
Contents

Contributors to Volume 61	xv
Series Editor's Preface	xix
Preface	xxi

Part I

Advances in GC-MS and GC-MS-MS. Environmental Applications

1. Gas Chromatography-Mass Spectrometry Techniques for Multiresidue Pesticide Analysis in Agricultural Commodities	3
<i>Jon W. Wong, Douglas G. Hayward, and Kai Zhang</i>	
1. Gas Chromatography	3
2. Gas Chromatography with Element Selective Detection for Multiresidue Pesticide Analysis	4
3. Capillary GC-MS	5
4. Gas Chromatography-Ion Trap-Mass Spectrometry	6
5. Gas Chromatography-Single Quadrupole-Mass Spectrometry	8
6. GC-QQQ-MS/MS	10
7. Capillary GC-TOF-MS	12
8. Limitations and Future Outlook of GC-MS	15
9. Conclusions	17
References	17
2. Microextraction Techniques Coupled to Advanced GC-MS Techniques for Analysis of Environmental Samples	23
<i>Dimitra A. Lambropoulou</i>	
1. Introduction	23
2. Microextraction Techniques	25
2.1. Sorptive Microextraction Techniques	26
2.2. Solvent-Based Microextraction	44
3. Concluding Remarks, Trends, and Perspectives in Microextraction	50
References	53

3. Determination of Pesticide Residues in Environmental and Food Samples Using Gas Chromatography–Triple Quadrupole Mass Spectrometry	55
<i>Kai Zhang, Jon W. Wong, Douglas G. Hayward, and Paul Yang</i>	
1. Introduction	55
2. Method Development	57
3. Applications of GC–QqQ-MS	58
3.1. Determination of Pesticides in Environmental Samples	58
3.2. Determination of Pesticides in Food Samples	85
4. Challenges Issues of GC–QqQ-MS	88
5. Future of GC–QqQ-MS	90
References	92
4. Environmental Odor Pollution: A Complex GC–MS, Olfactometry and Diffusion Modeling Approach to Define Air Quality	97
<i>Giancarlo Bianchi, Marinella Palmiotto, Michele Giavini, and Enrico Davoli</i>	
1. Environmental Odor Pollution	97
2. Analytical Methods	99
2.1. Air Sampling	99
2.2. Instrumental Analysis	99
2.3. Olfactometry	100
2.4. Diffusion Modeling	101
2.5. Chemometric Analysis	101
3. Results for VOCs	102
4. Case Studies: Landfills and Composting Plants	107
5. Conclusions	113
References	113
5. Injection Port Derivatization for GC/MS–MS: Analysis of Hormones in Water	115
<i>E. Michael Thurman, Jeff H. Writer, and Imma Ferrer</i>	
1. Introduction	115
2. Experimental Methods and Sample Preparation	120
2.1. On-Column Derivatization Method for Hormones and Bisphenol A	120
2.2. Comparison Method: U.S. Geological Survey Method for Hormones	121
3. Results and Discussion	122
3.1. Derivatization by BSTFA/TMCS/Pyridine	122
3.2. Derivatized Hormone Mass Spectra	125

3.3. Building the MRM Table for Hormones and Endocrine Disruptors	137
3.4. Analysis of Water Samples	138
4. Conclusions	140
Acknowledgments	140
References	140
6. High-Throughput Analysis of PPCPs, PCDD/Fs, and PCBs in Biological Matrices Using GC–MS–MS	143
<i>Sascha Usenko, Bikram Subedi, Lissette Aguilar, and Eleanor Robinson</i>	
1. Introduction	143
2. Sample Preparation Overview	144
2.1. Pretreatment	144
2.2. Extraction	145
2.3. Cleanup	147
3. Next-Generation PLE Techniques	147
3.1. Case Study #1: San Jacinto River Waste Pits	150
4. Gas Chromatography Tandem MS for Trace Analysis in Biological Matrices	152
4.1. Case Study #2: PPCP Nationwide Study	156
References	157
7. GC–MS Applied to the Monitoring of Pesticides in Milk and Blackberries and PAHs in Processed Meats of Colombia	159
<i>Gustavo Antonio Peñuela Mesa, Andrés Fernando Gallo Ortiz, Duvan Esteban Hoyos Ossa, and Andrés Ramírez Restrepo</i>	
1. Introduction	159
2. Materials and Methods	161
2.1. Equipment	161
2.2. Sampling	161
2.3. Reactives and Reference Materials	161
2.4. Methods	164
3. Validation	164
3.1. Validation Process	164
3.2. Validation Results	169
4. Monitoring	178
4.1. Raw Cow's Milk	178
4.2. Blackberry	178
4.3. Processed Meats	179
5. Conclusions	179
Acknowledgments	180
References	180

