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The Rapid Determination of Heavy Metals in Sediment by Means of X-ray Fluorescence Analysis*

Modification of the X-ray Intensity Using Scattered Radiation

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The present method was developed as a way of modifying intensity using the mass-absorption coefficient of the matrix, which is itself obtained from the measurement of the intensity at an arbitrary scattered wavelength. This modification, derived from the simplified equation by the utilization of the known matrix composition, has been empirically demonstrated, and it has been applied to various river-sediment samples. Repeated analyses on copper and zinc in representative sediments were carried out, and the average ($\bar{x}$) and the coefficient of the variation (*c.v.*) obtained by the present method and by the atomic-absorption method were compared. In the former method, $\bar{x}$=1,550 μg/g, *c.v.*=4.25% on copper, $\bar{x}$=4,400 μg/g, and *c.v.*=7.11% on zinc; in the latter method, $\bar{x}$=1,500 μg/g, *c.v.*=9.87% on copper, $\bar{x}$=4,330 μg/g, and *c.v.*=13.03% on zinc.

The X-ray fluorescence method, the atomic-absorption method, and the colorimetric method have all been used to determine the elements in a samples with a homogeneous composition of samples. Of these analytical methods, the X-ray fluorescence method has these advantages compared with the others;

(1) many elements can be analyzed rapidly, (2) the samples need not be destroyed, and (3) the X-ray spectro-chemical analysis of heavy metals does not generally depend on any of the chemical properties of the elements in which they are present.

There is, however, a problem related to the analysis of sediments by the X-ray fluorescence method-the matrix effect. Therefore, many investigators have reported modifications.

There have been modifications derived from the theoretical equation on the basis of the absorption and excitation effects of X-ray emission,[1–3] and experimental modifications derived by assuming a definite relation between the X-ray intensities and constituent elements of a sample.[4–6]

Taylor and Andermann[7–8] adopted a technique which involves the utilization of a modification using the value of the ratio of the $K\alpha$- or $L\alpha$-ray intensity to the scattered radiation at an empirically selected wavelength. With this method, the variation in the X-ray intensity with the matrix effect could be modified at lower concentrations (less than 500 μg/g content of copper).[9] However, at higher concentrations, differences in the mass-absorption coefficients at the constituent elements of the substructure for both wavelengths appeared in the intensity ratio, an example is shown in Fig. 1.

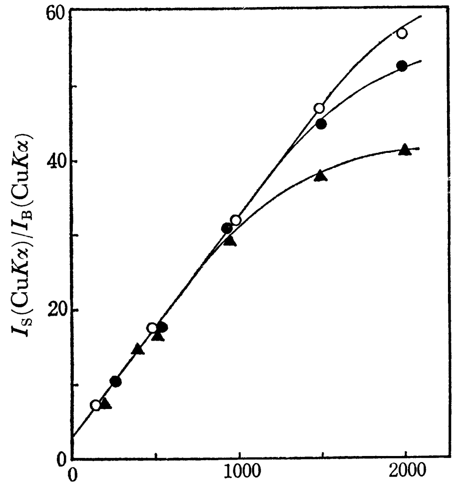

Fig. 1. Calibration curves of Cu on $I_S(\mathrm{Cu}K\alpha)/I_B(\mathrm{Cu}K\alpha)$ ratio.
○: H_3BO_3, ●: Cellulose powder, ▲: Silicic acid.

The present modification was developed by using the modification factor of the variation in the fluorescence intensity, which was determined from the measurement of the scattered radiation at an arbitrary wavelength.

This paper will deal with the modification and with the analytical results on metals in the river- and sea-sediments.

Experimental

Sample Treatment and Analytical Conditions of the X-ray Measurements. The sediment was sufficiently separated from water and then displaced on the evaporating dish. After dehydration for three hr at 110 °C in a drying oven, the sample was moderately crushed by a pestle, sieved to obtain a fine fraction, and finally crushed by means of a mixer-mill until the particle size became smaller than 100 μ. The specimen was molded at a pressure of 15 t/cm² and then analyzed by using a X-ray spectrometer.

A Rigaku Denki Geigerflex X-ray spectrometer equipped with a D9C-type constant-potential X-ray generator and a KG-X-type goniometer was used for the X-ray emission measurements.

The analytical conditions of the X-ray spectra are shown in Table 1.

