STRATEGY OF FUSION BEAD CORRECTION IN XRF ANALYSIS OF POWDERS

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ABSTRACT

An empirical calibration method for fused bead analysis by XRF spectrometry with advanced corrections has been established. These calibrations include matrix effects, weighing inaccuracies, loss on ignition (LOI), gain on ignition (GOI), decomposition of oxidizing agent and evaporation of flux. The corrections for these common sources of error in the fusion method are incorporated into the basic calibration equation using actual weights for the sample, oxidizing agent, flux and fused bead. There are two correction models, a flux weight model using sample and flux weights and a bead weight model using sample and fused bead weights. The latter model is advantageous in correcting for flux evaporation when required.   The fusion bead corrections are applied in the analysis of iron ore and copper concentrates to demonstrate how the various source of error are successfully corrected in a universal fashion using the advanced method.

INTRODUCTION

The fusion bead method is an effective sample preparation technique for accurate analysis of a wide variety of powder samples by XRF spectrometry such as ores, rocks and refractory materials since it eliminates heterogeneity effects associated with grain size and mineralogical composition. In order to obtain highly accurate results, it is necessary to provide a constant flux-to-sample ratio (flux ratio) in each preparation of a given sample type.   Even if weighing is performed precisely, variation in flux ratio may occur owing to loss on ignition (LOI) or gain on ignition (GOI) of the sample, evaporation of the flux or decomposition of oxidizing agents during fusion.   These influences introduce analytical errors in the fused bead method by altering the flux ratio and x-ray absorption properties of the matrix.

Prior attempts to correct these sources of variation based on flux weight and sample weight and to correct for LOI/GOI were applied in the calibration equation for ore analysis via the fusion method (ISO9516-1: 2003(E)), but the application of these corrections is limited and inflexible. We have established a unique, easy-to-use, universal fusion bead correction method for the empirical calibration method with matrix correction for fusion bead analysis.   The advanced correction equation has been derived from a theoretical intensity equation based on the principle of X-ray absorption characteristics.   The equation consists of alpha coefficients computed by a fundamental parameter (FP) method.   The software computing alpha coefficients is capable of

calculating the coefficients for weight ratios of flux : sample, bead : sample and oxidizing agent : sample, as well as matrix correction coefficients to account for the influence of coexisting elements in fused bead samples.   It is also possible to calculate coefficients for the composition of a fused bead when the weight after fusion exceeds 100% of the starting weight owing to GOI from oxidation of elements in reduced states during fusion.   Thus, the correction method can be used to correct LOI/GOI, flux evaporation and variations in flux ratio due to inaccuracies in weighing the sample and fusion reagents.   We have demonstrated that the method accurately corrects for such effects in the analysis of iron ore and copper concentrate using the fusion method.

THEORY

Figure 1 shows changes of component weights during fusion, which can cause analytical errors. In the model in Figure 1, weight change of oxidizing agent is also considered.   For example, when sodium nitrate is added as an oxidizing agent, sodium nitrate (X) breaks down during fusion and sodium oxide (X') is left in bead while nitrogen oxide is evaporated.   X' can be obtained by simple calculation from X because the decomposition reaction of oxidizing agent during fusion is known.

The bead weight is expressed by Equation (1).

$$B = F + S + X - L \qquad\qquad (1)$$

L represents the total of LOI and GOI.   When the GOI of sample during fusion is larger than the LOI of sample during fusion, L is negative value.   For simplicity, decomposed oxidizing agent

