

Contents

Preface *xv*

About the Editor *xvii*

1	Introduction of Mass Spectrometry and Ambient Ionization Techniques	1
	<i>Yiyang Dong, Jiahui Liu, and Tianyang Guo</i>	
1.1	Evolution of Analytical Chemistry and Its Challenges in the Twenty-First Century	1
1.2	Historical Overview of Mass Spectrometry and Its Role in Contemporary Analytical Chemistry	5
1.3	Desorption/Ionization in Mass Spectrometry	12
1.3.1	Electronic Ionization (EI)	13
1.3.2	Chemical Ionization (CI)	14
1.3.3	Fast Atom/Ion Bombardment Ionization (FAB)	15
1.3.4	Electrospray Ionization (ESI)	16
1.3.5	Matrix Assisted Laser Desorption/Ionization (MALDI)	18
1.3.6	Field Desorption (FD) or Field Ionization (FI)	19
1.3.7	Plasma Desorption (PD) (ICP, LTP, DART)	19
1.4	Ambient Ionization and Direct Analysis in Real Time	21
1.4.1	Ambient Ionization	21
1.4.2	Direct Analysis in Real Time	24
1.4.2.1	Mechanisms	24
1.4.2.2	Parameters	27
1.4.2.3	Devices	29
	References	30
2	DART Mass Spectrometry: Principle and Ionization Facilities	43
	<i>David Rondeau</i>	
2.1	Introduction	43
2.2	Metastable Gas Stream Formation	43
2.3	Ionization Mechanisms in Positive DART	45
2.3.1	Generation of Primary Ions by Ambient Air Ionization	46
2.3.2	Formation of the Protonated Molecules	50

2.3.3	Formation of the Ammonium Adducts	54
2.3.4	Formation of the Radical Cations and Their Fragments	55
2.3.5	Matrix Effects in DART Due to Sample Solvents	59
2.4	Ionization Mechanisms in Negative DART	65
2.4.1	Generation of Primary Ions by Ambient Air Ionization	65
2.4.2	Formation of Deprotonated Molecules	68
2.4.3	Formation of Radical Anions	69
2.4.4	Formation of Anionic Adducts	70
2.5	Some Parameters Affecting the DART Mass Spectra	71
2.5.1	Substitution of Helium by Nitrogen or Argon	71
2.5.2	The Temperature of the Gas Stream	75
2.5.3	The Internal Energy of Ions in DART-MS	76
2.6	Conclusion	78
	References	78
3	Sampling and Analyte Enrichment Strategies for DART-MS	81
	<i>Wen Ma, Xianjiang Li, and Huwei Liu</i>	
3.1	Dilution Strategy for Sticky Sample Analysis	81
3.2	Purification Strategy for Eliminating the Matrix Interference	82
3.2.1	Liquid Phase Extraction	82
3.2.2	Solid Phase Extraction (SPE)	86
3.2.3	Solid Phase Microextraction (SPME)	87
3.3	Derivatization Strategy to Decrease Polarity and Enhance Volatility	89
3.4	Conclusions	91
	References	91
4	Optimization of DART and Mass Spectrometric Parameters	97
	<i>Guohua Wu and Wushuang Li</i>	
4.1	Introduction	97
4.2	Effect of Working Gas Type, Gas Flow Rate, and Its Temperature	98
4.2.1	Gas Type	98
4.2.2	Gas Flow Rate	99
4.2.3	The Working Gas Temperature of DART Ionization Source	100
4.3	Effects of Grid Electrode Voltage and Sampling Speed	102
4.3.1	Effect of Grid Electrode Voltage	102
4.3.2	Effect of Sampling Speed	103
4.4	Effect of the Sampling Mode	104
4.4.1	Sampling Methods	104
4.4.2	Position and Angle of the DART Ion Source	105
4.5	Effect of Ion Mode	106
4.6	Effect of Solvent Type and Reagents	108
4.7	Summary	109
	References	109

