

MTP International Review of Science

**Physical Chemistry
Series One**

**Consultant Editor
A. D. Buckingham**

Volume 13

Analytical Chemistry—Part 2

Edited by T. S. West

MTP International Review of Science

Analytical Chemistry—Part 2

THE BUTTERWORTH GROUP

ENGLAND

Butterworth & Co (Publishers) Ltd
London: 88 Kingsway, WC2B 6AB

AUSTRALIA

Butterworths Pty Ltd
Sydney: 586 Pacific Highway 2067
Melbourne: 343 Little Collins Street, 3000
Brisbane: 240 Queen Street, 4000

NEW ZEALAND

Butterworths of New Zealand Ltd
Wellington: 26-28 Waring Taylor Street, 1

SOUTH AFRICA

Butterworth & Co (South Africa) (Pty) Ltd
Durban: 152-154 Gale Street

ISBN 0 408 70274 5

UNIVERSITY PARK PRESS

U.S.A. and CANADA

University Park Press Inc
Chamber of Commerce Building
Baltimore, Maryland, 21202

Library of Congress Cataloging in Publication Data

West, Thomas Summers.

Analytical chemistry.

(Physical chemistry, series one, v. 12-13)

(MTP international review of science)

1. Chemistry, Analytic. I. Title.

QD453.2.P58 Vol. 12-13 [QD75.2] 541'.3'08s [543]

ISBN 0-8391-1026-X (pt. 1) 72-8644

First Published 1973 and © 1973

MTP MEDICAL AND TECHNICAL PUBLISHING CO. LTD.

Seacourt Tower

West Way

Oxford, OX2 0JW

and

BUTTERWORTH & CO. (PUBLISHERS) LTD.

Filmset by Photoprint Plates Ltd., Rayleigh, Essex

Printed in England by Redwood Press Ltd., Trowbridge, Wilts
and bound by R. J. Acford Ltd., Chichester, Sussex

MTP International Review of Science

Publisher's Note

The MTP International Review of Science is an important new venture in scientific publishing, which we present in association with MTP Medical and Technical Publishing Co. Ltd. and University Park Press, Baltimore. The basic concept of the Review is to provide regular authoritative reviews of entire disciplines. We are starting with chemistry because the problems of literature survey are probably more acute in this subject than in any other. As a matter of policy, the authorship of the MTP Review of Chemistry is international and distinguished; the subject coverage is extensive, systematic and critical; and most important of all, new issues of the Review will be published every two years.

In the MTP Review of Chemistry (Series One), Inorganic, Physical and Organic Chemistry are comprehensively reviewed in 33 text volumes and 3 index volumes, details of which are shown opposite. In general, the reviews cover the period 1967 to 1971. In 1974, it is planned to issue the MTP Review of Chemistry (Series Two), consisting of a similar set of volumes covering the period 1971 to 1973. Series Three is planned for 1976, and so on.

The MTP Review of Chemistry has been conceived within a carefully organised editorial framework. The over-all plan was drawn up, and the volume editors were appointed, by three consultant editors. In turn, each volume editor planned the coverage of his field and appointed authors to write on subjects which were within the area of their own research experience. No geographical restriction was imposed. Hence, the 300 or so contributions to the MTP Review of Chemistry come from many countries of the world and provide an authoritative account of progress in chemistry.

To facilitate rapid production, individual volumes do not have an index. Instead, each chapter has been prefaced with a detailed list of contents, and an index to the 13 volumes of the MTP Review of Physical Chemistry (Series One) will appear, as a separate volume, after publication of the final volume. Similar arrangements will apply to the MTP Review of Organic Chemistry (Series One) and to subsequent series.

