



Contents

Preface XV
List of Contributors XIX

1	The Isotopic Composition of the Elements	1
	<i>Frank Vanhaecke and Kurt Kyser</i>	
1.1	Atomic Structure	1
1.2	Isotopes	2
1.3	Relation Between Atomic Structure and Natural Abundance of Elements and Isotopes	3
1.4	Natural Isotopic Composition of the Elements	5
1.4.1	Elements with Radiogenic Nuclides	7
1.4.1.1	Radioactive Decay	7
1.4.1.2	Elements with Radiogenic Nuclides	9
1.4.2	Effects Caused by Now Extinct Radionuclides	13
1.4.3	Mass-Dependent Isotope Fractionation	13
1.4.3.1	Isotope Fractionation in Physical Processes	15
1.4.3.2	Isotope Fractionation in Chemical Reactions	16
1.4.4	Mass-Independent Isotope Fractionation	20
1.4.5	Interaction of Cosmic Rays with Terrestrial Matter	23
1.4.6	Human-Made Variations	24
	References	26
2	Single-Collector Inductively Coupled Plasma Mass Spectrometry	31
	<i>Frank Vanhaecke</i>	
2.1	Mass Spectrometry	31
2.2	The Inductively Coupled Plasma Ion Source	32
2.3	Basic Operating Principles of Mass Spectrometers	34
2.3.1	Mass Spectrometer Characteristics	34
2.3.1.1	Mass Resolution	34

2.3.1.2	Abundance Sensitivity	35
2.3.1.3	Mass Spectral Range	36
2.3.1.4	Scanning Speed	36
2.3.2	Quadrupole Filter	36
2.3.3	Double-Focusing Sector Field Mass Spectrometer	38
2.3.4	Time-of-Flight Analyzer	43
2.3.5	Comparison of Characteristics	45
2.4	Quadrupole-Based ICP-MS	45
2.5	Sample Introduction Strategies in ICP-MS	47
2.6	Spectral Interferences	50
2.6.1	Cool Plasma Conditions	51
2.6.2	Multipole Collision/Reaction Cell	52
2.6.2.1	Overcoming Spectral Interference via Chemical Resolution	53
2.6.2.2	Overcoming Spectral Interference via Collisional Deceleration and Kinetic Energy Discrimination	55
2.6.3	High Mass Resolution with Sector Field ICP-MS	55
2.7	Measuring Isotope Ratios with Single-Collector ICP-MS	56
2.7.1	Isotope Ratio Precision	57
2.7.1.1	Poisson Counting Statistics	57
2.7.1.2	Isotope Ratio Precision with Single-Collector ICP-MS	58
2.7.2	Detector Issues	62
2.7.2.1	Electron Multiplier Operating Principles	62
2.7.2.2	Detector Dead Time	62
2.7.3	Instrumental Mass Discrimination	66
	References	68

3 Multi-Collector Inductively Coupled Plasma Mass Spectrometry 77

Michael Wieser, Johannes Schwieters, and Charles Douthitt

3.1	Introduction	77
3.2	Early Multi-Collector Mass Spectrometers	78
3.3	Variable Multi-Collector Mass Spectrometers	79
3.4	Mass Resolution and Resolving Power	81
3.5	Three-Isotope Plots for Measurement Validation	84
3.6	Detector Technologies for Multi-Collection	87
3.7	Conclusion	90
	References	91

4 Advances in Laser Ablation–Multi-Collector Inductively Coupled Plasma Mass Spectrometry 93

Takafumi Hirata

4.1	Precision of Isotope Ratio Measurements	93
4.2	Stable Signal Intensity Profiles: Why So Important?	94
4.3	Signal Smoothing Device	99

