

# X-ray fluorescence analysis by fusion bead method for ores and rocks

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## 1. Introduction

The fusion bead method is an effective sample preparation technique for accurate XRF analysis results of ores, rocks and refractory materials since the technique eliminates heterogeneity due to grain size and mineralogical effect.

This report describes various data processing methods to obtain more accurate analysis results showing practical examples of analysis obtained by using a wavelength dispersive X-ray fluorescence spectrometer (WDXRF), ZSX Primus II, and its data processing system.

## 2. What is fusion beads method?

Table 1 shows the application fields of XRF analysis and of fusion beads method (underlined). Wide application range for oxide powder can be seen.

The fusion bead method is an advanced analysis

**Table 1.** Application fields of XRF analysis and fusion beads method.

Iron and Steel	Non-ferrous	Environment
Special steel	Aluminum can	Drain, River water
Coated steel sheet	Shape-memory alloy	Soil pollution
Ferro-alloy	Copper alloy	Air pollution
Cast iron	Precious metal	Industrial waste
<u>Iron ore</u>	Nickel alloy	Mud polluted
Plating solution	Soldering paste	Coal ashes
Mining	Oil, Coal	Ceramics
<u>Ore</u>	Grease	Silicon nitride
<u>Rock</u>	Lubricant oil	<u>Alumina</u>
<u>Volcanic ashes</u>	Cutting oil	<u>Glass</u>
	Kerosene, Heavy oil	<u>Firebricks</u>
	Coal	Glaze
		<u>Kaolin</u>
Electro-Magnetic material	Cement	Chemical Ind.
LSI	<u>Cement</u>	Catalyst
Memory	<u>Slug</u>	Polymer
Opt-magnetic disk	<u>Recycle source</u>	Medicine,
Magnetic head	<u>Eorcement</u>	Cosmetic
LCD · CRT		Fertilizer
Magnetic materials		Paints
		Oil & fat, Detergent

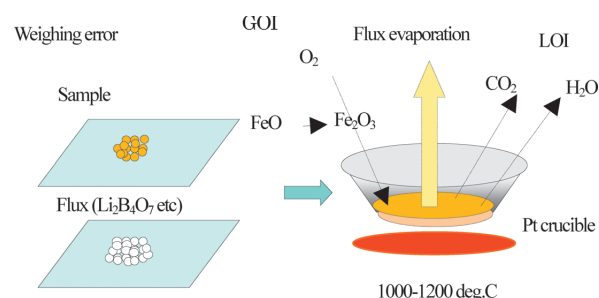
method having advantages shown below and registered as an international standard analysis method for refractory and iron ore.

- ISO12677: Chemical analysis of refractory products by XRF—fused cast bead method
  - ISO9516: Iron ores—Determination of various elements by X-ray fluorescence spectrometry
- ◆ Features
- Eliminate the mineralogical effect and grain size effect
  - Reduce coexisting component effect by dilution effect
  - Possible to make standard samples from synthetic oxides.

## 3. Error in fusion bead method

Dominant causes of various analytical errors in fusion bead method<sup>(1),(2)</sup> are shown below, and also in the image shown in Fig. 1.

- ◆ Weighing error (Dilution factor error)
- Sample powder and flux must be weighed accurately down to 0.1 mg unit for designated amount, but it is time consuming so that magnitude of the error depends on the operators skill.
- ◆ Loss on ignition (LOI), Gain on ignition (GOI)
- If there is water of crystallization or a carbonate present in the sample, volatilization of these compounds leads to an analytical error due to the loss of these compounds in the high temperature of the fusion melt.
- For example, in case of iron ore, the oxidization reaction of Fe<sup>2+</sup> to Fe<sup>3+</sup> when the melt occurs causes weight gain (GOI), and it becomes a source of error.
- ◆ Flux evaporation (Dilution factor error)
- Using low melting point flux or fusions that take place over a long period of time makes flux evaporate; this becomes a source of dilution error.



**Fig. 1.** Image of analytical errors of fused bead method.

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**4. Study of correction against Dilution factor, Loss on ignition (LOI) and Gain on ignition (GOI)**

Image of 4 models of Dilution factor, LOI and GOI<sup>(1),(2)</sup> are shown in Fig. 2.

In the above figures, the left side is the sample model including LOI and GOI, and the right side expresses the effect these factors have on the weight of the sample-flux mixture.

Figure 2 (a) is the case of no LOI and no GOI; the dilution factor can be calculated with the weights of sample and flux.

Figure 2 (b) is the case that an LOI component is included. As the LOI does not exist in the glass beads any more due to evaporation, concentration of components in a sample becomes higher from the viewpoint of concentration in the fused bead.

Figure 2 (c) is the case that GOI takes place. Concentration of component in a fused bead sample becomes lower.

Figure 2 (d) is the case that both LOI and GOI take place. Concentration of component in a sample may be higher or lower depending on the respective amount of LOI and GOI.

As mentioned above, concentration of components in the fused bead sample can vary due to the LOI or GOI, and it has an effect on the analysis result.

This phenomenon is treated by assuming total concentration in a sample is 100%, the LOI is considered as a positive concentration, and GOI as LOI having a negative concentration.

