

Contents

Contributors to Vol XLV	vii
Volumes in the Series	xi
Series Editor's Preface	xxv
Preface	xxvii

Chapter 1. Fundamentals of capillary electrophoresis

María Luisa Marina, Angel Ríos, Miguel Valcárcel

1.1	Introduction	1
1.2	Basic Concepts	2
1.2.1	Electrophoretic mobility and electroosmotic flow	2
1.2.2	Migration time, efficiency, and resolution.	4
1.2.3	Experimental variables affecting the electrophoretic resolution.	6
1.3	Instrumentation	11
1.3.1	High-voltage power supply	12
1.3.2	Injection systems	12
1.3.3	Capillaries	14
1.3.4	Detection systems	18
1.4	Separation Modes	19
1.5	Hyphenated Capillary Electrophoretic Techniques.	21
1.6	Field of Application and Trends	23
1.6.1	Role of CE techniques with respect to the analytical potential of other separation techniques	23
1.6.2	Field of application of CE.	24
1.6.3	Trends	27
	References	28

Chapter 2. Separation modes in capillary electrophoresis

María Ángeles García, María Luisa Marina, Angel Ríos, Miguel Valcárcel

2.1	Introduction	31
2.2	Separation Modes in CE Based on Pure Electrophoretic Principles	34

Contents

2.2.1	Capillary zone electrophoresis	34
2.2.2	Capillary gel electrophoresis	45
2.2.3	Capillary isoelectric focusing	50
2.2.4	Capillary isotachopheresis	56
2.3	Separation Modes in CE Combining Electrophoretic and Chromatographic Principles	60
2.3.1	Electrokinetic chromatography	60
2.3.2	Capillary electrochromatography	95
2.4	Nonaqueous Capillary Electrophoresis.	108
2.4.1	Introduction	108
2.4.2	Electrolytic solutions	110
2.4.3	Analyte-additive interactions.	112
2.4.4	Methodological aspects.	114
2.4.5	Applications.	116
2.5	Selection of the CE Mode and Separation Conditions.	118
	Acknowledgments.	118
	References	122

Chapter 3. On-line sample preconcentration techniques in capillary electrophoresis

Hong Chen, Shigeru Terabe

3.1	Introduction	135
3.2	Sample Stacking Technique.	137
3.2.1	Basic principle of stacking	137
3.2.2	Normal stacking mode	139
3.2.3	Large-volume sample stacking	140
3.2.4	Electrokinetic injection	142
3.2.5	pH-mediated stacking	143
3.2.6	Sample stacking of analytes in micellar electrokinetic chromatography	143
3.2.7	Applications of sample stacking	147
3.3	ITP Preconcentration	147
3.3.1	Principle of ITP	147
3.3.2	Normal ITP-zone electrophoresis mode	150
3.3.3	Transient ITP mode	153
3.3.4	Applications of ITP preconcentration technique.	154

Contents

3.4	Dynamic pH Junction Preconcentration	154
3.4.1	Principle of dynamic pH junction.	154
3.4.2	Applications of dynamic pH junction	158
3.5	Sweeping.	159
3.5.1	Basic theory of sweeping	159
3.5.2	Selective exhaustive injection-sweeping	163
3.5.3	Dynamic pH junction sweeping	164
3.5.4	Applications of sweeping	165
	References	166

Chapter 4. Coupling continuous flow systems to capillary electrophoresis

Bartolomé M. Simonet, Angel Ríos, Miguel Valcárcel

4.1	Introduction	173
4.2	Role of CFSs	174
4.3	Interfaces for Coupling Flow Systems to CE	175
4.3.1	CFSs to homemade CE arrangements	176
4.3.2	Coupling flow systems to commercial CE equipments	179
4.3.3	Flow injection-CE integrated microchips	182
4.4	Sample Injection and On-line Preparation.	185
4.4.1	On-line clean-up and preconcentration.	185
4.4.2	Online extraction/filtering	189
4.4.3	On-line dialysis	190
4.4.4	On-line membrane and hollow fibre system	192
4.4.5	On-line gas extraction and gas diffusion.	194
4.4.6	On-line sample treatment and separations performed in auxiliary equipments	194
4.5	Automatic Calibration in CE through CFS	200
4.6	Screening Flow Units-CE Analysis Arrangements	204
4.7	Analytical Applications by CFS-CE	207
4.7.1	Biomedical and pharmaceutical analysis.	207
4.7.2	Environmental analysis	213
4.7.3	Food analysis.	216
4.8	Future Prospects.	219
	Acknowledgements	220
	References	220

