

Wilson and Wilson's

COMPREHENSIVE ANALYTICAL CHEMISTRY

Edited by

G. SVEHLA, PH.D., D.SC., F.R.I.C.

*Reader in Analytical Chemistry
The Queen's University of Belfast*

VOLUME III

Elemental Analysis with Minute Samples
Standards and Standardization
Separations by Liquid Amalgams
Vacuum Fusion Analysis of Gases in Metals
Electroanalysis in Molten Salts



ELSEVIER SCIENTIFIC PUBLISHING COMPANY
AMSTERDAM OXFORD NEW YORK
1975

ELSEVIER SCIENTIFIC PUBLISHING COMPANY
335 JAN VAN GALENSTRAAT
P.O. BOX 211, AMSTERDAM, THE NETHERLANDS

AMERICAN ELSEVIER PUBLISHING COMPANY, INC.
52 VANDERBILT AVENUE
NEW YORK, NEW YORK 10017

LIBRARY OF CONGRESS CARD NUMBER: 58-10158

ISBN 0-444-41162-3

WITH 86 ILLUSTRATIONS AND 22 TABLES

COPYRIGHT © 1975 BY ELSEVIER SCIENTIFIC PUBLISHING COMPANY,
AMSTERDAM

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,
PHOTOCOPYING, RECORDING, OR OTHERWISE, WITHOUT THE PRIOR
WRITTEN PERMISSION OF THE PUBLISHER,
ELSEVIER SCIENTIFIC PUBLISHING COMPANY, JAN VAN GALEN-
STRAAT 335, AMSTERDAM

PRINTED IN THE NETHERLANDS

COMPREHENSIVE ANALYTICAL CHEMISTRY

COMPREHENSIVE ANALYTICAL CHEMISTRY

ADVISORY BOARD

R. Belcher, PH.D., D.SC., F.INST.F., F.R.I.C.

Professor of Analytical Chemistry, The University of Birmingham

The late F. Feigl, ENG., D.SC.

Laboratório da Produção Mineral, Ministério da Agricultura, Rio de Janeiro;
Professor at the University of Brazil

L.T. Hallett, PH.D.

Formerly Editor, *Analytical Chemistry*, Washington, D.C.

J. Haslam, D.SC., F.R.I.C.

Formerly Chief Analyst, Imperial Chemical Industries (Plastics Division),
Welwyn Garden City

H.M.N.H. Irving, M.A., D.PHIL., F.R.I.C.

Professor of Inorganic Chemistry, The University, Leeds

E.B. Sandell, PH.D.

Professor of Analytical Chemistry, The University of Minnesota, Minneapolis,
Minn.

A.A. Smales, O.B.E., D.SC., F.R.I.C.

Head of Analytical Chemistry Division, Atomic Energy Research Establishment,
Harwell

P.W. West, PH.D., D.SC.

Boyd Professor of Chemistry, Louisiana State University, Baton Rouge, La.

Contributors to Volume III

R.A. Chalmers, Department of Chemistry, University of Aberdeen,
Aberdeen

W.T. Elwell, Imperial Metal Industries Ltd., P.O. Box 216,
Birmingham

K.W. Fung, Department of Chemistry, University of Malaysia, Kuala Lumpur,
Malaysia

The late M. Kozłowski, Kazach State University, Alma Ata, U.S.S.R.

G. Mamantov, Department of Chemistry, University of Tennessee, Knoxville,
Tenn., U.S.A.

O. Songina, Kazach State University, Alma Ata, U.S.S.R.

G. Tölg, Max-Planck-Institut für Metallforschung, Schwäbisch Gmünd,
Germany

D.F. Wood, Imperial Metal Industries Ltd., P.O. Box 216, Birmingham

WILSON & WILSON'S

COMPREHENSIVE ANALYTICAL CHEMISTRY

VOLUMES IN THE SERIES

Vol. IA	Analytical Processes Gas Analysis Inorganic Qualitative Analysis Organic Qualitative Analysis Inorganic Gravimetric Analysis
Vol. IB	Inorganic Titrimetric Analysis Organic Quantitative Analysis
Vol. IC	Analytical Chemistry of the Elements
Vol. IIA	Electrochemical Analysis Electrodeposition Potentiometric Titrations Conductometric Titrations High-frequency Titrations
Vol. IIB	Liquid Chromatography in Columns Gas Chromatography Ion Exchangers Distillation
Vol. IIC	Paper and Thin-Layer Chromatography Radiochemical Methods Nuclear Magnetic Resonance and Electron Spin Resonance Methods X-Ray Spectrometry
Vol. IID	Coulometric Analysis
Vol. III	Elemental Analysis with Minute Samples Standards and Standardization Separations by Liquid Amalgams Vacuum Fusion Analysis of Gases in Metals Electroanalysis in Molten Salts

