

Silicate Rock Analysis by Fusion Method

Application

silicate rock,
petrology,
geology



Copyright
Shandchem

Instrument

Wavelength dispersive
X-ray fluorescence
spectrometer
ZSX PrimusII



Keywords

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Introduction

Geochemical data set for silicate rocks are essential for modern petrology. Concentrations of major and trace component in igneous rock sample provide many kinds of information about rock history such as eruption or solidification, magma evolution, magma genesis and source materials as well as petrographical classification.

X-ray fluorescence spectrometry for silicate rock analysis has been developed for the last few decades. XRF technique is currently used as standard analytical method to determine the chemical composition of major elements in silicate rocks.

Rock analysis which is demanded high accuracy requires fusion method to eliminate sample heterogeneity, such as grain size and mineralogical effect, owing to various rock-forming minerals. Conventional fusion method has been dominantly used for determination of major elements in silicate rock because dilution by flux significantly reduces sensitivities of trace elements. Pressed powder method is, therefore, applied to trace element analysis. Since it is not efficient and time-consuming that one sample analysis requires two preparation methods, low dilution fusion method was developed. The low dilution fusion bead technique is a method to improve sensitivity of trace elements, which enables to determine the concentrations of trace elements

accurately and reliably as well as major element determination by XRF.

This note demonstrates advanced method to determine the chemical composition in silicate rocks by XRF.

Instrument

The ZSX PrimusII is floor-standing sequential wavelength dispersive X-ray fluorescence (WDXRF) spectrometer, which has advantages in high spectral resolution and high sensitivity in light elements. The instrument is designed to provide reliable analysis results and its flexibility provides multipurpose availability to wide range applications.

The ZSX PrimusII is equipped with a high performance 4 kW Rh target X-ray tube with ultra-thin beryllium window. The tube provides unconventional high sensitivity for light element analysis. Analyzing crystals cover from beryllium to uranium measurement.

The instrument has also built-in intelligent auto sample changer (ASC). The ASC is upgradable up to 48 samples for demand.

The ZSX PrimusII has a unique optical configuration designed to minimize errors caused by uneven bead surface. It enables to measure fused beads with high precision in which the surface becomes curved by deformation of platinum crucible in continuous fusion operation.

Operation software provides non-specialist users with easy-to-use operation. In particular, flowbar system fully supports the user's operation on the setting-up of quantitative analysis.

Sample and sample preparation

The standard samples used for calibration were 14 certified reference materials (CRMs) supplied from the Geological Survey of Japan (GSJ). These standards are composed of basic to acidic igneous rocks. Range of SiO₂ content in these CRMs is wide from 43.6 to 76.8 in mass%.

The well-dried (2 hours at 105 degrees C) samples were fused with mixed flux of Spectroflux 100B (4LiBO₂:1LiB₄O₇) supplied from Johnson Matthey with sample to flux ratio 1:2 by using a fusion machine.

Measurement

The ZSX PrimusII with 4kW Rh target X-ray tube was used for measurement. Each measurement was performed at the tube condition in full load. All of trace elements were measured with primary beam filter to reduce background. Counting times for the rare earth elements were 400 – 800 seconds and for the other trace elements, 100 – 200 seconds.

Matrix correction coefficients (alpha) in the calibration were theoretically calculated by built-in FP software. In the calculation of theoretical alpha, ignition loss was set as balanced component.

Results

Calibration curves for major elements are shown in Figure 1. Accuracy of SiO₂ is less than 0.2 in such a wide concentration range. Other calibration show also excellent accuracy.

