Energy Dispersive X-Ray Spectroscopy for the Determination of Trace and Main Elements

M. Haschke

► To cite this version:

M. Haschke. Energy Dispersive X-Ray Spectroscopy for the Determination of Trace and Main Elements. Journal de Physique IV Proceedings, 1996, 06 (C4), pp.C4-619-C4-625. 10.1051/jp4:1996458 . jpa-00254341

HAL Id: jpa-00254341

<https://hal.science/jpa-00254341>

Submitted on 1 Jan 1996

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.

Energy Dispersive X-Ray Spectroscopy for the Determination of Trace and Main Elements

M. Haschke

SPECTRO Analytical Instruments, Kleve

Abstract: The results from various samples reported here show that energy dispersive x-ray spectroscopy is available as an efficient analytical method; one that has emerged from the qualitative and semi-quantitative overview analysis phase.

Particularly the ability to improve sensitivity or reduce statistical error using optimized excitation has led to an important advancement in capturing the primary signal. The simultaneous measurement of a wide range of elements enables utilization of all of the information contained in a spectra for the evaluation; allowing for new approaches for the evaluation of spectra, particularly for the consideration of matrix influences.

1. INTRODUCTION

Many laboratories have already shown interest in energy dispersive x-ray spectroscopy. The reasons for this are:

- Different sample types (solid materials, liquids, powders, metals, minerals, etc.) can be analyzed with simple sample preparation.
- Analysis over a wide range of concentrations (from traces to main components) is possible without dilution.
- A wide range of elements can be analyzed simultaneously.

Energy dispersive x-ray spectroscopy is, however, often viewed as a screening method. Using the results from various applications, this paper will show that this method is extremely flexible; that it can be viewed as a true alternative to wavelength dispersive x-ray spectroscopy for many applications.

The results presented here were obtained with the SPECTRO X-LAB. This instrument is characterized by its use of special techniques for the excitation of fluorescence radiation. The sample is not directly excited. The tube radiation is modified by different targets in order to achieve optimal excitation for the given analytical application.

The different targets used and their advantages are summarized in table 1. Up to 8 of these targets can be simultaneously utilized in one instrument.

Table 1: Targets used in the SPECTRO X-LAB for optimization of the excitation conditions

Target type	Excitation with	Result of the excitation	Application
BARKLA scatterer example: B ₄ C, Al ₂ O ₃	polarized radiation	reduced spectral background due to directionally dependent scattering of the polarized radiation	- trace analysis of heavier elements in light matrices (e.g., geology, soil, oil, plastic, biological samples, etc.)
Secondary target example: Si, Co, Zn, Mo, Pd, Sm	monoenergetic characteristic radiation of the target material	Highly effective for the excitation of certain groups of elements due to the closeness of exciting and excited radiation energies	- analysis of main components - trace analysis for light elements - analysis of small sample amounts - analysis of dust on filters
Combination targets example: HOPG	polarized monoenergetic radiation (Rh-L-radiation) and polarized bremsstrahlung	effective excitation of light elements due to Rh-L-radiation, measuring channels are not overloaded by excitation radiation, because, due to polarization, this is not scattered	- main component analysis from F to Fe with one excitation - trace analysis of light elements

2. ANALYTICAL CAPABILITIES

The analytical capabilities of a method or a measuring instrument are described by the following parameters:

- sensitivity (detection limits)
- precision (reproducibility)
- stability (longterm behavior)
- analytical exactness (correctness)

These parameters are displayed for energy dispersive x-ray spectroscopy for various analytical applications:

2.1 Sensitivity

The sensitivity of a method can be described by the achievable detection limits. The detection limit is calculated according to the IUPAC definition

$$C_{\text{LOD}} = 3 (\sqrt{U / I_s}) C_s$$

The detection limits that can be achieved with various excitation parameters for several elements are summarized in table 2. These values apply to silicate powders (for example geological samples, soils, slags).

The high sensitivity for heavy elements is achieved by excitation with polarized radiation. This radiation gives improved peak-background-ratios for light matrices because of significantly reduced scattering in the polarization plane.

The results for the light elements were achieved with a special radiation entrance window.

