the solutions, add 1 ml of $SnCl_2 \cdot 2H_2O$ solution, water to the mark, and allow to stand for 30 minutes. Measure the absorption of the solutions on an absorptiometer with a blue optical filter (a light path, 1 cm). Construct the calibration curve using the data obtained.

Procedure

Mix a sample of molybdenite weighing 0.3-3 g with 0.2 g of $KMnO_4$ in a porcelain crucible. Add 2-4 g of CaO (calcined before the test) and mix again. Cover the mixture with 1.0-2.0 g of calcium oxide and place the crucible in a cold muffle furnace. Raise slowly the temperature in the furnace to 650-700°C and maintain it at this level for two hours. Cool the crucible and leach its contents with 40-50 ml of water for an hour with periodically stirring. Pass the solution through a filter into a 100-ml volumetric flask. Wash the precipitate on the filter 3-4 times with water and add water to the filtrate to make 100 ml.

Transfer 10 ml of the obtained solution into a 25-ml volumetric flask and proceed as for the construction of the calibration curve. Determine the rhenium content from the calibration curve.

Note. Leaching with water dissolve 93-96 per cent of Re, while the main part of molybdenum remains in the precipitate as $CaMoO_4$. 100 ml of the filtrate contains from 0.6 to 1.0 mg of Mo. The molybdenum content in the aliquot decreases to 100 μg. But during the analysis of materials containing about 10^{-4} per cent of Re it is not reasonable to take an aliquot. The molybdenum concentration is therefore decreased by adding $BaCl_2$ solution to the filtrate. 100 ml of the solution contain now 30 μg of Mo and less than 3 μg of W. About 5-6 ml of 10 per cent solution of $BaCl_2 \cdot 2H_2O$ are added to the filtrate and the mixture is evaporated to 35-40 ml. The precipitate is separated on a dense filter and washed two times with small portions of hot water. The filtrate and the washings are collected in a 50-ml volumetric flask. After dilution, 25 ml of the solution are evaporated to 7-8 ml, transferred into a 25-ml volumetric flask, and the procedure is continued as described above.

EXTRACTION-PHOTOMETRIC DETERMINATION OF RHENIUM WITH METHYL VIOLET

The compound of methyl violet with the perrhenate ion at pH 3.5-5 is extracted with toluene. The extract has the absorption maximum at 540 and 600 nm. The molar extinction coefficients are 2.80×10^4 and 3.95×10^4 respectively. Ti, Bi and Sb, as well as a 40-fold quantity of molybdenum, do not interfere with the determination of rhenium. If Mo, W, Ta, Nb are contained in large quantities sodium tartrate is added to the solution. The following anions must be absent: NO_3^-, ClO_4^-, ClO_3^-, CH_3COO^-, SCN^-, I^-, Br^-, MnO_4^-, $PtCl_6^{2-}$, $RuCl_5^{2-}$, RuO_4^{2-}, $OsCl_6^{2-}$, $IrCl_6^{2-}$, $AuCl_4^-$, $Cr_2O_7^{2-}$ and CrO_4^{2-}.

The method can be used for the analysis of raw materials containing much Mo, W, Ta, Nb, Ti and Zr. The detectable minimum of Re is 0.1 µg/ml.

Reagents

Potassium perrhenate, *standard solution*. 1 ml is equivalent to 10 µg of rhenium.
Sodium tartrate, saturated solution.
Methyl violet. 1 ml contains 30 mg of the reagent.
Toluene.
Calcium oxide, solid.
Sodium molybdate, solution. Dissolve 2.522 g of $Na_2MoO_4 \cdot 2H_2O$ in water in a 1-litre volumetric flask.
Hydrochloric acid, diluted 1 : 3.
Hydrogen peroxide, 30 per cent solution.

Constructing a Calibration Curve

Place 1, 2, 3, 4 and 5 ml of the potassium perrhenate standard solution into separating funnels, and add 40 ml of water and 1.25 ml of sodium molybdate solution (if molybdenum-containing material is under examination). Add 5 ml of sodium tartrate and water to 50 ml. Acidify the solutions with hydrochloric acid to pH 4-4.6, add 14 drops of methyl violet and extract the coloured rhenium compound 4-5 times with 4-5 ml portions of toluene (the last portion should be colourless). Collect the extracts in a 50-ml volumetric flask and add toluene to the mark.

Measure the absorption of the extracts by a model ФЭК-М absorptiometer with a green optical filter. Construct the calibration curve using the data obtained.

Procedure

Grind thoroughly a sample weighing 0.05-0.5 g (molybdenum glance, ferromolybdenum, molybdenum concentrate) containing 0.01-0.001 per cent of Re and mix with 3-5 weights of calcium oxide in a nickel crucible. Sinter the mixture in a muffle furnace at 700-750°C for 3.5-4 hours, then cool and leach with water containing 1 ml of 30 per cent hydrogen peroxide with heating on a hotplate for 5-10 minutes to gentle boiling. Pass the hot solution through a white ribbon filter and rinse the beaker walls and the filter several times with hot water. Evaporate the filtrate in a porcelain dish to 30 ml. Cool the solution, filter again, collect the filtrate in a separating funnel and proceed as for the construction of the calibration curve, except that do not add molybdate solution.

Determine the rhenium content from the calibration curve.

EXTRACTION-PHOTOMETRIC DETERMINATION OF RHENIUM WITH THIOOXINE

Thiooxine reacts with the perrhenate ion in a strong acid medium (8-11 *N* HCl) to form a compound extractable by chloroform. The maximum absorption of the extract is at 438 nm; the molar extinction coefficient is 8.5×10^3. The Bouguer-Lambert-Beer law holds for the rhenium concentrations in the range from 1 to 40 μg in 1 ml of chloroform.

Au, Pt (over 0.7 mg), Pd, Ru (over 1 mg), Os (over 0.15 mg), Rh (over 2 mg), Ir (over 10 mg) interfere with the determination of rhenium in a medium of 9-10 *N* HCl. Mo (100 mg), W (10 mg), As^{V} (17 mg), Se and Te (3-5 mg), Cu (4-5 mg), Sn^{II} ($\leqslant$ 5 mg), Sn^{IV} ($\leqslant$ 50 mg) and large amounts of Cr, Ni, Co, Zn, Cd, In, Sb, Bi, Mn, U, Pb, Tl^{I}, Ge, Th, Nb, Ta, Ga, Al, Zr, and rare earths do not interfere. The following anions do not interfere: Br^-, I^-, F^-, SO_4^{2-}, PO_4^{3-} and ClO_4^-. The ions NO_3^- and AsO_3^{3-} must be absent.

Reagents

Potassium perrhenate, standard solution. 1 ml is equivalent to 20 μg of rhenium.
Thiooxine hydrochloride, 6 per cent solution in concentrated hydrochloric acid.
Chloroform.
Hydrochloric acid, density 1.19 g/cu.cm, and 9 *N* solution.

Constructing a Calibration Curve

Place 1, 2, 3, 4 and 5 ml of the $KReO_4$ standard solution into 100-ml Erlenmeyer flasks, add 10 ml of hydrochloric acid, density 1.19 g/cu.cm, and 5 ml of thiooxine hydrochloride solution into each flask. Heat on a boiling bath for three minutes (not more), cool quickly in a stream of water and transfer the solution into separating funnels. Add 10 ml of chloroform and shake. Allow the liquids to separate, and pass the chloroform extract through a layer of dry glass wool into a cell with a light path of 1 cm. Measure the absorption of the extract by an absorptiometer with a blue optical filter. Construct the calibration curve using the data obtained.

Procedure

Treat the test solution as for the construction of the calibration curve except that if tervalent iron is present, wash the extract with a 9 *N* solution of HCl (22 ml of the acid containing 2.5 ml of the reagent solution). Determine the rhenium concentration from the calibration curve.

DIFFERENTIAL-SPECTROPHOTOMETRIC DETERMINATION OF RHENIUM WITH THIOCARBAMIDE

Thiocarbamide reacts with rhenium (V) to form a soluble coloured compound. Its solutions obey the Bouguer-Lambert-Beer law in the range of rhenium concentrations from 5 to 200 μg/ml. The maximum absorption of the solutions is at 390 nm. The optimum conditions for the formation of the complex are as follows: the concentration of hydrochloric acid, 2.5-5 *N*; the concentration of the reductant, stannous chloride, 0.8-1 per cent; and of thiocarbamide, 1 per cent. The colour develops in 20 minutes and persists for over 5 hours.

Rhenium can be determined in the presence of 50 μg of *Mo* and 100 μg of W. Cd, Bi, Hg, Se, Te and As interfere with the determination. The anions of hydrofluoric, citric, tartaric, and oxalic acid do not interfere provided their concentration does not exceed 0.1 *N*. The interfering effect of Sb^{III} can be removed by adding fluorides.

A solution containing the sought element in high concentration and all the necessary reagents is used as a blank solution in differential spectrophotometric determination. The method is used for the analysis of objects containing rhenium in large quantity.

Reagents

Potassium perrhenate solution. 1 ml contains 10 mg of Re. Place 1.00 g of pure rhenium metal in a beaker and dissolve in 25 ml of a 5 per cent nitric acid with slightly heating. Transfer the solution into a 100-ml volumetric flask and add water to the mark.

Thiocarbamide, 5 per cent solution.

Stannous chloride, 20 per cent solution in concentrated hydrochloric acid.

Hydrochloric acid, density 1.19 g/cu.cm and diluted 1 : 1.

Sodium hydroxide, solid.

Hydrofluoric acid, concentrated, 38-40 per cent solution.

Boric acid, crystalline.

Hydrogen peroxide, 3 per cent solution.

Sodium nitrate, crystalline.

Procedure

Dissolve alloys containing to 30 per cent of Re in a mixture of acids. To that end, place 50-100 mg of alloy in a 150-ml beaker, add 10 ml of hydrochloric (1 : 1) and 4 ml of HF, and dissolve in the cold. Add 4 g of boric acid to the solution and boil until the solution is almost completely colourless, adding water periodically so that the solution volume is 50-80 ml. Cool the solution, transfer into a 50-100 ml volumetric flask and add water to the mark.

Decompose alloys containing 30-40 per cent of Re by alkali fusion. To that end, place 50-100 mg of the alloy in a nickel or a silver crucible, add $NaNO_3$ (on the tip of a spatula), 2 g of NaOH, and fuse in a muffle furnace at 400-500°C to obtain a clear melt. Cool the fused material, add 20-40 ml of hot water, heat in a 150-ml beaker, add 20-30 ml of hydrochloric acid (1 : 1) to prepare a clear solution, cool it. transfer in a 50- or 100-ml volumetric flask and add water to the mark.

Transfer an aliquot into a 50-ml volumetric flask, add 10 ml of concentrated hydrochloric acid, 10 ml of thiocarbamide and 2 ml of stannous chloride solution. Add water to the mark and mix. Allow the solution to stand for 35-40 minutes and measure its absorption at 390 nm against a blank solution on the model СФ-4 spectrophotometer containing all the reagents and 2 mg of Re.

Calculation

Calculate the c_x from the formula:

$$c_x = c_0 + D_x F$$

where c_0 is the concentration of rhenium in the blank solution, mg/50 ml; D_x is the absorption of the solution; and F is a constant factor.

To calculate the constant factor F, measure the absorption of a series of solutions with Re concentration varying from 2.0 to 2.7 mg (gradient 0.1 mg) in 50 ml of solution. Calculate the factor using the formula:

$$F = \frac{\Delta c}{D}\ ;\ \Delta c = c_1 - c_0$$

where c_1 is the concentration of rhenium in the standard series solutions from 2.0 to 2.7 mg in 50 ml; D is the absorption of the solution with the rhenium concentration of c_1 measured with reference to the solution with the rhenium concentration of c_0.

SPECTROPHOTOMETRIC DETERMINATION OF RHENIUM WITH THIOGLYCOLIC ACID

In the presence of $SnCl_2$, thioglycolic acid reacts with Re^{VII} to form a complex with the component ratio of 1 : 2. The pink complex absorbs maximum at 320-350 nm, the molar extinction coefficient at 320 nm being 3.6×10^3. The complex is formed in a wide range of pH (from pH 3 to 4 N H_2SO_4 or HNO_3). The maximum intensity of the colour is at a ten-fold molar excess of thioglycolic acid and 40-fold excess of $SnCl_2$. The maximum absorption develops in 20-30 minutes and persists at this level for 24 hours. The Bouguer-Lambert-Beer law holds for the solutions with Re concentrations in the range from 0 to 700 μg in 25 ml. K, Na, Mg, Al, Co, Ni, Cr, Ge, Zn, In, Ga, Tl, Cd, small quantities of Mn, Fe, Cu, Mo^{VI} (2.5-fold quantities), UO_2^{2+} and the citrate, oxalate, tartrate and acetate ions do not interfere with the determination. The ferric ion can be masked by ascorbic acid.

Reagents

Rhenium, standard solution. 1 ml is equivalent to 50 μg of rhenium.
Thioglycolic acid, 0.01 N solution.
Stannous chloride, 0.1 M solution.
Sulphuric acid, 10 N solution.

Constructing a Calibration Curve

Place 50, 100, 150, 200 and 250 μg of rhenium (standard solution) into 25-ml volumetric flasks, and add 2 ml of sulphuric acid, 1 ml of thioglycolic acid and 1 ml of stannous chloride into each flask. Mix thoroughly and add water to the mark. Allow the solutions to stand for 30 minutes and measure their absorption on a model CФ-4 spectrophotometer at 320-350 nm using a blank solution as the standard.

Procedure

Place an aliquot of the test solution containing 60-200 μg of rhenium into a 25-ml volumetric flask and proceed as for the construction of the calibration curve.

Determine the rhenium content from the calibration curve.

EXTRACTION-PHOTOMETRIC DETERMINATION OF RHENIUM WITH THIOGLYCOLIC ACID

The ionic association of the complex anion of Re with thioglycolic acid and the cation of diantipyrylmethane is readily extractable by a mixture of isoamyl alcohol and chloroform from a solution of 3.2-8 *N* HNO_3. The absorption maximum of the pink extract is at 460 nm, the molar extinction coefficient being 1.7×10^4.

Reagents

Rhenium, standard solution. 1 ml is equivalent to 10 μg of Re.
Thioglycolic acid, 0.1 *M* solution.
Stannous chloride, 10 per cent solution in HCl (1 : 4).
Mixture of isoamyl alcohol and chloroform (1 : 1).
Diantipyrylmethane. 0.2 *M* solution in hydrochloric acid.
Nitric acid, 10 *N* solution.

Constructing a Calibration Curve

Place 10, 20, 30, 40 and 50 μg of the Re standard solution into separating funnels, add 10 ml of HNO_3, 3 ml of thioglycolic acid and 3 ml of stannous chloride solution and keep for two hours. Add 3 ml of diantipyrylmethane solution, and extract rhenium for 1-2 minutes with 5 ml of the extracting mixture. Measure the absorption of the extract at 460 nm against a blank extract and construct the calibration curve ($l = 0.5$ cm).

Procedure

Determine the rhenium content of an aliquot in the same conditions as for the construction of the calibration curve. Find the rhenium content from the calibration curve.

EXTRACTION-PHOTOMETRIC DETERMINATION OF RHENIUM IN ORES WITH BIS(4'-METHYLBENZYLAMINOPHENYL)-ANTIPYRYLCARBINOL

The method is based on the reaction of ReO_4^- with the dye of the antipyryle series, bis(4'-methylbenzylaminophenyl)-antipyrylcarbinol, with the formation of the ionic association extractable by benzene from a 0.3-1.5 *M* phosphoric acid solution. The molar extinction coefficient of the extract is 7.55×10^4. 100 μg of Mo, 300 μg of W; 1000 μg of Cu, 80 μg of V, 50 mg of sulphate, tartrate, oxalate, citrate, ethylenediaminetetraacetate, Ca, Ba, Fe, Co, Ni, Al, tartrate, Nb and Ta do not interfere with the determination of 10 μg of Re. The ions Cl^-, SCN^-, $AuCl_4^-$, $SnCl_3^{2-}$, $Ru(OH)Cl_5^{2-}$ interfere

Reagents

Rhenium, standard solution. 1 ml is equivalent to 10 μg of Re.
Bis(4'-methylbenzylaminophenyl)-antipyrylcarbinol, 0.05 per cent solution.
Phosphoric acid, 6 *M* solution.
Benzene.
Calcium oxide.
Hydrogen peroxide, 30 per cent solution.

Constructing a Calibration Curve

Place from 1 to 10 μg of Re into separating funnels, add 2 ml of phosphoric acid and water to 8 ml, and finally add 2 ml of the reagent and extract with 5 ml of benzene for two minutes. Measure the absorption of the benzene extracts at 580 nm in a cell with a light path of 0.5 cm against a blank solution. Construct the calibration curve using the data obtained.

Procedure

Grind a sample of ore weighing 0.5-2.0 g, place it in a porcelain crucible and mix with 3-4 g of CaO. Place the crucible into a muffle furnace and keep for 2.5 hours at a temperature of 600-700°C. Cool the sintered material, leach with hot water in a 100-150 ml beaker and add, drop by drop, 1.0 ml of hydrogen peroxide solution. Boil for 15-20 minutes using a glass rod to break lumps. Separate the precipitate on a filter (with a water-jet ejector) and wash several times with hot water. Collect the filtrate and the washings, evaporate, and transfer into a 25- or 50-ml volumetric flask. Add water to the mark. Choose the aliquot size depending on the rhenium content, add phosphoric acid to 8 ml, and continue as for the construction of the calibration curve. Determine the rhenium content from the calibration curve.

PHOTOMETRIC DETERMINATION OF RHENIUM BY CATALYTIC (KINETIC) METHOD

The method is based on the ability of rhenium to catalyze (accelerate) the reduction of sodium tellurate to tellurinium metal by stannous chloride. The liberated tellurium, in the presence of a protective colloid (gelatin), colours the solution brown-black. Cu, Hg, Ge, Sn, Pb, Sb, Bi, As, Ru or Os, contained in quantity over 100 μg do not interfere with the determination of 0.1-0.001 μg of Re. The interfering effect of Mo and W can be removed by binding them into a complex with tartaric acid. The method can be used for the determination of rhenium in rock after its separation as sulphide.

Reagents

Potassium perrhenate, standard solutions. 1 ml is equivalent to 0.05 or 0.005 μg of rhenium.

Reagent mixture. Mix 5 ml of a 0.5 per cent solution of sodium tellurate, 2 ml of tartaric acid solution (45 g in 100 ml), 1.5 ml of a 0.5 per cent solution of gelatin and a solution of $SnCl_2 \cdot 2H_2O$ obtained by dissolving 10 g of tin metal in 25 ml of concentrated hydrochloric acid with heating. Prepare the mixture immediately before the analysis.

Procedure

Place 1 ml of the test solution into three calibrated test tubes, add 0.05 μg of Re (standard solution) into one test tube, 0.005 μg of Re into another, and 1 ml of distilled water into the third test tube and add 1.0 ml of the reagent mixture into each of them. Mix the solutions and allow to stand for from 1-2 to 16-18 hours until the test solution develops colour of sufficient intensity. Measure its absorption on an absorptiometer with a blue optical filter using one of the standard solutions (in which the colour is more similar to that of the test solution) as a reference solution.

Calculation

Calculate the rhenium content, c_x, using the formula:

$$c_x = \frac{c_a D_x}{D_{x+a} - D_x}$$

where c_a is the quantity of Re added to the test solution; D_x is the absorption of the solution; D_{x+a} is the absorption of the solution containing the additive of Re.

DIFFERENTIAL-PHOTOMETRIC DETERMINATION OF RHENIUM IN ITS ALLOYS WITH NIOBIUM AND HAFNIUM

Rhenium reacts with dimethyl glyoxime in an acid medium, in the presence of stannous chloride as a reductant, to form a soluble compound with the absorption maximum at 440 nm (the molar extinction coefficient, 6.9×10^3). The components react in the ratio of 1 : 1. The composition of the complex varies depending on excess of stannous chloride and the time of standing of the solutions. The method is recommended for the determination of 5-50 per cent of rhenium in binary alloys with niobium or hafnium. Sulphuric acid is used instead of hydrochloric acid to dissolve the alloys. The optimum acidity is 1-2 *N* H_2SO_4. Hydrolysis of niobium is precluded by adding hydrogen peroxide. The analysis of the Hf-Re alloy continues for two hours; of Nb-Re, three hours. The relative standard deviation is, 0.005 for the rhenium content of 30-50 per cent and 0.027-0.019 for the rhenium content of 10-50 per cent.

Reagents

Rhenium, standard solutions. 1 ml is equivalent to 1 mg and 0.1 mg of rhenium.
Sulphuric acid, density 1.84 g/cu.cm and diluted 1 : 1.
Ammonium sulphate, crystalline.
Hydrogen peroxide, 30 per cent solution.
Dimethyl glyoxime, 1 per cent solution in ethyl alcohol.
Stannous chloride, 10 per cent solution in 2 *N* sulphuric acid.

Calculating Factor *F*

Place 1 ml of the standard rhenium solution containing 1 mg/ml of Re into 50-ml volumetric flasks, and add from 0 to 5 ml of standard rhenium solution containing 0.1 mg/ml of rhenium. Add 3 ml of sulphuric acid, (1 : 1), 15 ml of water, 5 ml of dimethyl glyoxime, 4 ml of stannous chloride solution, and dilute with water to the mark. Allow the solutions to stand for two hours and measure their absorption at 440 nm ($l = 1$ cm) using the first solution as a reference one. Calculate the factor F using the following equation:

$$F = \frac{\Delta c}{D_x}, \ \Delta c = c_x - c_0$$

where c_0 is the rhenium concentration in the solution which is used as the standard; c_x is the rhenium concentration in the other solutions in the series; D_x is the absorption of the solution in the series.

Procedure

Dissolve a sample of the alloy weighing 0.100-0.200 g in 3 ml of sulphuric acid, density 1.84 g/cu.cm and 0.3 g of ammonium sulphate with heating. Dissolve the melt in 30-40 ml of water containing 2 ml of hydrogen peroxide. Transfer the solution into a 250-ml volumetric flask (for the determination of rhenium contained in the concentration of 30-40 per cent) or into a 200-ml flask (if the rhenium content is 50 per cent) and add water to the mark. Transfer an aliquot containing 1.1-1.4 mg of rhenium into a 50-ml volumetric flask and proceed as for the calculation of the factor F. Find the rhenium content from the formula:

$$c_x = c_0 + D_x F$$

POLAROGRAPHIC DETERMINATION OF RHENIUM IN ITS ALLOYS WITH MOLYBDENUM

Rhenium is passed into solution and simultaneously separated from molybdenum by sintering the sample with calcium oxide. Rhenium is dissolved as perrhenate, while the greater part of molybdenum is removed as a sparingly soluble $CaMoO_4$. Rhenium is determined in the obtained solution polarographically at the potential from —0.3 to —0.4 V against the background of 5 *N* sulphuric acid.

Reagents

Calcium oxide, solid.
Ammonium persulphate, 10 per cent solution.
Sulphuric acid, 5 *N* solution.

Procedure

Mix a sample of alloy weighing 0.1 g with three weights of calcium oxide and sinter in a muffle furnace at 700-750°C. Cool the melt, transfer in a beaker containing 50 ml of water, remove the crucible from the beaker, and rinse. Add 5 ml of ammonium persulphate solution and heat to boiling. Separate the precipitate on a Büchner funnel and wash 2-3 times with hot water. Transfer the filtrate into a 100-ml volumetric flask and add water to the mark. Transfer an aliquot (10 ml) into a 100-ml volumetric flask and add sulphuric acid to the mark. Place the solution into an electrolyzer, pass nitrogen to remove oxygen; and carry out polarography at the potential from —0.3 to —0.4 V using a saturated calomel electrode.

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Gallium

Gallium, Ga, has the positive valency of 3 (predominantly). The compounds of divalent gallium, e.g. $GaCl_2$, are unstable.

The standard electrode potentials in the aqueous solutions at 25 °C (with reference to the standard hydrogen electrode) are as follows:

$$\begin{array}{ll} Ga \rightleftharpoons Ga^{3+} + 3e^- & -0.529 \text{ V} \\ Ga + 3H_2O \rightleftharpoons Ga(OH)_3 + 3H^+ + 3e & -0.419 \text{ V} \\ Ga + 3H_2O \rightleftharpoons GaO_3^{3-} + 6H^+ + 3e & +0.319 \text{ V} \end{array}$$

Ga^{3+} ions are colourless and their properties are similar to those of Al^{3+} and Zn^{2+}.

Gallium hydroxide, $Ga(OH)_3$, is colourless and has amphoteric properties; $pL_{Ga(OH)_3} = 35\text{-}36.5$. The hydroxide $Ga(OH)_3$ has more marked amphoteric properties than the hydroxide of indium, $In(OH)_3$. In contrast to $Al(OH)_3$, it is soluble in concentrated solution of ammonia (it has a more acid character); when boiled, gallium hydroxide re-precipitates. Practically, pure hydroxide can be obtained by adding 0.1 *M* solution of NaOH to a 0.01 *M* gallium chloride solution at room temperature. A colloidal solution is first formed at pH about 6.7 (when 2.9 equivalent weights of the alkali have been added) and the coagulation becomes vivid. And conversely, when a 0.1 *M* solution of NaOH is added to a 0.005 *M* solution of gallium sulphate, a precipitate of basic gallium sulphate is formed, which is fully coagulated at pH 4.5-5.0 (when 2.5-2.6 equivalent weights of NaOH have been added). When four equivalent weights of NaOH are added at pH 9.7, the substances precipitated by NaOH from the solutions of chloride or sulphate, are dissolved with the formation of sodium gallate which can probably be described by the formula $Na[GaO_2]$ or $Na[Ga(OH)_4]$.

Gallium chloride, in the form of $HGaCl_4$, is extracted from a 6 *N* solution of HCl by ether. This reaction is used for the separation of gallium from aluminium and many other elements. Fe^{III}, Au^{III}, Sb^{III}, Tl^{III}, As^{III}, Ge^{IV}, V^{V} and Mo^{VI} are extracted (partly or completely) together with gallium. Extraction is used for the separation of gallium from raw materials [1].

The sulphide Ga_2S_3 is easily converted to $Ga(OH)_3$ in the presence of water.

Potassium ferrocyanide, $K_4[Fe(CN)_6]$, precipitates white $Ga_4[Fe(CN)_6]_3$ even from strong acid solutions of gallium salts (33 per cent HCl). Indium reacts in the same conditions to form $KIn_5[Fe(CN)_6]_4$.

The azo compounds containing two OH groups in the ortho position to the azo group react with the gallium ion to form coloured and sometimes fluorescing compounds. These react also with the ions In^{3+}, Y^{3+}, Th^{4+}, Zn^{2+}, Ce^{3+}, Al^{3+}, Sc^{3+}, La^{3+}, Fe^{3+}, etc. [2]. 2,2′-Hydroxy-4-sulphonaphthalene azo-naphthalene induces an orange fluorescence in gallium salt solutions in the ultraviolet light [3]. Lumogallion reacts similarly. It is used for the fluirometric determination of gallium [4]. The reagent was used for the analysis of semiconductor materials.

Gallion (0.01 per cent aqueous solution) reacts with the gallium ions in a weak acid medium to form a blue compound. The optimum pH is 2.4-3.4. The absorption maximum is at 600 nm. The sensitivity of the method at pH 3.2 is 0.2 µg of Ga in 5 ml of solution. The selectivity of the reagent is not high (the ions of iron and other elements interfere). The reagent is used for the photometric determination of gallium after its separation from most accompanying elements [5, 6].

Sodium diethyldithiocarbamate precipitates the gallium ion at pH 1.5-6. The white precipitate is soluble in ethyl acetate [7]. Gallium diethyldithiocarbamate is less stable than indium diethyldithiocarbamate. This is used for the separation of gallium from indium [8].

Gallium 8-hydroxyquinolinate is extractable with chloroform at pH 2.6. The chloroform extract fluoresces in the ultraviolet light. This phenomenon underlies a highly sensitive method for the determination of gallium, for example in bauxites [9]. But the selectivity of the method is low ($pL_{GaOx_3} = 40.8$).

Morin induces fluorescence in solution of salts of gallium and indium as it does in aluminium salts. The difference resides in that the fluorescence of gallium solutions is not extinguished by the addition of fluoroborate, and of the indium solution, by NaF. This makes it possible to detect the ions of gallium and indium in the presence of Al^{3+} [10]. Morin is used as an indicator in complexometric determination of gallium.

Pyridine azo-compounds can also be used as reagents for gallium. For example, 1(2-pyridylazo)-2-naphthol reacts with the gallium ion in an acid medium (pH 3.2) to form a crimson compound with the molar ratio of 1 : 1 (the absorption maximum at 550 nm). The compound is difficultly soluble in water but readily soluble in methanol, ethanol, higher alcohols and carbon tetrachloride. The molar extinction coefficient [11] is 2.2×10^4 (solution in 50 per cent ethanol). Its soluble analogue, 1-(2-pyridylazo)resorcinol, is used as a complexometric indicator for titration of gallium ions [12].

7-(5-Sulpho-2-naphthylazo)-8-quinolinol-5-sulphonic acid, 7-(4-sulpho-1-naphthylazo)-8-quinolinol-5-sulphonic acid, 7-(4,8-disulpho-2-naphthylazo)-8-quinolinol-5-sulphonic acid, 7-(5,7-disulpho-

2-naphthylazo)-8-quinolinol-5-sulphonic acid and 7-(1-naphthylazo)-8-quinolinol-5-sulphonic acid [13, 14] react with the gallium ion in a weak acid medium in the molar ratio of 1 : 1. The molar extinction coefficients of the compounds formed are 2.1×10^4, 1.9×10^4, 1.6×10^4, 1.6×10^4 and 1.6×10^4 respectively. The equilibrium constants of the reactions of their formation are 0.9×10^2, 3.1×10^2, 8.4×10^2, 3.6×10^2 and 1.0×10^2. All these azo compounds on the basis of 8-quinolinol-5-sulphonic acid and sulpho-derivatives of naphthylamine are good indicators for direct complexometric titration of the gallium ion at pH 2.2 and over. But the most selective of them is 7-(4-sulpho-1-naphthylazo)8-quinolinol-5-sulphonic acid which can be used to determine gallium in the presence of sufficiently large quantities of ions of the alkaline earths, zinc, cadmium, manganese, and aluminium.

The azo compounds of the thiazole series react with the gallium ion to form intensely coloured compounds suitable for photometric determination of gallium [15].

Cupferron precipitates Ga^{III} from 10-20 per cent sulphuric acid like it does Fe^{III}, Nb^{V}, Ta^{V}, Ti^{IV}, Zr^{IV}, Ge^{IV}, and V^{V}. This reagent can be used to separate Ga from Al and Zn. The precipitate is calcined to Ga_2O_3 [16].

The basic triphenylmethane dyes and their antipyrine analogues react with the $GaCl_4^-$ ion in a strong hydrochloric acid medium to form intensely coloured compounds extractable with some organic solvents. Excess dye remains in the aqueous phase in some cases. This phenomenon has been used in the highly sensitive photometric methods for the determination of gallium after its separation from the interfering elements.

Rhodamine S is the most widely used basic triphenylmethane dye [17-22]. Butyl rhodamine B is more sensitive. It is used for the photometric determination of gallium in various materials [32]. In a hydrochloric acid solution (6-6.5 *N*) it reacts with gallium to form a compound extractable with benzene and toluene. The extract is pink-violet and absorbs maximum at 565 nm. The molar extinction coefficient is 9.00×10^4 [23]. The ions of Au^{III}, Fe^{III}, Sb^{V} and Ti^{III} are reduced by $TiCl_3$.

The chlorogallate ions $GaCl_4^-$ react in a strong hydrochloric acid solution with various antipyrine dyes [24]. Bis-(*p*-methylbenzylaminophenyl)-antipyrylcarbinol is a sufficiently sensitive and selective reagent for the spectrophotometric determination of gallium.

Diantipyrylpropylmethane precipitates gallium quantitatively from 5.5-6 *N* solutions of hydrochloric acid in the form of the compound $C_{25}H_{30}O_2N_4 \cdot HGACl_4$. This compound meets the requirements for the weighing form. The determination of gallium can be ended gravimetrically, by weighing the precipitate $C_{26}H_{30}O_2N_4 \cdot \times HGaCl_4$ or by complexometric titration of gallium in the precipitate in the presence of 1-(2-pyridylazo)-2-naphthol. Many ions do not interfere with the precipitation of gallium in the form of the above compound [25].

Diantipyrylmethane does not precipitate the gallium ion quantitatively from hydrochloric acid solutions. The composition of the isolated compound [26] is described by the formula $C_{23}H_{24}O_2N_4 \times \times HGaCl_4$.

Diantipyrylphenylmethane precipitates gallium quantitatively from solutions containing the chloride, bromide or iodide ions. The precipitates are readily soluble in chloroform. Diantipyrylphenylmethane can be used for the isolation of small quantities of gallium by extraction [26].

Tartrates and oxalates react with the gallium ion at pH 9-11 to form stable complex ions $[Ga(C_4H_4O_6)_3]^{3-}$ and $[Ga(C_2O_4)_3]^{3-}$. They are used to separate gallium in ammonia solutions from $[Zn(NH_3)_4]^{2+}$ on cation-exchange resins in the NH_4^+ form [27].

Gallium is detected by the spectral method by excitation in the spark. The spectrum has two intense violet lines at 294.4 and 287.4 nm. Volatile gallium salts colour the flame violet and the spectrum has a line at 417.2 nm.

The polarographic methods for the determination of gallium are also promising [28-30].

The literature contains reviews of the methods for the detection and determination of gallium [31, 32].

GRAVIMETRIC DETERMINATION OF GALLIUM WITH CUPFERRON

The method is based on the precipitation of gallium by cupferron from sulphuric acid solution in the form of the cupferronate with subsequent calcining and weighing as Ga_2O_3. The method is used to separate Ga from In, Fe, Al and the lanthanides.

Reagents

Cupferron, 6 per cent solution prepared before the analysis.
Sulphuric acid, diluted 1 : 1 and 5 per cent solution.

Procedure

Neutralize a cold sulphuric acid solution of the sample containing less than 0.1 g of Ga with ammonia, acidify with 10 ml of sulphuric acid (1 : 1), add cold water to 200 ml and add, drop by drop with stirring, a solution of cupferron until the precipitate coagulates. Separate the precipitate on a red ribbon filter, wash with 5 per cent sulphuric acid containing a small quantity of cupferron. If chlorides are present, they should be removed by washing (to preclude the loss of gallium on calcining in the form of an easily volatile chloride). Char the filter and the precipitate carefully on a low flame, then raise the temperature to burn out the cone and finally calcine at 1000-1300 °C to constant mass. Gallium oxide calcined at 1000 °C is hygroscopic and should therefore be weighed immediately in the crucible with a tightly fitting lid.

ISOLATION AND COMPLEXOMETRIC DETERMINATION OF GALLIUM

The method is based on the precipitation of gallium by diantipyrylpropylmethane from a 6 N hydrochloric acid solution in the form of $C_{26}H_{30}O_2N_4 \cdot HGaCl_4$. The precipitate is dissolved in water and gallium is titrated complexometrically in the presence of 1-(2-pyridylazo)-2-naphthol. The method is used for the separation of Ga from Zn, Cd, In, Cu, Al, Ni, Mn, Mg, Co, and Bi. Fe^{3+}, Tl^{3+}, Sb^{V} interfere with the determination. The former two elements are reduced before precipitation of gallium while Sb^{V} is masked with tartaric acid.

Reagents

Diantipyrylpropylmethane, 1 per cent solution in acetic acid (1 : 10).
Hydrochloric acid, density 1.19 g/cu.cm.
1-(2-Pyridylazo)-2-naphthol, 0.1 per cent solution in methanol.
Washing solution, containing 0.05 per cent of diantipyrylpropylmethane in a 6 M solution of hydrochloric acid.
EDTA, 0.05 M solution.
Ammonium acetate, crystalline.

Procedure

Add diantipyrylpropylmethane to the solution of the sample (1 ml of the solution per 1 mg of gallium). Add an equal volume of hydrochloric acid, cool the solution and separate the precipitate on a filter. Wash the precipitate several times with the washing solution. Dissolve the precipitate on the filter in 50-70 ml of water and wash the filter thoroughly with a few portions of water. Add ammonium acetate to the solution to adjust the pH to 4-5, heat to 70-80 °C, add a few drops of 1-(2-pyridylazo)-2-naphthol solution and titrate slowly with EDTA solution until the red solution turns yellow. Allow the solution to stand for 5 minutes (the red colour restores) and continue the titration until the red solution turns yellow again. Wait for another five minutes (with heating from time to time) and continue with the titration until the yellow colour becomes stable.

COMPLEXOMETRIC DETERMINATION OF GALLIUM

EDTA reacts with the gallium ion to form a stable complex compound ($pK = 20.26 \pm 0.1$) and gallium can therefore be determined in an acid medium (pH 2.0-3.0) in the presence of 7-(1-naphthylazo)-8-hydroxyquinoline-5-sulphonic acid or 7-(4-sulpho-1-naphthylazo)-8-quinolinol-5-sulphonic acid. At the point of equivalence, the yellow colour sharply changes to violet (the colour of the indicator in an acid medium). Gallium can be determined in the presence of large quantities of Mg, Ca, Ba, Zn, Mn, Cd, and Al (provided the latter is bound by NaF). The ions Fe^{3+}, In^{3+}, Tl^{3+}, Bi^{3+}, Cu^{2+}, Ni^{2+} and Co^{2+} interfere with the determination.

Reagents

7-(1-Naphthylazo)-8-quinolinol-5-sulphonic acid, 0.1 per cent solution in dimethyl formamide, or *7-(4-sulpho-1-naphthylazo)-8-quinolinol-5-sulphonic acid*, 0.1 per cent aqueous solution.
EDTA, 0.01 *M* solution.
Ammonia, 1 *N* solution.
Biphthalate buffer solution, pH 2.2-2.6.

Procedure

Adjust the pH of the solution to 2.0-2.6 by ammonia, add 15-20 ml of the biphthalate buffer solution, heat to 70-80 °C, and a few drops of the indicator and titrate with EDTA solution until the yellow colour changes to violet.

COMPLEXOMETRIC DETERMINATION OF GALLIUM WITH AMMONIUM SARCOSINEDITHIOCARBAMATE IN THE PRESENCE OF INDIUM, BISMUTH AND CADMIUM

Ammonium sarcosinedithiocarbamate is used to mask indium in complexometric titration. A fifty-fold quantity of bismuth does not interfere with the determination, provided the titration is carried out with a reference substance to compensate for the effect of the yellow colour of the bismuth complex with the reagent on the colour change of the indicator, 1(2-pyridylazo)resorcinol, at the end point of the titration.

Reagents

EDTA, 0.01 *M* solution.
Ammonium sarcosinedithiocarbamate, 1 per cent solution.
1-(2-Pyridylazo)resorcinol (PAR), 0.1 per cent solution.
Acetic acid, 1 *N* solution.
Ammonia, 25 per cent solution.

Procedure

Neutralize the solution with ammonia until turbidity develops, which can be dissolved by adding a few drops of acetic acid. Check the pH by a universal indicator paper (the pH should be 2-3), add the sarcosinedithiocarbamate in the quantity 25 times exceeding that of the interfering ion, 2-3 drops of PAR, and titrate with EDTA until the red solution turns pure yellow.

EXTRACTION-PHOTOMETRIC DETERMINATION OF GALLIUM IN BAUXITES WITH BUTYLRHODAMINE B

Gallium forms a coloured association with butylrhodamine B which is extractable with toluene. The absorption maximum of butylrhodamine B chlorogallate extract is at 565 nm. The detectable minimum is 0.005 μg of Ga in millilitre. The molar extinction coefficient is 9.0×10^4. The optimum acidity of the aqueous phase during extraction of the association with toluene is 6-6.5 *N* HCl. The Bouguer-Lambert-Beer law holds in the range of gallium concentrations from 0.005 to 2 μg/ml. Au^{III}, Fe^{III}, Sb^{V}, and Tl^{III} interfere and their effect is removed by adding titanium (III). If aluminium is present in large quantity, it should be separated by extraction of gallium with amyl acetate from a 6 *N* solution of HCl.

Reagents

Gallium salt, standard solution. 1 ml is equivalent to 10 μg of Ga.
Butyl rhodamine B, 0.1 per cent solution.
Hydrochloric acid, 6 *N* solution.
Titanium chloride, 20 per cent solution.
Amyl acetate.
Toluene.
Hydrogen peroxide.
Sodium hydroxide, crystalline.

Constructing a Calibration Curve

Place the standard gallium solution into separating funnels in quantities containing 2, 4, 6, 8 and 10 μg of Ga. Add 10 ml of hydrochloric acid and 2 ml of titanium trichloride into each funnel, shake and add 1 ml of butyl rhodamine B. Extract for two minutes with 10 ml of toluene. Separate the organic layers and measure their absorption at 565 nm in a cell with a light path of 1 cm, using a blank extract as the reference solution. Construct the calibration curve using the data obtained.

Procedure

Fuse a sample weighing from 0.1 to 0.5 g depending on the gallium concentration with 1-1.5 g of NaOH and 0.5 g of Na_2O_2 in a corundum crucible at a temperature of 600-650 °C. Leach the fused material with hot water and dissolve the precipitate of the hydroxides in hydrochloric acid. Evaporate the solution on a water bath until dry salts are obtained. Dissolve the residue in hydrochloric acid and transfer the solution into a separating funnel. Extract gallium three times with amyl acetate in the presence of titanium chloride, each time shaking for 90-120 seconds. Wash the extract three times with HCl and re-extract gallium three times with water. Evaporate the aqueous solutions on a water bath to prepare dry salts, dissolve the residue in 5 ml of hydrochloric acid and transfer into a 25-ml separating funnel. Rinse the porcelain dish where the solution was evaporated with 2 ml of hydrochloric acid and transfer the solution into the same separating funnel. Add 2 ml of titanium chloride, shake, and add 1 ml of butyl rhodamine B solution. Extract the ionic association with 10 ml of toluene, shaking the mixture for two minutes. When the phases have separated, remove the aqueous solution and pass the extract through a glass cotton filter to separate water droplets. Collect the filtrate in a cell with a light path of 1 cm. Measure the absorption of the extract in the above specified conditions. Determine the gallium content from the calibration curve.

EXTRACTION-PHOTOMETRIC DETERMINATION OF GALLIUM WITH RHODAMINE S

Rhodamine S reacts with the gallium ion in a 6 *N* solution of HCl, to form rhodamine chlorogallate extractable by benzene mixture with diethyl ether (3 : 1), butyl acetate (4 : 1), or a mixture (3 : 1) of chlorobenzene with carbon tetrachloride. The molar extinction coefficient of the benzene extract at 565 nm is 6.00×10^4, and of the chlorobenzene and carbon tetrachloride extract (3 : 1) at 562 nm, 7.89×10^4. Fe^{III}, Sb^{V}, As^{V}, Mo^{VI}, Tl^{III}, Te^{IV}, Se^{IV} Al (over 0.3 mg), Cu (over 2 mg) interfere with the determination. The aluminium and copper ions are separated from the gallium ion by extraction with butyl acetate from a 6 *N* solution of HCl. The effect of Fe, Sb, As, Mo, Tl, Te and Se is removed by adding titanium (III) chloride.

The accuracy of the method is ±5 per cent.

Reagents

Gallium salt, standard solution in 6 N HCl. 1 ml is equivalent to 1 μg of gallium.
Hydrochloric acid, 6 *N* solution.
Mixture of benzene and butyl acetate, 4 : 1.
Titanium (III) chloride, 5 per cent solution in HCl.
Rhodamine S, 0.5 per cent solution.

Constructing a Calibration Curve

Place 1, 2, 3, 4 and 5 ml of the gallium standard solution into 25-50 ml separating funnels and add hydrochloric acid to 5 ml. Add 0.2 ml of titanium chloride, 10 ml of the mixture of benzene and butyl acetate and 0.5 ml of rhodamine S in each unnel. Shake the mixtures for two minutes and discard the separated lower layer. Pass the coloured extract through a glass wool filter. Measure the absorption of the extracts on an absorptiometer with a green filter in a cell with a light path of 1 cm using benzene and butyl acetate as reference solutions. Construct the calibration curve using the data obtained.

Procedure

Determine gallium in the test solution as described for the construction of the calibration curve. Find the gallium content from the calibration curve.

