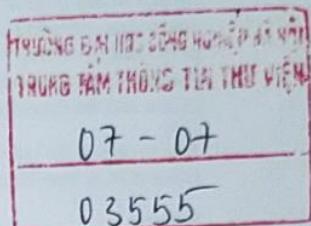


# THE APPLICATION OF GREEN SOLVENTS IN SEPARATION PROCESSES

EDITED BY  
FRANCISCO PENA-PEREIRA  
MAREK TOBISZEWSKI

# The Application of Green Solvents in Separation Processes



Edited by

**Francisco Pena-Pereira**

Campus As Lagoas-Marcosende s/n, Vigo, Spain

**Marek Tobiszewski**

Gdańsk University of Technology, Gdańsk, Poland



GIFT OF THE ASIA FOUNDATION  
NOT FOR RE-SALE

QUÀ TẶNG CỦA QUÝ CHÂU Á  
KHÔNG ĐƯỢC BÁN LẠI



[elsevier.com](http://elsevier.com)

# Contents

List of Contributors	xiii
----------------------	------

## Section I Introduction

### 1. Initial Considerations

*Francisco Pena-Pereira and Marek Tobiszewski*

1.1 The Need to Use Solvents	3
1.2 Traditional Solvents	4
1.3 Green Solvents	7
1.4 Greener Extraction Techniques	10
1.5 Green Sampling and Sample Preparation	11
1.6 Solvents for Analytical Separations	12
1.7 Concluding Remarks	12
Acknowledgments	13
References	13

## Section II Green Solvents

### 2. Water as the First Choice Green Solvent

*Kari Hartonen and Marja-Liisa Riekkola*

2.1 Introduction	19
2.1.1 Why to Use Water as a Solvent?	19
2.1.2 Water—The Most Green Choice	20
2.2 Solvent Properties of Water	20
2.3 Separation Techniques Utilizing Water	23
2.3.1 Extraction at HTs	23
2.3.2 Liquid Chromatography at HTs	26
2.4 Recent Applications in Extraction	28
2.4.1 Biorefinery (Chemicals From Biomass)	28
2.4.2 Bioactive Compounds	31
2.4.3 Energy Technology	34
2.4.4 Amino Acids—Searching for Extraterrestrial Life	36
2.4.5 Essential Oils	36
2.4.6 Other Applications	37

<b>2.5 Recent Applications Carried out by High-Temperature Chromatography</b>	39
2.5.1 Pharmaceuticals	39
2.5.2 Cosmetics	42
2.5.3 Food	43
2.5.4 Other Applications	44
<b>2.6 Conclusions and Future Trends</b>	46
<b>References</b>	47
<b>3. A Systematic Approach to Green Solvent Selection, Design, and Verification</b>	
<i>Deenesh K. Babi, Kusuma Kulajanpeng, Ananya Tongrod, Alisa Kammafoo, Khavinet Lourvanij and Rafiqul Gani</i>	
<b>3.1 Introduction</b>	57
<b>3.2 Solvent Selection and Design</b>	62
3.2.1 Problem Definition	62
3.2.2 Computer-Aided Molecular Design Concept	64
3.2.3 CAMD Technique Applied to Solvent Selection-Design	66
3.2.4 Separation Process Selection	67
3.2.5 Process Modeling	68
3.2.6 Property Modeling	69
<b>3.3 Application</b>	71
3.3.1 Vapor-Liquid Separation Using Organic Solvent	71
3.3.2 Vapor-Liquid Separation Using Ionic Liquids	74
3.3.3 Liquid-Liquid Separation	80
3.3.4 Solid-Liquid Separation	84
<b>3.4 Conclusions</b>	87
<b>References</b>	87
<b>4. Bio-Based Molecular Solvents</b>	
<i>J. Vovers, K.H. Smith and G.W. Stevens</i>	
<b>4.1 Introduction to Bio-Based Solvents and Solvent Extraction</b>	91
4.1.1 Bio-Based Solvents	91
4.1.2 Solvent Extraction	92
<b>4.2 Bio-Based Solvent Drivers</b>	93
4.2.1 Regulatory Pressures	94
4.2.2 Environmental and Health Concerns	94
4.2.3 Economic Drivers	95
<b>4.3 Selecting Solvents for Solvent Extraction Applications</b>	96
4.3.1 Green Solvent Selection Guides	96
4.3.2 Solvents and Their Characteristics	98
<b>4.4 Bio-Based Solvents</b>	99
4.4.1 Renewable Versions of Conventional Solvents	102
4.4.2 Glycerol Derivatives	103
4.4.3 Terpenes	104