Table 2: Detection limits for different excitation conditions in a silicate matrix (from /1/) [in µg/g]

Atomic number	Element	Detection limit		
		BARKLA	Secondary	Secondary
11	Na ₂ O		Cd -2000	Si -150
12	MgO		Cd -1000	Si - 50
13	Al ₂ O ₃		Cd - 600	HOPG -30
14	SiO ₂		Cd - 300	HOPG -20
15	P ₂ O ₅		Cd - 120	HOPG -15
16	SO ₄		Cd - 30	HOPG - 8
17	Cl		Cd - 10	HOPG - 4
20	CaO		Co - 80	
22	TiO ₂		Co - 25	
29	Cu	0.9		
30	Zn	0.8		
33	As	0.6		
35	Br	0.6		
42	Mo	2.0		
48	Cd	0.3		
50	Sn	0.6		
56	Ba	2.5		
80	Hg	1.7		
82	Pb	1.7		

An effective excitation is important for light elements because the fluorescent yield of this elements is small. The detection limits shown in table 2 for light elements are achieved with special targets and with a special entrance window for the detector.

Secondary targets are more suited to the trace analysis of metals, because these allow selective excitation. Thus, it is possible to excite lighter trace elements without exciting the main components. Results from the analysis of precious metals are summarized in table 3.

Table 3: Limits of detection for precious metal alloys (from /2/)
[in $\mu\text{g/g}$]

Element	Target Au/Ag	Matrix Au	Matrix Ag
Cr	Zn	2	-
Mn	Zn	4	-
Co	Zn	2	1
Ni	Ge	5	3
Cu	Ge	9	3
Zn	Ge	5	2
As	Pd	25	20
Ag	Sm/-	6	n.a.
Sn	Sm/-	0.3	25
Sb	Sm/-	3	25
Te	Sm/	2	20
Pd	Sm/	4	-
Rh	Sm/-	4	50
Pt	-/Pd	-	3
Au	-/Pd	n.a.	13
Bi	-/Pd	20	10
Pb	-/Pd	20	4

Excitation with secondary targets is also very effective for the analysis of small sample amounts. Examples of detection limits for dust on filters are shown in table 4.

Table 4: Detection limits for filter dust (from /3/)
[in ng/cm^2]

Element	Detection limit	
	membrane filter	quartz filter
Al	-	225
K	-	135
Ca	100	120
Cr	6	4.8
Mn	2	3.8
Fe	2	50
Ni	2.5	3.6
Cu	3	3.9
Zn	4	3.0
Ba	-	27
Pb	8	4.2
Cd	4	6.0

2.2 Reproducibility

The reproducibility of a method is determined by repeated measurements of the same sample. The results of measurements on a Basalt sample are presented here. The sample was prepared with a melt fusion and analyzed ten times.

The results of the individual measurements and the standard deviations for them are summarized for various elements in table 5.

Fusion tablets have a high homogeneity and a flat surface. The high reproducibility is a result of the low statistical error obtained by the high effective excitation.

Table 5: Reproducibility for a melt tablet (from /4/)
(Basalt sample, in %, measuring time: 100 s with HOPG target)

Meas.	1	2	3	4	5	6	7	8	9	10	Average	SD	RSD
MgO	12,21	12,28	12,26	12,21	12,03	12,04	12,05	12,07	12,38	12,18	12,171	0,1198	0,0098
Al ₂ O ₃	12	12,17	12,01	12,1	12,07	12,09	12,09	12,2	12,11	12,06	12,09	0,0622	0,0051
SiO ₂	43,31	43,41	43,54	43,56	43,49	43,49	43,62	43,49	43,76	43,54	43,521	0,1197	0,0398
P ₂ O ₅	0,46	0,46	0,47	0,52	0,47	0,46	0,49	0,47	0,49	0,47	0,476	0,0189	0,0398
K ₂ O	1,33	1,32	1,35	1,32	1,32	1,32	1,3	1,33	1,31	1,32	1,322	0,0132	0,0099
CaO	11,2	11,26	11,2	11,2	11,26	11,3	11,24	11,2	11,31	11,15	11,222	0,0655	0,0058
TiO ₂	2,41	2,41	2,42	2,42	2,42	2,43	2,4	2,42	2,42	2,41	2,416	0,0084	0,0035
Cr ₂ O ₃	0,06	0,06	0,06	0,06	0,06	0,06	0,06	0,06	0,06	0,06	0,06	0	0
MnO	0,19	0,19	0,19	0,19	0,19	0,19	0,19	0,19	0,19	0,19	0,19	0	0
Fe ₂ O ₃	12,29	12,34	12,31	12,35	12,34	12,4	12,35	12,36	12,36	12,34	12,344	0,0295	0,0024