SEPARATION OF GALLIUM IN THE ANALYSIS OF COMMERCIAL ALUMINIUM

The best method to separate gallium from the accompanying elements for subsequent photometric determination is extraction from a 6 *N* solution of hydrochloric acid by ethyl ether or a less volatile butyl acetate, the phase ratio being 1 : 1. The distribution coefficient in the latter case is 400. Gallium is re-extracted with water and determined by the thiocyanide method.

Reagents

Butyl acetate.
Hydrochloric acid, 6 *N* solution.
Titanium (III) *chloride*, 5 per cent solution
Sodium chloride, crystalline.

Procedure

Dissolve 0.25 g of aluminium metal in 20-30 ml of hydrochloric acid with moderate heating. Add titanium chloride solution, drop by drop, until violet colour develops. Allow the solution to stand for 2-3 minutes and transfer into a 100-ml separating funnel. Rinse the beaker with 3-5 ml of hydrochloric acid. Add an equal volume of butyl acetate to the solution and shake energetically for a minute. Discard the separated lower layer and wash the extract two times with hydrochloric acid (2-3 ml portions). Re-extract gallium with 10-15 ml of water for a minute. Transfer the lower layer into a porcelain dish. Repeat the re-extraction of gallium with water and add the re-extract to the dish contents. Add 0.1 g of NaCl and evaporate the solution on a water bath to dryness. Dissolve the residue in hydrochloric acid, transfer the solution into a 25-ml volumetric flask and add hydrochloric acid to the mark.

Transfer a 5-ml aliquot into a 25-50 ml separating funnel and proceed as in the previous procedure.

FLUORIMETRIC DETERMINATION OF GALLIUM WITH LUMOGALLION

The method is based on the reaction of the gallium ion with lumogallion, (2,2',4'-trihydroxy-5-chloro-(1-azo-1')benzene-3-sulphonic acid, at pH 1.7-4.0 with the formation of a complex compound fluorescing with an orange-red light. The reagent does not fluoresce in the same conditions in the absence of gallium. The compound is extractable with isoamyl alcohol. The extract fluoresces intensely. The dependence between the intensity of fluorescence and the gallium concentration to 0.5 μg in 5 ml is linear in the pH range from 1.7 to 4.0 for both the aqueous solution and the extract. The sensitivity of the determination of Ga in the aqueous solution is 0.01 μg/5 ml, and in the isoamyl alcohol extract 0.005 μg/5 ml.

Thousand-fold quantities of Li, Na, K, Cs, NH_4^+, Ag, Zn, Cd, Hg, Be, Mg, Ca, Sr, Ba, Tl, Ge, Pb, As, $Sb^{III, V}$, Bi, Cr, Se, Te, Mn, Ru, Co, Th, Nd, Ce, Pr, Ni, Cl, NO_3^-, SO_4^{2-}, phthalate, citrate and acetate ions do not interfere with the determination of 0.05 μg of gallium in 5 ml of solution in the pH range from 2.0 to 3.0. Less than 5 μg in 5 ml of solution of Sn, Zr, Pd, and less than 0.5 μg in 5 ml of Cu, Fe, V, and Mo do not interfere.

The fluorescence of aluminium in the presence of the reagent is markedly less intense. But if the gallium to aluminium ratio is

1 : 1 (pH 1.7-3.5), the presence of aluminium can be disregarded. To remove the effect of a ten-fold quantity of aluminium, it is necessary to build up the pH 1.7-2.7. If aluminium is contained in a hundred-fold quantity, the pH should be 1.7-2.2. The sensitivity of the reagent to gallium is preserved.

Reagents

Lumogallion, 0.01 per cent solution in acetone.
EDTA, 0.05 *M* solution.
Gallium salt, standard solution. Dissolve 0.100 g of gallium metal in 10 ml of hydrochloric acid (1 : 1) containing a few drops of 30 per cent hydrogen peroxide with heating on a water bath. Evaporate the solution to dryness with 1 ml of a 10 per cent solution of sodium chloride. Dissolve the residue in 2 *N* hydrochloric acid, transfer the solution into a 100-ml volumetric flask and add the acid of the same concentration to the mark (Solution A). Transfer 10 ml of solution A into a 100-ml volumetric flask, add 10 ml of sodium chloride solution, and add water to the mark (Solution B). On the day of the analysis, place 1 ml of solution B into a 100-ml volumetric flask and add water to the mark (Solution C). 1 ml of solution C contains 0.1 μg of gallium.
Buffer solution, pH 3.0.

Procedure

Adjust the pH of the test solution to pH 3.0-3.5 (to the universal indicator paper), transfer it into a 25-ml volumetric flask and add the buffer solution to the mark. Place 5 ml of the obtained solution into four test tubes. Add 0.1 ml of solution B into the first, the same volume of solution C into the second, 0.1 ml of EDTA solution into the third, and 0.1 ml of water into the fourth test tube. Add 0.2 ml of the reagent solution into each test tube and allow the solutions to stand for 60-80 minutes. Measure the intensity of the fluorescence in a 6-ml cell at 580 nm.

Calculation

Calculate the gallium content (x) using the formula:

$$x = \frac{\Delta a\,(I_x - I_m)}{I_a - I_x}$$

where Δa is the quantity of gallium added, in μg; I_x is the relative intensity of fluorescence of the sample solution; I_m is the reading of the blank solution with EDTA, and I_a is the intensity of fluorescence in the solution containing gallium.

FLUORIMETRIC DETERMINATION OF GALLIUM IN GERMANIUM PREPARATIONS WITH SULPHONAPHTHOLAZORESORCINOL

The method is based on the formation of Ga^{3+} complex with sulphonaphtholazoresorcinol, [4-sulpho-2-naphthol-(1-azo-1′)-2′, 4′-dihydroxybenzene]. The reagent reacts with Ga^{3+} in a water-ethanol mixture at pH 3 to form a bright orange-red fluorescing compound whose fluorescence intensity is proportional to the gallium concentration. Fluorescence develops gradually to attain its maximum in about 30 minutes (it remains further constant). The detectable minimum is 0.01 μg of Ga. The fluorescence quenching effect of the ferric ion is removed by adding hydroxylamine. Aluminium reacts like gallium and when contained in the quantity exceeding 15 mg, it interferes with the determination of gallium.

Reagents

Sulphonaphtholazoresorcinol, 0.01 per cent solution in ether.
Chloroacetate buffer solution, a mixture of equal volumes of 0.5 *M* solutions of $CH_2ClCOOH$ and $CH_2ClCOONH_4$.
Hydroxylamine chloride, 10 per cent solution.
Ethyl alcohol, 96 per cent solution.
Hydrochloric acid, 7-8 *N* and 0.2 *N* solutions.
Sodium chloride, 10 per cent solution.
Gallium salt, standard solution. 1 ml is equivalent to 0.2 μg of gallium. Prepare the solution to 0.2 *N* HCl.

Constructing a Calibration Curve

Place 0.25, 0.5, 0.75 and 1.0 ml of the standard solution of gallium salt into quartz test tubes and add 0.2 *N* HCl to 1.0 ml. Add 0.2 ml of the buffer solution, 0.2 ml of hydroxylamine chloride, 2 ml of ethanol and 0.2 ml of sulphonaphtholazoresorcinol into each test tube. Allow the solutions to stand for 30 minutes and measure their absorption fluorescence. Construct the calibration curve using the data obtained.

Procedure

Dissolve a sample of germanium dioxide or germanium metal. Remove germanium as $GeCl_4$ by evaporation with 7-8 *N* HCl. Add 0.3 ml of sodium chloride solution, 2 ml of 7 *N* hydrochloric acid to the residue, evaporate the solution to dryness, calcine the residue for two minutes on a gas burner. Cool the residue and dissolve in 0.2 ml of 0.2 *N* hydrochloric acid, and if necessary, pass the solution through a small filter. Wash the filter with 0.8 ml of water. Determine the gallium content from the calibration curve.

SPECTROPHOTOMETRIC DETERMINATION OF GALLIUM AND INDIUM WITH 1-(2-THIAZOLYLAZO)-2-NAPHTHOL-3,6-DISULPHONIC ACID WHEN BOTH ARE PRESENT

The reagent 1-(2-thiazolylazo)-2-naphthol-3,6-disulphonic acid (3,6-disulpho-TAN) reacts with the gallium ion in an acid medium to form a crimson-red compound and with the indium ion to form a dark-red (in transmitted light) and a violet (in reflected light) compound. Own colour of the reagent is orange yellow. The absorption spectra are characterized by two bands of maximum absorption, viz. at 530 nm and 570 nm (gallium) and 540 and 570 nm (indium). It is convenient for analytical purposes to measure the absorption at 580 nm. The molar extinction coefficients are $(1.93 \pm 0.12) \times 10^4$ and $(2.40 \pm 0.03) \times 10^4$ for the complexes of gallium and indium respectively. The molar extinction coefficient of the reagent is less than 300 in these conditions. Gallium and indium react with the reagent to form sufficiently stable compounds with the molar ratio of the components of 1 : 1; pK are 8.19 and 9.27 for gallium and indium respectively. The Bouguer-Lambert-Beer law holds for the range of concentrations from 0.2 to 2.5 μg/ml for gallium and from 0.5 to 5.0 μg/ml for indium. The effect of tartrate on the determination of gallium and indium is of special interest: a ten-fold excess of the tartrate ion destroys completely the gallium compound with 3,6-disulpho-TAN while the indium compound with this reagent is stable in the presence of a 250-fold excess of the tartrate ion. This makes it possible to determine indium in the presence of gallium. Gallium and indium can also be determined in one solution.

Reagents

Gallium salt, standard solution. 1 ml is equivalent to 10 μg of gallium.
Indium salt, standard solution. 1 ml is equivalent to 10 μg of indium.
3,6-Disulpho-TAN, 10^{-3} M solution.
Sodium tartrate, 0.01 M solution.

Constructing Calibration Curves for Gallium and Indium

Place from 10 to 50 μg of gallium and from 20 to 100 μg of indium into 25-ml volumetric flasks, add 4 ml of 3,6-disulpho-TAN, adjust the pH to 3-4, and add water to the mark. Mix the solutions and measure their absorption at 580 nm, using water as the reference solution. Construct the calibration curves using the data obtained.

Procedure

Place a solution containing 10-45 μg of gallium and 20-90 μg of indium into a 25-ml volumetric flask, add 4 ml of 3,6-disulpho-TAN solution, adjust the pH to 3-4, add water to the mark, mix, and measure the absorption of the resultant solution at 580 nm. The absorption is proportional to the total content of gallium and indium.

Place the same aliquot into another 25-ml volumetric flask, add 4 ml of 3,6-disulpho-TAN, 1 ml of sodium tartrate, adjust the pH to 3-4, add water to the mark, mix, and measure the absorption of the solution at 580 nm using water as a reference solution. The absorption corresponds to the indium content which should be found from the calibration curve. The difference of absorptions corresponds to the gallium content, which should be found from the calibration curve.

POLAROGRAPHIC DETERMINATION OF GALLIUM

Gallium (III) is reduced in an ammoniacal solution against the background of $(NH_4)_2SO_4$ or NH_4Cl on a dropping-mercury electrode at the potential of —1.4 to —1.8 V. The ammonia concentration of 1.3-6.6 N does not affect the limit current. The most reliable method to remove oxygen is with hydrogen. But sodium sulphite can be also used for gallium concentrations over 0.01 mg/ml. The method is suitable for the determination of 0.01-0.3 mg/ml of gallium.

For polarographic determination of gallium in polymetallic ore wastes, bauxites, and other materials, its small amounts can be separated from the accompanying elements by the ion-exchange chromatography with alternation of the anion- and cation-exchange processes. When a strong acid (6 *N* HCl) solution of the sample is passed through a column packed with the basic anion-exchange resin AB-17 in the Cl^- form, the elements which do not form chloride anion complexes (aluminium, chromium, nickel, cobalt, and others) are not sorbed, while the other elements remain in the column. When the anion-exchange column is then washed with 4 *N* hydrochloric acid, the greater part of copper and indium is eluted, while all gallium remains on the anion-exchanger together with tin, lead, cadmium, zinc, and other elements forming chloride complexes. Gallium is extracted by a 4 *N* solution of ammonia. The ammoniacal solution is separated finally from the accompanying elements on a cation-exchange resin CBC in the NH_4^+ form, on which all positively charged ammonia complexes are retained, while gallium passes into the eluate.

Reagents

Gallium salt, standard solution. 1 ml is equivalent to 0.5 mg of gallium.
Hydrochloric acid, density 1.19 g/cu.cm and 4 *N* solution.
Ammonia, 4 *N* solution.
Anion-exchange resin AB-17 in the Cl^- form.
Cation-exchange resin CBC in the NH_4^+ form.
Polarographic background. 2.6 *N* solution of ammonia and 1.8 *N* solution of $(NH_4)_2SO_4$ or NH_4Cl.
Sodium sulphite, saturated solution.
Gelatin, 0.2 per cent solution.

Constructing a Calibration Curve

Place 0.5, 1.0, 1.5, 2.0, 2.5, 3.0, 3.5, 4.0, 4.5, and 5.0 ml of the standard solution of gallium salt into 25-ml volumetric flasks, and add four drops of sodium sulphite, two drops of gelatin solution into each flask, and finally add polarographic background to the mark. Carry out polarography of the solutions and construct the calibration curve using the data obtained.

Procedure

Dilute the test solution with an equal volume of concentrated hydrochloric acid and pass it through a column packed with anion-exchange resin AB-17 in the Cl^- form. Wash the column with 100 ml of 4 *N* hydrochloric acid and then with 10 ml of water. Transfer the column contents into a separating funnel and extract gallium with four 20-ml portions of 4 *N* ammonia solution. Pass the obtained solution through a column packed with the cation-exchange resin

CBC in the NH_4^+ form, wash the resin with 20 ml of 4 *N* ammonia solution and evaporate the eluate to 10 ml. Further proceed as for the construction of the calibration curve. Determine the gallium content from the calibration curve.

EXTRACTION-POLAROGRAPHIC DETERMINATION OF GALLIUM

The selectivity of the polarographic method for the determination of gallium against the background of sodium salicylate can significantly be increased if gallium is first extracted with butyl acetate from a 6 *N* solution of hydrochloric acid. The polarographic background is homogenized at the ratio of butyl acetate to aqueous solution of the electrolyte and to ethanol of 1 : 1 : 2. The half-wave potential of gallium against this background is —1.45 V at pH 3.0. The method can be used for the determination of gallium in aluminium.

Reagents

Polarographic background. 0.5 *M* solution of lithium chloride plus 0.1 *M* solution of sodium salicylate.
Ethanol.
Butyl acetate.
Hydrochloric acid, 6 *M* solution.

Procedure

Add 5 ml of butyl acetate to 5 ml of the solution containing gallium and aluminium (6 *M* HCl), and extract gallium for a minute. Separate the organic phase, add 5 ml of ethanol and 10 ml of the background solution, and adjust the pH to 3.0. Remove oxygen by a current of pure nitrogen and carry out polarography. Note the current of gallium reduction at the mercury-dropping electrode at the potential of —1.45 V (using bottom mercury as the reference electrode). Determine gallium by the increment method.

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Indium

Indium, In, has the positive valency of 3. The compounds of indium in its lower valency states are unstable. The chlorides, InCl and $InCl_2$, disproportionate in the presence of water as follows:

$$3InCl \rightleftharpoons 2In + InCl_3$$

$$3InCl_2 \rightleftharpoons In + 2InCl_3$$

The standard electrode potentials in an aqueous medium at 25 °C are as follows (with reference to the standard electrode):

$In^+ \rightleftharpoons In^{3+} + 2e^-$	-0.443 V
$In + Cl^- \rightleftharpoons InCl + e^-$	-0.34 V
$In + 3H_2O \rightleftharpoons In(OH)_3 + 3H^+ + 3e^-$	-0.172 V
$In \rightleftharpoons In^+ + e^-$	-0.139 V
$In + 2H_2O \rightleftharpoons InO_2^- + 4H^+ + 3e^-$	$+0.146$ V

The ion In^{3+} is colourless.

The reactions of In^{III} resemble those of Al^{III} and Cd^{II}.

When NaOH solution is added to a 0.005 *M* solution of $InCl_3$ at pH 3.7, the hydroxide with a small admixture of the basic salt begins precipitating. The precipitation ends at pH 6.70.

A 0.0025 *M* solution of $In_2(SO_4)_3$ begins precipitating basic sulphate at pH 3.4. The precipitation ends at pH 3.75. A further addition of NaOH solution completely converts the basic sulphate into indium hydroxide [1].

The solubility product for indium hydroxide, p*L*, is 33.9. Indium hydroxide is soluble in a concentrated solution of caustic alkalis and has therefore marked amphoteric properties (see Fig. 6).

Hydrogen sulphide precipitates a yellow sulphide, In_2S_3, from neutral or weak acid (pH 3-4) solutions of indium salts. The compound is readily soluble in dilute hydrochloric acid. The properties of In_2S_3 are similar to those of CdS.

Ammonium sulphide precipitates a white hydroxide of indium, $In(OH)_3$, from solutions of indium salts (similarity of the In^{3+} and Al^{3+} ions). Potassium ferrocyanide precipitates the indium ion as a white compound $KIn_5[Fe(CN)_6]_4$, which is more soluble in hydrochloric acid than the corresponding gallium salt.

Indium forms oxalate, fluoride, bromide complexes, $In(C_2O_4)_2^-$, InF_4^{3-}, and $InBr_4^-$. The solubility of the compound $KIn(C_2O_4)_2$ is relatively low. The solubility of InF_3 is 0.5 mole/litre, while that of Na_3InF_6, is 0.35 mole/litre.

Indium in the form of $HInBr_4$ is extractable [2] with diethyl ether from 3-5 *N* solutions of HBr. Indium can afterwards be determined by the extraction-photometric method with 8-quinolinol. The method is highly selective [3].

Indium is extractable with benzene from 2.5 *N* solution of HBr in the presence of the basic dye rhodamine S with the addition of small amounts of acetone [4]. Fe^{II}, Ca, Ga, Cr^{III}, Ti, Th, Bi, Be, Pb, As^{III}, U^{IV}, V^{V}, Ni, Co, Zr do not interfere with the determination. Rhodamine 6G is recommended for the extraction-fluorimetric determination of indium in ores [5].

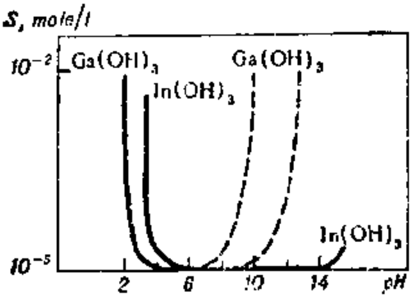

Fig. 6. Dependence of the solubility of gallium hydroxide and indium hydroxide, $Me(OH)_3$, on pH

Satisfactory results have been attained with the extraction-photometric determination of 6-22 μg of In [4]. There are a few variants for the photometric and fluorescence determination of indium [6-8] which are based on the above mentioned principle. Fluorescence is induced by the light of a mercury lamp.

Sodium diethyldithiocarbamate precipitates quantitatively the indium ion at pH 1.5-9 in the form of $[(C_2H_5)_2NC(S)S]_3In$ [9]. The precipitate is extracted with ethyl acetate, carbon tetrachloride and some other solvents. The reagent is used for the gravimetric determination of indium and its separation from gallium [10].

The ionic association InI_4^- with malachite green is extracted with carbon tetrachloride from a 2 *N* solution of H_2SO_4. The reagent is used for the extraction-photometric determination of indium in gallium [11].

Alizarine, quinalizarine, stilbazo, morin and other organic reagents react with In^{3+} as with Al^{3+}. The compound of In^{3+} with alizarine fluoresces [12].

1-(2-Pyridylazo)-2-naphthol and 1-(2-pyridylazo)resorcinol react with indium in the molar ratio of 1 : 1 with the formation of intensely coloured compounds [13, 14]. The solutions of the indium compounds with 1-(2-pyridylazo)-2-naphthol in a mixture of water and ethanol, water and dioxane, or water and acetone are crimson-red. Their absorption maximum is at 550 nm. The molar extinction coefficient is 1.87×10^4. The optimum pH is 4.3-6. 1-(2-Pyridylazo)-resorcinol is more sensitive. The reagents are used for the photometric determination of indium and as complexometric indicators [15-19] for titration of the indium ion at pH 2.3-2.5.

Azo-compounds with 8-quinolinol containing the OH group in the ortho-position to the azo group react with the indium ion to form specifically coloured compounds [20, 21]. The best indicators for direct complexometric titration of indium at pH 2.8-3.5 are 7-(1-naphthylazo)-8-quinolinol-5-sulphonic acid, 7-(4-sulpho-2-naphthylazo)-8-quinolinol-5-sulphonic acid, 7-(6-sulpho-2-naphthylazo)-8-quinolinol-5-sulphonic acid, 7-(4,8-disulpho-2-naphthylazo)-8-quinolinol-5-sulphonic acid, and 7-(5,7-disulpho-2-naphthylazo)-8-quinolinol-5-sulphonic acid. 7-(4,8-Disulpho-2-naphthylazo)-8-quinolinol-5-sulphonic acid and 7-(5,7-disulpho-2-naphthylazo)-8-quinolinol-5-sulphonic acid react with the indium ion in the molar ratio of 1 : 1. The aqueous solutions of the first reagent are crimson-red (the absorption maximum at 520 nm) in an acid medium, and yellow-orange (absorption maximum at 500 nm) in an alkaline medium. The second reagent reacts with the indium ion to form a yellow compound readily soluble in water. The absorption maximum of its solutions is at 420 nm. The indium compound is formed at pH 2.8-6.0. The molar extinction coefficient of this compound is 1.6×10^4 [20].

Trihydroxyfluorones offer good prospects for the photometric determination of indium.

Diphenylcarbazone reacts with the indium ion in a weak acid medium ($pH < 7$) to form violet compounds. The absorption maximum is at about 530 nm. If the indium concentration is high, a precipitate of the same colour is liberated [23]. In the absence of indium, the colour of the solution remains brownish-yellow. At pH 5-6, the ions of Mg, Ca, Al, Cr^{III}, Ti, Mn^{II}, U^{VI}, Cd, Pb, Bi, Sn^{IV}, Sb, As, Ag, Ge and Tl do not interfere with the determination provided the content of either of them does not exceed 50 μg. Cu^{II}, Zn, Ga, Fe^{III} interfere (the effect of a small quantity of the ferric iron being removed by thiocarbamide at pH 5.6). The reagent is used for the determination of more than 2×10^{-6} per cent of indium in germanium (sample weighing 2 g) after distillation of germanium as $GeCl_4$.

Indium is selectively extracted with chloroform and dichloroethane in the form of ionic associations of its halide complexes with diantipyrylmethane [24].

Alkylphosphoric acids extract indium from sulphuric acid solutions and are used for separation of indium from many ions. The selectivity of determination can be increased by re-extraction of indium by hydrobromic acid [25].

Indium compounds colour a flame in specific blue-violet shade. The absorption spectrum has an intense line at 451.1 nm and a weaker line at 410.2 nm. The spark spectrum has many lines; the main lines at 325.6 and 303.9 nm can be mistaken for the lines of Al, Cr, and Mn.

A selective amperometric method for the determination of indium in various materials with EDTA [26, 27] has been developed. Polarographic methods are widely used as well [28, 29].

The review of the methods for the determination of indium is given in the literature [9].

SEPARATION OF INDIUM AND GALLIUM WITH DIETHYLDITHIOCARBAMATE

The method of separation of indium and gallium is based on the precipitation (or extraction by ethyl acetate) at pH 3-5 in the form of diethyldithiocarbamate in the presence of excess sodium oxalate. Gallium remains in solution, and is determined by precipitation with 8-hydroxyquinoline.

Reagents

Ammonia, 1 *N* solution.
Sodium diethyldithiocarbamate, 1 per cent solution.
8-Quinolinol, 3 per cent solution in acetic acid.
Sodium oxalate, 2 per cent solution.
Methyl orange.

Procedure

Add sodium oxalate to the solution containing 2-10 mg of indium and 2.5-30 mg of gallium (1-2 ml of solution per mg of Ga). Dilute the solution to 40 ml and neutralize with ammonia to methyl orange. Add sodium diethyldithiocarbamate solution with stirring until precipitation stops. Add a small excess of the reagent (three-fold with respect to the indium content). Separate the precipitate in a glass crucible No. 3, wash with water, dry to constant weight at 105 °C, and weigh.

The conversion factor for indium is 0.2050.

Collect the filtrate and the washings and determine gallium with 8-quinolinol or EDTA (see page 280).

COMPLEXOMETRIC DETERMINATION OF INDIUM

Indium reacts with EDTA in the molar ratio of 1 : 1 with the formation of a stable complex ($\log K_{st} = 24.9 \pm 0.1$). The method is based on the titration in an acid medium (pH 2.3-2.5) of the indium ion In^{3+} with a standard solution of EDTA in the presence of 1-(2-pyridylazo)-2-naphthol. At the end point of titration, the red solution turns pure yellow. The ions Ga^{3+}, Tl^{3+}, Fe^{3+}, Bi^{3+}, Zr^{4+} and Th^{4+}, which form stable complexonates at this pH, interfere with the determination of indium. Pb^{2+}, Cd^{2+}, Zn^{2+} and the other cations reacting with EDTA in neutral or weak alkaline medium do not interfere. 1-(2-Pyridylazo)resorcinol can also be used as an indicator (the red colour changes to yellow). Various azoxines, e.g. 7-(1-naphthylazo)-8-quinolinol-5-sulphonic acid, 7-(4-sulpho-1-naphthylazo)-8-quinolinol-5-sulphonic acid, 7-(5-sulpho-2-naphthylazo)-8-quinolinol-5-sulphonic acid, and 7-(5,7-disulpho-2-naphthylazo)-8-quinolinol-5-sulphonic acid can be used (the yellow colour changes to crimson).

Reagents

EDTA, 0.01 *M* solution.
Ammonia, 1 *N* solution.
Acetic acid, density 1.05 g/cu.cm.
1-(2-Pyridylazo)-2-naphthol, 0.1 per cent solution in methyl alcohol.

Procedure

Neutralize the test solution with ammonia until white turbidity develops. Add 2 ml of acetic acid to dissolve the precipitate, add 2 drops of the indicator solution and titrate with EDTA, adding it dropwise, when the point of equivalence is approached, and thoroughly mixing until the red solution turns yellow.

1 ml of 0.0100 *M* solution of EDTA is equivalent to 1.148 g of indium.

EXTRACTION-PHOTOMETRIC DETERMINATION OF SMALL QUANTITY OF INDIUM WITH RHODAMINE S

Rhodamine S reacts with the bromide complex of indium, $InBr_4^-$, to form an ionic association extractable with a mixture of benzene and acetone (5 : 1) from a 2.5 *N* hydrobromic acid medium. The absorption maximum is at 530 nm. The selectivity of the method is low.

Reagents

Rhodamine S, 0.256 per cent solution.
Benzene.
Acetone.
Indium salt, standard solution. 1 ml is equivalent to 20 μg of indium. Prepare the solution in 2.5 *N* HBr.
Hydrobromic acid, 2.5 *N* solution.
Titanium trichloride, 5 per cent solution.

Constructing a Calibration Curve

Place 1, 2, 3, 4 and 5 ml of the standard solution of indium salt into separating funnels and add hydrobromic acid to 10 ml. Add 1 ml of rhodamine S, 0.2 ml of titanium chloride, 5 ml of benzene and 1 ml of acetone into each separating funnel. Shake the mixtures for a minute and after separation of the phases, measure the absorption of the extracts on an absorptiometer, model ФЭК-М, using a green filter and a blank extract as a reference solution. Construct the calibration curve using the data obtained.

Procedure

When determining indium in pure solutions, proceed as instructed for the construction of the calibration curve.

PHOTOMETRIC DETERMINATION OF INDIUM WITH 1-(2-PYRIDYLAZO)RESORCINOL

1-(2-Pyridylazo)resorcinol reacts with the indium ion to give a red complex with the absorption maximum at 500 nm and the molar extinction coefficient of 3.28×10^4. The constancy of the absorption of the coloured solutions is attained at pH 6-8. The Bouguer-Lambert-Beer law holds for the range of indium concentrations from 5 to 120 μg in 25 ml of solution.

1000-10,000-fold quantities of Na^+, K^+, Mg^{2+}, Ca^{2+}, Ba^{2+}, Cl^-, Br^-, I^-, SCN^-, CN^-, SO_4^{2-}, SO_3^{2-}, $S_2O_3^{2-}$, NO_3^-, ClO_3^-, BrO_3^-, IO_3^-, SiO_3^{2-}, BO_2^-, BF_4^-, WO_4^{2-}, CrO_4^{2-}, MoO_4^{2-} and CH_3COO^-, as also the citrate, tartrate, and sulphosalicylate ions do not interfere with the determination of indium. Fe^{3+}, Fe^{2+}, Co^{2+}, Ni^{2+}, V^V, Zr^{IV}, Bi^{3+}, Sn^{II}, F^-, NO_2^-, $P_2O_7^{4-}$, $C_2O_4^{2-}$ and ethylenediamine tetraacetate ions interfere. Small quantities of Zn^{2+}, Cd^{2+}, Al^{3+}, Mn^{3+}, Cr^{3+}, Pb^{2+}, Sn^{IV} and Cu^{2+} do not interfere if the determination is carried out at pH 3 and the Cu^{2+} ion is masked by thiosulphate.

The method is used for the determination of indium in its concentrates and sublimates with the separation of indium from the interfering elements by extraction in the form of the iodide from a 1.5 *N* solution of hydriodic acid.

Reagents

Indium salt, standard solution. 1 ml is equivalent to 20 μg of indium.
1-(2-Pyridylazo)resorcinol, 2×10^{-3} *M* solution.
Acetate buffer solution, pH 3.
Hydrochloric acid, density 1.19 g/cu.cm and diluted 1 : 1.
Nitric acid, density 1.4 g/cu.cm.
Hydrazine chloride, crystalline.
Potassium bromide, crystalline.
Ammonia, 25 per cent solution.
Ammonium chloride, 1 per cent solution.
Sulphuric acid, 1 per cent, 3 *N* and 3.5 *N* solutions.
Sodium thiosulphate, crystalline.
Potassium iodide, crystalline.
Ethyl ether.
Hydriodic acid, 1.5 *N* solution.

Constructing a Calibration Curve

Place 1, 2, 3, 4 and 5 ml of the standard solution of indium into 25-ml volumetric flasks and add 2 ml of 1-(2-pyridylazo)resorcinol into each flask and dilute with the acetate buffer solution to the mark. Measure the absorption of the solutions at 500 nm against a blank solution. Construct the calibration curve using the data obtained.

Procedure

Decompose a sample weighing from 0.1 to 1 g (depending on the indium concentration) with hydrochloric and nitric acids. Evaporate the solution almost to dryness, add 5 ml of hydrochloric acid, density 1.19 g/cu.cm, to the residue, add 0.1 g of hydrazine chloride, 0.1 g of potassium bromide, and evaporate the solution almost to dryness. Repeat the evaporation with hydrochloric acid two times more. Dissolve the residue in dilute hydrochloric acid, add concentrated sulphuric acid, evaporate to fumes of sulphuric acid, separate the precipitated lead sulphate, and wash it with a 1 per cent solution of sulphuric acid.

Add 2 ml of nitric acid to the filtrate, heat the solution to boiling and precipitate the hydroxides of tervalent metals with ammonium. Separate the precipitate on a loose filter and wash with ammonium chloride solution containing a small amount of ammonia. Dissolve the precipitate in dilute hydrochloric acid (1 : 1) and repeat the precipitation with ammonia. Dissolve the precipitate of the hydroxides in a hot 3.5 *N* sulphuric acid, transfer the solution into a 25-ml volumetric flask and add 3 *N* sulphuric acid to the mark.

Transfer a 10-ml aliquot into a separating funnel, add 10 ml of water, 0.1 g of sodium thiosulphate, 5 g of potassium iodide, mix the solution and extract with 20 ml of ethyl ether. Repeat extraction with ether. Join the extracts, wash them with hydriodic acid, add 5 ml of water, and evaporate the ether on a water bath. Filter the solution into a 25-ml volumetric flask and proceed as for the construction of the calibration curve. As soon as the absorption of the solution has been measured determine the indium content from the calibration curve.

EXTRACTION-PHOTOMETRIC DETERMINATION OF INDIUM IN ORES WITH 8-QUINOLINOL

The method is based on the extraction of indium 8-hydroxyquinolinate by carbon tetrachloride at pH 8.0±0.5. Indium is separated from most interfering elements in the form of $HInBr_4$ by ether, while traces of the interfering elements can be masked with citric acid and cyanide. Ferric iron is first reduced with ascorbic acid. Copper, nickel, zinc, cadmium and cobalt are masked in a weak alkaline medium with cyanide.

Reagents

Indium salt, standard solution. 1 ml is equivalent to 15 μg of indium.
Ammonium chloride, crystalline.
Hydrochloric acid, density 1.19 g/cu.cm, 3 *N*, 6 *N* and 2 per cent solutions.
Hydrobromic acid, concentrated, containing 1 per cent of Br.
Hydrofluoric acid.
Sodium bromide; dissolve 100 g of $NaBr \cdot 2H_2O$ in 50 ml of water.
Sodium sulphite, anhydrous.
Hydrogen peroxide, 30 per cent solution.

Methyl orange, 0.02 per cent solution.

Ethyl ether, saturated with sodium bromide. Add 56 ml of sulphuric acid (1 : 1) to 140 ml of sodium bromide solution (see above); cool the solution, add 20 g of sodium sulphite and mix to dissolve the salt. Transfer the solution into a 1000-ml separating funnel, add 600 ml of ether, shake for 2-3 minutes, and separate the aqueous phase.

Ethyl ether, saturated with hydrochloric acid. Shake equal volumes of ether and 6 N hydrochloric acid in a separating funnel for 2-3 minutes and discard the aqueous phase.

Sodium bromide solution in sulphuric acid. Use the aqueous phase obtained in the preparation of ether saturated with bromide. Separate the precipitated crystals on a filter.

Ascorbic acid, 5 per cent solution.

Sodium citrate, 20 per cent aqueous solution.

Potassium cyanide, 2 per cent solution. Add 150 ml of ammonia solution to 20 g of the reagent and dilute with water to 1000 ml.

8-Quinolinol, 0.15 per cent solution in carbon tetrachloride.

Nitric acid, density 1.4 g/cu.cm.

Sulphuric acid, 18 N solution.

Ammonia, 6 N solution.

Constructing a Calibration Curve

Place 2, 4, 6, 8 and 10 ml of the standard solution of indium salt into 50-ml separating funnels, add 3 ml of 3 N hydrochloric acid, 5 g of NH_4Cl, 2 ml of a 5 per cent solution of ascorbic acid, 2 ml of a 20 per cent sodium citrate solution, and 5 ml of potassium cyanide solution into each funnel and dilute the solutions with water to 25 ml. Stir the solutions, and 5 ml of 8-quinolinol solution and shake for 1-2 minutes. Allow the solutions to stand for 30 seconds and measure their absorption on an absorptiometer ($l = 1$ cm) using a blue optical filter. Construct the calibration curve using the data obtained.

Procedure

Place a sample of ore weighing 0.5-1.0 g in a 250-ml beaker and decompose it with heating in 15 ml of concentrated hydrochloric acid. When the main part of the sample has dissolved, add 5 ml of HNO_3 and evaporate the solution to dryness. Add 5-10 ml of concentrated hydrochloric acid and 50 ml of hot water to the residue and boil to dissolve the salts. Pass the solution through a white ribbon filter into a 250-ml beaker. Wash the residue on the filter with a 2 per cent solution of hot hydrochloric acid and then with water. When copper and lead-zinc ores are analyzed, discard the residue. When analyzing tin ores, transfer the residue into a nickel crucible, incinerate, wet with water, add 3-5 ml of hydrofluoric acid, and evaporate to dryness. Wash off the precipitate into a small beaker with a small amount of water and treat 2-3 times with a small amount of hydrobromic acid containing bromine. Evaporate the solution to dryness each time ($SnBr_4$ is distilled during this operation). Dissolve the residue in a 6 N solution of hydrochloric acid and add the solution to the main filtrate.

Add 10 ml of sulphuric acid to the filtrate and evaporate to heavy fumes of SO_3 (for 5-10 minutes). Cool the residue, rinse the beaker walls with a small amount of water and evaporate again to fumes of sulphuric acid. Cool the solution, rinse the beaker walls with a small quantity of water, add 18 ml of a hot solution of sodium bromide and evaporate the solution to about 20 ml.

Cool the solution and add 4 g of sodium sulphite. Stir the solution and allow to stand for 30 minutes. Transfer it into a 125-ml separating funnel with the minimum of water (not more than 5-10 ml). Add 25 ml of ether saturated with sodium bromide to the solution, shake for 1-2 minutes, and allow the ether layer to separate. Remove the aqueous layer into another separating funnel and extract again with 20 ml of ether saturated with sodium bromide. Discard the aqueous layer, join the extracts and wash 1-2 times with 10-ml portions of sodium bromide solution in sulphuric acid. If the washing is done in two steps, extract both portions of the washing solution, one after the other, with one portion of ether saturated with sodium bromide (10 ml) and add it to the main extract. Add 25 ml of 6 *N* hydrochloric acid and a few drops of 30 per cent hydrogen peroxide to the extract, cool the mixture and shake for 1-2 minutes. Transfer the acid solution into another separating funnel and shake the ether extract again with 10 ml of 6 *N* hydrochloric acid.

Each new acid solution should be shaken with one and the same portion of ether (10 ml) saturated with hydrochloric acid. If the hydrochloric acid solutions were joined, wash them twice with 10-ml portions of ether saturated with 6 *N* hydrochloric acid.

Shake the ether solutions obtained during washing the hydrochloric acid solutions, one after another, with the same 10-ml portion of 6 *N* hydrochloric acid. Join the hydrochloric acid solutions and discard the ether solutions.

Evaporate the acid solution to a small volume, add a few drops of hydrogen peroxide and continue evaporating almost to dryness. Dissolve the residue in water. Neutralize the obtained solution by 6 *N* ammonia solution to methyl orange until the indicator colour changes to yellow. Add 3 *N* hydrochloric acid until the solution turns orange and 3 ml in excess. Add 2 ml of ascorbic acid and 2 ml of sodium citrate, transfer the solution into a 50-ml separating funnel, rinse the beaker with the minimum quantity of water, add 5 g of NH_4Cl, 5 ml of potassium cyanide solution and dilute with water to 25 ml. Add 5 ml of 8-quinolinol solution, shake for 1-2 minutes, keep in the dark for 30 minutes, and transfer the solution, or its part, into a cell and measure the absorption on an absorptiometer. Find the indium content from the calibration curve.

EXTRACTION-FLUORIMETRIC DETERMINATION OF INDIUM IN ORES WITH RHODAMINE 6G

The method is based on the reaction between bromide complexes of indium with rhodamine 6G. The compound is extracted with benzene from 15 *N* sulphuric acid and the indium concentration is found from the intensity of the fluorescence of the extract. The interfering ions Fe^{3+}, Cu^{2+}, Sn^{IV}, Sb^{III}, Tl^{III}, Au^{III} and Hg^{2+} should be removed.

Reagents

Rhodamine 6G, 0.25 per cent solution.
Ammonia, 25 per cent solution.
Ammonium sulphate, 1 per cent solution.
Iron, reduced by hydrogen.
Sulphuric acid, density 1.84 g/cu.cm, 15 *N* and diluted 1 : 1 and 1 : 2.
Titanium trichloride, 5 per cent solution.
Potassium bromide, 40 per cent solution.
Indium salt, standard solution. 1 ml is equivalent to 1 μg of indium.
Benzene.
Aqua regia.

Constructing a Calibration Curve

Place a solution containing 0.1, 0.2, 0.3, 0.4, 0.5, 0.6, 0.7, 0.8, 0.9 and 1.0 μg of indium into 10-ml test tubes and dilute with 15 *N* sulphuric acid to 10 ml. Add 100 mg of iron into each test tube and keep for 30 minutes. Using a pipette, transfer 5-ml aliquots (through cotton wool) into 25-ml separating funnels. Add 0.1 ml of rhodamine 6G solution, 6 ml of benzene and 0.5 ml of potassium bromide solution and shake immediately for 30 seconds. Allow the phases to separate, transfer the extracts into dry test tubes and measure the intensity of fluorescence on a fluorimeter. Construct the calibration curve.

Procedure

Dissolve a sample of ore weighing 0.3 g in 25-30 ml of aqua regia with heating on a sand bath. As soon as the sample has dissolved, evaporate the solution to 5 ml and dilute the concentrate with water to 25-30 ml. Precipitate hydroxides by adding a small excess of ammonia solution. Separate the precipitate on a dense filter, wash 2-3 times with ammonium sulphate solution and dissolve in hot sulphuric acid (1 : 2). Wash the filter 2-3 times with water and collect the solution and the washings in the precipitation beaker. Precipitate the hydroxides again. Separate the precipitate on a filter, wash 3-4 times with ammonium sulphate solution and 1-2 times with water. Dissolve the precipitate on the filter in a 15 *N* solution of sulphuric acid and collect the filtrate in a test tube. Dilute it with the same sulphuric acid to 10 ml. Cool the solution, add 0.15-0.20 g of iron and allow to stand for an hour with periodically stirring. Transfer the solution into another test tube, add 100 mg of iron and keep for another 30 minutes. Take a 5-ml aliquot and proceed as for the construction of the calibration curve. Find the indium content from the calibration curve.

SEPARATION OF INDIUM BY EXTRACTION

The method is based on the extraction of indium with butyl acetate from a 5 *N* solution of hydrobromic acid.

Reagents

Hydrochloric acid, density 1.19 g/cu.cm and 6 *N* solution.
Hydrobromic acid, concentrated, 5 *N* and 2.5 *N* solutions.
Nitric acid, density 1.4 g/cu.cm.
Sulphuric acid, density 1.84 g/cu.cm.
Hydrogen peroxide, 30 per cent solution.
Butyl acetate.

Procedure

Treat a sample of ore weighing 0.1 g with 10 ml of nitric and 5 ml of hydrochloric acids, density 1.19 g/cu.cm, first without heating, then evaporate the solution to dryness, add 3-4 ml of concentrated hydrobromic acid to the dry residue, and evaporate to dryness again. Dissolve the residue in 5 ml of 5 *N* hydrobromic acid, transfer the solution into a separating funnel, and rinse the beaker with 5 *N* hydrobromic acid. Add 10 ml of butyl acetate to the solution and extract for one minute. Separate the extract, wash it with two 2-3 ml portions of 5 *N* hydrobromic acid with shaking for 10-15 seconds. Re-extract indium with two 20-ml portions of 6 *N* hydrochloric acid containing 1-2 drops of hydrogen peroxide. Evaporate the re-extract to dryness, add sulphuric acid to the residue and heat the solution to fumes of sulphuric acid. Treat the dry residue with 2.5 *N* hydrobromic acid.

Determine indium photometrically using rhodamine S.

SEPARATION OF INDIUM FROM TIN BY EXTRACTION

The method is based on the combined extraction of indium and tin from sulphuric acid solutions with a mixture of alkylphosphoric acid in octane with subsequent re-extraction of indium by hydrobromic acid. The method can be used to separate indium from a 1000-fold quantity of tin. The determination ends photometrically with rhodamine 6G. The method can be used for the determination of 0.01-0.0001 per cent of indium in sulphide and oxide concentrates containing large quantity (15-50 per cent) of tin.

Reagents

Ethylhexylphosphoric acid. Place 150 ml of 2-ethylhexyl alcohol and 150 ml of octane in a 400-500 ml beaker; add, with stirring, 70-75 g of P_2O_5, and maintain the temperature not above 70-75 °C. Allow the solution to stand for 90-120 minutes, dilute with octane or isooctane in the ratio of 1 : 1.5, and wash the diluted extracting agent with 1 *N* sulphuric acid to remove PO_4^{3-}, the ratio of the phases being 3 : 1.
Ammonium fluoride, 0.5 *N* solution.
Hydrobromic acid, diluted 5 : 1.
Sulphuric acid, 1 *N* and 3-4 *N* solutions.
Ascorbic acid, crystalline..
Ammonium sulphate, 1-2 per cent solution.
Sodium peroxide, crystalline.
Magnesium oxide, crystalline.

