Contents

1 Introduction
T. Arai 1
1.1 The Discovery of X-Rays and Origin of X-Ray Fluorescence Analysis 1
1.2 Historical Progress of Laboratory X-Ray Fluorescence Spectrometers 4
1.3 Measurement of Soft and Ultrasoft X-Rays 8
1.3.1 X-Ray Tubes for Soft and Ultrasoft X-Rays 8
1.3.2 Scientific Research Work on Soft and Ultrasoft X-Rays 9
1.3.3 Synthetic Multilayer Analyzers 9
1.3.4 Total Reflection Mirrors 13
1.4 Analytical Precision and Accuracy in X-Ray Fluorescence Analysis 15
1.4.1 Correction of Matrix Element Effects 16
1.4.2 Quantitative Analysis of Heat Resistance and High Temperature Alloys 19
1.4.3 Segregation Influencing Analytical Accuracy 25
1.5 Concluding Remarks 26
References 26

2 X-Ray Sources
2.1 Introduction
N. Langhoff and A. Simionovici 33
2.2 X-Ray Tubes
V. Arkadiev, W. Knüpfer and N. Langhoff 36
2.2.1 Basic Physical Principles 36
2.2.2 Technology of the Components 38
2.2.3 Vacuum Envelope of X-Ray Tubes 46
2.2.4 Tube Housing Assembly 47

2.2.5 Modern X-Ray Tubes 47
2.2.6 Some Applications 52
2.3 Radioisotope Sources
T. Čechák and J. Leonhardt 54
2.3.1 Basic Physical Principles 55
2.3.2 Radioisotope Sources 57
2.3.3 Production of Radioactive Sources 63
2.3.4 Radiation Protection Regulations 64
2.4 Synchrotron Radiation Sources
A. Simionovici and J. Chavanne 66
2.4.1 SR Basics 66
2.4.2 Storage Ring Description 67
2.4.3 Generation of SR 68
2.4.4 SRW Package 72
References 80

3 X-Ray Optics
3.1 Introduction
A. Erko 85
3.2 Mirror Optics
V. Arkadiev and A. Bjeoumikhov 89
3.2.1 Total External Reflection Mirrors 89
3.2.2 Capillary Optical Systems 89
3.3 Diffraction Optics – Elements of Diffraction Theory
A. Erko 111
3.3.1 Electromagnetic Wave Propagation 111
3.3.2 Fraunhofer Approximation 113
3.3.3 Fresnel Approximation 113
3.3.4 Bragg Diffraction 115
3.4 Optics for Monochromators
A. Antonov, V. Arkadiev, B. Beckhoff, A. Erko, I. Grigorieva, B. Kanngießer and B. Vidal 115
3.4.1 Diffraction Gratings 115
3.4.2 Multilayers for X-Ray Optics 129
3.4.3 HOPG-based Optics 143
3.4.4 Laterally Graded SiGe Crystals 157
3.5 Focusing Diffraction Optics
A. Erko 167
3.5.1 Zone Plates 167
3.5.2 Reflection Zone Plate and Bragg–Fresnel Optics 179
3.5.3 Bragg–Fresnel Holographic Optics 185
3.6 Refraction X-Ray Optics
A. Erko 187
3.6.1 Compound Refractive Lens 187
References 190

4 X-Ray Detectors and XRF Detection Channels
4.1 Introduction
F. Scholze . . . 199
4.2 X-Ray Detectors and Signal Processing
A. Longoni and C. Fiorini . . . 203
4.2.1 Introduction . . . 203
4.2.2 Basic Properties of X-Ray Detectors . . . 203
4.2.3 Classification of the Most Commonly Used X-Ray Detectors . . . 216
4.2.4 Semiconductor Detectors . . . 218
4.2.5 Silicon Drift Detectors . . . 222
4.2.6 Basics of Signal Electronics . . . 235
4.2.7 Shape Factors of some Filtering Amplifiers . . . 249
4.2.8 Auxiliary Functions . . . 252
4.2.9 Appendix 1 – The Laplace Transform . . . 256
4.2.10 Appendix 2 – Calculation of the ENC . . . 257
4.2.11 Appendix 3 – Digital Pulse Processing . . . 259
4.3 High Resolution Imaging X-Ray CCD Spectrometers
L. Strüder, N. Meidinger and R. Hartmann . . . 262
4.3.1 Introduction . . . 262
4.3.2 Fully Depleted Backside Illuminated pn-CCDs . . . 264
4.3.3 Frame Store pn-CCDs for ROSITA, and XEUS . . . 277
4.3.4 Conclusion . . . 284
4.4 Wavelength Dispersive XRF and a Comparison with EDS
N. Kawahara and T. Shoji . . . 284
4.4.1 Dispersion Materials for WDXRF . . . 285
4.4.2 Detectors and Electronics . . . 288
4.4.3 Optics Used for the WD Spectrometer and its Components . . . 293
4.4.4 Types of WDXRF Spectrometer . . . 296
4.4.5 Selected Applications Suitable for WDXRF . . . 299
4.4.6 Comparison of WDXRF and EDXRF . . . 301
References . . . 302