Since the LOI and GOI make concentration in a fused bead sample vary, matrix correction using the net effect of the concentration of LOI or concentration of the

negative GOI can be made.

**5. General calibration equation and dilution correction**

General calibration equation incorporating correction for LOI, GOI and dilution factor including a term of co-existing component correction is shown in the equation (1) below.

$$W_i = (aI_i^2 + bI_i + c) + (1 + \sum \alpha_j W_j + \alpha_{LOI} W_{LOI} + \alpha_F R_F + K_F) \quad (1)$$

Where

- $\alpha_j$ : Inter element correction factor
- $\alpha_{LOI}$ : LOI (GOI) correction factor
- $\alpha_F$ : Correction coefficient for dilution factor
- $R_F$ : Dilution factor (flux weight/Sample weight)
- $K_F$ : Constant

Term of  $\alpha_F R_F + K_F$  is a correction term of flux dilution factor. All co-existing component correction coefficients  $\alpha_j$ ,  $\alpha_{LOI}$ ,  $\alpha_F$  can be calculated using the fundamental parameter method (FP method). And, when co-existing component correction factors are calculated by FP method, in case that the LOI (GOI) is considered as a base component (except for correction component) in a correction model, the term of  $\alpha_{LOI} W_{LOI}$  is not used and the LOI (GOI) correction can be made without concentration information of the LOI (GOI).

The equation (2) below removes the term  $\alpha_{LOI} W_{LOI}$  from the equation (1).

$$W_i = (bI_i + c)(1 + \sum \alpha_j W_j + \alpha_F R_F + K_F) \quad (2)$$

In above (2),  $\alpha_F R_F + K_F$  is the term of dilution factor correction and it can be neglected when dilution factor is constant. This term of dilution factor is explained hereunder.

The equation (3) below is a calibration equation including dilution factor correction.

$$W_i = (bI_i + c)(1 + \sum \alpha_j W_j + \alpha_F \Delta R_F) \quad (3)$$

Regarding  $\bar{R}_F$  as a standard dilution factor and as the difference from standard dilution factor, the equation (4) can be shown.

$$\Delta R_F = R_F - \bar{R}_F \quad (4)$$

Substitution (4) for (3) makes equation (5) below.

$$W_i = (bI_i + c)(1 + \sum \alpha_j W_j + \alpha_F R_F - \alpha_F \bar{R}_F) \quad (5)$$

By defining equation (6) below, the equation (2) is obtained.

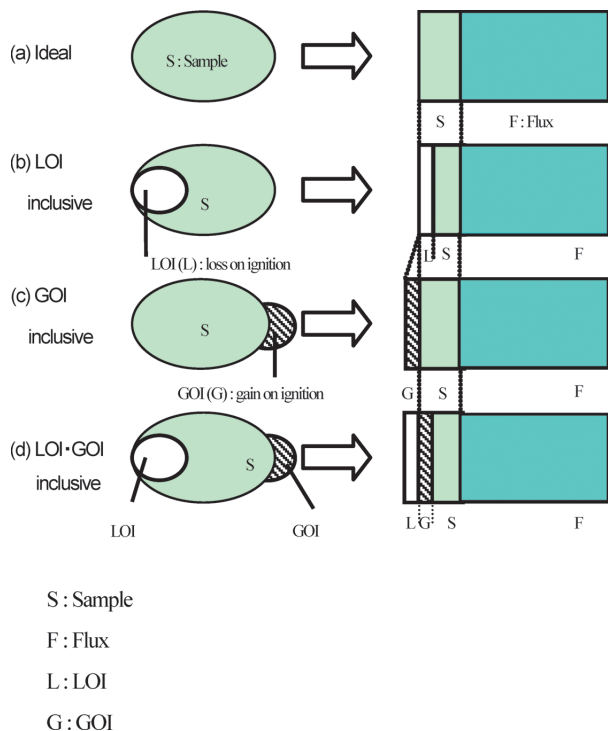


Fig. 2. Models of Dilution factor, LOI and GOI.

$$K_F = -\alpha_F - \bar{R}_F \quad (6)$$

It is understood that, even for fused beads with different dilution factors, the correction of difference of dilution factor can be made by using the equation (2).

### 5. Inter element correction model (Matrix correction model)

As an inter element correction model for iron and steel analysis, JIS method is popular in Japan. But there are 3 inter element influence coefficient correction models as shown below including JIS method.

#### ◆ Lachance-Traill model

This is a model considering all other components except for analysis component as correction components. Calibration equation is linear model. This model can not be used when the concentration of the LOI (including GOI) is unknown. If it is known, it can be applied as it is treated as one of the concentrations.

#### ◆ de Jongh model

This is a model handling all components including analysis component except for base component (as balance) as correction components. LOI (including GOI) correction can be made even if LOI (including GOI) is not known. Calibration equation is a linear model.

#### ◆ JIS model

This is a model designating all components except for analysis component and base component as correction components. When LOI (including GOI) is set as the except analysis component (base component), LOI (including GOI) correction can be made even if LOI (including GOI) is not known. Calibration equation used is a quadratic or linear model.

