

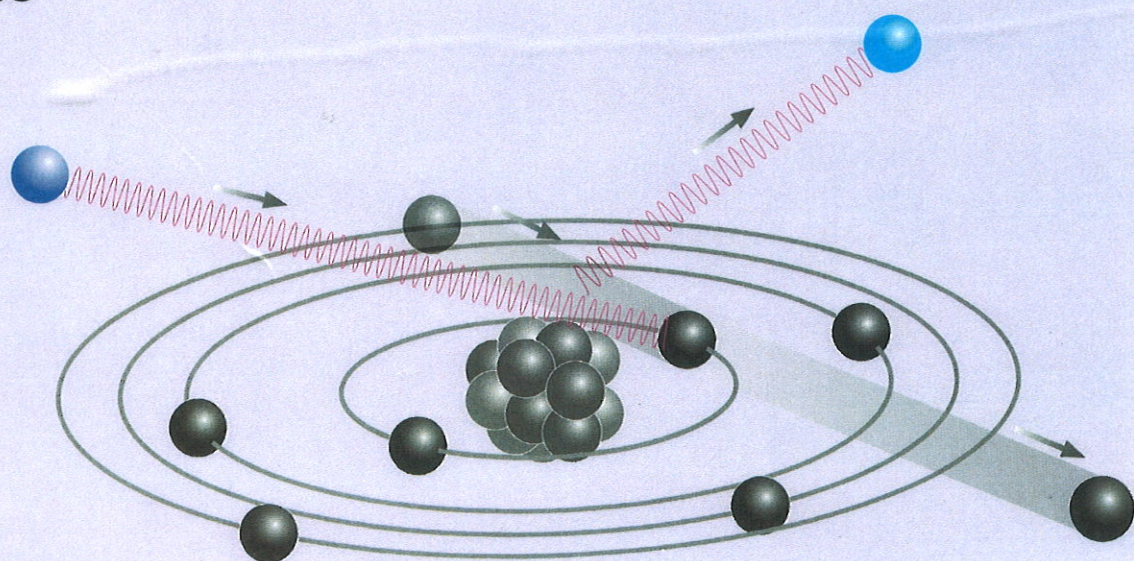
Understanding

XRF

Spectrometry

A practical guide
with worked
examples

James P. Willis
Andrew R. Duncan



Volume

Quantitative
analysis and special
sample preparation
and presentation
methods

2

Table of Contents

Foreword

F.1	INTRODUCTION.....	F-1
F.2	ACKNOWLEDGEMENTS	F-2
F.3	BIBLIOGRAPHY.....	F-3
F.4	SYMBOLS AND TERMINOLOGY.....	F-4
F.4.1	Symbols.....	F-6
F.4.2	Influence Coefficients.....	F-6
F.4.2.1	In the Rousseau algorithm.....	F-6
F.4.2.2	In the Lachance-Traill algorithm.....	F-6

Chapter 13: Introduction to Quantitative Analysis (1) - Choice of Counting Positions and Determination of Background Intensity

13.1	BASIC TERMINOLOGY	13-1
13.2	CHOICE OF INSTRUMENTAL PARAMETERS AND ANGULAR POSITIONS.....	13-1
13.2.1	Selection of X-ray Tube Anode	13-1
13.2.2	Selection of Analysing Crystal.....	13-2
13.2.3	Selection of Detectors	13-2
13.2.4	Selection of Analyte Lines	13-4
13.2.5	Infinite Thickness	13-4
13.2.6	Ba Case Study	13-7
13.2.7	Selection of Peak and Background Counting Positions	13-9
13.3	CALCULATION OF BACKGROUND INTENSITY BENEATH A PEAK	13-9
13.3.1	Introduction.....	13-11
13.3.2	Method (A)	13-11
13.3.3	Method (B)	13-12
13.3.4	Method (C)	13-12
13.3.5	Method (D)	13-12
13.3.6	Method (E)	13-13
13.3.7	Method (F)	13-13
13.3.8	Method (G)	13-15
13.3.9	Method (H)	13-16
13.3.10	Method (I)	13-16
13.4	REFERENCES	

