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A NEW EQUATION FOR WAVELENGTH DISPERSIVE X-RAY FLUORESCENCE ANALYSIS WITHOUT STANDARDS

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Summary—We derive an iteration equation for calculation of the concentrations of the elements in X-ray fluorescence analysis without standards. It does not require calculation of the intensity of primary spectra, which can excite the characteristic fluorescent X-ray, so its calculation is simpler. The experiments show that the results derived by the method without standards converged to those by chemical analysis, after three to four iterative calculations. The influence of the configuration of the specimen is negligible.

One of the difficulties in X-ray spectrometric analysis is the requirement for standards that are difficult to prepare. Therefore, some scientists initiated a study without standards,[1–4] and have applied the method in energy dispersive XRF. However, experiments of wavelength dispersive X-ray fluorescence analysis without standards have so far been carried out only with certain elements analysed using a crystal. On the other hand, the calculation of the intensity of primary spectra which can excite the characteristic fluorescent X-ray is tedious, and the discrepancy in the reference spectra and the actual spectra of the instrument involved will have an influence upon the accuracy of X-ray fluorescence analysis without standards. Therefore, in this manuscript we derive an iteration equation which does not require calculation of the intensity of primary spectra. The equation can be applied in combinatory analysis of a few crystals for both light and heavy elements. The results show that the iteration equation can be used in a wide range of concentrations of the elements.

The method without standards only requires the measurement of intensity of elements in the specimen but not the intensity of elements in standards. Therefore, the geometric configuration of the specimen need not be identical with standards, so the preparation of the specimen is simpler.

DERIVATION OF EQUATIONS

Equation (1) is the fundamental iteration equation:

$$C_A = C_B \frac{I'_L}{I'_K} \frac{P_B}{P_A} \frac{T_B}{T_A} \frac{(\mu/\rho)_{B,\lambda e}}{(\mu/\rho)_{A,\lambda e}} \times \frac{(\mu/\rho)_{M\lambda e} + A(\mu/\rho)_{M,\lambda L}}{(\mu/\rho)_{M,\lambda e} + A(\mu/\rho)_{M,\lambda K}}. \quad (1)$$

Its derivation is shown in the following: If the source which can excite the characteristic fluorescent X-ray is monochromatic, and the specimen is thick enough, near the surface of the sample the intensity of the characteristic fluorescent X-ray of the L line of element A is[5]

$$I_L = P_A I_{O,\lambda\ \mathrm{primary}} C_A \times \frac{(\mu/\rho)_{A,\lambda\ \mathrm{primary}}}{(\mu/\rho)_{M,\lambda\ \mathrm{primary}} + A(\mu/\rho)_{M,\lambda L}}, \quad (2)$$

where

$$P_A = \omega_A g_L \times \frac{\gamma_{A-1}}{\gamma_A} \frac{d\Omega}{4\pi} \quad (3)$$

$$A = \sin\phi \sin\psi. \quad (4)$$

The symbols in equations (1)–(4) are: C_A, concentration for the Ath element; C_B concentration for the *B*th element; I'_L detected intensity of the characteristic fluorescent X-ray of the L line of the Ath element; I'_K detected intensity of the characteristic fluorecent X-ray of the K line of the Bth element; ω_A fluorescence yield for the Ath element; g_L ratio of the intensity of the L line to all other lines in the spectral series; γ_A absorption jump ratio for the Ath element; Ω, solid angle; ϕ, incident angle; ψ, takeoff angle; T_A residual factor for the Ath element; T_B residual factor for the Bth element; λ_{primary} primary radiation wavelength from the excitation source; λ_e effective wavelength from the excitation source; λ_L wavelength of the characteristic fluorescent X-ray of the L line of the Ath element; λ_K wavelength of the characteristic fluorescent X-ray of the K line of the Bth element; $(\mu/\rho)_{M,\lambda\ \text{primary}}$ total specimen mass attenuation coefficient for the wavelength λ primary; $(\mu/\rho)_{M,\lambda L}$ total specimen mass attenuation coefficient for the wavelength λL: $(\mu/\rho)_{M,\lambda K}$ total specimen mass attenuation coefficient for the wavelength λK; $(\mu/\rho)_{M,\lambda e}$ total specimen mass attenuation coefficient for the effective wavelength λe; $(\mu/\rho)_{A,\lambda e}$ mass attenuation coefficient of the Ath element for the effective wavelength λe; $(\mu/\rho)_{B,\lambda e}$ mass attenuation coefficient of the Bth element for the effective wavelength λe.

