An Absorption Correction Formula for X-Ray Fluorescence Analysis Using Compton Scattering

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A correction method for X-ray fluorescence analysis of the heaviest element in a light element matrix was developed on the basis of the linear relationship between the Compton scattering intensity and the reciprocal of mass absorption coefficient. Using the equation obtained here, the heaviest element in the sample was determined over a large concentration range by measuring only the Compton scattering intensity of the primary X-rays and the fluorescent X-ray intensity for the analyte element. In this study, we employed copper in copper compounds as analyte element; the obtained copper concentrations agreed with the values calculated from chemical composition within 5% relative errors.

Keywords X-Ray fluorescence, absorption correction, light element matrix, Compton scattering, copper determination

In the X-ray fluorescence analysis of heavy elements in a light element matrix, a method employing Compton scattering X-rays as an internal standard^{1,2} can be used in addition to conventional calibration procedures. This method is based on the following theoretical assumptions:

1) the intensity of Compton scattering line is linearly related to the reciprocals of mass absorption coefficients for the analyte line wavelength as well as the Compton scattering wavelength;

2) in the X-ray fluorescence analysis of heavy elements in a light element matrix, only the absorption effect needs to be taken into account.

Assumption 1) is valid only when there is no major absorption edge between the Compton scattering line and the fluorescent X-rays used as an analyte line. However, this major absorption edge cannot be neglected in the general case as shown in Fig. 1, when an X-ray source of short wavelength such as Rh K_α is used. In a previous paper³, we have described a convenient method for determination of the heaviest element in a sample under the conditions where a major absorption edge is present between the Compton scattering line and the fluorescent X-rays, and we have reported the application data on the analysis of iron in iron compounds.

Here a brief outline of the principles is given and results of application to the determination of copper in copper compounds are described.

The equation for absorption correction was obtained on the basis of the following three relations:

1) the difference of the mass absorption coefficients of the sample between the longer and the shorter wave-

Fig. 1 Notation of wavelengths and mass absorption coefficients: λ_c , Rh K_α Compton wavelength; λ_e , equivalent wavelength; μ_c , mass absorption coefficient for Compton scattering; μ_e , that for equivalent wavelength; μ_s , that for short wavelength side of absorption edge; μ_i , that for long wavelength side of absorption edge; μ_f , that for analyte line. Curve A, $(\mu)_p$'s for pure copper; curve B, μ 's for copper gluconate.

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length sides of the absorption edge is proportional to the concentration of the analyte element whose absorption edge exists there;

2) the ratio of the mass absorption coefficients of the sample to those of the element concerned is almost constant on each side of the absorption edge (Hower's relation⁴);

3) an equivalent wavelength is used in polychromatic excitation.⁵

In order to use this equation, only the measurements of the intensities of the Compton scattering line and of the fluorescent X-rays for the analyte are required. In this study, we employed copper as the analyte element, and examined the validity of the equation.

Theory

We assumed that the heaviest element contained in the sample is the analyte element (see Fig. 1). When the mass absorption coefficient of the sample at the short wavelength side of the absorption edge is denoted by μ_s , and that at long wavelength side by μ_l , respectively, the difference between them can be represented by the following equation:

$$\mu_s - \mu_l = [\Sigma(\mu_s)_i C_i + (\mu_s)_p C] - [\Sigma(\mu_l)_i C_i + (\mu_l)_p C], \quad (1)$$

where C is the weight fraction of the analyte element contained in the sample. Subscript p represents the pure analyte element and i the matrix element, respectively. Since the mass absorption coefficients of the matrix element will not vary at the absorption edge,

$$\Sigma(\mu_s)_i C_i \approx \Sigma(\mu_l)_i C_i. \quad (2)$$

Then Eq. (1) can be rewritten as

$$\mu_s - \mu_l = [(\mu_s)_p - (\mu_l)_p] C. \quad (3)$$

Applying Hower's relation to the mass absorption coefficients for wavelength shorter than that of the absorption edge, we have

$$\mu_s / (\mu_s)_p = \mu_c / (\mu_c)_p, \quad (4)$$

where μ_c is the mass absorption coefficient of each specimen at the Compton scattering wavelength. Rewriting Eq. (4) and using the proportionality constant k_s , we have

$$\mu_s = k_s \mu_c, \quad \text{where } k_s = (\mu_s)_p / (\mu_c)_p \quad (5)$$

which shows that the mass absorption coefficient μ_s of the sample is represented by μ_c and k_s obtained from a pure substance of the analyte element. In this equation, μ_c can be obtained from the intensity of the Compton scattering line.

