Ion Chromatography

MODERN ANALYTICAL CHEMISTRY

Series Editor: David Hercules
University of Pittsburgh

ANALYTICAL ATOMIC SPECTROSCOPY

William G. Schrenk

APPLIED ATOMIC SPECTROSCOPY

Volumes 1 and 2

Edited by E. L. Grove

CHEMICAL DERIVATIZATION IN ANALYTICAL CHEMISTRY

Edited by R. W. Frei and J. F. Lawrence

Volume 1: Chromatography

Volume 2: Separation and Continuous Flow Techniques

COMPUTER-ENHANCED ANALYTICAL SPECTROSCOPY

Volume 1: Edited by Henk L. C. Meuzelaar and Thomas L. Isenhour

Volume 2: Edited by Henk L. C. Meuzelaar

ION CHROMATOGRAPHY

Hamish Small

ION-SELECTIVE ELECTRODES IN ANALYTICAL CHEMISTRY

Volumes 1 and 2

Edited by Henry Freiser

LIQUID CHROMATOGRAPHY/MASS SPECTROMETRY

Techniques and Applications

Alfred L. Yergey, Charles G. Edmonds, Ivor A. S. Lewis, and Marvin L. Vestal

MODERN FLUORESCENCE SPECTROSCOPY

Volumes 1-4

Edited by E. L. Wehry

PHOTOELECTRON AND AUGER SPECTROSCOPY

Thomas A. Carlson

PRINCIPLES OF CHEMICAL SENSORS

Jiří Janata

TRANSFORM TECHNIQUES IN CHEMISTRY

Edited by Peter R. Griffiths

A Continuation Order Plan is available for this series. A continuation order will bring delivery of each new volume immediately upon publication. Volumes are billed only upon actual shipment. For further information please contact the publisher.

Ion Chromatography

Hamish Small

*Formerly Research Scientist
The Dow Chemical Company
Midland, Michigan*

Springer Science+Business Media, LLC

Library of Congress Cataloging in Publication Data

Small, Hamish.

Ion chromatography / Hamish Small.

p. cm — (Modern analytical chemistry)

Includes bibliographical references.

ISBN 978-1-4899-2544-2

ISBN 978-1-4899-2542-8 (eBook)

DOI 10.1007/978-1-4899-2542-8

1. Ion exchange chromatography. I. Title. II. Series.

QD79.C453S63 1990

89-39790

543/.0893 — dc20

CIP

© 1989 Springer Science+Business Media New York

Originally published by Plenum Press, New York in 1989.

Softcover reprint of the hardcover 1st edition 1989

All rights reserved

No part of this book may be reproduced, stored in a retrieval system, or transmitted in any form or by any means, electronic, mechanical, photocopying, microfilming, recording, or otherwise, without written permission from the Publisher

To Beryl, Deborah, and Claire

Preface

Bewitched is an odd word with which to begin a chemical textbook. Yet that is a fair description of how I reacted on first learning of ion exchange and imagining what might be done with it. That initial fascination has not left me these many years later, and it has provided much of the motivation for writing this book. The perceived need for a text on the fundamentals of ion chromatography provided the rest.

Many readers will have a general idea of what ion chromatography is and what it does. Briefly, for those who do not, it is an umbrella term for a variety of chromatographic methods for the rapid and sensitive analysis of mixtures of ionic species. It has become highly developed in the last decade, and while it is now routinely used for the determination of organic as well as inorganic ions, its initial impact was greatest in the area of inorganic analysis. In the past the determination of inorganic ions, particularly anions, meant laborious, time-consuming, and often not very sensitive “wet chemical” methods. In the last ten years that has changed radically as ion chromatography has supplanted these older methods.

While ion chromatography (IC) is relatively new, the principles that underlie its practice and guide the development of its several parts have been laid down over decades of research in many diverse areas of chemistry. A primary purpose of this book is to provide a systematic account of this fundamental chemistry and the principles that underlie it.

Ion chromatography is a practical art, and this book is about practical matters. So although there is an emphasis on basic principles, I have placed equal importance on showing the direct relationship of the underlying scientific concepts to everyday practical matters of IC, such as the design and synthesis of ion exchange resins and the solution of real chromatographic problems. I have treated detection in IC at some length, in the first place because detection stands equal in importance to separation in modern chromatography, and second because new methods of detection are largely responsible for the renaissance of ion exchange in analytical chemistry. The book has also given me the opportunity to address

the specific area of conductometric detection, which, in IC, is still a source of some misunderstanding.