4.4	Multiple Ion Counting	101
4.5	Isotope Fractionation During Laser Ablation and Ionization	102
4.6	Standardization of the Isotope Ratio Data	107
	Acknowledgments	108
	References	108
5	Correction of Instrumental Mass Discrimination for Isotope Ratio Determination with Multi-Collector Inductively Coupled Plasma Mass Spectrometry	113
	<i>Juris Meija, Lu Yang, Zoltán Mester, and Ralph E. Sturgeon</i>	
5.1	Historical Introduction	113
5.2	Mass Bias in MC-ICP-MS	114
5.3	Systematics of Mass Bias Correction Models	115
5.3.1	External Gravimetric Calibration	116
5.3.2	Internal Double-Spike Calibration	117
5.3.3	Internal Calibration (Inter-Element)	117
5.3.4	External Bracketing Calibration (Inter-Element)	117
5.4	Logic of Conventional Correction Models	118
5.5	Pitfalls with Some Correction Models	119
5.5.1	Linear Law	119
5.5.2	Exponential Versus the Power Law	120
5.6	Integrity of the Correction Models	120
5.6.1	Russell's Law	120
5.6.2	Discrimination Exponent	121
5.6.3	Discrimination Function	122
5.6.4	Second-Order Terms	124
5.7	The Regression Model	124
5.8	Calibration with Double Spikes	126
5.8.1	Caveat of the Model Choice	129
5.9	Calibration with Internal Correction	130
5.9.1	Intra-Elemental Correction	130
5.9.2	Inter-Elemental Correction	130
5.10	Uncertainty Evaluation	131
5.10.1	Uncertainty Modeling and the Double Spikes	132
5.11	Conclusion	133
	References	134
6	Reference Materials in Isotopic Analysis	139
	<i>Jochen Vogl and Wolfgang Pritzkow</i>	
6.1	Introduction	139
6.2	Terminology	140
6.3	Determination of Isotope Amount Ratios	145
6.4	Isotopic Reference Materials	149

6.4.1	General	149
6.4.2	Historical Development	149
6.4.3	Requirements for Isotopic Reference Materials	151
6.5	Present Status, Related Problems, and Solutions	153
6.5.1	Present Status	153
6.5.2	Related Problems	154
6.5.3	Solution	156
6.6	Conclusion and Outlook	157
)	References	158

7 Quality Control in Isotope Ratio Applications 165

Thomas Meisel

7.1	Introduction	165
7.2	Terminology and Definitions	168
7.3	Measurement Uncertainty	174
7.3.1	Influence Quantities	177
7.3.1.1	Sampling	177
7.3.1.2	Sample Preparation	177
7.3.1.3	Isotope Amount Ratio Determination	177
7.3.1.4	Data Presentation with Isotope Notation	179
7.3.2	Example of Uncertainty Budget Estimation When Using Isotope Dilution	180
7.3.3	Alternative Approach	181
7.3.4	How to Establish Metrological Traceability	181
7.3.5	Method Validation	182
7.3.5.1	Limits of Detection, of Determination, and of Quantitation	182
7.3.5.2	Inter-Laboratory Studies	184
7.4	Conclusion	185
)	References	185

8 Determination of Trace Elements and Elemental Species Using Isotope Dilution Inductively Coupled Plasma Mass Spectrometry 189

Klaus G. Heumann

8.1	Introduction	189
8.2	Fundamentals	190
8.2.1	Principles of Isotope Dilution Mass Spectrometry	190
8.2.2	Elements Accessible to ICP-IDMS Analysis	194
8.2.3	Selection of Spike Isotope and Optimization of Its Amount	195
8.2.4	Uncertainty Budget and Limit of Detection	199
8.3	Selected Examples of Trace Element Determination via ICP-IDMS	200
8.3.1	Trends in ICP-IDMS Trace Analysis	200

8.3.2	Direct Determination of Trace Elements in Solid Samples via Laser Ablation and Electrothermal Vaporization ICP-IDMS	201
8.3.3	Representative Examples of Trace Element Determination via ICP-IDMS	203
8.3.3.1	Determination of Trace Amounts of Silicon in Biological Samples	203
8.3.3.2	Trace Element Analysis of Fossil Fuels	205
8.3.3.3	Trace Element Analysis via On-Line Photochemical Vapor Generation	207
8.3.3.4	Determination of Trace Amounts of Platinum Group Elements	208
8.3.3.5	Determination of Ultra-Trace Amounts of Transuranium Elements	211
8.3.4	ICP-IDMS in Elemental Speciation	212
8.3.4.1	Principles of ICP-IDMS in Elemental Speciation	212
8.3.4.2	Species-Specific ICP-IDMS	214
8.3.4.3	Species-Unspecific ICP-IDMS	221
	References	230

