

Contents

1	Origins and development	1
1.1.	Introduction	1
1.2	The ICP-MS system	5
2	Instrumentation for ICP-MS	10
2.1	The inductively coupled plasma	10
2.1.1	Torch and plasma	10
2.1.2	RF coupling	13
2.1.3	Sample introduction	13
2.1.4	Sample history	14
2.1.5	Plasma populations	15
2.1.6	Distribution of ions in the plasma	18
2.1.7	Other plasmas	21
2.2	Ion extraction	21
2.2.1	Boundary layer and sheath	22
2.2.2	Plasma potential and secondary discharge	23
2.2.3	Supersonic jet	26
2.2.4	Gas dynamics	28
2.2.5	Ion kinetic energies	30
2.3	Ion focusing	31
2.3.1	Operation of ion lenses	31
2.3.2	Ion lenses in ICP-MS	33
2.3.3	Space charge effects	35
2.4	Quadrupole mass spectrometers	37
2.4.1	Quadrupole configuration	37
2.4.2	Ion trajectories and stability diagrams	38
2.4.3	Characteristics of mass spectra from quadrupoles	41
2.4.4	RF-only quadrupoles	42
2.4.5	Scanning and data acquisition	44
2.5	Other mass spectrometers	45
2.6	Ion detection	48
2.6.1	Channeltron electron multipliers	48
2.6.2	Signal measurement by pulse counting	50
2.6.3	Other detectors	51
2.7	Vacuum considerations	51
2.7.1	Properties and flow of gases	51
2.7.2	A vacuum system for ICP-MS	53
2.7.3	Pumps used in ICP-MS	54
3	Instrument options	58
3.1	Introduction	58
3.2	Nebulisers	58
3.2.1	Introduction	58
3.2.2	Concentric nebulisers	59
3.2.3	Cross-flow nebulisers	64
3.2.4	Babington type nebuliser	65
3.2.5	Frit type nebuliser	66
3.2.6	Ultrasonic nebuliser	67

3.3	Spray chambers	68
3.3.1	Principles	68
3.3.2	Operation	69
3.3.3	Thermally stabilised spray chambers for ICP-MS	71
3.4	Torches	75
3.4.1	Construction	75
3.4.2	Demountable torches	75
3.4.3	Alignment	76
3.4.4	Specialised torches	76
3.5	Interface	78
3.5.1	Introduction	78
3.5.2	Sampling cones	78
3.5.3	Skimmer cones	80
4	Sample introduction for liquids and gases	81
4.1	Introduction	81
4.2	Electrothermal vaporisation	82
4.2.1	Principles	82
4.2.2	Instrumentation	83
4.2.3	Operating parameters	89
4.2.4	Applications and analytical performance of ETV-ICP-MS	93
4.3	Vapour generation and gas phase sample introduction	98
4.3.1	Introduction	98
4.3.2	Hydride generation	98
4.3.3	Osmium tetroxide vapour generation	105
4.3.4	Reactive gases	110
4.4	Liquid chromatography	112
4.4.1	Introduction	112
4.4.2	Principles	113
4.4.3	Instrumentation, reagents and operating parameters	118
4.4.4	Applications	118
4.5	Flow injection	119
4.5.1	Introduction	119
4.5.2	Apparatus	119
4.5.3	Sample introduction	120
4.5.4	Operating parameters	120
4.5.5	Applications	122
4.6	Direct sample insertion	124
4.6.1	Principles	124
4.6.2	Applications	124
5	Interferences	125
5.1	Introduction	125
5.2	Spectroscopic interferences	125
5.2.1	Isobaric overlap	125
5.2.2	Polyatomic ions	129
5.2.3	Refractory oxides	134
5.2.4	Doubly charged ions	143
5.2.5	Alleviation of spectroscopic interferences	145
5.3	Non-spectroscopic interferences	148
5.3.1	High dissolved solids	148
5.3.2	Suppression and enhancement effects	150
6	Calibration and data handling	153
6.1	Introduction	153