Butterworth & Co. (Publishers) Ltd

Physical Chemistry Series One

Consultant Editor
A. D. Buckingham
*Department of Chemistry
University of Cambridge*

Volume titles and Editors

- 1 THEORETICAL CHEMISTRY**
Professor W. Byers Brown, *University of Manchester*
- 2 MOLECULAR STRUCTURE AND PROPERTIES**
Professor G. Allen, *University of Manchester*
- 3 SPECTROSCOPY**
Dr. D. A. Ramsay, F.R.S.C.,
National Research Council of Canada
- 4 MAGNETIC RESONANCE**
Professor C. A. McDowell, F.R.S.C.,
University of British Columbia
- 5 MASS SPECTROMETRY**
Professor A. Maccoll, *University College, University of London*
- 6 ELECTROCHEMISTRY**
Professor J. O'M Bockris, *University of Pennsylvania*
- 7 SURFACE CHEMISTRY AND COLLOIDS**
Professor M. Kerker, *Clarkson College of Technology, New York*
- 8 MACROMOLECULAR SCIENCE**
Professor C. E. H. Bawn, F.R.S.,
University of Liverpool
- 9 CHEMICAL KINETICS**
Professor J. C. Polanyi, F.R.S.,
University of Toronto
- 10 THERMOCHEMISTRY AND THERMODYNAMICS**
Dr. H. A. Skinner, *University of Manchester*
- 11 CHEMICAL CRYSTALLOGRAPHY**
Professor J. Monteath Robertson, F.R.S.,
University of Glasgow
- 12 ANALYTICAL CHEMISTRY — PART 1**
Professor T. S. West, *Imperial College, University of London*
- 13 ANALYTICAL CHEMISTRY — PART 2**
Professor T. S. West, *Imperial College, University of London*

INDEX VOLUME

Inorganic Chemistry
Series One
Consultant Editor
H. J. Emeléus, F.R.S.
Department of Chemistry
University of Cambridge

Volume titles and Editors

- 1 MAIN GROUP ELEMENTS—
HYDROGEN AND GROUPS I–IV**
Professor M. F. Lappert, *University of Sussex*
- 2 MAIN GROUP ELEMENTS—
GROUPS V AND VI**
Professor C. C. Addison, F.R.S. and
Dr. D. B. Sowerby, *University of Nottingham*
- 3 MAIN GROUP ELEMENTS—
GROUP VII AND NOBLE GASES**
Professor Viktor Gutmann, *Technical University of Vienna*
- 4 ORGANOMETALLIC DERIVATIVES
OF THE MAIN GROUP
ELEMENTS**
Dr. B. J. Aylett, *Westfield College,
University of London*
- 5 TRANSITION METALS—PART 1**
Professor D. W. A. Sharp, *University of Glasgow*
- 6 TRANSITION METALS—PART 2**
Dr. M. J. Mays, *University of Cambridge*
- 7 LANTHANIDES AND ACTINIDES**
Professor K. W. Bagnall, *University of Manchester*
- 8 RADIOCHEMISTRY**
Dr. A. G. Maddock, *University of Cambridge*
- 9 REACTION MECHANISMS IN
INORGANIC CHEMISTRY**
Professor M. L. Tobe, *University College,
University of London*
- 10 SOLID STATE CHEMISTRY**
Dr. L. E. J. Roberts, *Atomic Energy
Research Establishment, Harwell*

INDEX VOLUME

Organic Chemistry
Series One
Consultant Editor
D. H. Hey, F.R.S.
Department of Chemistry
King's College, University of London

Volume titles and Editors

- 1 STRUCTURE DETERMINATION
IN ORGANIC CHEMISTRY**
Professor W. D. Ollis, F.R.S.,
University of Sheffield
- 2 ALIPHATIC COMPOUNDS**
Professor N. B. Chapman,
Hull University
- 3 AROMATIC COMPOUNDS**
Professor H. Zollinger, *Swiss Federal
Institute of Technology, Zurich*
- 4 HETEROCYCLIC COMPOUNDS**
Dr. K. Schofield, *University of Exeter*
- 5 ALICYCLIC COMPOUNDS**
Professor W. Parker, *University of
Stirling*
- 6 AMINO ACIDS, PEPTIDES AND
RELATED COMPOUNDS**
Professor D. H. Hey, F.R.S. and
Dr. D. I. John,
King's College, University of London
- 7 CARBOHYDRATES**
Professor G. O. Aspinall, *Trent University,
Ontario*
- 8 STEROIDS**
Dr. W. F. Johns, *G. D. Searle & Co.,
Chicago*
- 9 ALKALOIDS**
Professor K. F. Wiesner, F.R.S.,
University of New Brunswick
- 10 FREE RADICAL REACTIONS**
Professor W. A. Waters, F.R.S.,
University of Oxford

INDEX VOLUME

Physical Chemistry

Series One

Consultant Editor

A. D. Buckingham

MTP International Review of Science

Volume 13

Analytical Chemistry—Part 2

Edited by T. S. West

Imperial College, University of London

Butterworths · London
University Park Press · Baltimore

Consultant Editor's Note

The MTP International Review of Science is designed to provide a comprehensive, critical and continuing survey of progress in research. The difficult problem of keeping up with advances on a reasonably broad front makes the idea of the Review especially appealing, and I was grateful to be given the opportunity of helping to plan it.