Procedure

Place a sample weighing 0.1-2 g into a corundum crucible and fuse with 6-7 weights of sodium peroxide in the presence of 0.1-0.2 g of magnesia. Place the crucible into a cold muffle furnace, raise the temperature gradually to 650-700 °C and fuse the sample for 6-8 minutes to obtain a uniform melt. Cool the crucible, transfer it carefully into a beaker containing 60-70 ml of water, and cover the beaker with a watch glass. When the vigorous reaction stops, pass the solution through a filter and wash the precipitate on the filter with a solution of ammonium sulphate containing free ammonia. Wash the precipitate from the filter with 20-30 ml of 3-4 *N* sulphuric acid into the precipitation beaker, heat to dissolve the precipitate, transfer the solution into a 100-ml separating funnel and add 0.1-0.2 g of ascorbic acid. Mix 30-35 ml of the solution with an equal volume of the extracting agent and shake the mixture for 1-1.5 minutes. If a stable emulsion is formed in the aqueous phase in 5-10 minutes, add 8-10 ml of ammonium fluoride. After the phases have separated, wash the extract two times with 7-10 ml of 1 *N* sulphuric acid and three times with 2-ml portions of hydrobromic acid. Use the hydrobromic acid solution for the photometric determination of indium with rhodamine 6G.

PHOTOMETRIC DETERMINATION OF INDIUM WITH 8-QUINOLINOL WITH SEPARATION OF INDIUM HALIDE COMPLEXES BY DIANTIPYRYLMETHANE EXTRACTION

The selectivity of the photometric determination of indium with 8-quinolinol can markedly be increased if indium is first extracted as ionic associations of its iodide or bromide complexes with diantipyrylmethane using chloroform or dichloroethane as extracting agents. 8-Quinolinol is added to the extract and the absorption is measured at 395 nm. Al, Fe^{3+}, Ga, Zn, Cd, Cu, Mn, Th, Co, and Ni do not interfere with the determination. Ferric iron is reduced by ascorbic acid and copper is masked by thiocarbamide. Zr, Tl and Bi interfere.

Reagents

Indium salt, standard solution. 1 ml is equivalent to 50 μg of indium.
Diantipyrylmethane, 0.3 per cent solution in chloroform and 0.3 per cent solution in dichloroethane.
Sodium thiosulphate, crystalline.
8-Quinolinol, 0.5 per cent solution in chloroform and 0.5 per cent solution in dichloroethane.
Sulphuric acid, 1 *N* solution.
Acetate buffer solution, pH 5.
Chloroform.
Dichloroethane.
Potassium iodide, 5 *M* solution.
Potassium bromide, 5 *M* solution.

Constructing a Calibration Curve

Place the standard solution of indium salt containing 50, 100, 150, 200, 250 and 300 μg of indium into separating funnels and add 5 ml of the buffer solution into each funnel. Next add 10 ml of 8-quinolinol solution in chloroform (dichloroethane) and shake for two minutes. When the phases have separated, shake the aqueous phase with 5 ml of the solvent. Collect the extracts and dilute them with the solvent in a 25-ml volumetric flask to the mark. Measure the absorption at 395 nm in a cell with the layer thickness of 5 cm and construct the calibration curve.

Procedure

Place a solution containing 50-300 μg of indium (0.2 *N* sulphuric acid) into a separating funnel, add KBr or KI solution to the concentration of 1 *M* and dilute with sulphuric acid to 20 ml. Shake for two minutes with 10 ml of 0.3 per cent solution of diantipyrylmethane in chloroform (if the iodide complex is extracted) or with 10 ml of diantipyrylmethane solution in dichloroethane (if the bromide complex of indium is extracted). If indium is extracted from the iodide solutions, add a few crystals of sodium thiosulphate to the aqueous phase. After separation of the extract, shake the aqueous phase with 3 ml of the solvent and join the extracts. Wash the joined extracts by shaking with 10 ml of 1 *N* sulphuric acid solution of KI or KBr. (1 *M* solution of KI or KBr.) Transfer the organic phase into another separating funnel, add 6 ml of 8-quinolinol solution in the same solvent which was used for the extraction of indium in the form of the ionic association, and shake with 5 ml of the buffer solution to remove excess acidity. Transfer the organic phase into a 25-ml volumetric flask, wash the aqueous phase with 3 ml of pure solvent and add to the main extract. Dilute the extract in the volumetric flask with pure solvent to the mark and measure the absorption of the solution at 395 nm in a cell with a light path of 5 cm. Find the indium content from the calibration curve.

PHOTOMETRIC DETERMINATION OF INDIUM WITH SALICYLFLUORONE

Trihydroxyfluorones react with the indium ion at pH 3-6 to form from red to red-violet compounds soluble in water-ethanol mixtures. Salicylfluorone is the best reagent for the photometric determination of indium. The reagent solutions have the maximum absorption at 490 nm, the indium compound solution absorbs maximum at 535 nm, the optimum pH of the solution being 4.8. The molar extinction coefficient of the complex is 6.14×10^4, of the reagent solution (at the same acidity and the same wavelength), 2.0×10^3. The solutions obey the Bouguer-Lambert-Beer law with indium concentrations from 0.02 to 2.0 μg/ml. The reagent is used for the determination of 2×10^{-4} per cent of indium in sulphide ores, copper and sulphide concentrates, silicates, metallic lead and zinc.

Indium is first precipitated by ammonia in the form of hydroxide and then extracted as the iodide complex with ethyl ether from sulphuric acid solutions. Traces of iron can be masked by ortho-phenanthroline.

Reagents

Indium chloride, standard solution. 1 ml is equivalent to 5 μg of indium.

Salicylfluorone, 0.05 per cent solution. Dissolve 50 mg of the reagent with moderate heating in 99 ml of 96 per cent ethanol and 1 ml of 6 *N* hydrochloric acid.

Acetate buffer solution, pH 4.6-4.8. Mix equal volumes of 1 *M* solutions of sodium acetate and acetic acid.

Gelatin, 1 per cent solution.

Hydrofluoric acid, 40 per cent solution.

Nitric acid, density 1.4 g/cu.cm and diluted 1 : 1.

Sulphuric acid, 1 *N*, 1.8 *N*, 2 *N* solutions and diluted 1 : 1.

Hydrochloric acid, density 1.17 g/cu.cm and diluted 1 : 1.

Ammonia, 25 per cent solution.

Ammonium chloride, 1 per cent solution with pH adjusted to 9 with ammonia.

Potassium iodide, crystalline.

Sodium thiosulphate, crystalline, and 5 per cent solution.

Thymol blue, 0.1 per cent solution in water-ethanol mixture containing 20 per cent (v/v) of ethanol.

Ethyl ether, free from peroxides. Keep over sodium metal and then distil.

Ammonium fluoride, 1 per cent solution.

Ascorbic acid, 2 per cent solution prepared for the analysis.

ortho-Phenanthroline, 0.24 per cent solution.

Hydrogen peroxide, 30 per cent solution.

Washing liquid. Dissolve 8 g of potassium iodide in 50 ml of 1 *N* sulphuric acid and add a few drops of a 5 per cent solution of sodium thiosulphate until the solution becomes colourless.

Ferric salt solution. 1 ml is equivalent to 20 mg of iron. Dissolve ferriammonium sulphate in 0.1 *N* hydrochloric acid.

Constructing a Calibration Curve

Place 1, 2, 3, 4, 5, 6, 7 and 8 ml of the standard solution of indium chloride, into 50-ml volumetric flasks and add 0.5 ml of ammonium fluoride, 0.5 ml of ascorbic acid, 1 ml of ortho-phenanthroline, 2 ml of gelatin and 2 ml of salicylfluorone, 20 ml of the buffer solution into each flask and dilute with water to the mark. Allow the solutions to stand for 45 minutes and measure their absorption at 535 nm against a blank solution in a cell with a light path of 20-50 mm. Construct the calibration curve using the data obtained.

Procedure

(a) *Determining Indium in Silicates.* Treat a sample weighing 0.5-1 g in a platinum dish with 5 ml of hydrofluoric and 15 ml of sulphuric acids (1 : 1) with heating first on a water and then a sand bath to fumes of sulphuric acid. Cool the residue, dissolve in 100 ml of water with heating, filter, and dilute the filtrate with water to 200 ml. If the sample contains sulphides, it should first be calcined in a muffle furnace. Proceed further as in item (f).

(b) *Determining Indium in Sulphides.* Heat a sample weighing 0.5-1 g in nitric acid or a mixture of nitric and hydrochloric acids (density 1.4 and 1.17 g/cu.cm respectively) to oxidize sulphur, then add 15 ml of sulphuric acid (1 : 1) and heat to heavy white fumes of sulphuric acid. Dilute the solution with water to 100 ml, heat to boiling, cool, filter, and dilute the filtrate with water to 200 ml. Proceed further as in item (f).

(c) *Determining Indium in Iron Ores.* Dissolve a sample weighing 1 g, with heating, in 15 ml of hydrochloric acid, density 1.17 g/cu.cm; filter and wash the residue on the filter with hydrochloric acid (1 : 1) and hot water, dilute the filtrate and the washings with water to 200 ml. Proceed further as in item (f).

(d) *Determining Indium in Lead Metal.* Dissolve a sample weighing 1 g in nitric acid (1 : 1), add 15 ml of sulphuric acid (1 : 1) and evaporate to fumes of sulphuric acid. Dilute the residue with water and evaporate again to fumes of sulphuric acid. Cool the solution, separate the precipitated lead sulphate on a filter, wash with water, and dilute the filtrate and the washings with water to 200 ml. Proceed further as in item (f).

(e) *Determining Indium in Zinc Metal.* Dissolve a sample weighing 1 g in hydrochloric acid (1 : 1) with heating, and add 1 ml of nitric acid at the end of dissolution. Dilute the solution with water to 200 ml.

(f) *Separation of Indium from Accompanying Ions.* Add 3 ml of hydrogen peroxide to the obtained solution. If the sample contains a very small quantity of iron, add 40 mg of ferric iron (as sulphate). Add ammonia solution drop by drop with stirring until a precipitate falls out and 2 ml in excess. Pass the settled solution through a filter, wash the precipitate on the filter with ammonium chloride solution, dissolve in 100 ml of warm 2 *N* sulphuric acid, dilute with water to 200 ml, add 3 ml of hydrogen peroxide solution and repeat precipitation with ammonia. Wash the precipitate, dissolve in 60 ml of 1.8 *N* sulphuric acid, add 8 g of potassium iodide, and then sodium thiosulphate, drop by drop until the solution becomes colourless, and add 1-2 drops in excess. If the sample is rich in iron, first add crystalline sodium thiosulphate to decolourize the solution and then add the solution.

Transfer the colourless solution into a separating funnel, shake two times with 30 ml of ethyl ether for two minutes. Add 2-3 drops of sodium thiosulphate solution to the aqueous phase before the second extraction, join the ether layers, wash them 4 times with 10-ml portions of the washing liquid, adding 2-3 drops of sodium thiosulphate to each portion of the washing solution. Re-extract indium from the washed extracts by shaking three times with 15 ml of water for two minutes. Collect the re-extracts in a 50-ml volumetric flask and add water to the mark.

Transfer an aliquot of the solution containing 2-35 μg of indium into a 50-ml volumetric flask and determine indium.

EXTRACTION-PHOTOMETRIC DETERMINATION OF INDIUM IN GALLIUM WITH MALACHITE GREEN

The method is based on the extraction of the ionic association of InI_4^- with the cation of malachite green by carbon tetrachloride from a 2 *N* solution of sulphuric acid. The absorption maximum of the extract is at 633 nm, the molar extinction coefficient, 8.3×10^4. Au^{3+} and Tl^{3+} interfere. The interfering effect of Au^{3+} is removed by extraction from 3-4 *N* H_2SO_4.

Reagents

Indium salt, standard solution. 1 ml is equivalent to 5 µg of indium.
Malachite green, 10^{-3} *M* solution.
Carbon tetrachloride.
Potassium iodide, 6 *M* solution.
Sulphuric acid, 1 *N* and diluted 1 : 1.
Nitric acid, density 1.4 g/cu.cm.

Constructing a Calibration Curve

Place 0.2, 0.3, 0.4, 0.5, 0.6, 0.7, 0.8, 0.9 and 1 ml of the standard solution of indium salt in 20-ml separating funnels, add 25 ml of KI solution, 0.3 ml of sulphuric acid (1 : 1) and 0.8 ml of malachite green solution into each funnel. Dilute the solution with bidistillate to 6 ml, add 6 ml of carbon tetrachloride and extract for a minute. After the phases have separated, measure the absorption of the extracts at 633 nm ($l = 1$ cm) against a blank extract. Construct the calibration curve using the data obtained.

Procedure

Dissolve a sample of gallium weighing 0.5 g in 5 ml of a mixture (1 : 1) of nitric and sulphuric acids. Evaporate the solution to moist salts, add sulphuric acid and evaporate again. Dissolve the residue in 1 *N* sulphuric acid and dilute the solution with 1 *N* sulphuric acid to 10 ml. Place a 1-2 ml aliquot into a 25-ml separating funnel and proceed as for the construction of the calibration curve. Determine the indium content from the calibration curve.

AMPEROMETRIC DETERMINATION OF INDIUM IN CONCENTRATES

The method is based on the titration of indium with EDTA solution at pH 1.0. The equivalence point is detected by the disappearance of the diffusion current of the ion In^{3+} reduction on the dropping-mercury electrode at the potential of —0.7 to —0.8 V with reference to the saturated calomel electrode.

Many elements occurring in the materials containing indium, e.g. Zn, Mn, Cd, Co, Al, do not interfere with the determination. Considerable quantities of ferrous iron (not more than 10 mg) do not interfere with the titration either. Ferric iron is reduced to Fe^{2+}. The effect of the Sn ion (less than 5 mg) and Sb ion (less than

2 mg) can be removed by adding tartaric acid. Indium can be determined in the presence of a small quantity of copper (less than 0.5 mg), provided it is masked with thiocarbamide, and also Pb and As (less than 2 mg). Large quantities of these elements interfere with the detection of the equivalence point since copper, lead and arsenic cause diffusion current. But they can easily be separated from indium during the analysis: arsenic and lead, by the decomposition with a mixture of hydrochloric and sulphuric acid, with evaporation to fumes of sulphuric acid; and copper, during precipitation of hydroxides with excess ammonia. The bismuth ion interferes.

Reagents

Hydrochloric acid, density 1.19 g/cu.cm.
Sulphuric acid, density 1.84 g/cu.cm.
Ammonia, solution, density 0.9 g/cu.cm.
Tartaric acid, crystalline.
Ascorbic acid, 4 per cent solution.
Thiocarbamide, 5 per cent solution.
Tropaeolin 00, indicator solution.
Buffer solution, pH 1.0. Mix 50 ml of a 0.2 *M* solution of potassium chloride with 97 ml of 0.2 *N* hydrochloric acid and dilute with water to 200 ml.
EDTA, 0.005 or 0.02 *M* solution.

Procedure

Decompose a sample weighing 0.5 g with a mixture of hydrochloric and sulphuric acid (5 ml of each acid) and evaporate the solution to fumes of sulphuric acid. Dilute the residue with water to 5 ml and filter. Precipitate hydroxides from the filtrate by excess ammonia. Separate the precipitate and dissolve in hydrochloric acid. Transfer the solution into a 50-100 ml volumetric flask and add water to the mark. Place a 10-20 ml aliquot into a titration beaker, add 0.5-1 g of tartaric acid, 1-2 ml of ascorbic acid, and 0.2 ml of thiocarbamide solution. Neutralize the solution with ammonia to tropaeolin 00 until the red colour changes to yellow. Add 15-20 ml of the buffer solution and titrate with EDTA solution from a 5-ml semimicro-burette. Detect the equivalence point graphically by the change in the diffusion current of indium depending on the amount of the EDTA solution added.

POLAROGRAPHIC DETERMINATION OF INDIUM

All elements which interfere with the determination are removed before polarography by amalgamated zinc in the presence of not less than 20 per cent of a sulphate of an alkali metal. As, Sb, Bi, Cu, Tl, Se, Sn, Ti, Fe^{III}, V^{V} and Cr^{VI} are reduced energetically to their elemental state or compounds of their lower valencies in this reaction. Indium is determined in the obtained solution polarographically after adding sodium chloride in the quantity of 10 per cent by weight. The half-wave potential for indium is —1.06 V with reference to the saturated calomel half-cell.

The method can be used for the determination of indium in industrial materials and wastes.

Reagents

Nitric acid, density 1.4 g/cu.cm.
Sulphuric acid, density 1.84 g/cu.cm.
Amalgamated zinc. Dissolve zinc in mercury with heating in the presence of diluted (1 : 5) sulphuric acid.
Sodium chloride, crystalline.

Procedure

Add a mixture of nitric and sulphuric acid to a sample weighing 1-3 g and heat to white fumes. Add hot water to the cooled residue and separate the precipitate on a filter. Add an equal quantity of sulphuric acid (or an equivalent quantity of sulphate) to the solution so that the acid concentration is not less than 20 per cent. Next add amalgamated zinc to the solution, mix by a stirrer at a speed of 350-400 r.p.m. for 45 minutes. Filter the solution, add about 10 per cent (by weight) of sodium chloride and carry out polarography at a potential of —1.06 V. Determine the indium content by the increment method.

POLAROGRAPHIC DETERMINATION OF INDIUM IN SULPHIDE ORES

The method is based on the polarographic determination of indium in a medium of 3 *N* hydrochloric acid at a potential of from —0.4 to —0.8 V with reference to the saturated calomel electrode. Cu, Pb, Cd and Sn ions interfere with the determination. Indium is precipitated as its hydroxide, using ferric hydroxide as the collecting agent. The precipitation is carried out from a hot strong alkaline solution in the presence of EDTA. When the precipitate has dissolved in hydrochloric acid, oxygen and ferric iron are reduced with iron metal.

Reagents

Hydrochloric acid, density 1.19 g/cu.cm and 3 *N* solution.
Perchloric acid, 60 per cent solution.
EDTA, 5 per cent solution.
Sodium hydroxide, 10 and 5 per cent solutions.
Iron, reduced by hydrogen.
Sodium chloride, 1 per cent solution.
Indium salt, standard solution. 1 ml is equivalent to 0.1 mg of indium.

Procedure

Decompose a sample of ore weighing 0.1-1.0 g in 3 ml of concentrated hydrochloric acid and a few millilitres of perchloric acid with heating. Evaporate the solution almost to dryness. Add 40-50 ml of hot water to the residue and heat to the boil. Separate the insoluble residue on a filter, wash with hot water and discard. Add 20-25 ml of EDTA to the solution and then add 10 per cent solution of sodium hydroxide until the solution reacts alkaline. Add 15-20 ml in excess. Dilute the solution with water to 150-200 ml, heat slowly to the boil, maintain boiling for 3-5 minutes, and allow the solution to stand on a boiling water bath until the precipitate fully coagulates (30-40 minutes). Separate the precipitate on a filter washed preliminarily with a hot 5 per cent solution of NaOH. Wash the precipitate on the filter with a hot solution of sodium chloride and 1-2 times with hot water. Dissolve the precipitate in hot 3 *N* hydrochloric acid, evaporate the solution (if necessary), transfer into a 25-ml volumetric flask and add 3 *N* hydrochloric acid to the mark. Place the solution into an electrolyzer, add 0.2-0.3 g (on a spatula tip) of iron metal and carry out polarography in 40-50 minutes. Determine the indium content by the increment method.

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Thallium

Thallium, Tl, has the positive valency of 1 and 3. The standard electrode potentials in an aqueous medium at 25 °C are as follows (with reference to the standard hydrogen electrode):

$2Tl + S^{2-} \rightleftharpoons Tl_2S + 2e^-$	−0.93 V
$Tl + I^- \rightleftharpoons TlI + e^-$	−0.753 V
$Tl + Br^- \rightleftharpoons TlBr + e^-$	−0.658 V
$Tl + Cl^- \rightleftharpoons TlCl + e^-$	−0.557 V
$Tl \rightleftharpoons Tl^+ + e^-$	−0.336 V
$TlOH_{(TB)} + 2OH^- \rightleftharpoons Tl(OH)_{3(TB)} + 2e^-$	−0.05 V
$Tl + H_2O \rightleftharpoons TlOH_{TB} + H^+ + e^-$	+0.778 V
$Tl^+ \rightleftharpoons Tl^{3+} + 2e^-$	+1.252 V

The Tl^{3+} ion is colourless and easy to hydrolyse. Solutions contain the ions $TlOH^{2+}$, TlO^+ and others. The pK of the reaction $Tl^{3+} + H_2O \rightleftharpoons TlOH^{2+} + H^+$ is −0.8 (the ionic strength at 25 °C is 3.0).

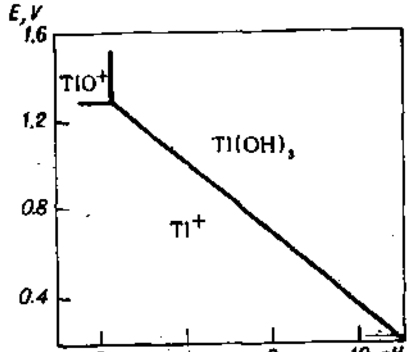

Fig. 7. Dependence of approximate potentials of the system Tl^{III}/Tl^{I} on pH. Concentration of thallium, 10^{-2} *M*

The ion of tervalent thallium in acid solutions is a strong oxidant; it is easily reduced to a colourless Tl^+ ion (Fig. 7). The formation of a sparingly soluble compound TlCl promotes reduction. But the chloride, bromide and iodide ions decrease the oxidizing potential of thallium (III) due to complex formation. Monovalent thallium is oxidized only by energetic oxidants (MnO_4^-, Cl_2) in a strong acid medium. Potassium bromate oxidizes quantitatively Tl^I to Tl^{III} in an acid medium and is used for the titrimetric determination of thallium (I). On the other hand, the ion Tl^+ is an energetic reductant in an alkaline medium. The chemical properties of the Tl^+ ion are similar to those of the alkali metals, silver, and also the ion Pb^{2+}.

Thallium (I) hydroxide is soluble in water and is a strong base.

Thallium (I) salts of strong acids react neutral. Most of them are soluble in water except the halides TlCl, TlBr, TlI (only TlF is soluble), azide TlN_3, sulphide Tl_2S, chromate Tl_2CrO_4, chloroplatinate $Tl_2[PtCl_6]$, and cobaltinitrite $Tl_3[Co(NO_2)_6]$.

Thallium (I) does not form more or less stable complexes. For example, it does not form complex compounds with the ion $S_2O_3^{2-}$ (as distinct from Pb^{II} and Ag^I) or ammonia (in contrast to Ag^I). Thallium (I) belongs to the silver analytical subgroup since its chloride is sparingly soluble in water. Dilute hydrochloric acid precipitates white TlCl from solutions containing the Tl^I ion. The precipitate is sparingly soluble in water at room temperature and in dilute acids; better soluble in hot water; $pL_{TlCl} = 3.7$. Potassium iodide precipitates a yellow sparingly soluble TlI; $pL_{TlI} = 7.2$. The precipitate is insoluble in solutions of $Na_2S_2O_3$ (in contrast to AgI and PbI_2). EDTA does not interfere with the precipitation of TlI [1]. This sharply increases the selectivity of precipitation of the iodide. The interfering elements can also be masked by tartrate or cyanide ions. Tl^I can be determined in TlI microcrystalloscopically.

Hydrogen sulphide precipitates a black substance Tl_2S ($pL_{Tl_2S} = 22.2$-23.9) from a neutral solution.

Ammonium sulphide also precipitates Tl_2S which is insoluble in excess precipitant.

Potassium chromate precipitates yellow Tl_2CrO_4, sparingly soluble in dilute acids. It is used for the gravimetric determination of thallium [2, 3]. Acid solutions precipitate an orange-red bichromate $Tl_2Cr_2O_7$. When boiled in concentrated hydrochloric acid, the precipitate dissolves and the solution liberates beautiful red crystals on cooling.

Chloroplatinic acid precipitates an orange substance, Tl_2PtCl_6 insoluble in cold water. Hot acid solutions of Tl^I salts precipitate yellowish octahedral crystals suitable for microcrystalloscopic detection of thallium.

Potassium ferricyanide oxidizes Tl^I in an alkaline medium to give a brown precipitate $Tl(OH)_3$.

Iodobismuthates of the alkali metals react with Tl^I to form a red precipitate [4]. The reaction is selective for Tl^I in the presence of $Na_2S_2O_3$ which removes the interfering effect of Fe^{III}, Ce^{IV}, Hg^{II}, Cu^{II}, Pt^{IV}, As^V and Sb^V. Selenious and tellurous acid interfere (precipitate a black substance).

Dipicrylamine is a selective reagent for the Tl^+ ion. Unlike the other ions of the silver subgroup (Ag^+, Hg_2^{2+}, Pb^{2+}), it precipitates a red substance. The ions K^+, NH_4^+, Rb^+ and Cs^+ interfere with the determination. The reagent is used [5] for microcrystalloscopic detection of Tl^+.

Thiocarbamide precipitates white crystals from salt solutions acidified with perchloric acid. The reaction is highly selective [6].

Thionalide precipitates selectively the Tl^I ion in the presence of KCN, NaOH and tartaric acid. The reagent reacts only with the Au^{III} ion in these conditions [7].

Thallium (III) salts are soluble only in the presence of strong acids. The salts are easily hydrolysed.

The hydroxide $Tl(OH)_3$ is a reddish brown amorphous substance. It begins precipitating from a 0.01 *M* solution of Tl^{III} salt at pH of about 0.3 ($pL = 43$-45). It has no amphoteric properties.

The trioxide Tl_2O_3 is black.

Thallium (III) ion forms many complex compounds. For example, thallium (III) readily forms complexes of the type $[TlX_4]^-$ and $[TlX_6]^{3-}$ ($X = F^-, Cl^-, Br^-$ and others). The complex compound $H[TlCl_4]$ is extracted with ethyl ether from hydrochloric acid solutions. Sulphate complexes of thallium (III) are not very stable. Thallium (III) forms complex compounds with organic oxy-acids (tartaric, citric and others), oxalic acid and other dicarboxylic acids.

The formation of thallium (III) complexes in solutions with the chloride or bromide ions occurs in steps [8]. The following instability constants have been established for the chloride complexes; $pK_1 = 7.50$; $pK_2 = 4.50$; $pK_3 = 2.75$; $pK_4 = 2.25$; $pK_5 = 1.95$; $pK_6 = 1.75$ (for the ionic strength of 0.4 and the temperature of 20 °C; the concentration of $HClO_4$ is 0.34 mole/l). The instability constants for the bromide complexes of thallium (III) in solutions of the same ionic strength and concentration of $HClO_4$ are as follows: $pK_1 = 8.3$; $pK_2 = 6.3$; $pK_3 = 4.6$; $pK_4 = 3.1$; $pK_5 = 2.5$, and $pK_6 = 1.7$ (20 °C).

The chloride and bromide ions interfere with the complexometric titration of thallium (III) and colour reactions with some organic reagents.

Thallium (III) is reduced quickly and quantitatively to Tl^I by hydrazine sulphate in weak sulphuric acid solutions [9]. This makes it possible to titrate the Tl^{III} ion potentiometrically using platinum-graphite electrodes.

Diantipyrylpropylmethane precipitates quantitatively the Tl^{III} ion from solutions containing the chloride ion in the form of the compound $C_{26}H_{30}O_2N_4 \cdot HTlCl_4$, which meets the requirements for the weighing form [10].

The pyrazolone derivatives, amidopyrine, antipyrine, diantipyrylmethane, diantipyrylphenylmethane, diantipyrylpropylmethane, precipitate the Tl^{III} ion as crystalline compounds in the presence of the bromide ion [10, 11]. Thallium can be determined gravimetrically as $C_{23}H_{24}O_2N_4 \cdot HTlBr_4$ and $C_{26}H_{30}O_3N_4 \cdot HTlBr_4$ [10, 11] in the presence of Cu, Zn, Cd, Bi, Fe, Sb. The reagents are also used for the extraction-photometric determination of thallium [12].

The thallium (III) ion reacts with basic dyes in the presence of the chloride and bromide ions to form sparingly soluble compounds. The bromide and chloride complexes of thallium react with the basic dye rhodamine B to form a red-violet precipitate [13] extractable with organic solvents as bright red liquids. The reagent itself is not extracted. The anions $TlCl_4^-$ and $TlBr_4^-$ react similarly in a weak acid solution with methyl violet [14-18] and other basic dyes of the diaminotriphenylmethane series [18-21]. The benzene extract of $HTlCl_4$ with rhodamine B intensely fluoresces in the ultra-violet light.

The named reagents are used for the extraction-photometric determination of thallium, and also for its detection.

When KI solution is added gradually to a dilute solution of $Tl_2(SO_4)_3$, the following reactions occur, one after another [22]:

$$Tl^{3+} + 2I^- \rightleftharpoons Tl^+ + I_2 \qquad (I)$$

$$I_2 + I^- \rightleftharpoons I_3^- \qquad (II)$$

$$Tl^+ + I^- + I_3^- \rightleftharpoons TlI_4^- \qquad (III)$$

Under certain conditions, tervalent thallium oxidizes the iodide ion quantitatively to the elementary iodine. When excess I^- ion is added, the thallium (I) ion, which is first formed, is oxidized by the elementary iodine to form a stable iodide complex anion of tervalent thallium, TlI_4 (the reaction of complexation is stepwise). The reaction is feasible due to a strong reduction of the oxidation potential of thallium (III) during the complex formation reaction. If the formed TlI ion is removed from the reaction sphere by precipitation with organic bases, e.g. pyrazolone derivatives, the reaction III will shift completely from left to right.

The ion of tervalent thallium forms sufficiently stable tartrate complexes under certain conditions [23]. The ion of tartaric acid does not practically reduce tervalent thallium at pH 3-7 to its monovalent state for several hours, while in an acid solution (pH 0.8-0.9) the reduction is effected by 8-10 per cent during two hours. The composition of the precipitate liberated from the solution containing Tl^{3+} and $C_4H_4O_6^{2-}$ at pH 2, corresponds to the formula $Tl_2(C_4H_4O_6)_3$. The solubility of this compound in water at 20 °C is $(1.0 \pm 0.1) \times 10^{-4}$ mole/l and it increases sharply in the presence of tartrate at pH higher than 2, probably due to the formation of $Tl(C_4H_4O_6)_2^-$ and other complexes. At pH 4, thallium enters the composition of the complex anion. At a temperature of 20 °C and the ionic strength of 1, the general successive stability constants of the tartrate complexes of thallium (III) are:

$$\beta_1 = 3.7 \times 10^{11}; \quad \beta_2 = 6\,5 \times 10^{12} \text{ and } \beta_3 = 2.2 \times 10^{13}$$

EDTA reacts with the ion of tervalent thallium to form a stable complex compound [24]. Its stability constant at 20 °C and the ionic strength of 0.4 is 3 × 10^{23}.

The value of log β at 20 °C and the ionic strength of 0.1 is 22.5 ± 0.5.

Several variants of the complexometric determination of thallium have been developed [25].

Various hydroxy-azo compounds react with tervalent thallium to form coloured compounds.

1-(2-Pyridylazo)-2-naphthol reacts with Tl^{III} in the molar ratio of 1 : 1 to form a red-violet compound sparingly soluble in water. The solubility increases in the presence of water-miscible organic solvents: methanol, ethanol, acetone. The absorption maximum of the compound solutions at pH 4.5 is at 560 nm (the absorption maximum of the reagent solution is at 470 nm in these conditions). The molar extinction coefficient is 2.2 × 10^4 (the solvent —50 per cent methanol, pH 2.2). The equilibrium constant of the reaction of formation of the complex compound is 1.9 × 10^2. The reagent is used as a complexometric indicator [26] for titration of Tl^{III}.

In order to increase the selectivity of the photometric determination of thallium, it is extracted by a solution of di-2-ethylhexylphosphoric acid and then determined in the extract with 1-(2-pyridylazo)-2-naphthol [27].

4-(2-Pyridylazo)resorcinol also reacts with the ion of Tl^{III} to form a red compound well soluble in water, butyl and isoamyl alcohol but insoluble in ethyl ether, benzene, carbon tetrachloride and chloroform. The absorption maximum of the aqueous solution of the compound is at 550 nm (pH 2.2); the absorption maximum of the reagent solution is at 415 nm. The molar extinction coefficient of the thallium compound is 1.9 × 10^4. The reagent is used as a complexometric indicator for titration of Tl^{III}.

7-(1-Naphthylazo)- and 7-(5,7-disulpho-2-naphthylazo)-8-quinolinol-5-sulphonic acids react with the ion of Tl^{III} at pH 2 and higher to form soluble yellow compounds. When EDTA is added to these solutions, a complexonate of Tl^{III} is formed and free azo-compounds are liberated. The solution is coloured violet in this reaction. The change of colour is distinct. The reagents are used as complexometric indicators for titration of Tl^{III} [28].

Xylenol orange reacts with Tl^{III} at pH 2.50 in the molar ratio of 1 : 1 to form a compound whose solution has the absorption maximum at 580 nm. The molar extinction coefficient is 2 × 10^4. The reagent is used as a complexometric indicator for titration of tervalent thallium.

Thallium compounds colour flame into emerald-green shades. The wide line of thallium in the visible region of the spectrum at 535 nm is close to that of barium, but thallium's line is more intense. Thallium is detected and determined by the spectral method and by the colour of flame.

Tl^{I} is determined polarographically in an ammonia medium in the presence of many ions. The method is used for the determination of thallium in cadmium [29].

The literature contains a review of the analytical methods for detection and determination of thallium [30, 31].

GRAVIMETRIC DETERMINATION OF THALLIUM (I) AS THIONALIDATE

The method is based on the precipitation of monovalent thallium in the form of a sparingly soluble thionalidate, $C_{10}H_7NHCOCH_2STl$. Thionalide reacts also with the cations of heavy metals capable of forming sparingly soluble sulphides. Solutions containing the tartrate ion and NaOH precipitate also Cu^{2+}, Cd^{2+}, Hg^{2+} and Au^{III} by the action of thionalide. Thionalide also precipitates Pb^{2+}, Bi^{3+}, Sb^{III}, Sn^{II} and Au^{III} from solutions containing the tartrate ion and KCN. If a solution contains the tartrate ion, KCN and NaOH, thionalide precipitates only Tl^{+} and Au^{III}.

Reagents

Thionalide, 5 per cent solution in acetone. 0.4-0.5 g of thionalide in 8-10 ml of acetone are required per 0.1 g of Tl.
Sodium tartrate, crystalline.
Potassium cyanide, crystalline.
Sodium hydroxide, 2 *N* solution.

Procedure

Neutralize 10-20 ml of the sample solution (containing 0.1-0.025 g of Tl) by NaOH solution to phenolphthalein, add 2 g of sodium tartrate, 3-5 g of KCN, and add an equal volume of NaOH solution. Dilute with water to 100 ml. Add a 4-5-fold excess of thionalide solution. Mix and heat to the boil: the amorphous precipitate turns into crystals. Cool the mixture, separate the lemon-yellow precipitate on a glass crucible, wash with cold water to remove KCN, and with acetone to remove excess reagent. Dry the residue at 100 °C and weigh. The conversion factor for Tl is 0.4859.

GRAVIMETRIC DETERMINATION OF THALLIUM (I) AS CHROMATE

The method is based on the precipitation of thallium from an alkaline solution by potassium chromate in the form of a sparingly soluble Tl_2CrO_4 (the solubility in water at 20°C is 8.15×10^{-5} mole/l; in 96 per cent ethanol, 1.14×10^{-5} mole/l). The ions reducing CrO_4^{2-} (e.g. SO_3^{2-}), and also the ions precipitating from an ammoniacal solution of chromate as hydroxides (Al, Fe, Cr) or chromates (Ag, Pb, Bi, Ba and Sr) interfere with the determination. The interfering effect of extraneous ions is removed by EDTA which reacts with them in an alkaline medium to form stable soluble complex compounds.

Reagents

Potassium chromate, 10 per cent and 1 per cent solutions.
Ammonia, 20 per cent solution.
Ethyl alcohol, 50 per cent solution.

Procedure

Heat a neutral solution of the sample (containing about 1 mg of Tl in 1 ml) to 70-80°C, add ammonia solution (4 ml per each 100 ml) and 10 per cent potassium chromate solution (10 ml per each 100 ml). Cool the solution and allow it to stand for at least 12 hours. Separate the precipitate of thallium chromate on a glass crucible No. 3, using 1 per cent potassium chromate solution to transfer the mixture onto the filter. Wash the precipitate 2 or 3 times with small portions of ethanol until the yellow colour of the filtrate vanishes, dry the precipitate to constant mass at 120-130°C, and weigh. The conversion factor for Tl is 0.7789.

GRAVIMETRIC DETERMINATION OF THALLIUM (III) WITH DIANTIPYRYLPROPYLMETHANE

The method is based on the precipitation of Tl^{III} as $C_{28}H_{30}O_2N_4 \cdot HTlCl_4$ from hydrochloric acid solution by diantipyrylpropylmethane. The solubility of the precipitate in water at 20°C is 5.7×10^{-5} mole/l. The variation of the acidity in the range from 1 to 6 *N* does not affect the results of the determination, the chloride ion concentration being higher than 0.1 *M*. In^{3+}, Bi^{3+}, Zn^{2+}, Cd^{2+}, Fe^{3+}, Mg^{2+}, PO_4^{3-}, and AsO_4^{3-} do not interfere with the determination of thallium (III) in a medium of 3 *N* hydrochloric acid.

Reagents

Diantipyrylpropylmethane, 1 per cent solution in CH_3COOH (1 : 1).
Washing solution, 0.05 per cent diantipyrylpropylmethane in 1 *M* hydrochloric acid.
Hydrochloric acid, 1 *M* solution.
Sodium chloride, crystalline.

Procedure

Add NaCl to an acid solution of Tl^{III} salt to adjust the chloride ion concentration to not lower than 0.1 *M*. Add diantipyrylpropylmethane with stirring until the formation of precipitate discontinues. Allow the precipitate to coagulate and separate on a glass filter No. 3 washing it several times with small portions of the washing solution and then with hydrochloric acid. Dry to constant weight at 110-120°C and weigh. The conversion factor for Tl is 0.2628.

BROMATOMETRIC DETERMINATION OF THALLIUM (I)

The method is based on the oxidation of Tl^{I} with potassium bromate in a hydrochloric acid medium (5-8 per cent HCl solution):

$$3Tl^{+} + BrO_3^{-} + 6H^{+} \rightleftharpoons 3Tl^{3+} + Br^{-} + 3H_2O$$

The point of equivalence is established potentiometrically by the change of the platinum electrode potential. A compensation potentiometer is used for the purpose. A saturated calomel half-cell is used as the reference electrode.

As, Sb, Tl, and Cu interfere with the determination. If the Fe^{3+} ion is present, ammonium phosphate should be added before titration.

Reagents

Potassium bromate, 0.02 *N* solution.
Hydrochloric acid, density 1.19 g/cu.cm.

Procedure

Dilute the solution of the sample (containing 0.05-0.01 g of Tl) with water, adding it to the mark in a 50-ml volumetric flask. Transfer a 20-ml aliquot of the solution into a titration beaker, add 15 ml of hydrochloric acid and titrate with potassium bromate solution until the potential jumps abruptly. During the first titration (tentative), add potassium bromate by 1-ml portions, while in the second (accurate) titration, add potassium bromate solution in 0.1 ml portions when the point of equivalence is approached. 1 ml of 0.0200 *N* solution of potassium bromate is equivalent to 2.044 mg of thallium.

COMPLEXOMETRIC DETERMINATION OF THALLIUM (III) IN ALLOYS

The method is based on the titration of tervalent thallium at pH of about 2 by a standard solution of EDTA. The equivalence point is located with 1-(2-pyridylazo)-2-naphthol or 4-(2-pyridylazo)resorcinol which react with Tl^{3+} to form red-violet or red complexes respectively. The complexes convert into thallium complexonates by the action of EDTA. The colour abruptly changes to yellow at the point of equivalence (own colour of the indicator).

Thallium can be determined in the presence of prevailing quantities of Zn, Pb and Cd, and also in the presence of the ions of metals forming stable complexonates only in neutral or weak alkaline medium (Ca, Mg, Al). Fe^{3+}, Bi^{3+}, In^{3+}, Ga^{3+}, Cu^{2+}, MnO_4^- and also the chloride, bromide and iodide ions, which destroy the thallium complex with the dye, interfere with the determination. Thallium can be determined in the presence of the Bi^{3+} ion by titrating the sum of Bi^{3+} and Tl^{3+} at pH 4-5. Tl^{3+} is then reduced to Tl^{+} and the liberated EDTA is titrated with a standard solution of a copper salt.

The method can be used for the analysis of magnesium and other alloys containing not less than 0.5 per cent of Tl. The error of determination of thallium does not exceed 0.5 per cent. The determination continues for 20-25 minutes.

Reagents

Sulphuric acid, diluted 1 : 2.
Ammonium persulphate, crystalline.
Sodium fluoride, crystalline.
Ammonia, 2 *N* solution.
Monochloroacetic acid, 1 *M* solution.
Potassium bromide, 2 *M* solution.
Sulphosalicylic acid, 20 per cent solution.
EDTA, 0.01 *M* solution.
Ammonium acetate, crystalline.
1-(2-Pyridylazo)-2-naphthol, 0.1 per cent solution in ethanol.
1-(2-Pyridylazo)resorcinol, 0.1 per cent aqueous solution.

Procedure

Determining Thallium in Magnesium Alloys. Dissolve a sample of the alloy weighing 0.2-0.5 g in 10 ml of sulphuric acid, dilute the solution with water to 100 ml (the final acid concentration should be 1-2 *N*), add 0.5 g of ammonium persulphate and boil for a few minutes to destroy its excess. Add 1-2 g of potassium fluoride (if the sample contains Zr or a large quantity of Al) and ammonia to the solution until it turns pale yellow ($Tl(OH)_3$ begins precipitating). Then add monochloroacetic acid, adjust the pH to 2 to universal test paper, and add a few drops of 1-(2-pyridylazo)-2-naphthol solution. Titrate with EDTA solution until the red-violet colour changes to yellow.

Determining Thallium in the Presence of Iron. Add 5-10 ml of potassium bromide solution to 50-70 ml of the solution containing Fe^{3+} and Tl^{3+} (to mask Tl^{III}) and adjust the pH of the solution to 2 by adding ammonia dropwise. Heat the solution to 40-60°C, add 3-5 drops of sulphosalicylic acid and titrate Fe^{III} with EDTA solution until the red-brown colour vanishes. Add ammonium acetate (to adjust the pH to 4-5), a few drops of 4-(2-pyridylazo)resorcinol solution (until the solution colour is distinct red) and titrate Tl^{III} with EDTA solution until the colour changes to orange yellow.

If the thallium and iron contents are about the same, one and the same solution of EDTA can be used for titration. If the iron content exceeds that of thallium, use a more concentrated solution of EDTA for the first titration.

EXTRACTION-PHOTOMETRIC DETERMINATION OF THALLIUM (III)

The method is based on the formation of an iodide complex of thallium (III) with diantipyrylmethane or diantipyrylpropylmethane, ($C_{23}H_{24}O_2N_4 \cdot HTlI_4$ or $C_{26}H_{30}O_2N_4 \cdot HTlI_4$) with subsequent extraction of the complex with benzene. The molar extinction coefficient of the benzene extract at 400-405 nm is 1.20×10^4. It does not depend on the nature of the base. Cu^{2+}, Fe^{3+}, Bi^{3+}, Cd^{2+}, Pb^{2+}, Zn^{2+}, Ga^{3+} and In^{3+} do not interfere with the determination in the presence of EDTA at pH 2-3.

Reagents

Diantipyrylmethane or diantipyrylpropylmethane, 0.05 per cent solution in acetic acid (1 : 10).
Potassium iodide, 0.1 per cent solution.
Sulphuric acid, 1 *N* solution.
Bromine water.
Benzene.
Thallium (I) salt, standard solution. 1 ml is equivalent to 40 μg of thallium.

Constructing a Calibration Curve

Place 1, 2, 3, 4 and 5 ml of the thallium (I) salt standard solution into small beakers and add 2-3 ml of bromine water into each of them. Heat the solutions to the boil and maintain boiling to remove excess bromine. Transfer cold solutions into 25-30 ml separating funnels, rinse the beakers with 2-3 ml of sulphuric acid, and add 2-3 ml of potassium iodide solution and 1-2 ml of diantipyrylmethane (or diantipyrylpropylmethane). Extract with 10 ml of benzene. Discard the separated lower layer, and pass the upper layer through a dry paper filter. Measure the absorption of the filtered extract at 400 nm in a cell with a light path of 1 cm on a spectrophotometer using benzene as a reference solution. Construct the calibration curve using the data obtained.