Chapter 14: Introduction to Quantitative Analysis (2) - Correction Procedures for Spectral Interference and Crystal Fluorescence

14.1	CORRECTION PROCEDURES FOR SPECTRAL INTERFERENCE (1).....	14-1
14.1.1	Interference from elements present in the sample	14-1
14.1.2	Example 1 – analysis of Rb, Sr and Y	14-3
14.1.3	Example 2 – analysis of Ce and Nd	14-9
14.2	CORRECTION PROCEDURES FOR SPECTRAL INTERFERENCE (2).....	14-13
14.2.1	Interference from elements present in the X-ray tube.....	14-13
14.2.2	Removal of interfering tube peaks.....	14-14
14.2.3	Correction using intensity ratio to a tube line.....	14-15
14.2.4	Correction using MACs	14-15
14.2.5	Example 3 – correction for tube-peak interference (method 1).....	14-18
14.2.6	Example 4 – correction for tube-peak interference (method 2).....	14-21
14.3	CORRECTION PROCEDURES FOR CRYSTAL FLUORESCENCE.....	14-23
14.4	REFERENCES	

Chapter 15: Introduction to Quantitative Analysis (3) - Methods of Trace Element Standardisation, Determination of Counting Error and Lower Limit of Detection

15.1	INTRODUCTION.....	15-1
15.2	METHOD OF STANDARD ADDITION	15-2
15.2.1	Technique.....	15-2
15.2.2	Notes.....	15-3
15.3	METHOD OF STANDARD DILUTION.....	15-3
15.3.1	Technique.....	15-3
15.3.2	Notes.....	15-3
15.4	USE OF AN INTERNAL STANDARD	15-3
15.4.1	Technique.....	15-4
15.4.2	Notes.....	15-6
15.5	EXTERNAL COMPARISON STANDARDS	15-6
15.5.1	Without correction for matrix effects	15-7
15.5.2	With correction for matrix effects.....	15-8
15.5.2.1	Regression of Y on X.....	15-8
15.5.2.2	Reduced Major Axis (RMA) Regression.....	15-8
15.5.2.3	Constrained regression through the origin.....	15-9
15.5.2.4	Single point calibration.....	15-9
15.5.2.5	Weighted regression	15-10
15.5.3	Advantages of using constrained regression	15-11
15.5.4	Using regression.....	15-11
15.6	COUNTING ERROR AND LOWER LIMIT OF DETECTION	15-13
15.7	EXAMPLE - CALCULATION OF CONCENTRATIONS, ERRORS AND LLDs.....	15-17
15.8	REFERENCES	15-17

Chapter 16: Standards and Standard Reference Materials

16.1	INTRODUCTION.....	16-1
16.2	LIFE OF STANDARD MATERIALS.....	16-1
16.3	IN-HOUSE STANDARDS	16-2
16.3.1	Natural standards	16-2
16.3.2	Artificial solid standards.....	16-2
16.3.3	Artificial liquid standards	16-2
16.4	STORAGE OF SRMS	16-3
16.5	WHERE DO YOU OBTAIN SRMS?.....	16-4
16.6	FINDING INFORMATION FOR ANALYTE CONCENTRATIONS	16-5
16.7	HOW ARE RECOMMENDED VALUES DETERMINED?	16-5
16.7.1	Statistical Methods	16-7
16.7.2	Abbey's "Select Laboratories" method.....	16-7
16.8	DIFFERENT TYPES OF DATA VALUES.....	16-8
16.9	PROFICIENCY TESTING	16-9
16.10	REFERENCES	16-9

Chapter 17: Introduction to Influence Coefficients

17.1	INTRODUCTION.....	17-1
17.1.1	Basic equations for concentration vs intensity.....	17-2
17.1.2	What are influence coefficients and correction terms?.....	17-2
17.1.3	Factors to be considered in influence coefficient equations.....	17-4
17.1.3.1	Excitation	17-4
17.1.3.2	Absorption.....	17-5
17.1.4	Some simple concentration vs intensity equations.....	17-6
17.1.5	Some influence coefficient equations	17-6
17.1.5.1	Lachance-Trail (L-T) algorithm	17-6

