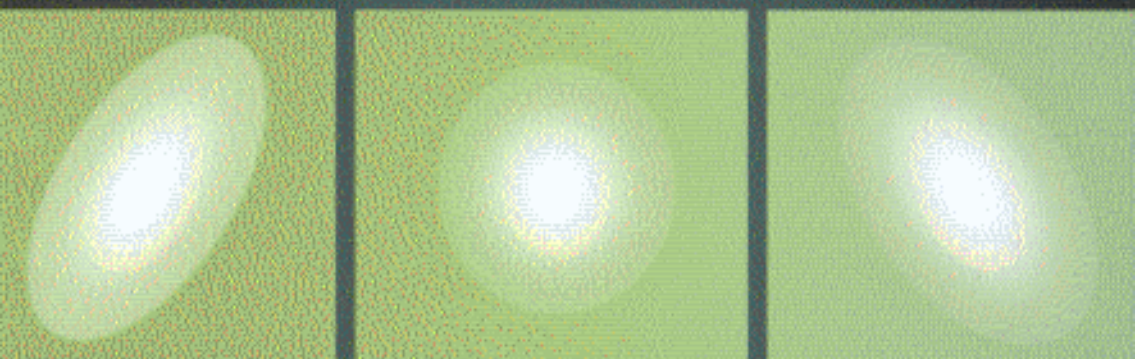


Atomic Spectroscopy in Elemental Analysis



Blackwell
Publishing



CRC Press

Edited by
Michael Cullen

Contents

<i>Contributors</i>	xi
<i>Preface</i>	xiii

1 Method validation for atomic spectroscopy	1
MICHAEL CULLEN and VICKI BARWICK	
1.1 Introduction	1
1.2 The process	2
1.3 Create the validation plan	3
1.4 Precision	4
1.5 Bias	10
1.6 Ruggedness	12
1.7 Limit of detection, limit of quantification and selectivity	13
1.8 The working range and linearity	15
1.9 Equipment qualification	17
1.10 Assessment of uncertainty	19
1.11 Has the method met the requirements set out in the validation plan?	21
Acknowledgements	21
References	22
2 Inductively coupled plasma mass spectrometry	23
ED MCCURDY and DON POTTER	
2.1 Introduction	23
2.2 History and development	24
2.3 Instrumentation	24
2.3.1 Sample introduction	24
2.3.2 Plasma	26
2.3.3 Interface	28
2.3.4 Vacuum system	30
2.3.5 Ion focusing	30
2.3.6 Collision cells	32
2.3.7 Mass analyser	35
2.3.8 Detector	38
2.4 Operation	39
2.4.1 Sample preparation and introduction	39
2.4.2 Plasma optimisation	40
2.4.3 Control of interferences	41
2.4.4 Data acquisition	44
2.4.5 Calibration and quantification	45

2.5	Applications	46
2.5.1	Environment, agriculture and food	46
2.5.2	Semiconductor	48
2.5.3	Clinical and pharmaceutical	49
2.5.4	Geological and nuclear	49
2.5.5	Forensic and archaeological	50
2.5.6	Chemical, petrochemical and material testing	50
	Acknowledgements	51
	References	51

3 Inductively coupled plasma atomic emission spectrometry **55**

STEPHEN J. HILL and ANDREW FISHER

3.1	Introduction	55
3.2	Theory	55
3.2.1	How a plasma is formed?	55
3.2.2	Atomic emission theory	56
3.2.3	Interferences	59
3.3	Instrumentation	61
3.3.1	Generators	61
3.3.2	Line isolation devices	62
3.3.3	Detectors	65
3.3.4	Radial and axial ICPs	68
3.3.5	Sample introduction	69
3.3.5.1	Nebulisers and spray chambers	69
3.3.5.2	Torches	73
3.3.5.3	Other sample introduction methods	77
3.4	Applications	80
3.4.1	Simple applications	81
3.4.2	Pre-concentration methods	82
3.4.3	Speciation and coupled techniques	83
3.4.4	Analysis of gases and high resolution applications	85
3.5	Alternative plasmas	85
3.6	Chemometrics and data manipulation	86
3.7	Conclusions	87
	References	88

