

## Optimization of analytical conditions for major element analysis of geological samples with XRF using glass beads

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Masatsugu Ogasawara, Masumi Mikoshiba, Nobuo Geshi, Gen Shimoda and Yoshihiro Ishizuka (2018) Optimization of analytical conditions for major element analysis of geological samples with XRF using glass beads. *Bull. Geol. Surv. Japan*, vol. 69 (2), p. 91–103, 4 figs, 6 tables.

**Abstract:** The major element XRF analytical program, Bead03, has been prepared for geological samples. The analytical condition suitable for the samples was optimized considering sensitivity, precision, and the lower limit of detection. The detailed analytical protocol of Bead03 has been described, and Bead03 has been successfully used at the shared facility of the GSJ laboratory. Bead03 is generally used without the need for frequent calibration. As such, any user can perform analysis with a minimum number of steps and simple operation. Bead03 can also 1) perform overlapping correction of Br  $L\alpha$  on Al  $K\alpha$ , eliminating the effect of releasing agent LiBr, and 2) apply curve fitting of backgrounds for Na  $K\alpha$  and Mg  $K\alpha$ . The present report also describes the quality of calibration lines for silicate rock samples and analytical precision.

**Keywords:** XRF, glass bead, geological samples, major elements, analytical conditions

### 1. Introduction

X-ray fluorescence spectrometry (XRF) is a standard technique for obtaining major and trace element compositions of geological samples (Potts, 1987). For XRF analysis of major elements, glass beads (or glass discs) are typically prepared from powdered samples (e.g., Norrish and Hutton, 1969; Norrish and Chappell, 1977).

The shared research facility at the Geological Survey of Japan (GSJ) provides various analytical instruments (Ogasawara, 2013), including an XRF system. A Philips PW-1404 XRF was introduced in 1987 as part of the shared research facility and has been used extensively to obtain major and trace element data of geological samples. In 2007, as the PW1404 had been used for 20 years and spare parts became difficult to obtain, a new XRF, the PANalytical Axios Advanced, was acquired in order to improve efficient analysis at the GSJ. Since the introduction of the new Axios Advanced XRF, most researchers have been using the new XRF, although the PW1404 is still used to obtain various analytical results.

For major element analysis using the Axios Advanced XRF, a public analytical program, Bead03, was prepared

for users in 2007. The Bead03 program requires a minimum number of steps to obtain major element data. As such, any user can operate the Axios Advanced XRF with minimal experience. Due to the extremely stable condition of the Axios Advanced XRF, calibration of the analytical program is not required for most users. Users can check the quality of the calibration by analysis of a reference rock standard (e.g., JB-1a) before analysis. If the results are satisfactory, then unknown samples can be analyzed subsequently. If the results are not satisfactory, the person in charge of the XRF will check the condition of the equipment and will perform a new calibration. In general, a new calibration might be necessary after more than a half year. The analytical protocol of Bead03 uses only natural silicate rock references for calibration, although it is possible to extend the calibration range with standards prepared from chemicals (e.g., Tsuchiya *et al.*, 1989; Seno and Motoyoshi, 2004; Yamasaki, 2014). Bead03 has been used for more than 8 years, providing excellent major element data. This report presents the results of examination under various analytical conditions and an optimized analytical protocol of major element analysis of geological samples with the Axios Advanced

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Table 1 Compositional ranges in routine analysis of geological samples

(wt.%)	GSJ Igneous standards			GSJ Sedimentary standards			Target range	
	Average	Min	Max	Average	Min	Max	Min	Max
SiO <sub>2</sub>	60.02	42.38	76.83	63.24	57.16	76.00	40.00	80.00
TiO <sub>2</sub>	0.64	0.01	1.60	0.63	0.40	0.75	0.00	2.00
Al <sub>2</sub> O <sub>3</sub>	13.72	0.66	23.48	14.89	9.91	18.17	0.00	25.00
Fe <sub>2</sub> O <sub>3</sub> *	6.78	0.77	15.06	6.90	4.37	11.65	0.00	15.00
MnO	0.12	0.02	0.22	0.13	0.06	0.27	0.00	0.30
MgO	6.78	0.04	44.60	2.04	1.17	2.73	0.00	45.00
CaO	6.03	0.09	15.02	1.88	0.56	3.66	0.00	15.00
Na <sub>2</sub> O	2.76	0.02	4.69	1.69	0.41	2.73	0.00	5.00
K <sub>2</sub> O	2.00	0.00	4.71	2.33	1.15	3.01	0.00	5.00
P <sub>2</sub> O <sub>5</sub>	0.10	0.00	0.29	0.15	0.08	0.21	0.00	0.30