In the case of polychromatic excitation and a

sufficiently thick sample, the following relation between the mass absorption coefficient μ_e for the equivalent wavelength λ_e and μ_l for the fluorescent X-rays λ_l can be derived from the general formula for primary fluorescence

$$\frac{\mu_e + (\sin \phi_1 / \sin \phi_2) \mu_l}{(\mu_e)_p + (\sin \phi_1 / \sin \phi_2) (\mu_l)_p} = \frac{(I)_p}{I} C. \quad (6)$$

Here I is the intensity of fluorescent X-rays of the analyte in the sample, $(I)_p$ that of the pure element, ϕ_1 the incident angle of primary X-rays, and ϕ_2 the emergence angle of fluorescent X-rays. To simplify the expression of Eq. (6) using a geometrical factor A ($= \sin \phi_1 / \sin \phi_2$), $\mu^* (= \mu_e + A \mu_l)$ and $R_l (= I / (I)_p)$, we have

$$\frac{\mu_e + A \mu_l}{(\mu_e)_p + A (\mu_l)_p} = \frac{\mu^*}{(\mu^*)_p} = \frac{C}{R_l}. \quad (7)$$

Applying Hower's relation to μ_e and μ_c , we have

$$\mu_e / \mu_c = (\mu_e)_p / (\mu_c)_p = k_e \quad (8)$$

and also for μ_l and μ_l

$$\mu_l / \mu_l = (\mu_l)_p / (\mu_l)_p = k_l. \quad (9)$$

If we combine Eqs. (3), (5), (7), (8) and (9), the weight fraction can be represented as

$$C = \frac{(k_e + A k_s k_l) \mu_c}{(\mu^*)_p / R_l + A k_l [(\mu_s)_p - (\mu_l)_p]}. \quad (10)$$

In this equation, μ_c and R_l are values related to an unknown sample, and all other factors except for A and k_e are values obtained from the mass absorption coefficients of analyte element. In these equations, factor A is determined by the optical geometry, and k_e is estimated on the basis of some representative samples. We can use the equations by measuring the intensities of Compton scattering and fluorescent X-rays of pure analyte element and samples.

Experimental, Results and Discussion

The testing conditions are listed in Table 1. Samples listed in Table 2 were ground in an agate mortar, and molded in an aluminum ring of 3 cm in diameter under a pressure of 1×10^3 kg/cm².

Determination of geometrical factor A

In order to obtain A in Eq. (7), the wavelengths of Compton scattering of Rh K_α were measured using copper gluconate. The Compton wavelength was 0.643 Å, and the scattering angle $\phi (= \phi_1 + \phi_2)$ was obtained as 97.9° from the following equation

$$\lambda_c - \lambda_R = 0.02426(1 - \cos \phi), \quad (11)$$

Table 1 The testing conditions

Spectrometer	Phillips PW 1540
Applied potential	50 kV
Tube current	21 mA
Target	Rh
Analyte line	Cu K β
Analyzing crystal	LiF
Detector	scintillation counter
Counting time	100 s for Rh K α Compton scattering 100 s for Cu K β 10 s for background at 41.43° 2 θ
Copper compounds	reagent grade

Table 2 Copper compounds used in this work

No.	Reagent	Chemical formula
1	Copper(I) oxide	Cu ₂ O
2	Copper(II) oxide	CuO
3	Copper(II) sulfide	CuS
4	Copper(I) chloride	CuCl
5	Copper(II) chloride	CuCl ₂ ·2H ₂ O
6	Copper(II) citrate	Cu ₂ C ₆ H ₄ ·2.5H ₂ O
7	Copper(II) acetate, cryst.	Cu(CH ₃ COO) ₂ ·H ₂ O
8	Copper(II) sulfate, cryst.	CuSO ₄ ·5H ₂ O
9	Copper(II) potassium chloride	CuCl ₂ ·2KCl·2H ₂ O
10	Copper(II) gluconate	(C ₆ H ₁₁ O ₇) ₂ Cu
11	Copper sheet	Cu

where λ_c is the wavelength of the Compton scattering and λ_R that of the coherent scattering, 0.613 Å.

The angle ϕ_1 and ϕ_2 were estimated on the basis of instrumental design as follows: The angle 2 θ was 73.0°, when the analyzing crystal was kept parallel to the surface of sample holder. We obtained ϕ_2 as 36.5° and ϕ_1 as 61.4°. Then coefficient A becomes 1.476.