5	Interfacing DART to Extend Analytical Capabilities	115
	<i>Yiding Zhang, Shuting Xu, and Yu Bai</i>	
5.1	Introduction	115
5.2	Interfacing DART with Different Separation Techniques	116
5.2.1	Solid Samples	116
5.2.2	Gaseous Samples	118
5.2.3	Liquid Samples	119
5.2.3.1	Liquid Chromatography	119
5.2.3.2	Capillary Electrophoresis	123
5.3	Techniques of Interfacing DART with Other Analytical Techniques	125
5.3.1	Surface Plasmon Resonance	125
5.3.2	Ion Mobility Spectrometry	126
5.4	Conclusion and Perspectives	129
	References	129
6	Application of DART-MS in Foods and Agro-Products Analysis	133
	<i>Canping Pan and Lei Wang</i>	
6.1	Introduction	133
6.2	Applications of DART-MS in Agriculture and Food Science	134
6.2.1	DART-MS in Pesticide Residue Analysis	134
6.2.1.1	Fast Screening Purposes	134
6.2.1.2	Screening Highly Hazardous Pesticides in Agrochemical Formulations	140
6.2.1.3	Quantitative MRM Residue Method	147
6.2.2	Veterinary Drug Residue Detection	148
6.2.3	Fast Detection of Melamine in Milk	149
6.2.4	Detection of Mycotoxins in Cereals	150
6.2.5	Food Component Rapid Analysis	151
6.2.6	Contaminations in Food Contact Materials (FCMs)	156
6.3	Conclusion	156
	References	157
7	Application of DART-MS for Industrial Chemical Analysis	163
	<i>Qiang Ma</i>	
7.1	Application on Household Items	163
7.1.1	Polydimethylsiloxane (PDMS) Analysis in Articles for Daily Use	163
7.1.2	Identification of Sulfides in Drywall	165
7.1.3	Phosphoric Acid Esters Screening in Aqueous Samples	168
7.2	Application on Food Packaging Safety and Quality Control	172
7.2.1	Identification of PDMS in Food Packaging Materials	172
7.2.2	Identification of Polymer Additives in Food and Food Packaging	175
7.2.3	Identification of Residue Primary Aromatic Amines (PAAs) in Food Packaging Materials	176
7.3	Application on Pharmaceutical Products	177
7.3.1	Toxic Glycols Identification	177

7.3.2	Identification of Active Ingredients in Chinese Herbal Medicines	179
7.4	Application on Cosmetics Quality Control	182
7.4.1	Screening of Glucocorticoids Illegal Addition	182
7.5	Application on Other Industrial Chemical Fields	184
7.5.1	Ink Discrimination on Questioned Document	184
7.5.2	Ionic Liquids Identification	189
7.6	Conclusions	190
	References	190
8	Application of Direct Analysis in Real Time Coupled to Mass Spectrometry (DART-MS) for the Analysis of Environmental Contaminants	193
	<i>Maxime C. Bridoux and Sébastien Schramm</i>	
8.1	Introduction	193
8.2	Screening and Quantitative Analysis of Pesticides	194
8.3	Flame Retardants DART-MS Analysis	204
8.3.1	Organophosphorus Flame Retardants (OPFRs)	204
8.3.2	Brominated Flame Retardants (BFRs)	207
8.4	Use of DART-MS for the Analysis of Personal Care Products (PCPs)	210
8.4.1	Screening of Organic UV Filters in Water	210
8.4.2	Screening of Phthalic Acid Diesters	211
8.4.3	HPLC-DART-MS Analysis of Parabens	211
8.5	Use of DART-MS for the Analysis of Aerosols	212
8.5.1	Online DART for Aerosols Analysis	212
8.5.2	Offline DART Methods	213
8.5.3	Advantages and Limitations of DART-MS for Aerosols Characterization	213
8.6	Miscellaneous Environmental Application of DART-MS	214
8.7	Conclusions	215
	References	216
9	Application of DART-MS in Clinical and Pharmacological Analysis	223
	<i>Yue Li</i>	
9.1	Introduction	223
9.2	Sample Preparation	224
9.3	Applications of DART-MS	225
9.3.1	Rapid Determination of Small Organic Compounds in Biological Samples	225
9.3.1.1	Analysis of a Bitter Herbal Medicine <i>Gentiana scabra</i> Root Extract	225
9.3.1.2	Simultaneous Determination of 3-Chlorotyrosine and 3-Nitrotyrosine in Human Plasma	226
9.3.1.3	Rapid Screening for Methamphetamine, 3,4-Methylene-dioxymethamphetamine, and Their Metabolites in Urine	227