This particular 13-volume section is concerned with Physical Chemistry, Chemical Crystallography and Analytical Chemistry. The subdivision of Physical Chemistry adopted is not completely conventional, but it has been designed to reflect current research trends and it is hoped that it will appeal to the reader. Each volume has been edited by a distinguished chemist and has been written by a team of authoritative scientists. Each author has assessed and interpreted research progress in a specialised topic in terms of his own experience. I believe that their efforts have produced very useful and timely accounts of progress in these branches of chemistry, and that the volumes will make a valuable contribution towards the solution of our problem of keeping abreast of progress in research.

It is my pleasure to thank all those who have collaborated in making this venture possible – the volume editors, the chapter authors and the publishers.

Cambridge

A. D. Buckingham

Preface

During recent years analytical chemistry has probably undergone more radical change than most other branches of chemistry. The increased sophistication of instrumentation has of course been an outstanding feature, but more fundamental changes are also evident in the type of information which is now being provided. On the elemental side, techniques such as atomic absorption and atomic fluorescence spectroscopy have provided completely unequivocal direct elemental analysis for virtually every metal in the periodic table. Selective-ion electrodes take over for anions and non-metals where flame spectroscopy leaves off and immobilised enzyme and antibiotic membranes offer particularly exciting new vistas of development. Not only do analytical techniques now offer increased sensitivity and selectivity of analysis, they also provide information on structure, conformation, location on surfaces and many other aspects. In common with the other volumes of this series, these on analytical chemistry present reviews of selected areas by authors who are readily recognised authorities on their topics. Each contributor has been asked, wherever practical, to make a selective assessment of the present status of the subject rather than write a comprehensive review. Some areas are 'new', e.g. electron spectroscopy for chemical analysis and selective-ion electrodes, whilst others are well tried and fully recognised, but have been subject to recent developments, e.g. organic microanalysis and liquid-liquid distribution (solvent extraction). In all cases, the authors have been given complete freedom to review their topics individually within a minimum framework of size and scope. The authors have been drawn deliberately from a wide range of countries in an attempt to present as geographically balanced a view of analytical chemistry as possible. The editor has made a conscious effort to avoid duplication, but obviously some repetition is inevitable in topics which are inter-related. It is probable, however, that such duplication as exists may be beneficial rather than otherwise since two ways of expressing a common theme, particularly from different individual and national backgrounds, are more likely to be complementary and enlightening than purely repetitive or confusing. Many topics that could or should have been reviewed are obviously missing; the selection of topics is, arbitrarily, that of the editor.

London

T. S. West

Contents

Organic microanalysis	1
A. D. Campbell, <i>University of Otago, New Zealand</i>	
Organic reagents	43
Keihei Ueno, <i>Kyushu University, Fukuoka, Japan</i>	
Thermometric analysis	71
A. E. Beezer, <i>Chelsea College, University of London</i>	
x-Ray fluorescence analysis	95
R. Jenkins, <i>Philips Electronic Instruments, Mount Vernon, New York</i>	
Mass spectrometric analysis	127
A. J. B. Robertson, <i>King's College, University of London</i>	
Flame emission spectrometry	153
E. Pungor and L. Pólos, <i>Technical University, Budapest</i>	
Thermal methods of analysis	177
W. W. Wendlandt, <i>University of Houston</i>	
Electrochemical methods of analysis	201
A. Hulanicki, <i>Institute of Fundamental Problems of Chemistry, University of Warsaw</i>	
Light scattering methods	235
M. G. Huglin, <i>University of Salford</i>	

