

Contents

Volume 1

Foreword	<i>XV</i>
Preface to the Fourth Edition	<i>XVII</i>

1	Introduction	<i>1</i>
1.1	Historical Perspective	<i>1</i>
1.2	Types of Ion Chromatography	<i>4</i>
1.3	The Ion Chromatographic System	<i>5</i>
1.4	Advantages of Ion Chromatography	<i>8</i>
1.5	Selection of Separation and Detection Systems	<i>10</i>
	References	<i>12</i>
2	Theory of Chromatography	<i>15</i>
2.1	Chromatographic Terms	<i>15</i>
2.1.1	Asymmetry Factor A_s	<i>15</i>
2.2	Parameters for Assessing the Quality of a Separation	<i>17</i>
2.2.1	Resolution	<i>17</i>
2.2.2	Selectivity	<i>18</i>
2.2.3	Capacity Factor	<i>18</i>
2.3	Column Efficiency	<i>19</i>
2.4	The Concept of Theoretical Plates (van Deemter Theory)	<i>21</i>
2.5	van Deemter Curves in Ion Chromatography	<i>25</i>
	References	<i>27</i>
3	Anion-Exchange Chromatography (HPIC)	<i>29</i>
3.1	General Remarks	<i>29</i>
3.2	The Ion-Exchange Process	<i>30</i>
3.3	Thermodynamic Aspects	<i>31</i>
3.4	Stationary Phases	<i>36</i>
3.4.1	Polymer-Based Anion Exchangers	<i>37</i>

3.4.1.1	Poly(styrene-co-divinylbenzene)-Based Polymers	37
3.4.1.2	Polymethacrylate Resins	54
3.4.1.3	Polyvinylalcohol Resins	60
3.4.1.4	Nanobead-Agglomerated Anion Exchangers	63
3.4.1.5	Hyperbranched Condensation Polymers	95
3.4.1.6	Polymeric Monolithic Anion Exchangers	119
3.4.2	Silica-Based Anion Exchangers	126
3.4.3	Other Materials for Anion Separations	130
3.4.3.1	Crown Ether and Cryptand Phases	130
3.4.3.2	Alumina Phases	138
3.5	Eluents for Anion-Exchange Chromatography	142
3.6	Suppressor Systems in Anion-Exchange Chromatography	152
3.6.1	Suppressor Columns	153
3.6.2	Hollow Fiber Suppressors	158
3.6.3	Micromembrane Suppressors	161
3.6.4	Self-Regenerating Suppressors	167
3.6.5	Suppressors with Monolithic Suppression Beds	172
3.6.6	Capillary Suppressors	173
3.7	Anion-Exchange Chromatography of Inorganic Anions	175
3.7.1	Overview	175
3.7.2	General Parameters Affecting Retention	176
3.7.3	Experimental Parameters Affecting Retention when Applying Suppressor Systems	177
3.7.3.1	Choice of Eluent	177
3.7.3.2	Eluent Concentration and pH Value	193
3.7.3.3	Influence of Organic Solvents	198
3.7.4	Experimental Parameters Affecting Retention when Applying Nonsuppressed Conductivity Detection	201
3.7.4.1	Choice of Eluent	201
3.7.4.2	System Peaks	210
3.7.4.3	Eluent Concentration and pH Value	213
3.7.5	Polarizable Anions	216
3.8	Anion-Exchange Chromatography of Organic Anions	227
3.8.1	Carboxylic Acids	228
3.8.2	Organophosphates, Organosulfates, and Organosulfonates	244
3.8.3	Phosphonic and Phosphinic Acids	254
3.9	Gradient Elution Techniques in Anion-Exchange Chromatography of Inorganic and Organic Anions	267
3.9.1	Theoretical Aspects	268
3.9.2	Choice of Eluent	270
3.9.3	Possibilities for Optimizing Concentration Gradients	277
3.9.4	Isoconductive Techniques	278
3.10	Carbohydrates	281
3.10.1	Sugar Alcohols	287
3.10.2	Monosaccharides	290

