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XRF1048 - Fused bead analysis for wide concentration ranges of various oxide materials on benchtop WDXRF

Introduction

The fusion method in X-ray fluorescence (XRF) analysis is an effective sample preparation technique for getting accurate analysis results of powder samples, since the technique eliminates heterogeneity due to grain size and mineralogical difference. In addition, the homogenization of material property by vitrification makes it possible to expand the calibration range by the use of synthetic standards of fused beads with reagents or by using diverse reference materials. This application note demonstrates that single calibration for diverse materials, such as minerals, ores and refractories, was established by the fusion method on the Supermini200, a benchtop wavelength dispersive (WD) XRF spectrometer.

Instrument

The Supermini200, a benchtop sequential WDXRF spectrometer, is designed to minimize the peripherals in installation such as cooling water, power supply, installation area, etc. The Supermini200 has good sensitivity for the light elements such as Na, Mg and P, relative to energy dispersive (ED) XRF systems, and does not show any spectral overlap between typical analytes for cement, owing to high spectral resolution of the WD optics.

The Supermini200, equipped with an air-cooled 200 W X-ray tube and up to three analyzing crystals, can analyze the elements from oxygen to uranium.

Fusion bead correction

In XRF analysis by the fusion method for minerals, ores and refractories, it is necessary to apply different fusion conditions, such as dilution ratio, oxidizing agent, due to the difference of the optimum conditions for each material. In addition, some samples have crystal water or carbonate, which result in loss on ignition (LOI); on the other hand, some samples show gain on ignition (GOI).

“Fusion Bead Correction”, an optional program of the ZSX software, mounted on the Supermini200, can apply correction for error factors in the fusion method, such as difference of the mixing ratio of flux and oxidizing agent to sample, LOI and/or GOI, as well as matrix correction for absorption and enhancement by co-existing elements. The Fusion Bead Correction plays an important role in the analysis demonstrated in this application note.

Table 1: Standard materials used

BAS

Number	Material
BAS203a	Talc
BCS313-1	High purity silica
BCS314	Silica brick
BCS315	Fire brick
BCS368	Dolomite
BCS369	Magnesite chrome (Chrome-magnesia)
BCS370	Magnesite chrome (Chrome-magnesia)
BCS375	Soda feldspar
BCS376	Potash feldspar
BCS358	Zirconia
BCS389	High purity magnesia
BCS393	Limestone
BCS394	Calcined Bauxite
BCS395	Bauxite
BAS 683	Iron Ore

NIST

Number	Material
NBS98a	Plastic Clay
NBS120c	Florida Phosphate Rock
SRM 1c	Argillaceous Limestone
SRM 69b	Bauxite (Arkansas)
SRM 696	Bauxite, Surinam
SRM 697	Bauxite, Dominican
SRM 698	Bauxite, Jamaican
SRM 70a	Feldspar, Potash
SRM 99a	Feldspar, Soda
NIST81a	Glass Sand
NIST1413	Glass Sand (High Alumina)
NBS694	Phosphate Rock, Western

CSJ

Number	Material
R-603	Clay
R-701	Feldspar
R-801	Agalmatolite

TARJ

Number	Material
JRRM511	Chrom-magnesia refractory
JRRM602	Zircon-zirconia refractory
JRRM701	Alumina-zircon-silica refractory

JCA

Number	Material
RM-611	Portland cement
RM-612	Portland cement
RM-613	Portland cement

ECISS

Number	Material
ECISS782	Dolomite
ECISS776	Fire Brick

JSS

Number	Material
JSS009-2	Pure iron oxide (III)

Standard samples

Table 1 lists the certified reference materials used in this experiment. To expand the calibration range, reagents were used to make synthetic fused beads for some components, which is summarized in Table 2. Table 3 shows the concentration range of for only the reference materials and the calibration range including the synthetic fused beads for each component.

Sample preparation

Lithium tetraborate ($\text{Li}_2\text{B}_4\text{O}_7$), the flux used in this analysis, was dried at 675°C. The dilution (mixing) ratio of sample to flux in weight was 1:10 for all the materials except 1:20 for chrome-magnesia refractory. Lithium nitrate, an oxidizing agent, was used only for chrome-magnesia refractory, where the weight ratio of sample to flux was 1:10.

The samples were fused on Rigaku benchtop high-frequency fusion machine. The fusion temperature was 1200°C for all the materials except for Portland cement, which was fused at 1075°C to prevent volatilization of sulfur.

