

Contents

1 Fundamentals for the Chemical Measurement Process — 1

Gerhard Schlemmer and Mike Hinds

- 1.1 Analytical parameters — 2
 - 1.1.1 Define what is to be measured — 2
 - 1.1.2 How important is this analysis? — 2
 - 1.1.3 What is the sample, how is it sampled and how does it get to the lab? — 2
- 1.2 Sample preparation for elemental analysis — 3
 - 1.2.1 Sampling — 3
 - 1.2.2 Basic considerations of sample pretreatment — 4
 - 1.2.3 Drying — 5
 - 1.2.4 Grinding — 5
 - 1.2.5 Extraction/digestion/dissolution/decomposition: general comment — 6
 - 1.2.6 Chemistry for digestion — 7
 - 1.2.7 Traditionally heated systems — 9
 - 1.2.8 Systems using microwave energy — 10
 - 1.2.9 Conclusions — 25
- 1.3 Reference materials — 25
- 1.4 Validation — 27

2 Atomic absorption spectrometry and atomic fluorescence spectrometry — 30

Gerhard Schlemmer

- 2.1 Basic principles of atomic absorption spectrometry and atomic fluorescence spectrometry — 30
 - 2.1.1 Interaction of photons with electrons — 30
 - 2.1.2 Line width of absorbing atoms — 31
 - 2.1.3 Line width of emitting atoms in the source — 33
 - 2.1.4 Absorption process — 33
 - 2.1.5 Flame optical emission spectroscopy — 35
 - 2.1.6 Atomic fluorescence — 36
- 2.2 Technical means to facilitate AAS and AFS — 38
 - 2.2.1 General layout — 38
 - 2.2.2 Radiation source — 39
 - 2.2.3 Photometer and spectrometer — 46
 - 2.2.4 Counting photons and transfer to electrical information: principle way of operation and criteria for optimal use — 51
 - 2.2.5 Zero absorption: technical means to define the baseline — 54
 - 2.2.6 Separation of specific and nonspecific absorption — 57

2.2.7	Sample introduction and principles of atom generation in AAS —	66
2.3	Physicochemistry outside and inside the atomizer —	80
2.3.1	Flames —	80
2.3.2	Graphite furnace —	84
2.3.3	Chemical vapor generation —	87
2.3.4	Atomic fluorescence —	88
2.4	Mastering the spectrometer and its accessories —	89
2.4.1	Figures of merit —	90
2.5	Mastering the application; instrument suitability; method development; estimation on expected working range, basics of method optimization for flame, furnace, CVG, cold vapor, cold vapor fluorescence. Special applications: coupling of methods. Analytical quality versus sample and element throughput —	105
2.5.1	Instrument performance verification —	105
2.5.2	Estimate of the expected working range —	108
2.5.3	Is the instrument suitable for the application? —	109
2.6	Typical applications in AAS and AFS —	119
2.6.1	Contaminated soils: an easy standard flame AAS application —	119
2.6.2	Geochemistry: the determination of refractory elements in refractory matrix —	121
2.6.3	Determinations in ultrapure materials: an unusual challenge —	122
2.6.4	Between liquid and solid: the direct analysis of clinical samples in GF-AAS —	128
2.6.5	Plants and other biological tissue: the way to fast GF-AAS determinations —	132
2.6.6	Element-matrix separation: the determination of As and Sb in water samples —	136
2.6.7	CVG with analyte trapping for ultra, ultra-traces —	138
2.6.8	The determination of mercury with the cold vapor technique and AFS —	140
3	Inductively coupled plasma and microwave-induced plasma optical emission spectroscopy —	147
	José-Luis Todolí	
3.1	Introduction to inductively coupled plasma optical emission spectroscopy —	147
3.2	Plasma generation and fundamental parameters —	150
3.2.1	Characteristics of the ICP —	150
3.2.2	Mixed gas plasmas —	157
3.2.3	Generators —	158
3.3	Sample introduction systems —	159
3.3.1	Conventional liquid sample introduction system —	160

3.3.2	Drawbacks of conventional liquid sample introduction system —	163
3.3.3	Efficient nebulizers/spray chambers —	165
3.3.4	High solid nebulizers —	169
3.3.5	Cooled spray chambers —	170
3.3.6	Desolvation systems —	171
3.3.7	Low sample consumption systems —	175
3.3.8	Chemical vapor generation —	177
3.3.9	Electrothermal vaporization —	179
3.4	Torch configuration —	181
3.4.1	General characteristics —	181
3.4.2	Low argon consumption torches —	184
3.4.3	Plasma viewing mode —	184
3.5	Optical system —	187
3.5.1	Dispersive system —	188
3.5.2	Detectors —	191
3.6	General configurations —	194
3.7	Interferences in ICP-OES —	198
3.7.1	Spectral interferences in ICP-OES —	199
3.7.2	Non-spectral interferences (matrix effects) in ICP-OES —	202
3.7.3	Comparing spectral and non-spectral interferences —	214
3.8	Effect of the analyte chemical form —	216
3.9	Optimizing an ICP-OES system —	217
3.9.1	Optimization from the point of view of analytical figures of merit —	220
3.9.2	Optimization from the point of view of accuracy —	223
3.10	Methods for analyte quantification by ICP-OES —	228
3.11	Troubleshooting and maintenance in ICP-OES —	230
3.12	Microwave plasma optical emission spectroscopy (MIP-OES) —	232
3.12.1	Introduction to MIP-OES —	232
3.12.2	Instrumentation in MIP-OES —	233
3.12.3	Microwave inductively coupled atmospheric-pressure plasma (MICAP) —	240
3.12.4	Microwave plasma characteristics —	242
3.12.5	Spectral interferences in MIP-OES —	244
3.12.6	Matrix effects in MIP-OES —	247
3.12.7	Removal of matrix effects in MIP-OES —	249
3.12.8	Optimization in MIP-OES —	250
3.13	Comparison of ICP-OES and MIP-OES with other spectrochemical techniques —	251
3.14	Selected applications —	256