4 Analytical glow discharges **91**

NORBERT JAKUBOWSKI, ANNEMIE BOGAERTS and VOLKER HOFFMANN

4.1	Introduction	91
4.2	Basic principles of the analytical GD	91
4.2.1	Introduction	91
4.2.2	Typical discharge conditions of analytical GD	93
4.2.3	Spatial regions in the analytical GD	95
4.2.4	Species present in the analytical GD	98

4.2.5	Most important collision processes in the plasma	104
4.2.5.1	Elastic collisions	106
4.2.5.2	Ionization and excitation of argon atoms	106
4.2.5.3	Ionization and excitation of sputtered (analyte) atoms	109
4.2.5.4	Positive ion-electron recombination	111
4.2.5.5	De-excitation	113
4.2.6	Processes occurring at the walls	114
4.2.6.1	Secondary electron emission	114
4.2.6.2	Sputtering	116
4.3	Glow discharge optical emission spectroscopy	120
4.3.1	Introduction	120
4.3.2	Source and instrumental development	121
4.3.3	Quantitative depth profile analysis	122
4.3.4	Application of a CCD detector	125
4.3.5	Radio frequency GD and interference effect	127
4.3.6	Quantification approaches and measurement of electrical parameters	131
4.4	Glow discharge mass spectrometry	132
4.4.1	Source and instrumental development	133
4.4.2	Instrumentation	137
4.4.3	Sample preparation	140
4.4.4	Quantification	141
4.4.5	Analytical figures of merit	143
4.4.5.1	Sensitivity	143
4.4.5.2	Limit of detection	143
4.4.5.3	Reproducibility and precision	144
4.4.5.4	Robustness	144
4.4.5.5	Accuracy	144
4.4.6	Applications	145
4.4.6.1	Bulk analysis of conducting and semi-conducting samples	147
4.4.6.2	Bulk analysis of non-conducting samples	148
4.4.6.3	In-depth analysis of surface layers	148
4.5	Conclusion	152
	References	152

5 Microwave plasma atomic emission spectroscopy 157

PETER C. UDEN

5.1	Introduction	157
5.2	Microwave-induced plasmas (MIP)	157
5.3	MIPs as chromatographic detectors	159
5.3.1	Analytical information from GC-AED	166
5.4	GC-AED detection of non-metallic elements	168
5.5	GC-AED detection of metallic elements	172
5.5.1	Main group metallic compounds	172
5.5.2	GC-AED of transition metal compounds	175
5.6	Isotope detection by GC-AED	181
5.7	Analytical derivatization in GC-AED	182
5.8	Liquid and supercritical fluid chromatographic applications of AED detection	183
5.9	The role and future development of MIP-AED chromatographic detection	185
	References	185