4.4.4 Ethers	106
4.4.5 Ethyl Lactate	106
<b>4.5 Conclusions</b>	107
<b>References</b>	107
<b>5. Supramolecular Solvents for Green Chemistry</b>	
<i>Carmen Caballo, María D. Sicilia and Soledad Rubio</i>	
<b>5.1 Introduction</b>	111
<b>5.2 Synthesis of Supramolecular Solvents</b>	112
5.2.1 Self-Assembly and Coacervation of Amphiphiles	113
5.2.2 Strategies to Induce Coacervation	115
<b>5.3 Tailoring Composition and Nanostructure of Supramolecular Solvents</b>	119
5.3.1 Tailoring SUPRAS Composition	119
5.3.2 Tailoring SUPRAS Nanostructures	123
<b>5.4 Solubilization of Solutes in Supramolecular Solvents</b>	125
<b>5.5 Applications</b>	126
<b>5.6 Conclusions</b>	132
<b>Acknowledgments</b>	132
<b>References</b>	133
<b>6. Ionic Liquids, Switchable Solvents, and Eutectic Mixtures</b>	
<i>Pablo Domínguez de María</i>	
<b>6.1 Motivation for Research in Neoteric Solvents: Ionic Liquids, Switchable Solvents, and Deep Eutectic Solvents</b>	139
<b>6.2 Recent Trends in Using ILs for Separation Processes</b>	142
<b>6.3 Recent Trends in Using DESs for Separation Processes</b>	143
<b>6.4 Recent Trends in Using Switchable Solvents for Separation Processes</b>	147
<b>6.5 Concluding Remarks</b>	149
<b>References</b>	149
<b>7. Supercritical Fluids and Gas-Expanded Liquids</b>	
<i>Larissa P. Cunico and Charlotta Turner</i>	
<b>7.1 Introduction</b>	155
<b>7.2 Physicochemical Properties of SCFs</b>	159
7.2.1 Density	160
7.2.2 Viscosity and Mass Transfer	161
7.2.3 Dielectric Properties	164
<b>7.3 Physicochemical Properties of GXLs</b>	166
7.3.1 Density	167
7.3.2 Compressibility	170
7.3.3 Viscosity and Mass Transfer	172
7.3.4 Dielectric Properties	174

<b>7.4 Phase Equilibria and Phase Diagrams</b>	177
7.4.1 Introduction to Phase Equilibria—SCFs and GXLs	177
7.4.2 PV and PT Phase Diagrams	182
7.4.3 Thermodynamic Modeling of SCFs and GXLs Properties	185
<b>7.5 Solubility of Compounds in SCFs and GXLs</b>	189
<b>7.6 Experimental Procedures</b>	194
<b>7.7 Examples of Applications</b>	197
<b>7.8 Greenness of SCFs and GXLs</b>	199
<b>7.9 Conclusions</b>	201
<b>List of Abbreviations</b>	201
<b>Acknowledgments</b>	201
<b>References</b>	202

## Section III

### Green Extraction Techniques

#### 8. Green-Membrane Extraction

*Pavel Kubáň and Petr Boček*

<b>8.1 Lead-In</b>	217
<b>8.2 Green-Membrane Classification</b>	222
8.2.1 Porous vs Nonporous Membranes	222
8.2.2 One-phase vs Multiple-phase Membrane Extractions	224
<b>8.3 Porous Membrane Extractions</b>	225
8.3.1 Porous Membranes and Their Classification	225
8.3.2 Driving Forces and Principles in Porous Membrane Extractions	226
<b>8.4 Nonporous Membrane Extractions</b>	229
8.4.1 Supported Liquid Membranes	229
8.4.2 Polymer Inclusion Membranes	234
8.4.3 Polymeric Membranes	240
8.4.4 Bulk Liquid and Other Unique Membranes	242
<b>8.5 Conclusions</b>	244
<b>Acknowledgments</b>	245
<b>References</b>	245

