

A HANDBOOK OF
**DECOMPOSITION
METHODS
IN ANALYTICAL
CHEMISTRY**

Rudolf Bock
translated by Iain L Marr

DECOMPOSITION METHODS IN ANALYTICAL CHEMISTRY

R

C.N.R.
I.C.M.M.

BIBLIOTECA

INVENTARIO

564/L
QD 75.3

1983

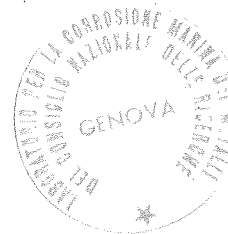
11958

A Handbook of Decomposition Methods
in Analytical Chemistry

567/L - 2450

A Handbook of Decomposition Methods in Analytical Chemistry

RUDOLF BOCK
formerly Professor of Analytical Chemistry
University of Mainz



CONSIGLIO NAZIONALE DELLE RICERCHE
INVENTARIO N. 567/L

2450

translated and revised by

Dr Iain L. Marr
Lecturer in Chemistry
University of Aberdeen

International Textbook Company

International Textbook Company Limited
A member of the Blackie Group
Bishopbriggs
Glasgow G64 2NZ

450 Edgware Road
London W2 1EG

© 1979 the Blackie Group
First published 1979

Based on
Aufschlußmethoden der anorganischen und organischen Chemie
Copyright © 1972 by Verlag Chemie GmbH, Weinheim/Bergstr.

*All rights reserved.
No part of this publication may be reproduced,
stored in a retrieval system, or transmitted,
in any form or by any means,
electronic, mechanical, recording or otherwise,
without prior permission of the Publishers*

*International Standard Book Number
Hardback 0 7002 0269 2*

Printed in Great Britain by
T. & A. Constable Ltd., Edinburgh

Preface

THE GERMAN EDITION OF THIS BOOK APPEARED IN 1972, AND MANY IMPORTANT improvements in the field of decomposition methods have been made since then. Much of the stimulation for this work has been provided by the basic research of T. T. Gorsuch since 1959. The text has therefore been expanded considerably and several sections completely rewritten. The tables have been enlarged and new ones added. It is hoped that the reader will be able to use the information provided in the tables directly, without having to resort to the original publications. However, if necessary, more detailed information can be found from the extensive list of references.

I should like to thank Dr Iain Marr for his able translation of a complex German text, and for valuable additions of his own. Mr K. Beyermann has translated many Russian publications for me, and Mr H. Kürner and Mr B. Bernas have compiled information from various sources and provided descriptions of apparatus. The drawings were made by Mr W. Kelp with the help of Mrs I. Datz and Mr J. Möhner. All these people have contributed to the book, and I should like to express my gratitude. Finally, I wish to thank the authors and editors of journals who have permitted the reproduction of figures.

Appendices 1–3 are new compilations, for which many colleagues have generously supplied information from their specialized fields. Their names are given at the appropriate places, as there are too many to be mentioned here.

RUDOLF BOCK
La Tour de Peilz

Contents

Chapter 1.	INTRODUCTION	1
1.1	Definitions; Literature	1
1.2	The Technique of Opening-out	1
1.2.1	Opening-out by heating in a gas	1
1.2.2	Dissolution and opening-out with liquids	1
1.2.3	Opening-out in melts	5
1.3	Container Materials	6
1.3.1	Glass	6
1.3.2	Porcelain	8
1.3.3	Fused quartz	8
1.3.4	Various oxides	9
1.3.5	Metals	9
1.3.6	Graphite	11
1.3.7	Plastics	11
1.4	Sources of Error Pertaining to the Dissolution and Opening-out Processes	12
1.4.1	Losses as spray or dust	13
1.4.2	Losses through volatilization	14
1.4.3	Losses due to adsorption	17
1.4.4	Losses due to reaction with the container	27
1.4.5	Blank values	28
1.4.6	Removal of foam	31
1.5	Speeding up the Dissolution and Opening-out Processes — Automation	31
1.5.1	Speeding up the dissolution and opening-out	31
1.5.2	Automation	32
Chapter 2.	DISSOLUTION WITHOUT CHEMICAL REACTION	35
2.1	Solvents for Inorganic Substances	35
2.2	Solvents for Organic Substances	35