6	X-ray fluorescence analysis (XRF)	189
	BRUNO VREBOS	
6.1	Introduction	189
6.2	Physics of X-ray absorption and excitation	189
6.2.1	Introduction	189
6.2.2	Absorption	190
6.2.3	The photoelectric effect	191
6.2.4	Scattering of X-rays	193
6.2.5	Nomenclature of characteristic X-rays	194
6.2.6	The fluorescence yield	194
6.2.7	Excitation of X-rays	195
6.2.7.1	Radio-isotopes	195
6.2.7.2	X-ray tubes	196
6.2.7.3	Synchrotron radiation	197
6.3	Principal components of wavelength dispersive XRF spectrometers	198
6.3.1	Introduction	198
6.3.2	Bragg's law for diffraction	199
6.3.3	Analyzer crystal	201
6.3.4	Goniometer	203
6.3.5	Collimators	204
6.3.6	Detectors	204
6.3.6.1	Gas-filled detectors	205
6.3.6.2	Scintillation detectors	207
6.3.7	Other arrangements	207
6.4	Principal components of EDS	208
6.4.1	Introduction	208
6.4.2	Detectors	209
6.4.2.1	Introduction	209
6.4.2.2	Si(Li) detectors	209
6.4.2.3	Si-PIN detectors	209
6.4.2.4	Si-drift chamber detectors	210
6.4.2.5	High-resolution detectors	210
6.5	Applications	210
6.5.1	Qualitative analysis	210
6.5.2	Quantitative analysis	211
6.5.2.1	Absorption	211
6.5.2.2	Enhancement	213
6.5.3	Correction for matrix effects	215
6.5.3.1	Fundamental parameter method	215
6.5.3.2	Compton correction	215
6.5.3.3	Influence coefficient algorithms	216
6.6	Notes on specimen preparation	217
6.7	Conclusion	218
	References	218
7	Electrothermal atomic absorption spectrometry	221
	ALBERT KH. GILMUTDINOV	
7.1	Introduction	221
7.2	Graphite atomizers	222

7.3	Graphite furnace analysis	225
7.3.1	Drying	226
7.3.2	Pyrolysis	227
7.3.3	Cool-down (optional)	227
7.3.4	Atomization	227
7.3.5	The clean out	228
7.4	Electrothermal atomization	228
7.5	Interferences in graphite furnace AAS	232
7.6	The relative merits of ETAAS	237
	References	238

8 Flame atomic absorption spectroscopy, including hydride generation and cold vapor techniques **239**

JULIAN F. TYSON and EMILY YOURD

8.1	Introduction	239
8.1.1	Why flame atomic absorption spectrometry?	239
8.1.2	The current status of FAAS	240
8.1.3	Closely related techniques: hydride generation, cold vapor mercury, AFS and AES	241
8.2	Basic principles	242
8.3	How do FAAS instruments work?	244
8.3.1	Sample introduction	245
8.3.1.1	Nebulizers	245
8.3.1.2	Spray chamber	246
8.3.2	Flames	246
8.3.3	Light sources	248
8.3.3.1	Atom source emission	250
8.3.3.2	Stray radiation	250
8.3.4	Detectors	251
8.3.5	Optical system	252
8.4	Instruments for hydride generation	253
8.5	Instruments for cold vapor mercury determination	254
8.6	Instruments for AFS	255
8.7	Limitations to performance	256
8.7.1	Instrument effects	257
8.7.2	Analyte effects (or why all elements do not have the same detection limit)	258
8.7.3	Sample effects	259
8.8	How to get the right answer?	260
8.8.1	How to deal with interference effects?	260
8.8.2	Separation and preconcentration	262
8.8.3	Flow injection techniques	264
8.8.4	Other possibilities for improving analytical performance	264
8.9	Some practical points	265
8.9.1	Safety	265
8.9.2	Nebulizers (sensitivity drift)	266
8.9.3	Light sources	266
8.9.4	Calibration	266
8.9.5	Achieving very low detection limits	267

8.10	Sample preparation issues	267
8.11	Representative applications	268
8.11.1	Earth sciences	268
8.11.2	Environmental	270
8.11.3	Petroleum related	273
8.11.4	Food and beverages	274
8.11.5	Clinical and forensic	276
8.12	Bibliography	277
	References	279

9 Chemometrics in elemental analysis **282**

MICHAEL J. ADAMS and MELISSA J. ROMEO

9.1	Introduction	282
9.2	Experimental design and optimization	282
9.3	Multi-variate statistics	288
9.4	Exploratory data analysis	293
9.4.1	Cluster analysis	293
9.4.2	Principal components analysis	295
9.5	Discriminant analysis	299
9.6	Calibration models	301
9.7	Conclusion	306
	References	306