

Contents

1 SFC and SFE: An Introduction for Novices	
BERND WENCLAWIAK	1
2 Physico-chemical Principles of Supercritical Fluid Separation Processes	
GERHARD M. SCHNEIDER	9
2.1 Introduction	9
2.2 Physico-chemical Properties of Pure Supercritical Solvents	10
2.2.1 Thermodynamic Properties	10
2.2.2 Dielectric Properties	10
2.2.3 Transport Properties	12
2.3 Phase Equilibria of Fluid Mixtures	13
2.3.1 Phase-Theoretical Aspects	13
2.3.2 Classification of Binary Critical Phase Behavior by "Families"	14
2.3.3 Ternary Systems	16
2.3.4 Quaternary Systems	19
2.3.5 Solubility of Solids in Supercritical Solvents	21
2.3.6 Isothermal Pressure (Concentration) Phase Diagrams	21
2.3.7 Calculation and Correlation of Fluid Phase Equilibria	24
2.4 Physico-chemical Applications of SFC	26
2.4.1 Capacity Ratios	26
2.4.2 Diffusion Coefficients	28
References	30
3 Basic Principles of Analytical Supercritical Fluid Extraction	
JERRY W. KING and JOHN E. FRANCE	32
3.1 The Development of Analytical SFE	32
3.1.1 Sample Preparation in Analytical Chemistry	32
3.1.2 Utilization of Supercritical Fluids in Analytical-Scale Extractions	33
3.1.3 Features of Analytical SFE	33

3.2	Fluid Properties in SFE	34
3.2.1	Selection of the Supercritical Fluid	34
3.2.2	Unique Properties of Supercritical Fluid Carbon Dioxide	36
3.2.3	The Use of Cosolvents in SFE	37
3.3	Optimizing Experimental Conditions for Analytical SFE	39
3.3.1	Objectives of the Extraction	39
3.3.2	Critical Parameters Pertinent to SFE	41
3.3.3	A Theoretical Approach for Optimizing SFE	42
3.4	The Relevance of SFC-Derived Data to Analytical SFE	43
3.4.1	Relevant Measurements by SFC	44
3.4.2	Implications for SFE	45
3.5	The Practice of Analytical SFE	46
3.5.1	Equipment Requirements	46
3.5.2	Experimental Considerations in Analytical SFE ..	49
3.6	Sample Matrix Effects in SFE	51
3.6.1	Physical Matrix Effects	52
3.6.2	Chemical Changes in the Sample Matrix	52
3.6.3	Impact of Matrix on Extraction Kinetics	53
3.7	Problems and Future Research Needs in Analytical SFE	55
	References	57

4 Coupled Supercritical Fluid Extraction-Capillary Gas Chromatography (SFE-GC)

STEVEN B. HAWTHORNE	61
4.1 Introduction	61
4.2 Performing SFE-GC	61
4.2.1 Instrumentation and Methods	61
4.2.2 Fluids and Extraction Conditions Used for SFE-GC	64
4.3 Abilities and Limitations of Split and On-Column SFE-GC	65
4.3.1 Chromatographic Peak Shapes Obtained Using SFE-GC	65
4.3.2 Quantitation Using SFE-GC	67
4.3.3 Speed of SFE-GC Analyses	67
4.3.4 Sensitivity and Sample Sizes	68
4.3.5 Sample Types and Matrix Considerations	70
4.4 Summary	72
References	72

5 Gradients in SFC

ERNST KLESPIER and FRANZ P. SCHMITZ	74
5.1 Overview	74
5.2 Temperature Gradients	79
5.3 Pressure Gradients	81
5.4 Density Gradients	87
5.5 Velocity Gradients	94
5.6 References	97

6 Injection Techniques in SFC

TYGE GREIBROKK	100
6.1 Introduction	100
6.2 The Physical State of the Sample	100
6.3 Introduction of Supercritical Fluid Extracts	100
6.4 Introducing a Solution	101
6.5 Peak Focusing	102
6.6 Direct Injection	103
6.7 Open Split (Dynamic Split) Injection	103
6.8 Timed Split Injection	105
6.9 Solvent Effects on Peak Shape	106
6.10 Solvent Venting with a Precolumn	107
6.11 Solvent Backflush	109
6.12 Solvent Venting with Gas Purging	111
6.13 Sample Losses in the Injector	114
References	115