#### 9. Microwaves for Greener Extraction

*Inmaculada de la Calle and Marta Costas-Rodríguez*

<b>9.1 Introduction</b>	253
<b>9.2 Types of Microwave Systems</b>	255
<b>9.3 Experimental Variables Affecting Microwave-Assisted Extraction</b>	257
9.3.1 Solvent Properties and Solvent-to-Solid Ratio	257
9.3.2 Nature of the Matrix	257
9.3.3 Stirring	258
9.3.4 Microwave Power and Temperature	258
9.3.5 Extraction Time and Cycles	259

9.4	Green Aspects of Microwave-Assisted Extraction	259
9.5	Standardized Procedures Using Microwave-Accelerated Extraction Techniques	261
9.6	Selected Applications Using Microwaves	265
9.6.1	Classical Microwave-Assisted Extraction	265
9.6.2	Microwave-Assisted Extraction Using Green Solvents	266
9.6.3	Microwave-Assisted Preconcentration Techniques	281
9.6.4	Combination of Microwave Energy With Other Preconcentration Techniques	284
9.6.5	MAE and Separate-Step Preconcentration Outside the Microwave	287
9.6.6	Cloud-Point Extraction and Microwave-Assisted Back-Extraction	289
9.7	Conclusions	289
	Acknowledgments	290
	References	290
10.	<b>Ultrasound-Assisted Extraction</b>	
	<i>Małgorzata Rutkowska, Jacek Namieśnik and Piotr Konieczka</i>	
10.1	Introduction	301
10.2	Ultrasound Principles	301
10.2.1	Physical Parameters Affecting UAE	304
10.2.2	Medium Parameters Affecting UAE	306
10.3	Kinetics of Ultrasound-Assisted Extraction	307
10.4	Typical Ultrasound Devices Used in Analytical Laboratories	307
10.4.1	Ultrasonic Bath	310
10.4.2	The Ultrasonic Probe	311
10.5	Application of UAE	313
10.6	Conclusion	318
	References	319
11.	<b>Environmentally Benign Supercritical Fluid Extraction</b>	
	<i>Marcelo M.R. de Melo, Inês Portugal, Armando J.D. Silvestre and Carlos M. Silva</i>	
11.1	Introduction	325
11.2	Supercritical Fluid Extraction Technology	326
11.2.1	Supercritical Fluids	326
11.2.2	Operating Conditions	327
11.2.3	Typical Layouts of Supercritical Fluid Extraction Units	329
11.3	Process and Natural Products Improvements Based on SFE Technology	331
11.3.1	SFE Suitability for Intensification and Integration of Processes	331
11.3.2	Enhancement of Vegetal Extracts By SFE	333
11.3.3	Advantages of SFE in Food Processing	336

<b>11.4 Prospective Applications of Supercritical Fluids at Industrial Scale</b>	339
11.4.1 Nutraceutical and Medicinal Formulations	339
11.4.2 Supercritical CO <sub>2</sub> as a Breakthrough Technology for the Pulp and Paper Industry	340
11.4.3 Defatting Animal Crude Leather, Wool, and Related Products	341
11.4.4 Violent CO <sub>2</sub> Decompression for Mechanical Grinding	342
11.4.5 Power (Co)Generation Opportunities Through SC-CO <sub>2</sub>	342
<b>11.5 Final Remarks</b>	343
<b>Acknowledgments</b>	343
<b>References</b>	343
 <b>12. Surfactant-Mediated Extraction Techniques</b>	
<i>Evangelos K. Paleologos</i>	
<b>12.1 Introduction</b>	349
<b>12.2 Cloud Point and Coacervate Extraction</b>	349
12.2.1 Beneficial Features of CPE	350
12.2.2 Application of CPE on Metal Preconcentration and Determination	350
12.2.3 Application of Ultrasounds or Microwaves on Surfactant Systems	354
12.2.4 Application of CPE on Solid Samples	355
12.2.5 Application of CPE on Electroanalysis	356
12.2.6 Application of CPE for the Extraction of Organic Compounds	356
<b>12.3 Combination of Surfactants With Other Techniques and Substances</b>	358
12.3.1 Surfactants and Ionic Liquids	358
12.3.2 Surfactants and Microextraction Techniques	359
<b>12.4 Nonanalytical Application of Surfactants</b>	368
<b>12.5 Conclusions</b>	370
<b>References</b>	370

## Section IV **Green Sampling and Sample Preparation Techniques**

### 13. Green Sample Collection

*Mariusz Marć, Monika Śmiełowska and Bożena Zabiegała*

<b>13.1 Introduction</b>	379
<b>13.2 Green Sample Collection Techniques in Air Quality Monitoring</b>	382
13.2.1 General Information—Theory and Basic Design Principles of Sampling Devices to be Used in Gaseous Media	382

