

Contents

	Foreword	<i>xvii</i>
	Preface to the Fourth Edition	<i>xix</i>
1	Introduction	<i>1</i>
1.1	The Historical Development of the GC-MS Technique	<i>4</i>
	References	<i>7</i>
2	Fundamentals	<i>9</i>
2.1	Sample Preparation	<i>9</i>
2.1.1	QuEChERS Sample Preparation	<i>11</i>
2.1.2	Dispersive Liquid/Liquid Microextraction	<i>17</i>
2.1.3	Solid Phase Extraction	<i>19</i>
2.1.3.1	Online Solid Phase Extraction	<i>24</i>
2.1.3.2	Micro Solid Phase Extraction	<i>25</i>
2.1.4	Solid Phase Microextraction	<i>27</i>
2.1.4.1	Solid Phase Microextraction Devices	<i>28</i>
2.1.4.2	Solid Phase Microextraction Operation for GC-MS	<i>36</i>
2.1.4.3	Solid Phase Microextraction Sorbent Materials	<i>42</i>
2.1.5	Static Headspace Technique	<i>49</i>
2.1.5.1	Measures for Improved Headspace Response	<i>53</i>
2.1.5.2	Quantitation by Multiple Headspace Extraction	<i>56</i>
2.1.5.3	Headspace Analysis Operation	<i>59</i>
2.1.6	Dynamic Headspace – Purge & Trap Technique	<i>62</i>
2.1.6.1	Coupling of Purge and Trap with GC-MS Systems	<i>63</i>
2.1.6.2	Modes of Operation of Purge and Trap Systems	<i>64</i>
2.1.6.3	Static Headspace vs. Purge and Trap	<i>70</i>
2.1.7	Dynamic Headspace – In-Tube Extraction	<i>76</i>
2.1.8	Adsorptive Enrichment and Thermal Desorption	<i>77</i>
2.1.8.1	Sample Collection	<i>81</i>
2.1.8.2	Calibration	<i>82</i>
2.1.8.3	Desorption	<i>84</i>
2.1.9	Stir Bar Sorptive Extraction	<i>87</i>
2.1.10	Pyrolysis	<i>88</i>

- 2.1.10.1 Foil Pyrolysis 90
- 2.1.10.2 Curie Point Pyrolysis 92
- 2.1.10.3 Micro-Furnace Pyrolysis 94
- 2.1.11 Thermal Extraction (Outgassing) 95
- 2.1.12 Liquid Chromatography Clean-up 98
- 2.1.13 Pressurized Liquid Extraction 100
- 2.1.13.1 In-Cell Clean-up 103
- 2.1.13.2 In-Cell Hydrocarbon Oxidation 105
- References 105
- 2.2 Gas Chromatography 128
 - 2.2.1 Sample Inlet Systems 128
 - 2.2.2 Carrier Gas Regulation 129
 - 2.2.2.1 Forward Pressure Regulation 130
 - 2.2.2.2 Back Pressure Regulation 131
 - 2.2.2.3 Carrier Gas Saving 132
 - 2.2.3 Injection Port Septa 134
 - 2.2.3.1 Septum Purge 136
 - 2.2.3.2 The MicroSeal Septum 136
 - 2.2.4 Injection Port Liner 138
 - 2.2.4.1 Split Injection 138
 - 2.2.4.2 Splitless Injection 139
 - 2.2.4.3 Liner Activity and Deactivation 140
 - 2.2.4.4 Liner Geometry 142
 - 2.2.5 Hot Split/Splitless Sample Injection Techniques 143
 - 2.2.5.1 Hot Needle Thermospray Injection Technique 144
 - 2.2.5.2 Cold Needle Liquid Band Injection Technique 147
 - 2.2.5.3 Filled Needle Injections 147
 - 2.2.5.4 Split Injection 148
 - 2.2.5.5 Splitless Injection (Total Sample Transfer) 148
 - 2.2.5.6 Concurrent Solvent Recondensation 150
 - 2.2.5.7 Concurrent Backflush 151
 - 2.2.6 Temperature Programmable Injectors 155
 - 2.2.6.1 PTV Injection Modes 159
 - 2.2.6.2 Cryofocusing 166
 - 2.2.7 Non-Vaporizing Injection Techniques 168
 - 2.2.7.1 On-Column Injection 168
 - 2.2.7.2 PTV On-Column Injection 171
 - 2.2.7.3 LC-GC Coupling 171
 - 2.2.8 Capillary Column Choice and Separation Optimization 173
 - 2.2.8.1 Choice of Carrier Gas 174
 - 2.2.8.2 Optimization of the Carrier Gas Flow 197
 - 2.2.8.3 Sample Capacity 200
 - 2.2.8.4 Internal Diameter 200
 - 2.2.8.5 Film Thickness 202
 - 2.2.8.6 Column Length 204