3.10.3	Oligosaccharides	308
3.10.4	Polysaccharides	314
3.10.5	Carbohydrates Derived from Glycoproteins	320
3.10.5.1	Compositional and Structural Analysis	323
3.10.5.2	Chosen Examples	338
3.11	Amino Acids	341
3.12	Anion-Exchange Chromatography of Proteins	351
3.12.1	Grafted Anion-Exchange Resins	351
3.12.2	Monolithic Anion-Exchange Media	359
3.13	Nucleic Acids	368
	References	390
4	Cation-Exchange Chromatography (HPIC)	401
4.1	Stationary Phases	401
4.1.1	Polymer-Based Cation Exchangers	401
4.1.1.1	Poly(styrene- <i>co</i> -divinylbenzene)-Based Polymers	401
4.1.1.2	Grafted Ethylvinylbenzene/Divinylbenzene Copolymers	404
4.1.1.3	Polymethacrylate and Poly(vinylalcohol) Resins	432
4.1.1.4	Nanobead-Agglomerated Cation Exchangers	434
4.1.2	Silica-Based Cation Exchangers	439
4.2	Eluents in Cation-Exchange Chromatography	448
4.3	Suppressor Systems in Cation-Exchange Chromatography	450
4.3.1	Suppressor Columns	450
4.3.2	Hollow Fiber Suppressors	451
4.3.3	Micromembrane Suppressors	451
4.3.4	Self-Regenerating Suppressors	452
4.3.5	Suppressors with Monolithic Suppression Beds	457
4.3.6	Capillary Suppressors	458
4.4	Cation-Exchange Chromatography of Alkali Metals, Alkaline-Earth Metals, and Amines	460
4.5	Transition Metal Analysis	468
4.5.1	Basic Theory	468
4.5.2	Transition Metal Analysis by Nonsuppressed Conductivity Detection	472
4.5.3	Transition Metal Analysis with Spectrophotometric Detection	474
4.5.4	Chelation Ion Chromatography	490
4.6	Analysis of Polyamines	496
4.7	Gradient Techniques in Cation-Exchange Chromatography of Inorganic and Organic Cations	498
4.8	Cation-Exchange Chromatography of Proteins	505
4.8.1	Grafted Cation-Exchange Resins	507
4.8.2	Monolithic Cation-Exchange Media	523
	References	529

Volume 2

5	Ion-Exclusion Chromatography (HPICE)	533
5.1	The Ion-Exclusion Process	533
5.2	Stationary Phases	535
5.3	Eluents for Ion-Exclusion Chromatography	542
5.4	Suppressor Systems in Ion-Exclusion Chromatography	543
5.5	Analysis of Inorganic Acids	545
5.6	Analysis of Organic Acids	550
5.7	HPICE/HPIC-Coupling	553
5.8	Analysis of Alcohols and Aldehydes	558
5.9	Amino Acids Analysis	561
5.9.1	Separation of Amino Acids	562
5.9.2	Postcolumn Derivatizations of Amino Acids	570
5.9.3	Sample Preparation	572
5.10	Size-Exclusion Chromatography of Proteins	573
	References	580
6	Ion-Pair Chromatography (MPIC)	583
6.1	Survey of Existing Retention Models	584
6.2	Suppressor Systems in Ion-Pair Chromatography	588
6.3	Experimental Parameters that Affect Retention	589
6.3.1	Type and Concentration of Lipophilic Counterions in the Mobile Phase	590
6.3.2	Type and Concentration of the Organic Modifier	593
6.3.3	Inorganic Additives	596
6.3.4	pH Effects and Temperature Influence	597
6.4	Analysis of Surface-Inactive Ions	599
6.5	Analysis of Surface-Active Ions	615
6.6	Applications of the Ion-Suppression Technique	636
6.7	Applications of Ion Chromatography on Mixed-Mode Stationary Phases	640
6.7.1	Polymer-Based Mixed-Mode Columns	641
6.7.2	Silica-Based Mixed-Mode Columns	657
	References	679
7	Hydrophilic Interaction Liquid Chromatography (HILIC)	683
7.1	Separation Mechanism in Hydrophilic Interaction Liquid Chromatography	685
7.2	Stationary Phases for HILIC	686
7.2.1	Underivatized Silica	687
7.2.2	Neutral Bonded Phases	690
7.2.3	Charged Bonded Phases	696
7.2.4	Zwitterionic Bonded Phases	698
7.2.5	Mixed-Mode Bonded Phases	701