1

Organic Microanalysis

A. D. CAMPBELL

University of Otago, New Zealand

1.1	INTRODUCTION	3
1.2	STANDARD COMPOUNDS AND SAMPLE PREPARATION	4
1.2.1	<i>Standard compounds</i>	4
1.2.2	<i>Purification of samples</i>	4
1.2.3	<i>Hygroscopic and air-sensitive samples</i>	5
1.3	CARBON AND HYDROGEN	5
1.3.1	<i>Sample additives</i>	5
1.3.1.1	<i>Metals not requiring additives</i>	6
1.3.1.2	<i>Elements requiring additives</i>	6
1.3.1.3	<i>Explosive samples</i>	6
1.3.2	<i>Combustion aids</i>	7
1.3.3	<i>Removal of halogens and sulphur</i>	7
1.3.3.1	<i>Fluorine</i>	7
1.3.3.2	<i>Chlorine, bromine, iodine and sulphur</i>	8
1.3.4	<i>Adsorbents for oxides of nitrogen</i>	8
1.3.5	<i>Measurement of water and carbon dioxide</i>	9
1.3.5.1	<i>Gravimetric procedures</i>	9
1.3.5.2	<i>Non-gravimetric procedures</i>	9
1.3.6	<i>Automatic carbon and hydrogen and carbon, hydrogen and nitrogen analysers</i>	10
1.3.6.1	<i>Measurement by thermal conductivity detectors</i>	10
	(a) <i>Separation by adsorption</i>	10
	(b) <i>Separation by gas chromatography</i>	11
1.3.6.2	<i>Conductimetric and coulometric measurement</i>	12
1.3.6.3	<i>Colorimetric end-point measurement</i>	12
1.3.7	<i>Simultaneous determination of other elements</i>	12
1.4	NITROGEN	13
1.4.1	<i>Nitrogen measured as nitrogen gas</i>	13
1.4.1.1	<i>Carbon dioxide generator</i>	13
1.4.1.2	<i>Combustion packings and procedures</i>	14
1.4.1.3	<i>Decomposition of nitrogen oxides</i>	14

1.4.1.4	<i>Automatic analysers</i>	15
1.4.1.5	<i>Submicro-methods</i>	15
1.4.2	<i>Nitrogen measured as ammonia</i>	15
1.4.2.1	<i>Sample digestion</i>	16
	(a) <i>Catalysts</i>	16
	(b) <i>Temperature</i>	16
	(c) <i>Oxidising agents</i>	16
	(d) <i>Reducing agents</i>	16
1.4.2.2	<i>Distillation apparatus</i>	17
1.4.2.3	<i>Absorption and titration of ammonia</i>	17
1.4.2.4	<i>Non-distillation methods</i>	17
1.4.2.5	<i>Submicro-methods</i>	18
1.4.2.6	<i>Nitrogen by hydrogenation</i>	18
1.5	OXYGEN	18
1.5.1	<i>General methods</i>	18
1.5.1.1	<i>Gravimetric finish</i>	18
1.5.1.2	<i>Titrimetric finish</i>	18
1.5.2	<i>Catalytic carbons</i>	19
1.5.3	<i>Static combustion</i>	19
1.5.4	<i>Sulphur interference</i>	19
1.5.5	<i>Oxidation of carbon monoxide</i>	19
1.5.6	<i>Instrumental detection</i>	20
1.5.7	<i>Sample additives</i>	20
1.6	SULPHUR	21
1.6.1	<i>Combustion methods</i>	21
1.6.1.1	<i>Combustion in a stream of oxygen</i>	21
1.6.1.2	<i>Wet combustion methods</i>	21
1.6.1.3	<i>Fusion with sodium peroxide</i>	21
1.6.1.4	<i>Combustion in an oxygen-filled flask</i>	22
1.6.2	<i>Adsorption of sulphur oxides on silver</i>	22
1.6.3	<i>Titrimetric methods for the determination of sulphate</i>	22
1.6.4	<i>Reductive methods</i>	23
1.7	HALOGENS	23
1.7.1	<i>Chlorine, bromine and iodine</i>	23
1.7.1.1	<i>Chlorine (oxygen-filled flask)</i>	24
1.7.1.2	<i>Bromine and iodine (oxygen-filled flask)</i>	24
1.7.1.3	<i>Adsorption on silver</i>	25
1.7.1.4	<i>Distillation methods</i>	25
1.7.2	<i>Fluorine</i>	25
1.7.2.1	<i>Sample decomposition</i>	25
1.7.2.2	<i>Determination of fluoride</i>	26
1.8	PHOSPHORUS	26
1.8.1	<i>Sample decomposition</i>	26
1.8.1.1	<i>Wet oxidation</i>	26
1.8.1.2	<i>Fusion methods</i>	27
1.8.1.3	<i>Combustion in an oxygen-filled flask</i>	27