To whom is the book addressed and to whom might it appeal? Modern instrumentation, with its emphasis on operator convenience and its ability to automate, has been a tremendous boon to the analyst in increased productivity and decreased tedium. On the other hand, it tends increasingly to insulate the user from the underlying science, so texts and the like that emphasize the theoretical bases of methods provide a necessary counterbalance to this “black box” tendency. I believe such texts to be especially necessary in chromatography, where the operator is such an active participant in the analytical process, in that decisions must often be made on such matters as separation method, stationary and mobile phases, and modes of detection. So in considering to whom the book should appeal I always had in mind the practicing chromatographer. I hope also that the book will be of help to those who are involved in the design of new chromatographic phases since I have endeavored to treat the synthesis of exchangers and the origins of ion selectivity at some length. And an early chapter on the chromatographic process is intended as a bridge that practitioners of LC and GC will find useful in making the transition to ion exchange chromatography.

In the research phase of *Ion Chromatography*, and particularly in the writing of the book, I have been keenly aware of the rich hinterland from which we drew much of our resources. I hope the book goes at least a short way in recognizing those who, though they could not know it at the time, have contributed so significantly to the birth and success of this most recent offspring of Ion Exchange.

ACKNOWLEDGMENTS. I am especially indebted to Dr. Ed. Johnson and Ted Miller for their critical reading of the entire manuscript and for the many improvements that they suggested. Also my sincere thanks go to Rosanne Slingsby and Nancy Jensen for their help with many of the figures.

Hamish Small

Leland, Michigan

Contents

Chapter 1

Introduction

1.1. Background to Ion Chromatography	1
1.2. The Book	6
1.2.1. Aims	6
1.2.2. Organization	6
1.2.3. Terminology	7
References	8

Chapter 2

The Chromatographic Process

2.1. Introduction	11
2.2. A Description of a Chromatographic Separation	11
2.3. Thermodynamic Aspects of Chromatographic Separation	13
2.3.1. Distribution of a Solute between Two Phases	13
2.3.2. Chromatographic Separation of Solutes	14
2.3.3. Relationship between k' and K_D	16
2.3.4. Variation of K_D with Concentration—Nonideal Behavior	17
2.3.5. Isotherms and Peak Shape in Chromatography	20
2.4. Dynamic Aspects of the Chromatographic Process	22
2.4.1. Band Broadening in Chromatography	22
2.4.2. Band Broadening—Some Experimental Observations	23
2.4.3. The Plate Theory of Band Broadening	24
2.5. Rate Theories of Band Broadening	31
2.5.1. The Origins of Band Broadening	31
2.6. Resolution	36
2.7. Summary	38
References	38

Chapter 3

The Materials of Ion Chromatography

3.1. Introduction	41
-------------------------	----

3.2. Ion Exchangers	41
3.2.1. Polymer Precursors of Ion Exchange Resins	42
3.2.2. Cation Exchange Resins	43
3.2.3. Anion Exchange Resins	45
3.2.4. Surface Agglomeration Method for Preparing Low-Capacity Ion Exchangers ...	46
3.2.5. Silica- and Methacrylate-Based Ion Exchangers	51
3.2.6. Exchangers with Weakly Functional Groups	52
3.2.7. Chelating Resins	52
3.3. Ion Interaction Reagents	53
References	54

Chapter 4

Ion Exchange in Ion Chromatography

4.1. Introduction	57
4.2. Ion Exchange Selectivity and Equilibria	57
4.2.1. Selectivity and the Selectivity Coefficient	57
4.2.2. The Distribution Coefficient K_D	61
4.2.3. The Donnan Potential and Ion Exchange Equilibrium	65
4.2.4. A General Expression for K_D	67
4.2.5. K_D and k' for Low-Capacity Resins	70
4.2.6. Effects Attributable to the pH of the External Phase	73
4.2.7. Complexation and Ion Exchange Equilibria	74
4.2.8. Theories on the Causes of Ion Exchange Selectivity	85
4.3. Ion Exchange Kinetics	90
4.3.1. Band Broadening in Ion Exchange Chromatography	94
4.3.2. Chemical Rate Control	97
4.4. Ion Exchange Chromatography	98
4.4.1. Elution Development	98
4.4.2. Frontal Analysis	99
4.4.3. Displacement Development	99
4.4.4. Peak Shape in Elution Development	102
4.4.5. Base-Line Disturbances, "System" Peaks	104
4.5. Ion Interaction Chromatography	106
4.5.1. The Electrical Double Layer	107
4.5.2. The "Capacity" of the Adsorbed Double Layer	108
4.5.3. Retention of Surface Active Elutes	112
4.5.4. IIC and IEC—A Comparison	113
References	115