7.3	Factors Affecting Retention in HILIC	707
7.3.1	Organic Solvents	707
7.3.2	Ionic Additives	708
7.3.3	Mobile-Phase pH	709
7.4	Applications	710
7.4.1	Carbohydrates and Amino Acids	710
7.4.2	Organic Acids	713
7.4.3	Hydrophilic Active Pharmaceutical Ingredients	718
7.4.4	Buffer Salts for Biopharmaceutical Applications	720
7.4.5	Nucleobases, Nucleosides, and Nucleotides	721
7.4.6	Melamine and Cyanuric Acid	725
	References	728
8	Detection Methods in Ion Chromatography	731
8.1	Electrochemical Detection Methods	731
8.1.1	Conductivity Detection	731
8.1.1.1	Theoretical Principles	732
8.1.1.2	Application Modes of Conductivity Detection	738
8.1.2	Amperometric Detection	743
8.1.2.1	Fundamental Principles of Voltammetry	744
8.1.2.2	Amperometry	748
8.1.3	Charge Detection	771
8.1.3.1	The Charge Signal	774
8.1.3.2	Calibration Behavior in Charge Detection	776
8.1.3.3	Example Applications	778
8.2	Spectrometric Detection Methods	782
8.2.1	UV/Vis Detection	782
8.2.1.1	Direct UV/Vis Detection	782
8.2.1.2	UV/Vis Detection in Combination with Derivatization Techniques	783
8.2.1.3	Indirect UV Detection	799
8.2.2	Fluorescence Detection	803
8.3	Aerosol-Based Detection Methods	810
8.3.1	Evaporative Light Scattering Detection	811
8.3.1.1	Advantages and Limitations of ELSD	814
8.3.1.2	Applications of ELSD	816
8.3.2	Condensation Nucleation Light Scattering Detection	819
8.3.3	Charged Aerosol Detection	822
8.3.3.1	Applications of CAD	829
8.4	Other Detection Methods	844
8.4.1	Refractive Index Detection	844
8.4.2	Radioactivity Monitoring	847
8.4.3	Chemiluminescence Detection	848
8.5	Hyphenated Techniques	853
8.5.1	IC-ICP Coupling	853
8.5.2	IC-MS Coupling	865

8.5.2.1	Electrospray Interface	867
8.5.2.2	IC–MS Applications	875
	References	926
9	Quantitative Analysis	935
9.1	General	935
9.2	Analytical Chemical Information Parameters	936
9.3	Determination of Peak Areas	937
9.3.1	Manual Determination of Peak Areas and Peak Heights	938
9.3.2	Electronic Peak Area Determination	940
9.4	Statistical Quantities	944
9.4.1	Mean Value	944
9.4.2	Standard Deviation	945
9.4.3	Scatter and Confidence Interval	945
9.5	Calibration of an Analytical Method (Basic Calibration)	946
9.5.1	Acquisition of the Calibration Function	947
9.5.1.1	Method Characteristic Parameters of a Linear Calibration Function	948
9.5.1.2	Method Parameters of a Calibration Function of Second Degree	950
9.5.2	Testing of the Basic Calibration	952
9.5.3	Testing the Precision	953
9.5.3.1	Homogeneity of Variances	953
9.5.3.2	Outlier Tests	953
9.5.4	Calibration Methods	955
9.5.4.1	Area Normalization	955
9.5.4.2	Internal Standard	956
9.5.4.3	External Standard	957
9.5.4.4	Standard Addition	958
9.6	Detection Criteria, Limit of Detection, Limit of Determination	960
9.6.1	Determination of Detection Criteria, Limit of Detection, and Limit of Determination	961
9.7	The System of Quality Control Cards	964
9.7.1	Types of Quality Control Cards and Their Applications	965
	References	972