2.2.8.7	Properties of Column Phases	205
2.2.8.8	Ionic Liquid Phases	209
2.2.9	Chromatography Parameters	212
2.2.9.1	The Chromatogram and its Meaning	214
2.2.9.2	Capacity Factor k'	216
2.2.9.3	Chromatographic Resolution	216
2.2.9.4	Factors Affecting the Resolution	218
2.2.9.5	Maximum Sample Capacity	222
2.2.9.6	Peak Symmetry	222
2.2.9.7	Effect of Oven Temperature Ramp Rate	225
2.2.10	Fast Gas Chromatography Solutions	227
2.2.10.1	Fast Chromatography	227
2.2.10.2	Vacuum Outlet (Low Pressure) Chromatography	233
2.2.10.3	Ultra-Fast Chromatography	235
2.2.10.4	Flow-Field Thermal Gradient Gas Chromatography	237
2.2.11	Multi-Dimensional Gas Chromatography	239
2.2.11.1	Heart Cutting	241
2.2.11.2	Comprehensive GC – GC \times GC	241
2.2.11.3	Modulation	245
2.2.11.4	Detection	246
2.2.11.5	Data Handling	248
2.2.11.6	Moving Capillary Stream Switching	249
2.2.12	Classical Detectors for GC-MS Systems	251
2.2.12.1	Atomic Emission Detector (AED)	253
2.2.12.2	Electron Capture Detector (ECD)	254
2.2.12.3	Electrolytical Conductivity Detector (ELCD)	256
2.2.12.4	Flame-Ionization Detector (FID)	257
2.2.12.5	Flamephotometric Detector (FPD)	258
2.2.12.6	Helium Ionization Detector (HID)	258
2.2.12.7	Nitrogen-Phosphorous Detector (NPD)	259
2.2.12.8	Pulsed Discharge Detector (PDD)	261
2.2.12.9	Photo Ionization Detector (PID)	262
2.2.12.10	Sulfur Chemiluminescence Detector (SCD)	265
2.2.12.11	Thermal Conductivity Detector (TCD)	265
2.2.12.12	Vacuum Ultra Violet Detector (VUV)	266
2.2.12.13	Olfactometry	268
2.2.12.14	Classical Detectors Parallel to the Mass Spectrometer	268
2.2.12.15	Microchannel Devices	271
	References	273
2.3	Mass Spectrometry	291
2.3.1	Ionization	292
2.3.1.1	Electron Ionization	292
2.3.1.2	Chemical Ionization	295
2.3.2	Mass Analysis	313
2.3.2.1	Resolving Power and Resolution in Mass Spectrometry	314