9 Geochronological Dating 235

Marlina A. Elburg

9.1	Geochronology: Principles	235
9.1.1	Single Phase and Isochron Dating	235
9.1.2	Closure Temperature	237
9.2	Practicalities	240
9.2.1	Isobaric Overlap	240
9.2.2	ICP-MS versus TIMS for Geochronology	241
9.3	Various Isotopic Systems	242
9.3.1	U/Th-Pb	242
9.3.1.1	LA-ICP-MS U-Pb Dating of Zircon	244
9.3.1.2	Laser Ablation U/Th-Pb Dating of Other Phases	254
9.3.1.3	Solution Pb-Pb Dating	257
9.3.2	Lu-Hf System	257
9.3.2.1	Lu-Hf Isochrons with Garnet	258
9.3.2.2	Lu-Hf on Phosphates	259
9.3.2.3	Zircon Hf Isotopic Model Ages	259
9.3.3	Re(-Pt)-Os System	261
9.3.3.1	Re-Os Molybdenite Dating	262
9.3.3.2	Re-Os Dating of Black Shales	262
9.3.3.3	Pt-Re-Os on Mantle Peridotites	263
9.4	Systems for Which ICP-MS Analysis Brings Fewer Advantages	265
	Acknowledgments	266
	References	266

10	Application of Multiple-Collector Inductively Coupled Plasma Mass Spectrometry to Isotopic Analysis in Cosmochemistry	275
	<i>Mark Rehkämper, Maria Schönbächler, and Rasmus Andreasen</i>	
10.1	Introduction	275
10.2	Extraterrestrial Samples	276
10.2.1	Introduction	276
10.2.2	Classification of Meteorites	277
10.2.3	Chondritic Meteorites	279
10.2.4	Non-Chondritic Meteorites	281
10.3	Origin of Cosmochemical Isotopic Variations	281
10.3.1	Radiogenic Isotope Variations from the Decay of Long-Lived Radioactive Nuclides	282
10.3.2	Radiogenic Isotope Variations from the Decay of Extinct Radioactive Nuclides	282
10.3.3	Nucleosynthetic Isotope Anomalies	283
10.3.4	Mass-Dependent Isotope Fractionation	284
10.3.5	Cosmogenic Isotope Anomalies	284
10.4	Use of MC-ICP-MS in Cosmochemistry	285
10.4.1	Specific Advantages of MC-ICP-MS	286
10.4.2	Analytical Procedures	287
10.5	Applications of MC-ICP-MS in Cosmochemistry	289
10.5.1	Nucleosynthetic Isotope Anomalies	289
10.5.2	Long-Lived Radioactive Decay Systems	293
10.5.2.1	The ^{87}Rb - ^{87}Sr Decay System	293
10.5.2.2	The ^{147}Sm - ^{143}Nd Decay System	293
10.5.2.3	The ^{176}Lu - ^{176}Hf Decay System	294
10.5.2.4	The U/Th-Pb Decay Systems	295
10.5.3	Extinct Radioactive Decay Systems	297
10.5.4	Stable Isotope Fractionation	300
10.5.5	Cosmogenic Isotope Variations	306
10.6	Conclusion	307
	Acknowledgments	308
	References	308
11	Establishing the Basis for Using Stable Isotope Ratios of Metals as Paleoredox Proxies	317
	<i>Laura E. Wasyljenki</i>	
11.1	Introduction	317
11.2	Isotope Ratios of Metals as Paleoredox Proxies	319
11.2.1	Molybdenum Isotope Ratios and Global Ocean Paleoredox	320
11.2.2	Cr Isotope Ratios and Paleoredox Conditions of the Atmosphere	329

11.2.3	Uranium Isotope Ratios and Marine Paleoredox	338
11.3	Diagenesis: a Critical Area for Further Work	344
	References	346
12	Isotopes as Tracers of Elements Across the Geosphere–Biosphere Interface	351
	<i>Kurt Kyser</i>	
12.1	Description of the Geosphere–Biosphere Interface	351
12.2	Elements That Typify the Geosphere–Biosphere Interface	354
12.3	Microbes at the Interface	355
12.4	Element Tracing in Environmental Science and Exploration of Metal Deposits	356
12.5	Isotopes as Indicators of Paleoenvironments	360
12.6	Tracing the Geosphere Effect on Vegetation and Animals	360
12.7	Tracing in the Marine Environment	364
12.8	Future Directions	367
	References	368
13	Archeometric Applications	373
	<i>Patrick Degryse</i>	
13.1	Introduction	373
13.2	Current Applications	375
13.2.1	Lead	375
13.2.2	Strontium	377
13.2.2.1	Inorganics: Glass and Iron	377
13.2.2.2	Organics: Skeletal Matter	378
13.2.3	Neodymium	379
13.2.4	Osmium	379
13.3	New Applications	380
13.3.1	Copper	380
13.3.2	Tin	380
13.3.3	Antimony	380
13.3.4	Boron	381
13.4	Conclusion	382
	References	382
14	Forensic Applications	391
	<i>Martín Resano and Frank Vanhaecke</i>	
14.1	Introduction	391
14.1.1	What is Forensics?	391
14.1.2	The Role of ICP-MS in Forensics	391