Volume 3

10	Applications	975
10.1	Ion Chromatography in Environmental Analysis	977
10.1.1	Conventional Water Analysis	977
10.1.2	Analysis of Water Disinfection By-Products	996
10.1.2.1	Analysis of Bromate and Other Oxyhalides	997
10.1.2.2	Analysis of Haloacetic Acids	1021

10.1.3	Perchlorate Analysis	1024
10.1.4	Analysis of Highly Contaminated Water Samples	1038
10.1.4.1	Seawater Analysis	1041
10.1.4.2	Soil Analysis	1048
10.1.4.3	Air Analysis	1053
10.1.5	Other Environmental Applications	1066
10.2	Ion Chromatography in Power Plant Chemistry	1068
10.2.1	High-Purity Water Analysis	1069
10.2.1.1	Conventional Preconcentration Techniques	1070
10.2.1.2	Large-Volume Direct Injection Techniques	1077
10.2.1.3	RFIC-ESP	1081
10.2.1.4	Capillary Ion Chromatography	1084
10.2.2	Analysis of Conditioned Waters	1085
10.2.3	Cooling Water Analysis	1094
10.2.4	Flue Gas Scrubber Solutions	1106
10.2.5	Analysis of Chemicals	1111
10.3	Ion Chromatography in the Semiconductor Industry	1114
10.3.1	High-Purity Water Analysis	1115
10.3.2	Surface Contaminations	1123
10.3.3	Solvents	1128
10.3.4	Acids, Bases, and Etching Agents	1132
10.3.4.1	Solar Cell Manufacturing	1142
10.3.5	Other Applications	1143
10.4	Ion Chromatography in the Electroplating Industry	1148
10.4.1	Analysis of Inorganic Anions	1149
10.4.2	Analysis of Metal Complexes	1157
10.4.3	Analysis of Organic Acids	1159
10.4.4	Analysis of Inorganic Cations	1161
10.4.5	Analysis of Organic Additives	1162
10.5	Ion Chromatography in the Detergent and Household Product Industry	1175
10.5.1	Detergents	1175
10.5.2	Household Products	1184
10.6	Ion Chromatography in the Food and Beverage Industry	1194
10.6.1	Beverages	1197
10.6.2	Dairy Products	1224
10.6.3	Meat Processing	1233
10.6.4	Baby Food	1237
10.6.5	Groceries and Luxuries	1254
10.6.6	Sweeteners	1264
10.7	Ion Chromatography in the Pharmaceutical Industry	1271
10.7.1	Counterion Analysis	1272
10.7.2	Analysis of Amines	1283
10.7.3	Analysis of Organic Acids	1291
10.7.4	Antibiotics	1295

10.7.5	Ionic Drugs	1311
10.7.6	Assays for Active Pharmaceutical Ingredients and Counterions	1315
10.7.7	Other Pharmaceutical Applications	1318
10.7.8	Biotechnology Applications	1325
10.8	Ion Chromatography in Clinical Chemistry	1336
10.9	Oligosaccharide Analysis of Membrane-Coupled Glycoproteins	1361
10.10	Chemical and Petrochemical Applications	1367
10.10.1	Chemical Applications	1367
10.10.2	Petrochemical Applications	1393
10.10.2.1	Combustion Ion Chromatography	1407
10.10.2.2	Biofuel Applications	1409
10.11	Other Applications	1417
10.12	Sample Preparation and Matrix Problems	1423
10.12.1	Sample Filtration and Preservation	1425
10.12.2	Sample Dilution	1431
10.12.3	Sample Pretreatment Cartridges	1437
10.12.4	Sample Neutralization	1443
10.12.5	Combustion Techniques	1446
10.12.6	Dialysis Techniques	1453
10.12.7	Chemical Modifications of Samples	1455
10.13	Concluding Remarks	1459
	References	1461
	Index	1485