When the source is the broadband spectra, the $I_{O,\lambda\ \text{primary}}$ in equation (2) may be interchanged by $I_{O,\lambda\ \text{effective}}$ $\lambda_{\text{effective}}$ can be written as λ_e for simplification. On the other hand, the intensity I_L is absorbed by the analyser crystal and the window of the detector. The detected intensity (I'_L) is only the the residual part of the intensity I_L of the surface of the sample. If the residual factor of element A is shown by T_A, then

$$I'_L = T_A I_L = T_A P_A I_{0,\lambda e} C_A \times \frac{(\mu/\rho)_{A,\lambda e}}{(\mu/\rho)_{A,\lambda e} + A(\mu/\rho)_{M,\lambda L}}. \quad (5)$$

If the element B in the sample is the one with the highest concentration, it can be chosen as the reference element for the calculation. From equation (5), the intensity of line K of element B can be written as

$$I'_K = T_B P_B I_{O,\lambda e} C_B \frac{(\mu/\rho)_{B,\lambda e}}{(\mu/\rho)_{B,\lambda e} + A(\mu/\rho)_{M,\lambda K}} \quad (6)$$

putting (5)/(6), where the $I_{O,\lambda e}$ cancel out:

$$\frac{I'_L}{I'_K} = \frac{T_A}{T_B}\frac{P_A}{P_B}\frac{C_A}{C_B}\frac{(\mu/\rho)_{A,\lambda e}((\mu/\rho)_{M,\lambda e} + A(\mu/\rho)_{M,\lambda K}}{(\mu/\rho)_{B,\lambda e}((\mu/\rho)_{M,\lambda e} + A(\mu/\rho)_{M,\lambda L}}, \quad (7)$$

therefore,

$$C_A = C_B \frac{I'_L}{I'_K}\frac{T_B}{T_A}\frac{P_B}{P_A}\frac{(\mu/\rho)_{B,\lambda e}}{(\mu/\rho)_{A,\lambda e}} \times \frac{(\mu/\rho)_{M,\lambda e} + A(\mu/\rho)_{M,\lambda L}}{(\mu/\rho)_{M,\lambda e} + A(\mu/\rho)_{M,\lambda K}}. \quad (8)$$

The equation is the fundamental iteration one as equation (1).

THE EQUATION FOR THE DETERMINATION OF THE RELATIVE RESIDUE FACTOR OF THE INSTRUMENT

The residue factors T_A and T_B depend on the construction of the instrument used and the wavelength of the characteristic fluorescent X-ray, and not on the shapes or sizes of the samples. Once a residue factor and each element are specified, the residue factor can be regarded as a constant instrumental parameter and can be stored on the computer. From equation (5) we know:

$$T_A = \frac{I'_L}{I_L}.$$

If the attenuation of the characteristic fluorescent X-ray in the path increases, the detected intensity I'_L will decrease, and T_A will decrease. Therefore, T_A is called the residue factor, and not the attenuation factor.

From equation (7) the residue factors of element B related to element A can be calculated using equation (9):

$$\frac{T_B}{T_A} = \frac{C_A}{C_B}\frac{I'_K}{I'_L}\frac{P_A}{P_B}\frac{(\mu/\rho)_{A,\lambda e}}{(\mu/\rho)_{B,\lambda e}} \times \frac{(\mu/\rho)_{M,\lambda e} + A(\mu/\rho)_{M,\lambda K}}{(\mu/\rho)_{M,\lambda e} + A(\mu/\rho)_{M,\lambda L}}. \quad (9)$$

If we have some samples in which the concentrations of elements are known, and whose relative intensities have been measured, the relative residue factor of the elements can be calculated by equation (9). If we have some pure elements, and their relative intensities have been measured, the relative residue factors of the elements can be calculated by equation (10):

$$\frac{T_B}{T_A} = \frac{I'_K}{I'_L}\frac{P_A}{P_B}\frac{(\mu/\rho)_{A,\lambda e}}{(\mu/\rho)_{B,\lambda e}}\frac{(\mu/\rho)_{B,\lambda e} + A(\mu/\rho)_{B,\lambda K}}{(\mu/\rho)_{A,\lambda e} + A(\mu/\rho)_{A,\lambda L}}. \quad (10)$$

We need not calculate T_B and T_A, but the ratio T_B/T_A.