17.1.5.2	Claisse-Quintin (C-Q) algorithm.....	17-7
17.1.5.3	COLA (Comprehensive Lachance) algorithm	17-7
17.1.5.4	Rousseau (RR) algorithm.....	17-7
17.1.6	Summary	17-10
17.1.7	Link between measured and calculated theoretical "emitted intensities"	17-13
17.2	PRIMARY FLUORESCENCE EMISSIONS DUE TO ABSORPTION.....	17-17
17.2.1	The concept of absorption correction coefficients.....	17-17
17.2.2	Derivation of a'_s and a''_s	17-17
17.2.3	Calculating theoretical intensities, measured intensities and concentrations using MACs	17-19
17.3	THE CONCEPT OF ABSORPTION INFLUENCE COEFFICIENTS: a_{ij}	17-21
17.3.1	Derivation of expressions for $a_{ij\lambda}$	17-22
17.3.2	Detailed derivation of absorption influence coefficient, $a_{ij\lambda}$	17-24
17.3.3	Calculation of μ_s^* , $I_{i\lambda}$, $a_{ij\lambda}$, C_i , $I_{(i)\lambda}$ and g_i (numerical example).....	17-24
17.3.4	Transformations of equations (17.11b) and (17.3)	17-25
17.4	THE CONCEPT OF ENHANCEMENT INFLUENCE COEFFICIENTS: $e_{ij\lambda}$	17-25
17.4.1	Derivation of expressions for $e_{ij\lambda}$	17-26
17.4.1.1	Detailed derivation of enhancement influence coefficient, $e_{ij\lambda}$	17-27
17.4.1.2	Multi-element context	17-29
17.4.2	Use and derivation of e^* to correct for enhancement	17-34
17.5	SUMMARY.....	17-34
17.6	REFERENCES	17-35
17.7	APPENDICES.....	
17.7.1	Appendix 17A: Numerical example of the calculation of μ_s^* , $I_{Ni\lambda}$, $a_{NiFe\lambda}$, C_{Ni} , $I_{(Ni)\lambda}$ and g_{Ni}	17-35
17.7.2	Appendix 17B: A numerical example of the calculation of the enhancement influence coefficient $e_{FeNi\lambda}$ and its application in calculating $I_{i\lambda}$	17-37
17.7.3	Table 17B-1. Data for computing $a_{FeNi\lambda}$, $e_{FeNi\lambda}$ and $I_{Fe\lambda}$	17-38

Chapter 18: Mathematical Matrix Correction Techniques

18.1	INTRODUCTION.....	18-1
18.2	XRF EMISSIONS AND INFLUENCE COEFFICIENTS FOR POLYCHROMATIC EXCITATION SOURCES	18-4
18.2.1	The process of summing monochromatic entities	18-4
18.2.2	Fundamental parameters method	18-5
18.2.3	Influence coefficient algorithms for polychromatic incident radiation	18-5
18.3	A COMPARISON OF SOME CHARACTERISTICS OF SELECTED INFLUENCE COEFFICIENT ALGORITHMS	18-6
18.3.1	Broll-Tertian (B-T) algorithm.....	18-6
18.3.2	Rousseau (RR) algorithm	18-6
18.3.3	Lachance-Claisse (L-C) algorithm	18-7
18.4	UNDERSTANDING INFLUENCE COEFFICIENTS.....	18-7
18.4.1	Introduction.....	18-10
18.4.2	Summary	18-10
18.5	THE CONCEPT OF α_{ij} IN DIFFERENT INFLUENCE COEFFICIENT ALGORITHMS.....	18-16
18.5.1	The modified Claisse-Quintin (C-Q+) and COLA Algorithms.....	18-16
18.5.1.1	Cross-correction coefficients, α_{ijk}	18-18
18.5.2	"Eliminated element" algorithms.....	18-21
18.6	EMPIRICAL INFLUENCE COEFFICIENTS: r_{ij}	18-22
18.6.1	Empirical Coefficient r_{ij} in the Lachance-Trail Algorithm.....	18-22
18.6.2	Empirical Coefficient r_{ij} in the Lucas-Tooth and Price Algorithm	18-23
18.6.3	Empirical Coefficients r_{ij} and r_{jk} in the Raspberry-Heinrich Algorithm	18-23
18.7	SOME OF THE MORE FREQUENTLY USED CALIBRATION EQUATIONS AND MATRIX CORRECTION ALGORITHMS.....	18-25
18.8	THE EMPIRICAL APPROACH.....	18-25