Contents

Chapter 5. UV-Vis absorbance detection in capillary electrophoresis

Antonio L. Crego, Maria Luisa Marina

5.1	Introduction	225
5.2	UV-Vis Absorbance Detection in CE	231
5.2.1	Basic principles	231
5.2.2	Detector design	232
5.2.3	Derivatization and complexation procedures	261
5.2.4	Indirect absorbance detection	269
5.3	Thermo-optical Detection in CE	278
5.3.1	Thermal lens detection	278
5.3.2	Photoacoustic detection	287
5.4	UV-Vis Absorbance Detection in Microchip electrophoresis	291
	Acknowledgments	296
	References	296

Chapter 6. Fluorescence detection in capillary electrophoresis

Maria Teresa Veledo, Pilar Lara-Quintanar, Mercedes de Frutos,
Jose Carlos Díez-Masa

6.1	Introduction	305
6.1.1	Objectives and outline of this chapter	305
6.1.2	Basic concepts	306
6.2	Instrumental Setup	307
6.2.1	Light sources	307
6.2.2	Optical train for LIF	310
6.2.3	Light measuring devices for LIF	314
6.3	Derivatization Methods	320
6.3.1	Pre-capillary derivatization	321
6.3.2	On-capillary derivatization	326
6.3.3	Post-capillary derivatization	328
6.3.4	Protein detection with and without derivatization	329
6.4	Miniaturized Fluorescence Detection for Microchips	335
6.4.1	On-chip fluorescence detection	340
6.4.2	Miniaturized fluorescence detection	343

Contents

6.5	Indirect Fluorescence Detection.	347
6.5.1	Background concepts: transfer ratio (TR) and dynamic reserve (DR)	347
6.5.2	Choice of the background electrolyte (BGE): types of electrolyte additives used in indirect fluorescence detection	349
6.5.3	Direct versus indirect fluorescence detection	351
6.5.4	Applications of indirect fluorescence detection	351
6.6	Conclusions and Future Trends.	353
6.6.1	Multiphoton fluorescence detection	357
6.6.2	Wavelength-resolved LIF detection	359
6.6.3	Time-resolved LIF	361
6.6.4	New approaches to fluorescent labeling of proteins at low concentrations.	363
6.7	Selected Applications.	363
	Acknowledgments.	364
	References	364

Chapter 7. Novel optical detection techniques in CE based on phosphorescence or chemiluminescence

Jacobus Kuijt, Freek Ariese, Cees Gooijer

7.1	Introduction	375
7.2	Phosphorescence Detection in CE	376
7.2.1	Introduction	376
7.2.2	Basic features of phosphorescence	377
7.2.3	Coupling of phosphorescence detection to CE.	379
7.2.4	Applications of CE-phosphorescence	380
7.2.5	Concluding remarks on CE-phosphorescence	385
7.3	Chemiluminescence Detection in CE.	388
7.3.1	Introduction	388
7.3.2	Development of CL detection in CE	388
7.3.3	CL reactions	389
7.3.4	Post-capillary CL reactors	394
7.3.5	Applications of CE-CL.	396
7.3.6	Concluding remarks on CE-CL	407
	References	408

Contents

Chapter 8. Electrochemical detection in capillary electrophoresis

Kim M. Hanson, Theron J. Pappas, Lisa A. Holland

8.1	Introduction	413
8.2	Modes of EC Detection	414
8.2.1	Amperometry	414
8.2.2	Voltammetry	419
8.2.3	Conductivity	421
8.2.4	Potentiometry	422
8.3	Decoupling	422
8.4	Applications	424
8.4.1	Neurochemistry	425
8.4.2	Biomarkers	427
8.4.3	Physiological activity	428
8.4.4	Environmental monitoring	428
8.5	Conclusions and Future Prospects	430
	Acknowledgments	431
	References	431

Chapter 9. Mass spectrometry detection in capillary electrophoresis

Carolina Simó, Alejandro Cifuentes

9.1	Introduction	441
9.2	Principles and Instrumentation	442
9.2.1	Electrospray ionization	443
9.2.2	Mass analyzers	452
9.2.3	CE-MS compatibility	453
9.2.4	Chip-based CE-MS	477
9.3	Applications	481
9.3.1	Proteins and peptides	481
9.3.2	Drugs and metabolites	487
9.3.3	Pesticides	494
9.3.4	Other compounds	498
9.4	Future Outlook	504
	Acknowledgments	505
	References	505