Table 1. Compositions of the five alloys of aluminium determined (in weight fraction)

No.	Mn%	Fe%	Cu%	Mg%	Si%	Al%
1	0.39	0.18	2.30	1.10	8.20	87.83
2	0.93	0.74	1.20	0.56	9.35	87.22
3	0.59	0.38	1.48	0.74	11.22	85.59
4	0.79	1.08	1.89	0.94	12.49	82.81
5	0.22	0.33	0.73	0.27	13.96	84.49

Table 2. Crystals and detectors of six elements used

Detector	PET	LiF-200†	TAP‡	LiF-200	Rx-4†	LiF-200
Element	Al	Cu	Mg	Fe	Si	Mn
Crystal	PET*	LiF-200†	TAP‡	LiF-200	Rx-4§	LiF-200
Detector	PC¶	SC‖	PC	SC	PC	SC

*PET, Pentaerythritol.
†LiF(200), Lithium fluoride.
‡TAP, Thallium acid phthalate.
§Rx-4, Citrate, ammonium hydrogen.
‖SC, NaI(Tl) scintillation detector.
¶PC, Gas-flow proportional counter.
The filter was not used.

If the vacuum path is to be used, the absorption of the X-ray in the path mainly depends on the analyser crystal and the window of the detector. Although the residue factor (T_A or T_B) shows some changes when the geometry of the sample changes, the change in the ratio T_B/T_A will be small.

THE ITERATION PROCEDURE

If the zero-order approximation of the concentration for the ith element in sample consisting of N elements is $C_i^{(0)}$, $C_i^{(0)}$ may be calculated from the detected intensity:[4]

$$C_i^{(0)} = \frac{I_i'}{\sum\limits_{i=1}^{n} I_i'} \tag{11}$$

in $C_i^{(0)}$ including the $C_B^{(0)}$ and $C_A^{(0)}$.

The total specimen mass attenuation coefficient may be calculated from the following equations:[5]

$$(\mu/\rho)_{M,\lambda L} = \sum_{i=1}^{n} C_i(\mu/\rho)_{i,\lambda L} \tag{12}$$

$$(\mu/\rho)_{M,\lambda K} = \sum_{i=1}^{n} C_i(\mu/\rho)_{i,\lambda K} \tag{13}$$

$$(\mu/\rho)_{M,\lambda e} = \sum_{i=1}^{n} C_i(\mu/\rho)_{i,\lambda e}. \tag{14}$$

The zero-order approximation of $(\mu/\rho)_{M,\lambda L}$; $(\mu/\rho)_{M,\lambda K}$; $(\mu/\rho)_{M,\lambda e}$ may be calculated from the zero-order approximation of the element concentrations. P_A/P_B and A are calculated from equations (3) and (4), respectively. $(\mu/\rho)_{B,\lambda e}$ and $(\mu/\rho)_{A,\lambda e}$ were obtained from references. So the first-order approximation of $C_A^{(1)}$ could be obtained after the zero-order approximations $[C_B^{(0)};(\mu/\rho)_{M,\lambda L}^{(0)};(\mu/\rho)_{M,\lambda K}^{(0)};(\mu/\rho)_{M,\lambda e}^{(0)}]$ are inserted into equation (1). The first-order approximation of $C_B^{(1)}$ could be obtained after the $(N-1)$ piece of $C_A^{(1)}$ was calculated. The first-order approximations of $(\mu/\rho)_{M,\lambda L}^{(0)}$; $(\mu/\rho)_{M,\lambda K}$; $(\mu/\rho)_{M,\lambda e}$ could be calculated from $C_i^{(1)}$ by equations (12)–(14). So the second-order approximation of $C_A^{(2)}$

Table 3. The 1st-order to 4th-order iteration approximation of concentration (Mn)

	Sample				
	1	2	3	4	5
1st-order (%)	0.2914	0.7727	0.4789	0.6218	0.1922
2nd-order (%)	0.4043	0.9524	0.6026	0.8133	0.2250
3rd-order (%)	0.3882	0.9270	0.5894	0.7885	0.2190
4th-order (%)	0.3899	0.9304	0.5896	0.7896	0.2192
Chemical (%)	0.39	0.93	0.59	0.79	0.22
Difference (%)	−0.0001	0.0004	−0.0004	−0.0004	−0.0008

Table 4. The 1st-order to 4th-order iteration approximation of concentration (Fe)