2.3.2.2	Quadrupole and Quadrupole Ion Trap Mass Spectrometer	325
2.3.2.3	Sector Field Mass Spectrometer	327
2.3.2.4	Orbitrap Mass Spectrometer	329
2.3.2.5	Time-of-Flight Analyzer	333
2.3.2.6	Ion Mobility Analyzer	336
2.3.2.7	High and Low Mass Resolution in the Case of Dioxin Analysis	339
2.3.3	Isotope Ratio Monitoring GC-MS	344
2.3.3.1	The Principles of Isotope Ratio Monitoring	345
2.3.3.2	Notations in irm-GC-MS	346
2.3.3.3	Isotopic Fractionation	347
2.3.3.4	irm-GC-MS Technology	349
2.3.3.5	The Open Split Interface	353
2.3.3.6	Compound Specific Isotope Analysis	353
2.3.3.7	Online Combustion for $\delta^{13}\text{C}$ and $\delta^{15}\text{N}$ Determination	354
2.3.3.8	The Oxidation Reactor	355
2.3.3.9	The Reduction Reactor	355
2.3.3.10	Water Removal	355
2.3.3.11	The Liquid Nitrogen Trap	357
2.3.3.12	Online High Temperature Conversion for $\delta^2\text{H}$ and $\delta^{18}\text{O}$ Determination	357
2.3.3.13	Mass Spectrometer for Isotope Ratio Analysis	359
2.3.3.14	Injection of Reference Gases	361
2.3.3.15	Isotope Reference Materials	361
2.3.4	Acquisition Techniques in GC-MS	363
2.3.4.1	Detection of the Complete Mass Spectrum (Full Scan)	363
2.3.4.2	Recording Individual Masses (SIM)	364
2.3.4.3	High Resolution Accurate Mass SIM Data Acquisition	374
2.3.4.4	MS/MS – Tandem Mass Spectrometry	380
2.3.5	Mass Calibration	388
2.3.6	Vacuum Systems	396
	References	400
3	Evaluation of GC-MS Analyses	413
3.1	Display of Chromatograms	413
3.1.1	Total Ion Current Chromatograms	413
3.1.2	Mass Chromatograms	415
3.2	Substance Identification	418
3.2.1	Reading Mass Spectra	418
3.2.2	Extraction of Mass Spectra	420
3.2.2.1	Manual Spectrum Subtraction	420
3.2.2.2	Deconvolution of Mass Spectra	425
3.2.3	The Retention Index	430
3.2.4	Libraries of Mass Spectra	434
3.2.4.1	Universal Mass Spectral Libraries	436
3.2.4.2	Application Libraries of Mass Spectra	438

3.2.5	Library Search Programs	443
3.2.5.1	The NIST Search Procedure	445
3.2.6	Interpretation of Mass Spectra	451
3.2.6.1	Isotope Patterns	461
3.2.6.2	Fragmentation and Rearrangement Reactions	468
3.2.6.3	DMOX Derivatives for Location of Double Bond Positions	471
3.2.7	Mass Spectroscopic Features of Selected Substance Classes	472
3.2.7.1	Volatile Halogenated Hydrocarbons	472
3.2.7.2	Benzene/Toluene/Ethylbenzene/Xylenes (BTEX, Alkylaromatics)	475
3.2.7.3	Polyaromatic Hydrocarbons	478
3.2.7.4	Phenols	480
3.2.7.5	Pesticides	482
3.2.7.6	Polychlorinated Biphenyls	492
3.2.7.7	Polychlorinated Dioxins/Furans (PCDDs/PCDFs)	495
3.2.7.8	Drugs	496
3.2.7.9	Explosives	498
3.2.7.10	Chemical Warfare Agents	498
3.2.7.11	Brominated Flame Retardants (BFRs)	504
3.3	Quantitation	505
3.3.1	Acquisition Rate	506
3.3.2	Decision Limit	507
3.3.3	Detection Limit	509
3.3.4	Limit of Quantitation	512
3.3.5	Sensitivity	514
3.3.6	The Calibration Function	514
3.3.7	Quantitation and Standardization	516
3.3.7.1	External Standardization	516
3.3.7.2	Internal Standardization	517
3.3.7.3	Standard Addition	522
3.4	Frequently Occurring Impurities	523
	References	531
4	Applications	541
4.1	Air Analysis According to U.S. EPA Method TO-14	541
4.1.1	Introduction	541
4.1.2	Analysis Conditions	543
4.1.3	Limit of Detection	544
4.1.4	Results	544
4.2	BTEX in Surface Water as of U.S. EPA Method 8260	549
4.2.1	Introduction	549
4.2.2	Sample Preparation	549
4.2.3	Experimental Conditions	550
4.2.4	Analysis Conditions	550
4.2.5	Results	551
4.2.6	Conclusions	553