When the concentration of LOI (including GOI) is not known, de Jongh model or JIS model can be applied.

### 6. Comparison between JIS and de Jongh models

When LOI (including GOI) is not known, both de Jongh and JIS model can be used. So, coexisting components correction factors (matrix correction coefficients) are calculated by FP method and compared. Analysis object is rock, and fusion beads are made with  $Li_2B_4O_7$  flux at a dilution factor of 5:1 (flux: sample). Si-K $\alpha$  and Ca-K $\alpha$  as representatives are used and calculated. Results are shown in Table 2 and Table 3.

It can be said that the factors for JIS and de Jongh model compare very closely to one another. The only difference is that the de Jongh model has a self absorption factor, by including the analysis component, in the correction term. In JIS model the combination of analysis component and base component is a snap-shot sample of the basic calibration line, therefore, the equation is linear in the case of a narrow concentration range, but quadratic if employed over a wide range. On the other hand, as the de Jongh model regresses nearly linearly due to self absorption correction including the analysis component in the correction term, the equation can be approximated linear over a wide range of concentrations.

Table 2. Comparison of SiO<sub>2</sub> coexisting component correction factors.

(Spectrum: Si-K $\alpha$ )

Model	JIS	de Jongh
Anal. Compo.	SiO <sub>2</sub>	
Spectrum Cor. Compo.	Si-K $\alpha$	
Na <sub>2</sub> O	0.005173	0.00515
MgO	0.00583	0.00581
Al <sub>2</sub> O <sub>3</sub>	0.00593	0.00592
SiO <sub>2</sub>		0.00278
P <sub>2</sub> O <sub>5</sub>	0.00275	0.00275
K <sub>2</sub> O	0.00268	0.00267
CaO	0.00296	0.00295
TiO <sub>2</sub>	0.00336	0.00335
MnO	0.00478	0.00477
Fe <sub>2</sub> O <sub>3</sub>	0.00513	0.00511

Base component is LOI for both models.

Table 3. Comparison of CaO coexisting component correction factors.

(Spectrum: Ca-K $\alpha$ )

Model	JIS	de Jongh
Anal. Compo.	CaO	
Spectrum Cor. Compo.	Ca-K $\alpha$	
Na <sub>2</sub> O	0.00569	0.00565
MgO	0.00656	0.00651
Al <sub>2</sub> O <sub>3</sub>	0.00693	0.00687
SiO <sub>2</sub>	0.00775	0.00770
P <sub>2</sub> O <sub>5</sub>	0.00851	0.00845
K <sub>2</sub> O	0.0249	0.0247
CaO	-	0.00724
TiO <sub>2</sub>	0.00381	0.00378
MnO	0.00414	0.00411
Fe <sub>2</sub> O <sub>3</sub>	0.00449	0.00446

Base component is LOI for both models.

Calibration lines of SiO<sub>2</sub> and CaO with the correction factors in Table 2 and 3 are shown in Fig. 3 and 4. There is no big difference between both models. The calibration lines were approximated with quadratic curve for JIS model and linear for de Jongh model.

### 7. Comparison of coexisting component correction factors (Matrix correction coefficients) for the analysis of various refractory by fusion beads method

Basically, matrix correction factors are calculated for each kind of materials and calibration lines are made for the same. JIS R 2216 (XRF analysis of refractory)

designates coexisting component correction factors for each kind of materials.

Meanwhile, making calibration lines for each kind of materials requires lots of preparation of calibration lines and analysis operation is troublesome, while making a universal calibration line covering many kinds of different materials makes a wide range of analyses with less calibration lines possible.

It is possible to apply a universal calibration line to the analyses of various kinds of materials if the differences of coexisting components correction factors among them are small. Table 4 is a list of concentration

ranges of major components of various refractory and dilution factors.

For the table, major component in each material is different and the concentration range of each component is very wide. And dilution factor of chrome-magnesia is different from others. (Dilution factor correction is discussed later in section 8.). Then, as an example, comparison of coexisting component correction factors among clay ( $\text{SiO}_2\text{-Al}_2\text{O}_3$  group), high alumina ( $\text{Al}_2\text{O}_3$  group) and alumina-zircon-silica ( $\text{SiO}_2\text{-ZrO}_2\text{-Al}_2\text{O}_3$  group) was calculated. Coexisting component correction factors for Si-K $\alpha$  and Fe-K $\alpha$  are shown in Table 5 and 6, respectively. Calculations of correction factors are made using the Lachance-Trail model.

It is obvious that the correction factors for both analysis lines are approximately the same for these different materials. This is due to the sample dilution by flux resulting that the sample matrices in fusion beads are similar in each material. It means that making calibration lines for each material is not necessary and analysis with single calibration line covering a wide range of materials. Then, the universal calibration lines of  $\text{SiO}_2$  and  $\text{Fe}_2\text{O}_3$  for various materials are shown in Fig. 5 and Fig. 6. Satisfactory calibration lines for various materials are obtained. Standard samples used for the study are shown in Table 7.