When analyzing powder samples, low reproducibilities of light elements are obtained as a result of grain size and surface influences. The values for 7 measurements on a stone sample are given in table 6.

Table 6: Standard deviations for powder samples

Element	1	2	3	4	5	6	7	Average	SD	RSD
Al ₂ O ₃ [%]	14,61	14,28	14,39	14,53	14,24	14,43	14,38	14,408	0.1303	0.0090
SiO ₂ [%]	67,86	67,40	66,74	68,33	66,31	67,21	68,04	67,27	0.8193	0,0121
MnO [µg/g]	1783	1736	1767	1775	1753	1743	1749	1758	17	0.0098
Fe ₂ O ₃ [%]	6,191	6,213	6,260	6,163	6,155	6,189	6,162	6,190	0.0369	0.0059
Rb [µg/g]	2013	2000	2023	2011	2006	2010	2027	2012	0,9	0,0046
Sn [µg/g]	1894	1851	1885	1873	1877	1882	1872	1876	1,3	0,0071
Pb [µg/g]	20,1	19,6	28,0	20,6	18,5	19,5	19,2	20,78	3,2	0,156

The influence of sample preparation on the reproducibility can be neglected for these examinations,. When these influences are taken into consideration, the standard deviation is markedly increased; factors from 2 - 5 may occur depending on sample homogeneity, care in sample preparation and sample quality.

2.3 Longterm Stability

The longterm stability of an instrument is a measure of the reliability of the analysis over a longer period of time or of the necessity for regular standardizations.

Energy dispersive x-ray spectroscopy, with its simultaneous measurement of a wide range of elements, offers method specific standardization based on a current measurement. In this way:

- the energy-channel relationship for each spectra can be standardized, as several x-ray lines are always clearly identifiable or
- influences from instabilities in the excitation or from detection effects can be compensated for by using the relationship of line intensities on scattering intensities.

The longterm stability is displayed in table 7 using measurements on the same standard sample over a period of 8 months.

Table 7: Longterm stability of the SPECTRO X-LAB using daily measurements of the GSS 1 standard sample (from /5/)

Element	Reference sample GSS1		SPECTRO X-LAB			
	C _{cert} [μg/g]	SD [μg/g]	C _{av} [μg/g]	SD _{abs} [μg/g]	RSD [%]	RSD _{month} [%]
Ti	8056	417	7921	203.0	2.56	1.61
Zn	680	53	666.24	7.95	1.19	1.18
Sr	155	10	155.3	1.58	1.02	1.02
Cd	4.3	0.6	5.01	0.5	10.1	5.38
Ba	590	50	551.2	10.5	1.91	1.06
Pb	98	8	97.2	1.78	1.8	2.04

2.4 Analytical Exactness

The assessment of the analytical exactness is often the deciding criteria for the evaluation of the capabilities of an analytical instrument. Normally, however, this question can only be decided as a comparison with other methods. This can take place in different ways:

- analysis of samples with known contents (reference materials)
- participation in round robin tests

To validate energy dispersive x-ray spectroscopy, examinations with the SPECTRO X-TEST were conducted with all of the above named methods.

Comparison with Reference Materials

This method is the simplest and is the standard method for the calibration of a spectrometer. These types of comparisons are summarized for main components and trace elements in several geological samples in tables 8 and 9.

