

Contents

PREFACE	IX
PREFACE TO THE ENGLISH EDITION	X
 <i>Chapter 1. FUNDAMENTALS</i>	 1
1.1 Energy quantization	1
1.2 Distribution of electrons in an atom	5
1.3 Atom excitation	6
1.3.1 Atom excitation by photons	6
1.3.2 Yield of photon excitation	7
1.3.3 Atom excitation by charged particles	16
1.4 Atom deexcitation	18
1.4.1 Characteristic radiation	18
1.4.2 Auger effect	25
1.4.3 Fluorescence yield	27
1.4.4 Chemical influences in X-ray emission	30
15 Photon scattering	31
1.5.1 Incoherent (Compton) scattering	31
1.5.2 Coherent scattering	34
1.5.3 Scattered radiation in X-ray fluorescence analysis	35
1.6 Attenuation of X-ray beam	37
1.7 Mean and effective atomic number	48
 <i>Chapter 2. SOURCES OF PRIMARY (EXCITING) RADIATION</i>	 50
2.1 Properties of radioisotope sources	50
2.2 Production of radioisotope sources	55

23	Isotope X-ray sources	57
2.3.1	Beta-excited X-ray sources	59
2.3.2	Photon-excited X-ray sources	64
2.4	Influence of measuring conditions on the shape of X-ray spectrum	67
25	Low-power X-ray tubes	68
25.1	Construction of X-ray tubes	70
25.2	Power-supply systems and the problem of stability of photon output	73
 Chapter 3. SECONDARY RADIATION OF SAMPLE		75
3.1	Intensity of fluorescence radiation	76
3.1.1	Thin samples	77
3.1.2	Thick samples	78
3.2	Intensity of scattered radiation	84
 Chapter 4. DETECTION OF X-RAYS		86
4.1	Proportional counter	86
4.1.1	Escape peaks	92
4.1.2	Proportional flow counter	95
4.2	Scintillation counter	97
4.2.1	Scintillator NaI(Tl)	97
4.2.2	Photomultiplier	100
4.3	Solid-state detector	102
4.3.1	Electron energies in an ideal (pure) crystal	102
4.3.2	Local energy levels associated with crystal impurities	107
4.3.3	Leakage current	109
4.3.4	The p-n junction	110
4.3.5	Lithium-drifted detectors	112
4.3.6	Solid-state room-temperature X-ray detectors	114
4.4	Detection efficiency	114
4.5	Energy resolution	122
4.5.1	Intrinsic energy resolution	125
4.5.2	Noise sources	127
4.6	Gas proportional-scintillation counters	129

<i>Chapter 5. X-RAY SPECTROMETRY</i>	131
5.1 Electronic methods (pulse-height selection)	133
5.1.1 Calibration of a spectrometer	135
5.1.2 Multichannel analysis	137
5.1.3 Measurements in a chosen channel; measurements with a single discriminator	140
5.2 Filter methods	141
5.2.1 Techniques of manufacturing and balancing the filter as- sembly	144
5.2.2 Advantages and shortcomings of balanced filter technique	146
5.2.3 Single-filter method	148
5.3 Radiator methods	150
5.3.1. Balanced radiator method	151
 <i>Chapter 6. SELECTION OF OPTIMUM CONDITIONS FOR ANALYSIS</i>	 153
6.1 Calibration	153
6.1.1 Standard samples	155
6.1.2 Establishing a calibration curve	159
6.2 Sensitivity of analysis	160
6.3 Factors influencing sensitivity	163
6.3.1 Selection of measurement geometry	163
6.3.2 Selection of detector	167
6.3.3 Selection of primary radiation energy	169
6.3.4 Selection of source activity	173
6.3.5 Selection of measuring channel width	175
6.3.6 Influence of matrix composition on sensitivity	177
 <i>Chapter 7. DISTURBING EFFECTS</i>	 178
7.1 Interelement radiation	178
7.2. Matrix effects	179
7.2.1 Absorption effect	179
7.2.2 Enhancement effect	182

7.3 Particle-size effects	185
7.3.1 Influence of sample granulation on fluorescence radiation intensity	185
7.3.2 Influence of sample granulation on transmitted radiation intensity	202
7.3.3 Influence of sample granulation on scattered radiation intensity	205
7.3.4 Application of particle-size effects	207
7.4 Mineralogical effects	209
7.5 Surface effects	210