Average, minimum, and maximum values of GSJ Igneous standards are obtained from 16 standards; JA-1, JA-2, JA-3, JB-1, JB-2, JB-3, JG-1, JG-2, JG-3, JGb-1, JGb-2, JH-1, JP-1, JR-1, JR-2, and JR-3 (Imai *et al.*, 1995; Imai *et al.*, 1999)

Average, minimum, and maximum values of GSJ Sedimentary standards are obtained from 6 standards; Jlk-1, JSI-1, JSI-2, JSd-1, JSd-2, and JSd-3 (Imai *et al.*, 1996;)

Fe<sub>2</sub>O<sub>3</sub>\*: Total Fe as Fe<sub>2</sub>O<sub>3</sub>

XRF using glass beads. The precision and accuracy of analysis using Bead03 are also discussed, although a new analytical program, Bead04, has been used for glass discs prepared with the TK-4500 fully automatic glass bead sampler, which is same as Bead03, and calibration lines were established using standard glass beads prepared with TK-4500.

## 2. Specifications and characteristics of XRF at the GSJ shared research facility

The XRF is used in a wide range of applications in scientific research and industry. Various options for a standard model of XRF can generally be selected to meet the requirements for the specific application. Thus, the selection of such options is important to perform accurate and efficient analysis.

Geological samples analyzed at the shared research facility of the GSJ are typically igneous and sedimentary rocks. Analysis of carbonate rocks can be performed with other analytical techniques using acid digestion for sample preparation. Table 1 shows typical compositional ranges of major elements of igneous and sedimentary rocks, estimated from the chemical compositions of GSJ standard reference materials. For the composition range of the sediments and sedimentary rocks (Table 1), chert and carbonate rocks are not included. The compositional ranges required for analysis using XRF in the GSJ are indicated in Table 1. The specifications of XRF and the analytical protocol are selected so as to provide precise analytical results for the compositional ranges.

Detailed specifications of the Axios Advanced XRF at the GSJ shared research facility are listed in Table 2. The Axios Advanced XRF at the GSJ shared research facility uses a 4 kW power Rh end window-type X-ray

tube. Although X-ray tubes with Sc or Cr anodes are effective for generating X-rays of major elements of geological samples (Norrish and Chappell, 1977), modern wavelength dispersive XRF instruments mostly use Rh X-ray tubes, which effectively generate specific X-rays of light elements and heavy elements. The maximum voltage applied to the X-ray tube is 60 kV. As the tube is a 4 kW tube, it is possible to apply a tube current of 66 mA at a maximum voltage of 60 kV. The Axios Advanced XRF at the GSJ shared research facility has four tube filters, Pb 1 mm (beam stopper), Al 200 µm, Al 750 µm, and brass 400 µm. The tube filter can be placed between the X-ray tube and the sample, eliminating any specific X-ray lines from the X-ray tube, although with some reduction of X-ray intensity. The Al filters can be used to reduce background counts for the analysis of transition elements, such as Cu. The brass 400 µm filter reduces Rh K $\alpha$  and K $\beta$  from the X-ray tube and can be applied to the analysis of Ag, Cd, and Rh.

A collimator mask is placed between the sample and the collimator and eliminates any fluorescence X-rays generated by the sample holder. The Axios Advanced XRF has six different sizes of collimator mask (Table 2). Three types of collimators can be selected in the Axios Advanced XRF. The Soller slit spacings of 150 µm, 300 µm, and 700 µm are those for the very fine, fine, and coarse collimators, respectively.

The Axios Advanced XRF can accommodate up to eight analysing crystals. The analysing crystals of the XRF at the GSJ shared research facility are listed in Table 2. PX1, PX4A, PX7, PX8, and PX10 are synthetic layer analyzers prepared by PANalytical Co. PX1 and PX8 have better diffraction efficiencies than TAP and can be used to analyze Na and Mg. PX4A is used for the analysis of carbon. PX7 can be used for the analysis of boron.