	Sample				
	1	2	3	4	5
1st-order (%)	0.1350	0.6164	0.3095	0.8517	0.2874
2nd-order (%)	0.1867	0.7581	0.3878	1.111	0.3377
3rd-order (%)	0.1794	0.7377	0.3795	1.077	0.3287
4th-order (%)	0.1802	0.7405	0.3803	1.078	0.3288
Chemical (%)	0.18	0.74	0.38	1.08	0.33
Difference (%)	0.0002	0.0005	0.0003	−0.002	−0.0012

Table 5. The 1st-order to 4th-order iteration approximation of concentration (Cu)

	Sample				
	1	2	3	4	5
1st-order (%)	1.750	1.018	1.221	1.554	0.677
2nd-order (%)	2.365	1.213	1.499	1.912	0.7839
3rd-order (%)	2.294	1.197	1.479	1.892	0.7660
4th-order (%)	2.300	1.201	1.480	1.889	0.7666
Chemical (%)	2.30	1.20	1.48	1.89	0.73
Difference (%)	0	0.001	0	−0.001	0.0366

Table 6. The 1st-order to 4th-order iteration approximation of concentration (Mg)

	Sample				
	1	2	3	4	5
1st-order (%)	1.196	0.5868	0.7874	1.018	0.2783
2nd-order (%)	1.083	0.5559	0.7316	0.9234	0.2734
3rd-order (%)	1.103	0.5609	0.7402	0.9422	0.2701
4th-order (%)	1.100	0.5600	0.7398	0.9391	0.2698
Chemical (%)	1.10	0.56	0.74	0.94	0.27
Difference (%)	0	0	−0.0002	−0.0009	−0.0002

could be obtained after the first-order approximations $[C_B^{(1)};(\mu/\rho)^{(1)}_{M,\lambda L};(\mu/\rho)^{(1)}_{M,\lambda K};(\mu/\rho)^{(1)}_{M,\lambda e}]$ were inserted into equation (1).

This iterative calculation is repeated until the difference between the $C_A^{(m)}$ and the $C_A^{(m-1)}$ is small enough to be determined by the materials tested.

THE PRACTICAL APPLICATION OF THE ITERATION EQUATION

We single out aluminium alloy as an example to verify the above equation. The concentrations of five samples of aluminium alloy are given in Table 1.

The instrument used was a Rigaku (Japan) X-ray fluorescence spectrometer with a rhodium

Table 7. The 1st-order to 4th-order iteration approximation of concentration (Si)

	Sample				
	1	2	3	4	5
1st-order (%)	6.181	7.862	9.253	10.03	12.25
2nd-order (%)	8.729	9.762	11.76	13.30	14.60
3rd-order (%)	8.115	9.285	11.13	12.24	13.78
4th-order (%)	8.212	9.362	11.23	12.50	13.94
Chemical (%)	8.20	9.35	11.22	12.49	13.96
Difference (%)	0.012	0.012	0.01	0.01	−0.02

Table 8. The 1st-order to 4th-order iteration approximation of concentration (Al)

	Sample				
	1	2	3	4	5
1st-order (%)	90.45	89.14	87.95	85.92	86.31
2nd-order (%)	87.23	86.76	85.02	81.94	83.78
3rd-order (%)	87.92	87.29	85.68	82.96	84.64
4th-order (%)	87.82	87.21	85.58	82.80	84.47
Chemical (%)	87.83	87.22	85.59	82.81	84.49
Difference (%)	−0.01	−0.01	−0.01	−0.01	−0.02

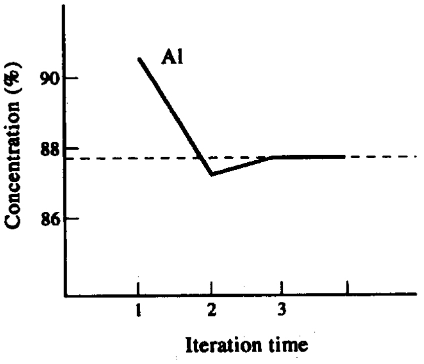

Fig. 1. The converging status of the result by the iteration calculation method (high concentration element).

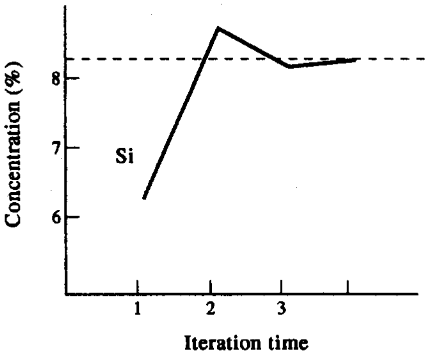

Fig. 2. The converging status of the result by the iteration calculation method (middle concentration element 1).

