

Analytical Chemistry
of the
Condensed Phosphates

GREENFIELD
AND
CLIFT

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**ANALYTICAL CHEMISTRY
OF THE
CONDENSED PHOSPHATES**



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**ANALYTICAL CHEMISTRY
OF THE
CONDENSED PHOSPHATES**

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CONTENTS

Foreword	viii
Preface	x
Acknowledgements	xi
1. General Properties of the Condensed Phosphates	1
Classification	1
Structure	2
Physical Properties	5
Chemical Properties	13
Stability in Solution: Degradation Products on Hydrolysis	18
Reaction with Metal Salts in Solution—Sequestering Action	32
References	34
2. Gravimetric Methods	37
Heavy-metal Salts	37
Cobalt Complexes	44
Chromium Complexes	49
Other Metal Complexes	49
Organic Bases as Precipitants	49
References	50
3. Titrimetric Methods	51
Titration of the Free Acids	51
Chain-length Determinations	52
Titration of Hydron produced in Precipitation Reactions	61
EDTA Complexes	63
Thermometric Titrations	64
References	65
4. Electrometric Methods (other than Potentiometry)	66
Amperometric Titrations	66
Conductimetric Titrations	68
Polarographic Methods	69
References	72

5. Chromatographic Methods	73
Paper Chromatography	73
Thin-layer Chromatography "Adsorption"	88
Thin-layer Chromatography (ion exchange)	96
Electrophoresis	97
Ion Exchange Column Chromatography	98
Gel Filtration	103
References	106
6. Automated Methods	108
Automated Ion Exchange	108
Automated Temperature Rise	117
Appendix I: Automated Ion Exchange Computer Program Description	120
Reference	122
7. Physical Methods other than Chromatography	123
Ultracentrifugation	123
Dialysis	124
Intrinsic Viscosity in Salt Solutions	124
Light Scattering in Salt Solutions	125
Flow Birefringence	126
Anisotropy in Electrical Conductivity	127
Solubility Fractionation	127
Refractive Index	128
Temperature Rise Test	129
Infrared	132
X-ray Diffraction	142
Nuclear Magnetic Resonance	146
References	153
8. Methods for the Determination of Esters of the Condensed Phosphates	156
Determination of Tetra-alkylpyrophosphates	162
Determination of Tetra-arylpyrophosphates	170
Determination of Nucleotides containing Condensed Phosphates	171
References	173
9. Modus Operandi	174
Preparation of Samples for Analysis	174
Qualitative Tests	177
Preferred Methods of Quantitative Analysis	180
References	183
10. Preparation of Pure Samples	184
Orthophosphoric Acid	184
Orthophosphate	185
Pyrophosphate	186

CONTENTS

vii

Triphosphate	186
Sodium Trimetaphosphate	188
Sodium Tetraphosphate	188
Sodium Tetrametaphosphate	190
Sodium Hexametaphosphate and Sodium Pentametaphosphate	191
Sodium Octanoctaphosphate	192
Madrell's Salt-insoluble Sodium "Metaphosphate"	193
Graham's Salt—Sodium Polyphosphate Glass	194
Potassium Kurrol Salt—Insoluble Potassium "Metaphosphate"	195
References	195
Index	197

FOREWORD

THE fact that phosphoric acid loses water when heated, and gives a product of different chemical properties was reported by Berzelius early in the nineteenth century. In 1845 Fleitmann and Henneberg proposed the concept of a series of polyphosphoric acids in which each member would be formed by addition of a molecule of phosphoric acid to the previous member, with loss of a molecule of water.

While the lowest member of this series, Graham's pyrophosphoric acid, $H_4P_2O_7$, was readily isolated both in the free state and as its salts, higher members were not so readily identified, and many chemists felt that they were mixtures of pyrophosphoric acid and the so-called "metaphosphoric acid" HPO_3 . The final confirmation of their structure thus awaited the development, in the twentieth century, of the analytical techniques described in this monograph, and without these techniques the situation would still be in doubt.

Even if the chemical interest of the polyphosphates had not given this impetus to the development of analytical methods for their detection and determination, the increasing realization of their importance, both in nature and in commerce, would have done so. The part played by adenosine triphosphate in biological processes of all kinds is well known, and the intermediary of polyphosphates in the synthesis of proteins or the nucleic acids, scarcely less.

Whilst in nature the polyphosphates appear to play their role by means of the rapid equilibration which they can undergo, in industry they are mainly used as sequestering agents towards metal ions and as mild acids which, because of their low toxicity, are acceptable in food uses. The first commercial use of the polyphosphates was that of disodium pyrophosphate in World War I as a replacement for tartaric acid in baking powder. This application, which has persisted to the present day, was

followed by the discovery of the water-softening powers of the soluble polyphosphate glasses and of tetrasodium pyrophosphate. The real explosion in the use of polyphosphates came with the discovery of the "building" properties of pentasodium triphosphate ("tripolyphosphate") used with alkylaryl sulphonate acid in synthetic detergents. From a small start in Germany in the 1930s these have grown in importance such that sodium triphosphate, a laboratory curiosity in 1930, is now made all over the world on a scale of many hundreds of thousands of tons.

For the analysis of these and other materials, practically every type of analytical method has been pressed into service in the laboratories of the authors. Classical chemical (gravimetric and titrimetric) methods were first used, but the major developments have come in the fields of chromatography (paper, thin layer, and ion exchange) as well as from the use of more sophisticated techniques such as electrophoresis, X-ray diffraction, and infrared and nuclear magnetic resonance spectrometry. These and other methods are discussed in this monograph, as well as automatic analytical techniques, to which the authors have made their own considerable contribution.

The value of a book such as this, however, lies not only in collation of the literature and the assembly of recommended analytical procedures — important though this is: even more vital is the stimulus it gives to further work. Thus, to give only two examples of unsolved problems, we still have no unequivocal way of determining the instantaneous composition of a liquid polyphosphoric acid or of a polyphosphate melt. Again, in spite of the pioneering work of van Wazer, we have no clear picture of the structure of the "ultraprophosphates" which contain an excess of phosphorus pentoxide over that required for the "infinite" polyphosphate molecule (NaPO_3): for their solution these and similar questions await the development of a new generation of analytical techniques.

A. F. CHILDS

PREFACE

THIS book is designed as a practical text. The practical information is supported by sufficient theoretical knowledge for a full understanding of the processes involved. Although the book is primarily intended for non-phosphorus chemists, it does contain original work and hence may be of value to the expert.

The authors are indebted to a number of their colleagues for the assistance which they have given in providing specialist information for inclusion in certain chapters. Particularly they are indebted to the following: D. A. Brown, R. Harper, R. T. Jones, H. McD. McGeachin, G. Miller, D. R. Peck, R. A. Smith, T. P. Sutton, R. H. Tomlinson and F. R. Tromans.

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S. GREENFIELD
M. CLIFF

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