

SPECTRAL INTERFERENCE IN X-RAY FLUORESCENCE ANALYSIS OF COMMON MATERIALS

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ABSTRACT

Quantitative X-ray fluorescence analysis of most common materials (major ores and alloys) is affected by several adverse factors that influence accuracy of element determinations. Most attention over the past two decades or so was focussed on inter-element interactions and their mathematical corrections using various fundamental-parameters methods. However, spectral interference plays a role, which is very often not properly recognized and has even been neglected. Spectral interference considered important in the authors' practice was identified and characterized for 38 elements in the range B(5) – Bi(83). Selected examples demonstrate the magnitude of the analytical error occurring if spectral interference has not been corrected. An example of a complex application involving analysis of 26 elements in aluminum alloys is shown. The standard error obtained in the calibration process is compared for three cases: inter-element correction alone, inter-element and spectral correction, and no correction at all. The effect of spectral correction on standard error obtained in the calibration process is assessed.

INTRODUCTION

In modern quantitative XRF analysis of materials it is necessary to apply matrix corrections that compensate for the interactions among the elements and their radiation. Most attention over the past two decades or so was focused on inter-element interactions and their mathematical corrections using various fundamental-parameters methods. However, wavelength spectral interference plays a role, which is very often not properly recognized and has even been neglected. Spectral interference is defined as a condition when radiation corresponding to a specific analyte line and radiation of another line enter the detector at the same time[1]. Another type of spectral interference originating during the pulse-height distribution analysis is not dealt with in this work.

Unlike atomic spectra that are characterized by a large number of spectral lines the X-ray characteristic radiation of elements is relatively simple. Low atomic number elements are characterized by just a few major spectral lines. Middle atomic number and heavy elements have an increased potential for spectral interference. Nevertheless, the number and magnitude of possible spectral interference is limited and can be handled mathematically. This work deals with spectral interference that we managed to come across in our practice. The paper does not pretend to be a complete document on spectral interference in XRF analysis. Although the work does not cover all spectral interference, it would apply to most common materials encountered in daily practice. Another objective was to demonstrate on selected examples the magnitude of analytical error occurring if spectral interference was not corrected.

SPECTRAL-LINE INTERFERENCE

In order to minimize analytical error it is important to identify potential spectral interference and to estimate its impact. Surely, the lower the concentration (and intensity) of the measured line and the higher the intensity of the interfering line, the more serious is the interference. Hence, the most

important interference to be corrected is that that is caused by major or minor element occurring in the matrix. The more their content varies the more important is the spectral correction. The magnitude of the interference increases with angular proximity of the analyte and the interfering line. In trying to increase the angular spacing between two lines the choice of crystal or collimator plays a very important role. Several middle atomic elements and almost all heavy elements require that a fine collimator be used. However, increase in the angular spacing (usually accomplished by selecting another crystal with smaller d spacing), or selection of a finer collimator generally comes at the expense of measured intensity.

Much interference is inconsequential when the concentration of the interfering element and the relative intensity of its interfering line are both on the low end. For example, interference of Mo $K\alpha$ third order line at 2.13 Å on the Mn $K\alpha$ line at 2.103 Å is weak as long as Mo remains a trace constituent.

Interference of tube spectral lines with a number of analyte elements is most of the time unavoidable. Fortunately, this contribution to analyte intensity is almost constant. For example, in the case of the Ti $K\alpha$ line both Rh and Sc target tube primary radiation interferes. The Rh $K\beta_1$ line (5th order) and Rh $K\beta_3$ line (5th order) make a systematic contribution at all times. If a Sc target tube is used the unavoidable contribution is made by the Sc $K\beta_{1,3}$ line of the 1st order.

When using an Rh target tube there is an unavoidable interference of the Rh $L\alpha$ line with Cd $K\alpha$ line. Using a 300 µm brass filter can minimize this interference.

The interference of the 2nd order Nb $K\beta_1$ and Nb $K\beta_3$ lines on the first-order Ta $L\beta_1$ line can be easily avoided by decreasing the tube excitation potential. Setting the tube potential at 19 kV for selective excitation of the Ta $L\beta_1$ line (9.342 KeV) eliminates the Nb $K\beta_1$ line (18.619 KeV) and the Nb $K\beta_3$ line (18.603 KeV)[2].