	CONTENTS	ix
6.2 General concepts		153
6.2.1 Mass scale calibration		153
6.2.2 Accuracy, precision and reproducibility		154
6.3 Instrumental modes of data collection		154
6.3.1 Peak hopping		154
6.3.2 Scanning		155
6.4 Linearity of response		157
6.5 Blanks		158
6.6 Factors affecting signal stability		158
6.7 Qualitative analysis		160
6.8 Semi-quantitative calibration		160
6.9 Quantitative analysis		162
6.9.1 External calibration techniques		162
6.9.2 Raw data correction procedures		162
6.9.3 Standard additions		167
6.9.4 Isotope dilution		168
7 Sample preparation for ICP–MS	172	
7.1 Introduction		173
7.2 General considerations		173
7.2.1 Laboratory equipment and practices		173
7.2.2 Choice of mineral acids		174
7.2.3 Limits of quantitative analysis		180
7.2.4 Precision and accuracy: assessing a digestion procedure		181
7.3 Digestion procedures		181
7.3.1 Open vessel digestions		182
7.3.2 Closed vessel digestions		192
7.3.3 Alkali fusions		196
7.3.4 Microwave digestion		202
7.4 Separation and pre-concentration methods		209
7.4.1 Rare earth elements		210
7.4.2 Precious metals		216
7.4.3 Petrogenic discriminators: Hf, Nb, Ta, Zr		221
7.5 Conclusions and overview		224
8 Elemental analysis of solutions and applications	225	
8.1 Introduction		225
8.2 Multi-element determinations		225
8.3 Geological applications		228
8.3.1 Rare earth elements		229
8.3.2 Platinum group metals		235
8.3.3 Zirconium, niobium, hafnium, tantalum, thorium and uranium		240
8.3.4 Molybdenum, tungsten and thallium		242
8.3.5 Analysis of specific sample types		244
8.4 Environmental applications		247
8.4.1 Multi-element applications		247
8.4.2 Single-element applications		249
8.5 Nuclear applications		251
8.5.1 Uranium matrices		251
8.5.2 Lithium and boron matrices		252
8.5.3 Zirconium and hafnium alloys		253
8.6 Industrial applications		253
8.6.1 Metals		254
8.6.2 Hydrocarbons		256
8.6.3 Other sample types		259

8.7 Biological applications	260
8.7.1 Foods	260
8.7.2 Animal tissue	261
8.7.3 Medical applications	263
8.8 Summary	264
9 The analysis of natural waters by ICP-MS	265
9.1 Introduction	265
9.2 Water sampling procedures for ICP-MS	267
9.2.1 Filtration, acidification and storage	267
9.3 Direct water analysis by ICP-MS	269
9.3.1 Pneumatic nebulisation	269
9.3.2 Electrothermal vaporisation and direct sample insertion	269
9.3.3 Gas phase injection	270
9.4 Water analysis with chemical separation and/or pre-concentration	271
9.4.1 Seawater	271
9.4.2 Freshwater	273
9.4.3 On-line separation and pre-concentration	274
9.5 Calibration strategies	276
9.5.1 External calibration	276
9.5.2 Standard additions	277
9.5.3 Isotope dilution	277
10 Analysis of solid samples	279
10.1 Introduction	279
10.1.1 Calibration	280
10.2 Slurry nebulisation	281
10.2.1 Grinding techniques	281
10.2.2 Dispersing agents	283
10.2.3 Particle size distributions	283
10.2.4 Applications of slurry nebulisation	284
10.3 Laser ablation	290
10.3.1 What is a laser?	291
10.3.2 Modes of operation	291
10.3.3 System configuration	292
10.3.4 Laser operation	294
10.3.5 Sample preparation	295
10.3.6 Calibration	296
10.3.7 Interferences	299
10.3.8 Detection limits	301
10.3.9 Practical considerations	302
10.3.10 Applications	305
10.4 Direct sample insertion	308
10.5 Powdered solids	308
10.6 Arc nebulisation	309
11 Isotope ratio measurement	310
11.1 Introduction	310
11.1.1 Traditional methods of isotope ratio determination	311
11.2 Instrument performance	312
11.2.1 Sensitivity and counting statistics	312
11.2.2 Dead time	312
11.2.3 Resolution and abundance sensitivity	313
11.2.4 Mass bias	315

CONTENTS

xi

11.3 Applications and methods of isotope analysis	315
11.3.1 Lithium	315
11.3.2 Boron	316
11.3.3 Iron	320
11.3.4 Copper	324
11.3.5 Zinc	324
11.3.6 Rhenium and osmium	327
11.3.7 Lead	331
11.3.8 Uranium	334
11.3.9 Other isotopic ratios determined by ICP-MS	336
Appendices	338
Appendix 1 Originators of reference material cited in the text	338
Appendix 2 Naturally-occurring isotopes—useful data	341
Appendix 3 Glossary	348
References	355
Index	377