Measurement condition

Each fused bead was measured under vacuum on the Supermini200, a benchtop WDXRF spectrometer, which was equipped with an end-window Pd-target 200 W X-ray tube, operating at 50 kV and 4.0 mA, with the measurement area 30 mm in diameter. The measurement condition of each component was tabulated in Table 4. The counting time for each element is 20 seconds each for peak and background. The total measurement time for the analysis of the 15 components per sample was approximately 12 minutes.

Table 2: Synthetic fused bead (unit: mass%)

Reagent	Component	Content of component	Content of LOI
Na_2CO_3	Na_2O	25	75
Al_2O_3	Al_2O_3	100	0
Li_3PO_4	P_2O_5	25	75
K_2CO_3	K_2O	50	50
CaCO_3	CaO	100	0
TiO_2	TiO_2	10	90

Table 3: Concentration range of the reference materials and the calibration (unit: mass%)

Component	Concentration range of the reference materials	Calibration range
Na_2O	0.003 - 10.4	0.003 - <u>25.0</u>
MgO	0.001 - 96.7	0.001 - 96.7
Al_2O_3	0.036 - 88.8	0.036 - <u>100</u>
SiO_2	0.2 - 99.78	0.2 - 99.78
P_2O_5	0.004 - 33.34	0.004 - 33.34
K_2O	0.004 - 11.8	0.004 - <u>50.0</u>
CaO	0.006 - 66.25	0.006 - <u>100</u>
TiO_2	0.004 - 4.961	0.004 - <u>10.0</u>

MnO	0.000 - 0.596	0.000 - 0.596
Fe ₂ O ₃	0.012 - 99.84	0.012 - 99.84
Cr ₂ O ₃	0.001 - 52.51	0.001 - 52.51
ZrO ₂	0.034 - 92.7	0.034 - 92.7
HfO ₂	0.00 - 1.63	0.00 - 1.63
SO ₃	0.001 - 6.07	0.001 - 6.07
SrO	0.003 - 0.28	0.003 - 0.28
LOI	0.00 - 47.4	0.00 - <u>90.0</u>

Note) Underlined numbers denote the concentration of the synthetic fused bead.

Table 4: Measurement condition

Element	Na	Mg	Al	Si	P	S	K	Ca
Line	Kα	Kα	Kα	Kα	Kα	Kα	Kα	Kα
Filter	Out	Out	Out	Out	Out	Out	Al	Out
Crystal	RX25	RX25	PET	PET	PET	PET	PET	PET
Detector	PC	PC	PC	PC	PC	PC	PC	PC
Element	Ti	Cr	Mn	Fe	Sr	Zr	Hf	
Line	Kα	Kα	Kα	Kα	Kα	La	Lβ1	
Filter	Out	Out	Out	Out	Out	Out	Out	
Crystal	LiF	LiF	LiF	LiF	LiF	PET	LiF	
Detector	SC	SC	SC	SC	SC	PC	SC	

Note) LiF: LiF(200), PC: F-PC

Calibration result

The calibration results are summarized in Table 5 and typical calibration curves are shown in Figures 1 – 8, where some typical materials are displayed on the charts in order to indicate that various materials were used for the calibration.

The accuracy of calibration is calculated by the following formula:

$$Accuracy = \sqrt{\frac{\sum_i (C_i - \hat{C}_i)^2}{n-m}}$$

C_i : calculated value of standard sample

\hat{C}_i : reference value of standard sample

n : number of standard samples.

m: degree of freedom (linear 2, quad. 3)

When matrix correction coefficients were calculated theoretically, LOI/GOI was designated as the balance component in the de Jongh model, where an analyte is included in the correcting components, to compensate for the influence of LOI/GOI. Therefore, it is not necessary to obtain LOI/GOI content or to ignite samples prior to the analysis of unknown samples though the LOI/GOI content is unknown.

The calibration results show that excellent accuracy was obtained for each and all of the analytes even though various standard materials and additional synthetic standards were used for making the calibration curves.

When an element line of an analyte is interfered with by other element lines, it is necessary to apply appropriate overlap correction. In this analysis, correction for overlap of Zr-La to P-K α , of Cr-K β 1 to Mn-K α , of P-K α to Zr-La and of Zr-Ly1 to S-K α was carried out.

