Handbook of Green Analytical Chemistry

Edited by

MIGUEL DE LA GUARDIA
Department of Analytical Chemistry, University of Valencia, Valencia, Spain

SALVADOR GARRIGUES
Department of Analytical Chemistry, University of Valencia, Valencia, Spain

WILEY

A John Wiley & Sons, Ltd., Publication

Contents

List of Contributors xv
Preface xix

Section I: Concepts **1**

1 The Concept of Green Analytical Chemistry **3**
Miguel de la Guardia and Salvador Garrigues

1.1 Green Analytical Chemistry in the frame of Green Chemistry 3
1.2 Green Analytical Chemistry versus Analytical Chemistry 7
1.3 The ethical compromise of sustainability 9
1.4 The business opportunities of clean methods 11
1.5 The attitudes of the scientific community 12
References 14

2 Education in Green Analytical Chemistry **17**
Miguel de la Guardia and Salvador Garrigues

2.1 The structure of the Analytical Chemistry paradigm 17
2.2 The social perception of Analytical Chemistry 20
2.3 Teaching Analytical Chemistry 21
2.4 Teaching Green Analytical Chemistry 25
2.5 From the bench to the real world 26
2.6 Making sustainable professionals for the future 28
References 29

3 Green Analytical Laboratory Experiments **31**
Suparna Dutta and Arabinda K. Das

3.1 Greening the university laboratories 31
3.2 Green laboratory experiments 33
3.2.1 Green methods for sample pretreatment 33
3.2.2 Green separation using liquid-liquid, solid-phase and solventless extractions 37
3.2.3 Green alternatives for chemical reactions 42
3.2.4 Green spectroscopy 45
3.3 The place of Green Analytical Chemistry in the future of our laboratories 52
References 52

4 Publishing in Green Analytical Chemistry 55
Salvador Garrigues and Miguel de la Guardia

4.1 A bibliometric study of the literature in Green Analytical Chemistry 56
4.2 Milestones of the literature on Green Analytical Chemistry 57
4.3 The need for powerful keywords 61
4.4 A new attitude of authors faced with green parameters 62
4.5 A proposal for editors and reviewers 64
4.6 The future starts now 65
References 66

Section II: The Analytical Process 67

5 Greening Sampling Techniques 69
José Luis Gómez Ariza and Tamara García Barrera

5.1 Greening analytical chemistry solutions for sampling 70
5.2 New green approaches to reduce problems related to sample losses, sample contamination, transport and storage 70
5.2.1 Methods based on flow-through solid phase spectroscopy 70
5.2.2 Methods based on hollow-fiber GC/HPLC/CE 71
5.2.3 Methods based on the use of nanoparticles 75
5.3 Greening analytical in-line systems 76
5.4 In-field sampling 77
5.5 Environmentally friendly sample stabilization 79
5.6 Sampling for automatization 79
5.7 Future possibilities in green sampling 80
References 80

6 Direct Analysis of Samples 85
Sergio Armenta and Miguel de la Guardia

6.1 Remote environmental sensing 85
6.1.1 Synthetic Aperture Radar (SAR) images (satellite sensors) 86
6.1.2 Open-path spectroscopy 86
6.1.3 Field-portable analyzers 90
6.2 Process monitoring: in-line, on-line and at-line measurements 91
6.2.1 NIR spectroscopy 92
6.2.2 Raman spectroscopy 92
6.2.3 MIR spectroscopy 93
6.2.4 Imaging technology and image analysis 93
6.3 At-line non-destructive or quasi non-destructive measurements 94
6.3.1 Photoacoustic Spectroscopy (PAS) 94
6.3.2 Ambient Mass Spectrometry (MS) 95
6.3.3 Solid sampling plasma sources 95
6.3.4 Nuclear Magnetic Resonance (NMR) 96

6.3.5 X-ray spectroscopy 96
6.3.6 Other surface analysis techniques 97
6.4 New challenges in direct analysis 97
References 98

7 Green Analytical Chemistry Approaches in Sample Preparation **103**
Marek Tobiszewski, Agata Mechlińska and Jacek Namieśnik

7.1 About sample preparation 103
7.2 Miniaturized extraction techniques 104
7.2.1 Solid-phase extraction (SPE) 104
7.2.2 Solid-phase microextraction (SPME) 105
7.2.3 Stir-bar sorptive extraction (SBSE) 106
7.2.4 Liquid-liquid microextraction 106
7.2.5 Membrane extraction 108
7.2.6 Gas extraction 109
7.3 Alternative solvents 113
7.3.1 Analytical applications of ionic liquids 113
7.3.2 Supercritical fluid extraction 114
7.3.3 Subcritical water extraction 115
7.3.4 Fluorous phases 116
7.4 Assisted extractions 117
7.4.1 Microwave-assisted extraction 117
7.4.2 Ultrasound-assisted extraction 117
7.4.3 Pressurized liquid extraction 118
7.5 Final remarks 119
References 119