Procedure

Add all the required reagents to the solution of the sample as instructed for the construction of the calibration curve, and measure the absorption of the solution. Find the thallium content from the calibration curve.

EXTRACTION-PHOTOMETRIC DETERMINATION OF SMALL QUANTITY OF THALLIUM (III) WITH METHYL VIOLET

The method is based on the extraction with toluene (or benzene) of a coloured compound of the anion $TlCl_4^-$ with the cation of methyl violet. The absorption maximum of the extract is at 570 nm. The molar extinction coefficient is about 5.0×10^4. The change in the acidity from 0.2 to 0.8 *N* (HCl) does not affect the results of the determination. The interfering effect of antimony can be removed by oxidizing Tl^{I} to Tl^{III}, the chloride ion concentration not exceeding 0.1-0.2 g-eq./l ($SbCl_6^-$ ion is not formed in these conditions). The interfering effect of Au^{III} and Hg^{II} can be removed by (calorization) of the elements with copper metal.

Reagents

Methyl violet, 0.2 per cent solution.
Phosphoric acid, density 1.46 g/cu.cm.
Hydrogen peroxide, 30 per cent solution.

Ferric chloride, 20 per cent solution.
Copper spiral.
Thallium (I) salt, standard solution. 1 ml is equivalent to 10 μg of thallium.
Hydrochloric acid, density 1.19 g/cu.cm.
Nitric acid, density 1.4 g/cu.cm.
Toluene.

Constructing a Calibration Curve

Place the thallium (I) salt standard solution in 100-ml beakers so that they contain 1, 5, 15, and 20 μg of Tl. Add 30 ml of phosphoric acid, 1 ml of ferric chloride and 7-8 drops of hydrogen peroxide into each beaker and allow the solutions to stand for 30-40 minutes. Transfer the solutions into separating funnels, dilute with water to 40 ml, add 25 ml of toluene, 1.0 ml of methyl violet solution and shake for a minute. Allow the phases to separate and transfer the extract into a dry 50-ml beaker. Allow the solutions to stand for 20 minutes and measure their absorption by an absorptiometer in a cell with a light path of 1 cm using a green optical filter. Construct the calibration curve using the data obtained.

Procedure

Place a sample of ore weighing 1 g into a 150-ml beaker and add 20-40 ml of a mixture of hydrochloric and nitric acid (3 : 1). As soon as the vigorous reaction stops, heat the solution and evaporate to 3-5 ml. Transfer the beaker onto a water bath and evaporate the solution to dryness. Treat the residue with 5-10 ml of hydrochloric acid and evaporate again on a water bath to dryness. If a sample contains thallium bound with a silicate base, silicon is distilled as SiF_4. The residue is treated with concentrated hydrochloric acid with subsequent removal of its excess by evaporation on a water bath.

Add 30 ml of phosphoric acid to the obtained solution, heat it to boiling and immerse a copper spiral (washed preliminarily with dilute nitric acid and water). Remove the beaker from the hotplate in ten minutes. Remove the spiral, wash it with a small amount of water. Separate the undissolved residue on a filter and wash it 1-2 times with water. The volume of the filtrate and the washings should not exceed 30-35 ml. Proceed further as for the construction of the calibration curve. Find the thallium content from the calibration curve.

EXTRACTION OF THALLIUM (III) FROM ORES AND THEIR PRODUCTS

Thallium (III) is separated by extraction with ethyl ether from a 1 *N* solution of hydrobromic acid. Hg^{2+}, Sb^{V} and Au^{III} are extracted together with Tl^{III}.

Reagents

Nitric acid, density 1.4 g/cu.cm.
Hydrochloric acid, diluted 1 : 1 and 10 per cent solution.
Sulphuric acid, diluted 1 : 1.

Hydrobromic acid, 40 per cent solution saturated with bromine and 1 *N* solution saturated with ether.
Ether, saturated with 1 *N* hydrobromic acid.
Bromine.

Procedure

Dissolve a sample of ore weighing 0.2-0.5 g in 20-50 ml of hydrochloric acid (1 : 1) with heating on a sand bath, add 2-3 ml of nitric acid and evaporate to dryness. Treat the residue two times with 2-3 ml portions of hydrochloric acid (1 : 1), and evaporate to dryness each time. Next, add 20-30 ml of a 10 per cent solution of hydrochloric acid, heat the solution, then cool it and separate the undercomposed residue and $PbCl_2$ on a filter. Wash the precipitate two or three times with a 10 per cent solution of hydrochloric acid. Evaporate the filtrate to dryness, treat the residue with 5-7 ml of a 40 per cent solution of hydrobromic acid saturated with bromine and evaporate almost to dryness. Repeat this operation three times.

Dissolve the dry residue in 8-10 ml of 1 *N* hydrobromic acid saturated with bromine, transfer the solution into a separating funnel and rinse the beaker once or twice with 2-3 ml portions of the same acid. Add an equal volume of ether to the solution and shake for a minute. Allow the mixture to separate, transfer the aqueous layer into another separating funnel washed with 1 *N* hydrobromic acid saturated with ether, and repeat extraction. Wash the ether extracts two times with 5-ml portions of the same acid, each time shaking for 15-20 seconds. Remove ether by heating on a water bath and evaporate the solution to dryness. Add 0.5 ml of sulphuric acid and evaporate the solution on a sand bath to fumes of H_2SO_4. (To oxidize organic impurities, add a few drops of nitric acid.) Add 2-3 ml of water and evaporate again to fumes of H_2SO_4. Repeat this operation two or three times. Evaporate for the last time almost to dryness and determine thallium in the residue polarographically or photometrically.

POLAROGRAPHIC DETERMINATION OF THALLIUM (I) IN CADMIUM

The thallium (I) ion is reduced reversibly on a dropping-mercury electrode at the potential of about —0.50 V with reference to a saturated calomel electrode. The half-wave potential does not depend on the composition of the electrolyte. The wave height is proportional to the thallium concentration in the solution against the background of NH_3 or HCl. Monovalent thallium is easy to determine in cadmium or its salts in an ammonia medium in the absence of copper. The half-wave potentials for Tl^+ and Sn or Pb are indiscriminate. To discriminate between the Sn and Tl waves, the tartrate ion is added to suppress the Sn wave, while to distinguish between the waves of Pb and Tl, it is recommended to add EDTA, which shifts the half-wave potential of Pb in a weak acid medium to the region of more negative values (—1.1 V). The method is used for the determination of thallium in lead as well. In these conditions, copper is reduced at the potential of —0.3 V. Polarography is usually carried out after separation of thallium by extraction.

Reagents

Sulphuric acid, diluted 1 : 1.
Ammonia, 25 per cent solution.
Sodium sulphite, crystalline.
Joiner's glue, 0.25 per cent solution.
Hydrogen peroxide, 30 per cent solution.

Procedure

Distil ether from its extracts from 1 *M* HBr solutions containing thallium on a water bath. Add 3 ml of sulphuric acid (1 : 1) to the residue and evaporate the solution to fumes of H_2SO_4. Add 3-5 drops of hydrogen peroxide to the hot solution in order to decolourize it. Cool the solution, wash the flask walls with 5 ml of water and heat the solution again to fumes of SO_3. Add 10-15 ml of water and 0.2-0.3 g of sodium sulphite to the residue and boil for 5 minutes until SO_2 odour is felt no longer. Transfer the solution into a 25-ml volumetric flask, neutralize to Congo red with ammonia solution and add 2.5 ml in excess. Cool the solution, add water to the mark and mix thoroughly. Transfer 15 ml of the solution into a beaker, add 1 g of sodium sulphite, 5 drops of joiner's glue, mix, and carry out polarography.

EXTRACTION OF THALLIUM WITH DI-2-ETHYLHEXYLPHOSPHORIC ACID AND ITS PHOTOMETRIC DETERMINATION WITH 1-(2-PYRIDYLAZO)-2-NAPHTHOL

Thallium (III) can be separated from Zn, Cd, Hg, Cu, Al, Co, Ni, Ag, Mg, Cr and Mn by its extraction with di-2-ethylhexylphosphoric acid in heptane from 0.1-0.5 *N* solutions of sulphuric, nitric and perchloric acids. Ga, In, Sb, Bi, Fe and the rare earths are extracted together with thallium (III). But only thallium (III) practically reacts in benzene extract with 1-(2-pyridylazo)-2-naphthol and this ensures sufficient selectivity in the determination of thallium. Hundredfold quantities of Ga and Fe do not interfere with the determination. The molar extinction coefficient of the extract is $(15.6 \pm 0.6) \times \times 10^3$ at 560 nm.

Reagents

Thallium (III), standard solution. 1 ml is equivalent to 5 μg of thallium.
Di-2-ethylhexylphosphoric acid, 0.3 *N* solution in heptane.
Benzene.
Sulphuric acid, 0.5 *N* solution.
1-(2-Pyridylazo)-2-naphthol, 0.01 per cent solution in benzene.

Constructing a Calibration Curve

Place 1, 2, 3, 4, 5 and 6 ml of the standard solution of thallium into 25-ml separating funnels and adjust the pH of the solutions to 0.1-0.5 *N* H_2SO_4. Add 10 ml of *di-2-ethylhexylphosphoric acid* and extract thallium for two minutes. Allow the phases to separate, wash the organic layer two times with sulphuric acid, add 2 ml of 1-(2-pyridylazo)-2-naphthol, transfer the mixtures into 25-ml volumetric flasks and add benzene to the mark. Measure the absorption of the extracts at 560 nm in cells with a light path of 1 cm. Construct the calibration curve using the data obtained.

Procedure

Take an aliquot of the solution containing from 5 to 30 μg of thallium and proceed as for the construction of the calibration curve. Find the thallium content from the calibration curve.

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Germanium

Germanium, Ge, has the positive valency of 4 and 2 and the negative valency of 4. Compounds of Ge^{IV} (GeO_2, $GeCl_4$, many complex compounds, etc.) are most important in analytical chemistry. Compounds of divalent germanium easily oxidize to Ge^{4+}. The gaseous hydride GeH_4 is a compound in which germanium has the negative valency of 4. When heated to 360°C, it decomposes to Ge and H_2. It is more stable than SbH_3. The hydride GeH_4 is formed during reduction of germanium compounds with zinc metal or amalgamated sodium. Black Ag_4Ge is known.

The standard electrode potentials in aqueous solutions at 25°C are as follows (with reference to the standard hydrogen potential:)

$$Ge^{2+} + 3H_2O \rightleftharpoons H_2GeO_3 + 4H^+ + 2e^- \qquad -0.363\ V$$

$$Ge + 2H_2O \rightleftharpoons GeO_2 + 4H^+ + 4e^- \qquad -0.246\ V$$

$$Ge + 3H_2O \rightleftharpoons H_2GeO_3 + 4H^+ + 4e^- \qquad -0.182\ V$$

$$Ge \rightleftharpoons Ge^{2+} + 2e^- \qquad 0.000\ V$$

Germanium (II) forms a tartrate complex from whose solutions germanium cannot be precipitated by ammonia or hydrogen sulphide.

Germanium sulphide, GeS, is a reddish-orange substance soluble in concentrated hydrochloric acid and solutions of ammonium sulphide. Concentrated hydrochloric acid solutions contain the anion GeC[illegible] and others. Sulpho salts are present in solutions of ammonium sulphide.

Germanium hydroxide, $Ge(OH)_2$, is an orange-red substance soluble in hydrochloric acid and alkalies, and very difficultly soluble in ammonia solutions.

The compounds of divalent germanium easily oxidize in air. Dark brown or black GeO is known.

The ion of divalent germanium is formed during reduction of tetravalent germanium compounds by hypophosphorous acid in hydrochloric acid solutions. Arsenic is reduced to its elemental state and precipitates in these conditions. The reaction is used for the separation of germanium and arsenic [1].

Germanium (IV) in aqueous solutions can be present in the form of various anions and also cations (Ge^{4+}, $Ge(OH)_3^+$, etc.).

Aqueous solutions of germanium dioxide contain ions of metagermanic acid (H_2GeO_3) and pentagermanic acid ($H_2Ge_5O_{11}$), the equilibrium between them being dependent on the pH and the total concentration of the tetravalent germanium ion. The dissociation constants of metagermanic acid are $k_1 = 1.86 \times 10^{-9}$ and $k_2 = 1.9 \times \times 10^{-13}$. Equilibrium between germanic acid or germanium dioxide and the anion $GeCl_5^-$ or $GeCl_6^{2-}$ is established in hydrochloric acid solutions of germanium dioxide. One or two intermediate acid complexes $[Ge(OH)_xCl_{5-x}]^-$ or $[Ge(OH)_x Cl_{6-x}]^{2-}$ (where x is 3 or 4) are probably involved in the equilibrium. Solutions of germanium dioxide, in addition to anions, contain also cations [2, 3]. Germanium cations are absent from an alkaline solution but appear at pH below 7. The ion Ge^{4+}, germanyl GeO^{2+} or $Ge(OH)_2^{2+}$ are formed in solutions. Their concentration in weak or moderately acid solution is small, but despite this many reactions of germanium with organic reagents occur only due to the presence of these cations. For example, the germanium cation reacts with EDTA in acid solutions.

Hydrogen sulphide precipitates white GeS_2 from strong acid solutions. The compound is sparingly soluble in 3 *N* hydrochloric acid. It is easily hydrolyzed, and is soluble in solutions of sulphides of the alkali metals with the formation of the ion GeS_3^{2-} and others.

Germanium (IV) forms complex compounds with the chloride, fluoride, and oxalate ions, polyhydric alcohols (glycerol, mannitol), phenols, containing not less than two oxy-groups in the ortho-position. The fluoride complex (GeF_6^{2-}) and oxalate complexes of germanium (IV) are very low dissociated. Germanium can be masked by potassium fluoride (or oxalate). Germanium is not precipitated by hydrogen sulphide in the presence of KF from acid solutions. Arsenic (III) can therefore be separated from germanium (the sulphide As_2S_3 is precipitated in the presence of KF). Hexafluorogermanates are completely destroyed by alkalies.

Ammonium molybdate reacts with germanic acid in nitric, sulphuric or hydrochloric acid solution (like silicic acid) with the formation of yellow molybdogermanic acid $H_4[Ge(Mo_3O_{10})_4]$. Germanium can be determined photometrically in the form of this compound, either directly or after reduction to a blue compound [4].

EDTA reacts with the germanium (IV) ion in acid solutions (0.02-0.05 *N*) in the molar ratio of 1 : 1. The reaction is completed in ten minutes with boiling only on the condition that the solutions contain at least a 2.5-fold excess of EDTA. The reaction is slow in the cold. Germanium cannot be displaced from the formed complex by the zinc ion in an alkaline medium, by the bismuth ion in a weak acid medium and by zirconium ion in a strong acid medium. This makes it possible to determine germanium by titrating excess EDTA with a solution of a salt of bismuth, zinc or zirconium using suitable indicators [5].

Excess polyhydric alcohols or monosaccharides (glycerol, mannitol, fructose, galactose, etc.) react with the solution of germanium dioxide in the molar ratio of 2 : 1 with the formation of monobasic complex acids. The thermodynamic constants of ionization of the formed difructosogermanic, digalactosogermanic, dimannitogermanic, diglucosogermanic and diglycerogermanic acids are (1.04 ±

± 0.01) × 10^{-4}, (2.39 ± 0.01) × 10^{-5}, (1.21 ± 0.01) × 10^{-5}, (8.35 ± 0.03) × 10^{-6} and (5.05 ± 0.02) × 10^{-6}, respectively (at 25°C) [6]. The thermodynamic instability constants [7] of these compounds at 25°C are 4.24 × 10^{-5}, 7.64 × 10^{-3}, 4.04 × 10^{-4}, 3.54 × 10^{-2} and 7.85 × 10^{-2}, respectively. A relatively great increase in the solution acidity during the reaction between a weak germanic acid and mannitol or fructose makes it possible to easily determine germanium by titration with a suitable indicator.

Germanium dioxide reacts in aqueous solutions with simple diphenols to form two series of complex compounds, viz. sparingly soluble complexes $GePh \cdot 2H_2O$ (so-called germanium-diphenols) and soluble complexes H_2GePh_3 (phenol-germanic acids). Tripyrocatecholgermanic and tripyrogallolgermanic acids in 0.01 *M* (and more dilute) solutions are completely ionized at the first step. The second ionization constants are 1.85 × 10^{-2} and 2.21 × 10^{-3} respectively (at 25°C).

The dissociation constants of complexes according to the equation

$$HGePh_3^- + 3H_2O \rightleftharpoons HGeO_3^- + 3H_2Ph$$

are 2.16 × 10^{-9} and 0.88 × 10^{-9}, respectively (at 25°C). When diphenol is added to the solution of GeO_2, only one soluble complex acid is formed [8]. Phenolgermanic acids form salts with pyridine, piperidine, quinoline, triphenylmethane dyes, cations of orthophenanthrolinic complexes of Co, Ni, Cu, Zn and Cd.

The formation of tripyrocatecholgermanic acid underlies the alkalimetric method for the determination of germanium (the end point of titration is established potentiometrically or to bromcresol purple). The method ensures good reproducibility and accuracy of the results [9, 10]. The same reaction is used for the gravimetric determination of germanium [11].

Dinitropyrocatecholgermanic acid reacts with brilliant green to form an ionic association (extractable with carbon tetrachloride) suitable for the extraction-photometric determination of germanium [12].

Orthodihydroxyazo compounds react with the ion of tetravalent germanium to form coloured products [13]. Resarsone is used for fluorimetric determination of germanium [14-16]. Various substitutes of 2,3,7-trihydroxy-6-fluorones react with the germanium (IV) ion to form coloured compounds [17-19]. Phenylfluorone is the most suitable reagent for the photometric determination of microgram quantities of germanium [20]. The reagent is used for the photometric determination of 0.0001-0.2 per cent of germanium in silicates, in sulphide and other ores, and coals. Germanium is first separated as $GeCl_4$ by exctraction with carbon tetrachloride from 9 *N* solutions of hydrochloric acid or by distillation from solutions of hydrochloric and phosphoric acid.

o-Dihydroxychromenols react with the germanium (IV) ion to form coloured compounds [21]. 6,7-Dihydroxy-2,4-diphenylbenzopyrilium chloride has the highest sensitivity. The reagent is used for the photometric determination of germanium. The method is used for the analysis of various materials. EDTA masks Zr, Th, Fe^{3+}, Sn^{IV}, Bi^{III}. Phosphoric acid masks the titanium (III) ion, hydrogen peroxide, and decreases the effect of the ions of Mo^{VI}, W^{VI}, Sb^{III} and V^{V}.

Purpurogallin reacts with germanium (IV) in the molar ratio of 2 : 1 in a wide range of pH [22] to form pale yellow or pale pink soluble compounds. On standing the solution precipitates a pink substance. The solutions remain clear in the presence of ethanol and gelatin. The absorption curves of purpurogallin complex of germanium have the maximum at 340 nm. Purpurogallin is suitable for the spectrophotometric determination of germanium. The molar extinction coefficient in a 3 *N* hydrochloric acid solution is 3.4×10^4 at 340 nm. The absorption is proportional in the range of Ge concentrations from 0.1 to 3.4 μg/ml.

For the detection and determination of germanium, it is separated by distillation as $GeCl_4$ (b.p. 86°C) from hydrochloric acid solution in a current of chloride and in the presence of an oxidant. As^{III} converts into a non-volatile As^{V} in this process. A more convenient method to separate germanium from many accompaning elements is extraction of $GeCl_4$ with carbon tetrachloride from 8-10 *N* solutions of hydrochloric acid. Small quantities of germanium are separated by co-precipitation with ferric hydroxide and also by precipitation with tannic acid and by some other methods.

A relatively large quantity of germanium can be determined by the alkalimetric titration with a monobasic mannitolgermanic acid or dibasic tripyrocatecholgermanic acid. The methods give satisfactory results. The gravimetric methods (weighing as GeO_2, Mg_2GeO_4, molybdogermanates of organic bases, etc.) are relatively seldom used. The method based on weighing tripyrocatecholgermanate of cadmium phenanthroline $[CdPhen_2]\,[Ge(O_2C_6H_4)_3]$ is also important.

A small quantity of germanium is determined photometrically as a molybdogermanic complex with 9-phenyl-2,3,7-trihydroxyfluorone and also other hydroxyl-containing organic substances. Polarographic and spectral methods of determining germanium are also practically used.

The literature contains a review of the analytical methods for the determination of germanium [23, 24] and a review of the chemistry of germanium [24] (complex formation and the state of germanium in solutions).

GRAVIMETRIC DETERMINATION OF GERMANIUM AS TRIPYROCATECHOLGERMANATE

Tripyrocatecholgermanic acid is precipitated at pH 3.5-4.5 by a doubly charged cation complex of cadmium with *o*-phenanthroline. The obtained compound $[CdPhen_2]\,[Ge(O_2C_6H_4)_3]$ is weighed. The error of the determination of 0.5-20 mg of Ge is less than 2 per cent. The method is used after the separation of germanium by distillation or extraction.

Reagents

Cadmium complex with o-phenanthroline, 0.01 *M* solution. Dissolve separately 0.21 g of anhydrous cadmium sulphate in 50 ml of water and 0.364 g of *o*-phenanthroline in 50 ml of water, and mix the solutions.
Acetate buffer solution, pH 4.
Pyrocatechol, 10 per cent solution, prepared for the test.
Sodium sulphate, 5 per cent solution.
Ethyl alcohol, 96 per cent.

Procedure

Add 5 ml of pyrocatechol to 15 ml of the solution containing 0.5-20 mg of Ge. Next add 2 ml of sodium sulphate (for a better coagulation of the precipitate) and 8 ml of the acetate buffer solution. Stir the solution and add 25 ml of the cadmium complex with phenanthroline. In 15-30 minutes separate the precipitate on a glass filter No. 3 or 4, wash with two 5-ml portions of water, once with 3 ml of ethanol, dry to constant weight at 100-110°C, and weigh. The conversion factor for Ge is 0.08347.

POTENTIOMETRIC TITRATION OF TRIPYROCATECHOLGERMANIC ACID

Tripyrocatecholgermanic acid is titrated with sodium hydroxide solution with detecting the end point by a glass electrode. The end point can also be located by using bromcresol purple. B, Sb^{III}, Sn^{IV} and Fe^{III} interfere with the determination. Germanium is determined as $GeCl_4$ by extraction or distillation.

Reagents

Pyrocatechol, crystalline.
Sodium hydroxide, 1 *N* and 0.02 *N* solutions free from Na_2CO_3. Standardize a 0.02 *N* solution of NaOH against pure GeO_2. To that end, dissolve a sample of GeO_2 in NaOH solution free from Na_2CO_3 and proceed as in the Procedure.
Hydrochloric acid, 1 *N* solution.

Procedure

Add 1 *N* solution of sodium hydroxide or hydrochloric acid to pH 5 (glass electrode) to 250 ml of the test solution containing 20-100 mg of Ge. Then add 3 g of pyrocatechol and titrate with a 0.02 *N* solution of NaOH to pH 5 at a rate of one drop per second.

COMPLEXOMETRIC DETERMINATION OF GERMANIUM (IV)

An acid solution of germanium dioxide is heated with excess EDTA during which germanium (IV) complexonate is formed quantitatively. Excess EDTA is titrated with a solution of a zirconium or zink salt in the presence of a suitable indicator. Magnesium, alkaline-earth metals, zinc, lead, aluminium and many ter- and divalent metals do not interfere with the titration of excess EDTA by a zirconium salt in a hydrochloric acid medium. 100 mg of arsenic, less than 50 mg of antimony or less than 15 mg of molybdenum do not interfere either. Magnesium, alkaline earths and all metals forming complexonates in an ammonia medium interfere with the determination of germanium by titration with a solution of a zinc salt. 100 mg of arsenic, to 10 mg of antimony and to 15 mg of molybdenum do not interfere.

Iron and tin interfere with the titration of excess EDTA both in alkaline and acid medium. Complexometric determination of germanium in substances of complex composition is therefore possible only after its separation from many elements by distillation of $GeCl_4$ or extraction of $GeCl_4$ with carbon tetrachloride.

The method can be used to determine from 0.05 to dozens of per cent of germanium in commercial materials.

The method is used for the analysis of ash, coals rich in germanium, concentrates of germanium dioxide containing 20-60 per cent of Fe_2O_3, 10-20 per cent of SiO_2, a few per cent of As_2O_3, Al_2O_3, CaO, MgO and oxides of other elements. During the analysis of ash, germanium is separated by extraction with carbon tetrachloride, and during the analysis of concentrates, by distillation from 6 *N* hydrochloric acid. It is unnecessary to separate germanium from arsenic during extraction or distillation because arsenic does not interfere with subsequent complexometric determination of germanium.

Reagents

Nitric acid, density 1.4 g/cu.cm.
Hydrofluoric acid, 40 per cent solution.
Orthophosphoric acid, density 1.8 g/cu.cm.
Hydrochloric acid, density 1.19 g/cu.cm and 1 and 6 *N* solutions.
Carbon tetrachloride, pure.
Hydroxylamine chloride, 2 per cent solution in 9 *N* HCl.
Phenolphthalein, 0.1 per cent ethanol solution.
Sodium hydroxide, 18 *N* solution.
EDTA, 0.005, 0.05 and 0.1 *M* solutions.
Xylenol orange, 0.1 per cent solution.
Zirconium oxychloride, 0.005, 0.05 and 0.1 *M* solutions in 1 *N* hydrochloric acid.
Ammonia, 25 per cent solution.
Chromogen black, *ET*-00, 0.1 per cent solution.
Zinc sulphate, 0.005, 0.05 and 0.1 *M* solutions.

Procedure

Determining Germanium in Ash. Add 2 ml of nitric acid and 5 ml of hydrofluoric acid to a sample of ash weighing 0.5-1 g in a platinum dish and evaporate on a water bath to 1.0-1.5 ml. Add 2 ml of nitric, 5 ml of hydrofluoric, and 3 ml of orthophosphoric acid. Evaporate first on a water bath and then on a sand bath to a syrupy consistency, cool, wash the dish walls with water and evaporate again to prepare a thick syrup. Transfer the liquid into a separating funnel with 25 ml of water, add 75 ml of concentrated hydrochloric acid and extract three times with 10-ml portions of carbon tetrachloride. Wash the extracts three times with 10-ml portions of hydroxylamine chloride solution and extract $GeCl_4$ three times with 10-ml portions of water in another separating funnel.

Add a drop of phenolphthalein to the re-extract in a conical flask and then add 18 N sodium hydroxide solution, drop by drop, until the pink colour appears. The colour is destroyed by adding 2-3 drops of 1 N hydrochloric acid. Add 2.5 ml of 1 N hydrochloric acid, dilute with water to 50 ml, add 25 ml of 0.005 M EDTA solution, heat to boiling and boil carefully for 15 minutes, adding water from time to time to replenish the evaporated water. Titrate EDTA excess by zirconium oxychloride solution. To that end, add 3 ml of 1 N hydrochloric acid, 3 drops of xylenol orange to the solution, cool it to 55°C and titrate with a 0.005 M solution of zirconium oxychloride in 1 N hydrochloric acid until the yellow solution turns bright pink.

Excess EDTA can be titrated with a solution of zinc sulphate. Cool the solution to room temperature, add 2 ml of ammonia solution, 5 drops of chromogen black ET-00 solution and titrate with a 0.005 M solution of zinc sulphate until the blue-green solution turns pink without a blue hue.

1 ml of a 0.005 M solution of EDTA is equivalent to 0.363 mg of germanium.

Determining Germanium in Concentrates. Take a sample of concentrate weighing 0.25-1.0 g (depending on the germanium content) and distil $GeCl_4$ from 15 ml of 6 N hydrochloric acid in a special apparatus. Instal a partial condenser in a rubber plug of a 100-ml round-bottomed flask with a 9-cm neck. The distance from the end of the widened part of the condenser to the outlet tube should be 7-8 cm. The condenser should be filled with glass fragments and closed with a rubber stopper. Connect the condenser outlet tube (end-to-end connection with a piece of rubber tubing) with a vertical condenser tube bent at an obtuse angle. The inner tube should be 20-25 cm long. Pass its lower end into a 100-ml conical flask containing 20 ml of water.

Place the receptacle into cold water during distillation and pass a fast stream of water through the condenser.

Place the sample of the concentrate into the flask of the apparatus and add 15 ml of 6 N hydrochloric acid. Close the flask with a plug carrying the partial condenser, assemble the apparatus, heat the flask on a gas burner, and distil for 15 minutes until the residual volume of the liquid is 2-3 ml. Cool the still, add 15 ml of 6 N hydrochloric acid through the partial condenser and distill again at the same rate to reduce the liquid volume in the flask to 2-3 ml. Repeat the operation once again.

Transfer the obtained distillates into a 500-ml Erlenmeyer flask, add 2-3 drops of phenolphthalein and 18 N sodium hydroxide, drop by drop until the solution turns pink. The colour should be destroyed by 3-5 drops of 1 N hydrochloric acid. Add 4.5 ml of 1 N hydrochloric acid, 50 ml of 0.1 M (or 0.05 M) solution of EDTA and water to make 150 ml. Heat to the boil and maintain the liquid boiling quietly for 15 minutes. Add water from time to time to replenish the loss on evaporation. Titrate excess EDTA with a 0.1 M (or 0.05 M) solution of zirconium oxychloride. To that end, dilute the solution with water to 300 ml, heat to 55 °C, add 20 ml of 1 N hydro-
and 0.5 ml of 0.1 per cent solution of xylenol orange, and
(or 0.05 M) solution of zirconium oxychloride.
ated with zinc sulphate solution. Cool
emperature, add water to 300 ml, 6 ml
ml of chromogen black ET-00 solution,
(or 0.05 M) solution of zinc sulphate.

1 m
a of EDTA is equivalent to 7.26 mg of germanium.

PHOTOMETRIC DETERMINATION OF GERMANIUM AS MOLYBDOGERMANIC HETEROPOLYACID

Germanium is separated by extraction from a 9 N solution of hydrochloric acid with carbon tetrachloride (the distribution coefficient, 500). As^{III} and osmic acid are extracted together with germanium. Germanium is re-extracted with water and the determination ends photometrically (molybdogermanic acid is yellow). Thousand-fold quantities of Si, Fe^{III} and As^{V} do not interfere with the determination.

Reagents

Germanium compound, standard solution. 1 ml is equivalent to 0.2 mg of GeO_2.
Carbon tetrachloride, pure.
Hydrochloric acid, density 1.19 g/cu.cm and 9 N solution.
Ammonium molybdate, 5 per cent solution.
Sulphuric acid, 2 N solution.

Constructing a Calibration Curve

Place 1, 2, 3, 4 and 5 ml of the standard solution of germanium into five separating funnels, add 20 ml of hydrochloric acid, density 1.19 g/cu.cm, to each funnel and water to make 25 ml. Cool the solutions, add 10 ml of CCl_4 and shake for two minutes. Repeat the extraction two times with 5-ml portions of carbon tetrachloride. Collect the extracts in other separating funnels, wash with 5 ml of 9 N HCl, separate the phases, and re-extract germanium two times with 6 ml of water for 2 minutes. Add 10 ml of ammonium molybdate and 5 ml of sulphuric acid solution to the aqueous phase and water to the mark (25 ml). Allow the solutions to stand for 10 minutes and measure their absorption on an absorptiometer using a blue optical filter. (The light path 5 cm.) Construct the calibration curve using the data obtained.

Procedure

Add all the required reagents to the test solution and proceed as for the construction of the calibration curve. Measure the absorption of the solution obtained, and find the germanium content from the calibration curve.

PHOTOMETRIC DETERMINATION OF GERMANIUM WITH PHENYLFLUORONE

The germanium (IV) ion reacts with phenylfluorone (9-phenyl-2,3,7-trihydroxy-6-fluorone) in an acid solution in the molar ratio of 1 : 2 to form a red substance. If the germanium content is low, a suspension is formed which can be stabilized by a protective colloid. The variation of acidity within a comparatively wide range (0.3-1.5 N) does not affect the formation of a phenylfluorone compound of germanium. The reagent precipitates at acidity below 0.3 N. 0.5-1.5 N solutions of hydrochloric acid develop colour in 15-20 minutes.

The absorption maximum of colloidal solutions is at 500 nm but the absorption should be measured with an optical filter with the maximum transmittance at 530 nm. The molar extinction coefficient is 3.85×10^4.

Ti, Zr, Hf, Sn^{IV}, Nb, Ta, Sb^{III}, Te, Mo^{VI}, W^{VI}, V^{V}, Cr^{VI}, Mn^{VII} and Ce^{IV} interfere with the determination. Ga and As do not react with phenylfluorone in acid solutions. F^- (less than 1 mg in 10 ml) and Fe^{3+} (less than 100 g in 10 ml) do not interfere. In the analysis of various materials, germanium is separated from the interfering ions by extraction with carbon tetrachloride from 9 N solution of hydrochloric acid or by distillation of $GeCl_4$ (in the presence of an oxidant).

Reagents

Calcium oxide, solid.
Calcium nitrate, saturated aqueous solution.
Nitric acid, density 1.4 g/cu.cm.
Hydrofluoric acid, concentrated (38-40 per cent solution).
Phosphoric acid, density 1.7 g/cu.cm.
Sulphuric acid, diluted 1 : 1 and 1 : 16.
Sodium peroxide, solid.
Ammonium nitrate, 2 per cent solution.
Hydroxylamine chloride, 2 per cent solution in 9 N HCl.
Carbon tetrachloride, pure.
Germanium, standard solution. 1 ml is equivalent to 5 μg of germanium.
Hydrochloric acid, 9 N and 12 N solutions.
Gelatin, 1 per cent solution.
Phenylfluorone, 0.05 per cent solution. Dissolve 50 mg of the reagent in 100 ml of 96 per cent ethyl alcohol with heating, and add 0.5 ml of 6 N hydrochloric acid.

Constructing a Calibration Curve

Place 1, 2, 3, 4 and 5 ml of the standard solution of germanium into five 25-ml volumetric flasks, and add 4 ml of 6 N HCl, water to 20 ml, and 1 ml of gelatin solution into each flask. Mix the contents and add 1.5 ml of phenylfluorone, Mix again and add water to the mark. Measure the absorption of the solutions in 30 minutes on an absorptiometer or a photometer with an optical filter with the maximum transmittance at 530 nm. Use a blank solution as the standard. Construct the calibration curve using the data obtained.

Procedure

Dissolving Sample. Place a sample of coal or coke weighing 1 g in a platinum dish, add 0.5 g of CaO, mix, add 6 ml of $Ca(NO_3)_2$ solution and evaporate, first almost to dryness on a water bath, and then on a sand bath. Heat the residue slowly in a muffle furnace to 400-450°C (the greater part of carbonaceous particles burn out) and elevate the temperature to 700-800°C. If the heating is too fast, the material will take flame and be dispersed. Some coals should be incinerated without $Ca(NO_3)_2$ to avoid flashing and dispersion of the material. When the main part of coal has burnt, stir the residue by a spatula two or three times to accelerate incineration (the residue is a white or a brownish substance). Cool the residue, add 5 ml of HNO_3 dropwise, and evaporate on a water bath to dryness. Add 5 ml of hydrofluoric acid to the residue and evaporate to dryness again. Add 5 ml of hydrofluoric acid and 10 ml of phosphoric acid, evaporate on a water bath and then on a sand bath to remove hydrofluoric acid. Wash the syrupy residue with 25 ml of water into a beaker and heat to destroy lumps.

When ferric oxide ores are analysed, germanium can be extracted by decomposing a sample with hydrofluoric, nitric and phosphoric acid. Place the sample of ore weighing 0.5-1.0 g into a platinum dish, add dropwise, from a pipette, 5 ml of nitric acid avoiding vigorous reaction, and evaporate on a water bath to dryness. Repeat the nitric acid treatment and evaporation one or two times. Add 5 ml of hydrofluoric acid and 5 ml of phosphoric acid to the residue and evaporate to remove hydrofluoric acid. Wash the syrupy residue with 25 ml of water into a beaker and heat to dissolve the solid.

To analyze silicates, they are decomposed with a mixture of hydrofluoric, sulphuric and nitric acid (or a mixture of hydrofluoric, phosphoric and nitric acid). Place a sample weighing 0.5 g into a platinum dish, treat with 3 ml of sulphuric acid (1 : 16), 0.5 ml of concentrated HNO_3 and 5 ml of hydrofluoric acid. Evaporate to white fumes. Add 5 ml of water to the residue and dissolve it with heating.

In analysing sulphide ores, heat a sample weighing 0.5-1 g in a crucible in a muffle furnace at 400-500°C and treat the residue with a mixture of acids (as instructed above) or heat with calcium oxide and calcium nitrate (as in the analysis of coals).

Separating Germanium by Extraction. Cool the obtained solution (25 ml) to room temperature, add 75 ml of concentrated hydrochloric acid (disregarding possible turbidity), cool, transfer into a 200-ml separating funnel, add 20 ml of carbon tetrachloride, and extract two times for two minutes. Wash the extract three times with hydroxylamine chloride solution in 9 *N* hydrochloric acid (10-ml portions) with shaking. Re-extract germanium by two 6-ml portions of water, shaking each time for one minute.

Transfer the aqueous solutions into a 25-ml volumetric flask and proceed further as for the construction of the calibration curve. Find the germanium content of the sample from the calibration curve.

PHOTOMETRIC DETERMINATION OF GERMANIUM WITH 6,7-DIHYDROXY-2,4-DIPHENYLBENZOPYRANOL

The method is based on the formation of an orange-red complex germanium with 6,7-dihydroxy-2,4-diphenylbenzopyranol hydrochloride. The absorption maximum of solutions of this complex is at 470 nm. The molar extinction coefficient of the complex is $2.50 \times \times 10^4$. The optimum acidity, 0.1-0.6 *N* HCl. Zr, Hf, Ti, Th, Mo, W, V, Ta, Nb, and Sn interfere with the determination, and germanium should therefore be separated by extraction. The method can be used to determine 0.1-25 μg of Ge in 10 ml.

Reagents

6,7-Dihydroxy-2,4-diphenylbenzopyranol hydrochloride, 0.2 per cent solution in ethyl alcohol.
Gelatin, 1 per cent solution.
Hydrochloric acid, 5 *N* solution.
Germanium, standard solution, 1 ml is equivalent to 5 μg of germanium.

Constructing a Calibration Curve

Place 1, 2, 3, 4 and 5 ml of the standard solution of germanium into volumetric flasks and add 1 ml of hydrochloric acid, 1 ml of gelatin solution and 1.25 ml of the reagent solution into each flask. Now add water to 25 ml and, in three minutes, measure the absorption of the solutions on an absorptiometer with a green optical filter using a blank solution as the standard. Construct the calibration curve using the data obtained.

Procedure

Add all the requisite reagents to the test solution and measure its absorption. Find the germanium content from the calibration curve.

EXTRACTION-PHOTOMETRIC DETERMINATION OF GERMANIUM

The method is based on the extraction by carbon tetrachloride of an ionic association formed by dinitropyrocatecholgermanic acid with the cation of brilliant green. The molar extinction coefficient of the extract at 625 nm is 1.41×10^5. Germanium should be separated by extraction with carbon tetrachloride from 9 *N* HCl solution before the determination.

Reagents

Nitric acid, density 1.4 g/cu.cm.
Hydrofluoric acid, 40 per cent solution.
Phosphoric acid, concentrated.

Magnesium nitrate, 40 per cent solution.
Hydrochloric acid, 11, 9 and 2 *N* solutions.
Carbon tetrachloride.
o-Nitrophenol, 0.1 per cent solution.
Sodium hydroxide, 0.1 *N* solution.
3,5-Dinitropyrocatechol, 0.02 per cent solution in ethyl alcohol.
Brilliant green, 0.05 per cent solution.
Germanium, standard solution. 1 ml is equivalent to 1 μg of germanium.

Constructing a Calibration Curve

Place 0.5, 1.0, 1.5, 2.0 and 2.5 ml of the germanium standard solution into 50-ml separating funnels and add three volumes of 11-12 *N* solution of hydrochloric acid and extract two times with 10-ml portions of carbon tetrachloride. Wash the extract two times with 10-ml portions of a 9 *N* solution of hydrochloric acid. Add 10 ml of water to the washed extract and shake for a minute. Without separating CCl_4, add a drop of 0.1 per cent o-nitrophenol solution and alkalize with NaOH solution until the solution turns yellow. Add 1 ml of 2 *N* HCl, 1.5 ml of 3,5-dinitropyrocatechol, 6 ml of brilliant green, mix, and shake for 1 minute. After the phases have separated, transfer the organic phase into a 50-ml volumetric flask, extract two times with 10-ml portions of carbon tetrachloride, and collect the extracts in the same volumetric flask. Add 5 ml of 96 per cent ethanol and CCl_4 to the mark. Mix the solution and measure its absorption at 625 nm in a cell with a light path of 5 cm using carbon tetrachloride as a reference solution. Construct the calibration curve using the data obtained.

Procedure

Dissolve a sample weighing 0.1-1 g in a platinum dish in a mixture of 5 ml of HNO_3, 5 ml of HF and 5 ml of H_3PO_4, evaporate on a water bath to remove HNO_3 and HF and then heat on a sand bath. If a sample of sulphide ore, or material containing carbon is analyzed, wet the sample with 2.5 ml of $Mg(NO_3)_2 \cdot 6H_2O$, dry on a sand bath and place into a muffle furnace heated to 800-850°C for ten minutes. Cool the dish, add 5 ml of the acid mixture and continue the destruction of the sample. Rinse the dish walls with water and keep it on a sand bath until a clear syrup is obtained. If the germanium content is low transfer the residue into a separating funnel with 15 ml of water. If the germanium content is high, dilute the residue with water in a volumetric flask to 50 ml and determine germanium in an aliquot as for the construction of the calibration curve. Find the germanium content from the calibration curve.

FLUORIMETRIC DETERMINATION OF GERMANIUM WITH RESARSONE IN NATURAL MATERIALS

Resarsone (2′,2′,4′-trihydroxy-3-arsono-5-chlorazobenzene) reacts in an acid medium with germanium in the ratio of 1 : 1 to form an orange-red soluble compound fluorescing with a pink light, the maximum fluorescence being at 610 nm. Equal quantities of other cations, 10 μg of Cu, 500 μg of Al and Zr, 1 mg of Fe^{III} do not interfere with the determination of 0.03 μg of germanium. Fluorescence is quenched by 1 μg of Nb, 100 μg of Cu and 10 mg of Fe^{III}. The determination of germanium by this method is only possible after the separation of the interfering ions by extraction from hydrochloric acid solution with carbon tetrachloride.

Reagents

Germanium salt, standard solution. 1 ml is equivalent to 1 μg of germanium.

Resarsone, 0.005 per cent solution in a mixture of water and acetone (1 : 1).

Acid mixture. Dilute 52 ml of HCl, density 1.19 g/cu.cm, and 250 ml of H_3PO_4, density 1.7 g/cu.cm, with water to make 1 litre.

Nitric acid, density 1.4 g/cu.cm.

Hydrochloric acid, density 1.19 g/cu.cm and 9 *N* solution.

Phosphoric acid, density 1.7 g/cu.cm.

Hydrofluoric acid, 40 per cent solution.

Sulphuric acid, density 1.84 g/cu.cm.

Sodium hydrosulphite, crystalline.

Boric acid, 2 per cent solution.

Carbon tetrachloride.

Constructing a Calibration Curve

Place 0.2, 0.4, 0.6, 0.8 and 1.0 ml of the germanium solution into 100-ml separating funnels rinsed with 9 *N* HCl and add 70 ml of hydrochloric acid, density 1.19 g/cu.cm, and 10 ml of carbon tetrachloride into each funnel, and shake for one minute. After the phases have separated, wash the organic layer with 5 ml of 9 *N* HCl for a minute. Transfer the extract into a quartz test tube, add 8 ml of the acid mixture and 2 ml of the reagent solution. Shake the solution for a minute, allow it to stand for an hour and measure fluorescence of the solution. Construct the calibration curve using the data obtained.

Procedure

Roast sulphide ores before the analysis in a muffle furnace at 500-600°C with sufficient air to burn out the sulphide sulphur. Incinerate coals by raising the temperature slowly to 500-550°C to burn out carbonaceous material completely.