4.3	Volatile Priority Pollutants	554
4.3.1	Introduction	554
4.3.2	Analysis Conditions	556
4.3.3	Results	557
4.4	MAGIC 60 – VOC Analysis	560
4.4.1	Introduction	560
4.4.2	Analysis Conditions	561
4.4.3	Results	569
4.5	irm-GC-MS of Volatile Organic Compounds	569
4.5.1	Introduction	569
4.5.2	Analysis Conditions	570
4.5.3	Results	571
4.6	Organotin Compounds in Water	572
4.6.1	Introduction	572
4.6.2	Analysis Conditions	573
4.6.3	Experimental Conditions	574
4.6.4	Results	577
4.7	Analysis of Dithiocarbamate Pesticides	577
4.7.1	Introduction	577
4.7.2	Analysis Conditions	578
4.7.3	Sample Preparation	580
4.7.4	Preparation of Standard Solutions and Reaction Mixture	580
4.7.4.1	Carbon Disulfide Standard Solution	580
4.7.4.2	Standard Solution of Thiram	580
4.7.4.3	Preparation of Reaction Mixture	580
4.7.4.4	Calibration Standards	580
4.7.5	Experimental Conditions	581
4.7.6	Sample Measurements	581
4.7.7	Results	583
4.7.7.1	Sensitivity	583
4.7.7.2	Recovery	583
4.7.7.3	Accuracy	583
4.7.8	General Guidelines for DTC Analysis	583
4.7.9	Conclusions	584
4.8	Pesticides Multi-Method by Single Quadrupole MS	584
4.8.1	Introduction	584
4.8.2	Analysis Conditions	592
4.8.3	Results	593
4.9	QuEChERSER Analysis of Pesticides	594
4.9.1	Introduction	594
4.9.2	Analysis Conditions	595
4.9.3	Analysis	597
4.9.4	Results	598
4.10	Pesticide Analysis with Ethyl Acetate Extraction and Automated Micro-SPE Clean-up	599

4.10.1	Introduction	599
4.10.2	Analysis Conditions	600
4.10.3	Ethyl Acetate Extraction	601
4.10.3.1	Micro-SPE Clean-up	601
4.10.4	Results	601
4.11	Multi-Residue Pesticides Analysis in Ayurvedic Churna	603
4.11.1	Introduction	603
4.11.2	Analysis Conditions	604
4.11.3	Sample Preparation	605
4.11.4	Experimental Conditions	605
4.11.5	Results	612
4.11.6	Conclusions	612
4.12	Polar Aromatic Amines by SPME	614
4.12.1	Introduction	614
4.12.2	Analysis Conditions	614
4.12.3	Results	616
4.13	Phthalates in Liquors	619
4.13.1	Introduction	619
4.13.2	Analysis Conditions	619
4.13.3	Sample Preparation	620
4.13.4	Experimental Conditions	621
4.13.5	Sample Measurements	621
4.13.6	Results	622
4.13.7	Quantitation	623
4.13.8	Sensitivity	624
4.13.9	Method Precision and Recovery	625
4.13.10	Conclusions	625
4.14	Natural Spice Ingredients Capsaicin, Piperine, Thymol, and Cinnamaldehyde	626
4.14.1	Introduction	627
4.14.2	Analysis Conditions	627
4.14.3	Experimental Conditions	628
4.14.4	Sample Measurements	629
4.14.5	Results	631
4.14.6	Conclusions	632
4.15	Geosmin and Methylisoborneol in Drinking Water	632
4.15.1	Introduction	632
4.15.2	Analysis Conditions	633
4.15.3	SPME Method	634
4.15.4	Results	634
4.16	Flavor and Fragrance Profiling by Dual-Column GC-MS	637
4.16.1	Introduction	637
4.16.2	Analysis Conditions	638
4.16.3	Sample Preparation	638
4.16.4	Experimental Setup	639