18.9	ALPHA COEFFICIENT MODELS	18-26
18.10	THE FUNDAMENTAL INFLUENCE COEFFICIENT APPROACH	18-27
18.10.1	Comments on, and explanation of, data in Table 18.9.	18-31
18.10.2	The de Jongh and JIS Algorithms (eliminating one component)	18-33
18.10.3	Models Requiring On-line Fundamental Parameters Software	18-33
18.10.3.1	Broll-Tertian algorithm.....	18-33
18.10.3.2	Rousseau algorithm	18-33
18.10.3.3	Lachance-Claisse algorithm.....	18-33
18.11	THE FUNDAMENTAL PARAMETERS ALGORITHM/METHOD	18-34
18.12	COMPARISON OF RESULTS FROM SOME INFLUENCE COEFFICIENT ALGORITHMS	18-41
18.13	DEFINING COMPREHENSIVE ANALYTICAL CONTEXTS	18-41
18.13.1	Monitors.....	18-42
18.13.2	Condensed numerical example of analytical context data	18-43
18.13.3	Analytical Strategy.....	18-44
18.14	INFLUENCE COEFFICIENT MODELS - LIMITATIONS, PITFALLS	18-44
18.15	SOME OF THE COMMONLY USED INFLUENCE COEFFICIENT MODELS.....	18-45
18.16	TYPES OF INFLUENCE COEFFICIENT MODELS	18-46
18.16.1	Algorithms using the empirical approach (MRA)	18-47
18.16.2	The fundamental influence coefficient approach	18-48
18.16.3	Alpha coefficient models (models requiring off-line fundamental parameters software).....	18-48
18.16.3.1	Claisse-Quintin (C-Q) algorithm.....	18-48
18.16.3.2	COLA and Lachance-Traill (L-T) algorithms	18-48
18.16.4	The de Jongh and JIS algorithms	18-48
18.16.4.1	de Jongh algorithm (DJ)	18-49
18.16.4.2	Japanese Industrial Standard algorithm (JIS)	18-49
18.16.5	Models requiring on-line fundamental parameters software	18-49
18.16.5.1	Broll-Tertian.....	18-50
18.16.5.2	Rousseau model.....	18-50
18.16.5.3	COLA algorithm.....	18-50
18.17	SUMMARY.....	18-52
18.18	ACKNOWLEDGEMENT	18-52
18.19	REFERENCES	
18.20	APPENDIX. NUMERICAL EXAMPLE OF THE CALCULATION OF INFLUENCE COEFFICIENTS FOR THE C-Q+ AND COLA ALGORITHMS	18-54
18.20.1	C-Q+ algorithm.....	18-55
18.20.2	COLA algorithm.....	18-55

Chapter 19: Glass Disks by Borate Fusions

19.1	INTRODUCTION.....	19-1
19.1.1	Undesirable effects of using powders in XRFS	19-1
19.1.2	Advantages of using fusion techniques	19-2
19.2	PREPARATION OF GLASS DISKS	19-2
19.2.1	General procedure	19-2
19.2.1.1	Typical simplified procedure	19-3
19.2.1.2	A limitation to borate fusion.....	19-3
19.2.2	Fluxes and additives	19-3
19.2.2.1	Fluxes.....	19-4
19.2.2.2	Properties of borate fluxes	19-5
19.2.2.3	Impurities in fluxes.....	19-5
19.2.2.4	Additives	19-5
19.2.2.5	Releasing agents	19-7
19.2.3	Preparation before fusion.....	19-7
19.2.3.1	Fusion mixture.....	19-10
19.2.3.2	Crucibles and moulds.....	