	ORGANIC MICROANALYSIS	3
1.8.2	<i>Measurement of phosphate</i>	27
1.8.2.1	<i>Gravimetric methods</i>	27
1.8.2.2	<i>Titrimetric methods</i>	28
1.8.2.3	<i>Colorimetric methods</i>	28
1.9	OTHER ELEMENTS	28
1.9.1	<i>Arsenic</i>	28
1.9.2	<i>Boron</i>	29
1.9.3	<i>Selenium</i>	29
1.9.4	<i>Silicon</i>	29
1.9.5	<i>Determination of other elements</i>	30
1.10	FUNCTIONAL GROUP ANALYSIS	31
1.10.1	<i>Alkoxy determination</i>	31
1.10.1.1	<i>Ether cleavage</i>	31
1.10.1.2	<i>Carrier gas</i>	32
1.10.1.3	<i>Scrubbing reagents</i>	32
1.10.1.4	<i>Estimation of alkyl halide</i>	32
1.10.1.5	<i>Range of application</i>	32
1.10.1.6	<i>Other methods</i>	33
1.10.2	<i>Alkyl groups attached to nitrogen</i>	33
1.10.3	<i>Acyl groups</i>	34
1.10.3.1	<i>Hydrolysis of acetyl groups</i>	34
1.10.3.2	<i>Distillation apparatus</i>	34
1.10.3.3	<i>Titration of acetic acid</i>	34
1.10.3.4	<i>Other methods</i>	35
	ACKNOWLEDGEMENT	35

1.1 INTRODUCTION

There has been a series of significant advances throughout the history of organic analysis. Initially there was the development of satisfactory methods of analysis by Liebig, Dumas, Kjeldahl and Carius and then, near the beginning of this century, the outstanding contribution of Pregl who refined existing methods to the micro-scale and developed new techniques. Today organic analysis is again on the move, but this time on a broad front taking in research workers throughout the world. The newer techniques of separation and measurement are being combined with the methods of automation to provide apparatus which permits repetitive analyses to be carried out with the minimum of attention from the operator. Hand in hand with this development, and a necessary part of the move, is the thorough investigation of the various processes involved in each analytical operation. These studies promote a better understanding of the limitations of an analytical method and ultimately lead to the design of equipment of more universal application.

For many years the 3-5 mg sample of Pregl was accepted as the ultimate goal, but with the isolation of pure samples of new compounds on a very small scale, using the techniques of thin-layer and gas-phase chromatography and electrophoresis, it became obvious that further decrease in sample size,

and inevitable refinement in methods, was necessary. Although they are unlikely to be used in normal routine work, the methods developed by Belcher and co-workers¹, using 40–80 μg samples, provide techniques for elemental and group analysis on an appropriate scale to meet this eventuality. The newer instrumental methods using measuring techniques such as the thermal conductivity (katharometer type) detector which permit electronic amplification, also lend themselves to refinement for the analysis of samples on a submicro-scale.

Many thought that with the wide availability of modern instruments for physical measurement the need for organic elemental analysis might decrease, but this has not been the case. Schöniger² in a lecture entitled *Trends in Organic Elemental Microanalysis* states 'Despite the fact that in recent years the physico-chemical methods, infrared, ultraviolet, n.m.r. spectroscopy, and mass spectroscopy, have been widely used, the number of elemental analyses made is increasing at a steady rate. This is because as the chemist is getting more detailed information, he can work more rapidly and, therefore, he needs more primary information, . . .'. It must be admitted that some very elegant work has resulted from the application of high resolution mass spectroscopy, but it is also apparent that elemental analysis and physical methods are complementary. Both are indispensable in the research laboratory. However, one area which has been very significantly displaced by physical methods is the field of functional group analysis.