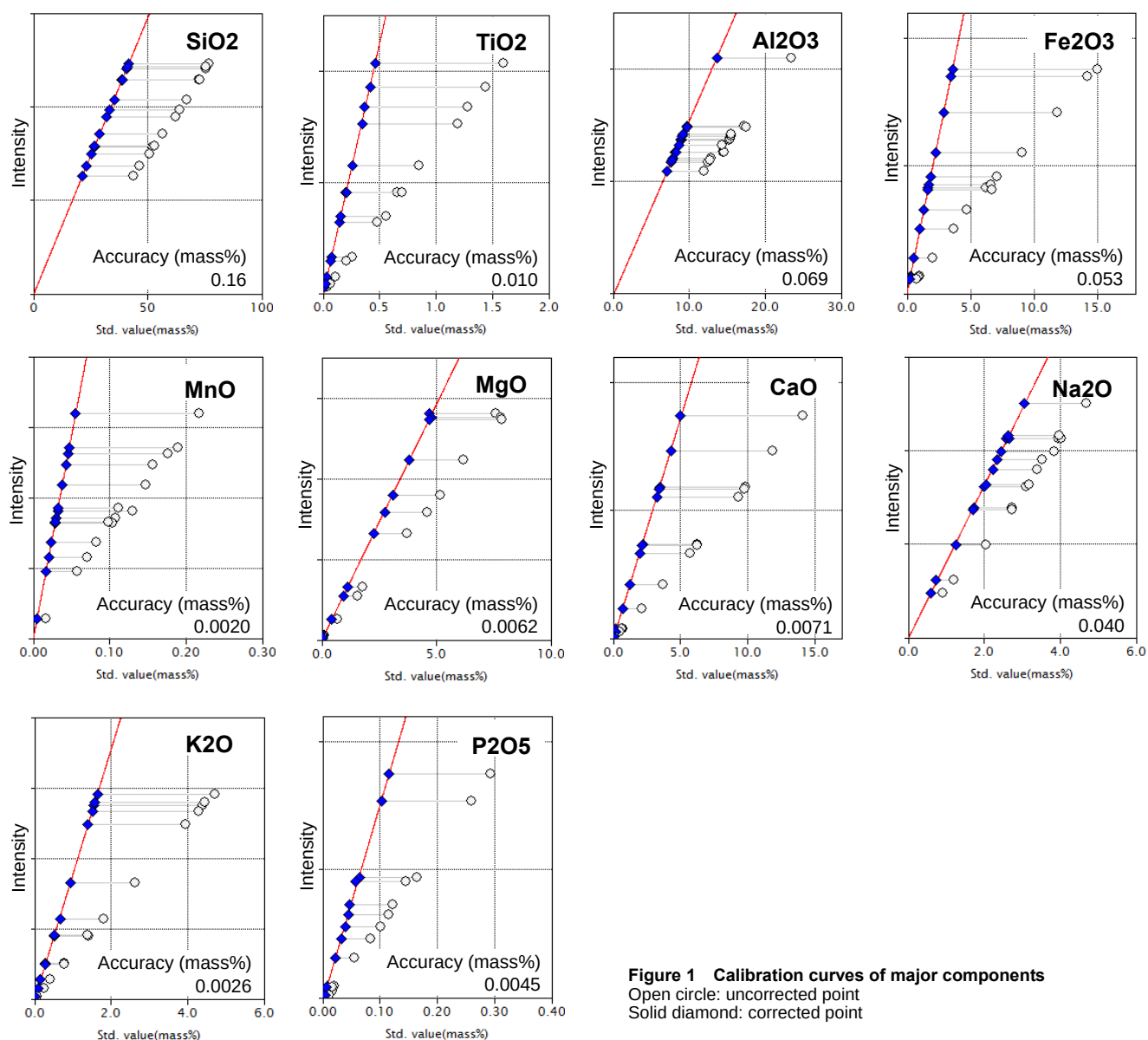


Figure 1 Calibration curves of major components
Open circle: uncorrected point
Solid diamond: corrected point

The accuracy is calculated by the following formula.

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

C_i : calculated value of standard sample i

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

n : number of standard samples.