$$B = F + S + X - (l_S - g_S + l_F + l_X)$$
$$\Downarrow$$
$$B = F + S + X' - L$$
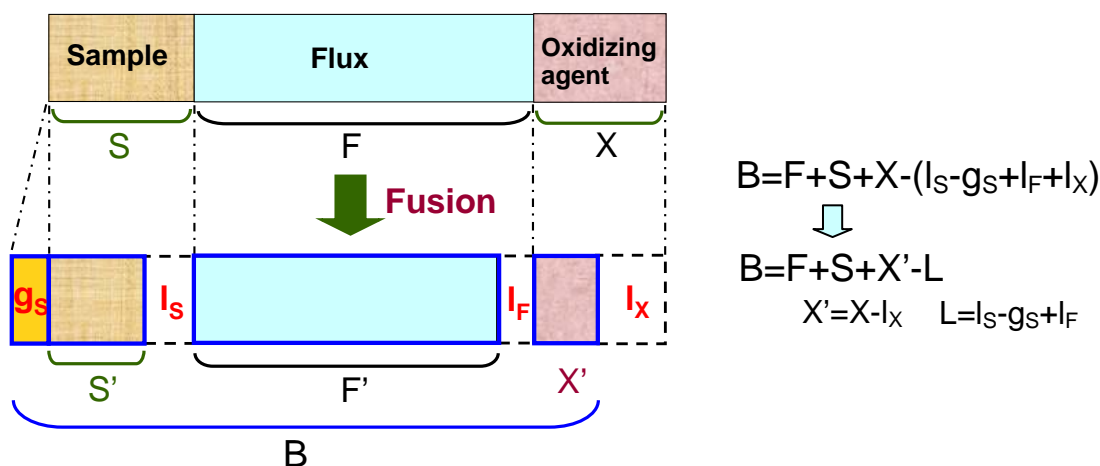$$X' = X - l_X \qquad L = l_S - g_S + l_F$$

Figure 1.   Weight changes in fusion.
S: sample, B: bead, F: flux, X: oxidizing agent, S': sample left in bead, F': flux in bead, X': decomposed oxidizing agent in bead, g_S: GOI of sample, l_S: LOI of sample, l_F: evaporation of flux, l_X: evaporated component in oxidizing agent.

X' is expressed as X. Henceforth, in this paper, X represents decomposed oxidizing agent left in bead. The weight of decomposed oxidizing agent is calculated from the original weight before fusion described above.

In addition to those changes during fusion, variation of weights of sample and reagents, which causes variation of flux ratio to standard ratio, has to be included in correction factors.

Simplified X-ray intensity equation

Fluorescent X-ray intensity of element i can be described using weight fraction in bead by the following simplified equation.

$$I_i = \frac{k_i \times W_i}{\mu_1 W_1 + \cdots\cdots + \mu_n W_n + \mu_F W_F + \mu_X W_X} \tag{2}$$

I_i	: X-ray intensity of element line of analyte i
$W_1 \ldots W_n$	: weight fraction of each component in fused bead
W_F	: weight fraction of flux in fused bead
W_X	: weight fraction of a component of oxidizing agent left in fused after fusion
$\mu_1 \ldots \mu_n$	: absorption coefficient of each component for element line
μ_F	: absorption coefficient of flux for element line
μ_X	: absorption coefficient of the component of oxidizing agent left in fused bead
k_i	: constant

The weight fractions W_j, W_F and W_X in bead are described using concentrations in sample (C_i) and sample, flux and oxidizing (decomposed) agent weights as shown in Equation (3), (4) and (5), respectively.

$$W_i = \frac{S \times C_i}{B} = \frac{S \times C_i}{S + F + X - L} \tag{3}$$

$$W_F = \frac{F}{B} = \frac{F}{S + F + X - L} \tag{4}$$

$$W_X = \frac{X}{B} = \frac{X}{S + F + X - L} \tag{5}$$

Then, Equation (2) can be rearranged substituting (3), (4) and (5) as follows:

$$I_i = \frac{k_i \times C_i}{\mu_1 C_1 + \cdots\cdots + \mu_n C_n + \mu_F \dfrac{F}{S} + \mu_X \dfrac{X}{S}} \tag{6}$$

When flux evaporation can be ignored, flux weight in fused bead F equals to flux weight at weighing F_0 and then Equation (6) is named "flux weight model". The term X/S is oxidizing agent ratio and F/S is flux ratio in weight.

There is a case where flux evaporation can not be ignored during fusion. In this case, flux weight left in bead F' is unknown (F $\neq$ F') and then F in bead is described by Equation (7).

$$F = B - S - X + L \tag{7}$$

Then, Equation (6) is rearranged substituting Equation (7) as follows:

$$I_i = \frac{k_i \times C_i}{\mu_1 C_1 + \cdots\cdots + \mu_n C_n + \mu_F C_L + \mu_F\left(\dfrac{B}{S} - 1\right) + \left(\mu_X - \mu_F\right)\dfrac{X}{S}} \tag{8}$$

Equation (8) is "bead weight model". In this model, LOI is included in the equation with the absorption coefficient of the flux and the flux ratio is described as B/S-1.