Table 8: Comparison of analytical results for main components (from /6/)
(Samples prepared as melt tablets) [in %]

Sample Element	PFA 1		KH		BHVO-1		RGM-1	
	Expect	X-LAB	Expect	X-LAB	Expect	X-LAB	Expect	X-LAB
Na ₂ O	1,31	1,28 ± 0,18	0,43	< 0,1	2,64	2,13 ± 0,19	4,05	4,07 ± 0,18
MgO	1,54	1,63 ± 0,08	0,77	0,73 ± 0,12	7,30	7,35 ± 0,12	0,33	0,33 ± 0,06
Al ₂ O ₃	26,7	26,55 ± 0,13	2,28	2,40 ± 0,05	13,7	13,69 ± 0,10	13,7	13,70 ± 0,09
SiO ₂	51,5	51,61 ± 0,20	8,70	8,60 ± 0,07	50,1	50,04 ± 0,19	72,9	73,3 ± 0,18
P ₂ O ₅	0,27	0,29 ± 0,01	0,11	0,12 ± 0,02	0,27	0,30 ± 0,01	0,04	0,07 ± 0,01
SO ₃	0,44	0,59 ± 0,01	0,28	0,33 ± 0,01	0,06	0,06 ± 0,01	0,06	< 0,02
K ₂ O	3,76	3,89 ± 0,02	0,44	0,41 ± 0,00	0,53	0,54 ± 0,01	4,30	4,41 ± 0,02
CaO	1,09	1,14 ± 0,01	47,2	47,99 ± 0,07	11,5	11,55 ± 0,03	1,15	1,20 ± 0,01
TiO ₂	0,97	0,96 ± 0,01	0,11	0,14 ± 0,01	2,76	2,75 ± 0,01	0,26	0,27 ± 0,01
MnO	0,06	0,07 ± 0,02	0,07	0,08 ± 0,00	0,17	0,17 ± 0,01	0,03	0,04 ± 0,00
Fe ₂ O ₃	9,37	9,27 ± 0,02	0,77	0,84 ± 0,01	12,4	12,21 ± 0,02	1,87	1,90 ± 0,01

Table 9: Comparison of analytical results for trace elements (from /6/)
(Samples prepared as powder tablets) [in µg/g]

Sample Element	GXR 4		GXR 6		BCR 141		SOIL 7	
	Expect	X-LAB	Expect	X-LAB	Expect	X-LAB	Expect	X-LAB
Cr	64.0	76.1 ± 1.5	96.0	93.8 ± 1.6	(75)	69.9 ± 1.5	60.0	68.2 ± 2.1
Ni	42.0	35.2 ± 1.5	27.0	28.3 ± 1.0	(28)	33.8 ± 1.0	-	28.2 ± 1.0
Cu	6520.0	6556 ± 14	66.0	64.2 ± 1.3	32.6	32.9 ± 0.9	11.0	12.9 ± 0.6
Zn	73.0	81.4 ± 1.5	118.0	127 ± 1.5	81.3	77.2 ± 1.1	104.0	100 ± 1.3
As	98.0	103 ± 1.1	330.0	316 ± 2	(5.4)	6.3 ± 0.5	13.4	11.8 ± 0.7
Br	-	< 0.6	(1.4)	2.0 ± 0.4	(5.0)	4.0 ± 0.2	-	20.0 ± 0.3
Cd	(0.9)	0.6 ± 0.2	(1.0)	< 0.3	0.4	0.6 ± 0.2	-	1.6 ± 0.2
Sn	5.6	6.4 ± 0.3	(1.7)	1.5 ± 0.2	(4.0)	4.8 ± 0.3	-	2.8 ± 0.2
Ba	1640.0	1832 ± 3	1300.0	1540 ± 2	(980)	280 ± 2	-	201.5 ± 2
Pb	52.0	54.6 ± 1.3	101.0	98.7 ± 1.5	29.4	29.4 ± 1.0	60.0	68.4 ± 1.3

Acknowledgments

Measurements from the following were used for this release:

- /1/ Landesumweltamt NRW, Recklinghausen
- /2/ Staatliche Bank von Kasachstan, Almaty
- /3/ Institut für anorganische und analytische Chemie der Universität Hamburg
- /4/ Rockwool Lapinus B.V., Roermond
- /5/ Gesellschaft für Wirtschafts- und Umweltgeologie, Berlin
- /6/ Institute of Geology, University of Sheffield