Estimation of equivalent wavelength

Equation (7) shows that $\mu^*/(\mu^*)_p$ varies with the equivalent wavelength λ_e . In this study, the equivalent wavelength was estimated as 0.8 Å from a slightly modified version of Tertian's method⁵, and regarded as a constant irrespective of the variety of samples.

Intensity of Compton scattering line and mass absorption coefficients

It is well known that the intensity of the Compton scattering line is linearly related to the reciprocal of the mass absorption coefficient. Results obtained with copper compounds and pure sulfur are shown in Fig. 2. The total intensity at the peak angle was taken as the Compton intensity, because of the large variation involved in background subtraction. The mass absorption coefficients ($\mu = \sum \mu_i c_i$) for these specimens were computed from the following equation and the chemical compositions:

$$\mu_i = c_i \lambda_i^{n_i} \quad (12)$$

Fig. 2 Compton scattering intensity I_c as a function of the reciprocal of mass absorption coefficient μ . The numbers corresponds to the numbers in Table 2.

Table 3 Values of factors in Eq. (10)

Factor	Value
k_s	7.922
k_e	1.808
k_f	1.024
$(\mu_s)_p - (\mu_l)_p$	263.9
$(\mu^*)_p$	130.9
A	1.476

here n_i and c_i are both constant. i denotes the element contained in the sample. To calculate the mass absorption coefficient of hydrogen, the estimated values 0.34 and 1.13 were obtained for c_i and n_i respectively from the literature.⁶

Calculation of factors

The values k_s , k_e , k_f , $(\mu^*)_p$ and $(\mu_s)_p - (\mu_l)_p$ for copper were calculated using Eqs. (5), (7), (8) and (12). They are listed in Table 3.

Results of quantitative analysis

The results of quantitative analysis using Eq. (10) are shown in Table 4. For the analyte line, the Cu K β was used instead of Cu K α in order to minimize the influence of detector dead time and to reduce errors arising from the application of Hower's relation by using a wavelength of the analyte line closest to the absorption edge. The maximum relative error was +4.5% for copper(II) potassium chloride. The maximum absolute error was -1.9% for copper(I) chloride.

Source of errors

The determination using Eq. (10) may involve the following sources of errors:

- 1) inaccuracy of mass absorption coefficients, especi-

Table 4 Accuracy of absorption correction

Sample No.	R_f	μ_c $\text{cm}^2 \text{g}^{-1}$	Concentration, %		Error, %	Relative error, %
			Obsd.	Content		
1	0.9801	33.99	88.5	88.8	-0.8	-0.9
2	0.9735	30.98	80.9	79.9	+1.0	+1.3
3	0.6757	27.66	65.4	66.5	-1.1	-1.7
4	0.6242	28.98	66.8	64.2	+2.6	+4.0
5	0.4674	17.70	36.8	37.3	-0.5	-1.3
6	0.8740	13.46	34.2	35.3	-1.1	-3.1
7	0.8717	12.14	30.8	31.8	-1.0	-3.1
8	0.5974	11.56	26.3	25.5	+0.8	+3.1
9	0.2071	14.96	20.8	19.9	+0.9	+4.5
10	0.6978	5.68	13.6	14.0	-0.4	-2.9

ally in a sample relatively thin compared to the critical depth;

2) calculation of mass absorption coefficients from Compton scattering;

3) application of Hower's relation;

4) estimation of equivalent wavelength;

5) inaccuracy of geometrical factors.

For 1), 2) and 3), it seems possible to reduce errors by using mass absorption coefficients of the same compilation for a sufficiently thick sample.

As a result of the examination in which the values of the equivalent wavelength and the geometrical factor were changed, it is found that the errors are insensitive to their values in the ranges $0.6 < \lambda_c < 1.0$ and $1.329 < A < 2.214$.

Limits to application of this method

This analytical method can be applied only to the heaviest element in the light element matrix. When absorption edges of matrix elements lie near that of the analyte element, the mass absorption coefficients of fluorescent X-rays are large, and the estimation of equivalent wavelength becomes important. If the content of the heaviest element is small, the second term of the denominator of Eq. (10) is so small compared with

the first term that it becomes negligible. In this case, this method is the same as Andermann's correction method.⁷ Thus the calibration curves can be estimated with the aid of mass absorption coefficient at Compton scattering wavelength.

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