Perhaps the most important challenge to the organic analyst today stems from the tremendous interest which the study of new and unusual oxidation states and the development of catalysts has brought to inorganic chemistry. Instead of purely organic substances it is not unusual for service laboratories to have to contend with more than half their samples containing metals or other elements 'unusual' to the organic chemist.

1.2 STANDARD COMPOUNDS AND SAMPLE PREPARATION

1.2.1 Standard compounds

It is necessary to have a wide range of reference substances, which are unlikely to vary in composition on storage, to test new analytical methods, and also to run as a check in routine analysis. Such a series has been prepared on the recommendation of the Microchemistry Group of the Society for Analytical Chemistry³ and is available from British Drug Houses Ltd.

1.2.2 Purification of samples

The analyst is seldom involved in the purification of samples, but he should ensure that the research worker appreciates the care which is necessary in sample preparation. High vacuum sublimation in glass tubes c. 8–10 mm i.d., sealed at one end, is a satisfactory method to remove adsorbent residues from many samples purified by thin-layer or column chromatography. Samples should be dried before analysis, but the research worker involved should supply relevant data if this operation is to be performed by the

analyst. It must be remembered that a small amount of moisture or inert material may have negligible effects on hydrogen or nitrogen values but a pronounced effect on carbon, the percentage of which is normally very much greater.

1.2.3 Hygroscopic and air-sensitive samples

Drying hygroscopic samples to constant weight in a platinum boat using a 'weighing pig' is tedious when large numbers are involved. Secor and White⁴ recommend weighing the sample into short sections of pure indium tubing which is crimped to provide a partial seal. When the sample is dried under suitable conditions of temperature and pressure, moisture escapes through the crimped seal, but moisture uptake is sufficiently slow to permit accurate weighing, and electrostatic charges, which can prove troublesome with a weighing pig, are avoided. A very simple modification which is suitable for a wide range of substances makes use of a small aluminium capsule⁵ fabricated from thin foil. The capsule readily disintegrates during combustion analysis and the residue is easily removed. Air-sensitive substances may be loaded into similar aluminium foil capsules in the inert atmosphere of a glove box and sealed by folding. Culmo and Fagans⁶ seal liquid samples in an aluminium pan under an atmosphere of helium or oxygen for combustion in a CHN analyser.

In many instances, where a number of determinations are to be made on the one sample, it is expedient to equilibrate a hygroscopic sample to the laboratory atmosphere, carry out all the analyses on this material, and make an appropriate correction following drying of a portion to constant weight.

1.3 CARBON AND HYDROGEN

The determination of carbon and hydrogen is the most well-known and frequently-performed analytical method in organic analysis and it is not surprising to find considerable research into automation.

The combustion train of Pregl^{7,8} needs little explanation. The sample (3–5 mg) is heated in a stream of oxygen, and combustion to carbon dioxide and water is completed by passage through heated copper oxide. Following removal of sulphur oxides and halogen by lead chromate and silver, and the removal of oxides of nitrogen by lead dioxide, water is adsorbed on anhydrous magnesium perchlorate (Anhydrone) and carbon dioxide on soda asbestos (Carbosorb). These latter reagents are contained in specially constructed absorption tubes which may be disconnected and weighed accurately.

It is convenient to divide the determination into the various processes involved and study each in detail, although some reagents may serve the dual role of combustion aid and adsorbent for the combustion products of interfering elements.

1.3.1 Sample additives

A wide range of organic compounds containing combinations of C, H, O, N, S, Cl, Br and I, may be combusted successfully in a sample boat without

additives. However, current investigations in inorganic chemistry require combustion methods to be suitable for the analysis of samples containing virtually any element or combination of elements. The use of additives has been reviewed by Fildes⁹. Additives are used to modify explosive properties, aid combustion, displace carbon from carbonaceous residues including carbonates and carbides, or withhold volatile interfering elements and their oxidation products.

1.3.1.1 Metals not requiring additives

Many metals do not interfere in combustion analysis and hence do not require the use of additives¹⁰. In such cases it is frequently possible to determine the element simultaneously by weighing the residue. Compounds containing silver, gold or platinum burn to leave a quantitative residue of the metal although hydrogenation of the platinum residue may be necessary if it is to be weighed. Normally aluminium, copper, chromium and iron remain as well defined oxides, but manganese, cobalt, and nickel tend to give mixed oxides of indefinite composition. Mercury will pass through most combustion packings, but it may be collected on cold gold before the hydrogen adsorption tube.