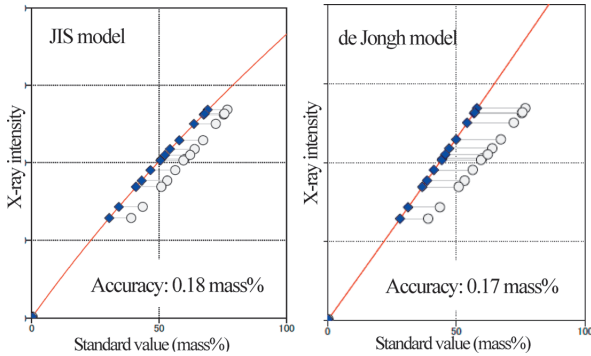


Fig. 3.  $\text{SiO}_2$  calibration lines applied JIS model and de Jongh model.

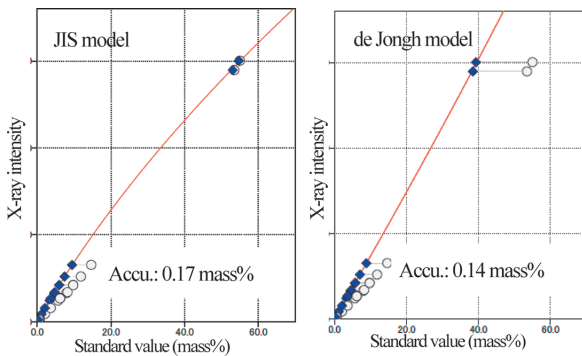


Fig. 4. CaO calibration lines applied JIS model and de Jongh model.

### 8. Application of dilution factor correction and coexisting component correction

Usually, sample is made at fixed dilution factor in fusion beads method. But the accurate weighing of sample and flux requires skill and time, and it is one of the sources of error at sample preparation stage. To overcome these problems, there is a method to make dilution factor correction using correction term of equation (1) in Section 5, which corrects a difference between dilution factor of each sample and standard factor using actual weights after designation of weighing allowance.

These dilution factor correction coefficients can be calculated along with the coexisting components

Table 4. List of concentration ranges of major components of various refractory and dilution factors.

Material	Major Component (mass%)						Dilution Factor (Flux / Sample)
	$\text{SiO}_2$	$\text{Al}_2\text{O}_3$	$\text{Fe}_2\text{O}_3$	MgO	$\text{Cr}_2\text{O}_3$	$\text{ZrO}_2$	
Clay	37~86	6~49	~5		~1	~1	10
Silica Stone	84~97	~10					10
High Alumina	~44	47~94					10
Magnesia				81~99			10
Chrome-Magnesia			~27	10~52	2~53		22.16
Zircon-Zirconia	~45					48~92	10
Alumina-Zirconia-Silica	~42	10~82				12~48	10
Alumina-Magnesia		10~93		3~79			10
All Materials	~97	~94	~27	~99	~53	~92	10~22.16

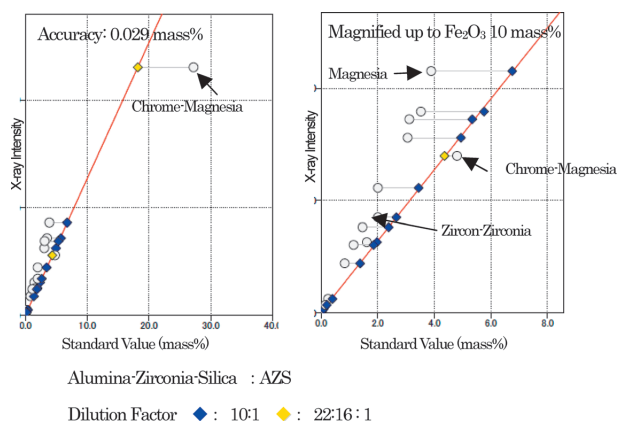
Flux:  $\text{Li}_2\text{B}_4\text{O}_7$  (Oxidizing agent  $\text{LiNO}_3$  was used for Chrome-Magnesia.)

**Table 5.** Comparison of coexisting components correction factors of clay (SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> group), High Alumina (Al<sub>2</sub>O<sub>3</sub> group) and Alumina-Zircon-Silica (SiO<sub>2</sub>-ZrO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> group) for analysis spectrum Si-K $\alpha$

Material Cor. Compo.	Clay	High Alumina	Alumina-Zircon-Silica
Al <sub>2</sub> O <sub>3</sub>	0.00138	0.00138	0.00137
Fe <sub>2</sub> O <sub>3</sub>	0.00102	0.00101	0.00102
TiO <sub>2</sub>	0.000244	0.000241	0.000243
MnO	0.000865	0.000862	
CaO	0.000691	0.000660	0.000681
MgO	0.00133	0.00133	0.00133
Na <sub>2</sub> O	0.00104	0.00104	0.00104
K <sub>2</sub> O	-0.000541	-0.000575	-0.000549
P <sub>2</sub> O <sub>5</sub>	-0.000188		
Cr <sub>2</sub> O <sub>3</sub>	0.000606		0.000607
ZrO <sub>2</sub>	0.000876		0.000868