13.2.2	Passive Sampling Technique	384
13.2.3	Active/Dynamic Sampling Technique	387
13.2.4	Commonly Applied Passive Sampling Devices in the Field of Air Quality Monitoring	389
13.2.5	Summary and Green Aspects of the Use of Sampling Techniques in Air Quality Monitoring	392
13.3	<b>Application of Green Sampling Techniques in the Field of Aquatic Medium Quality Monitoring</b>	393
13.3.1	General Information—Theory and Basic Design Principles of Passive Sampling Devices to be Used in Liquid Media	393
13.3.2	Effects of Environmental Factors on the Working Parameters of Passive Sampling Devices	397
13.3.3	Commonly Applied Passive Sampling Devices in the Field of Monitoring the Quality of Water Environment	401
13.3.4	Summary and Green Aspects of the Use of Sampling Techniques in Water Quality Assessment	406
	<b>Acknowledgment</b>	407
	<b>References</b>	407

## 14. Microextraction and Solventless Techniques

*Seyed Mohammad Majedi and Hian Kee Lee*

14.1	<b>Introduction</b>	415
14.2	<b>Sorption-Based Microextraction Techniques</b>	416
14.2.1	Solid-Phase Microextraction	416
14.2.2	Needle Trap Device	418
14.2.3	Onsite and In Vivo SPME	420
14.2.4	Stir-Bar Sorptive Extraction	422
14.2.5	Variants of SPE	425
14.2.6	New Sorbent Materials for SBSE and SPE	427
14.3	<b>LPME Techniques</b>	429
14.3.1	Single-Drop Microextraction (SDME)	429
14.3.2	Hollow Fiber LPME	430
14.3.3	Electromembrane Extraction	431
14.3.4	Micellar-Mediated Extraction	432
14.3.5	Dispersive Liquid–Liquid Microextraction	433
14.4	<b>Conclusion</b>	435
	<b>References</b>	436

## Section V Green Analytical Separations

### 15. Green Gas and Liquid Capillary Chromatography

*Heba Shaaban, Ahmed Mostafa and Tadeusz Górecki*

15.1	<b>Introduction</b>	453
15.2	<b>Green Aspects of Liquid Chromatography</b>	455

15.2.1	Replacement of Hazardous Solvents	455
15.2.2	Reduction of Organic Solvent Consumption	459
15.2.3	Miniaturization	460
15.2.4	Multidimensional Liquid Chromatography	466
<b>15.3</b>	<b>Green Aspects of Gas Chromatography</b>	<b>467</b>
15.3.1	Selection of an Appropriate Carrier Gas	467
15.3.2	Speeding up GC Analysis	469
15.3.3	Multidimensional Gas Chromatography	472
15.3.4	Other Approaches	473
<b>15.4</b>	<b>Conclusions</b>	<b>474</b>
	<b>References</b>	<b>475</b>
<b>16.</b>	<b>Supercritical Fluid Chromatography</b>	
	<i>Udi Jumhawan and Takeshi Bamba</i>	
16.1	Introduction	483
16.2	Supercritical Fluid Carbon Dioxide as Potent Green Solvent	484
16.3	Supercritical Fluid Chromatography as a New Approach in "Omics" Technology	485
16.4	The Evolution of SFC Technology	488
16.5	Detector and Ionization Mode in SFC	491
16.6	Supercritical Fluid Chromatography/Mass Spectrometry	495
16.7	Application of Supercritical Fluid Chromatography	500
16.7.1	Food Science	500
16.7.2	Food Safety and Quality	501
16.7.3	Early Disease Diagnosis and Biomarker Discovery	505
16.8	Conclusions and Future Perspective	508
	<b>References</b>	<b>510</b>
<b>17.</b>	<b>Capillary Electrophoresis as a Green Alternative Separation Technique</b>	
	<i>Alain Wuethrich and Joselito P. Quirino</i>	
17.1	Chromatographic and Electrokinetic Separations	517
17.1.1	Chromatographic Separations	517
17.1.2	Electrokinetic Separations	524
17.2	The Greenness of CE	528
17.3	Conclusion	530
	<b>Acknowledgment</b>	<b>531</b>
	<b>References</b>	<b>531</b>
	<b>Index</b>	<b>533</b>