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Table 1. Analytical conditions of X-ray

X-Ray tube	Tungsten target
Generator suplied	47.5 kV-40 mA
Analyzing crystal	LiF
Detector	Scintillation countor
Path	About 10^{-2} Torr
Counting time	10 s (Fix time)
Measuring method	To detect by using the pulse height analyzer and the differential method

Results and Discussion

The Intensity of the Scattered Radiation and the Mass-absorption Coefficient. The background of the X-ray fluorescence analysis is composed of the coherent scattering of photons of the given wavelength by the sample, the Compton scattering of the photons of the given wavelength by the sample, the scatter of radiation by the analyzing crystal, and fluorescence by the crystal. The intensity of the scattered radiation is approximately equal to that of the background, therefore, it can be expressed by the following equation.[10]

$$I_B=K_1[\{J_{(\lambda k)}\sum(C_iF_i^2/A_i)\}/\{\mu_{m(\ k)}(\sec\theta_1+\sec\theta_2)\}$$
$$+\{J_{(\lambda k)}\sum C_i(Z_i-f_i^2)r\}/\{\mu_{m(\lambda c)}(\sec\theta_1+\sec\theta_2)\}] \quad (1)$$

where J is the photon flux which is the intensity distribution of the exciting source; λ_k is the $K\alpha$ wavelength for the i element; μ is the mass-absorption coefficient; m is the matrix; θ_1 and θ_2 are the angles of incidence and excitation (from the normal state to the sample surface); λ_c is the Compton scattering of the photons of the given wavelength; K is a factor which is decided by the k element and the geometrical conditions of the instrument; C is the concentration; A is the atomic number; F is the atomic scattering power, f is the incoherent scattering power, and r is a recoil factor. Equation(1) is expressed as the background intensity underneath a peak.

Now, if the k element to be analyzed is rarely present in the sample, this intensity can be regarded as that of the radiation scattered at the same arbitrary wavelength. Therefore, λ_k was experimentally selected to be 0.906 Å of the scattered radiation at an arbitrary wavelength which was not influenced by the coexisting elements and which was obtained with a relatively high intensity.

Equation (1) can be simplified by noting that, since $\lambda_k-\lambda_c=0.03\ \text{Å}\fallingdotseq 0$, $\mu_{(\lambda c)}=\mu_{(\lambda k)}$.
Thus,

$$I_B=K_2\cdot K_s/\mu_{m(0.906\text{Å})} \quad (2)$$

where:

$$K_s=\sum\{C_i(K_s)_i\} \text{ and } (K_s)_i=\{F_i^2+(Z_i-f_i^2)r\}/A_i$$

$$K_2=K_1\cdot J_{(\lambda k)}/(\sec\theta_1+\sec\theta_2)=\text{const.}$$

The values of $(K_s)_i$ for each element can be calculated from the values of F and f^2, which are available in the standard text by Lonsdal.[11]

Equation (3) can be obtained by the conversion of the logarithms with regard to two variables, I_B and μ_m (0.906 Å), on both sides of Eq. (2):

$$\log I_B+\log\mu_{m(0.906\text{Å})}=K_3 \quad (3)$$

The mass-absorption coefficient of the X-ray is expressed as a function of the wavelength, containing the photoelectric absorption coefficient (τ) and the scattering coefficient (δ). The photoelectric absorption coefficient increases in proportion to the third power of the wavelength in the region from a remote absorption edge. On the other hand, however, the scattering coefficient is constant and independent of the wavelength in the first approximation.[12] Therefore, the mass-absorption coefficient of the X-ray is generally expressed as $\mu=\delta+\tau$. Then, $\tau=CZ^m\lambda^3$; thus, $\mu=\delta+n\lambda^3$.

The mass-absorption coefficient of the scattered radiation at the arbitrary wavelength is

$$\mu_{m(0.906\text{Å})}=\delta+n(0.906)^3, \quad (4)$$

while that of the $K\alpha$-line to be analyzed is expressed as

$$\mu_{m(\lambda s)}=\delta+n\cdot\lambda_s^3, \quad (5)$$

where λ_s is the wavelength of the $K\alpha$-line to be analyzed.

The relation between $\mu_{m(\lambda s)}$ and $\mu_{m(0.906\text{Å})}$ can be expressed as follows from Eqs. (4) and (5):

$$\log\mu_{m(0.906\text{Å})}=\log\mu_{m(\lambda s)}+K_4 \quad (6)$$

When Eq. (6) is substituted in Eq. (3), Eq. (7) is obtained:

$$\log I_B+\log\mu_{m(\lambda s)}=K_5 \quad (7)$$

Thus, Eq. (7) shows that the mass-absorption coefficient for the given wavelength, λ_s, can be determined by the measurement of I_B.