**Table 6.** Comparison of coexisting components correction factors of clay (SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> group), High Alumina (Al<sub>2</sub>O<sub>3</sub> group) and Alumina-Zircon-Silica (SiO<sub>2</sub>-ZrO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> group) for analysis spectrum Fe-K $\alpha$

Material Cor. Compo.	Clay	High Alumina	Alumina-Zircon-Silica
SiO <sub>2</sub>	-0.00188	-0.00187	-0.00206
Al <sub>2</sub> O <sub>3</sub>	-0.00219	-0.00218	-0.00237
TiO <sub>2</sub>	0.00393	0.00395	0.00364
MnO	-0.000194	-0.000193	
CaO	0.00403	0.00404	0.00372
MgO	-0.00237	-0.00236	-0.00254
Na <sub>2</sub> O	-0.00262	-0.00261	-0.00279
K <sub>2</sub> O	0.00394	0.00396	0.00364
P <sub>2</sub> O <sub>5</sub>	-0.00165		
Cr <sub>2</sub> O <sub>3</sub>	0.00727		0.00691
ZrO <sub>2</sub>	0.00109		0.00130



**Fig. 6.** Fe<sub>2</sub>O<sub>3</sub> calibration lines.

**Table 7.** Standard samples for firebrick.

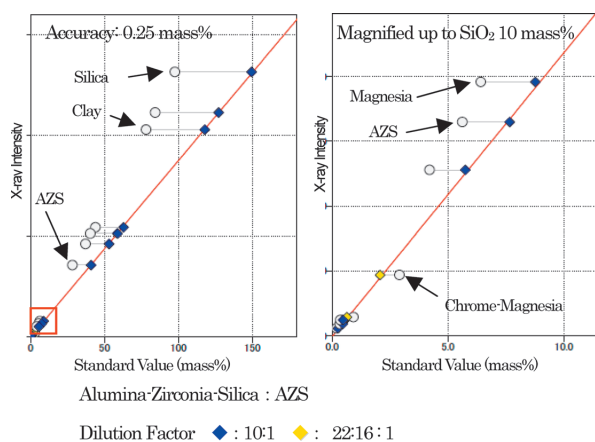
Material	Sample Name
Clay	JRRM 122
	JRRM 135
Silica Stone	JRRM 201
	JRRM 210
High Alumina	JRRM 301
	JRRM 310
Magnesia	JRRM 401
	JRRM 410
Chrome-Magnesia	JRRM 501
	JRRM 511
Zircon-Zirconia	JRRM 602
	JRRM 609
Alumina-Zirconia-Silica	JRRM701
	JRRM710
Alumina-Magnesia	JRRM801
	JRRM810

correction coefficients by the software. Example of application of the dilution factor correction is shown below.

Contents of samples used for this study are as follows.

- Sample: Rock
- Conditions for making fusion beads:  
Flux: Li<sub>2</sub>B<sub>4</sub>O<sub>7</sub>  
Dilution factor (Flux: Sample): 10 : 1 and 5 : 1
- Analysis component: SiO<sub>2</sub>
- Spectrum: Si-K $\alpha$
- Standard samples used:  
CCRMP: SY-2, SY-3  
GSJ: JA1, JA2, JA3, JB2, JB3, JG1A, JG2, JG3, JGb1, JR1, JR2, JLS1, JCP1

Figure 7 shows SiO<sub>2</sub> calibration line without correction. Big error due to difference of dilution factor is observed. Figure 8 is the line with dilution factor correction only. Dilution factor correction improves the error due to difference of dilution factor significantly. But error due to coexisting component matrix effect is still there. Figure 9 shows the calibration line after



**Fig. 5.** SiO<sub>2</sub> calibration lines.

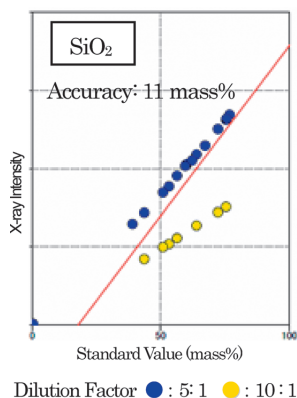


Fig. 7. Uncorrected calibration line.

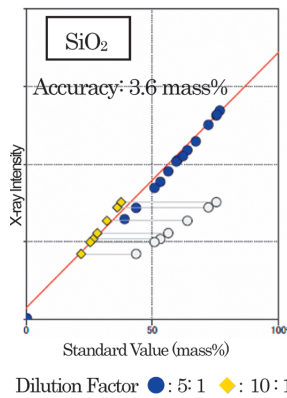


Fig. 8. Calibration line applied dilution factor correction only.

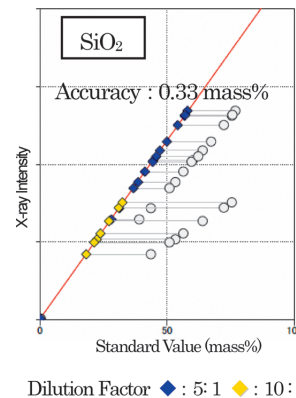


Fig. 9. Both dilution factor correction and coexisting component correction are applied.

applying the coexisting component correction as well. It can be said that application of both corrections makes correlation better and improves accuracy by one order of magnitude.