Grind thoroughly a sample of silicate rock weighing 0.5-1 g, place it in a platinum dish, wet with water, add 5 ml of nitric acid and evaporate on a water bath to dryness. Add 5 ml of hydrofluoric acid and 5 ml of phosphoric acid stirring the mixture occasionally. Heat on a water bath for 1-2.5 hours to remove excess HF. Add 0.5 ml of sulphuric acid, place on an electric hotplate and evaporate at moderate temperature to fumes of SO_3. If the decomposition is incomplete, repeat the evaporation with hydrofluoric acid. If the residue is violet, add a small amount of water, sodium hydrosulphite by portions, and evaporate again to white fumes. Transfer the remaining syrup with 25 ml of a hot solution of boric acid into a 50-ml beaker, cool the solution, wash the dish with 5 ml of hydrochloric acid, density 1.19 g/cu.cm, and add the liquid to the main solution. Proceed further as for the construction of the calibration curve. Find the germanium content from the calibration curve.

POLAROGRAPHIC DETERMINATION OF GERMANIUM IN SULPHIDE ORE

The method is based on the extraction of germanium tetrachloride with CCl_4 and its polarography in the carbonate-complexonate solution at pH 8.0-9.0. The half-wave potential of germanium is —1.5 V (with reference to the saturated calomel electrode). The method can be used to determine 0.0005-0.01 per cent of germanium in a sample weighing 1 g or 0.001-0.02 per cent of Ge in a sample weighing 0.5 g.

Reagents

Nitric acid, density 1.4 g/cu.cm.
Hydrochloric acid, density 1.19 g/cu.cm and 9 *N* solution.
Sulphuric acid, diluted 1 : 100.
Phosphoric acid, density 1.17 g/cu.cm.
Hydrofluoric acid, 40 per cent solution.
Carbonate mixture. Grind 2 g of anhydrous Na_2CO_3 with 20 g of sodium hydrocarbonate in a mortar.
Sodium sulphate, crystalline.
Sodium hydroxide, 10 *M* solution.
Carbon tetrachloride, pure.
EDTA, 0.1 *M* solution.
Phenolphthalein, 0.1 per cent solution in ethyl alcohol.
Germanium, standard solution. 1 ml is equivalent to 25 μg of germanium. Dilute the solution with ten volumes of water to construct a calibration curve.

Constructing a Calibration Curve

Place 0.0, 0.2, 0.4, 1.0, 2.0 and 4.0 μg of germanium into 100-ml beakers and extract with carbon tetrachloride as described in Sec. Photometric Determination of Germanium with Phenylfluorone (separation of germanium by extraction) and then re-extract germanium. Add 2.5 ml of sodium hydroxide solution, neutralize excess alkali with hydrochloric acid to phenolphthalein, and add 1-2 drops of the alkali until pink colour develops. Boil a weak alkaline solution for 3-5 minutes, evaporate to 4-7 ml and, depending on the anticipated germanium content, transfer into a 25-ml volumetric flask or into a 10-ml test tube. Add 0.4 g of dry mixture of sodium carbonate and bicarbonate, 1 ml of EDTA solution and 0.2 g of sodium sulphite per each 10 ml of the final solution and dilute with water to the mark. Transfer a part of the solution into an electrolyzer, pass a stream of pure hydrogen or nitrogen and carry out polarography in the voltage range from —1.2 to —1.8 V. Measure the height of the polarographic wave and construct the calibration curve using the data obtained.

Procedure

Grind thoroughly a sample of sulphite ore weighing 0.5-1.0 g, dissolve it with HNO_3, HF and H_3PO_4. Proceed further as for the construction of the calibration curve. Find the germanium content from the calibration curve.

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Bismuth

Bismuth, Bi, has the positive valency of 3 and 5. Compounds of tetravalent bismuth can also exist. In the hydride BiH_3, bismuth has the negative valency of 3. Various bismuth (III) compounds are very important for analytical chemistry.

The standard electrode potentials in an aqueous medium at 25°C are as follows (with reference to the standard hydrogen electrode):

$Bi + H_2O + Cl^- \rightleftharpoons BiOCl + 2H^+ + 3e^-$	+0.16 V
$Bi + 4Cl^- \rightleftharpoons BiCl_4^- + 3e^-$	+0.16 V
$Bi \rightleftharpoons Bi^{3+} + 3e^-$	+0.215 V
$Bi + H_2O \rightleftharpoons BiOH^{2+} + H^+ + 3e^-$	+0.254 V
$Bi + H_2O \rightleftharpoons BiO^+ + 2H^+ + 3e^-$	+0.320 V
$2Bi + 3H_2O \rightleftharpoons Bi_2O_3 + 6H^+ + 6e^-$	+0.371 V
$2Bi_2O_3 + H_2O \rightleftharpoons Bi_4O_7 + 2H^+ + 2e^-$	+1.338 V
$Bi_4O_7 + H_2O \rightleftharpoons 2Bi_2O_4 + 2H^+ + 2e^-$	+1.541 V
$Bi_2O_4 + H_2O \rightleftharpoons Bi_2O_5 + 2H^+ + 2e^-$	+1.607 V
$2Bi^{3+} + 5H_2O \rightleftharpoons Bi_2O_5 + 10H^+ + 4e^-$	+1.759 V

Compounds of pentavalent bismuth, bismuthates of the alkali metals, can exist only in the solid state. The bismuth (V) ion does not exist in solution. Bismuthates have strong oxidizing properties. In acid solutions they oxidize the manganese (II) ion to permanganate, and the tervalent cerium ion to the tetravalent ion.

The cation Bi^{3+} prevails in the solution of bismuth perchlorate at pH 0 and at a higher acidity. Less acid solutions contain the ions $BiOH^{2+}$, BiO^+, Bi_2O^{4+}, $Bi_3O_2^{5+}$ and others. All of them are colourless.

Bismuth oxide, Bi_2O_3, is a yellow substance, practically insoluble in water and soluble in acids. It meets the requirements for the weighing form and can be obtained by calcining bismuth hydroxide, basic bismuth carbonate, and some bismuth compounds with organic reagents.

Unlike antimony (III) hydroxide, bismuth hydroxide, $Bi(OH)_3$, has a marked basic character and does not show amphoteric properties. It is soluble in acids and practically insoluble in alkali solution. Small quantities of $[Bi(OH)_4]$ can only be obtained by boiling the hydroxide in concentrated (50 per cent) solutions of the alkali metal hydroxides.

Salts of Bi^{III} are hydrolyzed in an aqueous solution at pH 2 to precipitate basic salts. At higher alkalinity, the basic salts are converted into an amorphous hydroxide Bi(OH)$_3$, which forms a yellow compound BiO(OH) on heating. Bismuth salts are hydrolyzed in solutions when ammonia, caustic alkalies, carbonates of the alkali metals, sodium formate or sodium acetate, various organic bases, and solid oxides of zinc or mercury are added. The chloride of tervalent bismuth is the easiest to hydrolyze. Next follow the nitrate and perchlorate. The degree of hydrolysis of BiCl$_3$ in solution decreases with increasing concentration of the ions H$^+$ and Cl$^-$ (when chlorides of the alkali metals are added) because chloride complexes of bismuth are formed. When acidity decreases, BiCl$_3$ and Bi(NO$_3$)$_3$ solutions precipitate white basic chlorides and nitrates. Their composition corresponds approximately to the formulas BiOCl and BiONO$_3$. The precipitates of the basic salts are insoluble in a 2 *N* solution of NaOH (in contrast to the products of hydrolysis of salts of Sb^{III}, Sn^{II}, and Sn^{IV}).

Hydrogen sulphide precipitates brown Bi$_2$S$_3$ which is insoluble in cold dilute acids, solutions of ammonium sulphide and ammonium polysulphide (in contrast to Sb$_2$S$_3$, SnS and SnS$_2$). The sulphide Bi$_2$S$_3$ is soluble in hot dilute nitric and concentrated hydrochloric acid.

Acid sodium phosphate precipitates white BiPO$_4$ from solutions of tervalent bismuth. Unlike the phosphates of other metals, it is practically insoluble in 0.2 *N* nitric acid. The solubility product index, pL_{BiPO_4}, is 19-20. The solubility of BiPO$_4$ in HNO$_3$ sharply increases in the presence of the chloride ion (due to complexation). Only Zr^{IV}, Th^{IV} and Ti^{IV} form sparingly soluble phosphates in a 0.2 *N* solution of nitric acid. The phosphate BiPO$_4$ is comparatively well soluble in dilute solutions of hydrochloric acid.

Bismuth (III) forms various complex ions with the chloride ions BiCl$_4^-$, BiCl$_5^{2-}$, BiCl$_6^{3-}$, Bi$_2$Cl$_9^{2-}$ and others, with mannitol, SCN$^-$, S$_2$O$_3^{2-}$, etc. The orange complexes BiI$_4^-$, BiI$_5^{2-}$, BiI$_6^{3-}$ and others are more stable.

Tartrate complexes of bismuth are less stable than their analogues with Sb^{III}. Citrate and oxalate complexes are known.

Bismuth does not form ammonia complexes (in contrast to Cu^{II}, Ag^{I}, Cd^{II}, and others).

A black-brown iodide BiI$_3$ which precipitates when KI is added to a solution of a bismuth salt, and also a red oxyiodide BiOI (the product of hydrolysis of BiI$_3$) are soluble in excess KI solution to form yellow iodobismuthite solutions. The iodobismuthite ion is precipitated by various organic bases (quinine, cinchonine, and many others) in the form of BH[BiI$_4$] and other yellow or red compounds (B is the molecule of base). The precipitates are soluble in organic polar liquids.

EDTA reacts with the bismuth ions [1] in the molar ratio of 1 : 1. The reagent is used for the titrimetric determination of bismuth in various materials [2]. The end point of titration is established amperometrically or by chemical indicators, viz., pyrocatechol violet, xylenol orange, 1-(2-pyridylazo)-2-naphthol, etc. The complexometric method is superior to all other titrimetric methods for the determination of bismuth by its selectivity, accuracy, speed and reliability.

8-Quinolinol precipitates quantitatively the bismuth ion from a weak acetic acid solution in the form of a compound $Bi(C_9H_6ON)_3$ of constant composition. The formation of this compound underlies the gravimetric, titrimetric and photometric methods of determination of bismuth. It is convenient to titrate 8-quinolinol after dissolution of the filtered and washed precipitate of bismuth 8-hydroxyquinolinate, using an apparatus for potentiometric (bromatometric) non-compensated titration [3].

Thiocarbamide, $CS(NH_2)_2$, reacts with the bismuth ion in nitric or sulphuric acid solution to form a bright yellow compound [4]. Thiocarbamide is a highly selective reagent for the detection and photometric determination of small quantities of bismuth in various materials [5-7]. Derivatives of thiocarbamide are even more sensitive and selective (e.g. *o*-tolylthiocarbamide, which is used for the extraction-photometric determination of bismuth [8]. O,O-Diethyl ether of dithiophosphoric acid, $(C_2H_5O)_2PSSH$, precipitates quantitatively the bismuth ion from acid solutions in the form of the compound $[(C_2H_5O)_2PSS]_3Bi$. A greenish-yellow precipitate, melting at 55°C, has a constant composition. It is practically insoluble in water or acids and well soluble in organic solvents. Solutions of $[(C_2H_5O)_2PSS]_3Bi$ in organic solvents are greenish-yellow and absorb in the ultraviolet and visible regions of the spectrum. The solutions of this compound in CCl_4 are quite stable and obey the Beer law. The molar extinction coefficient at 330 nm is 1.6×10^4, and at 400 nm, 4.5×10^3. Diethyldithiophosphoric acid is used in the form of its nickel salt for the gravimetric, titrimetric, and extraction-photometric determination of bismuth in the presence of some elements [9].

Bismuthol I and bismuthol II react with the Bi^{3+} ion in an acid medium to form a red precipitate. The ions of other metals form precipitates of other colours. The reagents are used for the identification of bismuth after its separation from other elements [10].

1,5-Diphenylthiocarbazone (dithizone), dinaphthylthiocarbazone and their numerous derivatives react with the bismuth ion to form intensely coloured compounds extractable with chloroform and other organic solvents [11, 12]. Dithizone, dinaphthylthiocarbazone and some of their derivatives are valuable reagents for the extraction-photometric determination of small amounts of bismuth.

Zinc reduces the ions of Bi^{III} (and Sb^{III}) in hydrochloric acid solutions to black metal which (after removal of zinc) is insoluble in hydrochloric acid (in contrast to Sn). The ions of silver and mercury can be masked by adding excess KCN [13, 14].

Sodium stannite (Na_2SnO_2) solution reduces bismuth salts in an alkaline medium with liberation of a dark brown precipitate of elemental bismuth.

The ions of divalent chromium (solutions of the salts $CrCl_2$, $CrSO_4$) reduce quantitatively the tervalent bismuth ion to the elemental state [15-17]. The reaction is strictly stoichiometric:

$$Bi^{3+} + 3Cr^{2+} = Bi_{solid} + 3Cr^{3+}$$

At the end of the reduction reaction, the potential of the platinum or tungsten indicator electrode jumps abruptly and this makes it possible to titrate bismuth potentiometrically in the presence of lead, cadmium, and other elements.

Potassium hexacyanomanganate, $K_4[Mn(CN)_6]$, whose solution can be prepared by the reaction of Mn^{II} with excess KCN, precipitates a black substance, probably a mixture of BiO and bismuth metal from an acidified solution of a bismuth salt. The reagent is oxidized in this reaction to $[Mn(CN)_6]^{3-}$. The ions Ag^+, Hg_2^{2+} and Hg^{2+} can be masked by cyanide [18].

Traces of bismuth stimulate the reduction of Pb^{II} by formaldehyde in the presence of excess alkali [19]. This is used to detect small amounts of bismuth in the presence of Pb.

The review of the methods for the determination of bismuth is given in the literature [4].

COMPLEXOMETRIC DETERMINATION OF BISMUTH WITH PYROCATECHOL VIOLET AS INDICATOR

Bismuth reacts with EDTA to form a stable soluble compound ($\log \beta = 27.94$; 20°C, $\mu = 0.1$, KNO_3). Pyrocatechol violet is the most convenient indicator for this reaction. At pH 2.0-2.5 it forms a blue bismuth complex. Own colour of the indicator at this acidity is yellow. Large amounts of divalent cations, or a 5000-fold quantity of lead do not interfere with the determination. Fe^{III}, Hg^{II}, Sb^{III}, V, Zr, Th, phosphates, tartrates, chlorides, citrates, oxalates and fluorides interfere. The interfering effect of Fe^{III} and Hg^{II} can be removed by adding ascorbic acid. Hg^{II} can be reduced to its elemental state by formic acid.

Reagents

EDTA, 0.01 *M* solution.
Ammonia, 1 *M* solution.
Sulphosalicylic acid, 2 per cent solution.
Ascorbic acid, 1 per cent solution.
Pyrocatechol violet, 0.1 per cent solution.
Formic acid, 5 per cent solution.
Nitric acid, density 1.4 g/cu.cm and 0.1 *M* solution.

Procedure

Determining Bismuth in the Presence of Iron (III). **Dissolve the sample in nitric acid, density 1.4 g/cu.cm, evaporate to a small volume, transfer into a 50-ml volumetric flask and add 0.1 *M* nitric** acid to the mark. Take an aliquot containing 10-15 mg of bismuth, dilute with water to make about 50 ml, adjust the pH of the solution to 2.0-2.5 with ammonia to universal test paper, and add 5 drops of sulphosalicylic acid and ascorbic acid to decolourize the solution. Add 1-2 ml in excess. About 1 ml of ascorbic acid is required to reduce 4 ml of Fe^{III}. Add 1-2 drops of pyrocatechol violet solution and titrate with EDTA until the blue solution turns lemon-yellow.

1 ml of 0.0100 *M* EDTA solution is equivalent to 2.09 mg of bismuth.

Determining Bismuth in the Presence of Mercury (II). Adjust the pH of the solution of nitrates to 2.0-2.5 with ammonia, and add formic acid (1.5 ml per each 10 mg of mercury, and 0.5 ml in excess). Heat the solution to boiling, maintain boiling for 1-2 minutes, cool, add 1-2 drops of pyrocatechol violet and titrate as for the determination of bismuth in the presence of iron.

PHOTOMETRIC DETERMINATION OF BISMUTH WITH THIOCARBAMIDE

Bismuth reacts with thiocarbamide to form compounds which are approximately described by various formulas: $Bi(CSN_2H_4)_3Cl_3$, $Bi(CSN_2H_4)\cdot(NO_3)_2OH$, or $Bi(CSN_2H_4)Cl_3$. The determination is carried out in a nitric acid medium at the optimum concentration of 0.4-1.2 *N*. The concentration of thiocarbamide is 1 per cent. The absorption of the solutions of thiocarbamide complexes is proportional to the bismuth concentration in the range from 2 to 16 μg/ml. The colour of the solutions persists for about 90 minutes. The method is suitable for the determination of bismuth in lead and aluminium alloys and in many other materials.

Pb, Cu and many other elements do not interfere with the determination. Large quantity of Sb^{III} which forms a yellow compound with thiocarbamide, interferes. Au^{III} (brown) and large quantities of Hg^{I} and Se^{IV} also interfere.

Determining Bismuth in Aluminium Alloys

Alloys are dissolved in hydrochloric acid. All bismuth and the main bulk of copper and lead precipitate. The precipitate is separated on a filter, dissolved in nitric acid and bismuth is determined photometrically in the obtained solution. The method can be used for the determination of bismuth in aluminium alloys containing 3.5-6 per cent of copper and 0.2-0.6 per cent of lead.

Reagents

Bismuth nitrate, standard solution. 1 ml is equivalent to 0.1 mg of bismuth. Dissolve 0.1115 g of bismuth oxide in 20 ml of nitric acid (1 : 1) and dilute carefully with water in a volumetric flask to make 1 litre of the solution.

Hydrochloric acid, diluted 1 : 1.
Nitric acid, diluted 1 : 1 and 1 : 10.
Thiocarbamide, saturated solution.

Constructing a Calibration Curve

Place the standard solution of bismuth nitrate containing from 0.05 to 0.25 mg of bismuth into 50-ml volumetric flasks and add 7 ml of nitric acid (1 : 1), if bismuth is determined in aluminium alloys, or nitric acid (1 : 4) if bismuth is determined in lead, into each flask. Next add 10 ml of thiocarbamide solution and water to the mark. Mix the solutions and measure their absorption on an absorptiometer with a blue filter. Construct the calibration curve using the data obtained.

Procedure

Treat a sample of an aluminium alloy weighing 0.1 g in 5 ml of hydrochloric acid without heating in a 100-150 ml beaker. Aluminium, magnesium, and other elements are dissolved, while all bismuth and the main part of lead and copper precipitate. When the reaction has been completed, add immediately 5 ml of distilled water and separate the insoluble precipitate on a small filter washing it quickly two times with small portions of hot water. The filtration and washing operations should be as rapid as possible since otherwise the results will be low. Dissolve the precipitate on the filter in 5-10 ml of hot nitric acid (1 : 1) and collect the liquid in a 50-ml volumetric flask. Wash the filter with small portions of nitric acid (1 : 10) and then with water. Collect the washings in the same flask, add 10 ml of thiocarbamide solution and water to make 50 ml. Measure the absorption of the solution on an absorptiometer.

Find the bismuth content from the calibration curve.

Determining Bismuth in Lead

Bismuth is separated from the main bulk of lead by precipitation in the form of bismuth carbonate. The bismuth ion is precipitated quantitatively from a weak nitric acid solution at pH 4.1 ± 0.2 while lead is precipitated as its basic salt from a dilute solution of lead nitrate at pH 6. Zn, Cd, Co, Ni, Cu, As ($\leqslant 1$ per cent), Sn (< 0.1 per cent), Fe^{III} (< 0.05 per cent) and a small quantity of the chloride ion does not interfere with the determination. The ions which form coloured compounds with thiocarbamide interfere. The interfering effect of antimony is removed by adding tartaric acid to the solution.

Reagents

Bismuth nitrate, standard solution (see the previous section)
Nitric acid, diluted 1 : 4 and 1 : 1.
Sodium carbonate, 2 *N* solution.
Tartaric acid, crystalline.
Thiocarbamide, saturated solution.

Constructing a Calibration Curve

Construct the calibration curve as in the previous section

Procedure

Dissolve a sample of lead weighing 1 g and containing 0.005-0.05 per cent of bismuth (or weighing 10 g, if the bismuth content is 0.0005-0.005 per cent) in nitric acid (1 : 1) with heating. Remove excess acid by evaporation, dissolve the residue in a small quantity of distilled water and neutralize with sodium carbonate solution until turbidity develops (basic salts precipitate). Add 4-5 ml of sodium carbonate in excess and boil for 1-2 minutes. The precipitate contains all bismuth and a small quantity of lead.

Decant as much as possible of the liquid through a small filter, transfer the filter with the precipitate without washing into the beaker where the sample was dissolved, and dissolve the precipitate in 5-10 ml of nitric acid (1 : 4). If considerable quantity of antimony is present in the lead, add 1-2 g of tartaric acid. Transfer the solution into a 50-ml volumetric flask, add 10 ml of thiocarbamide solution and water to the mark, and measure the absorption of the resultant solution.

Find the bismuth content from the calibration curve.

EXTRACTION-PHOTOMETRIC DETERMINATION OF BISMUTH IN NICKEL ALLOYS AND IN LEAD CONCENTRATES USING *o*-TOLYLTHIOCARBAMIDE

Bismuth reacts with N-phenyl-substituted thiocarbamides, such as *o*-tolyl-, diphenyl-, di-*o*-tolyl-thiocarbamides in the presence of the anions I^-, SCN^-, ClO_4^- to form coloured compounds. The determination of bismuth is most sensitive and selective with *o*-tolylthiocarbamide in the presence of the perchlorate ion and perchloric acid. The formed compound $BiR_5(ClO_4)_3 \cdot nH_2O$ is extractable with dichloroethane and chloroform from 1-6.5 M $HClO_4$ in the presence of about 3 g-ion/l of ClO_4^-. The molar extinction coefficient of the dichloroethane solution is 1.14×10^4. The extracts absorb maximum at 425-430 nm. Large quantities of nickel, cobalt, lead and iron, moderate quantities of zinc (2.5 mg), copper (1 mg) and indium (5 mg) do not interfere with the determination. The method is used for the determination of $(3.3\text{-}6) \times 10^{-3}$ per cent of bismuth in nickel metal, 2.6×10^{-3} per cent of Bi in nickel alloys and 2.7×10^{-2} per cent of Bi in lead concentrate.

Reagents

Bismuth perchlorate, standard solution. 1 ml is equivalent to 10 μg of bismuth.
Sodium perchlorate, 3 M solution.
Perchloric acid, 42 per cent solution.
o-Tolylthiocarbamide, 0.03 M solution in dichloroethane (or chloroform).

Constructing a Calibration Curve

Place the standard bismuth perchlorate solution containing 0, 20, 40, 60, 80 and 100 μg of Bi in separating funnels and add 5 ml of sodium perchlorate and 5 ml of perchloric acid into each funnel. Add 5 ml of the reagent and extract for one minute. Separate the extracts and measure their absorption at 480 nm in a cell with a light path of 1 cm using water as a reference solution. Construct the calibration curve using the data obtained.

Procedure

Dissolve a sample of a nickel alloy or lead concentrate weighing 0.5-1 g and containing from 10 to 100 μg of bismuth in 10 ml of perchloric acid and evaporate to white fumes. Transfer the solution into a separating funnel and proceed further as for the construction of the calibration curve, without adding any perchloric acid. It is recommended that the extract be washed with perchloric acid and then its absorption measured. Find the bismuth content from the calibration curve.

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Selenium and Tellurium

Selenium, Se, and tellurium, Te, have the positive valency of 2, 4 and 6, and also the negative valency of 2. The compounds of tetravalent selenium and tellurium are most important for analytical chemistry [1].

Many compounds of selenium and tellurium in the same valency states have similar properties and are very much like analogous compounds of sulphur.

Elemental selenium and tellurium exist in several allotropic modifications. During the reduction of selenites or during oxidation of hydrogen selenide, H_2Se, a red amorphous selenium is liberated. This modification of selenium is only slightly (0.05 per cent) soluble in carbon disulphide. It is soluble in ammonium sulphide, $(NH_4)_2S$. Red-brown monoclynic prisms or needles are precipitated from CS_2 solutions. When heated to 90-100°C, the red modification of selenium converts into its grey modification (m.p. 217°C, b.p. 690°C). The grey modification of selenium is insoluble in CS_2 and conducts electricity, the conductivity being dependent on the temperature and the intensity of illumination. A vitreous modification of amorphous selenium is also known. At 90°C it turns into the crystalline modification.

Colloidal solutions contain selenium in the amorphous form. They are brick-red and used for the photometric determination of selenium.

Several brown or black modifications are known for tellurium. When its compounds are reduced, brown-black amorphous tellurium is obtained. It easily forms colloidal solutions used for photometric determinations, and is soluble in solutions of ammonium sulphide, $(NH_4)_2S$.

The standard electrode potentials in the aqueous solutions at 25°C are as follows (with reference to the standard hydrogen electrode):

For selenium

$$Se^{2-} \rightleftharpoons Se + 2e^- \qquad -0.92\ V$$

$$Se + 3H_2O \rightleftharpoons H_2SeO_3 + 4H^+ + 4e^- \qquad +0.741\ V$$

$$2Se + 2Cl^- \rightleftharpoons Se_2Cl_2 + 2e^- \qquad +1.1\ V$$

For tellurium

$$Te_2^{2-} \rightleftharpoons 2Te + 2e^- \qquad -0.84\ V$$

The most important forms of selenium in various valency states and the corresponding actual oxidation-reduction potentials are given in Fig. 8.

When selenium and tellurium are dissolved in nitric acid, selenious and tellurous acids are formed. Tellurium is soluble in a mixture of nitric and hydrochloric acid with the formation of telluric and tellurous acid. Hydrochloric acid alone does not act on tellurium. Tellurium is soluble in concentrated sulphuric acid. A bright red solution precipitates black tellurium on dilution.

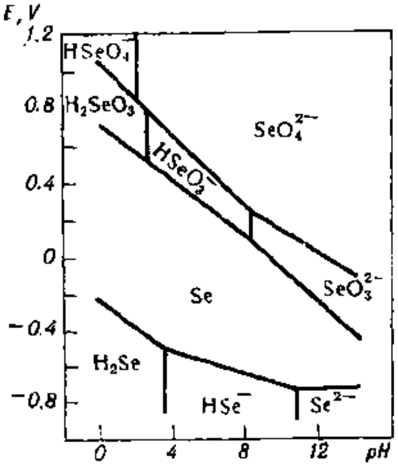

Fig. 8. Dependence of approximate potentials of selenium on pH. Selenium concentration, 10^{-2} M

Selenious acid is reduced to the red modification of selenium even by a weak reductant (salts of divalent iron, SO_2, iodides, organic acids, thiocarbamides, etc.). Hydrazine, hydroxylamine, ascorbic acid, ammonium thiocyanide, thiocarbamide, chlorides of tin (II) and titanium (III) or chromium (II), metallic zinc, magnesium, iron, copper and many others are used as reductants. Very energetic reductants reduce selenium partly to H_2Se.

Tellurous acid is reduced to tellurium by more active reductants ($SnCl_2$, zinc, etc.) than selenious acid. Sulphurous acid reduces tellurous acid only in weak acid solutions and does not reduce it in strong acid media. Hydroxylamine reduces tellurous acid in ammonia solutions and does not reduce it in acid solutions. Elemental tellurium is liberated in the form of a brownish-black powder.

Conditions can be provided in which selenious acid can be reduced, e.g. by hydroxylamine chloride or KI to the elemental selenium, while tellurous acid remains in solution.

When hydrogen sulphide is passed through a solution of selenious acid acidified with hydrochloric acid, a yellow substance precipitates in the cold, and an orange substance with heating (a mixture of sulphur and selenium). The precipitate is soluble in ammonium sulphide solutions.

Sulphur dioxide reduces selenious acid to the red modification of selenium in the cold in a medium of a dilute or concentrated solution of hydrochloric acid [2]. Tellurous acid is reduced in the medium of a 10 per cent solution of hydrochloric acid with heating (the reduction reaction discontinues in the cold). Selenious acid is also reduced in a medium of a 50 per cent sulphuric acid while tellurous acid is not reduced in these conditions.

A solution of sulphur dioxide in acetone is sometimes used for the quantitative reduction of selenious acid.

The reaction of reduction of selenious acid

$$SeO_3^{2-} + 4I^- + 6H^{\bullet} \rightleftharpoons Se + 2I_2 + 3H_2O$$

underlies various methods for the detection and for the photometric and titrimetric determination of selenium.

Ascorbic acid reduces quantitatively selenious acid to the elemental state in a medium of 0.1 *N* hydrochloric acid (with the formation of dehydroascorbic acid). Two moles of ascorbic acid are spent per mole of H_2SeO_3. This reaction is employed in the microtitrimetric determination of selenium in commercial selenium. Excess ascorbic acid is titrated with iodine solution in the presence of starch.

Ammonium thiocyanide reduces selenious acid in hydrochloric acid solutions (about 0.5 *N* HCl) with boiling. Tellurous and telluric acids are not reduced by this reaction.

Thiocarbamide reduces selenious acid to the elemental selenium in acidified solutions. Tellurous acid reacts with thiocarbamide to form yellow soluble complex compounds which are used for the photometric determination of tellurium [3]. Solutions contain complex ions of divalent tellurium $[Te(SCN_2H_4)_4]^{2+}$. Alkalization of these solutions precipitates black elemental tellurium.

If selenium and tellurium are to be precipitated together, $SnCl_2$, salts of hydrazine, or a solution of SO_2 and hydrazine salt should be used. Hydrazine is used to separate selenium from tellurium [4]. Selenious acid is oxidized to selenic acid in solution by oxidants which are more energetic than the oxidants required to oxidize sulphurous acid.

In contrast to selenious acid, selenic acid is reduced with difficulty and only by energetic reductants ($TiCl_3$, $CrCl_2$, hypophosphorous acid, etc.). Hydrogen sulphide, sulphurous acid anhydride and other mild reductants do not reduce selenic acid.

Selenic acid, H_2SeO_4, reacts with concentrated (12 *M*) hydrochloric acid:

$$H_2SeO_4 + 2HCl \rightleftharpoons Cl_2 + H_2SeO_3 + H_2O$$

The reaction is reversible. Chlorine oxidizes H_2SeO_3 to H_2SeO_4 in an alkaline medium.

Telluric acid (like selenic acid) is reduced only with energetic reductants. When reduced with tin ($SnCl_2$) or sodium hypophosphite in an acid medium, black elemental tellurium is precipitated.

Stannite reduces tellurate (and tellurites) to the elemental tellurium in a strong alkaline medium:

$$TeO_3^{2-} + 3SnO_2^{2-} \rightleftharpoons Te + 3SnO_3^{2-} + 2e^-$$

$$TeO_4^{2-} + 4SnO_2^{2-} \rightleftharpoons Te + 4SnO_3^{2-} + 2e^-$$

Selenium and tellurium form gaseous hydrogen selenide H_2Se, and hydrogen telluride, H_2Te. Hydrogen selenide in aqueous solutions is a stronger acid than hydrogen sulphide (pK_1 and pK_2 for H_2Se at 18°C are 3.77 and 11.0 respectively, while for H_2S at 25°C these are 7.2 and 14.0). The pK for H_2Te at 25°C is 3.0.

The oxidability increases in the series H_2S, H_2Se and H_2Te. These compounds are oxidized by atmospheric oxygen.

Hydrogen telluride, H_2Te, decomposes spontaneously into H_2 and Te. Aqueous solutions of H_2Te are unstable; they are easily oxidized by atmospheric oxygen with liberation of black tellurium.

Selenides and tellurides of metals resemble sulphides as regards their properties. Solutions of selenides and tellurides of the alkali metals are oxidized by atmospheric oxygen on standing, they liberate elemental tellurium and selenium and become turbid.

Salts of the alkali and alkaline earth metals and of hydroselenious and hydrotellurous acid are soluble in water. Selenides and tellurides of other metals are sparingly soluble. Silver telluride is less soluble than silver sulphide.

Polyselenides and polytellurides are red.

Selenium dioxide, SeO_2, has an acid character. When dissolved n water, it forms a weak selenious acid, H_2SeO_3, ($pK_1 = 2.46$ and $pK_2 = 7.3$).

The solutions of sodium selenite and potassium selenite react alkaline.

Selenites of most metals are sparingly soluble in water but are solved in solutions of strong acids.

Barium chloride precipitates a white substance, $BaSeO_3$, from solutions of selenites of the alkali metals. The precipitate is soluble in nitric or hydrochloric acid ($pL_{BaSeO_3} = 7.0$).

Lead acetate precipitates $PbSeO_3$. The white substance is sparingly soluble in hydrochloric or nitric acid ($pL_{PbSeO_3} = 1.0$).

Silver nitrate forms a white precipitate, Ag_2SeO_3.

Mercurous nitrate, $Hg_2(NO_3)_2$, in dilute nitric acid, forms a crystalline precipitate Hg_2SeO_3 which is suitable for microcrystalline detection of selenium.

Tellurium dioxide is a white amphoteric substance soluble in hydrochloric acid and in solutions of hydroxides of the alkali metals. TeO_2 is sparingly soluble in water. When an acid solution is diluted with water, it precipitates TeO_2.

Tellurous acid, H_2TeO_3, is weak ($pK_1 = 2.5$; $pK_2 = 7.7$). The solubility of tellurous acid is not high. It is precipitated from an acetate buffer solution and is relatively sparingly soluble in strong acids to form mainly the ions $TeOOH^-$ and Te^{4+}. The solubility of tellurous acid in 1 *N* hydrochloric acid or 1 *N* perchloric acid is 0.01 mole/l. Alkaline solutions contain the ion TeO_3^{2-}.

The following equilibria have been studied for Te^{IV}:

$$TeO_{2(solid)} + H_2O \rightleftharpoons HTeO_2^+ + OH^- \qquad pK = 16.1$$

$$H_2TeO_{3(solid)} \rightleftharpoons HTeO_2^+ + OH^- \qquad pK = 11$$

$$3H_2O + TeO_3^{2-} \rightleftharpoons Te^{4+} + 6OH^- \qquad pK = 46$$

$$Te^{4+} + 2H_2O \rightleftharpoons HTeO_2^+ + 3H^+ \qquad pK = 0.7$$

Most salts of tellurous acid are sparingly soluble in water. Tellurites are soluble in strong acids.

Barium chloride precipitates a white substance from tellurite solutions which is soluble in dilute nitric acid.

Tellurium (IV) is oxidized quantitatively to Te^{VI} by potassium bichromate in a sulphuric acid medium. This reaction underlies the titrimetric determination of tellurium [5].

Selenic acid, H_2SeO_4, is similar to sulphuric acid with respect to its strength. Selenates of most metals are soluble in water. Sparingly soluble are $BaSeO_4$, $SrSeO_4$, $PbSeO_4$ ($pL_{BaSeO_4} = 7.0$; $pL_{SrSeO_4} = 5.0$).

Telluric acid, $H_2TeO_4 \cdot 2H_2O$, is a colourless crystalline substance well soluble in water. It is a weak acid ($K_1 = 2 \times 10^{-8}$, $K_2 = 5 \times 10^{-11}$). Salts Ag_6TeO_6 or Hg_3TeO_6 are known. These are salts of ortho-telluric acid, H_6TeO_6. Tellurates of most metals are sparingly soluble in water. Potassium tellurate, $K_2H_4TeO_6 \cdot 3H_2O$, is well soluble in water while the sodium salt, $Na_2H_4TeO_6$, is only sparingly soluble. When heated, $H_2TeO_4 \cdot 2H_2O$ forms H_2TeO_4.

Hexavalent tellurium does not form cations.

Some organic reagents of various classes are used for the detection and determination of selenium and tellurium.

3,3′-Diaminobenzidine reacts with selenious acid at pH 2-3 with the formation of yellow diphenylpiazselenol [6, 7]. The reagent is used for the extraction-photometric determination of selenium [6-9].

3,3′-Diaminobenzidine is used to determine microgram quantities of selenium in the presence of grams of arsenic (without its separation) [7, 8]. The reagent can be used to determine selenium in gallium arsenide without its separation [8]. Large quantities of indium interfere with the determination of selenium. In this case, selenium (microgram quantities) is separated by reduction with a mixture of $SnCl_2$ and hypophosphite in hydrochloric acid solution (1 : 7) in the presence of a collecting agent (arsenic). This method is used in the analysis of indium, indium antimonide, and indium arsenide.

o-Phenylenediamine [10, 11] can be used instead of 3,3′-diaminobenzidine in the photometric determination of selenium. It reacts with selenious acid at pH 1.5-2.5 to form a practically colourless crystalline compound extractable with toluene. The absorption of a toluene extract is measured at 335 nm. Large quantities of ions do not interfere with the determination. Only Fe^{III}, Sn^{IV} and I^- interfere. The ferric ion can be masked with EDTA.

Some organic reagents containing the sulphohydryl group —SH react with selenious acid to form coloured compounds. 2-Mercaptobenzimidazol is among them. When a 1 per cent solution of the reagent is added to a dilute solution of selenious acid in 1-3 *M* hydrochloric acid, a yellow colour develops [12]. The formed compound is well extractable with a mixture of butyl alcohol and chloroform (1 : 5), the colour of the solution being persistent. The concentration of the reagent and selenious acid is high, the solution immediately precipitates yellow crystals. The precipitate is unstable. The extracts absorb maximum at 330 nm, the molar extinction coefficient being 1.05×10^4. Selenious acid reacts with the reagent in the molar ratio of 1 : 4. The reagent is used for the photometric determination of selenium, the absorption being measured not at the absorption maximum of the formed compound (the reagent proper absorbs at this wavelength as well) but at 420 nm. Hg, Ag, Au, Cd, Pb and others do not interfere with the determination. Te, Bi and Cu interfere.

When selenious acid is added to an acid solution of N-(mercaptoacetyl)-*p*-anizidine or *N*-(mercaptoacetyl)-*p*-toluidine, a yellow colour, yellowish-brown turbidity or precipitate (depending on the concentration of selenious acid) develop immediately. The formed compounds are well extractable with chloroform, carbon tetrachloride, benzene, toluene, isoamyl and isobutyl alcohol. The extracts are yellow. They are stable. The best extracting agent is a mixture of butyl alcohol and chloroform (1 : 5). The maximum absorption of the extract is in a medium of 0.05-0.5 *M* solution of hydrochloric acid. Elemental selenium is liberated from a 6 *M* solution of hydrochloric acid. The maximum absorption of the extracts is at 315-320 nm. The molar extinction coefficient is 1.2×10^3. The reagents react with selenious acid in the molar ratio of 2 : 1. They are used for the photometric determination of selenium in various technical materials [13]. Te^{IV}, Cu^{II}, Bi^{III}, and Mo^{VI} interfere with the determination.

The salt of divalent selenium $[(C_2H_5O)_2PSS]_2Se$ is a yellow crystalline substance. It is very stable and soluble in organic solvents [14].

Sodium diethyldithiocarbamate and other derivatives of dithiocarbamic acid are valuable reagents for the extraction-photometric determination of tellurium. The diethyldithiocarbamate method is used for the determination of microgram quantities of tellurium in the presence of up to 0.5 g of arsenic without separation [15]. In order to increase sensitivity, tellurium diethyldithiocarbamate in carbon tetrachloride is converted into copper diethyldithiocarbamate. Large quantities of indium and gallium interfere with the determination of tellurium. Therefore, during the determination of traces of tellurium in indium, indium arsenide and gallium arsenide, tellurium is separated by reduction with a mixture of $SnCl_2$ and hypophosphite in hydrochloric acid solution (1 : 7) using arsenic as a collector. Derivatives of carbamic acids containing heterocyclic substitutes are more promising [16].

Bismuthol II reacts with tellurous acid at pH 3.3-4.4 to form a yellow compound [17, 18]. Selenious acid reacts with bismuthol II also to form a yellow compound which, however, is very slowly extractable.

Selenium and tellurium form yellow complexes with 5-mercapto-3-(naphthyl-2)-1,3,4-thiadiazolthione-2 soluble in chloroform and benzene. Conditions have been found to separate extraction-photometric determination of selenium and tellurium [19].

Tellurium (IV) in hydrochloric, hydrobromic and hydriodic acid solutions is in the form of the halide complex ions. Crystals of various compounds containing the anions TeX_6^{2-} (here X is Cl, Br or I) and cations of the alkali metals or organic cations have been isolated from these solutions. The complex iodide TeI_6^{2-} is used for the photometric determination of tellurium in steel [20].

Diantipyrylmethane, diantipyrylmethylmethane, diantipyrylpropylmethane and diantipyrylphenylmethane precipitate compounds of tetravalent tellurium from hydrobromic acid solutions. The reaction, by which some of these compounds are formed, underlies the extraction-photometric determination of tellurium in lead and in some other materials [21-23].

The chloride complexes of tetravalent tellurium are not precipitated by the pyrazolone derivatives but are extractable quantitatively by dichloroethane in their presence. The selenium (IV) ion is not precipitated from hydrochloric acid solutions and is not extracted in the presence of pyrazolone derivatives either. Tellurium can therefore be easily separated from selenium. Chlorotelluric acid is extracted by a mixture of benzene and ethyl ether (2 : 1) from solutions of 5-7 per cent hydrochloric acid in the presence of rhodamine B. Tellurium is determined by the intensity of fluorescence of the extract in ultraviolet light [24]. Rhodamine 6G is less suitable for the determination of tellurium than rhodamine B.

Butyl rhodamine B is a highly sensitive reagent for the extraction-photometric determination of tellurium [25]. It can determine over 10^{-4} per cent of tellurium. A butyl rhodamine B compound with the bromide anion complex of tellurium is extractable by a mixture of benzene and ethyl ether (3 : 1). In, Sb, Au, Hg, large quantities of the ions of Fe^{III} and Cu^{I} interfere. When tellurium is determined in mineral raw materials, it is separated (simultaneously with selenium) by hypophosphite from a 6 *N* solution of hydrochloric acid using arsenic as a collecting agent, or by titanium trichloride from 2.5 *M* sulphuric acid medium and a 2.5 *N* hydrochloric acid medium.

Polarographic [26, 27] and extraction-polarographic [28] methods of determining selenium and tellurium are used.

GRAVIMETRIC DETERMINATION OF SELENIUM IN STEEL

Selenium is reduced to the elemental state by sulphur dioxide and weighed after drying at 105°C.

Reagents

Hydrochloric acid, density 1.19 g/cu.cm and diluted 1 : 1.
Nitric acid, density 1.4 g/cu.cm.
Sulphur dioxide. Act by concentrated sulphuric acid on Na_2SO_3.
Ethyl alcohol, 96 per cent solution.
Ethyl ether.

Procedure

Dissolve a sample of steel weighing 5 g (containing from 0.1 to 0.5 per cent of selenium) or 2 g (containing from 0.5 to 1 per cent of selenium) in 60 ml of a mixture of hydrochloric and nitric acid. Evaporate the solution on a water bath to dryness (without calcining), add 20 ml of hydrochloric acid (1 : 1), 20 ml of water, and dissolve the salts with slowly heating. Separate silicic acid on a filter and discard it. Add 60 ml of concentrated hydrochloric acid to the filtrate and dilute with water to 100 ml. Pass sulphur dioxide gas through the hydrochloric acid solution with stirring it to accelerate coagulation of selenium. Allow the mixture to stand overnight, then separate the precipitate on a glass filter No. 3 or 4, and wash the precipitate with hydrochloric acid (1 : 1), then with warm water to remove the acid, and finally with ethanol and once with ether. Dry to constant weight at 105°C.

DETERMINING SELENIUM AND TELLURIUM IN ORES AND INTERMEDIATES

Selenium and tellurium are separated by hydrazine in 9.5 *N* hydrochloric acid solution. The method is based on the interaction of selenious acid with excess standard solution of thiosulphate:

$$4Na_2S_2O_3 + H_2SeO_3 + 4HCl \rightleftharpoons Na_2SeS_4O_6 + Na_2S_4O_6 + 4NaCl + 3H_2O$$

The unreacted thiosulphate is titrated with iodine solution.

Tellurium is determined by the reaction between tellurous acid and excess potassium iodide:

$$H_2TeO_3 + 4I^- + 4H^+ \rightleftharpoons Te + 2I_2 + 3H_2O$$

Small quantities of selenium and tellurium are separated in the presence of a collecting agent (Hg_2Cl_2).

Reagents

Nitric acid, density 1.42 g/cu.cm.
Mixture of bromine and carbon tetrachloride, (2 : 3).
Sulphuric acid, concentrated.
Hydrochloric acid, density 1.19 g/cu.cm, 5 per cent solution and diluted 2 : 100.
Mercuric chloride, solution containing 1 mg Hg in 1 ml.