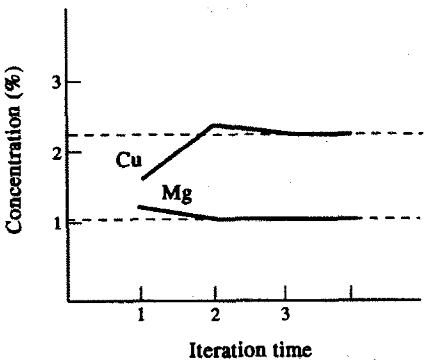

Fig. 3. The converging status of the result by the iteration calculation method (middle concentration element 2).

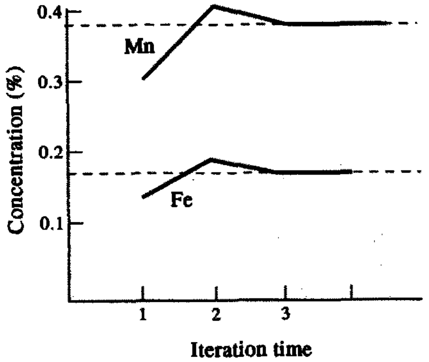

Fig. 4. The converging status of the result by the iteration calculation method (low concentration element).

target tube at an operating voltage of 50 kV and a tube current of 40 mA. The crystals and detectors used are given in Table 2.

The ratio P_B/P_A in equation (1) can be calculated from equation (3):

$$\frac{P_B}{P_A} = \frac{\omega_B}{\omega_A}\frac{g_K}{g_L}\frac{\gamma_{B-1}}{\gamma_{A-1}}\frac{\gamma_A}{\gamma_B}, \tag{15}$$

where $d\Omega/4\pi$ cancels out.

A in equation (1) is calculated from equation (4), in which ϕ and ψ are 63° and 40°, respectively. μ/ρ;ω;γ and g were taken from Refs 6–10. λ_e is 0.614 Å. The relative residue factor (T_B/T_A) and intensity $(I'_L; I'_K)$ were obtained by experimental measurement.

The first-order to fourth-order approximation of the concentration of the six elements of the five samples are given in Tables 3–8, in which the results of chemical analysis and difference between 4th-order approximation and the results of chemical analysis are also shown.

Figures 1–4 show that the results of iteration calculation converge with those of chemical analysis (dashed line in the figures), for high or low concentration elements.

CONCLUSIONS

A new practical iteration equation for wavelength dispersive X-ray fluorescence analysis without standards and a new equation for the calculation of relative residues factors are presented. It does not require calculation of the intensity of primary spectra. When the vacuum path to be used and the specimen is thick enough, equation (1) is valid.

The example of the analysis of aluminium alloy shows that the results agree well with the chemical values. Because standards are not needed, the geometric configuration of the sample is generally not required. We will present the results of experiments on other categories of samples in later papers.

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REFERENCES

1. K. Ohno, J. Fujiwara and I. Morimoto, *X-Ray Spectrom.*, 1980, **9**, 138.
2. M. Mantler, *X-Ray Spectrom.*, 1980, **9**, 143.
3. M. Mantler and H. Ebel, *X-Ray Spectrom.*, 1980, **9**, 146.
4. Yongzhong Wang and Zhimin Chen, *X-Ray Spectrom.*, 1987, **16**, 131.
5. E. P. Bertin, *Introduction to X-Ray Spectrometric Analysis*. Plenum Press, New York 1978.
6. R. Jenkins and J. L. de Vries, *Practical X-Ray Spectrometry*. Philips Technical Library, Springer, New York, 1975.
7. R. W. Fink, in *Handbook of Spectroscopy*, J. W. Robinson (ed.), Vol. 1, p. 221. CRC Press, Cleveland, 1974.
8. L. S. Birks, in *Handbook of Spectroscopy*, J. W. Robinson (ed.), Vol. 1, p. 230. CRC Press, Cleveland 1974.
9. J. H. Williams, *Phys. Rev.*, 1933, **44**, 146.
10. V. W. Slivisky and P. J. Ebert, *Phys. Rev. A. A*, 1972, **5**, 1581.