The above study was made with the case of a big difference of the dilution factor to show the effect of the dilution factor correction. From this result, it can be seen that an accurate analysis by means of making the dilution factor correction using actual weights of sample and flux when fusion beads are made is possible. Moreover, the correction can be made for the fusion beads with different dilution factors by group of the materials.

### 9. Application of LOI (including GOI) correction

When natural minerals containing crystal water and carbonate, etc. are used for fusion beads, they are volatile. (Corresponds to the model (b) of Fig. 2) In case of iron ore, FeO and Fe<sub>3</sub>O<sub>4</sub> is oxidized to Fe<sub>2</sub>O<sub>3</sub> the resulting GOI, and hydroxide (OH) volatiles (corresponds to the model (c)(d) of Fig. 2), then become sources of analysis error.

To verify the LOI correction, the fusion beads with dilution factor 10:1 made in the section 8, are set at a dilution ratio of 5:1 and the imaginary LOI at 50 mass%. The effect of LOI correction was verified with this imaginary model of SiO<sub>2</sub>.

Table 8 shows the coexisting component correction factors of analysis component SiO<sub>2</sub> for the cases of with and without LOI correction. The effect of LOI correction was discussed with these correction factors.

Figure 10 is the uncorrected calibration line, Figure 11 is the calibration line with coexisting component correction but without LOI correction, and Figure 12 is with both of them. In the case of with coexisting component correction but without LOI correction, accuracy of SiO<sub>2</sub> calibration line is 3.5 mass%, but it is improved up to 0.26 mass% using LOI correction. Thus it can be said that the accurate analysis is realized by employing coexisting component correction incorporated with the LOI correction.

Next, a study of fusion beads samples of which both

Table 8. Coexisting component correction factors without LOI correction and with it (Correction model: de Jongh).

Analysis Component Base Compo. Corr. Compo.	SiO <sub>2</sub>	
	Al <sub>2</sub> O <sub>3</sub>	LOI
Na <sub>2</sub> O	-0.000479	0.00515
MgO	-0.0000632	0.00581
Al <sub>2</sub> O <sub>3</sub>	-	0.00591
SiO <sub>2</sub>	-0.00197	0.00278
P <sub>2</sub> O <sub>5</sub>	-0.00199	0.00274
K <sub>2</sub> O	-0.00203	0.00267
CaO	-0.00187	0.00294
TiO <sub>2</sub>	-0.00161	0.00335
MnO	-0.000721	0.00476
Fe <sub>2</sub> O <sub>3</sub>	0.000503	0.00511

LOI and GOI take place at a same time using iron ore.

Contents of sample used for the study are shown below.

- Sample: Iron ore
- Dilution factor: 10:1
- Flux: Li<sub>2</sub>B<sub>4</sub>O<sub>7</sub>: 4 g, Sample: 0.4 g
- Oxidizing agent: NaNO<sub>3</sub>: 0.24 g
- Analysis component: Fe<sub>2</sub>O<sub>3</sub>
- Standard sample used:  
 JSS: 801, 803, 804, 805, 810, 812, 814, 820, 850, 851, 009  
 NBS: 692, 693  
 BS: 104  
 BCS: 301, 302, 175  
 BAS: 676, 683  
 NBS: 27e

Table 9 shows the coexisting component correction factors without LOI correction and with LOI correction and the study was made using those factors. Figure 13 shows an uncorrected calibration line. Figure 14 shows the one applied coexisting component correction only and Fig. 15 is the one applied both LOI correction and

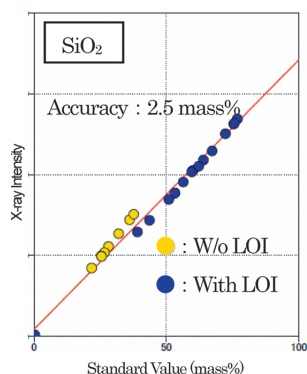


Fig. 10. Uncorrected calibration line.

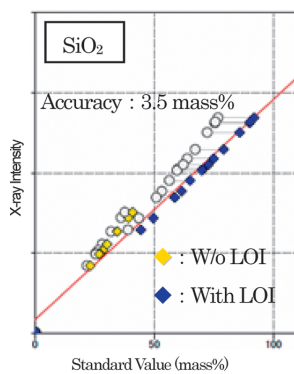


Fig. 11. Calibration line with coexisting component correction.

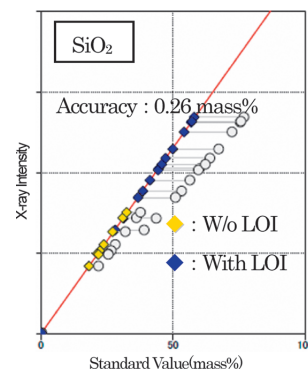


Fig. 12. Calibration line with corrections for LOI and coexisting component.

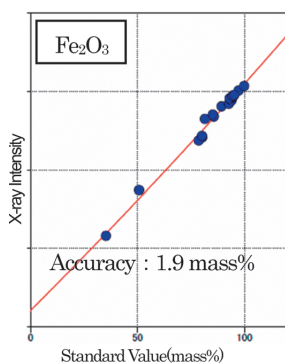


Fig. 13. Uncorrected calibration line.