Stannous chloride, crystalline, $SnCl_2 \cdot 2H_2O$, and 20 per cent solution in 20 per cent hydrochloric acid.
Hydrazine hydrochloride, 10 per cent solution.
Carbamide.
Sodium thiosulphate, 0.02 N solution.
Iodine, 0.02 N solution.
Potassium iodide, 30 per cent solution.

Procedure

Dissolving the Sample. Grind thoroughly a sample weighing 1.0-10 g, place it in a 300-800 ml refractory glass beaker, add 8-30 ml of a mixture of bromine and carbon tetrachloride, and allow the mixture to stand for 10-20 min. Add 10-75 ml of nitric acid by small portions with stirring, and allow the solution to stand in the cold. Then heat carefully and evaporate to a small volume. After the sample has completely decomposed, add 10-60 ml of sulphuric acid and evaporate the solution to H_2SO_4 fumes. Cool the residue, add a small amount of cold water and evaporate again to H_2SO_4 fumes. Repeat this operation until all nitrogen oxides and organic substances are completely removed.

Dissolve the residue in 60-200 ml of water and 10-50 ml of hydrochloric acid, density 1.19 g/cu.cm, with boiling in a beaker (covered with a glass) for 5-10 minutes. Separate the insoluble precipitate and wash with hot water. Depending on the size of the sample, add hydrochloric acid to adjust its concentration to 15 per cent (v/v). (The total volume of the solution, 100-300 ml.) Heat the solution to the boil. Add 5 ml of mercurous chloride solution to the boiling solution and reduce the ferric iron by small portions of 20 per cent solution of stannous chloride. When the solution becomes colourless, add 3-10 ml of the reductant in excess, a small amount of paper pulp, boil for five minutes and allow to stand for ten minutes at a temperature about the boiling point. Separate the selenium and tellurium precipitate on a paper pulp filter and wash 3-4 times with hot hydrochloric acid (2 : 100).

Separation of Selenium and Tellurium. Place the selenium and tellurium precipitates back in the precipitation beaker, add 20 ml of concentrated hydrochloric acid and 4-5 drops of nitric acid. Loosen the filter and heat on a water bath to dissolve the precipitate (the filter whitens). Add 40 ml of concentrated hydrochloric acid, 50 ml of water, heat the solution almost to the boil and add 15-20 ml of hydrazine solution. Stir the mixture and allow to stand for four hours in a warm place. Separate the selenium precipitate on a double filter and wash 7 or 8 times with a hot 5 per cent hydrochloric acid.

To isolate tellurium, dilute the filtrate with water to 250 ml, add a small quantity of filter pulp, heat to the boil, add 0.3 g of stannous chloride and boil until the solution fully clears. Separate the precipitated tellurium on a double filter and wash 7-8 times with a hot 5 per cent hydrochloric acid.

Determining Selenium. Transfer the selenium precipitate on the filter into a beaker, add 10 ml of concentrated hydrochloric acid, loosen the filter by a glass rod, add 3-4 drops of nitric acid and heat the mixture on a water bath to dissolve the precipitate completely. Add 150 ml of water, and 4 g of carbamide, and boil for 2-3 minutes. Cool the solution to room temperature, add 10-20 ml of sodium thiosulphate and titrate its excess with iodine solution in the presence of starch.

Determining Tellurium. Transfer the tellurium precipitate on the filter into a flask, add 10 ml of concentrated hydrochloric acid and 3-4 drops of nitric acid, and heat on a water bath to dissolve the precipitate completely. Add 100 ml of water, 4 g of carbamide, and boil for 2-3 minutes. Cool the solution, add 10 ml of potassium iodide solution and titrate excess iodine with sodium thiosulphate solution in the presence of starch until the blue or dark cherry solution (depending on the tellurium content) turns pale yellow.

BICHROMATOMETRIC DETERMINATION OF TELLURIUM IN TELLURIDES OF CADMIUM, ZINC AND MERCURY

The method is based on the oxidation of Te^{IV} to Te^{VI} by potassium bichromate in a sulphuric acid medium. The end point is established with phenylanthranilic acid. If hydrochloric acid is present, manganous sulphate should be added to preclude the oxidation of the chloride ion by potassium bichromate.

Reagents

Potassium bichromate, 0.05 *N* solution. 1 ml is equivalent to 3.19 mg of Te.
Mohr's salt. 0.05 *N* solution.
Sulphuric acid, density 1.84 g/cu.cm.
Phosphoric acid, 85 per cent solution.
Phenylanthranilic acid, 0.1 per cent solution.

Procedure

Grind thoroughly a sample of telluride weighing 0.1 g and dissolve it in 10 ml of sulphuric acid with heating on a hotplate (closed spiral). Cool the solution, mix with 50 ml of water, add 25 ml of potassium bichromate solution and allow to stand for 10-15 minutes. Next add 5 ml of H_3PO_4, 2-3 drops of phenylanthranilic acid and titrate with Mohr's salt until the red-violet solution turns purely green.

SPECTROPHOTOMETRIC DETERMINATION OF SELENIUM BY *o*-PHENYLENEDIAMINE IN METALLURGICAL PRODUCTS

The compound of Se^{IV} with *o*-phenylenediamine is extracted from a more acid medium than the compound with 3,3′-*diaminobenzidine*, which makes this reagent more selective. Many elements are hydrolyzed and therefore interfere with the determination of selenium by

3,3′-diaminobenzidine, but the same elements do not interfere with the determination of selenium by *o*-phenylenediamine. The interfering effect of iron and bismuth can easily be removed by binding them in complexes with phosphoric acid and EDTA in an acid medium (pH 1-2). This makes it possible to determine selenium in non-ferrous metallurgy products of complicated composition without its separation.

Reagents

Selenium, standard solution. 1 ml is equivalent to 5 μg of selenium.
Nitric acid, density 1.4 g/cu.cm.
Sulphuric acid, diluted 1 : 1 and 2 per cent solution.
Phosphoric acid, 85 per cent solution.
Formic acid, 85 per cent solution.
EDTA, 0.1 *M* solution.
Ammonia, 25 per cent solution.
o-Phenylenediamine, 1 per cent solution.
Toluene.

Constructing a Calibration Curve

Place 2.5, 5.0, 7.5, 10, 12.5 and 15 μg of selenium into separate 50-ml beakers and add 1 ml of formic acid, 5 ml of phosphoric acid, and 0.5 ml of EDTA solution into each beaker. Adjust the pH of the solutions to 1 by adding ammonia dropwise. Add 3 ml of *o*-phenylenediamine and allow the solutions to stand for 20 minutes. Transfer the solutions into separating funnels, add 5 ml of toluene and extract for two minutes. Transfer the extracts into dry test tubes and measure their absorption on a spectrophotometer at 335 nm in a cell with a light path of 1 cm. Use a blank extract as a reference solution. Construct the calibration curve using the data obtained.

Procedure

Place a sample weighing 0.25-1 g into a 100-ml Erlenmeyer flask, add 20 ml of nitric acid and allow to stand in the cold (if the sample contains sulphides). Heat the mixture to dissolve the sample, evaporate the solution to 4-5 ml, add 20 ml of sulphuric acid (1 : 1) and heat to white fumes. Add 5 ml of water and heat again to white fumes. Add 15-20 ml of water after the second evaporation and heat the solution to boiling. Cool the solution, filter it into a 50-ml volumetric flask, wash the precipitate first with a 2 per cent solution of sulphuric acid and then with water. Dilute the filtrate with water to the mark and mix thoroughly. Transfer an aliquot into a 100-ml Erlenmeyer flask, add water so that the final volume of the solution is not over 30-35 ml and proceed further as for the construction of the calibration curve. Find the selenium content from the calibration curve.

PHOTOMETRIC DETERMINATION OF SELENIUM WITH 3,3′-DIAMINOBENZIDINE WITHOUT EXTRACTION

The method is based on the reaction of the ion SeO_3^{2-} with 3,3′-diaminobenzidine in a neutral, acid, or alkaline medium, with the formation of a yellow sparingly soluble diphenylpiazselenol.

It is stable in acid, neutral, and alkaline solutions. It is well extractable by toluene and other organic solvents at pH 6-7. At pH 5 and below the extraction is slow.

Dilute aqueous solutions of diphenylpiazselenol obey Bouguer-Lambert-Beer law in the range of selenium concentrations from 0.25 to 2.5 μg/ml. The molar extinction coefficient at 347-349 nm is 1.02×10^4 (the acidity being 0.1 *N*). The colour of the solution develops in these conditions during 50 minutes and persists at this level for five hours. The ions of Al, Ba, Ca, Cd, Co, K, Cr^{III}, Mg, Mn, Mo^{VI}, Ni, Te^{IV}, Na, NH_4^+, Zn, Br, Cl, NO_3^-, PO_4^{3-}, SO_4^{2-}, and also the citrate, oxalate and tartrate ions do not interfere with the determination. The ferric ion can be masked by fluoride or oxalate.

Reagents

3,3′-Diaminobenzidine, 0.1 per cent solution of tetrachlorohydrate in dilute hydrochloric acid.
Hydrochloric acid, 5 *N* solution.
Selenious acid, standard solution. 1 ml is equivalent to 20 μg of selenium.

Constructing a Calibration Curve

Place 0.5, 1, 2, 3, 4 and 5 ml of the standard solution of selenious acid into 50-ml volumetric flasks, add 25 ml of the reagent into each flask and adjust the total acidity of the solutions to 0.1 *N* by adding 5 *M* hydrochloric acid. Add water to the mark, allow the solutions to stand for an hour and measure their absorption on an absorptiometer with a blue filter in a cell with a light path of 1 cm. Construct the calibration curve using the data obtained.

Procedure

Add all the requisite reagents into the solution of the sample and measure its absorption as instructed above. Find the selenium content from the calibration curve.

EXTRACTION-PHOTOMETRIC DETERMINATION OF SELENIUM WITH 3,3′-DIAMINOBENZIDINE

The toluene extract of diphenylpiazselenol has two absorption maxima, at 340 and 420 nm. 3,3′-Diaminobenzidine in toluene absorbs maximum at 340 nm, and the absorption of diphenylpiazselenol in toluene is therefore measured at 420 nm. V^V, Fe^{III}, Cu^{II} and other oxidants, which form coloured products, interfere with the determination. EDTA is used to mask all interfering ions except V^V. All coloured ions remain in the aqueous solution during extraction. Substances reducing the tetravalent selenium ion also interfere.

The method is used to determine selenium in tellurium, arsenic, sulphur, indium, copper, stainless steel, some semiconductor compounds and in ores.

The method can be used to determine 1×10^{-4} per cent of selenium in a sample weighing 1 g. The sensitivity of determination can be slighlty increased if fluorescence of the toluene extract of diphenylpiazselenium is measured (instead of its absorption). Diphenylpiazselenol fluoresces intensely at 580 nm while 3,3'-diaminobenzidine fluoresces at 420 nm. A 10-ml portion of the toluene extract is irradiated by a source of wavelengths at 420 nm and the induced fluorescence is measured at 550-600 nm. The selenium content is calculated with reference to the standard containing 0.5 μg of selenium in 10 ml.

Note. The sensitivity to Se of a naphthyl analogue of 3,3'-diaminobenzidine is higher both in spectrophotometric and fluorescence variants of the method.

Reagents

Sodium selenite, standard solution. 1 ml is equivalent to 2 μg of selenium.
Hydrochloric acid, density 1.19 g/cu.cm and diluted 1 : 7.
Nitric acid, density 1.5 g/cu.cm.
Ammonia, solution diluted 1 : 1.
EDTA, 2.5 per cent and 0.1 *M* solutions.
Formic acid, solution diluted 1 : 9.
Stannous chloride. Dissolve 10 g of the preparation in 4 ml of hydrochloric acid, density 1.19 g/cu.cm, with heating, and dilute with 16 ml of water. Prepare the solution immediately before the analysis.
Sodium hypophosphite, 10 per cent solution in hydrochloric acid (1 : 7).
Carbamide, 5 per cent solution.
Citric acid, 25 and 40 per cent solution.
Sodium arsenate solution. 1 ml is equivalent to 50 mg of arsenic.
Cresol red, 0.1 per cent solution in 20 per cent ethanol.
3,3'-Diaminobenzidine, 0.5 per cent solution. (Keep in the dark and cold.)
Toluene or benzene.

Constructing a Calibration Curve

Place solution containing 1.0, 3.0, 5.0 and 7.0 μg of selenium into 50-ml beakers and add 40 ml of water into each beaker. Now add 1 ml of a 2.5 per cent solution of EDTA, 2 ml of formic acid into each beaker and adjust the pH to 2-3 with ammonia to cresol red (the yellow colour of the indicator). Now add 2 ml of a 0.5 per cent solution of 3,3'-diaminobenzidine prepared for the analysis. Allow the solutions to stand for 30 minutes, add ammonia to adjust the pH to 8 (violet colour of the indicator), transfer the solutions to 75-100 ml separating funnels, add 11 ml of toluene or benzene and extract the coloured compound for one minute. Pass the extracts through dry paper filters into cells with a light path of 3 cm and measure the absorption of the solutions at 415-420 nm on a model ФЭКН-54 absorptiometer using a blank solution as the standard. Construct the calibration curve using the data obtained.

Procedure

Determining Selenium in Tellurium. Grind a sample of tellurium weighing 1.0 g and dissolve it with heating in a mixture of 15 ml of concentrated hydrochloric acid and 2 ml of nitric acid. Evaporate the solution to a very small volume (about 1 ml), add 20 ml of water, cool, transfer the solution into a 50-ml volumetric flask, and add water to the mark. Using a pipette, transfer 25 ml of the solution into a 100-ml beaker, dilute with water to 50 ml, add 3 ml of a 0.1 *M* solution of EDTA, 2 ml of formic acid, 10 ml of a 40 per cent solution of citric acid and ammonia solution, drop by drop, to pH 2.5-3.0

(universal test paper). Add 2 ml of 3,3′-diaminobenzidine solution, heat to the boil, allow to stand for ten minutes at room temperature, and then cool in a stream of tap water. Adjust the pH to 7.0-8.0, by ammonia solution: tellurous acid precipitates and then dissolves. Transfer the solution into a 100-ml separating funnel and extract diphenylpiazselenol for one minute with 11 ml of benzene or toluene. Proceed further as for the construction of the calibration curve.

Determining Selenium in Arsenic. Dissolve 1.0 g of arsenic in 6 ml of a mixture of equal volumes of concentrated nitric and hydrochloric acid with moderate heating (avoiding vigorous reaction). Evaporate the solution almost to dryness, add 15-20 ml of water, and heat to prepare a clear solution. Cool and dilute with water to 40 ml, add EDTA and formic acid and proceed further as for the construction of the calibration curve.

Determining Selenium in Indium. Dissolve 0.5 g of indium in 3 ml of nitric acid with moderate heating and evaporate the solution almost to dryness. Dissolve the residue in 20 ml of hydrochloric acid (1 : 7), add sodium arsenate solution, 1 ml of stannous chloride and 10 ml of sodium hypophosphite solution, and a small quantity of paper pulp (the liberated arsenic acts like a collector). Heat the solution to boiling, boil for 5-7 minutes until precipitation begins, dilute with hydrochloric acid (1 : 7) to 50 ml and allow to stand overnight.

Separate the precipitate on a filter with the paper pulp and wash 8-10 times with hydrochloric acid (1 : 7). Transfer the washed precipitate together with the filter pad into the precipitation beaker, add 6 ml of concentrated hydrochloric acid and 3-5 drops of nitric acid. Place the beaker on a water bath and keep at 70-80°C until the solid dissolves. Add 10-15 ml of hot water, 2 ml of carbamide solution to destroy excess oxidant, mix, and pass through a white ribbon filter. Wash the filter 2-3 times with warm water. Add 4 ml of citric acid to the filtrate, cool the solution, and proceed further as for the construction of the calibration curve.

Determining Selenium in Arsenide and Antimonide of Indium. Dissolve 0.5 g of indium arsenide or indium antimonide in 6 ml of a mixture of equal volumes of hydrochloric and nitric acid with moderate heating, and evaporate the solution almost to dryness.

If indium arsenide is analyzed, dissolve the residue in 20 ml of hydrochloric acid (1 : 7) with heating, add 1 ml of stannous chloride, 10 ml of sodium hypophosphite and a small amount of paper pulp. Add 1 ml of sodium arsenate solution (50 mg of arsenic) into the blank solution.

If indium antimonide is analyzed, dissolve the residue in 5 ml of a 25 per cent solution of citric acid with heating, add 20 ml of hydrochloric acid (1 : 7), 0.5 ml of sodium arsenate, 1 ml of stannous chloride and 10 ml of sodium hypophosphite solution and a small amount of filter paper pulp.

In both cases heat the solution to the boil, maintain boiling for 5-10 minutes until precipitate falls out, dilute with hydrochloric acid (1 : 7) to 50 ml and allow to stand overnight. Proceed further as for the determination of selenium in indium metal, except that in the case with indium antimonide add 4 ml (instead of 2 ml) of 3,3′-diaminobenzidine.

DETERMINING SMALL QUANTITY OF SELENIUM IN ORES

Reagents

Nitric acid, density 1.4 g/cu.cm.
Hydrochloric acid, density 1.19 g/cu.cm, and 3 per cent solution.
Sulphuric acid, diluted 1 : 1.
As_2O_3 solution. 1 ml is equivalent to 1 mg of arsenic.
Copper sulphate, $CuSO_4 \cdot 5H_2O$, crystalline.
Potassium (or sodium) hypophosphite, crystalline.
For the other reagents see Sec. Extraction-Photometric Determination of Selenium with 3,3′-Diaminobenzidine.

Constructing a Calibration Curve

Construct the calibration curve as instructed in Sec. Procedure.

Procedure

Treat a sample weighing 2 g with 40 ml of nitric acid. (If sulphide ore is analyzed, add 0.05-0.1 g of KI or 0.1-0.2 g of $KClO_3$.) Allow the mixture to stand overnight, then evaporate to 5-10 ml, add 10 ml of sulphuric acid, and evaporate to white fumes. Dissolve the residue in 5-10 ml of water and repeat the evaporation. Add 25-30 ml of water, heat to the boil, separate the insoluble precipitate on a filter, and collect the filtrate in a 150-ml beaker. Wash the precipitate on the filter with 2-3 small portions of hot water. Add an equal volume (50 ml) of hydrochloric acid to the filtrate, then add 1 ml of As_2O_3 solution and 0.1 g of copper sulphate. Add a small amount of paper pulp, heat to 80-90°C and then add potassium (or sodium) hypophosphite into the hot solution by small portions with stirring to reduce the ferric ion. Add 1-2 g in excess.

Heat the solution to the boil, maintain it boiling for ten minutes, and allow to stand for 2-3 hours or overnight. Separate the precipitate on a filter, wash it 4 or 5 times with a hot 3 per cent solution of hydrochloric acid and 3-4 times with water. Dissolve the precipitate on a filter in 5-8 ml of an acid mixture (5 ml of concentrated nitric acid and 2-3 drops of concentrated hydrochloric acid) and wash the filter with water. Add 2 ml of sulphuric acid to the solution and evaporate to white fumes. Wash the residue into a 10-ml test tube. Take a 3-ml portion of the solution and determine selenium as in Sec. Extraction-Photometric Determination of Selenium with 3,3′-Diaminobenzidine.

PHOTOMETRIC DETERMINATION OF TELLURIUM IN STEEL WITH POTASSIUM IODIDE

The absorption of yellow solutions of the iodide complex TeI_6^{2-}, which have two maxima, at 285 and 333 nm is measured. Fe^{III}, Cu^{II}, Bi^{III} and Se^{IV} interfere with the determination. Tellurium can be separated from the former three elements by reduction with stannous chloride. Selenium is also precipitated in this reaction. Therefore, if steel contains selenium, it should be separated. But as a rule, steels always contain either selenium or tellurium alone.

The optimum conditions for the determination of tellurium are as follows: the concentration of sulphuric acid is 1 *N*, of potassium iodide, 0.2 *M*, the time of retention, not less than ten minutes.

Reagents

Tellurous acid, standard solution. 1 ml is equivalent to 0.1 mg of tellurium.
Stannous chloride, 10 per cent solution. Dissolve 100 g of the reagent with heating in 250 ml of concentrated hydrochloric acid and then dilute to 1 litre.
Carbamide, crystalline.
Hydrochloric acid, density 1.19 g/cu.cm and diluted 1 : 20.
Nitric acid, density 1.4 g/cu.cm.
Potassium iodide, 2 *M* solution prepared for the test.
Sulphuric acid, diluted 1 : 5.

Constructing a Calibration Curve

Place 2, 4, 6, 8, and 10 ml of the standard solution of tellurous acid into 100-ml volumetric flasks, add 25 ml of water, 10 ml of concentrated hydrochloric acid, 10 ml of potassium iodide, and 3 g of carbamide into each flask, mix the solutions and allow to stand for 20 minutes in the dark. Measure the absorption of the solutions on an absorptiometer with a blue optical filter ($l = 1$ cm). Construct the calibration curve using the data obtained.

Procedure

Dissolve a sample of steel weighing 0.5-1.0 g (depending on the tellurium content) in 50-100 ml of sulphuric acid with moderate heating. When the sample has dissolved, separate the undissolved residue on a filter and wash several times with hot water. Transfer the filter with the precipitate into the dissolution beaker, add 10 ml of concentrated hydrochloric acid and 5-6 drops of nitric acid, and heat for 2-3 minutes to complete decomposition of the residue (more nitric acid is sometimes required). Add 25-30 ml of hot water to the solution, separate the paper pulp, and wash it several times with sulphuric acid (1 : 20). Heat the filtrate to boiling, add 3 g of carbamide and stannous chloride solution to discolour the solution, then add 5 ml in excess, and boil for ten minutes to coagulate tellurium precipitate. Add a small amount of paper pulp, heat the solution to the boil and allow it to stand in a warm place for 10-15 minutes. Separate the precipitate on a white ribbon filter and wash with hot hydrochloric acid (1 : 20).

Transfer the filter with the precipitate into the beaker where tellurium was precipitated, add 10 ml of hydrochloric acid, density 1.19 g/cu.cm, and 5-6 drops of nitric acid. Heat the solution with shaking the flask energetically from time to time. When the tellurium is all dissolved, dilute the solution to 30-40 ml, pass it through a white ribbon paper filter into a 100-ml volumetric flask and wash with hot water. Proceed further as for the construction of the calibration curve. Prepare a reference solution for the absorptiometric determination as follows: place 25-30 ml of distilled water into a 100-ml volumetric flask, add 10 ml of concentrated hydrochloric acid and two drops of nitric acid, and finally add 3 g of carbamide, 10 ml of potassium iodide solution and water to the mark.

EXTRACTION-PHOTOMETRIC DETERMINATION OF SELENIUM AND TELLURIUM IN NATIVE SULPHUR WITH 5-MERCAPTO-3-(NAPHTHYL-2)-1,3,4-THIADIAZOLTHIONE-2

The reagent forms yellow-orange complex compounds with Te^{IV} and Se^{IV}. These are practically insoluble (in water) substances, which are readily extractable by chloroform and benzene. The reaction with tellurium is more sensitive and occurs in a wide range of acidity, from 9 M H_2SO_4 to pH 6. The molar extinction coefficient is 2.95×10^4 at $\lambda = 320$ nm. Selenium forms compounds at pH $\leqslant 2$. At pH 4.8-5.0, only tellurium complex is extracted and tellurium can be determined by the extraction-photometric method in the presence of a 200-fold quantity of selenium. If selenium and tellurium are present in one solution, the absorption of the chloroform extract at pH 1.5 corresponds to the summary content of selenium and tellurium. The tellurium content is found from the calibration curve constructed at pH 4.8. The calibration graph for selenium is constructed at pH 1.5. The absorption corresponding to the selenium content is the difference in absorptions of the extracts obtained at pH of the aqueous phase 1.5 and 4.8 respectively. To remove the effect of the reagent, the absorption at pH 1.5 is measured against the reagent extract.

Reagents

Nitric acid, density 1.4 g/cu.cm.
Sulphuric acid, density 1.84 g/cu.cm.
Bromine.
Buffer solution, pH 1.5-2.0 and 4.8-5.0.
Chloroform.
5-Mercapto-3-(naphthyl-2)-1,3,4-thiadiazolthione-2, 0.1 per cent solution prepared for the test.

Constructing a Calibration Curve

For Selenium. Place 10 ml of the buffer solution with pH 1.5-2.0 into 10-ml separating funnels and add 1, 2, 3, 4 and 5 ml of the standard solution of selenious acid. Then add 2 ml of the reagent and 10 ml of chloroform into each funnel. Extract the coloured complex for 2-3 minutes and pass the extract through a dry paper filter into a dry cell with a light path of 1 cm. Measure the absorption of the extracts on an absorptiometer with an optical filter No. 2 using the reagent extract in chloroform as a reference solution.

For Tellurium. Place 10 ml of the buffer solution with pH 4.8-5.0 into separating funnels and add 1, 2, 3, 4 and 5 ml of the standard solution of tellurium (IV) respectively. Next add 2 ml of the reagent and 10 ml of chloroform and extract the complex for 5 minutes. Filter the extracts as described above and measure their absorption in the same conditions but using chloroform as a reference solution.

Procedure

Place a sample of ground sulphur weighing 1 or 2 grams in a 100-ml beaker and wet with water. Add 5-10 ml of nitric acid, and, carefully, a few drops of bromine. Heat on a water bath and add bromine again to decompose the sample completely. Add 2-3 ml of sulphuric acid and heat to white fumes. Cool, transfer into a 25-ml volumetric flask and add water to the mark.

To determine the summary content of selenium and tellurium, take a 10.0-ml aliquot, add 2 ml of the reagent solution and extract with 10 ml of chloroform for 5-7 minutes. After the phases have separated pass the extract through a dry paper filter into a dry cell with a light path of 1 cm and measure its absorption (D_2) on an absorptiometer with an optical filter No. 2 using the chloroform extract of the reagent as a reference solution.

To determine tellurium adjust the pH of another 10.0-ml aliquot to 4.8 by adding the buffer solution, add the reagent, and extract the tellurium complex with chloroform. Measure the absorption of the extract as described above (D_1).

Find the absorption corresponding to the selenium content as the difference $D_2 - D_1$. Determine the selenium and tellurium contents from the calibration curves.

SPECTROPHOTOMETRIC DETERMINATION OF TELLURIUM IN SELENIUM WITH SODIUM 3,5-DIPHENYLPYRAZOLINE-1-DITHIOCARBAMATE

The method is based on the formation of a tellurium compound with sodium 3,5-diphenylpyrazoline-1-dithiocarbamate. This is a yellow substance soluble in chloroform and carbon tetrachloride. It is extractable in a wide range of acidities, from 12 *M* HCl to pH 9. The absorption maximum of its chloroform extracts is at 415 nm. The apparent molar extinction coefficient is 2.04×10^4. The absorption of the extracts remains constant for a long time.

Microgram quantities of tellurium can be determined directly at pH about 8 in the presence of the tartrate ion, the tellurium to selenium ratio being 1 : 100.

The ions of all elements which react with dithiocarbamates in the specified conditions interfere with the determination. Selenium (over 1 g) and also As, Bi, Cd, Ni, Fe^{III}, Cu, Mn^{II}, Pd^{II}, Sb, Sn, Zn (over 1 mg each) and other elements can be masked during extraction of over 2 μg of tellurium. Tl^{III} and Tl^{I} also interfere but they can be extracted by pyrazolinedithiocarbamates in a strongly alkaline medium (pH 14, and higher).

The method can be used for the separation and determination of tellurium in selenious acid and semiconductor metal (selenium) and also in sulphur and phosphorus. The selenium ion and the ions of the accompanying elements can be masked with cyanide, EDTA, and tartrate in an alkaline medium at pH 8-9.

Reagents

Tellurium compound, standard solution. 1 ml is equivalent to 1 μg of tellurium.
Selenious acid. Purify the acid as follows. Dissolve the acid sample in water, adjust its pH to 8.7-8.9 with a 10 per cent solution of sodium hydroxide, and add 2 ml of a 0.1 per cent solution of sodium 3,5-diphenylpyrazoline-1-dithiocarbamate. Extract the turbidity several times with 10-ml portions of chloroform shaking for 2-3 minutes and adding 0.5-1.0 ml of the reagent before each extraction. Repeat the extraction until the addition of the reagent does not produce any turbidity. Discard the extracts and use the solution to prepare the standards.
Sodium 3,5-diphenylpyrazoline-1-dithiocarbamate, 1 per cent solution.
Chloroform.
Masking mixture. Mix 10 g of sodium cyanide, 1 g of EDTA, and 5 g of sodium tartrate and add water to make 100 ml.
Nitric acid, density 1.4 g/cu.cm.

Constructing a Calibration Curve

Place selenious acid purified from tellurium (about 1 g of Se) into separating funnels, add 10-15 ml of the masking mixture, adjust the pH of the solution to 8.6 and finally add 0.5, 1.0, 1.5, 2.0 and 2.5 ml of the standard solution of the tellurium compound. Now add 1-2 ml of a 1 per cent solution of the reagent and extract with chloroform (10, 10 and 5 ml portions). Filter the extracts into 25-ml volumetric flasks and add chloroform to the mark. Mix the solutions and measure their absorption on a spectrophotometer at 415 nm. Construct the calibration curve using the data obtained.

Procedure

Dissolve a sample of elemental selenium weighing 0.5-1.0 g in nitric acid, density 1.4 g/cu.cm, with very slightly heating on a water bath, and adding a few drops of concentrated hydrochloric acid. Transfer the acid solution into a 500-ml separating funnel, neutralize with sodium hydroxide solution and add the masking mixture. Adjust the pH to 8.5 and proceed as for the construction of the calibration curve. Find the tellurium content from the calibration curve.

PHOTOMETRIC DETERMINATION OF TELLURIUM BY COPPER DIETHYLDITHIOCARBAMATE IN COMMERCIAL INDIUM, ARSENIC, AND IN THEIR SEMICONDUCTOR COMPOUNDS

Tellurium reacts with diethyldithiocarbamate to form a coloured compound extractable by carbon tetrachloride. Only bismuth, gallium and antimony are extracted together with tellurium in the form of diethyldithiocarbamates in the presence of potassium cyanide and EDTA. The extract of tellurium compound with diethyldithiocarbamate is shaken with a solution of a copper salt: an intensely coloured solution of copper diethyldithiocarbamate in CCl_4 is formed. The absorption of the solution containing 1 μg of copper as the diethyldithiocarbamate is the same as the absorption of a solution containing 7 μg of tellurium in the form of a similar compound. The sensitivity of the photometric determination is thus increased.

The method can be used to determine 5×10^{-5} per cent of tellurium in a sample weighing 0.5 g.

Reagents

Sodium tellurite, standard solution. 1 ml is equivalent to 1 μg of tellurium.
Hydrochloric acid, density 1.19 g/cu.cm, and diluted 1 : 7 and 1 *N* solution.
Nitric acid, density 1.4 g/cu.cm.
Sulphuric acid, diluted 1 : 1.
Potassium hydroxide, 20 per cent solution.
Potassium cyanide, 10 per cent solution.
Buffer solution, pH 8.4-8.5. Dissolve 5 g of boric acid, 10 g of EDTA, and 10 g of KH_2PO_4 in 500-600 ml of hot water, neutralize to pH 8.5 with a 20 per cent solution of potassium hydroxide (potentiometric control) and dilute with water to 1 litre.
Sodium diethyldithiocarbamate, 0.5 per cent solution.
Copper sulphate, 0.02 per cent solution. Dissolve 0.1 g of anhydrous copper sulphate in 0.5 litre of water containing 7 ml of sulphuric acid. Before use, add anhydrous sodium carbonate to part of the solution until a pale blue colour develops. The solution must be clear.
Sodium arsenate, solution. 1 ml is equivalent to 50 mg of arsenic.
Sodium hypophosphite, 10 per cent solution in hydrochloric acid (1 : 7).
Stannous chloride, 10 per cent solution in 2 *M* HCl.
Citric acid, 25 per cent solution.
Phenolphthalein, 1 per cent solution in 60 per cent ethyl alcohol.
Carbon tetrachloride.

Constructing a Calibration Curve

Place 1, 2, 3, 4 and 5 ml of the standard solution of tellurium into 50-ml beakers, and add 20 ml of water, a drop of phenolphthalein, 4 drops of potassium cyanide solution and 5 ml of the buffer into each beaker. Adjust the pH to 8.4-8.5 and proceed as for the determination of tellurium in arsenic. Construct the calibration curve using the data obtained.

Procedure

Determining Tellurium in Arsenic. Dissolve 0.5 g of ground arsenic in 6 ml of a mixture of equal volumes of concentrated hydrochloric and nitric acid. Evaporate the greater part of the solution, add 1 ml of sulphuric acid (1 : 1) and continue evaporation to white fumes of sulphuric acid. Cool the solution, add 15 ml of water, a drop of phenolphthalein, and neutralize with a 20 per cent solution of potassium hydroxide until the solution becomes pale pink. Add 8-10 drops of potassium cyanide, 1 *N* hydrochloric acid until the solution becomes colourless, and 5 ml of the buffer solution (when pink colour develops, remove it by adding 1 *N* hydrochloric acid). Transfer the solution into a 75-100 ml separating funnel, add 2 ml of sodium diethyldithiocarbamate solution, keep for ten minutes in the dark, add 12 ml of carbon tetrachloride, and shake energetically for two minutes. Pass the extract through a dry filter into another separating funnel containing 10 ml of copper sulphate solution and shake energetically for a minute. Place the organic layer into a cell with a light path of 3 cm and measure the absorption on a model ФЭК-Н-54 absorptiometer using an optical filter No. 2 (transmitting maximum at 415 nm). Use chloroform as the standard.

Find the tellurium content from the calibration curve.

Determining Tellurium in Indium Metal. Dissolve 0.5 g of indium with moderate heating in 3 ml of nitric acid. Evaporate the solution almost to dryness, dissolve the residue in 20 ml of hydrochloric acid (1 : 7), add 1 ml of sodium arsenate solution, 1 ml of stannous chloride solution, 10 ml of sodium hypophosphite solution and a small amount of paper pulp. Boil the solution until precipitation begins, dilute with hydrochloric acid (1 : 7) to 50 ml, and allow to stand overnight.

Separate the precipitate on a filter with paper pulp and wash 8-10 times with hot hydrochloric acid (1 : 7). Dissolve the precipitate on the filter with 6-8 ml of hot nitric acid containing 2-3 drops of concentrated hydrochloric acid and wash the filter 2-3 times with hot water. Add 1 ml of sulphuric acid (1 : 1) to the filtrate and evaporate to fumes of sulphuric acid. Cool the solution, add 2 ml of citric acid solution, neutralize, and proceed as for the determination of tellurium in arsenic.

Determining Tellurium in Semiconductor Indium Arsenide. Act as for the determination of tellurium in indium metal. Use arsenic as the collector to precipitate microquantities of tellurium. Sodium arsenate should be added to the blank solution as well.

EXTRACTION-PHOTOMETRIC DETERMINATION OF TELLURIUM IN COMMERCIAL SELENIUM USING PYRAZOLONE DERIVATIVES

A chloride complex of tellurium (IV) with diantipyrylpropylmethane is exracted quantitatively by dichloroethane from hydrochloric acid solutions. All selenium (IV) remains in the aqueous phase (at any acid concentration). Any quantity of tellurium can thus be easily separated from selenium. To determine tellurium the chloride complex is converted into the bromide complex with diantipyrylpropylmethane and the absorption of the resultant solution is measured. The method is very simple and the results are reproducible. Moreover, it does not take much time.

The other methods of separating small quantities of tellurium from selenium when analysing commercial grades of selenium are very complicated, take much time (over two days) and involve the use of the strong poison, potassium cyanide. The analysis consists of many stages and this deteriorates the reliability of the results.

If the tellurium content of selenium exceeds 0.5 per cent, the determination can be ended titrimetrically.

Reagents

Nitric acid, density 1.4 g/cu.cm.
Sulphuric acid, diluted 1 : 1.
Hydrochloric acid, density 1.19 g/cu.cm and diluted 1 : 1.
Hydrobromic acid, 40 per cent, distilled.
Diantipyrylpropylmethane, 5 and 1 per cent solutions in acetic acid (1 : 1). Dissolve 5 g of antipyrine in a small quantity of water, add 2 ml of hydrochloric acid, 2 ml of distilled butyric aldehyde and heat on a water bath for 30 minutes. Cool, add water to about 200 ml and a 25 per cent solution of ammonia until a faint odour is felt. The oily liquid quickly crystallizes. Filter the crystals in a Büchner funnel, wash with water, and recrystallize from ethyl or methyl alcohol. The crystals melt at 156 °C.
1,2-Dichloroethane.
Tellurous acid, standard solution. 1 ml is equivalent to 0.001 g of tellurium. Dissolve 1 g of pure tellurium in nitric acid, density 1.4 g/cu.cm (add a small quantity of hydrochloric acid, if tellurium dissolves slowly). Transfer the solution into a 1-litre volumetric flask and add 5 per cent hydrochloric acid to the mark. 1 ml contains 0.001 g of tellurium (solution A). Place 1 ml of solution A into a 100-ml beaker, and evaporate twice with 5 ml of 1 per cent sulphuric acid. Transfer the residue into a 100-ml volumetric flask using sulphuric acid (1 : 1) and add the acid to the mark. 1 ml of the new solution contains 0.00001 g of Te (solution B).
EDTA, 0.02 *M* solution.
Ascorbic acid. Prepare the solution containing 1 g in 20 ml immediately before the analysis.

Constructing a Calibration Curve

Place 1, 2, 3, 4, 5, 6, 7, 8, 9 and 10 ml of tellurous acid (solution B) into ten 60-ml separating funnels, add water to 10 ml, 5 ml of distilled hydrobromic acid, and allow to stand for 1-2 minutes. Add 0.5 ml of ascorbic acid, 1 ml of a 1 per cent solution of diantipyrylpropylmethane, 5 ml of dichloroethane into each flask and shake the mixtures for a minute. When the phases have separated, pass the extracts through dry filters into cells with a light path of 1 cm and measure the absorption on an absorptiometer with the optical filter No. 3 or a spectrophotometer, using dichloroethane as the standard. Construct the calibration curve using the data obtained.

The colour of the extracts persists for a long time.

Procedure

Dissolve 0.5 g of selenium metal in 15-20 ml of nitric acid, add 5 ml of sulphuric acid and evaporate the solution to fumes of sulphuric acid. Cool the residue, add carefully 5 ml of water, and evaporate again to fumes of sulphuric acid. Cool the residue and transfer into a 50-ml volumetric flask using hydrochloric acid (1 : 1). Transfer a 5- or 10-ml aliquot (depending on the tellurium content) into a 100-ml separating funnel, add 1-2 ml of a 5 per cent solution of diantipyrylpropylmethane, hydrochloric acid (1 : 1) to 20 ml and 5 ml of dichloroethane, and shake for one minute.

After the phases have separated, transfer the extract into a clean 50-ml separating funnel. Add 5 ml of dichloroethane to the remaining aqueous phase, shake for a minute and separate the extract. Join the dichloroethane extracts and discard the aqueous solution. Wash the extracts two times with 10 ml of hydrochloric acid (1 : 1). Extract the tellurium compound from the joined extract by shaking with 10 ml of EDTA solution. When the phases have separated, discard dichloroethane. Add 5 ml of hydrobromic acid to the remaining aqueous solution and proceed as described above.

Find the tellurium content from the calibration curve.

EXTRACTION-PHOTOMETRIC DETERMINATION OF TELLURIUM IN COMMERCIAL LEAD AND BISMUTH WITH PYRAZOLONE DERIVATIVES

Tellurium is separated from lead and bismuth by extraction of the tellurium (IV) chloride complex with diantipyrylpropylmethane from hydrochloric acid solution (after adding EDTA). The procedure ends with the extraction-photometric determination of tellurium in the form of its bromide complex with pyrazolone derivatives (diantipyrylpropylmethane, diantipyrylmethane, diantipyrylmethylmethane). The yellow solutions of the bromide complexes of tellurium are stable for a long time. The method ensures accurate and reliable results, and takes relatively little time.

Reagents

EDTA, 0.1 *M* and 0.02 *M* solutions.
For the other reagents see the previous section.

Constructing a Calibration Curve

Place 1, 2, 3, 4, 5, 6, 7, 8, 9 and 10 ml of tellurous acid (solution B) into ten 50-ml separating funnels and dilute with water to 10 ml. Now add 5 ml of hydrobromic acid into each funnel and allow to stand for 1-2 minutes. Add 1 ml of a 1 per cent solution of diantipyrylpropylmethane, 5 ml of dichloroethane into each funnel and shake for a minute. Separate the extracts, pass them through dry filters into cells with a light path of 1 cm, and measure the absorptions of the extracts on an absorptiometer or spectrophotometer against dichloroethane. Construct the calibration curve using the data obtained. The colour of the extract persists for a long time.

Procedure

Dissolve 0.2-0.5 g of lead or bismuth in 20-25 ml of nitric acid (1 : 3). Evaporate the solution almost to dryness, rinse the flask walls with water and evaporate the solution to dryness. Dissolve the residue in 15-40 ml of 0.1 *M* solution of EDTA with heating, add an equal volume of concentrated hydrochloric acid and transfer the solution into a 100- or 200-ml separating funnel. Add 2 ml of 5 per cent diantipyrylpropylmethane solution, mix, add 5 ml of dichloroethane and shake for a minute. When the phases have separated, transfer the extract into a 50-ml separating funnel. Add 5 ml of dichloroethane to the remaining aqueous phase and shake for a minute again.

Join the extracts and discard the aqueous solution. Wash the extracts twice with 10 ml of hydrochloric acid (1 : 1). Separate tellurium from the extract by shaking with 10 ml of 0.02 *M* EDTA solution. Repeat this operation two times. As soon as the phases have separated, decant dichloroethane. Join the aqueous solutions and transfer them into a 50- or 100-ml volumetric flask. Add 0.02 *M* solution of EDTA to the mark.

Take a 5-ml aliquot of the solution, add 5 ml of 0.02 *M* EDTA solution, 10 ml of hydrobromic acid, 1 ml of a 1 per cent solution of diantipyrylpropylmethane and 5 ml of dichloroethane, and shake the mixture for a minute. Proceed further as for the construction of the calibration curve.

Find the tellurium content from the calibration curve.

Note. The reagents should be free from iron. If, however, small quantities of iron are present, add 0.5 ml of ascorbic acid solution (1 g per 20 ml of water) after adding hydrobromic acid.

EXTRACTION-PHOTOMETRIC DETERMINATION OF TELLURIUM IN COMMERCIAL COPPER WITH DIANTIPYRYLPROPYLMETHANE

Small amounts of tellurium are separated from copper by extraction of its chloride complex with diantipyrylpropylmethane by dichloroethane. Tellurium is then determined photometrically as its bromide complex with diantipyrylpropylmethane. The method is very simple. The other methods for determining tellurium in copper often give unreliable results, are complicated, and take much time.

Reagents

Nitric acid, diluted 1 : 3.
Sulphuric acid, diluted 1 : 1.
Hydrochloric acid, diluted 1 : 1.
Diantipyrylpropylmethane, 5 and 1 per cent solutions in acetic acid. Prepare as in Sec. Extraction-Photometric Determination of Tellurium in Commercial Selenium.
1,2-Dichloroethane.
Hydrobromic acid, 40 per cent solution, distilled.
Potassium bromide, saturated solution, containing about 60 g of KBr in 100 ml of water.
Tellurous acid. 1 ml is equivalent to 0.00001 g of Te.
Ascorbic acid, 5 per cent solution prepared before the test.

Constructing a Calibration Curve

Place 1, 2, 3, 4, 5, 6, 7 and 8 ml of tellurous acid into separating funnels, dilute with water to 5 ml, add 8 ml of saturated solution of potassium bromide and 0.5 ml of ascorbic acid into each funnel. Mix the solutions, add 3 ml of hydrobromic acid, 1 ml of a 1 per cent solution of diantipyrylpropylmethane and 5 ml of dichloroethane and shake the mixtures for a minute. Proceed further as in Sec. Procedure. Construct the calibration curve using the data obtained.

Procedure

Dissolve a sample of copper metal weighing 10 g in 50 ml of nitric acid. Transfer the solution into a 200-ml volumetric flask and add water to the mark. Take a 10-ml portion, add 5 ml of sulphuric acid and evaporate to fumes of sulphuric acid. Rinse the walls of the beaker with water and evaporate again to fumes of the acid. Dissolve the residue in 20 ml of hydrochloric acid, transfer the solution into a 100-ml separating funnel, add 2 ml of a 5 per cent solution of diantipyrylpropylmethane and 5 ml of dichloroethane, and shake the mixture for 2 minutes. Transfer the extract into a clean separating funnel. Add another 5-ml portion of dichloroethane to the remaining aqueous solution and shake the mixture for a minute.