Contents

Chapter 10. Inductively coupled plasma-mass spectrometry for specific detection in capillary electrophoresis

Gloria Álvarez Llamas, M^a del Rosario Fernández de la Campa, Elisa Blanco González, Alfredo Sanz Medel

10.1	The Inductively Coupled Plasma-mass Spectrometry (ICP-MS) as a specific atomic detector	519
10.1.1	ICP-MS fundamentals	519
10.1.2	ICP-MS as detection system in hyphenated techniques	522
10.2	Interfacing CE to ICP-MS: Potentials and Limitations	524
10.3	CE-ICP-MS Coupling via Nebulisation	525
10.3.1	The interface: key to success	525
10.3.2	Considerations about sensitivity/detection limits in CE-ICP-MS	529
10.3.3	The importance of the selected nebuliser in CE-ICP-MS couplings	530
10.4	CE-ICP-MS Coupling via Volatile Species generation	545
10.4.1	Advantages of volatile species generation in CE-ICP couplings	546
10.4.2	Interface designs based on VSG	546
10.5	Strategies to Improve Sensitivity in CE-ICP-MS Coupling	548
10.6	Some Selected Contributions and Applications	550
10.7	Conclusions and Future Prospects	552
	References	552

Chapter 11. Vibrational spectroscopic detection in capillary electrophoresis (CE)

Stephen Kulka, Bernhard Lendl

11.1	Introduction	557
11.2	IR Spectroscopy	558
11.2.1	On-line MIR spectroscopic detection in CE	558
11.2.2	FTIR spectroscopic detection in CE after solvent elimination	563

Contents

11.3	Raman Spectroscopy	566
11.3.1	Raman scattering in CE.	567
11.3.2	Surface-enhanced Raman scattering in CE.	573
	References	580

Chapter 12. Coupling nuclear magnetic resonance to capillary electrophoresis

Dimuthu A. Jayawickrama, Jonathan V. Sweedler

12.1	Introduction	583
12.1.1	NMR sensitivity improvements	584
12.1.2	CE and NMR hyphenation.	585
12.2	CE–NMR Hyphenation	586
12.2.1	The size-matched NMR probe	586
12.2.2	Interfacing CE to NMR	590
12.2.3	CE–NMR measurements	592
12.3	Applications.	597
12.3.1	CZE–NMR.	598
12.3.2	Sample concentration methods.	600
12.3.3	Diagnostic capabilities of CE/cITP–NMR	607
12.4	Conclusions and Future Directions	613
	References	614

Chapter 13. Chiral analysis by capillary electrophoresis

Carmen García-Ruiz, Maria Luisa Marina

13.1	Introduction	617
13.2	Separation Modes in CE for Chiral Analysis	622
13.2.1	Electrokinetic chromatography.	623
13.2.2	Capillary electrochromatography	639
13.2.3	Non-aqueous capillary electrophoresis	640
13.3	Improving the Detection Sensitivity for Chiral Analysis by CE	645
13.3.1	On-line preconcentration techniques employed in chiral analysis by CE.	647
13.3.2	Alternative detection systems to on-line UV detection employed in chiral analysis by CE	649

Contents

13.4	Applications of Chiral Analysis by CE	656
13.4.1	Pharmaceutical and biomedical analysis	656
13.4.2	Environmental analysis	668
13.4.3	Food analysis	679
13.4.4	Other applications	686
13.5	Chiral Analysis by Microchip Electrophoresis	687
13.6	Future Perspectives.	689
	Acknowledgments	692
	References	692

Chapter 14. Electrochemical detection in capillary electrophoresis on microchips

Antonio Javier Blasco, Alberto Escarpa

14.1	Introduction	703
14.2	Principles and Designs of Capillary Electrophoresis with Electrochemical Detection Microsystems	707
14.2.1	Materials and microfabrication techniques	708
14.2.2	Fluids moving: principles of injection	713
14.2.3	Detection implementation	716
14.2.4	Electrode materials	730
14.2.5	Modes of detection	734
14.3	Selected Analytical Applications	741
14.3.1	Neurotransmitters and related compounds	741
14.3.2	Bioanalytical and clinical	742
14.3.3	Environmental	746
14.3.4	Conductimetry	749
14.4	Conclusions and Future Direction	752
	Acknowledgements	754
	References	754

List of Abbreviations	759
Subject Index	761