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

Typical lower limit of detection (LLD) and typical accuracy of calibration curve for each trace element are shown in Table 1. The LLDs are calculated as following:

$$\text{LLD} = 3 \cdot \frac{1}{m} \cdot \sigma_B = 3 \cdot \frac{1}{m} \cdot \sqrt{\frac{I_B}{1000 \cdot t}}$$

m : sensitivity of calibration (kcps/mass%)

σ_B : standard deviation of blank intensity (kcps)

I_B : intensity of the blank (kcps)

t : counting time (s); 100 s is used

Table 1 Typical LLD and accuracy of calibration curve for trace elements

unit : ppm

Component / Element	Typical LLD (100s, 3 σ)	Typical accuracy
Ba	4.5	12.9
Ce	1.9	2.5
Co	0.2	1.3
Cr	0.5	2.5
Cu	0.2	5.9
Ga	0.2	0.6
La	1.9	2.4
Nb	0.5	1.1
Nd	4.2	2.5
Ni	0.2	3.3
Pb	0.1	0.5
Rb	0.1	3.5
Sc	0.5	3.7
Sm	2.5	1.3
Sr	0.1	4.6
Th	0.2	1.3
V	0.8	3.9
Y	0.1	0.6
Yb	1.3	0.7
Zn	0.1	1.7
Zr	0.1	6.0

The 4 kW high-power X-ray tube of ZSX PrimusII has great advantage in determination for trace elements. To test instrumental precision, 20 time measurements were performed with a granodiorite sample (JG-3). The results of average and standard deviation of each component are shown in Table 2.

Table 2 Result of precision test

unit : ppm

Component / Element	Certified value	Average of 20 measurement	Std. dev.	RSD%
SiO ₂ (mass%)	67.29	67.05	0.037	0.054
TiO ₂ (mass%)	0.48	0.48	0.002	0.34
Al ₂ O ₃ (mass%)	15.48	15.50	0.012	0.074
T.Fe ₂ O ₃ (mass%)	3.69	3.71	0.004	0.096
MnO (mass%)	0.071	0.071	0.0004	0.62
MgO (mass%)	1.79	1.80	0.007	0.40
CaO (mass%)	3.69	3.67	0.004	0.10
Na ₂ O (mass%)	3.96	4.02	0.018	0.44
K ₂ O (mass%)	2.64	2.61	0.002	0.086
P ₂ O ₅ (mass%)	0.122	0.128	0.0008	0.63
Ba	466	469	6.2	1.3
Ce	40.3	38	1.7	4.5
Co	11.7	11	0.38	3.4
Cr	22.4	23	0.80	3.5
Cu	6.81	6	0.34	6.1
Ga	17.1	16	0.37	2.3
La	20.6	21	1.5	7.2
Nb	5.88	8	0.23	2.9
Nd	17.2	16	0.82	5.3
Ni	14.3	15	0.32	2.1
Pb	11.7	11	0.45	4.0
Rb	67.3	71	0.28	0.40
Sc	8.76	9	0.99	10
Sm	3.39	3	0.56	19
Sr	379	367	0.45	0.12
Th	8.28	9	0.30	3.5
V	70.1	68	1.4	2.0
Y	17.3	18	0.20	1.1
Yb	1.77	2	0.28	18
Zn	46.5	46	0.34	0.74
Zr	144	152	0.29	0.19

Conclusions

X-ray fluorescence spectrometry is rapid, precise and accurate method to meet the requirements of silicate rock analysis. It can also minimize skill and time for the sample preparation compared to other spectroscopic analysis method which uses wet chemical technique. This note describes that XRF method with low dilution fusion technique applied to silicate rock samples can widely determine from major elements to trace elements with high accuracy.

The method covers almost all trace elements required for modern geochemical investigations. It also covers some rare earth elements.

The XRF analysis is the best method to obtain accurate and precise fundamental data required for scientific study in petrology and geochemistry. The method is also widely applicable for geological matters, such as environmental assessment of soil, exploring resources and process and quality control in mining as well as scientific investigations.



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