8 Green Sample Preparation with Non-Chromatographic Separation Techniques **125**
María Dolores Luque de Castro and Miguel Alcaide Molina

8.1 Sample preparation in the frame of the analytical process 125
8.2 Separation techniques involving a gas–liquid interface 127
8.2.1 Gas diffusion 127
8.2.2 Pervaporation 127
8.2.3 Membrane extraction with a sorbent interface 130
8.2.4 Distillation and microdistillation 131
8.2.5 Head-space separation 131
8.2.6 Hydride generation and cold-mercury vapour formation 133
8.3 Techniques involving a liquid–liquid interface 133
8.3.1 Dialysis and microdialysis 133
8.3.2 Liquid–liquid extraction 134
8.3.3 Single-drop microextraction 137
8.4 Techniques involving a liquid–solid interface 139
8.4.1 Solid-phase extraction 139
8.4.2 Solid-phase microextraction 141
8.4.3 Stir-bar sorptive extraction 142

8.4.4 Continuous filtration 143
8.5 A Green future for sample preparation 145
References 145

9 Capillary Electrophoresis **153**
Mihkel Kaljurand

9.1 The capillary electrophoresis separation techniques 153
9.2 Capillary electrophoresis among other liquid phase separation methods 155
9.2.1 Basic instrumentation for liquid phase separations 155
9.2.2 CE versus HPLC from the point of view of Green Analytical Chemistry 156
9.2.3 CE as a method of choice for portable instruments 159
9.2.4 World-to-chip interfacing and the quest for a 'killer' application for LOC devices 163
9.2.5 Gradient elution moving boundary electrophoresis and electrophoretic exclusion 165
9.3 Possible ways of surmounting the disadvantages of CE 167
9.4 Sample preparation in CE 168
9.5 Is capillary electrophoresis a green alternative? 169
References 170

10 Green Chromatography **175**
Chi-Yu Lu

10.1 Greening liquid chromatography 175
10.2 Green solvents 176
10.2.1 Hydrophilic solvents 176
10.2.2 Ionic liquids 177
10.2.3 Supercritical Fluid Chromatography (SFC) 177
10.3 Green instruments 178
10.3.1 Microbore Liquid Chromatography (microbore LC) 179
10.3.2 Capillary Liquid Chromatography (capillary LC) 180
10.3.3 Nano Liquid Chromatography (nano LC) 181
10.3.4 How to transfer the LC condition from traditional LC to microbore LC, capillary LC or nano LC 182
10.3.5 Homemade micro-scale analytical system 183
10.3.6 Ultra Performance Liquid Chromatography (UPLC) 184
References 185

11 Green Analytical Atomic Spectrometry **199**
Martín Resano, Esperanza García-Ruiz and Miguel A. Belarra

11.1 Atomic spectrometry in the context of Green Analytical Chemistry 199
11.2 Improvements in sample pretreatment strategies 202
11.2.1 Specific improvements 202
11.2.2 Slurry methods 204
11.3 Direct solid sampling techniques 205

11.3.1 Basic operating principles of the techniques discussed 205
11.3.2 Sample requirements and pretreatment strategies 207
11.3.3 Analyte monitoring: The arrival of high-resolution continuum source atomic absorption spectrometry 208
11.3.4 Calibration 210
11.3.5 Selected applications 210
11.4 Future for green analytical atomic spectrometry 213
References 215

12 Solid Phase Molecular Spectroscopy **221**
Antonio Molina-Díaz, Juan Francisco García-Reyes and Natividad Ramos-Martos

12.1 Solid phase molecular spectroscopy: an approach to Green Analytical Chemistry 221
12.2 Fundamentals of solid phase molecular spectroscopy 222
12.2.1 Solid phase absorption (spectrophotometric) procedures 222
12.2.2 Solid phase emission (fluorescence) procedures 225
12.3 Batch mode procedures 225
12.4 Flow mode procedures 226
12.4.1 Monitoring an intrinsic property 227
12.4.2 Monitoring derivative species 231
12.4.3 Recent flow-SPMS based approaches 232
12.5 Selected examples of application of solid phase molecular spectroscopy 233
12.6 The potential of flow solid phase envisaged from the point of view of Green Analytical Chemistry 235
References 240

