Analytical Chemistry of the Condensed Phosphates

GREENFIELD
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Publisher: Robert Maxwell M.C.

ANALYTICAL CHEMISTRY
OF THE
CONDENSED PHOSPHATES

INTERNATIONAL SERIES IN **ANALYTICAL CHEMISTRY**
VOLUME 57
GENERAL EDITORS: R. BELCHER AND H. FREISER

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S. GREENFIELD, A.I.M., F.R.I.C.

AND

M. CLIFT, A.I.R.C.

Albright & Wilson Limited,
Industrial Chemicals Division,
Oldbury Warley, West Midlands

PERGAMON PRESS

OXFORD · NEW YORK · TORONTO
SYDNEY · PARIS · BRAUNSCHWEIG

U. K.	Pergamon Press Ltd., Headington Hill Hall, Oxford OX3 0BW, England
U. S. A.	Pergamon Press Inc., Maxwell House, Fairview Park, Elmsford, New York 10523, U.S.A.
CANADA	Pergamon of Canada, Ltd., 207 Queen's Quay West, Toronto 1, Canada
AUSTRALIA	Pergamon Press (Aust.) Pty. Ltd., 19a Boundary Street, Rushcutters Bay, N.S.W. 2011, Australia
FRANCE	Pergamon Press SARL, 24 rue des Ecoles, 75240 Paris, Cedex 05, France
WEST GERMANY	Pergamon Press GmbH, D.3300 Braunschweig, Burgplatz 1, West Germany

First edition 1975

Library of Congress Cataloging in Publication Data

Greenfield, Stanley.
Analytical chemistry of the condensed phosphates.

(International series of monographs in analytical chemistry; v. 57)
Includes bibliographies.
1. Phosphates—Analysis. I. Clift, Martin, joint author. II. Title.
QD181. P1G74 1975 546'.712'6 74–32261
ISBN 0-08-018174-0

Printed in Hungary

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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 sulphonic 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 "ultraphosphates" 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.

They would also like to thank Messrs. E. T. Masters, J. Allen and G. Lewis for preparing some of the diagrams, Miss D. Priddey for typing the manuscript, and all those who made a smaller, but nevertheless significant, contribution.

S. GREENFIELD
M. CLIFT

ACKNOWLEDGEMENTS

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SAVILLE, B., *Analyst* **82,** 269 (1957),
(The Society of Analytical Chemistry, Analytical Division, Chemical Society).