EXPERIMENTAL

Interference identified in our practice and judged important is listed in Tables 1 and 2[3-5]. Spectral interference that was identified would apply to most raw materials like ores, and common products such as cement and alloys. Attention should also be given to the spectral lines whose half line wavelength might cause interference with the analyte line. A few selected examples demonstrate the magnitude of analytical error caused by spectral interference. Figure 1 shows a superposition of the Na $K\alpha$ line (second order) on the O $K\alpha$ line in bath electrolyte. Sodium is the major matrix constituent but its content does not change markedly (20-30%). Nevertheless, a suitable line overlap correction should be applied. The RMS (Root Mean Square) is 1.04% before (circles) and 0.59% after spectral correction (squares), respectively. Figure 2 shows a calibration curve for Na in pitch. The RMS is 0.008% before (circles) and 0.002% after spectral correction for Zn (squares), respectively. Zn in pitch is a trace constituent (0.008-0.08%) but it is a heavy element in a light matrix.

Table 1. Spectral Interference - Light and Ultra-light Elements

<i>Analyte line</i>	<i>Wave-length (Å)</i>	<i>Interference line</i>	<i>Interference Wave- length (Å)</i>	<i>Remarks</i>
B K α	67.0	3 O K α	70.93	1
C K α	44.0	2 Mn L α	44.63	1
O K α	23.707	2 Na K α	23.820	1
F K α	18.307	4 Rh L α	18.377	2
		Fe L α , L β	17.60, 17.29	1
Na K α	11.909	Zn L β	11.982	1
Mg K α	9.889	As L α	9.671	1
		3 Ca K α	10.078	1
		3 Sn L β_3	9.917	1
Al K α	8.339	3 Ti K α	8.250	1
		3 Sc K β	8.339	3
		Br L α	8.375	1
		4Cr K β	8.340	1
		3Ba L $\alpha_{1,2}$	8.325	1
P K α	6.155	Zr L α	6.076	1
		4 Cu K α	6.167	1
		Mo L α	6.151	1
S K α	5.373	Mo L $\alpha_{1,2}$	5.41	1
K K α	3.774	Cd L β	3.739	1

REMARK : Spectral interference becomes important

1 = if the interference is caused by major or minor element

2 = if the Rh tube is used

3 = if the Sc tube is used

Table 2. Spectral Interference – Mid-atomic Number and Heavy Elements

<i>Analyte line</i>	<i>Wavelength (Å)</i>	<i>Interference line</i>	<i>Interference Wavelength (Å)</i>	<i>Analyte line</i>	<i>Wavelength (Å)</i>	<i>Interference line</i>	<i>Interference Wavelength (Å)</i>
Ca K α	3.360	Sn L β	3.385	Rb K α	0.927	Bi L β	0.926, 0.939
Ti K α	2.750	Ba L α_1	2.776	Sr K α	0.877	2Sn K β	0.870, 0.850
V K α	2.505	Ti K β	2.514	Y K α	0.831	2Sb K β	0.834, 0.816
Cr K α	2.291	V K β	2.285			Rb K β	0.829
		2Bi L α	2.288	Zr K α	0.788	Sr K β	0.783
Mn K α	2.103	2BrK α	2.082, 2.088	Nb K α	0.748	Y K β	0.74
		Cr K β	2.085	Mo K α	0.710	Zr K β	0.701
		3Mo K α	2.13	Ag K α	0.561	Rh K β	0.546
Fe K α	1.937	Mn K β	1.910	Cd K α	0.536	Rh K β	0.546, 0.536
Co K α	1.791	Fe K β	1.757	Sn K α	0.492	3Pb K α	0.501
Ni K α	1.659	2YK α	1.660			3Bi K α	0.486
		3AgK α	1.683			Ag K β	0.497
Cu K α	1.542	Ta L α_2	1.533	Sb K α	0.472	Cd K β	0.475
Zn K α	1.437	3SbK α	1.416			3Bi K α	0.486
		2MoK α	1.420			Sn K α	0.492
		3SnK α	1.476	Ba L α	2.776	Sn Ly $_6$	2.778
Ga K α	1.341	Pb L β	1.350	Hf L α	1.569	2Zr K α	1.574
Ge K α	1.256	WL β	1.245	Ta L α	1.522	2Nb K α	1.494
As K α	1.177	Pb L α_1	1.175	Pb L α	1.175	As K α	1.177
Se K α	1.106	WL γ_1	1.098	Bi L α	1.144	3BaK α	1.161

Figure 1 Calibration curve for oxygen (Al_2O_3) in bath electrolyte. Effect of spectral correction (2Na $\text{K}\alpha$ on O $\text{K}\alpha$).