Join the dichloroethane extracts (discarding the aqueous solution) and wash two times with 10 ml of hydrochloric acid. Separate the tellurium compound by shaking with 10 ml of water. Repeat this operation two or three times. Collect the aqueous solutions in a 50-ml volumetric flask.

If the tellurium content is 0.02-0.01 per cent, take 5 ml of the solution from the volumetric flask, add 8 ml of a saturated solution of potassium bromide and 0.5 ml of ascorbic acid, stir the mixture, add 3 ml of hydrobromic acid, 1 ml of a 1 per cent solution of diantipyrylpropylmethane and 5 ml of dichloroethane, and shake the mixture for a minute.

Separate the extract from the aqueous phase, filter into a cell with a light path of 1 cm and measure the absorption of the extract on a model ФЭК-Н-57 absorptiometer, using a blue optical filter No. 3, or on a spectrophotometer. Find the tellurium content from the calibration curve.

Note. If the tellurium content of copper is high, the determination can be completed titrimetrically.

PHOTOMETRIC DETERMINATION OF TELLURIUM WITH BISMUTHOL II

The tellurium (IV) ion reacts with bismuthol II in an aqueous solution at pH 2.3 to form a complex with the absorption maximum at 395-400 nm and the molar extinction coefficient of 1.47×10^4. The absorption maximum of its chloroform extract is at 335-340 nm, the molar extinction coefficient being 2.80×10^4. The ions of Fe, Cu, Au^{III}, Pt^{IV}, V^{V}, Se and NO_2^- interfere with the determination. The other cations, those of Cd and Bi in particular, can be masked with EDTA and a citrate. The extraction-photometric variant of the method can be used to determine over 0.01 per cent of Te directly in ores. If the tellurium content is lower, it is first separated by reduction with $SnCl_2$ in the presence of a collecting agent.

Reagents

Bismuthol II, 1 per cent solution in 0.1 *N* solution of KOH.
Citric acid, 1 *M* solution.
EDTA, 0.1 M solution.
Ammonia, 6 *M* solution.

Polyvinyl alcohol, 2 per cent solution.
Ammonium sulphate, 50 per cent solution in sulphuric acid; pH 2.2.
Tellurous acid, standard solutions. 1 ml is equivalent to 25 and 10 μg of tellurium.

Constructing a Calibration Curve

For Determination of Te Without Extraction. Take 1, 2, 3, 4 and 5 ml of the standard solution of tellurous acid containing 25 μg of Te in 1 ml, and add 1 ml of citric acid, 1 ml polyvinyl alcohol and water to 15 ml. Now add 2 ml of bismuthol II to each solution and allow to stand for 20-30 minutes. Adjust the pH of the solutions to 6.5 with ammonia and dilute with water to 25 ml. Measure the absorption of the solutions at 400 nm ($l = 1$ cm) and construct the calibration curve using the data obtained.
For Determination of Te with Extraction. Place 1, 2, 3, 4 and 5 ml of the standard solution of tellurous acid with the concentration of tellurium of 10 μg/ml into 125-ml separating funnels and add 5 ml of ammonium sulphate solution (for a better extraction), 1 ml of citric acid, 3 ml of bismuthol II solution into each funnel and allow to stand for 20-30 minutes. Now adjust the pH to 6.5 ammonia solution, shake the solutions for a minute with 10 ml of chloroform and measure the absorption of the extracts at 340 nm. Construct the calibration curve using the data obtained.

Procedure

Add the requisite reagents to the test solution as for the construction of the calibration curve and measure the absorption of the resultant solution. Find the tellurium content from the calibration curve.

To determine tellurium by the extraction-photometric method add all the requisite reagents to the test solution, extract the tellurium compound by chloroform and measure the absorption of the extract at 340 nm. Find the tellurium content from the calibration curve.

POLAROGRAPHIC DETERMINATION OF SELENIUM AND TELLURIUM

The following background is recommended for the determination of selenium and tellurium contained in the concentration of 0.05-2 mmole/l:

Ammonium chloride	0.75 mole/l
Ammonia	0.25 mole/l
Sodium sulphite	0.1 mole/l
Gelatin	0.002 per cent

The tellurium concentration should not exceed that of selenium. The half-wave potential for tellurium is 0.83 V, and for selenium, −1.5 V (with reference to the saturated calomel electrode).

When selenium and tellurium are determined in ores, the sum of the elements is first precipitated, and the precipitate is then dissolved in hydrochloric acid containing an additive of potassium chlorate (which does not interfere with further polarographic determination).

Reagents

Hydrochloric acid, density 1.19 g/cu.cm.
Potassium chlorate, crystalline.
Sodium hydroxide, 30 per cent solution.
Background solution. Dissolve 56 g of NH_4Cl, 25 g of Na_2SO_4, 20 ml of concentrated ammonia solution and 20 mg of gelatin in one litre of water.

Procedure

Add 10 ml of hydrochloric acid to the precipitate of Se and Te, heat the mixture for 5-10 minutes on a water bath. Add periodically small quantities of potassium chlorate to complete dissolution of the solid. Cool the solution, and neutralize with sodium hydroxide to phenol red. Add 5 drops of sodium hydroxide in excess. (If the tellurium content is over 2 mg, add 7 drops of potassium hydroxide, and if the selenium content is low, add 1-2 drops.) Dilute the solution to 100 ml with the background solution and determine Te and Se polarographically at -0.4 to -1.0 V and from -1.2 to -1.8 V respectively.

EXTRACTION-POLAROGRAPHIC DETERMINATION OF TELLURIUM IN SULPHIDE ORE

The method is based on the separation of tellurium by extraction of a 4.5 *N* solution of hydrochloric acid with methyl isobutyl ketone and polarography of the extract on an AC polarograph model ЦЛА, using a dropping-mercury electrode. A mixture of equal volumes of 6 *N* HCl, methyl isobutyl ketone, and ethyl alcohol is used as the background solution. The elements, which are not extractable by methyl isobutyl ketone and are not reduced at potentials close to the half-peak potential of tellurium (Cu, Co, Ni, Cr), do not interfere. 200-fold quantities of zinc and cadmium do not interfere either. The interfering effect of a large quantity of tervalent iron can be removed by carrying out the extraction in the presence of ascorbic acid. The sensitivity of the determination of tellurium is 1×10^{-3} per cent in a sample weighing 0.5 g.

Reagents

Tellurium, standard solution. Dissolve tellurium metal in sulphuric acid. 1 ml is equivalent to 50 μg of Te.
Nitric acid, density 1.4 g/cu.cm.
Hydrochloric acid, density 1.18 g/cu.cm, 4.5 *N* solution saturated with methyl isobutyl ketone, and 6 *N* solution.
Bromine.
Ethyl alcohol.
Ascorbic acid, crystalline.
Methyl isobutyl ketone.

Constructing a Calibration Curve

Place 10, 20, 30, 40 and 50 μg of Te into separating funnels, and add 5.0 ml of 4.5 *N* HCl saturated with methyl isobutyl ketone. Then add 3 ml of methyl isobutyl ketone into each funnel, and extract for two minutes. Add 3 ml of ethyl alcohol, 2 ml of 6 N HCl to the organic extract, remove oxygen by bubbling a mixture of nitrogen and hydrogen for 20 minutes, and determine the peak at —0.6 V.

Procedure

Treat a finely ground sample of ore weighing 0.5 g with 10 ml of nitric acid with heating, add a few drops of bromine and heat on a closed-spiral hotplate. Continue adding bromine to complete dissolution of the sulphur. Add 5 ml of hydrochloric acid, density 1.18 g/cu.cm, and evaporate with 5 ml of 6 N HCl (to remove HNO_3 and reduce Te^{VI} to Te^{IV}). Using 6-9 ml of 4.5 N HCl saturated with methyl isobutyl ketone, transfer the dry residue into a separating funnel and add a precalculated quantity of ascorbic acid (so that the Fe^{III} to ascorbic acid ratio is 1 : 1). Add 3 ml of methyl isobutyl ketone, and extract tellurium for two minutes. Wash the organic layer two times with 5 ml of 4.5 N HCl saturated with methyl isobutyl ketone. Add 3 ml of ethyl alcohol and 2 ml of 6 N hydrochloric acid to the extract, remove oxygen by blowing a mixture of nitrogen and hydrogen for 20 minutes and determine the tellurium peak at —0.6 V with reference to bottom mercury. Find the tellurium content from the calibration curve.

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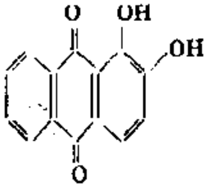
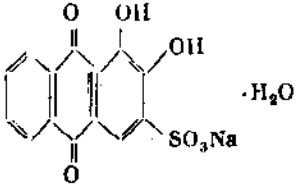
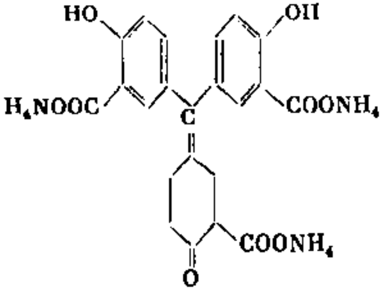
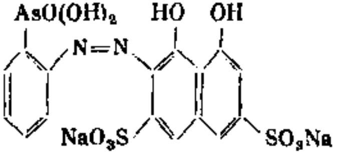
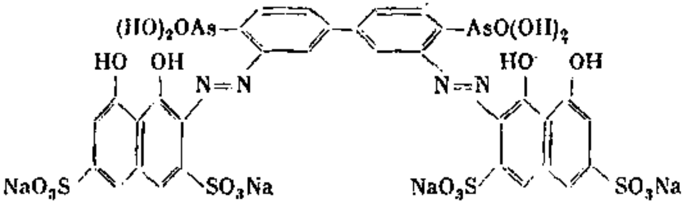
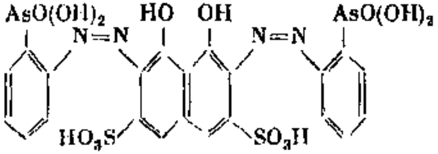
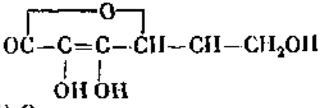
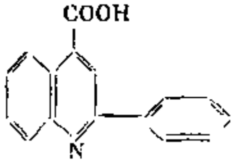
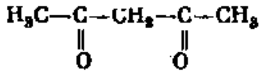
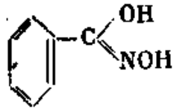
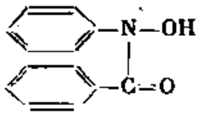
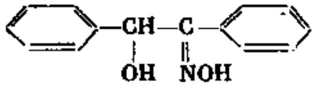
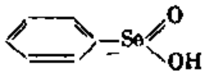
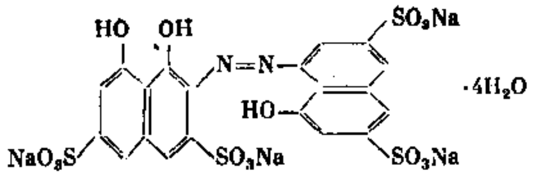
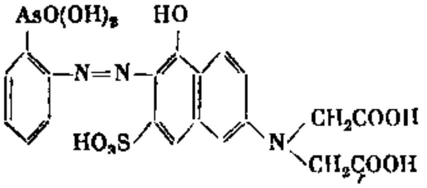
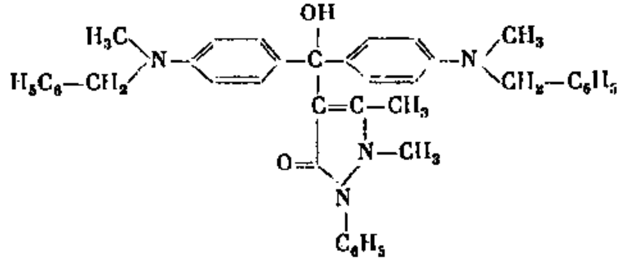
Appendices

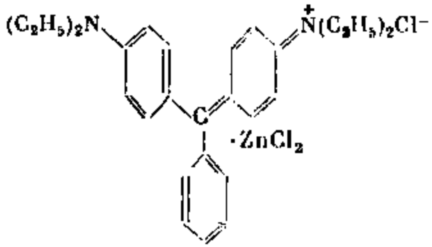
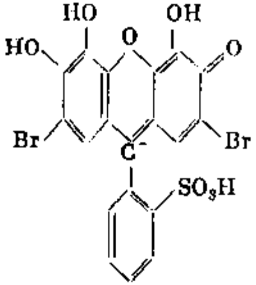
Appendix I. Important Organic Reagents for Determination of Rare Elements

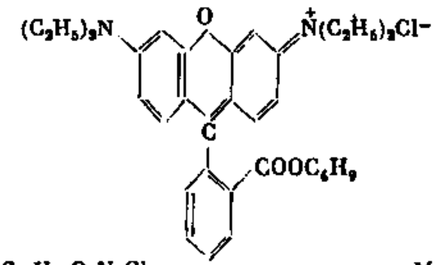
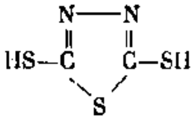
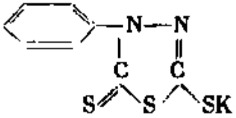
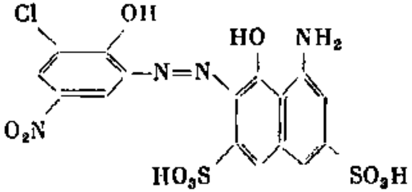
Name and its synonyms	Formula	Method of determination and elements determined
Alizarin (1,2-dihydroxyanthraquinone)	 $C_{14}H_8O_4$ Mol. wt. 240.22	Photometric determination of Ga, In, Ti, Th, U
Alizarin red S (1,2-dihydroxyanthraquinone-3-sulphonic acid, sodium salt)	 $C_{14}H_7O_7SNa \cdot H_2O$ Mol. wt. 360.28	Photometric determination of Be, Bi, Hf, Li, Sc, Tl, Ti, U, Zr
Aluminon (aurintricarboxylic acid, ammonium salt)	 $C_{22}H_{23}O_9N_3$ Mol. wt. 473.44	Detection and photometric determination of Be, Sc, Ce, La, Nd, Zr, Hf, Th, In, Ga

Arsenazo I [o-(1,8-dihydroxy-3,6-disulpho-2-naphthylazo)phenylarsonic acid, sodium salt, uranon]	 $C_{16}H_{11}O_{11}N_2S_2AsNa_2$ Mol. wt. 592.30	**Photometric determination of Th, Zr, U, Ti, Ta, lanthanides, Be, Ga, In. Complexometric indicator for titration of Th, Zr, U, lanthanides**
Arsenazo II [4,4′-diarsenodiphenyl-3,3′-bis-(2-azo-1,8-dihydroxynaphthalene-3,6-disulphonic acid), sodium salt]	 $C_{32}H_{20}O_{22}N_4S_4As_2Na_4$ Mol. wt. 1182.59	
Arsenazo III [1,8-dihydroxynaphthalene-3,6-disulphonic acid-2,7-bis-(azo-2-phenylarsonic acid)]	 $C_{22}H_{18}O_{14}N_4S_4As_2$ Mol. wt. 776.38	Complexometric indicator for titration of Th, U, Zr
Ascorbic acid	 $C_6H_8O_6$ Mol. wt. 176.13	Photometric determination of Se and Te. Reduction of Fe^{III} in determination of rare elements
Atophan (2-phenyl-quinoline-4-carboxylic acid)	 $C_{16}H_{11}O_2N$ Mol. wt. 249.26	Fluorimetric determination of Eu

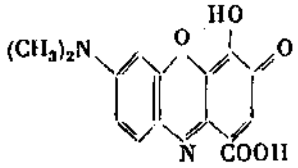
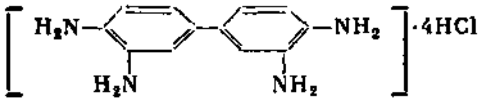
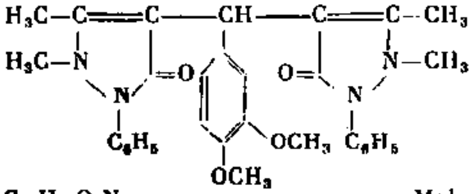
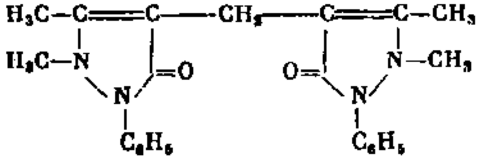
Name and its synonyms	Formula	Method of determination and elements determined
Acetylacetone	 $H_3C-\underset{\underset{O}{\Vert}}{C}-CH_2-\underset{\underset{O}{\Vert}}{C}-CH_3$ $C_5H_8O_2$ Mol. wt. 100.11	Separation and photometric determination of Be
Benzhydroxamic acid	 $C_7H_7O_2N$ Mol. wt. 137.14	Photometric determination of V and Nb
Benzidine sulphate	 $C_{12}H_{12}N_2 \cdot H_2SO_4$ Mol. wt. 282.32	Photometric determination of V^V, W^{VI}, Ce^{IV}, Ta, Tl, Ce^{IV}
N-Benzoyl-N-phenylhydroxylamine	 $C_{13}H_{11}O_2N$ Mol. wt. 213.24	Photometric determination of Ti, separation of Ta and Nb
α-Benzoinoxime	 $C_{14}H_{13}O_2N$ Mol. wt. 227.27	Gravimetric determination of V^V, Mo^{VI}
Benzeneseleninic acid	 $C_6H_6O_2Se$ Mol. wt. 189.07	Gravimetric determination of Sc

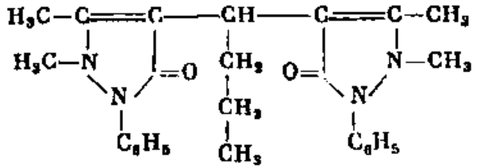
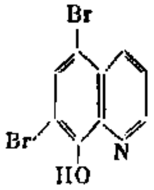
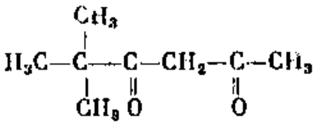
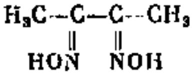
Beryllon II [8-hydroxynaphthalene-3,6-disulphonic acid-(1-azo-2')-1',8'-dihydroxynaphthalene-3', 6'-disulphonic acid, tetrasodium salt]	 $C_{20}H_{12}O_{16}N_2S_4Na_4 \cdot 4H_2O$ Mol. wt. 810.60	Photometric determination of Be
Beryllon IV [benzene-2-arsonic acid-(1-azo-2)-1-hydroxynaphthalene-6-iminodiacetic acid-3-sulphonic acid]	 $C_{20}H_{14}O_{11}N_3SAs$ Mol. wt. 579.31	Photometric determination of Be
Bis-(4'-methylbenzylaminophenyl)-antipyryl carbinol	 $C_{40}H_{41}O_2N_4$ Mol. wt. 609.73	Photometric determination of Re

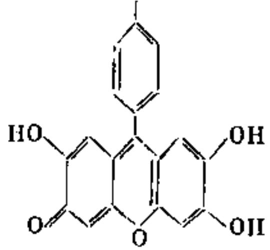
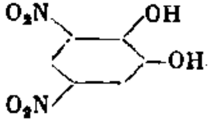
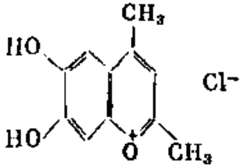
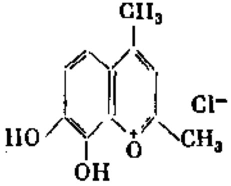
Name and its synonyms	Formula	Method of determination and elements determined
Brilliant green (ethyl green, diamant green G)	 $C_{27}H_{33}N_2Cl \cdot ZnCl_2$ Mol. wt. 557.31	Photometric determination of Tl^{III} (pH = 0.1-2.6), Ta, W, Ge
Brompyrogallol red (dibrompyrogallolsulphophthalein)	 $C_{19}H_{10}O_8SBr_2$ Mol. wt. 576.18	Complexometric indicator for titration of Bi, Ce^{III}, La, Pr, Nd, Sm

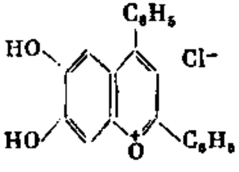
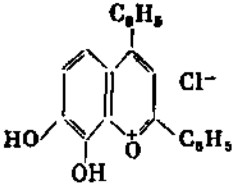
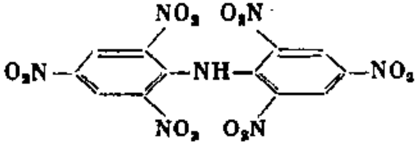
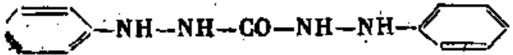
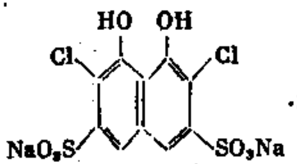
Butylrhodamine B	 $C_{28}H_{27}O_3N_2Cl$ Mol. wt. 460.97	Photometric determination of Ga
Bismuthol I (2,5-dimercapto-1,3,4-thiodiazolone)	 $C_2H_2N_2S_3$ Mol. wt. 150.24	Photometric determination of Bi, Te
Bismuthol II (5-mercapto-3-phenyl-2-thio-1,3,4-thiodiazolone, potassium salt)	 $C_8H_5N_2S_3K$ Mol. wt. 264.44	Photometric determination of Bi, Te
Gallion [8-amino-2-(3-chloro-2-hydroxy-5-nitrophenylazo)-1-naphthol-3,6-disulphonic acid]	 $C_{16}H_{11}O_{10}N_4S_2Cl$ Mol. wt. 518.89	Photometric determination of Ga

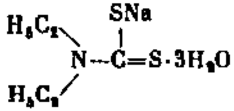
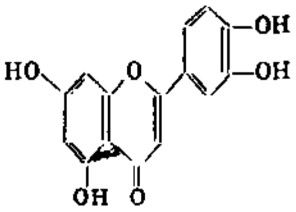
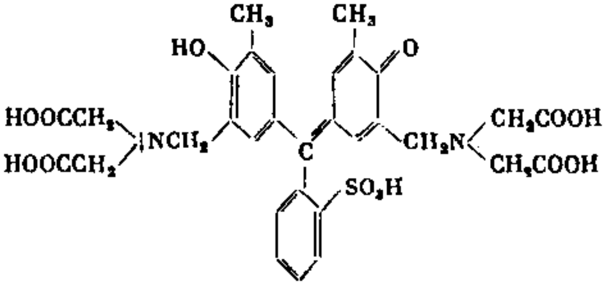
Ap. I (continued)

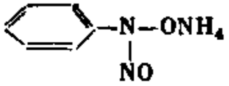
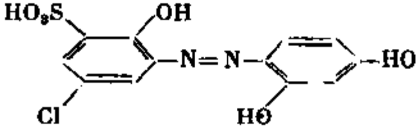
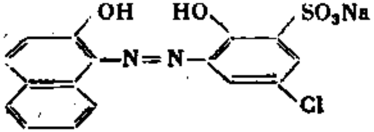
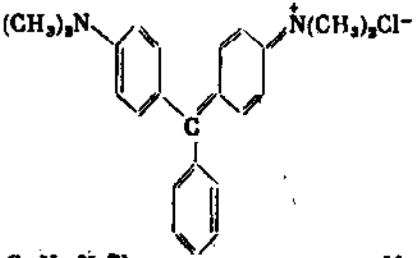
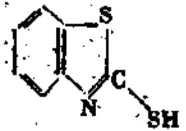
Name and its synonyms	Formula	Method of determination and elements determined
Gallocyanine (7-dimethylamino-4-hydroxy-3-oxo-3H-phenoxazine-1-carboxylic acid)	 $C_{15}H_{12}O_5N_2$ Mol. wt. 300.27	Photometric determination of Ca
3, 3'-Diaminobenzidine hydrochloride (3,3',4,4'-tetraaminodiphenyl tetrahydrochloride)	 $C_{12}H_{14}N_4 \cdot 4HCl$ Mol. wt. 360.12	Photometric determination of Se
Diantipyryl-3,4-dimethoxyphenylmethane	 $C_{31}H_{32}O_4N_4$ Mol. wt. 524.69	Photometric determination of V
Diantipyrylmethane	 $C_{23}H_{24}O_2N_4$ Mol. wt. 388.47	Photometric determination of Ti, I and Re

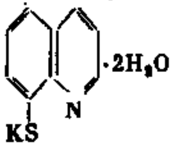
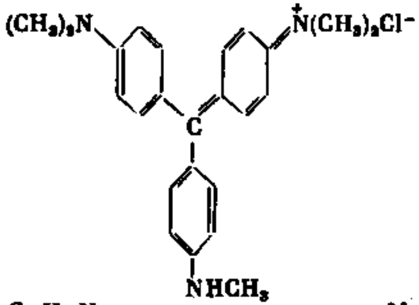
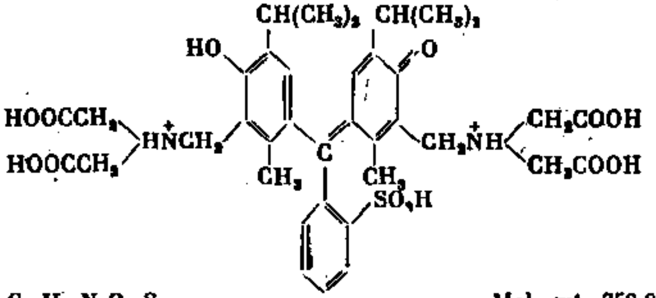
Diantipyrylpropylmethane	 $C_{26}H_{30}O_2N_4$ Mol. wt. 430.56	Photometric determination of Te, Ge, Tl
5,7-Dibromo-8-hydroxyquinoline	 $C_9H_5ONBr_2$ Mol. wt. 302.96	Photometric determination of V, Ga, Ti, Zr
2,2-Dimethylhexanedione-3, 5	 $H_3C-\underset{CH_3}{\overset{CH_3}{C}}-\underset{O}{\underset{\|}{C}}-CH_2-\underset{O}{\underset{\|}{C}}-CH_3$ $C_8H_{14}O_2$ Mol. wt. 142.19	Titrimetric determination of Be
Dimethylglyoxime	 $H_3C-\underset{HON}{\underset{\|}{C}}-\underset{NOH}{\underset{\|}{C}}-CH_3$ $C_4H_8O_2N_2$ Mol. wt. 116.12	Photometric determination of Re, V, Bi

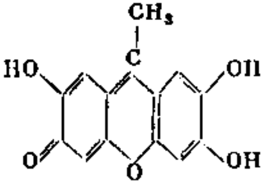
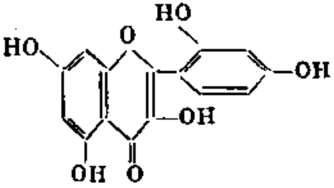
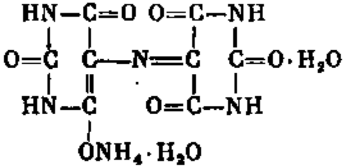
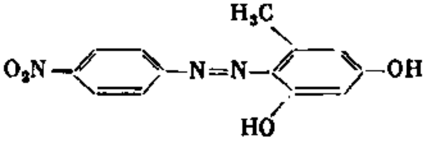
Name and its synonyms	Formula	Method of determination and elements determined
Dimethylfluorone (9-*p*-dimethylaminophenyl-2, 3, 7-trihydroxy-6-fluorone)	 $C_{21}H_{17}O_5N$ Mol. wt. 363.37	Photometric determination of Ta
3, 5-Dinitropyrocatechol	 $C_6H_4O_6N_2$ Mol. wt. 154.10	Photometric determination of W, Ge
o-Dihydroxychromenols (I. 6, 7-dihydroxy-2,4-dimethylbenzopyrilium chloride; II.7, 8-dihydroxy-2, 4-dimethylbenzopyrilium chloride;	 I  II $C_{11}H_{11}O_3Cl$ Mol. wt. 226.66	Photometric determination of Ge, Zr, Ti, Th, Mo, W, V, Ta, Nb, Sn

III.6,7-dihydroxy-2,4-diphenylbenzopyrilium chloride; IV.7,8-dihydroxy-2,4-diphenylbenzopyrilium chloride)	 III  IV $C_{21}H_{15}O_3Cl$ Mol. wt. 350.80	
Dipicrylamine (2,2′,4,4′,6,6′-hexanitrodiphenylamine)	 $C_{12}H_5O_{12}N_7$ Mol. wt. 439.213	Gravimetric determination of Rb, Cs
2,2′-Dipyridyl (α,α′-dipyridyl)	 $C_{10}H_8N_2$ Mol. wt. 156.19	Photometric determination of V, Mo, Re
Diphenylcarbazide (1,5-Diphenylcarbohydrazide)	 $C_{12}H_{14}ON_4$ Mol. wt. 242.28	Photometric determination of V, Mo
2,7-Dichlorochromotropic acid (1,8-dihydroxy-2,7-dichloronaphthalene-3,6-disulphonic acid, dihydrate)	 $\cdot 2H_2O$ $C_{10}H_4O_8S_2Cl_2Na_2$ Mol. wt. 469.18	Photometric determination of Ti

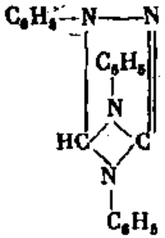
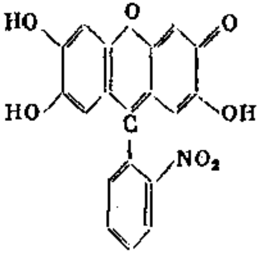
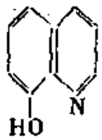
Name and its synonyms	Formula	Method of determination and elements determined
Sodium diethyldithiocarbamate	 $C_5H_{10}NS_2Na \cdot 3H_2O$ Mol. wt. 225.31	Photometric determination of Bi, In, Te
Quercetin (3,5,7,3′,4′-pentahydroxyflavone)	 $C_{15}H_{10}O_7$ Mol. wt. 302.24	Photometric determination of Th
Xylenol orange [3,3′-bis-(N,N-dicarboxylmethyl)-aminomethyl-*o*-cresolsulphophthalein]	 $C_{31}H_{32}O_{13}N_2S$ (as acid) Mol. wt. 672.670	Photometric determination of V, Bi, Nb, lanthanides, Sc, U, Zr, Hf, Ce

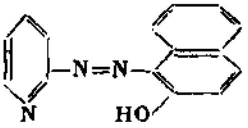
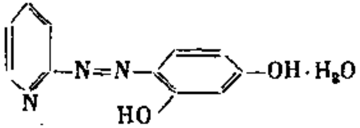
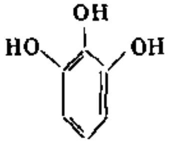
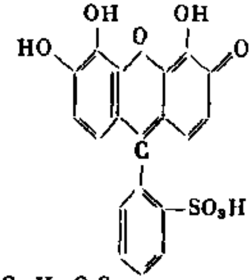
Cupferron (phenyl-α-nitrosohydroxylamine, ammonium salt)	 $C_6H_9O_2N_3$ Mol. wt. 155.16	Separation of V, Bi, Ga, Mo, Nb, Ta, Ti, Th, U, Zr
Lumogallion [2,2',4'-trihydroxy-5-chloro-(1-azo-1') benzene-3-sulphonic acid]	 $C_{12}H_9O_6N_2SCl$ Mol. wt. 344.73	Photometric determination of Ga
Magnezon [4-chloro-6-(2-hydroxy-1-naphthylazo)-1-phenol-2-sulphonic acid, Na salt]	 H_2O $C_{16}H_{11}O_6N_2SClNa$ Mol. wt. 418.79	Photometric determination of W
Malachite green B, base (Diamond green B)	 $C_{23}H_{25}N_2Cl$ Mol. wt. 364.92	Photometric determination of Tl, In
2-Mercaptobenzothiazol	 $C_7H_5NS_2$ Mol. wt. 167.25	Photometric determination of Bi, Tl

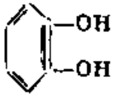
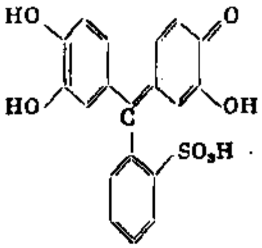
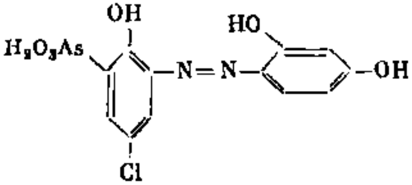
Name and its synonyms	Formula	Method of determination and elements determined
8-Mercaptoquinoline (thioxin), K salt	 $C_9H_6NSK \cdot 2H_2O$ Mol. wt. 235.34	Photometric determination of Re, Mo
Methyl violet (a mixture of several substances mainly of pentamethyl para-rosaniline with more or less methylated para-rosaniline)	 $C_{24}H_{28}N_3$ Mol. wt. 358.89	Photometric determination of Tl, Re, Ta
Methylthymol blue [3, 3′-bis-(N-di)carboxymethyl (aminomethyl) thymol sulphophthalein]	 $C_{37}H_{46}N_2O_{13}S$ Mol. wt. 758.89	Photometric determination of Hf. Complexometric indicator

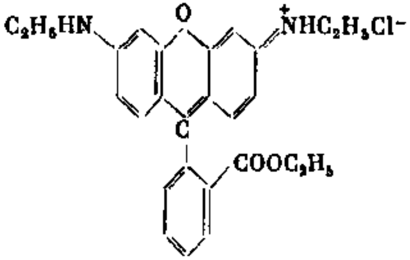
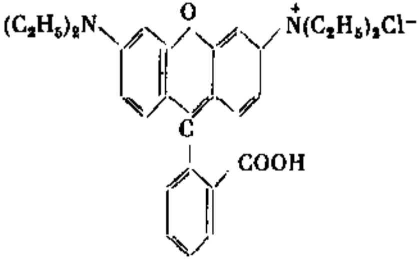
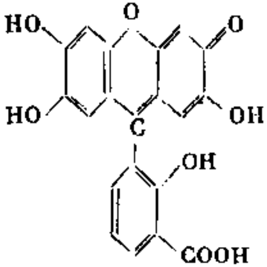
9-Methyl-2,3,7-trihydroxy-6-fluorone	 $C_{14}H_{10}O_5$ Mol. wt. 258.23	Photometric determination of Ge
Morin	 $C_{14}H_{10}O_7$ Mol. wt. 298.26	Fluorimetric determination of Be
Murexide (purpuric acid, NH_4 derivative)	 $C_8H_8O_6N_6 \cdot H_2O$ Mol. wt. 302.21	Complexometric indicator
p-Nitrobenzene azoorcinol	 $C_{13}H_{11}O_4N_3$ Mol. wt. 273.24	Photometric determination of Be

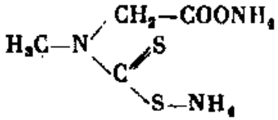
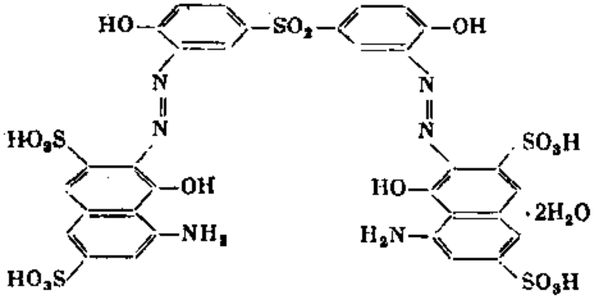
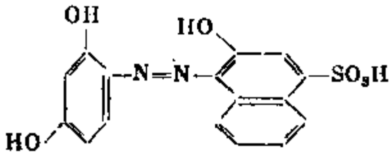
Ap. 1 (continued)

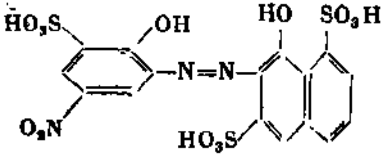
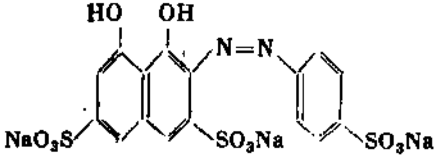
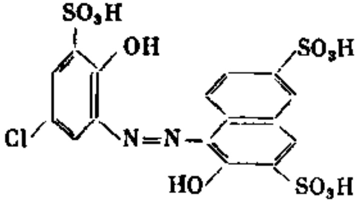
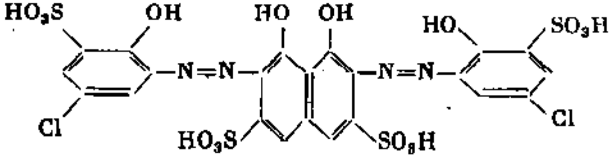
Name and its synonyms	Formula		Method of determination and elements determined
Nitron [1,4-diphenyl(3,5-endoanyl)dihydro-1,2,4-triazole]	 $C_{20}H_{16}N_4$	Mol. wt. 312.38	Gravimetric determination of W^{VI}, Re^{VII}
o-Nitrophenylfluorone	 $C_{19}H_9O_7N$	Mol. wt. 363.28	Photometric determination of Nb
8-Hydroxyquinoline	 C_9H_7ON	Mol. wt. 145.16	Gravimetric determination of Be, Ga, Ge, In, La, Li, Mo, Nb, Re, Ti, Ce, Zr, U

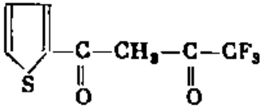
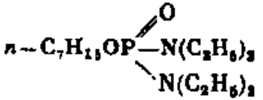
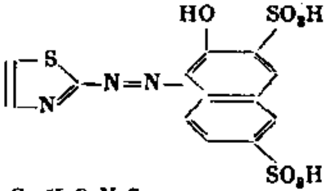
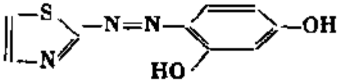
1-(2-Pyridylazo)-2-naphthol	 $C_{15}H_{11}ON_3$	Mol. wt. 249.27	Photometric determination of Ga, In, Tl, Sc, Th, Nb, Ta. Complexometric indicator for titration
4-(2-Pyridylazo)resorcinol, Na salt	 $C_{11}H_8O_2N_3Na \cdot H_2O$	Mol. wt. 255.21	Photometric determination of Sc, In, U, Nb Complexometric indicator
Pyrogallol (1,2,3-trihydroxybenzene)	 $C_6H_6O_3$	Mol. wt. 126.12	Photometric determination of Ta
Pyrogallol red (pyrogallol sulphophthalein)	 $C_{19}H_{12}O_8S$	Mol. wt. 418.38	Complexometric indicator

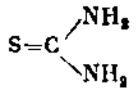
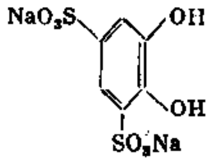
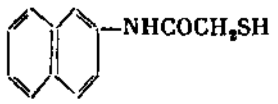
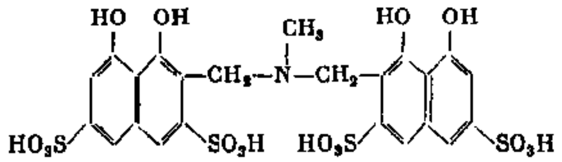
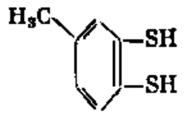
Name and its synonyms	Formula	Method of determination and elements determined
Pyrocatechol (1,2-dihydroxybenzene, *o*-dihydroxybenzene)	 $C_6H_6O_2$ Mol. wt. 110.11	Photometric determination of Ti, Mo, V
Pyrocatechol violet (pyrocatechol sulphophthalein)	 $C_{19}H_{14}O_7S$ Mol. wt. 386.38	Photometric determination of V Complexometric indicator
Resarson (2,2',4'-trihydroxy-3-arsono-5-chlorobenzene)	 $C_{12}H_{10}O_6N_2ClAs$ Mol. wt. 389.59	Fluorimetric determination of Ge

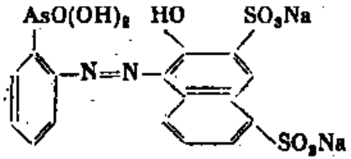
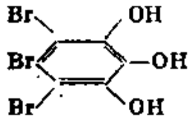
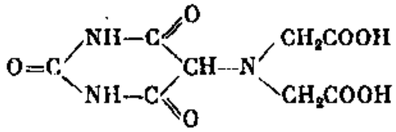
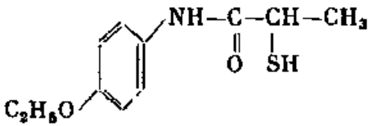
Rhodamine 6G (diethylamino-*o*-carboxyphenylxanthenyl chloride, ethyl ether)	 $C_{26}H_{27}O_3N_2Cl$ Mol. wt. 450.97	Fluorimetric determination of Re, In, Tl
Rhodamine S (tetraethyldiamino-*o*-carboxyphenyl xanthenyl chloride, rhodamine B)	 $C_{28}H_{31}O_3N_2Cl$ Mol. wt. 479.02	Fluorimetric determination of Tl and Ga
Salicyl fluorone	 $C_{20}H_{12}O_8$ Mol. wt. 380.30	Photometric determination of In, W

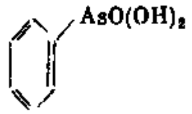
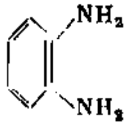
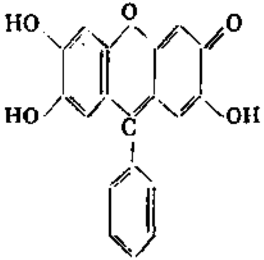
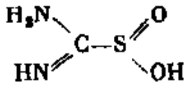
Name and its synonyms	Formula	Method of determination and elements determined
Sarcasine, dithiocarbamate	 $C_4H_{13}O_2N_3S_2$ Mol. wt. 178.29	Masking In, Bi, Cd
Sulphonazo [sulphon-bis-(4-hydroxyphenyl-(3-azo-2')-1'-hydroxy-8'-aminonaphtalene-3',6'-disulphonic acid]	 $C_{32}H_{24}O_{16}N_6S_6 \cdot 2H_2O$ Mol. wt. 976.93	Photometric determination of In, Sc and lanthanides
Sulphonaphtholazoresorcinol [4-sulpho-2-naphthol-(1-azo-1')-2',4'-dihydroxybenzene]	 $C_{16}H_{12}O_6N_2S$ Mol. wt. 360.35	Photometric determination of Ga

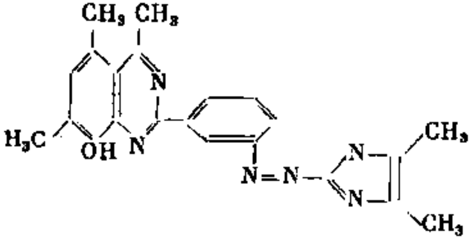
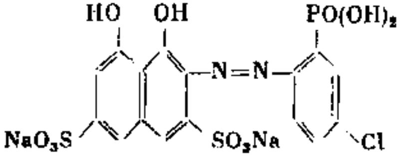
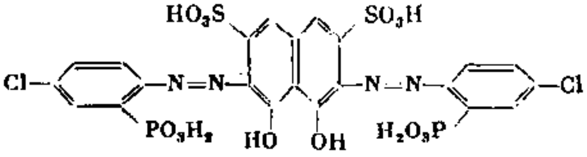
Sulphonitrazo [2-(2-hydroxy-5-nitro-3-sulphobenzeneazo)-1-naphthol-3,8-disulphonic acid]	 $C_{16}H_{11}O_{13}N_3S_3$ Mol. wt. 549.46	Photometric determination of V
4,5-Dihydroxy-3-(*p*-sulphophenylazo)-2,7-naphthalenedisulphonic acid, Na salt (SPANDS)	 $C_{16}H_9O_{11}N_2S_3Na_3$ Mol. wt. 570.42	Photometric determination of Th and Zr
2,4-Sulphochlorophenol R	 $C_{16}H_{11}O_{11}N_2S_3Cl$ Mol. wt. 538.9	Photometric determination of Sc
Sulphochlorophenol S	 $C_{22}H_{14}O_{16}N_4Cl_2S_2$ Mol. wt. 725.41	Photometric determination of Nb