Chapter 8. METHODS FOR ELIMINATING MATRIX EFFECTS 212

8.1 Analysis of three-component materials	212
8.1.1 Single-filter compensation method	213
8.1.2 Difference method with constant coefficient	216
8.1.3 Difference method with variable coefficient	218
8.1.4 Nomogram method	221
8.1.5 Method of generalized calibration curve	225
8.2 Analysis of multicomponent materials	226
8.2.1 Fluorescence-to-scatter ratio method	228
8.2.2 Fluorescence-to-scatter ratio method with the use of nomogram	231
8.2.3 Fluorescence-to-transmission ratio method	234
8.2.4 Absolute scatter intensity techniques	237
8.3 Calculation correction methods	238
8.3.1 Fundamental parameter method	238
8.3.2 Empirical coefficient method	246
8.3.3 Calculation methods in analysis of polymetallic ores	259
8.3.4 Multiple regression and analysis by computer	262
8.4 Methods requiring special preparation of samples	264
8.4.1 The method of thin samples	265
8.4.2 Eliminating matrix effects for samples of intermediate thickness	271
8.4.3 Internal standard method	278
8.4.4 Addition method	281
8.4.5 Dilution method	282

<i>Chapter 9. OTHER SOURCES OF ERRORS</i>	286
9.1 Errors due to statistical fluctuations	286
9.2 Equipment effects	293
9.2.1 Intrinsic disturbances	293
9.2.2 Disturbances arising from changes in external conditions	301
9.2.3 Methods for eliminating equipment errors	302
9.3 Background interference	303
9.3.1 Spectral interference	303
9.3.2 Linear interference	307
9.4 Effects due to the physical state of the sample	311
 <i>Chapter 10. PROCESSING OF MEASUREMENT DATA</i>	 313
10.1 Statistical distributions and their parameters	313
10.1.1 Mean value	314
10.1.2 Variance and standard deviation	315
10.1.3 Standard deviation of mean	316
10.1.4 Normal distribution	317
10.1.5 Student's distribution	317
10.1.6 Confidence intervals	319
10.2 Precision	322
10.3 Accuracy	323
10.4 Rejecting an outlier	326
10.5 Decision limit, detection limit, and determination limit	328
 <i>Chapter 11. APPLICATIONS OF ENERGY-DISPERSIVE X-RAY FLUORESCENCE ANALYSIS IN GEOLOGICAL PROSPECTING AND MINING</i>	 335
11.1 Field prospecting analyses	335
11.2 Analysis of drill cores and drillings	337
11.3 Analyses in boreholes (X-ray fluorescence logging)	338
11.4 Laboratory analyses of geological materials	341
11.4.1 Semi-quantitative selection analysis	341
11.4.2 Quantitative analysis	341

11.4.3	Determination of heavy ($Z > 73$) elements with the use of K-series X-rays	342
11.4.4	Determination of light ($Z < 16$) elements	344
11.5	Analyses of lunar and Martian surfaces	348
 Chapter 12. ON-STREAM ANALYSES		 350
12.1	Introduction	350
12.2	Mineral processing control	351
12.2.1	Sources of disturbances in analysis of flotation slurries	353
12.2.2	Immersion probes	357
12.2.3	Control of fineness of flotated ores	359
12.3	Calciferous sludge analysis	360
12.4	Analysis of loose materials	361
12.4.1	Determination of ash content in coal	362
12.4.2	Ore analysis on conveyor belts	362
 Chapter 13. TRACE ANALYSIS		 364
13.1	Introduction	364
13.2	Preconcentration methods	365
13.3	Analysis of water and effluent-waste pollutants	368
13.3.1	Analysis of suspensions and/or sediments	369
13.3.2	Analysis of the soluble fraction	371
13.4	Analysis of air pollutants	378
13.4.1	Analysis of particulates and aerosols	378
13.4.2	Analysis of gas pollutants	381
13.5	X-ray fluorescence analysis in medical applications	383
13.5.1	Stable-tracer method	383
13.5.2	Elemental analysis of biological materials	384
 Chapter 14. MISCELLANEOUS APPLICATIONS		 387
14.1	Alloy analysis	387
14.2	Analysis of solutions	389
14.3	Analysis of gases	390

14.4 Analysis of petroleum products	391
14.5 Analysis of paints and lacquers	392
14.6 EDXRF analysis in archaeology	392
14.6.1 Analysis of metallic and ceramic objects	392
14.6.2 Analysis of coins	393
14.6.3 Analysis of fossil bones	394
14.7 Coating thickness measurements	394
14.8 Other applications of EDXRF	398
REFERENCES	400
SUBJECT INDEX	421