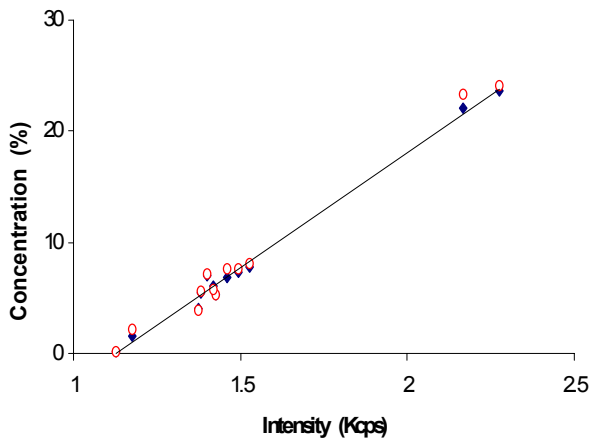
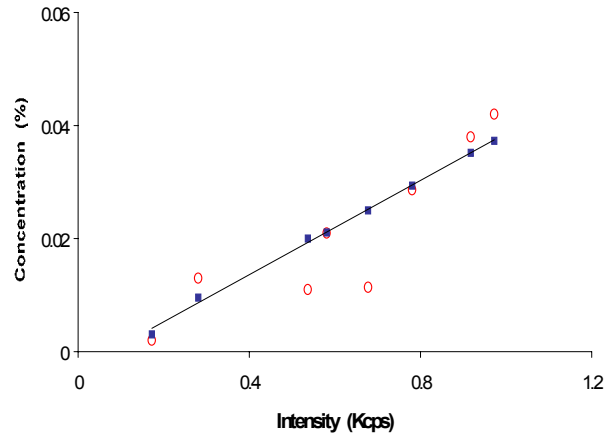


Figure 2 Calibration curve for Na in pitch. Effect of spectral correction (Zn $\text{L}\beta$ on Na $\text{K}\alpha$).



Another interesting example of interference is by Ca $\text{K}\alpha$ (third order) on Mg $\text{K}\alpha$. Using a multilayer PX-1 crystal and BA-12 Alcan bath standard the interference cannot be detected (Figure 3). Please note that the concentration of Mg is 0.08%, whereas Ca concentration is 3.1%. The interference can largely be overcome (Figure 4) if a TIAP crystal is used along with a fine collimator.

Figure 3 Mg scan in BA-12 Alcan bath standard measured with a PX-1 crystal.

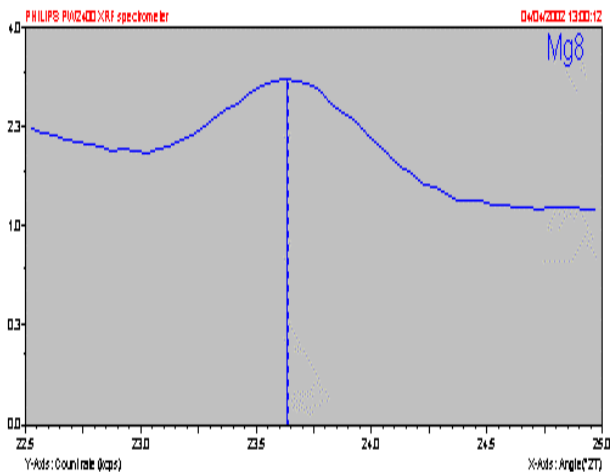


Figure 4 Mg scan in BA-12 Alcan bath standard measured with TIAP crystal. The peak to the left is due to Mg $\text{K}\alpha$.

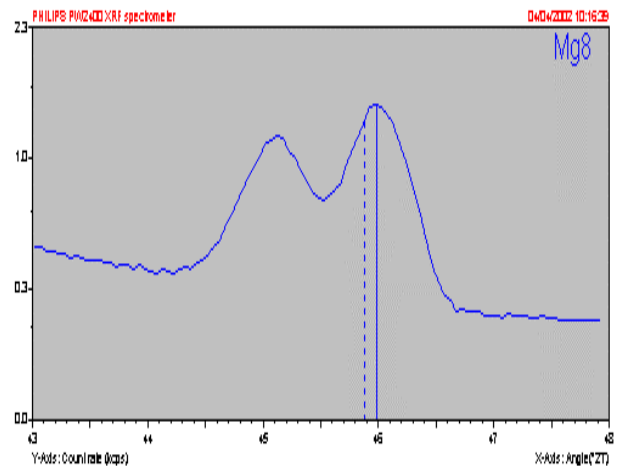


Table 3 gives selected data for a complex application involving analysis of aluminum alloys. One analytical program was established for determination of 26 major and minor elements. Sixty Alcan aluminum standard samples were employed in the calibration. Each sample surface was machined using Herzog automatic milling machine. Standard errors obtained in the calibration process are compared for three cases: inter-element correction alone, inter-element and spectral correction, and no correction at all.