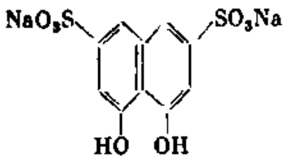
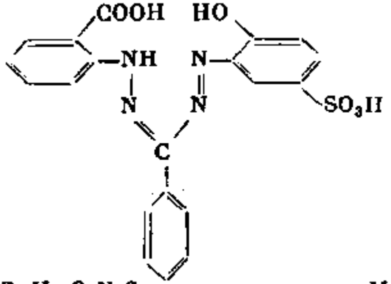
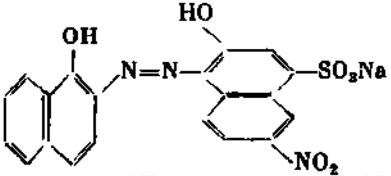
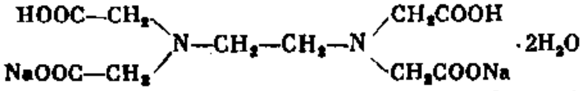
Name and its synonyms	Formula		Method of determination and elements determined
2-Tenoyl trifluoracetone	 $C_8H_5O_2SF_3$	Mol. wt. 222.24	Separation of Zr
Tetraethyldiamide heptylphosphate	 $n-C_7H_{15}OP(O)-[N(C_2H_5)_2]_2$ $C_{13}H_{29}O_2N_2P$	Mol. wt. 282.33	Separation of Zr
1-(2-Thiazolylazo)-2-naphthol-3,6-disulphonic acid	 $C_{13}H_9O_7N_3S_3$	Mol. wt. 394.41	Photometric determination of Ga
4-(2-Thiazolylazo) resorcinol	 $C_9H_7O_2N_3S$	Mol. wt. 221.22	Photometric determination of U
Thioglycolic acid	$HS—CH_2—COOH$ $C_2H_4O_2S$	Mol. wt. 92.12	Photometric determination of Re

Thiocarbamide	 CH_4N_2S Mol. wt. 76.12	Photometric determination of Bi, Re
Tiron (4,5-Dihydroxy-*m*-benzenedisulphonic acid, di-Na salt)	 $C_6H_4O_8S_2Na$ Mol. wt. 314.20	Photometric determination of Mo, Ti
Thionalide(β-aminonaphthalide of thioglycolic acid)	 $C_{12}H_{11}ONS$ Mol. wt. 217.29	Gravimetric determination of Bi, Ta
Trichromin [N-methyl-N,N-bis(methylenechromotropic acid)amine]	 $C_{23}H_{21}O_{16}NS_4$ Mol. wt. 695.66	Photometric determination of Ti
Toluene-3,4-dithiol	 $C_7H_8S_2$ Mol. wt. 156.27	Photometric determination of W, Mo

Name and its synonyms	Formula	Method of determination and elements determined
Thorin (thoron, APANS, *o*-(2-hydroxy-3,6-disulpho-1-naphthylazo) benzenearsonic acid, di-Na salt; thoronol)	 $C_{16}H_{11}O_{10}N_2S_2AsNa_2$ Mol. wt. 576.30	Photometric determination of Th, Hf, Zr
Tribrompyrogallol	 $C_6H_3O_3Br_3$ Mol. wt. 362.79	Photometric determination of V
Uramyl-N,N-diacetic acid (aminobarbituric-N, N-diacetic acid)	 $C_8H_9O_7N_3$ Mol. wt. 259.17	Amperometric determination of Be
p-Phenetidine-1-mercaptopropionic acid	 $C_{11}H_{15}O_2S$ Mol. wt. 225.31	Extraction-photometric determination of Mo

Phenylarsonic acid	 $C_6H_7O_3As$	Mol. wt. 201.96	Gravimetric determination of Zr
o-Phenylenediamine	 $C_6H_8N_2$	Mol. wt. 108.13	Photometric determination of Ge
Phenylfluorone (9-phenyl-2,3,7-trihydroxy-6-fluorone)	 $C_{19}H_{12}O_5$	Mol. wt. 320.30	Photometric determination of Ge
Formamidinesulphinic Acid (thiocarbamide dioxide)	 $CH_4O_2N_2S$	Mol. wt. 108.12	Complexometric determination of U

Name and its synonyms	Formula	Method of determination and elements determined
Quinazolinazo [2-(4″,5″-dimethylimidazole-2″-azo-2′-phenyl)-8-hydroxy-4,5,7-trimethylquinazoline]	 $C_{22}H_{21}ON_6$ Mol. wt. 385.43	Photometric determination of Li
Chlorophosphonazo I [2-(4-chloro-2-phosphinic acid phenylazo)-1,8-dihydroxynaphthalene-3,6-disulphonic acid, di-Na salt]	 $C_{16}H_{10}O_{11}N_2S_2ClPNa_2$ Mol. wt. 635.85	Photometric determination of U
Chlorophosphonazo III [2,7-bis-(4-chloro-2-phosphinic acid phenylazo)-1,8-dihydroxynaphthalene-3,6-disulphonic acid]	 $C_{22}H_{16}O_{14}N_4S_2Cl_2P_2$ Mol. wt. 757.38	Photometric determination of Sc, U

Chromotropic acid, di-Na salt (1,8-dihydroxynaphthalene-3,6-disulphonic acid, di-Na salt)	 $C_{10}H_6O_8S_2Na_2$ Mol. wt. 364.26	Photometric determination of Ti
Zincon [o-(2-α-(2-Hydroxy-5-sulphophenylazo) benzylidene hydrazino) benzoic acid]	 $C_{20}H_{16}O_6N_4S$ Mol. wt. 440.44	Complexometric indicator
Eriochrome black T [1'-(1-hydroxy-2-naphthylazo)-6'-nitro-2'-naphthol-4'-sulphoacid, Na salt]	 $C_{20}H_{12}O_7N_3SNa$ Mol. wt. 461.39	Complexometric indicator
EDTA (ethylenediamine tetraacetic acid, di-Na salt)	 $\begin{matrix}HOOC{-}CH_2 & & CH_2COOH\\ & N{-}CH_2{-}CH_2{-}N & \\ NaOOC{-}CH_2 & & CH_2COONa\end{matrix}\cdot 2H_2O$ $C_{10}H_{14}O_8N_2Na_2\cdot 2H_2O$ Mol. wt. 372.24	Complexometric determination of Sc, Ga, In, Tl, Y, Ge, lanthanides, Ti, Zr, Th, Bi, Mo

Appendix II. Masking Substances for Some Rare Elements

Element	Masking Substance
Be	Fluoride, tartrate, sulphosalicylic acid
Bi	Aminopolycarboxylic acids, chloride, dithizone, iodide, 1,2-dimercaptopropanol, citrate, $Na_5P_3O_{10}$, tartrate, triethanolamine
Ce	Aminopolycarboxylic acids, citrate, fluoride, tartrate, tiron
Ge	Oxalate, fluoride
Mo	Aminopolycarboxylic acids, ascorbic acid, citrate, oxalate, fluoride, H_2O_2, $Na_5R_3O_{10}$, hydroxylamine, thiocyanate, tartrate, tiron
Nb	Oxalate, fluoride, H_2O_2, OH^-, tartrate
Rare earths	EDTA
Sc	Tartrate
Se	Sulphide, sulphite
Sr	Aminopolycarboxylic acids, citrate, sulphate, tartrate
Ta	Citrate, fluoride, H_2O_2, OH^-, tartrate
Te	Iodide
Th	Aminopolycarboxylic acids, citrate, fluoride, sulphate, 4-sulphobenzenearsonic acid, tartrate, triethanolamine
Ti	Aminopolycarboxylic acids, ascorbic acid, citrate, fluoride, H_2O_2, OH^-, $Na_5P_3O_{10}$, sulphate, sulphosalicylic acid, tartrate, triethanolamine, tiron
Tl	Aminopolycarboxylic acids, citrate, chloride, cyanide, hydroxylamine, tartrate, triethanolamine
U	Citrate, carbonate, oxalate, fluoride, tartrate, H_2O_2
V	Ascorbic acid, EDTA, fluoride, H_2O_2, hydroxylamine, triethanolamine, tiron
W	Fluoride, H_2O_2, $Na_5P_3O_{10}$, hydroxylamine, thiocyanate, tartrate, tiron
Zr	Aminopolycarboxylic acids, tartrate, citrate, triethanolamine, oxalate, fluoride, H_2O_2, phosphate, pyrophosphate, sulphate

Appendix III. Elements Precipitated by General Analytical Reagents

1. The usual solvent for a precipitating agent is given in parentheses after its name.

2. The elements given in bold type may be quantitatively determined by the reagent in question.

3. The asterisk is used in the Table to mark the elements which are usually precipitated only in the presence of other members of the group.

4. Two asterisks mark the elements whose precipitation is prevented by tartrate.

Reagents	Conditions	Substance precipitated
Ammonia (aqueous solution)	After removal of H_2S, B, F group ions	**Al**, Au, **Be**, Co*, **Cr**, **Cu**, **Fe**, Ga, **In**, Ir, La, Nb, Ni, Os, P*, **Pb**, R.E., Sc, Si, **Sn**, **Ta**, **Th**, Tl, U, V*, W*, Y, Zn*, **Zr**
Ammonium polysulphide (aqueous solution)	After removal of H_2S and $(NH_4)_2S$ group, and B and F ions	Co, Mn, Ni, Si, Te, V*, W*, Zn
Anthranilic acid (ethyl alcohol solution)		**Ag**, **Cd**, Co, **Cu**, Fe, **Hg**, **Mn**, Ni, **Pb**, **Zn**
Benzidine (ethanol solution; 0.1 *M* HCl)		Cd, $[Fe(CN)_6]^{3-}$, IO_3^-, PO_4^{3-}, **SO_4^{2-}**, **W**
Cinchonine (6 *M* HCl solution)		Ir, Mo, **Pt**, **W**
Cupferron (aqueous solution)		**Al**, **Bi**, **Cu**, **Fe**, **Ga**, R.E., **Mo**, Nb, Pd, Sb, **Sn**, **Ta**, **Th**, **Ti**, Tl, **U**, V, W, **Zr**
Diammonium (or disodium) hydrogen phosphate (aqueous solution)	(a) acid medium (b) ammoniacal medium containing Cit or Tart	**Bi**, **Co**, **Hf**, **In**, Ti*, **Zn**, **Zr**, Au, **Ba**, **Be**, Ca, **Hg**, In, **Mg**, **Mn**, Pb, R.E., Sr, Th, U, Zr
Dimethylglyoxime (ethanol solution)	(a) Ammoniacal medium containing Tart	**Ni** (Co and Fe if present in very large amounts)
	(b) Dilute acid	**Au**, **Pd**, **Se**
Hexamethylenetetramine (aqueous solution)	See Ammonia	
Hydrazine (aqueous solution)		**Ag**, **Au**, Cu, **Hg**, Ir, Os, Pd, **Pt**, **Rh**, Ru, **Se**, **Te**
Hydrogen sulphide	(a) 0.2-0.5 *M* H^+	**Ag**, **As**, Au, **Bi**, Cd, **Cu**, Ge, **Hg**, In, Ir, **Mo**, Os, Pd, Pb, **Pt**, Re, **Rh**, Ru, **Sb**, **Se**, Sn, **Te**, **Tl**, V**, W*, Zn
	(b) Ammoniacal solution (after removal of H_2S group ions)	Co, Fe, Ga, In, Mn, Ni, Tl, U**, V**, Zn
p-Hydroxyphenylarsonic acid (aqueous solution)	Dilute acid soln.	Ce, **Sn**, **Th**, **Ti**, **Zr**

Reagents	Conditions	Substance precipitated
8-Quinolinol (ethanol solution)	(a) Acetate buffer solution	Ag, Al, Bi, Cd, Co, Cr, Cu, Fe, Ga, Hg, In, R.E., Mn, Mo, Nb, Ni, Pb, Pd, Sb, Ta, Th, Ti, U, V, W, Zn, Zr
	(b) Ammoniacal soln.	The same as in (a) except for Ag. Also Ba, Be, Ca, Mg, Sn, Sr
2-Mercaptobenzothiazole (acetic acid solution)	Ammoniacal soln. except for Cu, when dilute acid solution is used	Ag, Au, Bi, Cd, Cu, Hg, Ir, Pb, Pt, Rh, Tl
Neocupferron (aqueous solution)	See Cupferron	
Nitron (5 per cent acetic acid)	Dilute H_2SO_4 soln.	B, ClO_3^-, ClO_4^-, NO_3^-, ReO_4^-, W
1-Nitroso-2-naphthol (very dilute alkali)	Acid solutions	Ag, Au, B, Co, Cr, Cu, Fe, Mo, Pd, Ti, V, W, Zr
Oxalic acid (aqueous solution)	Dilute acid solution	Ag, Au, Cu, Hg, La, R.E., Ni, Pb, Sc, Th, U^{IV}, Zn
Phenylarsonic acid (aqueous solution)	Acid medium	Bi, Ce(IV), Fe, Hf, Nb, Sn, Ta, Th, Ti, U(IV), W, Zr
Phenylthiohydantoic acid (aqueous or alcoholic solution)	Acid soln.	Bi, Cd, Co, Cu, Fe, Hg, Ni, Pb, Sb
Picrolonic acid (aqueous solution)	Neutral soln.	Ca, Mg, Pb, Th
Pyridine and thiocyanate	Dilute acid solution	Ag, Cd, Cu, Mn, Ni
Quinaldic acid (acid solution)	Dilute acid solution	Ag, Cd, Co, Cu, Fe, Hg, Mo, Ni, Pb, Pd, Pt(II), U, W, Zn
Salicylaldoxime (ethanol solution)	Dilute acid solution	Ag, Bi, Cd, Co, Cu, Fe, Hg, Mg, Mn, Ni, Pb, Pd, V, Zn
Silver nitrate (aqueous solution)	Dilute HNO_3 solutions	As(V), Br^-, CN^-, OCN^-, SCN^-, Cl^-, I^-, IO_3^-, Mo(VI), N_3^-, S^{2-}, V(V)
Tannic acid (aqueous solution)	Ammoniacal soln. contg. Tart and electrolyte	Al, Be, Cr, Ga, Ge, Nb, Sb, Sn, Ta, Th, Ti, U, V, W, Zr
Tartaric acid (aqueous solution)		Ca, K, Nb, Sc, Sr, Ta
Tetraphenylarsonium chloride (aqueous solution)		Re, Tl
Thioglycolic-β-aminonaphthalide (ethanol solution)		Ag, As, Au, Bi, Cu, Hg, Os, Pb, Pd, Rh, Ru, Sb, Sn, Tl

Appendix IV. Solubility Products of Some Sparingly Soluble Compounds of Rare Elements at 18-25°C

Substance	pK_s	K_s	Substance	pK_s	K_s
Ag_2MoO_4	11.55	2.8×10^{-12}	KUO_2AsO_4	22.60	2.5×10^{-23}
$AgSeCN$	15.40	4.0×10^{-16}	$La_2(C_2O_4)_3\ 9H_2O$	26.60	2.5×10^{-27}
Ag_2SeO_3	15.01	9.7×10^{-16}	$La(IO_3)_3$	11.21	6.2×10^{-12}
Ag_2SeO_4	7.25	5.6×10^{-8}	$La(OH)_3$	18.7	2×10^{-19}
$AgVO_3$	6.3	5×10^{-7}	La_2S_3	12.70	2.0×10^{-13}
Ag_2HVO_4	13.7	2×10^{-14}	$LiUO_2AsO_4$	18.82	1.5×10^{-19}
Ag_2WO_4	11.26	5.5×10^{-12}	$Lu(OH)_3$	23.72	1.9×10^{-24}
$Be(NbO_3)_2$	15.92	1.2×10^{-16}	$Mg(NbO_3)_2$	16.64	2.3×10^{-17}
$Be(OH)_2$	21.2	7×10^{-22}	$MgSeO_3$	4.89	1.3×10^{-5}
$BiAsO_4$	9.36	4.4×10^{-10}	$MnSeO_3$	6.9	1×10^{-7}
BiI_3	18.09	8.1×10^{-19}	$NH_4UO_2AsO_4$	23.77	1.7×10^{-24}
$BiOOH$	9.4	4×10^{-10}	$NaUO_2AsO_4$	21.87	1.3×10^{-22}
$BiPO_4$	22.89	1.3×10^{-23}	$Nd(OH)_3$	21.49	3.2×10^{-22}
Bi_2S_3	97	1×10^{-97}	$NiSeO_3$	5	1×10^{-5}
$Ca(NbO_3)_2$	17.06	8.8×10^{-18}	$Pb(NbO_3)_2$	16.62	2.4×10^{-17}
$CaSeO_3$	5.53	3.0×10^{-6}	$PbSeO_3$	11.5	3×10^{-12}
$CaWO_4$	8.06	8.7×10^{-9}	$PbSeO_4$	6.84	1.4×10^{-7}
$CdSeO_3$	8.89	1.3×10^{-9}	$Pr(OH)_3$	21.17	6.8×10^{-22}
$Ce_2(C_2O_4)_3\cdot9H_2O$	28.5	3×10^{-29}	$Pu(OH)_3$	19.7	2×10^{-20}
$Ce_2(C_4H_4O_6)_3\cdot9H_2O$	19.01	9.7×10^{-20}	$RaSO_4$	10.37	4.3×10^{-11}
$Ce(IO_3)_3$	9.50	3.2×10^{-10}	$RbClO_4$	2.60	2.5×10^{-3}
$Ce(OH)_3$	19.8	2×10^{-20}	$Sc(OH)_3$	30.1	8×10^{-31}
Ce_2S_3	10.22	6.0×10^{-11}	$Sm(OH)_3$	22.08	8.3×10^{-23}
$Ce_2(SeO_3)_3$	24.43	3.7×10^{-25}	$Sr_3(AsO_4)_2$	18.09	8.1×10^{-19}
$CoSeO_3$	6.8	2×10^{-7}	$SrCO_3$	9.96	1.1×10^{-10}
$CsClO_4$	2.40	4.0×10^{-3}	$SrC_2O_4\cdot H_2O$	6.80	1.6×10^{-7}
$CuSeO_3$	7.68	2.1×10^{-8}	$SrCrO_4$	4.44	3.6×10^{-5}
$Er(OH)_3$	23.39	4.1×10^{-24}	SrF_2	8.61	2.5×10^{-9}
$Eu(OH)_3$	23.05	8.9×10^{-24}	$Sr(IO_3)_2$	6.48	3.3×10^{-7}
$Fe_2(SeO_3)_3$	30.7	2×10^{-31}	$Sr(NbO_3)_2$	17.38	4.2×10^{-18}
$Ga_4[Fe(CN)_6]_3$	33.82	1.5×10^{-34}	$SrSO_4$	6.49	3.2×10^{-7}
$Ga(OH)_3$	35.15	7.1×10^{-36}	$SrSeO_3$	5.74	1.8×10^{-6}
$Gd(HCO_3)_3$	1.7	2×10^{-2}	$Th(OH)_4$	44.4	4×10^{-45}
$Gd(OH)_3$	22.74	1.8×10^{-23}	$Th(HPO_4)_2$	20	1×10^{-20}
$Hf(OH)_4$	25.4	4×10^{-26}	$Ti(OH)_3$	40	1×10^{-40}
$HgSe$	59	1×10^{-59}	$TiO(OH)_2$	29	1×10^{-29}
Hg_2SeO_3	14.2	6×10^{-15}	$TlBr$	5.47	3.4×10^{-6}
$HgSeO_3$	13.82	1.5×10^{-14}	$TlBrO_3$	4.07	8.5×10^{-5}
Hg_2WO_4	16.96	1.1×10^{-17}	$Tl_2C_2O_4$	3.7	2×10^{-4}
$In_4[Fe(CN)_6]_3$	43.72	1.9×10^{-44}	$TlCl$	3.76	1.7×10^{-4}
$In(OH)_3$	33.2	6×10^{-34}	Tl_2CrO_4	12.01	9.8×10^{-13}

Substance	pK_s	K_s	Substance	pK_s	K_s
TlI	7.19	6.5×10^{-8}	$UO_2C_2O_4\cdot3H_2O$	3.7	2×10^{-4}
$TlIO_3$	5.51	3.1×10^{-6}	$(UO_2)_2[Fe(CN)_6]$	13.15	7.1×10^{-14}
TlN_3	3.66	2.2×10^{-4}	$UO_2(OH)_2$	21.95	1.1×10^{-22}
Tl_2S	20.3	5×10^{-21}	UO_2HPO_4	10.67	2.1×10^{-11}
TlSCN	3.77	1.7×10^{-4}	$VO(OH)_2$	22.13	7.4×10^{-23}
UO_2HAsO_4	10.50	3.0×10^{-11}	$(VO)_3(PO_4)_2$	24.1	8×10^{-25}
UO_2KAsO_4	22.60	2.5×10^{-23}	$Y(OH)_3$	22.1	8×10^{-23}
UO_2LiAsO_4	18.82	1.5×10^{-19}	$Yb(OH)_3$	23.6	3×10^{-24}
$UO_2NH_4AsO_4$	23.77	1.7×10^{-24}	$ZnSeO_3$	6.59	2.6×10^{-7}
UO_2NaAsO_4	21.87	1.3×10^{-22}	$Zr(OH)_4$	52	1×10^{-52}

Appendix V. Separation of Rare Elements by Extraction

The following abbreviations are used in this Table:

BPHA—benzoylphenylhydroxylamine, Na-salt; DDTC—diethyldithiocarbamate, Na-salt; SSA—sulphosalicylic acid; TBP—tributyl phosphate; TOPO—tri-*n*-octyl phosphine oxide, $(C_8H_{17})_3PO$; TTA—tenoyltrifluoracetone; EDTA—ethylenediamine tetracetic acid, disodium salt.

Element extracted	Separated from	Aqueous phase	Extracting agent
Ac	Ra	pH 5.5	0.25 *M* TTA/C_6H_6
Be	Al	2-Methyl-8-quinolinol, pH 8	Chloroform
	Al, Cu, Fe	Butyric acid, EDTA, KCl, pH 9.3-9.5	Chloroform
	Al, Sr, Y	pH 6-7	0.02 *M* TTA/C_6H_6
	Al, Zn	pH 2	Acetylacetone
	Divalent cations, elements in bronze	Acetylacetone, EDTA	Carbon tetrachloride
	Many elements	7 *M* NH_4SCN, 0.5 *M* HCl	Ethyl ether
	Many elements	EDTA, pH 5-7	Acetylacetone/C_6H_6
		Sodium benzoate, pH 7	Ethyl acetate, butanol or pentanol
		EDTA, pH 5-6	Acetylacetone
		2-Methyl-8-hydroxyquinaldine, pH 8.1	Chloroform
Bk		pH about 2.5	0.2 *M* TTA/C_6H_6
Ce	Ferrous materials	KCN, pH 9.9-10.5	3 per cent 8-quinolinol/$CHCl_3$
	Fission products	9 *M* HNO_3	Methyl isobutyl ketone
		0.5 *M* H_2SO_4	0.5 *M* TTA/xylene
	Many metals	EDTA, pH > 4	Acetylacetone
		Cupferron, pH 2	Butyl acetate
		8-10 *M* HNO_3 + +3 *M* $NaNO_3$	TBP
		8 *M* HNO_3	Ethyl ether

Element extracted	Separated from	Aqueous phase	Extracting agent
		Na tart., pH 8.5	0.1% 5,7-dibromo-8-quinolinol/$CHCl_3$
Cm		pH 3.5	0.2 *M* TTA/C_6H_6
Cs		Iodide soln. in KI	Nitromethane/C_6H_6
		0.4 *M* HPF_6	Nitromethane
		0.001 *M* $NaB(C_6H_5)_4$, pH 6.6	Nitrobenzene
Er		pH $\geqslant$ 8.3	0.02 *M* 5,7-dibromo-8-quinolinol/$CHCl_3$
Ga	Al, In	pH 1.2	Acetylacetone
		pH 3.0	1% 8-Quinolinol/$CHCl_3$
	Al, In, Sb, Tl, W, and others	Rhodamine B, 6 *M* HCl	Benzene
	Fe	6.5 *M* HCl, $TiCl_3$	Diisopropyl ether
	Many elements	HBr	Ethyl ether
	Many elements	HCl	Ethyl ether, diisopropyl ether, or TBP
	Many elements	3-7 *M* NH_4SCN, 0.5 *M* HCl	Ethyl ether
	Silicate rock	8-Quinolinol Hydroxylamine hydrochloride, CH_3COONa, pH 3.9	Chloroform
		Na benzoate, pH 7	Ethyl acetate, butanol or pentanol
		HCl	Amyl acetate
		Erio OS	$CHCl_3$
		5,7-Dibromo-8-quinolinol, KH phthalate, hydroxylamine hydrochloride	$CHCl_3$
		7 *M* HCl	0.1 *M* TOPO/cyclohexane
Ge	As, Hg, Sb, others	9 *M* HCl	Benzene, CCl_4, others
		Cupferron in weak acid solution	Methyl isobutyl ketone
		$(NH_4)_2MoO_4$, H_2SO_4	Isoamyl alcohol
Hf	Zr	SCN^-	Ethyl ether or methyl isobutyl ketone
		2 *M* $HClO_4$	0.1 *M* TTA/C_6H_6
		1 *M* HCl	0.1 *M* TOPO/cyclohexane
In	Al	pH 3	1% 8-Quinolinol/$CHCl_3$
	Al, Be, Bi, Fe, Ga, Mo, W	1.5 *M* KI, 0.75 *M* H_2SO_4	Ethyl ether
	Al, Ga	pH–3	Acetylacetone/$CHCl_3$ (1:1)
	Al, Ga, Tl, Zn, many others	0.5-6 *M* HBr	Ethyl ether or diisopropyl ether

Element extracted	Separated from	Aqueous phase	Extracting agent
Mo	W	Toluene-3,4-dithiol, H_3PO_4, citric acid	Light petroleum
	W, other ferrous materials	Strong acid	Toluene-3,4-dithiol/amyl acetate
	Zr	KSCN, acid solution	Butyl acetate
	All elements except W	Acid solution	α-Benzoinoxime/$CHCl_3$
	Ferrous alloys	EDTA, pH 1.5	1% 8-Quinolinol/$CHCl_3$
		3 *M* H_2SO_4	Acetyl acetone/$CHCl_3$ (1:1)
	Many elements	1-7 *M* NH_4SCN, 0.5 *M* HCl	Ethyl ether
	Most metals	NaF or EDTA, 0.1-0.5 *M* HCl	Morin/*n*-butanol
		SO_4^{2-}, pH 0.85	0.1 *M* TOPO/kerosene + +2% capryl alcohol
	Silicate rock	α-Benzoinoxime, $\leqslant$ 1.8 *M* HCl	Chloroform
		6 *M* HCl	Ethyl Ether
		EDTA, HCl	Chloroform
		1 *M* HCl	0.1 *M* TOPO/cyclohexane
		K ethyl xanthate, pH 1.11-1.56	$CHCl_3$, C_6H_5Cl, or toluene
Nb	Al, Fe, Ga, Mn, Sn, Ti, U, Zr	10 *M* HF, 2.2 *M* NH_4F, 6 *M* H_2SO_4	Methyl isobutyl ketone
	Pa	6 *M* HF, 6 *M* H_2SO_4	Diisobutylcarbinol
	Ta	Concd. HCl	Methyl dioctylamine/xylene or tribenzylamine /($CHCl_3$ or CH_2Cl_2)
	Fission products	HF, H_2SO_4	Tributyl phosphate
	Fission products	Oxalic acid, 1 *M* H_2SO_4, 2.5 *M* $(NH_4)_2SO_4$	0.6 *M* dibutylphosphoric acid/*n*-butyl ether
	Many elements	20 *M* HF	Ethyl ether
		F^-, pH 1	BPHA/$CHCl_3$
		Cupferron (acid soln.)	$CHCl_3$
		9 *M* HF, 6 *M* H_2SO_4	Diisopropyl ketone
		1 *M* Ammoniacal solution	8-Quinolinol/$CHCl_3$
		KSCN, $SnCl_2$, HCl	Ethyl ether
Nd		pH $\geqslant$ 8.3	5,7-Dichloro-8-quinolinol/$CHCl_3$
Np	Am, Bk, Cf, Cm	1 *M* HCl	TTA/xylene
	Pu, U, fission products		
		6-9 *M* HNO_3	Diethyl ether, methyl isobutyl ketone or dibutyl Carbitol

Element extracted	Separated from	Aqueous phase	Extracting agent
		HNO$_3$ satd. with NH$_4$NO$_3$	Ethyl ether
Pa	Al, Ba, Cr, Mg, Mn, Th, Ti, V	0.6 *M* HF, 8 *M* HCl satd. with AlCl$_3$	Diisopropyl ketone
	Mn, Ti, U, Zr	Cupferron, 0.1-4 *M* HCl	CHCl$_3$, C$_6$H$_6$ or amyl acetate
	Nb, Th	6 *M* HCl	Diisobutylcarbinol
	Ti, Zn and many others	6 *M* HCl satd. with MgCl$_2$	β,β′-Dichloroethyl ether
Pa^{233}	Nb^{95}	Oxalic acid, 6 *M* HCl	Diisobutylcarbinol
Pa (IV)	Pa(V)	6 *M* HCl	Hexone or TBP/C$_6$H$_6$
	All elements except Nb and Zr	4 *M* HNO$_3$	0.4 *M* TTA/C$_6$H$_6$
Po	Bi, Pb	6 *M* HCl	20% TBP/dibutyl ether
	Pa	7 *M* HCl	Diisopropyl ketone
		H$_2$O$_2$, 8 *M* HNO$_3$	Ethyl ether, hexone or diisopropyl ketone, *n*- or iso-amyl alcohol
		pH 0.2-5	Dithizone/CHCl$_3$
		pH 1.5-2.0	25 *M* TTA/C$_6$H$_6$
Pu	Al	Al(NO$_3$)$_3$, 5 *M* HNO$_3$	TBP
	Nb, Ru, Th, Zr, R.E., alk. and alk. earth metals	4.8 *M* HCl	5% Triisooctylamine/xylene
	Fission products	HNO$_3$ or HNO$_3$ + + Ca(NO$_3$)$_2$	Methyl *isobutyl* ketona
		pH 4.5	Acetylacetone/CHCl$_3$
		pH 2.5-4.5	Cinnamic acid/amyl acetate
		DDTC Na-salt, pH 3	Amyl acetate
	Fission products	HNO$_3$ satd. with NH$_4$NO$_3$	Amyl acetate
		pH 4-8	8-Quinolinol/amyl acetate
		0.5 *M* HNO$_3$	TTA/C$_6$H$_6$
		1 *M* HNO$_3$, NaNO$_2$, NH$_2$OH	0.5 *M* TTA/xylene
Rb		Iodine solution in KI	Nitromethane-C$_6$H$_6$
		NaB(C$_6$H$_5$)$_4$	Nitrobenzene
Re	Mo	Benzildioxime, 6 *M* H$_2$SO$_4$	Benzyl alcohol
	Mo	4-Hydroxy-3-mercaptotoluene, 6 *M* HCl	CHCl$_3$/isobutanol
	Mo, W	(C$_6$H$_5$)$_4$AsCl, pH 9	CHCl$_3$

Element extracted	Separated from	Aqueous phase	Extracting agent
	Many elements	20 M HF	Ethyl ether
		DDTA, concd. HCl	Ethyl acetate
		2,4-Diphenylthiosemicarbazide, 6 M HCl	$CHCl_3$
		4 M NaOH	Pyridine
		SKCN, HCl, $SnCl_2$	Butanol
		Toluene-3,4-dithiol in acid medium	$CHCl_3$ or amyl acetate
Sc	Al, Be, Cr, R.E., Ti	H_2O_2. HCl	Tributyl phosphate
	Al, Ca, Mg, Na, R.E., V	6 M HCl	Tributyl phosphate
	R.E., Y	pH 1.5	0.5 M TTA/C_6H_6
	Many elements	1 M HNO_3, satd. with $LiNO_3$ at 35°C	Ethyl ether
		7 M NH_4SCN, 0.5 M HCl	Ethyl ether
	Ores	SCN^-	Ethyl ether
		Na benzoate, pH 7	Ethyl acetate, butyl or amyl alcohol
		8-quinolinol, pH 9.7-10.5	C_6H_6
		pH 8.0-8.5	8-Quinolinol/$CHCl_3$
		Quinalizarine, alk. soln.	Isoamyl alcohol
Se	Cu, Fe, Te	3,3′-Diaminobenzidine	Toluene
		EDTA, pH 6-7	
	Many metals	Na diethyldithiocarbamate, EDTA, pH 5-6	CCl_4
		pH 11.3	1 M 8-Quinolinol/$CHCl_3$
		pH $>$ 10	TTA/C_6H_6
Ta	Al, Fe, Ga, Mn, Sn, Ti, U, Zr	10 M HF, 2.2 M NH_4F, 6 M H_2SO_4	Methyl isobutyl ketone
	Cr, Ge, Nb, Sb, Ti	HF, HCl	Hexone
	Hf, Mn, Nb, Se, Si, Sn, Ti, Zr	0.4 M HF, 6 M HCl	Diisopropyl ketone
	Nb, Ti	20% Pyrocatechol, $(NH_4)_2C_2O_4$, pH 3	n-Butanol
	Nb, Zr	HF, H_2SO_4	Cyclohexanone
	Nb, Zr	HF, HNO_3, $(NH_4)_2SO_4$	Acetone/isobutanol
	All metals except Nb	0.4 M HF, 6 M H_2SO_4	Methyl isobutyl ketone
	All elements except elemental halogens, Nb, Se, Te	0.4 M HF, 6 M H_2SO_4	Diisopropyl ketone
	Many elements	20 M HF	Ethyl ether
		F^-, pH 1	BPHA/$CHCl_3$

Element extracted	Separated from	Aqueous phase	Extracting agent
		1 *N* HNO_3	0.6 *M* Dibutylphosphoric acid/*n*-dibutyl ketone
		Methyl violet, HF, pH 2.3	C_6H_6
Tc	Mo, U	$(C_6H_5)_4AsCl$, pH 10-11	$CHCl_3$
		4 *M* NaOH	Pyridine
Te	Bi, Cb, Cu	HCl, $SnCl_2$	Ethyl acetate
	Se, other metals	DDTC, NaCN, EDTA pH 8.5-8.8	CCl_4
	Sepn. of Te(IV) from Te(VI)	2-10 *M* HCl	Tributyl phosphate
	Many elements	0.6 *M* NaI, 1 *M* HCl	Ethyl ether/*n*-isoamyl alcohol
		3-6 *M* HCl	DDTC/TBP
		pH 1	Dithizone/CCl_4
Th	Al	$HNO_3 + LiNO_3$	Mesityl oxide
	Am, Cm, Np, Pu, Ra, U	HNO_3, pH 1.4-1.5	0.5 *M* TTA/xylene
	Ce, V, Y	$Al(NO_3)_3$	Mesityl oxide
	La, U(VI)	pH 2	0.1 *M* BPHA/$CHCl_3$
	R.E.	NH_4SCN	*n*-Amyl alcohol
	R.E., Sc, Y	6 *M* NH_4NO_3+ +0.3 *M* HNO_3	Ethyl ether/dibutoxytetraethylene glycol (1:2)
	R.E., Zr	Satd. $Th(NO_3)_4$	Methyl-*n*-hexyl ketone, *n*-hexanol, hexone or ethyl butyrate
	All elements except Po	pH 1	0.25 *M* TTA/C_6H_6
	Divalent metals	Cupferron, pH 0.3-0.8	C_6H_6/isoamyl alcohol
	Many metals	$Ca(NO_3)_2 + HNO_3$	TBP
	Ores	$Al(NO_3)_3 + HNO_3$	Mesityl oxide, or hexone/TBP
		pH > 5.8	Acetylacetone/C_6H_6
		Cupferron, 0.25 *M* H_2SO_4	Butyl acetate
		1 *M* HNO_3, satd. with Al, Ca, Fe, Li, Mg or Zn nitrate	Ethyl ether
		Phenylcarboxylic acids	$CHCl_3$ or methyl isobutyl ketone
		Quercetin, pH 6.5	Isoamyl alcohol
		pH 4	5,7-Dichloro-8-quinolinol/$CHCl_3$
		pH > 4.9	8-Quinolinol/$CHCl_3$
		pH 2.0	0.5 *M* TTA/CCl_4

Element extracted	Separated from	Aqueous phase	Extracting agent
Ti	Al	8-Quinolinol, H_2O_2, pH 2.2	$CHCl_3$
	Al, Cr, Ga, V	Cupferron, HCl (1:9)	$CHCl_3$
	Al, Fe	pH 5.3	2-Methyl-8-quinolinol/$CHCl_3$
	Co, Ni, Zn	pH 1.6	Acetylacetone-$CHCl_3$
	Cu	Salicylaldoxime, thiourea, pH 5.3	Isobutyl alcohol
	Nb	20% catechol, $C_2O_4^{2-}$, pH 3	*n*-Butanol
	Nb, Ta	Cupferron, $(NH_4)_2$ Tart, pH 5	Isoamyl alcohol
	Many metals	EDTA, pH 8-9	8-Quinolinol/$CHCl_3$
	Many elements	3 *M* NH_4SCN, 0.5 *M* HCl	Ethyl ether
		Cupferron, EDTA, pH 5.5	Hexone
		Morin, acid soln.	Amyl alcohol
		7 *M* HCl	0.1 *M* TOPO/cyclohexane
		Sulphosalicylic acid, $(n\text{-Bu})_3$-NHOAc, pH 2.4-4	$CHCl_3$
Tl	Ag, Au, Cu, Fe, Hg, Pd, Sb, W, Zn	NaCN, pH 9-12	Dithizone/cyclohexane
	Bi, Mo, W	Bis(dimethylaminophenyl)-antipyrylcarbinol	C_6H_6/CCl_4 (2:3)
	All elements except Bi	DDTC, NaCN+EDTA, pH 11	CCl_4
	Many elements	1-6 *M* HBr	Ethyl ether
	Many metals	SSA, methyl violet, HCl	C_6H_6
	Many elements	Rhodamine B, Br_2 water	C_6H_6
		6 *M* HCl	Ethyl ether
		0.5 *M* HCl	Ethyl ether
		pH 6.5-7.0	8-Quinolinol/$CHCl_3$
		pH 3.8	0.25 *M* TTA/C_6H_6
U	Bi, Th	EDTA, pH 7	8-Quinolinol/hexone
	Bi and ores	4.7 *M* HNO_3	TBP-ethyl ether
	Co, Cr, Cu, Fe, Mn, Mo, Ni, Pb, Th	$Al(NO_3)_3$, pH 0-3	Methyl isobutyl ketone
	Fe, V	1-Nitroso-2-naphthol	Isoamyl alcohol
	La	pH 3.5	0.1 *M* BPHA/$CHCl_3$
	Nd, Pr	Acetate ion, pH 5.5-6	DDTC of diethylammonium/$CHCl_3$
	Th	NO_3^-, pH 1.0	0.1 *M* TOPO/CCl_4 or kerosene
	Th, others	1-(2-Pyridylazo)2-naphthol, EDTA	*o*-Dichlorobenzene
	Th, monazite	7 *M* HCl	TBP-methyl isobutyl ketone

Element extracted	Separated from	Aqueous phase	Extracting agent
	All elements except Be	$Ca(NO_3)_2$, EDTA, pH 7	Dibenzoylmethane/ethyl acetate
	All elements except Mo and V	H_2SO_4, pH 0.65	0.1 *M* TOPO/kerosene contg. 2% capryl alc.
U	Fission products	$HNO_3 + Ca(NO_3)_2$	Methyl isobutyl ketone
	Many elements	DDTC, EDTA, pyridine	C_6H_6, $CHCl_3$, ethyl acetate, or isoamyl alcohol/C_6H_6
	Many elements	HNO_3 + salting out agts. [$Al(NO_3)_3$, NH_4NO_3, $NaNO_3$, etc.]	Ethyl ether, ethyl acetate, nitromethane, methyl isobutyl ketone, TBP-($CHCl_3$, C_6H_6, or *i*-octane), hexone, 2-methyl cyclohexanone, or dibutylcarbinol
	Many elements	Pr_4HNO_3, $Al(NO_3)_3$	Hexone
	Many elements	1 *M* HCl	0.1 *M* TOPO/cyclohexane
	Many elements	7 *M* HCl	5% Triisooctylamine/xylene
	Most metals	EDTA, pH 4.6	Acetylacetone
	Most metals	EDTA, pH 8.8	8-Quinolinol/$CHCl_3$
	Monovalent and some divalent cations	Perfluorobutyric acid	Ethyl ether
		2-Acetoacetylpyridine pH 7.0-7.7	Butyl acetate
		Ascorbic acid, NH_4SCN, EDTA	TBP-CCl_4
		Phenylcarboxylic acids	$CHCl_3$ or hexone
		Dilute H_2SO_4	Cupferron/ethyl ether
		DDTC, pH 6	$CHCl_3$
		Weakly acid soln.	5,7-Dichloro-8-quinolinol/$CHCl_3$
		pH 3	0.2 *M* TTA/C_6H_6
V	Mo, U	Salicylhydroxamic acid, pH 3.0-3.5	Ethyl acetate
	Ti	DDTC, pH 4.5-5.0	$CHCl_3$
	U	DDTC, Tart., pH 0.4-0.5	Amyl acetate
	Ferrous materials	pH 2.0	Acetylacetone-$CHCl_3$
	Many elements	Cupferron, 1:9 HCl or H_2SO_4	Ethyl acetate, ethyl ether, or $CHCl_3$
	Many metals	Ca-EDTA, pH 5.0	8-Quinolinol/$CHCl_3$
		Benzohydroxamic acid in acid solution	*n*-Hexanol

Element extracted	Separated from	Aqueous phase	Extracting agent
		BPHA in acid solution	C_6H_6
		8-Quinolinol, acetate ion, pH 3.5-4.5	$CHCl_3$ or isoamyl alcohol
		KSCN, $SnCl_2$	Ethyl acetate or hexone
		7 *M* HCl	0.1 *M* TOPO/cyclohexane
		Nitric acid, pH 1.5-2.0	0.6 *M* TOPO/kerosene
W	Al, Cr, Mn, Nb, Ni, S, Ta, Ti, V	Toluene-3,4-dithiol $(NH_2OH)_2 \cdot H_2SO_4$, dilute HCl	Amyl acetate
	Mo	HCl, $SnCl_2$	Toluene-3,4-dithiol/amyl acetate
	All elements except Mo	α-Benzoinoxime, acid solution	$CHCl_3$
	Many elements	H_3PO_4, 3 *M* H_2SO_4	*n*-Amyl alcohol
	Most metals	EDTA, pH 2.4	8-Quinolinol/$CHCl_3$
		Cupferron, HCl (1:9)	Ethyl acetate
		DDTC, pH 1-1.5	Ethyl acetate
		Dithiol, HCl	Butyl acetate
		0.15 *M* KSCN, 6 *M* HCl	Ethyl ether
		SCN^-, $SnCl_2$, HCl	Ethyl ether, diisopropyl ketone or $i\text{-}C_5H_{11}OH\text{-}CHCl_3$
Y	Al, Mg, R.E.	15.6 *M* HNO_3	TBP
	La group of rare earths	1 *M* HNO_3, H_2O_2	0.6 *M* Dibutylphosphoric acid/$(n\text{-}Bu)_2O$
	R.E.	pH > 6	TTA/C_6H_6
	Sr	0.1 *M* HNO_3	Dibutylphosphoric acid/$CHCl_3$
		pH 8.5	8-Quinolinol/$CHCl_3$
Zr	Al, Fe, R.E., Th, V,	6 *M* HCl	0.5 *M* TTA/xylene
	Ce, V, Y	$Al(NO_3)_3$	Mesityl oxide
	Hf	HNO_3	TBP/dibutyl ether
	Nb, fission products	$H_2C_2O_4$, H_2O_2, 1 *M* H_2SO_4, 2.5 *M* $(NH_4)_2SO_4$	0.06 *M* Dibutylphosphoric acid/$(n\text{-}Bu)_2O$
	Divalent metals	Cupferron, pH 0.3-1.0	$C_6H_6\text{-}i\text{-}C_5H_{11}OH$
	Many elements	1 *M* HCl	0.1 *M* TOPO/cyclohexane
	Many elements	7 *M* HNO_3	TOPO/cyclohexane
	Many elements	NH_4SCN, 7 *M* HCl	TOPO/cyclohexane
		> 5 *M* $HClO_4$	TBP/CCl_4
		HCl	TBP/C_6H_6
		HNO_3	TBP/kerosene
		Cupferron, H_2SO_4 (1:9)	Ethyl acetate
		$HOAc + OAc^-$	8-Quinolinol/$CHCl_3$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