Chapter 3.	DECOMPOSITION BASED ON SUPPLY OF ENERGY	37
3.1	Decomposition by Action of Heat: Thermal Decomposition	37
3.1.1	Decomposition of inorganic materials	37
3.1.2	Decomposition of organic materials	37
3.2	Decomposition by Electrical Action	49
3.2.1	Decomposition of organic compounds by spark discharge	49
3.2.2	Irradiation of solids with high-energy electrons	49
3.2.3	Interaction between electrons and solutions	50
3.2.4	Ionization and fragmentation by electron impact in gases at low pressure	50
3.3	Decomposition by Photolysis and Radiolysis	51
Chapter 4.	DISSOLUTION AND OPENING-OUT BY CHEMICAL REACTION BUT WITHOUT CHANGE IN OXIDATION STATE	53
4.1	Dissolution with the Aid of Complexing Agents or Ion-exchangers	53
4.1.1	Dissolution with the aid of complexing agents	53
4.1.2	Dissolution with the aid of ion-exchangers	54
4.2	Dissolution with Hydrofluoric, Fluoboric and Fluosilicic Acids	55
4.2.1	General comments	55
4.2.2	Hydrofluoric acid decompositions without subsequent removal of fluoride ion	57
4.2.3	Hydrofluoric acid decompositions with subsequent removal of the fluoride ion	60
4.2.4	Dissolution with fluoroboric acid HBF_4 or fluorosilicic acid H_2SiF_6	62
4.3	Fluoride-fusion Decompositions	63
4.3.1	General comments	63
4.3.2	Decompositions with ammonium fluoride NH_4F and ammonium hydrogen difluoride NH_4HF_2	63
4.3.3	Decompositions with potassium hydrogen difluoride KHF_2 and potassium fluoride KF	64
4.3.4	Sodium fluorosilicate Na_2SiF_6 and fluoroborate NaBF_4	66
4.3.5	Sodium and lithium 'metafluoroborates'	66
4.4	Dissolution with HCl or HBr or HI	68
4.4.1	Dissolution with hydrochloric acid	68
4.4.2	Dissolution with hydrobromic acid	71
4.4.3	Dissolution with hydriodic acid	72
4.5	Volatilization by heating with Ammonium Chloride, Bromide or Iodide	72

4.6	Non-oxidizing Dissolution with Sulphuric Acid	74
4.7	Fusions with Hydrogen Sulphates or Pyrosulphates	77
4.8	Dissolution with Phosphoric Acid; Opening-out with Phosphate Melts	82
4.8.1	General considerations	82
4.8.2	Dissolution with phosphoric acid	82
4.8.3	Decompositions in phosphate melts	84
4.9	Dissolution by Double Decomposition with Various Acids	84
4.10	Fusions with Boric Acid, Boron Trioxide or Borates	86
4.10.1	General considerations	86
4.10.2	Fusions with boric acid H_3BO_3 or boron trioxide B_2O_3	86
4.10.3	Fusions with sodium tetraborate	88
4.10.4	Fusions with lithium tetraborate $\text{Li}_2\text{B}_4\text{O}_7$ and lithium metaborate LiBO_2	92
4.10.5	Fusions with various other borates	94
4.11	Decomposition with Enzymes	94
4.12	Pyrohydrolysis	97
4.13	Dissolution and Opening-out with Solutions of Alkali Metal Hydroxides or Carbonates, with Ammonia, Hydrazine and Organic Bases	101
4.14	Fusions with Alkali Metal Hydroxides	102
4.15	Fusions with Alkali Metal Carbonates	108
4.16	The Lawrence Smith Decomposition Method	116
4.17	Miscellaneous Fusion Decomposition Methods	121
Chapter 5.	OXIDIZING PROCEDURES	122
5.1	Oxidation with Oxygen or Ozone	122
5.1.1	Background	122
5.1.2	Dry-ashing in an open vessel	123
5.1.3	Combustion in a closed vessel under low pressure	153
5.1.4	Combustion in a closed vessel at normal or only slightly raised pressures	154
5.1.5	Combustion in a closed vessel at high pressure	168
5.1.6	Combustion in a stream of oxygen or air	172
5.1.7	Combustion in flames	183
5.1.8	Oxidation with excited oxygen or with ozone	189
5.2	Oxidation with Hydrogen Ions	192
5.3	Oxidation with Nitric Acid or Oxides or Nitrogen	195
5.3.1	General comments	195
5.3.2	Oxidation of inorganic materials	196
5.3.3	Oxidation of organic materials	201