19.2.4	Heating	19-11
19.2.4.1	Heating requirements	19-11
19.2.4.2	Heating steps.....	19-13
19.2.4.3	Heating steps for oxidation	19-13
19.2.4.4	Heating steps for fusion and homogenization.....	19-13
19.2.4.5	Heating steps for conditioning before casting	19-15
19.2.5	Casting and cooling.....	19-15
19.2.5.1	Casting into moulds	19-15
19.2.5.2	Solidification	19-15
19.2.6	Examples of fusions that require special techniques.....	19-18
19.2.6.1	Sulphide minerals.....	19-18
19.2.6.2	Copper compounds.....	19-19
19.2.6.3	Carbon.....	19-19
19.2.6.4	Metallic materials	19-20
19.2.6.5	Carbonates.....	19-20
19.3	PYROSULPHATE FUSIONS	19-20
19.3.1	Procedure.....	19-20
19.3.2	Automatic preparation.....	19-20
19.3.3	Requirements.....	19-21
19.3.4	Problems.....	19-21
19.3.5	Fusions of sulphide concentrates.....	19-21
19.3.6	Analysis of disks.....	19-21
19.3.7	Conclusions	19-22
19.4	FLUXERS	19-22
19.4.1	Fusion Instruments	19-22
19.5	CARE OF CRUCIBLES AND MOULDS.....	19-22
19.5.1	Crucibles	19-22
19.5.2	Moulds	19-23
19.6	MISCELLANEOUS	19-24
19.6.1	Contamination by crucibles	19-24
19.6.2	Blanks.....	19-24
19.6.3	Loss or gain on ignition (LOI or GOI)	19-24
19.7	ADVANTAGES AND LIMITATIONS OF FUSION	19-25
19.7.1	Advantages.....	19-25
19.7.1.1	Reproducibility	19-25
19.7.1.2	Accuracy	19-26
19.7.1.3	Preparation of standards	19-26
19.7.1.4	Versatility.....	19-26
19.7.1.5	Cost	19-26
19.7.2	Limitations	19-27
19.7.3	Environment	19-27
19.8	SELECTION OF FLUX	19-27
19.9	REFERENCES	19-28

Chapter 20: Sampling and Specimen Preparation of Geological Materials

20.1	INTRODUCTION.....	20-1
20.2	SAMPLING ERRORS.....	20-3
20.3	STANDARD SIEVE SIZES	20-4
20.4	ROCK SPLITTING, CRUSHING AND GRINDING	20-5
20.4.1	Grinding aids	20-6
20.5	SAMPLE SPLITTING/RIFFLING	20-6
20.6	POWDER BRIQUETTE PREPARATION	20-8
20.6.1	Binders	20-8
20.6.2	Specimen labelling.....	20-8
20.6.3	Briquetting pressure	20-8

20.6.4	Fracturing and pre-pumping of briquettes	20-8
20.6.5	Particle size effects	20-10
20.7	PREPARATION OF DISKS OF SOLID ROCK	20-11
20.8	FUSIONS	20-13
20.8.1	Low dilution fusions for trace element analysis	20-13
20.9	SPECIMEN STORAGE	20-13
20.9.1	Specimen contamination.....	20-14
20.10	WORN RIMS ON OFTEN-USED POWDER BRIQUETTES	20-16
20.11	REFERENCES	

Chapter 21: Special Sample Preparation Techniques

21.1	INTRODUCTION.....	21-1
21.2	LIQUIDS.....	21-1
21.3	VERY SMALL SAMPLES.....	21-1
21.4	THIN LAYER TECHNIQUES.....	21-4
21.4.1	Sample support media	21-4
21.4.2	Preparation of thin layers from solutions	21-5
21.4.3	Preparation of thin layers from powders.....	21-6
21.4.4	Coprecipitation	21-7
21.4.5	Use of ion exchangers	21-9
21.4.6	Preconcentration technique	21-10
21.5	CONTAMINATION.....	21-10
21.6	ELIMINATING RADIATION FROM THE SAMPLE CUP	21-11
21.7	CONCLUSION.....	21-12
21.8	REFERENCES	