14.2	Forensic Applications Based on ICP-MS Isotopic Analysis	393
14.2.1	Crime Scene Investigation	393
14.2.2	Nuclear Forensics	396
14.2.3	Food Authentication	399
14.2.4	Monitoring Environmental Pollution	404
14.2.5	Other Applications	408
14.3	Future Outlook	411
	Acknowledgments	412
	References	412
15	Nuclear Applications	419
	<i>Scott C. Szechenyi and Michael E. Ketterer</i>	
15.1	Introduction	419
15.2	Rationale	419
15.3	Process Control and Monitoring in the Nuclear Industry	422
15.4	Isotopic Studies of the Distribution of U and Pu in the Environment	424
15.5	Nuclear Forensics	429
15.6	Prospects for Future Developments	431
	Acknowledgment	431
	References	432
16	The Use of Stable Isotope Techniques for Studying Mineral and Trace Element Metabolism in Humans	435
	<i>Thomas Walczyk</i>	
16.1	Essential Elements	435
16.2	Stable Isotopic Labels Versus Radiotracers	436
16.3	Quantification of Stable Isotopic Tracers	438
16.4	Isotope Labeling Techniques	442
16.5	Concepts of Using Tracers in Studies of Element Metabolism in Humans	444
16.5.1	Overview	444
16.5.2	Fecal Balance Studies (Single Isotopic Label)	444
16.5.3	Fecal Balance Studies (Double Isotopic Label)	445
16.5.4	Plasma Appearance	446
16.5.5	Urinary Monitoring	447
16.5.6	Compartmental Modeling	447
16.5.7	Tissue Retention	448
16.5.8	Element Turnover Studies	449
16.5.9	Isotope Fractionation Effects	450
16.6	ICP-MS in Stable Isotope-Based Metabolic Studies	451
16.6.1	Measurement Precision	451
16.6.2	Mass Spectrometric Sensitivity	454

16.6.3	Measurement Accuracy and Quality Control	454
16.7	Element-by-Element Review	458
16.7.1	Calcium	458
16.7.2	Iron	462
16.7.3	Zinc	464
16.7.4	Magnesium	469
16.7.5	Selenium	471
16.7.6	Copper	474
16.7.7	Molybdenum	476
	Acknowledgments	477
	References	478
17	Isotopic Analysis via Multi-Collector Inductively Coupled Plasma Mass Spectrometry in Elemental Speciation	495
	<i>Vladimir N. Epov, Sylvain Berail, Christophe Péchéyran, David Amouroux, and Olivier F.X. Donard</i>	
17.1	Introduction	495
17.2	Advantage of On-Line versus Off-Line Separation of Elemental Species	497
17.3	Coupling Chromatography with MC-ICP-MS	498
17.3.1	Instrumentation: LC, GC, HPLC, and IC Coupled with MC-ICP-MS	498
17.3.1.1	Liquid Chromatography	500
17.3.1.2	Gas Chromatography	500
17.3.2	Acquisition, Mass Bias Correction, and Data Treatment Strategy	503
17.3.2.1	Signal Acquisition	503
17.3.2.2	Mass Bias Correction	504
17.3.2.3	Data Treatment Strategy	504
17.3.3	Consequences of the Transient Nature of the Signal	507
17.3.3.1	Shape and Width of the Peak	507
17.3.3.2	Drift of the Isotope Ratios During Peak Elution	507
17.4	Environmental and Other Applications	509
17.4.1	Mercury	509
17.4.2	Lead	511
17.4.3	Sulfur	511
17.4.4	Antimony	512
17.4.5	Halogens	512
17.5	Conclusion and Future Trends	513
	References	515
	Index	519