

# **Handbook of Inductively Coupled Plasma Mass Spectrometry**

K.E. JARVIS and A.L. GRAY

Geology Department

Royal Holloway and Bedford New College  
University of London

R.S. HOUK

Department of Chemistry  
Iowa State University

with additional invited chapters from

I. JARVIS, J.W. McLAREN and J.G. WILLIAMS



**BLACKIE ACADEMIC & PROFESSIONAL**

An Imprint of Chapman & Hall

London · Glasgow · Weinheim · New York · Tokyo · Melbourne · Madras

# Contents

<b>1</b>	<b>Origins and development</b>	<b>1</b>
1.1.	Introduction	1
1.2	The ICP-MS system	5
<b>2</b>	<b>Instrumentation for ICP-MS</b>	<b>10</b>
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
<b>3</b>	<b>Instrument options</b>	<b>58</b>
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
<b>4</b>	<b>Sample introduction for liquids and gases</b>	<b>81</b>
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
<b>5</b>	<b>Interferences</b>	<b>125</b>
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
<b>6</b>	<b>Calibration and data handling</b>	<b>153</b>
6.1	Introduction	153

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
<b>7</b>	<b>Sample preparation for ICP-MS</b>	<b>172</b>
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
<b>8</b>	<b>Elemental analysis of solutions and applications</b>	<b>225</b>
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
<b>9</b>	<b>The analysis of natural waters by ICP-MS</b>	<b>265</b>
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
<b>10</b>	<b>Analysis of solid samples</b>	<b>279</b>
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
<b>11</b>	<b>Isotope ratio measurement</b>	<b>310</b>
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

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
<b>Appendices</b>	<b>338</b>
Appendix 1 Originators of reference material cited in the text	338
Appendix 2 Naturally-occurring isotopes—useful data	341
Appendix 3 Glossary	348
<b>References</b>	<b>355</b>
<b>Index</b>	<b>377</b>