8. Applications and Strategies Based on Gas Chromatography–Low-Resolution Mass Spectrometry (GC–LRMS) for the Determination of Residues and Organic Contaminants in Environmental Samples	181
<i>Juan A. Padilla-Sánchez, Patricia Plaza-Bolaños, and Antonia Garrido Frenich</i>	
1. Introduction	182
2. Advanced Extraction Techniques in Environmental Analysis	184
2.1. Extraction of Water Samples	185
2.2. Extraction of Solid Samples	190
3. Derivatization Reactions of Compounds	193
4. GC–LRMS Analysis	194
4.1. GC Injection and Separation	194
4.2. LRMS Detection Strategies	196
5. Conclusions and Future Trends	198
Acknowledgments	199
References	199
9. Determination of Pyrethroid Insecticides in Environmental Samples by GC–MS and GC–MS–MS	203
<i>Cayo Corcellas, Ethel Eljarrat, and Damià Barceló</i>	
1. Introduction	203
1.1. Structures and Isomerism	204
1.2. Physicochemical Properties	205
1.3. Toxicity	211
2. Sample Preparation Methodologies	212
2.1. Environmental Samples	212
2.2. Biological Samples	216
3. Gas Chromatography Separation	218
3.1. Achiral Columns	218
3.2. Chiral Columns	220
4. Mass Spectrometry Detection	221
4.1. Mass Spectrometry	222
4.2. Tandem Mass Spectrometry	222
5. Levels of Real Samples	225
5.1. Environmental Samples	225
5.2. Biological Samples	225
5.3. Enantiomeric Results	226
Acknowledgments	227
References	228

10. GC–MS–MS for the Analysis of Phytoestrogens in the Environment	231
<i>Imma Ferrer and E. Michael Thurman</i>	
1. Introduction	231
2. Experimental	233
2.1. Chemicals and Reagents	233
2.2. Derivatization Procedure and Sample Preparation	233
2.3. GC–MS–MS Instrumentation	234
3. GC–MS–MS Analyses	235
3.1. Optimization of Derivatization and GC–MS Detection	235
3.2. Optimization of MS–MS Conditions	237
3.3. Chromatographic Separation of the Phytoestrogens	243
3.4. Analytical Performance	245
4. Application to Food and Environmental Samples	246
4.1. Application to Soy-Milk Analysis	246
4.2. Application to Wastewater Analysis	248
5. Conclusions	250
Acknowledgments	250
References	250

Part II

Advances in High Resolution and Accurate Mass GC–MS. Environmental Applications

11. Principles and Applications of Gas Chromatography Quadrupole Time-of-Flight Mass Spectrometry	255
<i>Jennifer N. Gushue</i>	
1. Introduction	255
2. Overview of GC/QTOF Instrumentation	256
2.1. Gas Chromatography	256
2.2. Ionization	258
2.3. Quadrupole Analyzers	262
2.4. Collision Cell	263
2.5. Time-of-Flight	264
3. Environmental Applications	266
3.1. Water Analysis	266
4. Conclusions	270
Acknowledgments	270
References	270

12. Gas Chromatography–Time-of-Flight Mass Spectrometry in Food and Environmental Analysis	271
<i>Tomas Cajka</i>	
1. Introduction	271
2. Gas Chromatography–Time-of-Flight Mass Spectrometry	272
3. Applications of GC–TOF–MS in Food and Environmental Analysis	280
3.1. Food and Environmental Contaminants	280
3.2. Aroma and Flavor Compounds	293
4. Conclusions	300
References	300
13. Ultra-High Mass Resolution Miniaturized Time-of-Flight Mass Spectrometer “infiTOF” for Rapid Analysis of Polychlorinated Biphenyls	303
<i>Shuichi Shimma, Shinichi Miki, Robert B. Cody, and Michisato Toyoda</i>	
1. Introduction	304
2. “On-Site Mass Spectrometry” Using Miniaturized Mass Spectrometers	304
2.1. On-Site Mass Spectrometry	304
2.2. Overview of Miniaturized Mass Spectrometers	305
2.3. Issues with Miniaturized Mass Spectrometers	306
3. Multiturn TOF Mass Spectrometers at Osaka University	307
4. Miniaturized Multiturn TOF Mass Spectrometer “infiTOF”	309
4.1. Overview of infiTOF System	309
4.2. Data Acquisition Methods	310
4.3. Ultra-High Mass Resolution Mass Spectra on infiTOF System	312
5. PCBs Analysis in GC–infiTOF System	315
5.1. Performance Evaluation Using Hepta-CB Standard	315
5.2. Fast GC/HRMS Using a Comprehensive PCBs Mixture	316
5.3. Separation of Contaminant Peaks in the Dielectric Coolant Fluid	318
6. Conclusions	322
References	322
14. Environmental Applications of Soft Ionization with GC–TOFMS and GC–QTOFMS	325
<i>Viorica Lopez-Avila, Patrick J. Roach, and Randall Urdahl</i>	
1. Introduction	325
2. Experimental	327