Derivation of calibration equation with alpha coefficients –flux weight model

The Equation (6) can be rearranged into Equation (9) as shown below. The component of LOI is added to the equation so as that total concentration of components becomes 100%. The concentration and absorption coefficient of LOI are C_0 and μ_0, respectively. Actually, LOI is not contained in fused beads, then μ_0 is zero.

$$C_i = b_i I_i\left(\mu_0 C_0 + \mu_1 C_1 + \cdots + \mu_n C_n + \mu_F \frac{F}{S} + \mu_X \frac{X}{S}\right) \tag{9}$$

where b_i is constant and $\displaystyle\sum_{j=0}^{n} C_j = 1.0$.

As flux ratio F/S and oxidizing agent ratio X/S can be described using standard ratio $\overline{R}$ and difference from standard ratio ΔR , Equation (9) is rearranged into Equation (10).

$$C_i = b_i I_i\left(\mu_0 C_0 + \mu_1 C_1 + \cdots + \mu_n C_n + \mu_F \overline{R}_F + \mu_F \Delta R_F + \mu_X \overline{R}_X + \mu_X \Delta R_X\right) \tag{10}$$

As the standard ratio $\overline{R}$ is fixed, $\mu_F \overline{R}_F$ and $\mu_X \overline{R}_X$ are constant.

By eliminating one component from the equation above as a balance component, Equation (10) can be rearranged into Equation (11).

$$C_i = b_i' I_i\left(1 + \sum^{j \neq b} \alpha_j C_j + \alpha_F \Delta R_F + \alpha_X \Delta R_X\right) \tag{11}$$

where, b represents balanced component and $b' = b(\mu_F \overline{R}_F + \mu_X \overline{R}_X)$.

Then, alphas described above are expressed as $\alpha_j = \dfrac{\mu_j}{\mu_F \overline{R}_F + \mu_X \overline{R}_X}$, $\alpha_F = \dfrac{\mu_F}{\mu_F \overline{R}_F + \mu_X \overline{R}_X}$

and $\alpha_X = \dfrac{\mu_X}{\mu_F \overline{R}_F + \mu_X \overline{R}_X}$, respectively.

Derivation of calibration equation with alpha coefficients –bead weight model

This model is for the case where flux evaporation can not be ignored.

Final weight of flux in fused bead F' is unknown (F'≠F). Flux ratio F'/S can be expressed using fused bead weight and sample weight as follows.

$$\frac{F'}{S} = \left(\frac{B}{S} - 1\right) - \frac{X}{S} + \frac{L}{S} = \left(\frac{B}{S} - 1\right) - \frac{X}{S} + C_0 \tag{12}$$

Equation (9) can be rearranged as shown below

$$C_i = b_i I_i \left[\mu_0 C_0 + \mu_1 C_1 + \cdots + \mu_n C_n + \mu_F \left(\frac{B}{S} - 1\right) + (\mu_X - \mu_F)\frac{X}{S} \right] \tag{13}$$

where, $\mu_0 = \mu_F$

Then, Equation (9) can be rearranged into Equation (14) as done in the flux weight model.

$$C_i = b_i'' I_i \left(1 + \sum^{j \neq b} \alpha_j C_j + \alpha_F \Delta R_F + \alpha_X \Delta R_X \right) \tag{14}$$

where, $b_i'' = b(\mu_F + \mu_F \overline{R}_F + (\mu_X - \mu_F)\overline{R}_X)$

The alphas denoted above are expressed as $\alpha_j = \dfrac{\mu_j - \mu_F}{\mu_F + \mu_F \overline{R}_F + (\mu_X - \mu_F)\overline{R}_X}$,

$\alpha_F = \dfrac{\mu_F}{\mu_F + \mu_F \overline{R}_F + (\mu_X - \mu_F)\overline{R}_X}$ and $\alpha_X = \dfrac{\mu_X - \mu_F}{\mu_F + \mu_F \overline{R}_F + (\mu_X - \mu_F)\overline{R}_X}$, respectively.

The alphas described for both models above are summarized in Table 1. In the case that oxidizing agents are considered, the alphas for components in samples, flux and oxidizing agents in both models can be approximately expressed by absorption coefficients and standard flux ratio and standard oxidizing agent ratio. Actual alphas to be used for calibration are obtained by computing with the FP method using a typical sample composition.

Table 1 includes the alpha equations for the case that oxidizing agents are not considered. In this case, the alpha for flux ratio is not dependent on any absorption coefficient and obtained simply by the standard flux ratio (Kataoka *et al.,* 1992).