Chapter 5

Ion Exchange Resins in Liquid Partition Chromatography

5.1. Introduction	119
5.2. Sorption Equilibria on Ion Exchange Resins	119
5.2.1. Sorption of Uncharged Species	120
5.2.2. Sorption of Strong Electrolytes	124
5.2.3. Thermodynamic Treatment of Electrolyte Distribution and Ion Exclusion	125
5.2.4. Sorption of Weak Electrolytes	127

5.3. Water as Eluent in Ion Chromatography	132
References	138

Chapter 6

Detection—General

6.1. Introduction	139
6.2. Detection in Chromatography	140
6.2.1. The Elements of Detection	140
6.2.2. The Requirements of a Detector	141
6.2.3. Sensitivity, Noise, and Limits of Detectability	142
6.2.4. Mobile Phase as a Source of Noise and Limitations on Detectability	144
6.2.5. Definition of Detectability	147
6.2.6. Detectability in Chromatography	147
References	148

Chapter 7.

Conductometric Detection

7.1. Introduction	149
7.2. Electrolyte Conductance—Theory and Measurement	151
7.2.1. Strong Electrolytes	151
7.2.2. Weak Electrolytes	153
7.2.3. Measurement of Conductance	154
7.3. Conductometric Detection: Suppressed	155
7.3.1. Eluent Suppression	155
7.3.2. Exhaustion and Regeneration of Column Suppressors	158
7.3.3. Eluents for Suppressed IC	160
7.3.4. Suppressor Column Effects	164
7.3.5. Problems with Column Suppressors	170
7.3.6. Membrane Suppressors	170
7.3.7. Removal of CO ₂ from Column Effluent	174
7.3.8. Nonlinearity Effects in Suppressed Conductometric Systems	175
7.4. Conductometric Detection: Nonsuppressed	177
7.4.1. The Basis of Nonsuppressed Conductometric Detection	178
7.4.2. Eluent Choice	179
7.5. A Comparison of Suppressed and Nonsuppressed Conductometric Detection	180
7.5.1. Simulated Experiments Using Suppressed and Nonsuppressed Methods	181
7.6. Gradient Elution and Conductometric Detection	186
7.7. Conductometric Detection in Ion Chromatography—A Summary	187
References	188

Chapter 8

Other Modes of Detection

8.1. Introduction	191
8.2. Photometers and Spectrophotometers	191
8.2.1. Principles of Photometric Detection	191

8.2.2. Sensitivity of Spectrophotometers	193
8.2.3. Photometric Detection with Postseparation Derivatization	195
8.2.4. Indirect Photometric Detection (IPD)	195
8.3. Electrochemical Detection	205
8.4. Miscellaneous Methods	206
8.5. Detection in IC—A Summary	208
References	210

Chapter 9

Selected Applications of Ion Chromatography

9.1. Introduction	213
9.2. Conductometric Detection in the IC of Common Inorganic Anions	213
9.3. Analysis of Alkali Metal and Alkaline Earth Metal Ion Mixtures	218
9.3.1. Alkali Metal and Alkaline Earth Metal Ions Together	218
9.3.2. A “Mechanical” Solution	221
9.3.3. Alkali Metal or Alkaline Earth Metal Ions Separately	223
9.4. IC of High-Affinity Ions	224
9.4.1. Polyphosphates and Similar Species	224
9.4.2. Polyamines	227
9.4.3. Hydrophobic Anions	228
9.5. Anions of Very Weak Acids	230
9.6. Ion Exclusion	234
9.7. Amino Acids	236
9.7.1. Acid–Base Chemistry of Alpha-Amino Acids	236
9.7.2. Ion Exchange Separation of Amino Acids	239
9.8. Carbohydrates	242
References	244

APPENDIXES

Appendix A. Logarithmic Diagrams	249
Appendix B. Limiting Equivalent Conductivities of Ions at 25°C	259
Appendix C. Conductance of Carbonic Acid as it is Neutralized by Sodium Hydroxide	261
Appendix D. Conductance of a Strong Acid in a Background of Weak Acid	263
Appendix E. Ionization Constants and pH Values at the Isoelectric Points (pI) of the Common Amino Acids in Water at 25°C	265
Appendix F. The Structure of Common Alpha-Amino Acids	267
References for Appendixes	271

Index	273
--------------------	-----