5 Quantitative Analysis
5.1 Overview
M. Mantler . . . 309
5.2 Basic Fundamental Parameter Equations
M. Mantler . . . 311
5.2.1 Fundamental Parameter Equations for Bulk Materials . . . 312
5.2.2 Direct Excitation . . . 317
5.2.3 Indirect Excitation . . . 322
5.2.4 Use of Standards . . . 325

5.3 Matrix Correction Methods and Influence Coefficients 327
5.3.1 The Nature of Influence Coefficients
M. Mantler 327
5.3.2 The Lachance–Traill Algorithm
J.P. Willis, G.R. Lachance 335
5.3.3 The Claisse–Quintin Algorithm
J.P. Willis, G.R. Lachance 340
5.3.4 The COLA Algorithm
J.P. Willis, G.R. Lachance 343
5.3.5 The de Jongh Algorithm
B.A.R. Vrebos 345
5.3.6 The Broll–Tertian Algorithm
K.-E. Mauser 347
5.3.7 The Japanese Industrial Standard Method
N. Kawahara 349
5.3.8 The Fundamental Algorithm
R.M. Rousseau 350
5.4 Compensation Methods 358
B.A.R. Vrebos 358
5.4.1 Internal Standards 358
5.4.2 Standard Addition Methods 361
5.4.3 Dilution Methods 362
5.4.4 Scattered Radiation – Compton Scatter 363
5.5 Thin and Layered Samples
P.N. Brouwer 369
5.5.1 Direct Excitation by Polychromatic Sources 369
5.5.2 Indirect Excitation by Polychromatic Sources 371
5.5.3 Back-Calculation Schemes 375
5.5.4 Solvability 376
5.5.5 Applications 377
5.6 Complex Excitation Effects and Light Elements
N. Kawahara 379
5.6.1 Indirect Excitation Processes in the Low Energy Region 379
5.6.2 Secondary Excitation by Electrons 379
5.6.3 Cascade Effect 382
5.7 Standardless Methods
K.-E. Mauser 384
5.7.1 Introduction 384
5.7.2 Semiquantitative Analysis 384
5.7.3 Requirements for a Standardless Method 385
5.8 Monte Carlo Methods
M. Mantler 394
5.9 Errors and Reliability Issues
M. Mantler 395
5.9.1 Mathematical Treatment of Statistical Errors 397

5.9.2 Counting Statistics . . . 398
5.9.3 Detection Limits . . . 398
5.10 Standardized Methods
K.-E. Mauser . . . 400
5.10.1 Introduction . . . 400
5.10.2 General Features of Standardized Methods . . . 400
5.10.3 Standardized Methods Versus Universal Calibrations and Standardless Methods . . . 403
5.10.4 Summary . . . 403
Symbols and Terminology . . . 404
References . . . 407

6 Specimen Preparation
J. Injuk, R. Van Grieken, A. Blank, L. Eksperiandova and V. Buhrke . . 411
6.1 Introduction . . . 411
6.2 Liquids . . . 412
6.2.1 Direct Analysis of Liquids and Solutions . . . 412
6.2.2 Conversion of Liquids into Quasi-Solid Specimens . . . 413
6.2.3 Conversion of Liquids into Organic Glassy Polymer Specimens . . . 414
6.2.4 Conversion of Liquids into Thin Films . . . 414
6.2.5 Analysis of Solutions after Preconcentration of Microimpurities . . . 415
6.3 Solid Specimens . . . 419
6.3.1 Metallic Specimens . . . 419
6.3.2 Powder Specimens . . . 421
6.3.3 Fused Specimens . . . 424
6.4 Biological Samples . . . 426
6.5 Aerosol and Dust Specimens . . . 427
6.6 Standards . . . 428
References . . . 429

7 Methodological Developments and Applications
7.1 Micro X-Ray Fluorescence Spectroscopy
B. Kanngießer and M. Haschke . . . 433
7.1.1 Introduction . . . 433
7.1.2 General Description of Micro-XRF Laboratory Units . . . 434
7.1.3 Applications of Micro X-Ray Fluorescence Analysis . . . 442
7.1.4 3D Micro X-Ray Fluorescence Spectroscopy . . . 462
7.2 Micro-XRF with Synchrotron Radiation
A. Simionovici and P. Chevallier . . . 474
7.2.1 Introduction . . . 474
7.2.2 The General Setup . . . 475
7.2.3 Quantitative Aspect . . . 481
7.2.4 Elemental Mapping . . . 484
7.2.5 Examples of Application . . . 488