Table 1. Alphas expressed by absorption coefficient

Model	Oxidizing agent is considered			Oxidizing agent is not considered	
	Correcting component	Flux ratio	Oxidizing agent ratio	Correcting component	Flux ratio
Flux weight (F/S)	$\dfrac{\mu_j}{\mu_F\overline{R}_F+\mu_X\overline{R}_X}$	$\dfrac{\mu_F}{\mu_F\overline{R}_F+\mu_X\overline{R}_X}$	$\dfrac{\mu_X}{\mu_F\overline{R}_F+\mu_X\overline{R}_X}$	$\dfrac{\mu_j}{\mu_F\overline{R}_F}$	$\dfrac{1}{\overline{R}_F}$
Bead weight (B/S-1)	$\dfrac{\mu_j-\mu_F}{\mu_F+\mu_F\overline{R}_F+(\mu_X-\mu_F)\overline{R}_X}$	$\dfrac{\mu_F}{\mu_F+\mu_F\overline{R}_F+(\mu_X-\mu_F)\overline{R}_X}$	$\dfrac{\mu_X-\mu_F}{\mu_F+\mu_F\overline{R}_F+(\mu_X-\mu_F)\overline{R}_X}$	$\dfrac{\mu_j-\mu_F}{\mu_F(\overline{R}_F+1)}$	$\dfrac{1}{\overline{R}_F+1}$

Calibration equation in practice and correction for weighing variation

The calibration equation can be generalized with flux ratio and oxidizing agent ratio using actual weight values.

$$C_i = (bI_i + c)\left(1 + \sum^{j\neq L}\alpha_j C_j + K + \alpha_F R_F + \alpha_X R_X\right) \tag{15}$$

where K is a constant denoted by $\alpha_F\overline{R}_F + \alpha_X\overline{R}_X$. $\overline{R}_F$ and $\overline{R}_X$ are denoted standard flux ratio and standard oxidizing ratio, respectively.

When flux evaporation can be ignored (flux weight model), the flux ratio R_F is expressed by F/S. On the other hand, in the case that flux evaporation can not be ignored (bead weight model), R_F is expressed by B/S-1. The oxidizing ratio is expressed by X/S for both models. Since LOI is eliminated in the equation by considering LOI as the balanced component, Equation (15) can be described by actually available weighted values. This correction principle also means that even though the flux ratio and/or oxidizing agent ratio in fused beads of unknown samples has large difference from target flux ratio and/or oxidizing agent ratio of a calibration, the difference can be corrected as well as weighing errors.

EXPERIMENTAL

Samples and sample preparations

Twenty one certified reference materials (CRMs) supplied from JSS, BAS, BCS, NBS, LKAB and CMSI were prepared for the experiments of iron ores. These CRMs are composed of iron ores and iron ore products, which are hematite ore, magnetite ore, iron sand, limonite, sinter, pellet and pure iron oxide.   Total iron content of the CRMs used in this experiments ranges from 24.7 to 71.1 mass%.

In a platinum crucible, 0.400 g of well-dried (2 hours at 105 °C) sample, 4.00 g of flux (lithium tetraborate) and 0.240 g of oxidizing agent (sodium nitrate) were weighed out. The flux ratio and oxidizing agent ratio for each fused bead were calculated by actual recorded weight so that precise weighing was not performed. The weighed sample and reagents were mixed well in a Pt crucible and fused at 1150 °C for 999 second by the high frequency (HF) type fusion machine of RIGAKU, in which fusion and casting are performed in the same crucible. As releasing agent, 50 µL of 50 % solution of LiI was added before fusion. Any pre-heating or calcination for sample before fusion was not performed.

For calibration of copper concentrates, fourteen certified reference materials of copper ores and concentrates were used. The procedure of making fused beads for copper ore and concentrate is as follows. The well-dried (2 hours at 105 °C) sample and flux (mixed flux: 35.3 % lithium tetraborate and 64.7 % lithium metaborate) were weighed out 0.2 g and 4.0g, respectively. The weighing was performed by recorded weight as well as iron ores. The sample and flux were mixed well in a Pt crucible and then 0.9 mL of 20 % solution of $LiNO_3$ (0.2 g as $LiNO_3$) with about 2 mL of pure water were added as oxidizing agent. The mixture was calcined in an electric furnace at 800 °C for 10 minutes for complete oxidization of S to SO_3. After cooling, 20 µL of 10 % solution of LiBr was added as releasing agent and then fused at 1050 °C for 420 second by the HF fusion machine.