4.16.5	Results	641
4.16.6	Conclusions	644
4.17	Aroma Profiling of Cheese	644
4.17.1	Introduction	644
4.17.2	Analysis Conditions	645
4.17.3	Sample Preparation	646
4.17.4	Experimental Conditions	647
4.17.4.1	Dynamic Headspace Sampling	647
4.17.4.2	Thermal Desorption	647
4.17.5	Sample Measurements	647
4.17.6	Results	648
4.17.7	Conclusions	649
4.18	Allergens	649
4.18.1	Introduction	649
4.18.2	Analysis Conditions	649
4.18.3	Sample Preparation	651
4.18.3.1	Extraction	651
4.18.4	Experimental Conditions	651
4.18.5	Results	651
4.18.6	Conclusions	656
4.19	Metabolite Profiling	656
4.19.1	Introduction	656
4.19.1.1	Workflow Phase I: Discovery	656
4.19.1.2	Workflow Phase II: Targeted Quantitation	658
4.19.2	Analysis Conditions	658
4.19.3	Sample Preparation	659
4.19.4	Results	660
4.19.5	Conclusion	664
4.20	Extractables and Leachables	665
4.20.1	Introduction	665
4.20.2	Analysis Conditions	666
4.20.3	Sample Preparation	668
4.20.4	Experimental Conditions	668
4.20.5	Data Processing and Results	668
4.20.6	AMDIS Chromatogram Deconvolution	668
4.20.7	Mass Frontier Spectrum Interpretation	673
4.20.8	Conclusions	675
4.21	Volatiles in Car Interiors	677
4.21.1	Introduction	677
4.21.2	Analysis Conditions	679
4.21.3	Sample Measurements	680
4.21.3.1	Sample Preparation	680
4.21.3.2	VOC testing	680
4.21.3.3	SVOC Testing	681
4.21.4	Conclusion	683

4.22	Azo Dyes in Leather and Textiles	683
4.22.1	Introduction	683
4.22.2	Analysis Conditions	685
4.22.3	Results	688
4.23	Fast GC of 16 Priority PAHs	691
4.23.1	Introduction	691
4.23.2	Analysis Conditions	694
4.23.3	Results	695
4.24	Environmental Contaminants in Fish	697
4.24.1	Introduction	698
4.24.2	Analysis conditions	698
4.24.3	Sample Preparation	700
4.24.4	Sample Measurements	700
4.24.5	Results	705
4.24.6	Method Limitations	711
4.24.7	Conclusions	712
4.25	Fast GC of PCBs	712
4.25.1	Introduction	712
4.25.2	Analysis Conditions	714
4.25.3	Results	716
4.26	Dioxin Screening in Food and Feed	718
4.26.1	Introduction	718
4.26.2	Analysis Conditions	720
4.26.3	Sample Preparation	721
4.26.4	Experimental Conditions	721
4.26.5	Results	724
4.26.6	Conclusions	729
4.27	Confirmation Analysis of Dioxins and Dioxin-like PCBs	730
4.27.1	Introduction	730
4.27.2	Analysis Conditions	732
4.27.2.1	Chromatographic Analysis	733
4.27.3	Results	736
4.28	U.S. EPA 1614 Brominated Flame Retardants PBDEs	739
4.28.1	Introduction	739
4.28.2	Analysis Conditions	739
4.28.3	Results	740
4.29	PBB Analysis by SPME	747
4.29.1	Introduction	747
4.29.2	Analysis Conditions	748
4.29.3	Results	749
4.30	THC-A in Urine by NCI	751
4.30.1	Introduction	751
4.30.2	Analysis Conditions	752
4.30.3	Sample Preparation	753
4.30.3.1	Hydrolysis	753

4.30.3.2	Extraction	754
4.30.3.3	Derivatization	754
4.30.4	Experimental Conditions	754
4.30.5	Sample Measurements	754
4.30.5.1	Reproducibility of Retention Times	754
4.30.5.2	Limit of Detection and Limit of Quantification	754
4.30.5.3	Recovery and Calibration	754
4.30.6	Results	755
4.30.6.1	Mass Spectra and GC Separation	755
4.30.7	Quality Control Samples	757
4.30.8	Conclusions	757
4.31	Comprehensive Drug Screening and Quantitation	757
4.31.1	Introduction	757
4.31.2	Analysis Conditions	758
4.31.3	Sample Preparation	759
4.31.4	Experimental Conditions	759
4.31.5	Sample Measurements	759
4.31.6	Results	761
4.31.7	Conclusions	761
4.32	Drugs of Abuse	762
4.32.1	Introduction	762
4.32.2	Analysis Conditions	763
4.32.3	Results	765
4.33	Structure Elucidation by CI and MS/MS	766
4.33.1	Introduction	766
4.33.2	Analysis Conditions	767
4.33.3	Experimental Conditions	768
4.33.4	Sample Measurements	768
4.33.5	Results	769
	References	770

Glossary 787

Further Reading 858

Author Index 859

Subject Index 861

Compound Index 881