Table 5: Calibration summary

Component	Calibration range (mass%)	Accuracy (mass%)	Figure
SiO ₂	0.2 - 99.78	0.27	1
Al ₂ O ₃	0.036 - 100	0.26	2
MgO	0.001 - 96.7	0.18	3
Na ₂ O	0.003 - 25.0	0.075	4
CaO	0.006 - 100	0.30	5
K ₂ O	0.004 - 50.0	0.032	
P ₂ O ₅	0.004 - 33.34	0.049	
TiO ₂	0.004 - 10.0	0.043	
MnO	0.000 - 0.596	0.067	
Fe ₂ O ₃	0.012 - 99.84	0.26	6
Cr ₂ O ₃	0.001 - 52.51	0.038	
ZrO ₂	0.034 - 92.7	0.34	7
HfO ₂	0.00 - 1.63	0.035	
SO ₃	0.001 - 6.07	0.031	8
SrO	0.003 - 0.28	0.003	

: Dilution ratio 1:20 + Oxidizer ratio 1:10

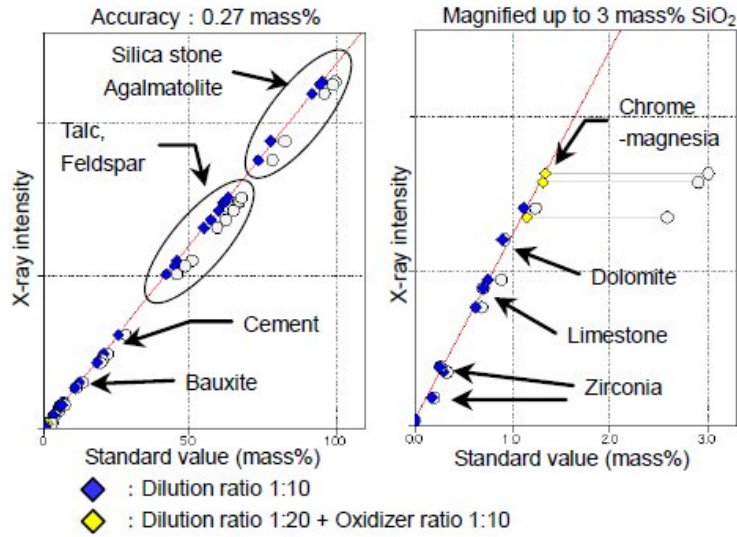


Figure 1: SiO₂ calibration curve

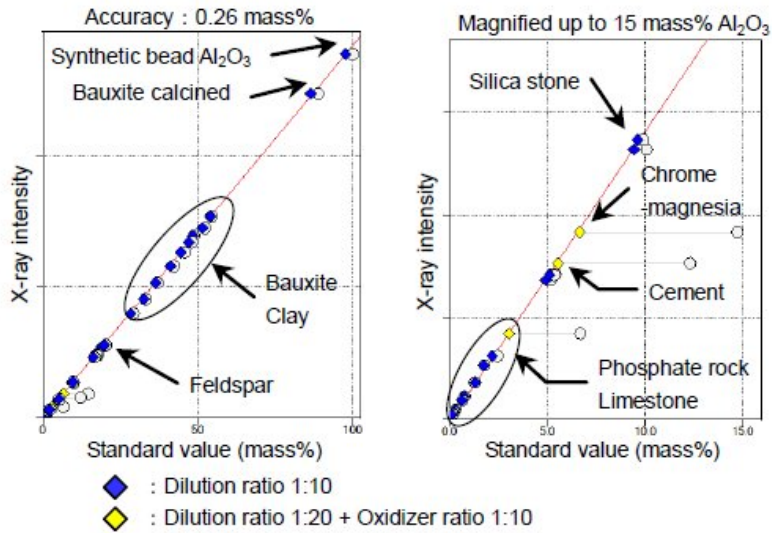


Figure 2: Al₂O₃ calibration curve

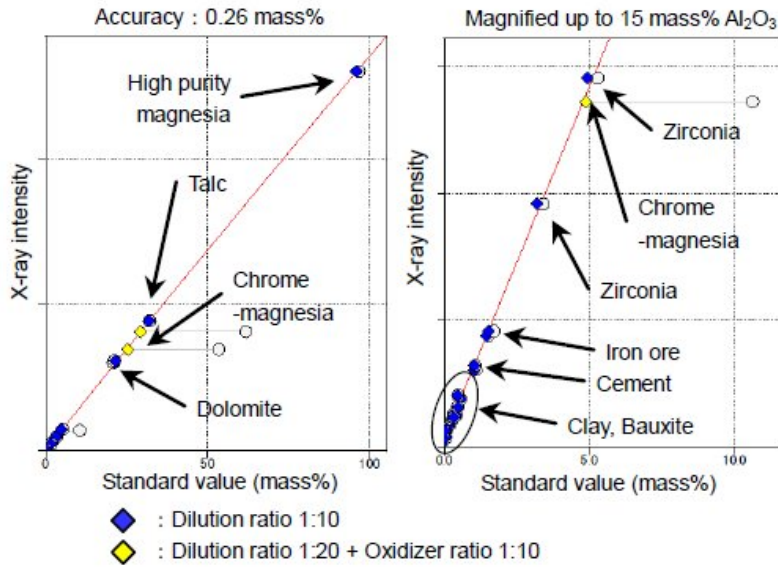


Figure 3: MgO calibration curve

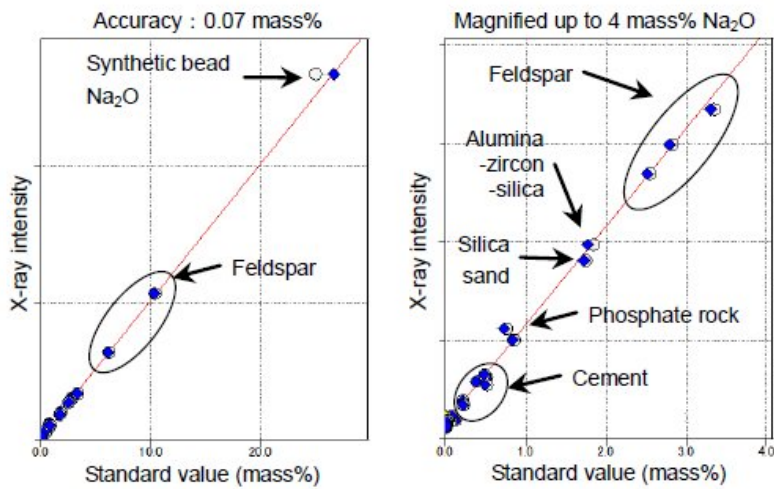