Table 2 Instrument details of the XRF (PANalytical Axios Advanced) at the GSJ

Component	Details
X-ray tube	Rh end window 4 kW (Super fine tube)
Tube Filter	Pb 1 mm (Beam stopper), Al 200 $\mu\text{m}$ , Al 750 $\mu\text{m}$ , Brass 400 $\mu\text{m}$
Collimator Mask	6 mm, 10 mm, 20 mm, 27 mm, 30 mm, 37 mm
Collimator	150 $\mu\text{m}$ , 300 $\mu\text{m}$ , 700 $\mu\text{m}$
Analyzing crystal	Ge(111)-C, PE(002)-C, LIF220, PX1, PX4A, PX7, PX8, PX10
Detector	Flow Proportional Counter, Xe Sealed counter, Scintillation counter, Duplex (FPC and Xe)

Ge(111)-C and PE(002)-C: curved crystals for high reflection efficiency

PX10 is equivalent to the LIF200 with a higher reflection efficiency. Ge (111)-C and PE(002)-C (Table 2) are curved crystals with a higher reflection efficiency than the crystals of the normal Ge and PET, respectively. In the minimum specifications, three analysing crystals, i.e., PX1 (or TAP), PET, and PX10 (or LiF200), will cover all of the necessary elements analyzed for the geological samples. The present specifications of the analysing crystals for the XRF at the GSJ shared research facility provide the opportunity to analyze any elements heavier than boron with the maximum efficiency.

The Axios Advanced XRF has three detectors: a flow proportional counter (FPC), a scintillation counter (SC), and a Xe sealed counter. A tandem combination of the FPC and Xe sealed counters, namely, the duplex detector system of PANalytical, can be used. The Duplex detector system is suitable for analyzing X-rays with energy from Ti K $\alpha$  to Co K $\alpha$ .

The XRF at the GSJ shared research facility is running continuously, except during annual maintenance of the electric power supply. When not in use, the X-ray tube is kept in standby mode at 50 kV and 20 mA. The standby mode of the X-ray tube allows a better lifetime of the tube and quick startup to the analytical mode.

In the glass bead analysis, only one sample holder is used. The glass beads are placed directly on trays and are supplied to the sample holder from the trays through an automatic sample handling system. The sample holder with the glass bead is then introduced into the spectrometer for analysis. Although the sample holders have been manufactured with high precision, their dimensions may still vary slightly. If multiple sample holders are used, the distance between the end of X-ray tube and the sample surface may vary, which could affect the intensity of fluorescence X-rays. The present Axios Advanced XRF system eliminates such variation using only one sample holder. A sample tray accommodates 12 glass discs. Eight trays can be placed on the sample changer. Thus, a maximum of 96 glass beads can be placed on the Axios Advanced XRF sample changer surface. The XRF can analyze up to 96 glass beads without any user attendance.

### 3. Sample preparation

A brief description of the sample preparation method for glass beads is presented in the following. There are three basic parameters to be selected for preparing glass beads: the type of flux and other chemicals, the mixing ratio of the flux and the sample, and the glass making method.

#### 3.1 Flux and other chemicals and sample-flux mixing ratio

Several types of fluxes are used for the analysis of geological samples (Table 3). A mixture of lithium tetraborate and lithium carbonate with lanthanum oxide (LaO) heavy absorber was classically used (Norrish and Hutton, 1969, Norrish and Chappell, 1977). Although LaO was used to reduce matrix effects, advanced software matrix corrections reduced the necessity of the heavy absorber. Lithium metaborate or a mixture of lithium metaborate and lithium tetraborate provides a lower fusion temperature than lithium tetraborate alone and is suitable for preparing low dilution glass beads (e.g., Kimura and Yamada, 1996; Goto *et al.*, 2002). As the present protocol of sample preparation uses a 1:10 sample:flux ratio, a mixture of lithium metaborate and lithium tetraborate is not required. Lithium tetraborate is more acidic compared to lithium metaborate and is compatible with basic materials (Claisse, 1989). Although a mixture of lithium metaborate and lithium tetraborate is suitable for fusing silicate rock samples, mixing the flux requires additional sample preparation work by users. Pre-mixed fluxes are commercially available, however it may be necessary to check the composition of the mixed flux for each new bottles. Based on these considerations, sample preparation for the Bead03 analytical program uses lithium tetraborate (Li<sub>2</sub>B<sub>4</sub>O<sub>7</sub>; Merck, Spectromelt A10).