7 Stationary Phases for Packed Column**Supercritical Fluid Chromatography**

COLIN F. POOLE, JOHN W. OUDSEMA, THOMAS A. DEAN, and SALWA K. POOLE	116
7.1 Introduction	116
7.2 Physical Properties of Column Packings	116
7.3 Influence of Substrate Morphology on the Properties of Chemically Bonded Phases in SFC ..	121
7.4 Influence of Surface Heterogeneity on the Properties of Chemically Bonded Phases	122
7.4.1 Chemical Interactions with Silanol Groups	122
7.4.2 Deactivation of Silanol Groups with Mobile Phase Modifiers	124

7.4.3	Shielding of Silanol Groups by Polymer Encapsulation	126
7.5	Macroporous Polymeric Packings	127
7.6	Column Packings Used for Special Applications ..	127
7.7	Conclusions	131
	References	132

8 Enantiomer Separation by Capillary Supercritical Fluid Chromatography

	MICHAEL SCHLEIMER and VOLKER SCHURIG	134
8.1	Introduction	134
8.2	General Aspects	135
8.2.1	Temperature	135
8.2.2	Speed of Analysis and Efficiency	136
8.2.3	Mobile Phase	138
8.2.4	Column Loadability	139
8.3	Packed Column SFC	140
8.4	Open Tubular Column SFC	140
8.5	Conclusion	146
	References	149

9 Supercritical Fluid Chromatography/ Mass Spectrometry

	J. DAVID PINKSTON	151
9.1	Introduction	151
9.2	Early Investigations of SFC/MS	151
9.3	SFC/MS Using Direct Introduction Interfaces ...	152
9.3.1	Flow Restriction	153
9.3.2	Ionization Methods	154
9.3.2.1	Chemical Ionization	154
9.3.2.2	Electron Ionization and Charge Exchange	155
9.3.2.3	Secondary Ion Mass Spectrometry	156
9.3.3	Type of Mass Analyzer	157
9.3.3.1	DFI SFC/MS Using Quadrupole Mass Spectrometers	157
9.3.3.2	DFI SFC/MS Using Double-Focussing Sector Mass Spectrometers	158
9.3.3.3	DFI SFC/MS Using Fourier Transform Mass Spectrometers	158
9.4	SFC/MS Using High-Flow-Rate Interfaces	161
9.4.1	SFC/MS Using the Moving Belt Interface	162
9.4.2	SFC/MS Using the Particle Beam Interface	163

9.4.3	Off-line SFC/MS	164
9.4.4	SFC/MS Using Direct Introduction of Split Effluents	164
9.4.5	SFC/MS Using Post-Expansion Splitting	165
9.4.6	SFC/MS Using the Thermospray Interface	170
9.5	Supercritical Fluid Injection/Mass Spectrometry ..	172
9.6	Conclusion	174
	References	175

10 Supercritical Fluid Chromatography with FT-IR Detection

	LARRY T. TAYLOR and ELIZABETH M. CALVEY	178
10.1	Introduction	178
10.2	Flow Cell Approach	178
10.3	Solvent Elimination Approach	184
10.4	Summary	188
	References	188

11 Supersonic Jet Spectroscopy with Supercritical Fluids

	CHUNG HANG SIN, STEVEN R. GOATES, MILTON L. LEE, and DAVID M. LUBMAN	190
11.1	Introduction	190
11.2	Supersonic Jet Spectroscopy	191
11.2.1	Principles of Supersonic Expansions	191
11.2.2	Spectroscopic Methods for Detection	192
11.3	High Pressure Fluid Injection for Nonvolatile Samples	193
11.3.1	Experimental	193
11.3.2	Supercritical Fluid Injection	194
11.3.3	High Pressure Liquid Injection	196
11.4	Supercritical Fluid Chromatography and Supersonic Jet Spectroscopy	197
11.4.1	Experimental	198
11.4.2	The Interfaces	199
11.5	Conclusions	202
	References	202

	Basic References Analytical Scale SFC/SFE	203
--	--	------------

	Recommended Literature	207
--	-------------------------------------	------------

	Subject Index	211
--	----------------------------	------------