The relation between the background intensity at 0.906 Å and the mass-absorption coefficient for the $K\alpha$-line to be analyzed on various model matrices was examined. Copper oxide, zinc carbonate, chromium oxide, arsenic trioxide, cadmium oxide, and stannous chloride were used as the standards. The concentrations of copper, zinc, chromium, arsenic, cadmium, and tin were adjusted to 1000 μg/g for each portion of boric acid, anhydrous aluminium sulfate, potassium sulfate, sodium sulfate, and sodium carbonate respectively used as the model materices.

The calculated results of the mass-absorption coefficients with the Cu$K\alpha$-, Zn$K\alpha$-, Cr$K\alpha$-, Cd$K\alpha$-, As$K\alpha$, and Sn$K\alpha$-emission spectra for the matrices are shown in Table 2.

The relation between the background intensity at 0.906 Å and the mass-absorption coefficient for Cu$K\alpha$-

Table 2. Values of mass absorption coefficient of K-emission spectra for various matrices

K-Emission spectrum	Matrix				
	H_3BO_3	Na_2CO_3	Na_2SO_4	$Al_2(SO_4)_3$	K_2SO_4
Cu$K\alpha$	10.56	17.15	28.53	31.43	63.30
Zn$K\alpha$	8.60	13.97	23.27	25.64	51.76
Cr$K\alpha$	32.21	53.09	87.54	96.12	155.64
As$K\alpha$	4.24	6.58	10.74	11.81	23.76
Cd$K\alpha$	0.74	1.02	1.55	1.69	3.27
Sn$K\alpha$	0.60	0.84	1.25	1.34	2.56

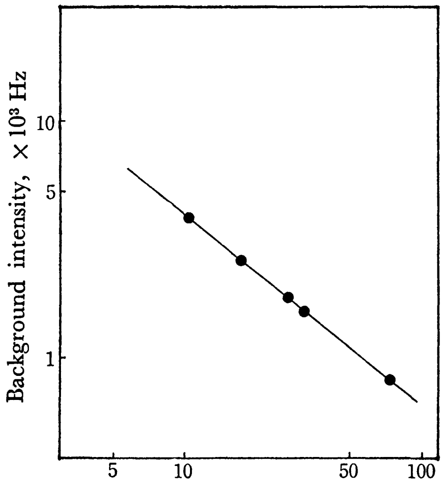

Fig. 2. Relationship between mass-absorption coefficient for Cu$K\alpha$-line and background intensity at 0.906 Å.

line is shown in Fig. 2 as representative of the standard elements.

A satisfactory reciprocity was obtained between I_B and μ_m(Cu$K\alpha$).

Fluorescence X-Ray Intensity and Mass-absorption Coefficient. Kalman and Heller[13] have shown that the intensity of the fluorescence X-ray can be represented by:

$$I_S = K_6C_s/\{\mu_{m(\bar{\lambda})} \sec\theta_1 + \mu_{(\lambda s)} \sec\theta_2\} \qquad (8)$$

where I_S is the intensity of the fluorescence peak of the s element, $\bar{\lambda}$ is the effective exciting wavelength, and K_6 is a factor which is decided by the s element and the geometrical conditions of the instrument. The constancy of $\bar{\lambda}$ in the case of a measurable $K\alpha$-line excited by operating an X-ray tube continuously with a constant power input has been verified.[11]

Equation (8) can be simplified as follows:

$$I_S = K_6C_s/N\cdot\mu_{m(\lambda s)} \qquad (9)$$

where:

$$N = \mu_{m(\bar{\lambda})}/\mu_{m(\lambda s)} + \sec\theta_2/\sec\theta_1 \qquad (10)$$

Compton has proved that N can be considered a constant if, for all the matrices, $\mu_{(\lambda)}\infty\lambda^n$ (where n is independent of the matrix) over the range from $\bar{\lambda}$ to λ_s.[10]

As is shown Eq. (9), the intensity of the fluorescence is a function of the concentration and the mass-absorption coefficient. The relation between I_S and C_s can be represented as the calibration curve on an identical matrix; however, the relation between the $\mu_{m(\lambda s)}$ obtained from Eq. (8) and I_S should be examined further.