Vol. IV

Instrumentation for Spectroscopy

Atomic Absorption and Fluorescence Spectroscopy

Diffuse Reflectance Spectroscopy

Preface

In *Comprehensive Analytical Chemistry* the aim is to provide a work which, in many instances, should be a self-sufficient reference work; but where this is not possible, it should at least be a starting point for any analytical investigation.

It is hoped to include the widest selection of analytical topics that is possible within the compass of the work, and to give material in sufficient detail to allow it to be utilised directly, not only by professional analytical chemists, but also by those workers whose use of analytical methods is incidental to their other work rather than continual. Where it is not possible to give details of methods, full reference to the pertinent original literature is made.

With the large number of contributors to *Comprehensive Analytical Chemistry*, it has become increasingly difficult to publish volumes with the originally planned contents. Volume III should have contained optical methods of analysis. Though some of the authors have submitted their chapters some time ago, others were late and some chapters are still outstanding. It has been decided, therefore, to give up the original editorial plans and to publish volumes of miscellaneous contents as soon as there is enough material available. At the same time, it was decided to give each new bound volume a new number instead of breaking one volume into parts A, B, etc. as done with Volumes I and II. It is hoped that the new editorial policy will speed up publication.

Volume III contains contributions on a wide range of subjects. There are chapters on elemental analysis with minute samples (Chap. I), standards and standardization in chemical analysis (Chap. II), separations with liquid amalgams (Chap. III), vacuum-fusion analysis of gases in metals (Chap. IV) and electroanalysis in molten salts

(Chap. V). All these topics deal with problems which confront the modern analytical chemist. As usual, these contributions are written by outstanding internationally known experts in their fields.

It is with the deepest regret that I have to report the sudden death of Professor Cecil L. Wilson, one of the founders of *Comprehensive Analytical Chemistry*. The death of Cecil Wilson is a loss to the international community of analytical chemists of an outstanding researcher, a gifted teacher, a prolific writer and a warm-hearted human being. He will be long remembered.

Dr. C.L. Graham of the University of Birmingham assisted in the production of the present volume; his contribution is acknowledged with many thanks.

June 1974

G. Svehla

Contents

<i>Preface</i>	ix
--------------------------	----

<i>Chapter I. ELEMENTAL ANALYSIS WITH MINUTE SAMPLES</i> , by G. Tölg	1
---	---

1. Introduction	1
1.1 Method nomenclature	1
1.2 Historical development	2
1.3 The application of microanalytical methods of elemental analysis	4
1.4 Limits of detection and reliability of the methods	6
2. Sources of error in microchemical analysis	10
2.1 Methods for concentrations $\geq 0.01 M$	11
2.2 Methods for concentrations $< 0.01 M$	12
2.2.1 Laboratories, 13 — 2.2.2 Interactions between solutions and containers, 16 — 2.2.3 Reagents, 21 — 2.2.4 Losses through volatilization, 25	
3. Sampling and sample preparation	26
4. Weighing in of sample	29
4.1 Direct weighing in	29
4.1.1 Weighing principles, 31 — 4.1.2 Comments on weighing in minute quantities of substance by means of quartz thread torsion balances, 37	
4.2 Indirect weighing in	41
4.2.1 By measuring volume and density, 41 — 4.2.2 By solution partition, 42	
5. Dissolution and decomposition of the sample	43
5.1 Methods of classical microanalysis	43
5.2 Methods for solution concentrations $\leq 0.01 M$	46
5.2.1 Requirements to be met by the decomposition reagents, 47 — 5.2.2 Exclusion of impurities from	