1.3.1.2 Elements requiring additives

Thermally stable carbonates are formed on combustion of samples containing the alkali and alkali-earth metals. The sample may be covered with potassium dichromate, vanadium pentoxide or potassium persulphate¹¹ to ensure displacement of carbon dioxide, but these reagents spatter on heating and require the sample boat to be enclosed in a platinum sheath to avoid attack on the combustion tube. Kissa¹² found tungstic oxide to be a superior reagent. This involatile oxide, which is readily obtained pure and anhydrous, does not melt during the combustion and is normally easily removed from the sample boat. Gawargious and Macdonald¹³ found tungstic oxide to be a suitable additive for samples containing a range of elements including phosphorus and boron. Belcher, Fildes and Nutten¹⁴ also used tungstic oxide in the presence of phosphorus, but included a boat containing further tungstic oxide in front of the combustion zone to retain volatile phosphorus oxides. Butterworth¹⁵ reports that certain boron-containing samples require induction heating to displace carbon from the sample residues.

The use of a silica capsule, open at only one end, to hold the sample has been adopted by several workers when combusting samples which are difficult to burn¹⁶ or require sample additives¹⁷. Reagents may be added to retain otherwise volatile oxidation products and the simultaneous determination of other elements is possible on analysis of the capsule-enclosed residue.

1.3.1.3 Explosive samples

Organometallic perchlorates and nitrates should be treated with caution for they may decompose with sufficient violence to shatter the combustion tube. No difficulties have been encountered in the analysis of a wide range of

samples mixed with freshly ignited copper oxide in the vertical combustion tube of a Coleman Model 33 carbon and hydrogen analyser¹⁸.

1.3.2 Combustion aids

Complete combustion of sample decomposition products is ensured by passage of the gases through a packing containing various aids and/or catalysts. The universal combustion tube packing of Niederl and Niederl¹⁹ was a development of the original Pregl^{7,8} method and incorporated platinised asbestos used with success by Friedrich²⁰. However, these methods and other variations such as the use of the mixed oxide catalyst Vinosit B²¹ all necessitate considerable skill, and each determination requires about one hour.

An important development, used extensively today, is the introduction of the combustion catalysts, silver permanganate decomposition product and cobalt oxide by Körbl²² and Večeřa²³ respectively. Both of these reagents catalyse the combustion of the sample decomposition products ensuring complete combustion at temperatures as low as 550–650 °C. They are readily made in the laboratory, permit a much faster gas flow to be used with corresponding reduction in time per combustion (20–25 min), and require only a short (4–5 cm) hot zone. The only disadvantage seems to be related to their ability to produce rather more oxides of nitrogen than other packings. As might be expected many variations have appeared in the literature: Uhle²⁴ has used cobalt oxide on pumice for the analysis of compounds containing silicon while others²⁵ have used the catalysts in series.

The empty tube combustion method²⁶ makes use of the technique introduced by Belcher and Spooner²⁷. Samples are burnt in a rapid flow of oxygen and oxidation is completed at a relatively high temperature in a modified combustion tube containing a series of baffle plates. The technique was reviewed by Schöniger²⁸. An interesting development is the introduction of static combustion methods probably inspired by the success of the oxygen-filled flask method of combustion popularised by Schöniger^{29,30}. Ingram³¹ describes an apparatus in which the sample is introduced into a hot oxygen-filled combustion volume where conversion to carbon dioxide and water is complete within a minute. The combustion products are then swept into adsorption tubes using a rapid flow of oxygen. This method, which combines the advantage of static combustion with the use of adsorbents for the removal of interfering gases, has been modified by the introduction of a vertical combustion tube³² and applied to the analysis of a range of research compounds. Others have analysed for carbon by electrical ignition of the sample in porcelain boats³³ or glass fibre paper³⁴ in an oxygen-filled flask, the carbonate being precipitated and collected as barium carbonate which is estimated titrimetrically.

1.3.3 Removal of halogens and sulphur

1.3.3.1 Fluorine

Little trouble is normally encountered in the analysis of samples containing small numbers of fluorine atoms, but highly fluorinated materials require