The result obtained by taking a intensity ratio on any matrix (m_i) and the standard model matrix (m_1) of the element to be analyzed at a constant concentration is shown in Eq. (11):

$$I_{S_1}/I_{S_i} = K_7\mu_{m_i(\lambda s)}/\mu_{m_1(\lambda s)} \qquad (11)$$

Equation (12) is obtained by the conversion of the logarithms on both sides Eq. (11), when the value of $\mu_{m_1(\lambda s)}$ is a unit:

$$\log I_{S_1}/I_{S_i} + \log\mu_{m_1(\lambda s)} = K_8 + \log\mu_{m_i(\lambda s)} \qquad (12)$$

The main components in river- and sea-sediments are light elements, such as silicon and aluminium; the heavy metals to be analyzed in these samples usually comprize less than 0.2—0.3% of the total (by weight). Therefore,

$$C_s \ll C_1+C_2+C_3+\cdots\cdots+C_n \text{ and } \mu_s \lesssim \mu_i$$
$$i = 1, 2, 3, \cdots\cdots\cdots, n$$

Then,

$$\mu_m = \mu_1C_1+\mu_2C_2+\mu_3C_3+\cdots\cdots+\mu_nC_n+\mu_sC_s$$
$$\fallingdotseq \mu_1C_1+\mu_2C_2+\mu_3C_3+\cdots\cdots\cdots+\mu_nC_n$$

If it should happen that the metal content in the standard model sample varies, the value of the mass-absorption coefficient for the measurable metal can be regarded as approximately constant in the range of lower concentrations.

The relation between I_{S1}/I_{Si} and $\mu_{m(\lambda s)}$ was examined on various matrices. Boric acid, sodium sulfate, anhydrous alminium sulfate, potassium sulfate, and sodium carbonate were used as the model matrices. The standard model matrix selected was anhydrous alminium sulfate, which had a mass-absorption coefficient close to that of the usual sediments. The samples containing 1000 μg/g copper in each matrix were used; the results are shown in Fig. 3.

The technique for the quantitative determination of elements in unknown samples is as follows: first, I_{S1}/I_{Si} is calculated from the value of $\mu_{mi(\lambda s)}$ (Fig. 3), which can be obtained by measuring the background intensity at 0.906 Å (Fig. 2); the peak intensity (I_{Si}) of an element in the sample is determined subsequently. Then, I_{Si} multiplied by I_{S1}/I_{Si} is transformed into I_{S1} for the matrix based on $\mu_{m_1(\lambda s)}$, and the concentration of the element with the transformed I_{S1} is determined from the calibration curve between C_s and I_{S1} on the standard model matrix.

Calibration Curves for Copper on Various Matrices. The calibration curves for copper in the concentration range

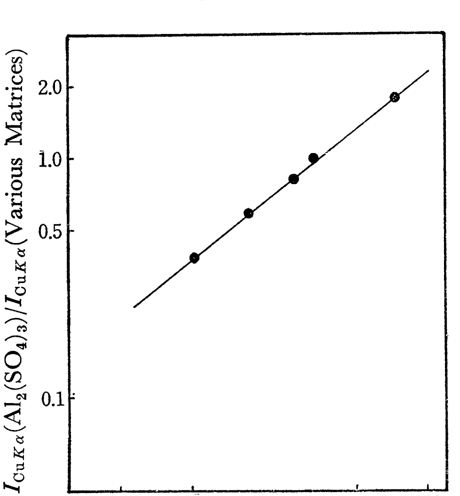

Fig. 3. Relationship between mass-absorption coefficient and intensity ratio of Cu$K\alpha$-line.

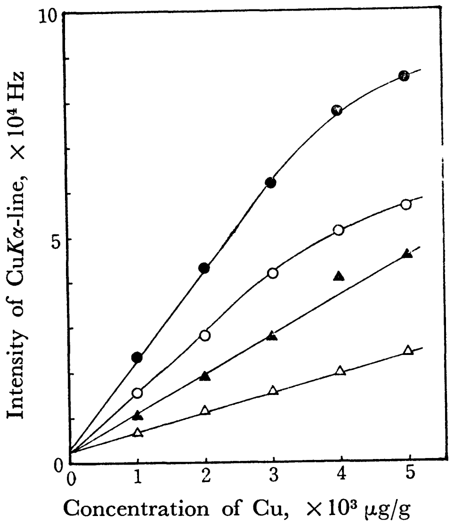

Fig. 4. Calibration curves for Cu on various matrices.
○: H_3BO_3, ●: Na_2CO_3, △: $Al_2(SO_4)_3$, ▲: K_2SO_4