Chapter 22: Software

22.1	INTRODUCTION.....	22-1
22.2	NRLXRF.....	22-1
22.2.1	Description	22-1
22.2.2	Source	22-2
22.3	VXRF	22-2
22.4	NBSGSC	22-3
22.4.1	CALCO	22-3
22.4.2	CALCOMP	22-3
22.4.3	Source	22-3
22.5	XRFWIN	22-4
22.6	ROUSSEAU SOFTWARE.....	22-4
22.7	XRF Direct (CLAISSE ON-LINE MATRIX CORRECTION SOFTWARE)	22-4
22.7.1	Claisse Calculator for optimal flux composition.....	22-4
22.7.2	Claisse website.....	22-5
22.8	UniQuant®	22-5
22.8.1	UniQuant® website.....	22-5
22.9	XrfTable	22-6
22.10	SOME USEFUL WEBSITES	22-7
22.11	REFERENCE	

Summary and Conclusion

S.1	SUMMARY.....	S-1
S.2	ADVANTAGES OF XRFS	S-12
S.3	DISADVANTAGES OF XRFS.....	S-13
S.4	CONCLUSION.....	S-15
S.5	REFERENCE	S-16

X-ray Tables

T.1	COPYRIGHT PERMISSIONS	T-1
T.2	REFERENCES	T-3
	Periodic Table for XRFS	T-4
Table 1.	Wavelengths of the principal K X-ray spectral lines (Å).....	T-6
Table 1a.	Wavelengths of the principal K X-ray spectral lines (nm)	T-8
Table 2.	Wavelengths of the principal L X-ray spectral lines (Å)	T-10
Table 2a.	Wavelengths of the principal L X-ray spectral lines (nm).....	T-12
Table 3.	Wavelengths of the principal M X-ray spectral lines (Å)	T-14
Table 3a.	Wavelengths of the principal M X-ray spectral lines (nm).....	T-16
Table 4.	Photon energies of the principal K and L Series X-ray spectral lines	T-18
Table 4a.	Photon energies of the principal M Series X-ray spectral lines	T-20
Table 5.	Wavelengths of the K, L and M X-ray Absorption Edges (Å).....	T-22
Table 5a.	Wavelengths of the K, L and M X-ray Absorption Edges (nm)	T-24
Table 6.	K, L and M X-ray Excitation Potentials and Binding Energies.....	T-26
Table 7-1.	Parameters used in Leroux and Thinh equations: $\mu = C.E_{ab} \cdot \lambda^n = C.E_{ab} \cdot (12.3981/E)^n \text{ cm}^2 \cdot \text{g}^{-1}$	T-28
Table 7-2.	MACs for various wavelengths ($\lambda = 0.31 - 6.0 \text{ \AA}$)	T-31
Table 7-3.	MACs for $K\alpha$ lines of elements $Z = 11 - 60$ (Na - Nd).....	T-36
Table 7-4.	MACs for $L\alpha_1$ lines of elements $Z = 30 - 94$ (Zn - Pu).....	T-42
Table 7-5.	MACs for $L\beta_1$ lines of elements $Z = 30 - 94$ (Zn - Pu).....	T-48
Table 8.	K and L_{III} Absorption Edge Jump Ratios (r) and $(r - 1)/r$ values	T-49
Table 9.	Average K, L and M Fluorescence Yields for elements $Z = 4-94$	T-50
Table 10.	Relative K and some L Line Intensities within a Series (f_x).....	T-52
Table 11.	Some Useful "Oxide to Element" and "Element to Oxide" conversion factors (gravimetric factors)	T-53
Table 12.	International Atomic Weights	T-54
Table 13.	Correspondence between Siegbahn and IUPAC notation for X-ray diagram lines	T-54

Index