	the air, 48 — 5.2.3 Consideration of desorption, ion exchange and adsorption on the walls of vessels, 51 — 5.2.4 Avoidance of spattering and volatilization of components of the sample during decomposition, 52	
5.3	Decomposition combined with separation	56
6.	Methods of separation	58
6.1	Separation by precipitation	59
6.2	Volatilization	61
6.3	Liquid—liquid extraction	65
6.4	Ion exchangers	68
6.5	Thin layer chromatography, paper chromatography and electrophoresis	71
6.6	Gas chromatographic separation	73
6.7	Combined methods of separation	74
7.	Determination methods	75
7.1	Methods of analysis based on gravimetry and precipitation	76
7.2	Volumetric methods	80
	7.2.1 Direct measurement of minute quantities of volumetric solution and liquid, 81 — 7.2.2 Coulometric generation of volumetric and standard solutions, 87 — 7.2.3 Determination of titration end-points, 89	
7.3	Spectrophotometric methods	98
7.4	Fluorometric methods	103
7.5	Atomic absorption and atomic fluorescence spectrophotometry	103
7.6	Atomic emission spectroscopy	107
7.7	Voltammetric methods of analysis	109
7.8	X-ray fluorescence analytical methods	113
7.9	Electron beam microanalysis	117
7.10	Mass spectrometric methods	121
7.11	Radioanalytical methods	127
	7.11.1 Tracer methods, 128 — 7.11.2 Methods of activation analysis, 132 — 7.11.3 Methods of analysis based on scattering of charged particles, 134	
8.	Conclusion	137
	References	138

Chapter II. STANDARDS AND STANDARDIZATION IN
CHEMICAL ANALYSIS, by R.A. Chalmers 185

1.	General	185
2.	Apparatus	187
	(A) Balances and weights	187
	(B) Graduated glassware	189
	(C) Instrument scales	191
	(D) Pulse counting	193
3.	Standard chemicals	193
	(A) Definition of standards	193
	(B) Titrimetric standards	197
	Generalized schemes of standardization, 197 — Acid-base standards, 197 — Oxidation-reduction standards, 202 — Precipitation titration standards, 204 — Complexometric standards, 204	
	(C) Inorganic standards	206
	(D) Organic and organometallic standards	211
	(E) Clinical standards	212
	(F) Standards for pH measurement	212
	(G) Thermogravimetric standards	213
	(H) Spectrophotometric standards	213
	(I) Commercial concentrated solutions for dilution	213
4.	Standard reference materials	214
	(A) Rocks and minerals	214
	(B) Metals and alloys	216
	(C) Other reference materials	217
5.	Standardization of methods and analysts	218
	References	220

Chapter III. SEPARATION BY LIQUID AMALGAMS, by
M. Kozłowski and O. Songina 225

1.	Introduction	225
2.	Physico-chemical properties of amalgams	226
	(A) Solubility of metals in mercury	226
	(B) Electrochemical properties of liquid (homogeneous and heterogeneous) amalgams	228
3.	Intermetallic compounds in amalgams	234
4.	Theory of cementation (displacement) of metals by amalgams	239

5.	Displacement of metals from their amalgams	248
6.	Practical applications	252
	(A) Separation of bismuth from more electronegative metals	252
	(B) Titration of amalgams by a mercury salt solution	253
	(C) Other determinations involving amalgam separations	254
7.	Instrumentation and preparation of amalgams	256
	References	256

Chapter IV. DETERMINATION OF GASES IN METALS BY VACUUM-FUSION AND INERT-GAS FUSION

METHODS, by W.T. Elwell and D.F. Wood 259

1.	Introduction	259
2.	Historical review of the vacuum-fusion method	260
3.	Principles of the vacuum-fusion method	262
	(A) Reactions involved	262
	(B) Analysis of the evolved gas	266
4.	Apparatus designs	267
	(A) Furnace section	267
	(B) Gas-analysis system	268
5.	A semi-micro vacuum-fusion apparatus	269
	(A) Furnace unit	270
	(B) Analysis unit	271
	(C) Calibration of apparatus	271
	(D) Operation of apparatus	272
	Notes, 274	
6.	Commercially available vacuum-fusion units	274
7.	Applications of the vacuum-fusion method	274
	(A) Ferrous materials	274
	(B) Non-ferrous materials	280
	Titanium, 280 — Zirconium etc., 283 — Molybdenum, tungsten, niobium and tantalum, etc., 284 — Aluminium, 286 — Beryllium etc., 286 — Chromium, 287 — Copper, 287 — Gallium and indium, 287 — Magnesium alloys, 287 — Rare-earth metals and lanthanum, etc., 288 — Rhenium, 288 — Uranium, 288 — Vanadium, 289 — Metal oxides, 289	
8.	Reviews of the vacuum-fusion method	289