13 Derivative Techniques in Molecular Absorption, Fluorimetry and Liquid Chromatography as Tools for Green Analytical Chemistry **245**
José Manuel Cano Pavón, Amparo García de Torres, Catalina Bosch Ojeda, Fuensanta Sánchez Rojas and Elisa I. Vereda Alonso

13.1 The derivative technique as a tool for Green Analytical Chemistry 245
13.1.1 Theoretical aspects 246
13.2 Derivative absorption spectrometry in the UV-visible region 247
13.2.1 Strategies to greener derivative spectrophotometry 248
13.3 Derivative fluorescence spectrometry 250
13.3.1 Derivative synchronous fluorescence spectrometry 251
13.4 Use of derivative signal techniques in liquid chromatography 254
References 255

14 Greening Electroanalytical Methods **261**
Paloma Yáñez-Sedeño, José M. Pingarrón and Lucas Hernández

14.1 Towards a more environmentally friendly electroanalysis 261
14.2 Electrode materials 262
14.2.1 Alternatives to mercury electrodes 262
14.2.2 Nanomaterial-based electrodes 268
14.3 Solvents 270

14.3.1 Ionic liquids 271
14.3.2 Supercritical fluids 273
14.4 Electrochemical detection in flowing solutions 274
14.4.1 Injection techniques 274
14.4.2 Miniaturized systems 276
14.5 Biosensors 278
14.5.1 Greening biosurface preparation 278
14.5.2 Direct electrochemical transfer of proteins 281
14.6 Future trends in green electroanalysis 282
References 282

Section III: Strategies **289**

15 Energy Savings in Analytical Chemistry **291**
Mihkel Koel

15.1 Energy consumption in analytical methods 291
15.2 Economy and saving energy in laboratory practice 294
15.2.1 Good housekeeping, control and maintenance 295
15.3 Alternative sources of energy for processes 296
15.3.1 Using microwaves in place of thermal heating 297
15.3.2 Using ultrasound in sample treatment 299
15.3.3 Light as a source of energy 301
15.4 Using alternative solvents for energy savings 302
15.4.1 Advantages of ionic liquids 303
15.4.2 Using subcritical and supercritical fluids 303
15.5 Efficient laboratory equipment 305
15.5.1 Trends in sample treatment 306
15.6 Effects of automation and micronization on energy consumption 307
15.6.1 Miniaturization in sample treatment 308
15.6.2 Using sensors 310
15.7 Assessment of energy efficiency 312
References 316

16 Green Analytical Chemistry and Flow Injection Methodologies **321**
Luis Dante Martínez, Soledad Cerutti and Raúl Andrés Gil

16.1 Progress of automated techniques for Green Analytical Chemistry 321
16.2 Flow injection analysis 322
16.3 Sequential injection analysis 325
16.4 Lab-on-valve 327
16.5 Multicommutation 328
16.6 Conclusions and remarks 334
References 334

17 Miniaturization **339**
Alberto Escarpa, Miguel Ángel López and Lourdes Ramos

17.1 Current needs and pitfalls in sample preparation 340
17.2 Non-integrated approaches for miniaturized sample preparation 341

17.2.1 Gaseous and liquid samples 341
17.2.2 Solid samples 350
17.3 Integrated approaches for sample preparation on microfluidic platforms 353
17.3.1 Microfluidic platforms in sample preparation process 353
17.3.2 The isolation of analyte from the sample matrix: filtering approaches 356
17.3.3 The isolation of analytes from the sample matrix: extraction approaches 360
17.3.4 Preconcentration approaches using electrokinetics 365
17.3.5 Derivatization schemes on microfluidic platforms 372
17.3.6 Sample preparation in cell analysis 373
17.4 Final remarks 378
References 379

18 Micro- and Nanomaterials Based Detection Systems Applied in Lab-on-a-Chip Technology **389**
Mariana Medina-Sánchez and Arben Merkoçi

18.1 Micro- and nanotechnology in Green Analytical Chemistry 389
18.2 Nanomaterials-based (bio)sensors 390
18.2.1 Optical nano(bio)sensors 391
18.2.2 Electrochemical nano(bio)sensors 393
18.2.3 Other detection principles 395
18.3 Lab-on-a-chip (LOC) technology 396
18.3.1 Miniaturization and nano-/microfluidics 396
18.3.2 Micro- and nanofabrication techniques 397
18.4 LOC applications 398
18.4.1 LOCs with optical detections 398
18.4.2 LOCs with electrochemical detectors 398
18.4.3 LOCs with other detections 399
18.5 Conclusions and future perspectives 400
References 401