2.1. Chemicals and Reagents	327
2.2. GC-MPPI High-Resolution TOF and QTOF Mass Spectrometer	328
3. Results and Discussion	329
3.1. Aliphatic Hydrocarbons	329
3.2. PASHs	333
4. Conclusions	345
Acknowledgments	345
References	345
15. Compound-Specific Stable Isotope Analysis of Natural and Produced Hydrocarbon Gases Surrounding Oil and Gas Operations	347
<i>Owen A. Sherwood, Patrick D. Travers, and Michael P. Dolan</i>	
1. Introduction	347
2. Hydrocarbon Gas Sampling Methods	350
3. Stable Isotope Background	352
3.1. Stable Carbon and Hydrogen Isotopes	352
3.2. Definitions	353
3.3. Stable Isotope Fractionation	353
4. Analytical Methods	355
4.1. Instrumentation	355
4.2. Stable Isotope Analysis of Hydrocarbons—Special Considerations	357
4.3. Standardization	358
5. Interpretation of Natural Gas Stable Isotopes	360
5.1. Natural Gas Types	360
5.2. Case Study: Wattenberg Field of Colorado	365
6. Conclusions	368
Acknowledgments	368
References	369
16. Analysis of Halogenated Flame Retardants by Gas Chromatography Coupled to LRMS, HRMS, MS–MS, and TOF-MS	373
<i>Enrique Barón, Ethel Eljarrat, and Damià Barceló</i>	
1. Introduction	373
1.1. Brominated Flame Retardants	374
1.2. Halogenated Norbornenes	379
1.3. Toxicity	380
2. Sample Treatment	381
2.1. PBDEs, Emerging BFRs, and Halogenated Norbornenes	381
2.2. MeO-PBDEs and OH-PBDEs	383

3. Instrumental Analysis	384
3.1. Chromatographic Separation	384
3.2. Mass Spectrometric Determination	385
4. Levels in Environmental Samples	392
References	396
17. Industrial Applications of High-Resolution GC/MS	403
<i>Jeffrey R. Gilbert, David McCaskill, Vyacheslav N. Fishman, Kathy Brzak, Dan Markham, Michael J. Bartels, Bill Winniford, Sheher Bano Mohsin, Jeffrie Godbey, Olujide Akinbo, and Paul Lewer</i>	
1. Introduction: Why GC/MS?	403
2. Industrial Applications of GC/MS	405
2.1. Environmental Analysis	405
2.2. Toxicology	408
2.3. Metabolomics in Agriculture	414
3. Recent Advances in GC/MS Technology	418
3.1. Comprehensive Two-Dimensional Gas Chromatography Time-of-Flight Mass Spectrometry (GC × GC–TOF-MS)	418
3.2. Accurate Mass GC/MS Instrumentation	421
3.3. GC/APCI/MS	422
4. Conclusions	425
References	427
18. Current Applications of GC-(Q)TOF and GC–HRMS for the Determination of Persistent Organic Pollutants in Water and Sediments Samples	431
<i>Patricia Plaza-Bolaños, Noelia M. Valera-Tarifa, and Antonia Garrido Frenich</i>	
1. Introduction	431
2. Sample Extraction	434
2.1. Extraction of Water Samples	434
2.2. Extraction of Sediments	436
3. Determination by Gas Chromatography Analysis Coupled to High-Resolution Mass Spectrometry	439
4. Applications and Quantification Strategies	450
5. Conclusions	452
Acknowledgments	452
References	452

19. A GC/MS–MS Versus GC/HRMS Dioxin Analysis Comparison. Some Critical Considerations for Low-Level Environmental Samples	455
<i>Marinella Palmiotto, Andrea Colombo, and Enrico Davoli</i>	
1. Introduction	455
2. Materials and Methods	457
3. Results	461
4. Conclusions	465
Acknowledgments	467
References	467
20. The Future of GC/Q-TOF in Environmental Analysis	471
<i>Anthony Macherone</i>	
1. Introduction	471
2. GC/MS and Environmental Analysis	473
2.1. A Brief Review of GC/MS Technologies	473
3. Biologically Relevant Chemical Space	480
4. The Exposome, Exposomics, and the Future of GC/Q-TOF	483
4.1. The Exposome	483
4.2. Exposomics	484
4.3. GC/TOF and Exposomics	484
5. Summary	488
References	489
Index	491