4 Inductively coupled plasma-mass spectrometry (ICP-MS) — 278

Frank Vanhaecke

- 4.1 Introduction and brief history — **278**
- 4.2 Instrumentation and principles of operation — **279**
 - 4.2.1 Sample introduction system — **279**
 - 4.2.2 Inductively coupled plasma (ICP) ion source — **279**
 - 4.2.3 Interface — **282**
 - 4.2.4 Mass spectrometer — **284**
 - 4.2.5 Detector — **294**
 - 4.2.6 Alternative sample introduction systems — **295**
- 4.3 Spectral interferences — **298**
 - 4.3.1 Types of interferences — **299**
 - 4.3.2 Methods to address spectral interferences — **300**
- 4.4 Non-spectral interferences — **310**
 - 4.4.1 Description of non-spectral interferences — **310**
 - 4.4.2 Methods to address non-spectral interferences — **312**
- 4.5 Analytical performance — **314**
- 4.6 Examples of typical applications — **316**
 - 4.6.1 (Ultra-)trace element determination — **317**
 - 4.6.2 Isotopic analysis — **318**
 - 4.6.3 Speciation analysis — **335**
 - 4.6.4 Bulk and spatially resolved analysis by means of laser ablation-ICP-MS — **338**
 - 4.6.5 Single-particle ICP-MS — **341**
 - 4.6.6 Single-cell ICP-MS — **345**

5 X-ray fluorescence spectrometry — 362

Michael W. Hinds

- 5.1 Overview — **362**
 - 5.1.1 What is X-ray fluorescence (XRF) spectrometry? — **362**
 - 5.1.2 What distinguishes XRF from other atomic spectrometric techniques? — **362**
 - 5.1.3 Types: wavelength dispersive XRF and energy dispersive XRF — **363**
- 5.2 Physics of X-rays — **364**
 - 5.2.1 Introduction — **364**
 - 5.2.2 Characteristic fluorescence lines — **366**
 - 5.2.3 Absorption and fluorescence — **370**
 - 5.2.4 Generation of X-rays within the X-ray tube — **373**
 - 5.2.5 Production of fluorescence X-rays within the sample — **374**
 - 5.2.6 Infinite thickness and analysis depth — **375**
 - 5.2.7 Fluorescence yield — **376**
- 5.3 WDXRF spectrometer and components — **377**

5.3.1	X-ray tube — 378
5.3.2	Primary beam filters — 382
5.3.3	Atmosphere — 382
5.3.4	Sample cups and aperture — 383
5.3.5	Mask — 384
5.3.6	Collimators — 385
5.3.7	Crystals or analyzer crystals — 386
5.3.8	Goniometer — 387
5.3.9	Detectors — 388
5.3.10	Pulse height selection — 390
5.3.11	Auxiliary services — 392
5.3.12	Optimization of parameters — 393
5.4	EDXRF spectrometer and components — 393
5.4.1	X-ray sources — 394
5.4.2	Atmosphere — 395
5.4.3	Primary beam filters — 395
5.4.4	Sample cups and aperture — 396
5.4.5	Detectors — 396
5.4.6	Multichannel analyzer — 400
5.4.7	Auxiliary services — 400
5.4.8	Handheld EDXRF spectrometer — 401
5.4.9	Total reflection XRF — 402
5.4.10	Comparison between EDXRF and WDXRF — 402
5.5	Obtaining optimized net intensities and counting times — 403
5.5.1	Background corrected peaks WDXRF — 403
5.5.2	Background correction EDXRF — 406
5.5.3	Peak overlap corrections — 408
5.5.4	Measurement time — 410
5.6	Matrix effects specific to XRF — 412
5.6.1	Absorption — 413
5.6.2	Enhancement — 414
5.6.3	Particle size effects — 415
5.6.4	Mineralogical effects — 416
5.6.5	Chemical state effects — 416
5.7	Calibration and mathematical correction models — 417
5.7.1	Reference materials — 417
5.7.2	Matrix correction algorithms — 418
5.7.3	Calibration — 422
5.7.4	Validation — 422
5.7.5	Drift correction — 423
5.8	Universal calibration XRF analysis — 424
5.8.1	How it works — 425

5.8.2	Applications — 425
5.8.3	Advantages and disadvantages — 425
5.9	Sample preparation — 426
5.9.1	Air sample preparation — 426
5.9.2	Liquid sample preparation — 426
5.9.3	Solid sample preparation — 428
5.10	Application Examples — 433
5.10.1	EDXRF: determination of Ag, As, and Zn in lead concentrate — 434
5.10.2	WDXRF: determination of Ag, Cu, and P in Sterling Silver — 436
5.11	Different applications and current trends in XRF — 441
5.11.1	Combination of WDXRF and EDXRF in one instrument — 441
5.11.2	Microfocusing optics and element concentration mapping — 441
5.11.3	X-ray tube advances — 441
5.11.4	Automation — 442
5.11.5	Advances in EDXRF — 442
5.11.6	Research to revise fundamental parameters — 443
5.11.7	Gamma activation analysis — 443
5.12	Concluding remarks — 443
5.13	Appendix — 444
5.13.1	Appendix 1: table of photon energies of the principle K and L X-ray spectral lines — 444
5.13.2	Appendix 2: table of K, L, and M X-ray excitation potentials of the elements — 447
5.13.3	Appendix 3: table of mass attenuation coefficients for K α line energies of selected elements — 449