7.3 Total-Reflection X-Ray Fluorescence (TXRF) Wafer Analysis
C. Streli, P. Wobrauschek, L. Fabry, S. Pahlke, F. Comin, R. Barrett, P. Pianetta, K. Lüning and B. Beckhoff 498
7.3.1 Introduction 498
7.3.2 Analysis of Metallic Surface Contamination by Means of TXRF 500
7.3.3 Historic Background 500
7.3.4 Instrumentation of Total Reflection X-Ray Fluorescence Analysis 502
7.3.5 Quantification of TXRF Analysis 503
7.3.6 Surface Analysis 508
7.3.7 Statistical Process Control (SPC) 516
7.3.8 Automated Vapor Phase Decomposition (VPD) Preparation 517
7.3.9 Low $\boldsymbol{Z}$ Determination – Problems – Solutions and Results 519
7.3.10 Synchrotron Radiation Induced TXRF 522
7.3.11 Conclusion and Outlook 553
7.4 Analysis of Layers
V. Rößiger and B. Nensel 554
7.4.1 Introduction to the Analysis of Layers 554
7.4.2 Theory of the Quantitative Layer Analysis: Yield Calculation 555
7.4.3 Calculation of the Unknown Measurement Quantities X_{ij} . . 563
7.4.4 The WinFTM® Program 567
7.4.5 Instruments 579
7.4.6 Application Examples 586
7.4.7 Summary and Outlook 600
7.5 Environmental Studies
S. Kurunczi, J. Osán, S. Török and M. Betti 601
7.5.1 Introduction 601
7.5.2 Water 604
7.5.3 Atmospheric Aerosol 620
7.5.4 Monte Carlo Based Quantitative Methods for Single Particles 627
7.5.5 Radionuclides and Radioactive Materials 635
7.6 Geology, Mining, Metallurgy
D. Rammlmair, M. Wilke, K. Rickers, R.A. Schwarzer, A. Möller and A. Wittenberg 640
7.6.1 Introduction 640
7.6.2 Macroscale 642
7.6.3 Mesoscale 648
7.6.4 Microscale 668
7.6.5 Conclusions 685

7.7 Application in Arts and Archaeology
O. Hahn, I. Reiche and H. Stege 687
7.7.1 General Remarks 687
7.7.2 Materials Groups 689
7.7.3 Conclusions and Perspectives 700
7.8 XRF-Application in Numismatics
J. Engelhardt 700
7.8.1 Introduction 700
7.8.2 History of XRF Investigations of Coins 701
7.8.3 General Remarks 701
7.8.4 Preparation of Coins for Surface and Bulk Analysis 705
7.8.5 Metals and Standards 706
7.8.6 Accuracy and Precision 706
7.8.7 Some Examples of Typical Questions of the Numismatist . . . 707
7.8.8 Conclusion 711
7.8.9 Recommended Reading 712
7.9 Analysis for Forensic Investigations
J. Zięba-Palus 712
7.9.1 The Specificity of Forensic Research 712
7.9.2 The XRF Method in Forensic Research 714
7.9.3 Conclusions 728
7.10 X-Ray Fluorescence Analysis in the Life Sciences
G. Weseloh, S. Staub and J. Feuerborn 728
7.10.1 Introduction 728
7.10.2 X-Ray Fluorescence Analysis by Means of X-Ray Tubes and Radioisotopes 729
7.10.3 Total Reflection X-Ray Fluorescence Analysis (TXRF) 736
7.10.4 Synchrotron Radiation Induced TXRF 748
7.10.5 X-Ray Fluorescence Analysis Using Synchrotron Radiation . 751
7.11 Non-Invasive Identification Of Chemical Compounds by EDXRS
P. Hoffmann 769
7.11.1 Introduction 769
7.11.2 Experimental Part 770
7.11.3 Results 771
7.11.4 Discussion 780
References 783

8 Appendix
8.1 X-Ray Safety and Protection
P. Ambrosi 835
8.1.1 Introduction 835
8.1.2 Radiation Protection Quantities 836
8.1.3 Health Hazards 839

8.1.4 Measuring Instruments 841
8.1.5 System of Radiation Protection 843
References 845
8.2 Useful Data Sources and Links
R. Wedell and W. Malzer 845

Index 849