19 Photocatalytic Treatment of Laboratory Wastes Containing Hazardous Organic Compounds **407**
Edmondo Pramauro, Alessandra Bianco Prevot and Debora Fabbri

19.1 Photocatalysis 407
19.2 Fundamentals of the photocatalytic process 408
19.3 Limits of the photocatalytic treatment 408
19.4 Usual photocatalytic procedure in laboratory practice 408
19.4.1 Solar detoxification of laboratory waste 409
19.5 Influence of experimental parameters 411
19.5.1 Dissolved oxygen 411
19.5.2 pH 411
19.5.3 Catalyst concentration 412
19.5.4 Degradation kinetics 412
19.6 Additives reducing the e^-/h^+ recombination 412
19.7 Analytical control of the photocatalytic treatment 413
19.8 Examples of possible applications of photocatalysis to the treatment of laboratory wastes 413
19.8.1 Percolates containing soluble aromatic contaminants 414

19.8.2 Photocatalytic destruction of aromatic amine residues in aqueous wastes 414
19.8.3 Degradation of aqueous wastes containing pesticides residue 415
19.8.4 The peculiar behaviour of triazine herbicides 416
19.8.5 Treatment of aqueous wastes containing organic solvent residues 416
19.8.6 Treatment of surfactant-containing aqueous wastes 416
19.8.7 Degradation of aqueous solutions of azo-dyes 419
19.8.8 Treatment of laboratory waste containing pharmaceuticals 419
19.9 Continuous monitoring of photocatalytic treatment 420
References 420

Section IV: Fields of Application **425**

20 Green Bioanalytical Chemistry **427**
Tadashi Nishio and Hideko Kanazawa

20.1 The analytical techniques in bioanalysis 427
20.2 Environmental-responsive polymers 428
20.3 Preparation of a polymer-modified surface for the stationary phase of environmental-responsive chromatography 430
20.4 Temperature-responsive chromatography for green analytical methods 432
20.5 Biological analysis by temperature-responsive chromatography 432
20.5.1 Analysis of propofol in plasma using water as a mobile phase 434
20.5.2 Contraceptive drugs analysis using temperature gradient chromatography 435
20.6 Affinity chromatography for green bioseparation 436
20.7 Separation of biologically active molecules by the green chromatographic method 438
20.8 Protein separation by an aqueous chromatographic system 441
20.9 Ice chromatography 442
20.10 High-temperature liquid chromatography 443
20.11 Ionic liquids 443
20.12 The future in green bioanalysis 444
References 444

21 Infrared Spectroscopy in Biodiagnostics: A Green Analytical Approach **449**
Mohammadreza Khanmohammadi and Amir Bagheri Garmarudi

21.1 Infrared spectroscopy capabilities 449
21.2 Infrared spectroscopy of bio-active chemicals in a bio-system 451
21.3 Medical analysis of body fluids by infrared spectroscopy 453
21.3.1 Blood and its extracts 455
21.3.2 Urine 457
21.3.3 Other body fluids 457
21.4 Diagnosis in tissue samples via IR spectroscopic analysis 457
21.4.1 Main spectral characteristics 459
21.4.2 The role of data processing 460
21.4.3 Cancer diagnosis by FTIR spectrometry 465
21.5 New trends in infrared spectroscopy assisted biodiagnostics 468
References 470

22 Environmental Analysis **475**
Ricardo Erthal Santelli, Marcos Almeida Bezerra, Julio Carlos Afonso, Maria de Fátima Batista de Carvalho, Eliane Padua Oliveira and Aline Soares Freire

22.1 Pollution and its control 475
22.2 Steps of an environmental analysis 476
22.2.1 Sample collection 476
22.2.2 Sample preparation 476
22.2.3 Analysis 479
22.3 Green environmental analysis for water, wastewater and effluent 480
22.3.1 Major mineral constituents 480
22.3.2 Trace metal ions 481
22.3.3 Organic pollutants 483
22.4 Green environmental analysis applied for solid samples 485
22.4.1 Soil 485
22.4.2 Sediments 488
22.4.3 Wastes 492
22.5 Green environmental analysis applied for atmospheric samples 496
22.5.1 Gases 496
22.5.2 Particulates 497
References 497

23 Green Industrial Analysis **505**
Sergio Armenta and Miguel de la Guardia

23.1 Greening industrial practices for safety and cost reasons 505
23.2 The quality control of raw materials and end products 506
23.3 Process control 510
23.4 Effluent control 511
23.5 Working atmosphere control 514
23.6 The future starts now 515
References 515

Index 519