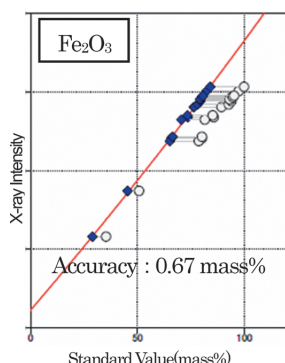


Fig. 14. Calibration line with coexisting component correction.

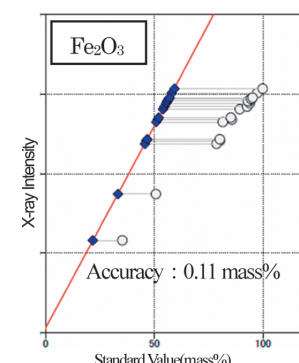


Fig. 15. Calibration line with corrections for LOI and coexisting component.

Table 9. Coexisting component correction factors without LOI correction and with it (Correction model: de Jongh).

Analysis Component Base Compo. Cor. Compo.	Fe <sub>2</sub> O <sub>3</sub>	
	SiO <sub>2</sub>	LOI
Fe <sub>2</sub> O <sub>3</sub>	0.00188	0.00687
SiO <sub>2</sub>	-	0.00419
MnO	0.00165	0.00655
P <sub>2</sub> O <sub>5</sub>	0.000262	0.00457
SO <sub>3</sub>	0.000560	0.00499
TiO <sub>2</sub>	0.00681	0.0139
CaO	0.00692	0.0140
MgO	-0.000577	0.00338
Al <sub>2</sub> O <sub>3</sub>	-0.000368	0.00367

coexisting component correction for Fe<sub>2</sub>O<sub>3</sub>.

This correction for iron ore is an application example in case of practical appearance of LOI and GOI, and we learn that this method is the effective method for making LOI (including GOI) correction.

### 10. Application of flux volatilization correction

There is a type of error made by dilution factor

change due to flux volatilization during fusion at high temperature making difference of flux weights before and after fusion.

Correction of flux volatilization effect can be made by using weight of fusion beads instead of flux weight for dilution factor calculation.

Equation for dilution factor R<sub>F</sub> calculation without LOI (including GOI) is as below.

$$R_F = \frac{F}{S} = \frac{B - S}{S} = \frac{B}{S} - 1 \tag{7}$$

where F: Weight of flux  
S: Weight of sample  
B: Weight of fusion beads

As shown in the equation (7) above, dilution factor correction can be applied by using dilution factor calculated from fusion beads weight (B) and sample weight (S).

Next, let's study the case of sample including LOI. The relation among sample, LOI and weight of flux in this case is explained by an image of Fig. 16.

As shown in the image above, it is understood that the LOI is replaced with a part of flux. Therefore, the LOI (including GOI) correction can be made by designating base component (balance) for calculation of coexisting component correction factor as a component of flux.

Flux volatilization correction was discussed with Fe<sub>2</sub>O<sub>3</sub> in the glass beads used in the Section 9 and one of two kinds of iron ore of which volatilization amounts are quite different each other.

Following is the comparison between the method without flux volatilization correction and with the said correction.

Coexisting component correction factors for each method are shown in Table 10. Calculation of the correction factor was made as follow.

- ◆ Without volatilization correction: Coexisting component correction factors were calculated with dilution factor (Flux/Sample) correction and incorporation of the LOI correction designating LOI as a base component.
- ◆ With volatilization correction: The factors were calculated with flux volatilization correction using the dilution factor using fusion beads and sample weights, and adding LOI correction of which base component is the flux component which is the LOI amount.

Besides, as the flux used are Li<sub>2</sub>B<sub>4</sub>O<sub>7</sub> 4g and oxidizing agent NaNO<sub>3</sub> 0.24 g (corresponding to Na<sub>2</sub>O 0.0875 g

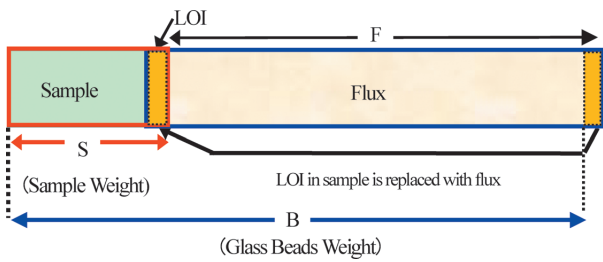


Fig. 16. Image of Flux Volatilization Correction.

Table 10. Coexisting component correction factors for Fe<sub>2</sub>O<sub>3</sub>.