Instruments

The measurements were performed on RIGAKU ZSX PrimusII sequential WDXRF spectrometer. The spectrometer is equipped with a Rh target end-window X-ray tube.

Measurement conditions were 50 kV and 50 mA of tube load.

The FP program calculating theoretical alpha coefficients is integrated in the operation software and is improved to calculate appropriate alphas for large GOI sample models in which the total sample concentration exceeds 100 % during fusion.

Calibration of iron ores

Eleven elements, Fe, Si, Al, P, Mg, S, Ca, K, Mn, V and Ba, were measured for iron ore calibration. The fusion bead correction method applied to the iron ore analysis is the flux weight model. Matrix effects were corrected by theoretical alpha coefficients calculated by the FP method.

Figure 2 is a calibration curve of total iron content in iron ore expressed as ferric oxide. The accuracy
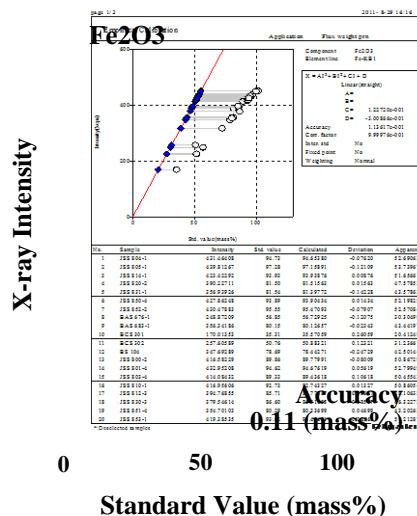

Figure 2. Calibration curve of total iron content in iron ores obtained by 29 CRMs.
Blue diamond: corrected point, open circle: uncorrected point.

of calibration is 0.11 mass%.   The accuracy is 0.08 mass% as total metal iron.

Total iron calibration shown in Figure 2 is obtained in accordance with the fused bead correction equation (19), in which the theoretical alphas are calculated with the LOI as balanced component. When the LOI is not considered in the correction, the accuracy of calibration for total Fe2O3 is degraded to 0.73 mass% even though the matrix correction and correction for weighing variation are applied.

Calibration of copper ores and concentrates

The correction method applied to the fused bead analysis of copper ores and concentrates is the bead weight model using the bead weight after fusion.   Sixteen elements, Pb, As, Zn, Cu, Co, Fe, Mn, Ti, Ca, K, S, P, Si, Al, Mg and Na, were measured for copper concentrate.   The theoretical alpha coefficients to correct matrix effects were obtained by the FP method as well as iron ore calibrations.

Figure 3 shows calibration curves of representative components in copper ores and concentrates. All components in calibration are expressed as oxide. The concentration range of certified values and obtained accuracy in metal form for representative components are shown in Table 2.
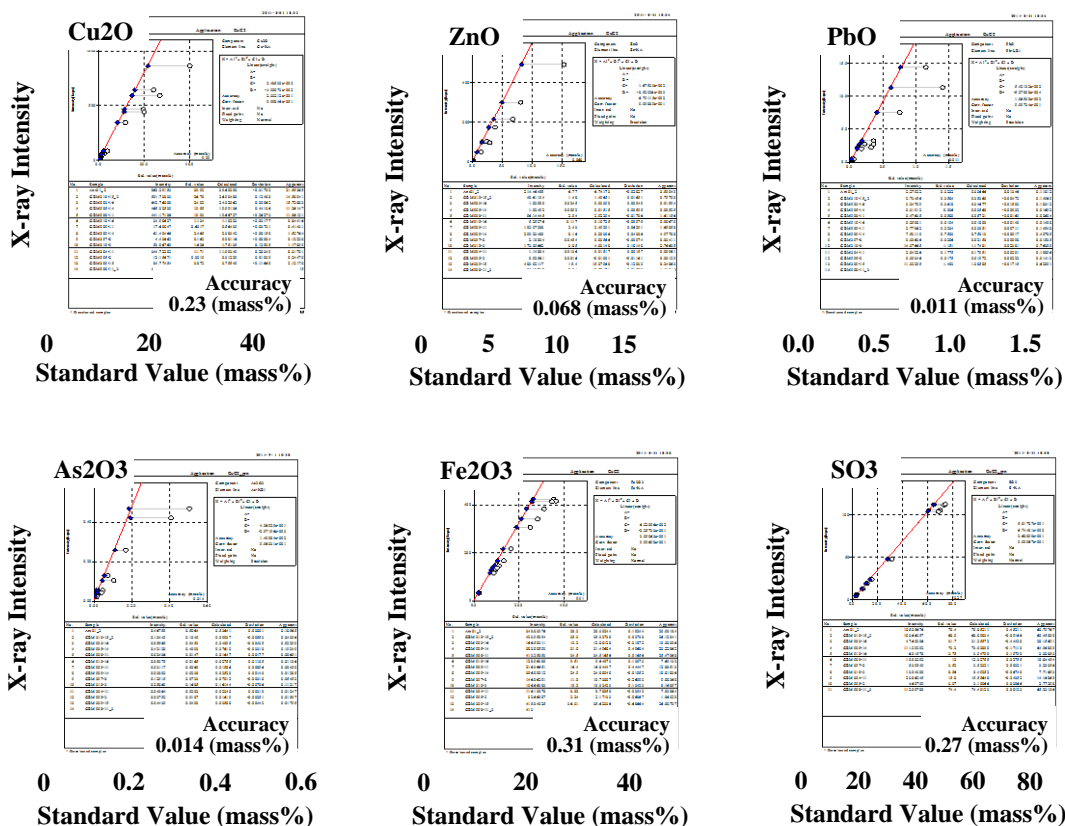

