

Short Communication

A GENERAL X-RAY FLUORESCENCE SPECTROMETRIC TECHNIQUE BASED ON SIMPLE CORRECTIONS FOR MATRIX EFFECTS

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X-ray fluorescence spectrometry is highly selective but, as is well known, problems arise when the x-rays are absorbed in different ways by the samples and standards. When the composition of the samples is approximately known, these matrix effects can be prevented by preparing standards and samples in the same way, e.g. by a borax fusion technique [1–5]. This procedure, when it is used correctly, ensures sufficient compensation of matrix effects. If, however, almost nothing is known about the composition of the samples, this method is not applicable. Even when it is applied, much work is involved in the preparation of new standards. Accordingly, several methods of correcting for matrix effects have been suggested [6–11]; some of them give good results but are rather complicated, while others may be restricted to certain wavelengths.

The method reported here, which is relatively simple and generally applicable for most materials, involves a combination of borax fusion with matrix effect corrections. The latter are done with algorithms, which are derived from the intensity formulae, together with empirical coefficients.

Experimental

Sample preparation. Accurately weigh two different amounts of the same sample (S_1 g and S_2 g on an ignited base) into Pt–5% Au crucibles, and add 6.000 g (dry weight) of borax. Mix well and fuse in a furnace at about 1000°C. Cast the melt into Pt–5% Au moulds, maintained at about 800°C, to produce glass discs of 30-mm diameter. For the determination of an element j , measure the intensities at a certain wavelength (λ_j) and correct for the background and dead-time; the corrected intensities are I_{jS_1} , and I_{jS_2} , respectively.

Standard preparation. If possible, use only the anhydrous oxides of the required elements, although other inorganic anhydrous compounds may be used at need. For element j , weigh two different amounts of its compound (m_1 g and m_2 g on an ignited base) and prepare glass discs as described above. The respective corrected measured intensities are I_{jm_1} and I_{jm_2} .

Matrix absorption corrections

Excitation by the total primary spectrum of an x-ray tube can be replaced by excitation by a hypothetical effective wavelength (λ_e). The absorption coefficients for this wavelength, $\mu_i(\lambda_e)$, are then used to calculate the primary absorption of the sample. The total sample absorption for element j is given by: $\Sigma_i W_i [\mu_i(\lambda_e) + A\mu_i(\lambda_j)]$, where the first term indicates the absorption for the effective wavelength of element j , and the second term the absorption for the characteristic wavelength.

Let the absorption coefficients for the borax be K'_j for the effective wavelength and K''_j for the characteristic wavelength of element j , and let the absorption coefficients for the sample be a'_j and a''_j for the effective wavelength and characteristic wavelength of element j , respectively. The absorption for the glass disc with S_1 g of sample (see sample preparation) can then be described by

$$\frac{6}{(6 + S_1)} (K'_j + AK''_j) + \frac{S_1}{(6 + S_1)} (a'_j + Aa''_j)$$

The terms $(K'_j + AK''_j)$ and $(a'_j + Aa''_j)$ depend on the wavelength, but are constants for element j measured under fixed conditions. A is an apparatus constant. Thus new combined absorption coefficients for primary and secondary radiation can be introduced.

If $(K'_j + AK''_j) = K_j$ and $(a'_j + Aa''_j) = A_j$, the expression becomes $(6K_j + S_1A_j)/(6 + S_1)$. Analogously, the absorption of the glass disc with S_2 g of sample can be described by $(6K_j + S_2A_j)/(6 + S_2)$, and the absorptions of the standard discs (see standard preparation) by $(6K_j + m_1B_j)/(6 + m_1)$ and $(6K_j + m_2B_j)/(6 + m_2)$, respectively. Here, B_j is the so-called combined absorption coefficient for primary and secondary absorption of the compound used for making standard discs of element j .

Calculations of absorption coefficients. For the sample the following expression now holds:

$$S_2 I_{jS_1} (6 + S_1) \frac{6K_j + S_1A_j}{(6 + S_1)} = S_1 I_{jS_2} (6 + S_2) \frac{6K_j + S_2A_j}{(6 + S_2)}$$

Thus A_j can be calculated in terms of K_j ; and the real value of K_j is not important, because all the absorption coefficients are in terms of K_j . If K_j is taken as a constant parameter of 1 for every wavelength, rearrangement gives for A_j (and analogously for B_j):

$$A_j = 6(S_1 I_{jS_2} - S_2 I_{jS_1}) / S_1 S_2 (I_{jS_2} - I_{jS_1})$$

$$B_j = 6(m_1 I_{jm_2} - m_2 I_{jm_1}) / m_1 m_2 (I_{jm_2} - I_{jm_1})$$

The amount of element j in the disc with S_1 g sample is then given by

$$C_j = b m_1 \frac{I_{jS_1}}{I_{jm_1}} \frac{(6 + S_1 A_j)}{(6 + S_1)} \frac{(6 + m_1)}{(6 + m_1 B_j)} \frac{(6 + S_1)}{(6 + m_1)} = b m_1 \frac{I_{jS_1}}{I_{jS_2}} \frac{(6 + S_1 A_j)}{(6 + m_1 B_j)}$$

where b is a conversion factor for the compound of element j which is used for making standards. The concentration of element j in the sample can then be easily calculated.

Results and discussion

Several ceramic materials were analysed as described above. The amounts weighed for the sample (S_1 g and S_2 g, respectively), were about 0.5 g and 0.3 g, while the weights (m_1 g and m_2 g) of the oxides used for making the standard discs were about 0.12 g and 0.07 g, respectively. To prevent loss of lead, samples and standards containing lead were fused first at 800°C and then at 1000°C. The results are shown in Table 1.

Some B.C.S. alloys were also analysed (Table 2). These alloys were dissolved in acid, and two different aliquots of the same solution were transferred to platinum crucibles, evaporated to dryness and ignited. Glass discs were prepared from the ignited materials. A synthetic mixture of Fe, Cr and Ni solutions was also analysed (Table 3).

TABLE 1

Results (in %) for some ceramic samples

	Sample 1		Sample 2		Sample 3	
	Present	Found	Present	Found	Present	Found
Pb	57.6	57.7	57.6	57.4	—	—
Ti	17.08	17.02	17.16	17.20	—	—
Sm	8.02	7.95	8.03	7.97	48.38	48.50
Zr	—	—	—	—	32.52	32.63

TABLE 2

Results (in %) for some B.C.S. alloys

Alloy	B.C.S. 218/2		B.C.S. 263/1		B.C.S. 330		B.C.S. 235/2	
	Present	Found	Present	Found	Present	Found	Present	Found
Fe	—	—	0.35	0.36	—	—	—	—
Cr	0.10	0.11	0.24	0.26	—	—	18.60	18.57
Ni	0.18	0.18	—	—	—	—	9.38	9.58
Mn	0.63	0.63	0.36	0.36	0.45	0.46	—	—

TABLE 3

Results (in mg) for a synthetic Fe—Cr—Ni solution

	Fe	Cr	Ni
Present	886	102.8	609.7
Found	885	102.5	607.2

The influence of possible enhancement on this technique is not known exactly, but in practice good results are obtained, where enhancement could be expected, so that probably only slight interference will occur. It is clear that, for every wavelength measured, the discs must be infinitely thick.

It can be concluded that the method described is reliable with an acceptable accuracy for most materials. The applicability of the technique to specific materials is under investigation and will be reported later.

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