9.	Historical review of the inert-gas fusion method	289
10.	Principle of inert-gas fusion	292
11.	Apparatus designs	292
(A)	Furnace section	292
(B)	Analysis section	293
12.	Applications of the inert-gas fusion method	294
(A)	Ferrous materials	294
(B)	Non-ferrous metals	295
	Beryllium, boron, thorium, uranium, etc., 295 —	
	Cadmium, magnesium and zinc, 295 — Niobium,	
	tantalum, vanadium and yttrium, 295 — Titanium	
	and zirconium, 296 — Various metals, 296 —	
	Metal oxides and nitrides, 297 — Other applications,	
	298	
13.	Reviews of the inert-gas fusion method	298
	References	299

Chapter V. ELECTROANALYTICAL CHEMISTRY IN MOLTEN

SALTS, by K.W. Fung and G. Mamantov 305

1.	Introduction	305
2.	Experimental techniques	305
(A)	Melt purification	305
	LiCl—KCl eutectic, 306 — Equimolar NaCl—KCl,	
	307 — $AlCl_3$ -alkali chloride mixtures, 307 —	
	Fluorides, 308 — Nitrates, 308 — Miscellaneous, 308	
(B)	Reference electrodes	309
	Pt^{2+}/Pt electrode, 309 — Ag^+/Ag electrode, 309 —	
	Al^{3+}/Al electrode, 310 — Ni^{2+}/Ni electrode, 310 —	
	The quasi reference electrode, 310	
(C)	Electrodes and cell design	311
	Working (indicator) electrodes, 311 — Counter	
	electrode, 312 — Cell design, 312	
(D)	Heating and temperature control	313
(E)	Instrumentation	314
3.	Electroanalytical methods and their application	314
(A)	Potentiometry	314
(B)	Voltammetry and polarography	317
	Conventional, 317 — Rotating disc electrode, 321 —	
	A.c. polarography, 323 — Integral (normal) pulse	
	polarography, 324	

(C)	Chronoamperometry	326
(D)	Linear sweep voltammetry	328
(E)	Chronopotentiometry	333
(F)	Coulometry	336
	Controlled current, 337 — Controlled potential, 338	
(G)	Miscellaneous	339
	Thin layer electrochemistry, 339 — Spectro- electrochemical studies, 339	
4.	Summary of results	341
5.	Acknowledgements	341
	References	341
	<i>Index</i>	372

Chapter I

Elemental Analysis with Minute Samples

GÜNTHER TÖLG

1. Introduction

1.1. METHOD NOMENCLATURE

“Elemental analysis with minute samples” or “microanalytical methods” (in contrast to the “macroanalytical methods”) refer to all those cases where the analysis of elements is accomplished with maximum accuracy on minute samples of inorganic or organic substances or when particularly small samples are excited to send out signals which are specific to the elements and which can be analyzed. These microanalytical methods differ from the “methods of trace analysis” by means of which very low contents ($< 10^{-3}\%$) of minor elements have to be determined in large quantities of sample [1].

In these cases, the bulk of the matrix elements can pose additional difficulties in the analysis of small quantities of elements. After initial isolation using special methods of separation, the trace components can frequently be detected by means of microanalytical methods which are appropriately arranged according to sample size [2–4] (Table 1).

Even though the concept of “microanalysis” is actually reserved for milligram methods, it will be used subsequently in a larger sense for all “methods with samples below the milligram range”.

As is usual in chemical analysis, a distinction is made in microanalysis between qualitative and quantitative methods. In the first case, one aims at limits of identification as low as possible, in the latter case one aims in addition at high precision. This subdivision is justified particularly in the case of methods of detection and analysis based on chemical reactions since in these cases, qualitative and