Figure 3.   Representative calibration curves for copper ore and concentrates.
Blue diamond: corrected point, open circle: uncorrected point.

The accuracy of sulfur calibration indicates the sulfur was successfully retained in beads during fusion and sulfur evaporation was minimized.

Table 2.   Concentration range and accuracy of calibration for representative components of copper ore and concentrates

	Cu (mass%)	Zn (mass%)	Pb (mass%)	As (mass%)	Fe (mass%)	S (mass%)
Concentration range	0.144 – 35.4	0.001 – 12.4	0.016 – 0.336	0.005 – 0.380	1.57 – 25.4	1.23 – 29.8
Accuracy of calibration	0.20	0.055	0.010	0.011	0.22	0.11

Accuracy is converted to metal form from the value in calibration curve.

CORRECTION FOR LARGE GOI WITH WEIGHING VARIATION

Copper concentrate is dominantly composed of sulfide minerals consistent of copper, iron and sulfur.   Therefore, large GOI occurs by oxidizing those elements during the fusion.   The amount of gain in weight for copper, iron and sulfur by oxidization is 113 %, 143 % and 250%, respectively.

One copper concentrate bead with different weights of sample, flux and oxidizing agent to the standard weight (Table 3) was analyzed as example of bead correction for variation of weighing values with large GOI.   Table 4 shows the large gain on ignition, weighing variation for samples, flux and oxidizing agent are successfully corrected.

Table 3.   Sample weight for a test of correction for GOI and weighing variation in copper concentrate

	Sample (g)	Flux (g)	LiNO3 (g)	Bead (g)
Reference	0.2	4.0	0.2	4.2433
Test bead	0.2163	4.1298	0.4	4.5343

Table 4.   Results of correction for GOI and weighing variation

	Cu (mass%)	Zn (mass%)	Pb (mass%)	As (mass%)	Fe (mass%)	S (mass%)
Certified value	23.79	1.19	0.333	0.080	24.7	27.6
Analyzed value	23.89	1.21	0.337	0.079	24.8	28.2

In the copper concentrate analysis, the fusion bead correction using the bead weight model, which can correct for the flux evaporation, was applied. When the flux evaporation is small enough to be ignored, results of both models are essentially identical.   In this study, accuracy of calibration obtained by the flux weight model is equivalent to the accuracy of the bead weight model, so that effect of the flux evaporation is considered negligible or restricted in this experiment.

CONCLUSION

The advanced fusion bead correction method is established as universal correction method for LOI/GOI, weighing variation and flux evaporation in the fusion bead method. The correction method includes correction for oxidizing agent weight variation.
The two correction models, the flux weight model and the bead weight model, applied in the fusion bead correction method were verified by X-ray intensity equation.   The alpha coefficients in the correction models can be roughly estimated using absorption coefficients.
The method can be applied to variety of ores and concentrates such as sulfide samples of concentrates, containing high GOI content, and also to samples with large LOI as well. It indicates that the correction method for fusion bead analysis has high versatility to analyze various powder samples as well as ores.

REFERENCES

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