5.4	Fusion Decompositions with Nitrate Melts	205
5.4.1	General comments	205
5.4.2	Application in inorganic analysis	207
5.4.3	Applications in organic analysis	210
5.5	Fusion Decompositions with Nitrite Melts	211
5.6	Oxidation with Sulphuric Acid	211
5.6.1	General comments	211
5.6.2	Oxidation of metals, alloys, and inorganic compounds	211
5.6.3	Oxidation of organic materials	212
5.7	Oxidation with Nitric plus Sulphuric Acids	215
5.7.1	Oxidation of inorganic materials	215
5.7.2	Oxidation of organic materials	215
5.8	Oxidation with Chloric Acid, Chlorates, Chlorite and Hypochlorite	218
5.8.1	General comments	218
5.8.2	Oxidation of inorganic substances with chlorates	219
5.8.3	Oxidation or organic substances with chloric acid or chlorates	219
5.8.4	Oxidation with chlorite or hypochlorite	221
5.9	Oxidation with Perchloric Acid	221
5.9.1	General comments	221
5.9.2	Danger of explosions	222
5.9.3	Oxidation of inorganic substances	224
5.9.4	Oxidation of organic substances	226
5.10	Oxidation with Iodic Acid, Iodates, and Periodates	232
5.10.1	Oxidation with iodic acid and iodates	232
5.10.2	Oxidation with periodate	233
5.11	Oxidation with Potassium Permanganate	234
5.12	Oxidation with Chromium (VI) and with $K_2CrO_7 + KIO_3 + H_2SO_4 + H_3PO_4$	236
5.12.1	Oxidation with CrO_3 or chromates	236
5.12.2	Oxidation with $K_2Cr_2O_7 + KIO_3 + H_2SO_4 + H_3PO_4$	239
5.13	Oxidation with Hydrogen Peroxide	240
5.13.1	General comments	240
5.13.2	Oxidation of inorganic substances	242
5.13.3	Oxidation of organic substances	243
5.14	Oxidation with Sodium Peroxide	247
5.14.1	General comments	247
5.14.2	Oxidation of inorganic substances	249
5.14.3	Oxidation of organic substances	252

5.15	Oxidations with Peroxydisulphate and other Peroxy-compounds	254
5.15.1	Oxidations with peroxydisulphate	254
5.15.2	Oxidation with various peroxides	257
5.15.3	Oxidation with peroxy-acids	257
5.16	Decomposition Reactions with Sulphur	257
5.16.1	General comments	257
5.16.2	The Freiburger decomposition	258
5.16.3	Decompositions with sulphur, H_2S , and S_2Cl_2	259
5.17	Decompositions with Halogens or their Compounds	261
5.17.1	Fluorination	261
5.17.2	Chlorination	262
5.17.3	Bromination	270
5.17.4	Oxidation with iodine	274
5.18	Electrolytic Oxidation	274
5.18.1	General	274
5.18.2	Electrolytic oxidation of metallic samples	275
5.18.3	Electrolytic isolation of inclusions and structural components	277
5.18.4	Electrolytic oxidation of organic compounds	282
5.19	Miscellaneous Oxidizing Decompositions	283
5.19.1	Miscellaneous oxidants for inorganic substances	283
5.19.2	Miscellaneous solid oxidants for organic substances	283

Chapter 6.	DECOMPOSITION PROCEDURES INVOLVING REDUCTION	287
6.1	Reduction with Hydrogen or Ammonia	287
6.1.1	Applications in inorganic analysis	287
6.1.2	Applications in organic analysis	288
6.2	Reduction with Carbon	292
6.2.1	Applications in inorganic analysis	292
6.2.2	Applications in organic analysis	293
6.3	Decompositions Involving Reduction with Metals	294
6.3.1	General comments	294
6.3.2	Fusion of the sample with a metal	295
6.3.3	Decomposition of samples with a metal plus a base	298
6.3.4	Decomposition of samples with a metal dissolved in liquid ammonia or in an amine	299
6.3.5	Decomposition of samples with an organometallic compound	300

6.4	Miscellaneous Reducing Decompositions	300
6.4.1	Reduction of sulphate to H_2S	300
6.4.2	Reduction with hydrazine	301
6.4.3	Decomposition with $\text{NaOH} + \text{NaCN}$	301
6.4.4	Decomposition with calcium hydride	301
6.4.5	Reduction with tin(II) chloride	302
6.4.6	Reduction with sodium formate	302
6.4.7	Reduction with lithium aluminium hydride	302
6.4.8	Reduction with $\text{NH}_4\text{H}_2\text{PO}_2$	302
6.4.9	Reduction with sodium borohydride	302
6.4.10	Reduction with chromium (II)	302
	References	303
	Appendix 1.	
	A systematic approach to dissolution of a sample of unknown composition: from Noyes and Bray	396
	Appendix 2.	
	Historical survey	397
	Appendix 3.	
	A compilation of decomposition methods which have proved themselves satisfactory in routine use	398
	Index	431