9.3.2	Newborn Screening for Phenylketonuria	227
9.3.3	DART-MS Analysis of Skin Metabolome Changes in Ultraviolet B-Induced Mice	228
9.3.4	Application in Detection of Breast Cancer	231
9.3.5	Transmission Mode DART-MS for Fast Untargeted Metabolic Fingerprinting	232
9.3.6	Applications of Confined DART Ion Source for Online <i>In vivo</i> Analysis of Human Breath	233
9.3.6.1	Real-Time Analysis of Exhaled Breath	234
9.3.6.2	Real-Time Monitoring of Oral Anesthetic Drug	235
9.4	Challenges and Limitations	236
9.5	Recent Advancements	237
	References	238
10	DART-MS Applications in Pharmaceuticals	241
	<i>Karina G. Putri, Qianwen Wu, and Young P. Jang</i>	
10.1	Pharmaceutical Analysis	241
10.2	Quality Assurance	243
10.3	Illegal Active Pharmaceutical Ingredients and Counterfeit Drugs	244
10.4	Drug Development	247
	References	251
11	Application of DART-MS in Natural Phytochemical Research	255
	<i>Vikas Bajpai, Awantika Singh, Brijesh Kumar, and Kunnath P. Madhusudanan</i>	
11.1	Introduction	255
11.2	Direct Analysis in Real Time (DART) Mass Spectrometry	256
11.3	DART-MS Parameter Optimization for Phytochemical Analysis	256
11.4	Applications of DART-MS in Phytochemical Research	257
11.4.1	Qualitative Phytochemical Analysis	257
11.4.2	Cell Culture Analysis	261
11.4.3	Analysis of Volatiles	261
11.4.4	Species Identification	262
11.4.5	Metabolic Profiling and Multivariate Analysis	263
11.4.6	Quantitative Analysis	274
11.5	Hyphenated DART-MS Techniques for Phytochemical Analysis	276
11.5.1	GC and HPLC-DART-MS	276
11.5.2	TLC/HPTLC-DART-MS	276
11.5.3	Capillary Electrophoresis-DART MS	277
11.5.4	DART-IMS-MS	277
11.5.5	Other Coupling Techniques	277
11.6	Improving Sensitivity of DART-MS for Phytochemical Analysis	278
11.6.1	Solvents and Gases	278
11.6.2	Matrix Suppression	279
11.7	DART -MS as Process Analytical Technology	279
11.8	Future Perspective	280
	References	280

12	Miscellaneous Applications of DART-MS	291
	<i>Yoshihito Okada</i>	
12.1	Introduction	291
12.2	Usefulness of Negative-Ion Mode	292
12.3	Application to Archeology and Conservation	293
12.4	Application by Using TLC	293
12.5	Application to Low Volatility, Chemical Warfare, and Homeland Security	294
12.6	Pheromone Profiles from Live Animals in Parallel with Behavior	295
12.7	Application to Distinction of Plants with Similarity	296
12.8	Application to Space	298
12.9	Application to Bituminous Coals	298
12.10	Application to Detection of Nicotine	298
12.11	Other Potential Applications of DART-MS	299
12.11.1	Instantaneous Screening for Counterfeit Drugs with No Sample Preparation [26-1]	299
12.11.2	Direct Analysis of Drugs in Pills and Capsules with No Sample Preparation [26-2]	300
12.11.3	Detection of Lycopene in Tomato Skin [26-3]	300
12.11.4	Distribution of Capsaicin in Chili Peppers [26-4]	302
12.11.5	Detection of Unstable Compound Released by Chopped Chives [26-5]	302
12.11.6	Rapid Detection of Fungicide in Orange Peel [26-6]	304
12.11.7	"Laundry Detective": Identification of a Stain [26-7]	304
12.11.8	Detection of the Peroxide Explosives TATP and HMTD [26-8]	306
12.11.9	Instantaneous Detection of Explosives on Clothing [26-9]	306
12.11.10	Rapid Detection and Exact Mass Measurements of Trace Components in a Herbicide [26-10]	308
12.11.11	Rapid Analysis of <i>p</i> -Phenylenediamine Antioxidants in Rubber [26-11]	308
	Acknowledgment	309
	References	309
13	Inherent Limitations and Prospects of DART-MS	313
	<i>Tim T. Häbe, Matthias Nitsch, and Gertrud E. Morlock</i>	
13.1	Aspects of Inherent Limitations of DART-MS	313
13.1.1	Gas Settings	314
13.1.1.1	Type of Gas	314
13.1.1.2	Gas Temperature	314
13.1.1.3	Gas Flow Rate	317
13.1.2	Voltage of Electrodes	317
13.1.3	Sample Introduction and Positioning	318
13.1.4	Detection System and Mass Range	318
13.1.5	Matrix Effects and the Need for Chromatography	319
13.1.6	Buffer and Salt Effects	321
13.1.7	Sample Carrier and Solvent	322
13.1.8	Humidity Effects	322

13.1.9	Use of Isotopically Labeled Standards	322
13.1.10	Dopant and Derivatization	323
13.2	DART versus Other Ambient Ion Sources	324
13.3	Prospects of DART-MS	326
13.3.1	Automation and Miniaturized DART-MS	326
13.3.2	Sample Preparation, Preconcentration, and Introduction	327
13.3.3	Ion Focusing and Flexible Ion Transportation	327
13.3.4	Quantitative Surface Scanning and Imaging by DART-MS	328
13.3.5	Hyphenation of Effect-Directed Analysis and DART-MS	331
13.3.6	Thermal Separations by Temperature Gradients	331
13.3.7	Aerosol, <i>in situ</i> and <i>in stillo</i> Chemical Reaction and Kinetic Monitoring	332
13.3.8	High Resolution and Data Analysis	332
13.4	Concluding Remarks	333
	References	333
	Index	345