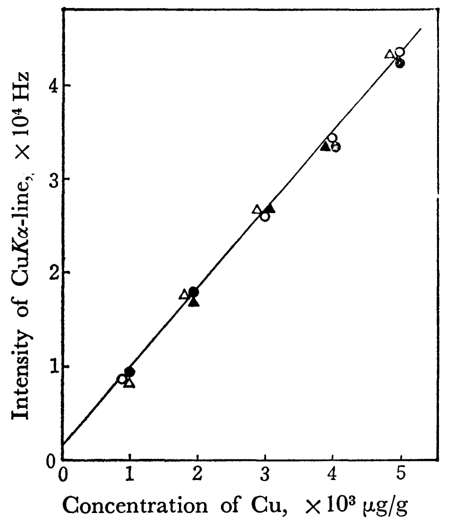

Fig. 5. Calibration curve for Cu converted into $Al_2(SO_4)_3$ matrix.
○: H_3BO_3, ●: Na_2CO_3, △: $Al_2(SO_4)_3$ ▲: K_2SO_4

of 500—5000 µg/g prepared in the various matrices described above are shown in Fig. 4. Each calibration curve for copper shows that the intensities become weak and become very different with an increase in the mass-absorption coefficient of the matrix for the *K*α-emission spectrum. Therefore, each calibration curve agreed very closely with that of the standard model matrix ($Al_2(SO_4)_3$ matrix) when this modification technique was used. The results are shown in Fig. 5.

Theoretically, this relation can be applied to any element except for an element in the vicinity of the absorption edges with the constituent element of the matrix. On the other hand, it is unnecessary to consider the excitation effect of measurable X-rays by the coexisting elements on the measurement of heavy metals in the sediments, because the elements forming the matrices of the sediments are mainly silicate and organic compounds.

The modification technique for the fluorescence intensities of other metals may be examined similarly.

Precision of Analytical Values. The results of the measurement of the copper and zinc contents by the present method and by the atomic-adsorption method on 10 specimens drawn as 1-lot sediment specimens are shown in Table 3.

The pretreatment of a sediment for the atomic-absorption method was carried out as follows: the metals to be analyzed, consisting of 10 g of portions the dried sediment, were extracted with 50 ml of 2 M-HNO_3 for 2 hr and then filtered. The extracted solution was heated and concentrated in a Kjeldahl flask, and the organic compounds in the sample were decomposed with 10 ml of 98% sulfuric acid and 10—20 ml

TABLE 3. MEASUREMENT OF Cu AND Zn CONTENT BY X-RAY FLUORESCENCE METHOD AND ATOMIC ABSORPTION METHOD ON 10 SPECIMENS DRAWN 1 LOT SEDIMENT

No.	X-Ray fluorescence method		Atomic absorption method	
	Cu (µg/g)	Zn (µg/g)	Cu (µg/g)	Zn (µg/g)
1	1530	4260	1520	4360
2	1540	4430	1510	4380
3	1520	4400	1490	4760
4	1590	4510	1550	4450
5	1570	4320	1420	4160
6	1540	4450	1500	4220
7	1550	4530	1510	4080
8	1580	4390	1450	4410
9	1570	4210	1510	4320
10	1540	4460	1560	4190
$\bar{x}$	1550	4400	1500	4330
c.v.%	4.52	7.11	9.87	13.03

TABLE 4. COMPARISON OF SEVERAL METALS CONTENT BY X-RAY FLUORESCENCE METHOD AND ATOMIC ABSORPTION METHOD

Sample No.	Cu		Zn		Cr		Sn	
	X[a] (µg/g)	A[b] (µg/g)	X[a] (µg/g)	A[b] (µg/g)	X[a] (µg/g)	A[b] (µg/g)	X[a] (µg/g)	A[b] (µg/g)
1	530	450	1250	1120	38	42	56	32
2	1940	1760	3620	3300	225	257	432	410
3	850	820	970	940	62	53	196	177
4	3750	3420	4820	4810	530	475	1260	1190
5	420	430	560	485	28	25	186	180
6	125	120	320	305	15	13.5	73	52

a) X-Ray fluorescence method. b) Atomic absorption method.

of 60% nitric acid. Then, the sample was analyzed by using the standard addition method.

The averages ($\bar{x}$) of the series of values obtained by the two analytical methods were approximately similar, but the coefficient of variation (*c.v.*) by the atomic-absorption method was larger than that by the X-ray fluorescence method.

Analysis of Several Metals in Sediments. The analytical values of copper, zinc, chromium, and tin in sediments obtained by the X-ray fluorescence method and the atomic-absorption method were compared. The results are listed in Table 4.

The standard addition technique was used for the atomic-absorption analysis. The values obtained by the two analytical methods agreed approximately.

The time required from pretreatment to the measurement of the sediments is shortened to about 30 min per sample, while 3 hr is needed for the atomic-absorption method. The present method is thus suitable for the rapid analysis of a number of samples, and good results are obtained for the concentration of each element in the range of 50—5000 μg/g.

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