Figure 4: Na_2O calibration curve

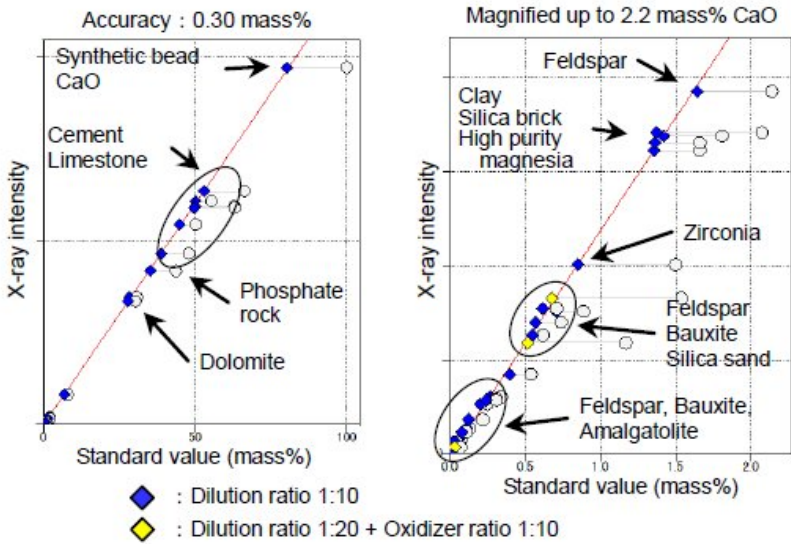


Figure 5: CaO calibration curve

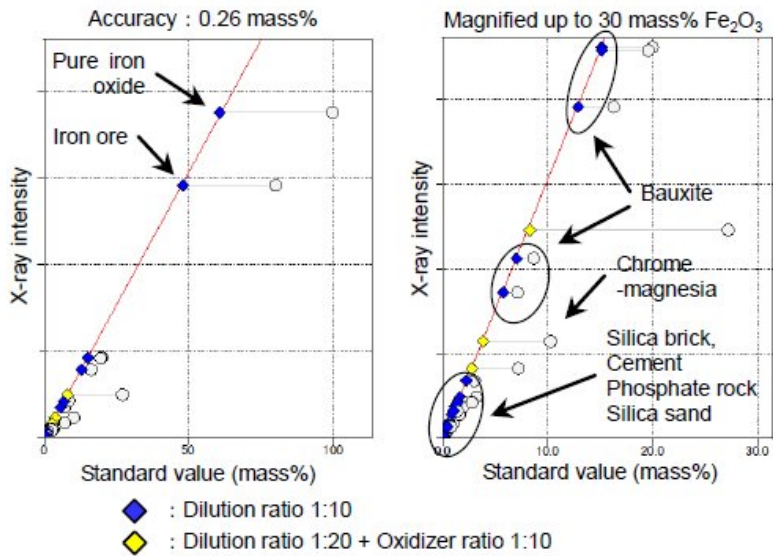


Figure 6: Fe₂O₃ calibration curve

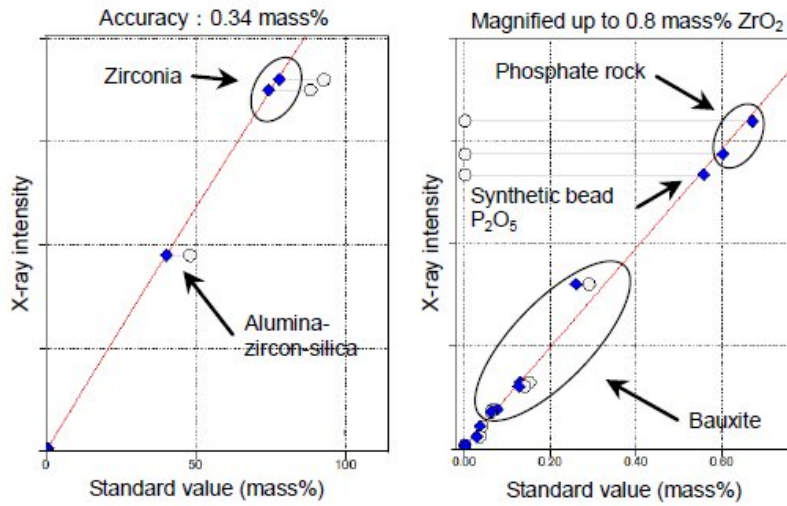


Figure 7: ZrO₂ calibration curve

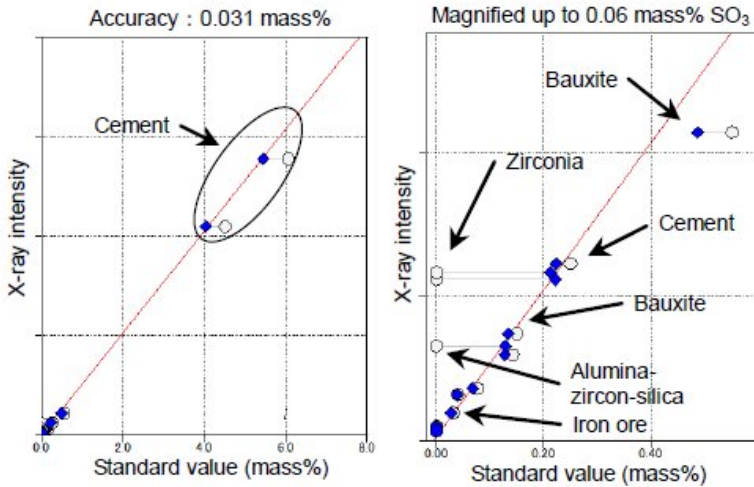


Figure 8: SO₃ calibration curve

Conclusion

This application note demonstrated that the fusion method and the corrections for LOI/GOI and dilution ratio of flux and oxidizing agent enable a single calibration with the wide range of concentration and for diverse materials, such as natural minerals and ores. In addition, the note also showed that it was possible to extend the calibration range by the use of a single agent to make a synthetic standard fused bead.

The Supermini200 is a benchtop WDXRF spectrometer equipped with an air-cooled 200 W X-ray tube to deliver excellent sensitivity and resolution from light elements to heavy elements while eliminating typical installation requirements, such as cooling water, special power supply and large floor space. Therefore, this system can be used for analysis of wide variety of natural minerals and ores under various environments.

References

- (1) Y. Yamada: *Rigaku Journal*, **28**[2] (2012), 15–21.
 - (2) Rigaku Application Note XRF5027, Determination of Metals in Copper Concentrate by Advanced Correction Method for Fused Beads
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Related products



Supermini200

Benchtop tube below sequential WDXRF spectrometer analyzes O through U in solids, liquids and powders