Table 3. Standard Errors (RMS %) Obtained in the Calibration Process for Al Alloys

Element	Range %	RMS (%)				Relative Improvement (%)	Interfering element
		No corrections	Inter-element correction	Inter-element + spectral	Spectral correction		
Mg	0 - 5	0.1033	0.0353	0.0347	0.0006	0.6	Sn
Al	80 - 100	2.0599	2.0338	0.4475	1.5863	77.0	Ti, Cu, Sn
Si	0 - 19	0.2123	0.1584	0.1573	0.0011	0.5	
P	0 - 0.008	0.0010	0.0007	0.0004	0.0003	32.4	Cu
Ca	0 - 0.06	0.0119	0.0121	0.0025	0.0097	81.5	Sn
Ti	0 - 0.25	0.0014	0.0015	0.0015	0.0000	0.0	
V	0 - 0.05	0.0018	0.0017	0.0008	0.0009	49.2	Ti
Cr	0 - 1.0	0.0044	0.0047	0.0045	0.0002	4.7	V
Mn	0 - 1.0	0.0050	0.0036	0.0036	0.0000	0.4	Cr
Fe	0 - 3.3	0.0110	0.0128	0.0128	0.0000	0.0	
Ni	0 - 5	0.0279	0.0071	0.0071	0.0000	0.0	
Cu	0 - 8	0.0525	0.0282	0.0270	0.0012	2.3	
Zn	0 - 10	0.0627	0.0138	0.0111	0.0028	4.4	Sn
Ga	0 - 0.05	0.0028	0.0008	0.0009	0.0000	1.4	
Sr	0 - 0.08	0.0008	0.0004	0.0003	0.0001	8.9	Sn
Zr	0 - 0.03	0.0011	0.0003	0.0003	0.0000	0.0	Sr
Cd	0 - 3	0.0497	0.0016	0.0016	0.0000	0.0	
Sn	0 - 20	1.4776	0.0580	0.0170	0.0409	2.8	
Sb	0 - 1	0.0230	0.0032	0.0031	0.0001	0.4	Cd
Pb	0 - 0.6	0.0132	0.0033	0.0033	0.0000	0.1	As
Bi	0 - 1.0	0.0073	0.0049	0.0049	0.0000	0.6	
Mo	0 - 0.001	0.0002	0.0001	0.0000	0.0000	11.1	Zn
Nb	0 - 0.001	0.0002	0.0000	0.0000	0.0000	0.0	
As	0 - 0.1	0.0037	0.0008	0.0008	0.0000	0.0	
Co	0 - 0.5	0.0010	0.0011	0.0010	0.0001	12.2	Fe
Ba	0 - 0.004	0.0003	0.0002	0.0002	0.0000	3.2	Sn

As evident in Table 3 the spectral corrections bring a certain improvement to the calibration process manifested by lower RMS. In order to quantify the effect of spectral correction the relative RMS was calculated using the RMS due to spectral correction alone and the RMS obtained when no correction has been applied. The degree of

improvement (%) for the elements concerned varies from 0 to over 80 %. Obviously, the elements for which no spectral correction was applied show no or almost no improvement. By contrast, for the elements with applied spectral correction the magnitude of improvement is as little as a fraction of a percent (Mg, Si, Mn, Sb, Pb, Bi), a few percent (Cr, Cu, Zn, Ga, Sr, Sn, Mo, Co, Ba), and as much as 81.5% (Ca). Thus, the spectral correction plays a very important role in lowering total analysis error. The degree of correction depends on the analyte and interfering element and the concentration level at which they occur.

CONCLUSION

Spectral interference plays a very important role in quantitative X-ray analysis and its correction cannot be ignored. Examples given in the work confirm that if spectral interference is not corrected the analytical error may increase by as much as 4 fold for Na in pitch, or 80% for Ca in Al alloys.

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