Method	W/o flux vol. correction	With flux vol. correction.
Base comp.	LOI	Flux component
Cor. comp.		
Fe <sub>2</sub> O <sub>3</sub>	0.00686	0.00538
SiO <sub>2</sub>	0.00419	0.00293
MnO	0.00654	0.00508
P <sub>2</sub> O <sub>5</sub>	0.00457	0.00327
SO <sub>3</sub>	0.00499	0.00365
TiO <sub>2</sub>	0.0139	0.0117
CaO	0.0140	0.0119
MgO	0.00338	0.00218
Al <sub>2</sub> O <sub>3</sub>	0.00367	0.00245
αF	0.0978	0.0891
KF (-α <sub>4</sub> R <sub>F</sub> )	-0.9998	-0.9110

- Dilution factor in case of w/o flux vol. correction: F/S
- Dilution factor in case of with flux vol. correction: B/S-1

which is a residual in the fusion beads), compound composition of the flux is set as Li: 1.518, B: 3.036, O: 5.375, Na: 0.089.

Moreover, standard dilution factor (R<sub>F</sub>) was set to 10.2188 (4.0875 g/0.4 g). De Jongh model was used for the coexisting component correction.

Calibration line of Fe<sub>2</sub>O<sub>3</sub> without volatilization correction is shown in Fig. 17.

Calibration line accuracy for all samples is 0.38 mass% which is rather big. Data of the fusion beads of which volatilization is big are shown by yellow markers. They obviously do not fall on the line. The difference between standard value and quantification value for the sample of which volatilization amount is as big as 1.43 mass%, and the difference for the sample of which volatilization amount is intermediate is 0.24 mass%. It can be said that the flux volatilization effect is quite big.

On the other hand, the calibration line for Fe<sub>2</sub>O<sub>3</sub> with flux volatilization correction is shown in Fig. 18. It is understood that the accuracy of the calibration line is improved greatly to 0.11 mass%. For the samples of which volatilization amount is rather big, as errors are as much as 0.07 mass% or 0.04 mass%, it is said that the flux volatilization correction is effective.

### 11. Precautions for glass beads method

Described above that the fusion beads method makes accuracy of the analysis improved by employing the above correction. The following are precautions for the

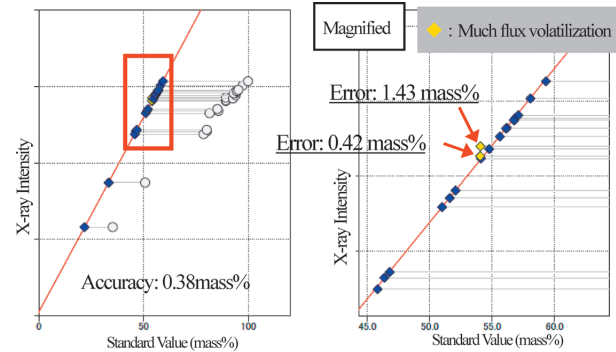


Fig. 17. Calibration line for Fe<sub>2</sub>O<sub>3</sub> without flux volatilization correction.

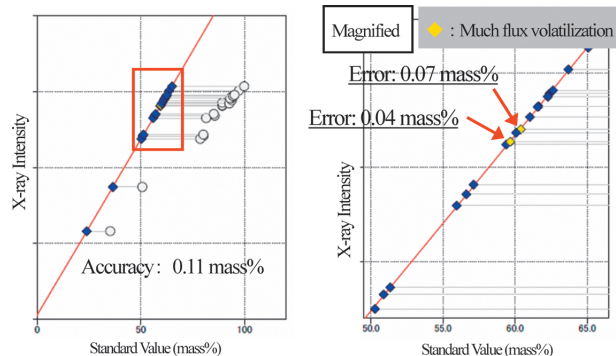


Fig. 18. Calibration line for Fe<sub>2</sub>O<sub>3</sub> with flux volatilization correction.



**Table 11.** Various dominant causes of error and its correction method in fusion beads method.

Cause of error	Weighing error	LOI	Weighing error LOI	Flux volatilization LOI
Correction method	Dilution factor correction	LOI correction	Dilution factor correction. LOI correction	Dilution factor correction LOI correction
Sample weight : S	Used	—	Used	Used
Flux weight : F	Used	—	Used	—
Beads weight : B	—	—	—	Used
Application	Sample not affected by LOI	Possible LOI correction at constant dilution factor	Applicable except for flux volatilization	Overall correction
Application example	Firebrick, etc.	Natural minerals like clay	Wide range of analytical objects	Possible most accurate correction for wide range of analysis object

fusion bead method.

- Analysis of elements with low boiling point (F, Cl, etc.) are difficult due to volatilization of sample during fusion.
- Metallic components [Not oxide; C (Organic matter) and sulfide (CuS<sub>2</sub>)] reacts with platinum so that the platinum crucible is damaged. Oxidization process of sample in advance is required for this kind of sample.

- Sensitivity of trace elements is decreased due to dilution by flux.

## 12. Conclusion

In conclusion, the above explanation of correction methods, a list of various dominant causes of error and their correction methods in fusion beads is shown in Table 11.

Accurate analysis can be made with corrections for LOI, GOI and the effect of flux volatilization by using appropriate coexisting component correction models. And the dilution factor correction is also possible even in case that dilution factors are varied. Moreover, use of actual weights of sample and flux, or sample and fusion beads, makes accurate weighing unnecessary, and operator is released from troublesome weighing. Accurate analysis covering wide concentration range from low to high can be made by employing coexisting component correction in this report to fusion beads method.

## References

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