Various sample-to-flux ratios, ranging from 1:1 to 1:10, have been used (e.g., Tani *et al.*, 2002). Glass beads with low dilution ratios are typically used to analyze trace elements as well as major elements, providing higher count rates of X-rays from trace elements. Bead03 was prepared for a sample-to-flux ratio of 1:10 to ensure complete fusion of typical rocks and to reduce the matrix effect. This ratio also contributes to an efficient weighing

Table 3 Characteristics of typical fluxes and other chemicals used to prepare glass beads

Flux/Chemical	Composition	Characteristics
<b>Flux</b>		
Lithium tetraborate*	Li <sub>2</sub> B <sub>4</sub> O <sub>7</sub>	Melting temperature: 930°C
Lithium metaborate	LiBO <sub>3</sub>	Melting temperature: 845°C
Mixture of lithium tetraborate and metaborate	Li <sub>2</sub> B <sub>4</sub> O <sub>7</sub> + LiBO <sub>3</sub>	Lower melting temperature
Flux with heavy absorber	Li <sub>2</sub> B <sub>4</sub> O <sub>7</sub> + Li <sub>2</sub> CO <sub>3</sub> + LaO	Addition of LaO reduces matrix differences (Norrish and Hutton, 1969)
<b>Oxidizing agent</b>		
Lithium nitrate	LiNO <sub>3</sub>	
<b>Releasing agent</b>		
Lithium bromide*	LiBr	Br overlaps on Al K $\alpha$ , Rb K $\alpha$
Lithium iodine	LiI	Strongly hygroscopic, I overlaps on Ti K $\alpha$

\*: used in Bead03 analytical protocol

procedure, as the weight of flux is 10 times the sample weight.

Lithium nitrate and sodium nitrate (Norrish and Hutton, 1969, Norrish and Chappell, 1977) have been used as oxidizing agents. An oxidizing agent is effective for samples that contain sulfide minerals, although ignition of such samples before the preparation of glass beads should be sufficient. As such, an oxidizing agent is not added in the present study.

### 3.2 Glass bead releasing agent

After fusion of the mixture of flux and sample in the crucible, melt is quenched to form glass bead. In order to ensure effective removal of the glass bead from the crucible, a releasing agent (non-wetting agent) is generally added. Table 3 lists the characteristics of two types of releasing agents commonly used in the analysis of geological samples: lithium bromide (LiBr) and lithium iodine (LiI). As Br K $\beta$  overlaps Rb K $\alpha$ , LiI is preferred for the analysis of Rb, which is an important lithophile trace element of geological samples. Br L $\alpha$  slightly overlaps Al K $\alpha$ . Iodine L $\beta$ 2 overlaps Ti K $\alpha$ . The present analytical protocol with Bead03 uses LiBr as the releasing agent. Lithium iodine is more hygroscopic than LiBr, and special care is necessary in its handling. The present analytical method is not intended to analyze Rb, and thus LiBr, which is easier to handle, is selected as a releasing agent.

### 3.3 Sample preparation procedure

The glass beads for XRF analysis can be prepared by gas heating, electric heating, or high-frequency induction heating methods. The GSJ shared facility provides high-frequency induction heating equipment, a TK-4100 bead sampler (Tokyo Kagaku Co., presently Amena Tech Co.)

and has been effectively used for the last 17 years. The TK-4100 bead sampler fuses the mixture of sample and flux in a crucible to make homogeneous melt and quenches the melt to form glass beads in the same crucible. A Mettler AG204 four-decimal-digit electric balance is used to weigh the sample and the flux. Lithium tetraborate flux is ignited before the use at 700 °C for approximately 2 hours and is kept in a plastic bottle. If the samples contain sulfide minerals or any reducing components, e.g., carbonaceous materials, then the samples can be ignited before weighing.

An outline of the procedures for preparing glass beads is presented here. Using a Mettler AG204 chemical balance, 0.5 g of sample is taken on weighing paper. The weight of the sample is recorded to four decimal digits. The weight of the sample need not be precisely 0.5000 g, but rather approximately 0.5 g. Then, a flux equal to 10 times the sample weight can be taken on another weighing paper with precisely three decimal digits, e.g., if the sample weight is 0.5007 g, then the weight of flux should be 5.007 g. As the PANalytical XRF generally accommodates glass beads of 32 mm in diameter as a standard, the weights of the sample and chemicals used are suitable for the preparation of glass beads of this diameter. It is important to have the sample-to-flux ratio be precisely 1:10. This weighing procedure is efficient and requires only one precise weighing. The sample powder can be placed on flux on the weighing paper, and mixed thoroughly with a spatula. Alternatively sample and flux powder can be transferred to an agate mortar and may be mixed thoroughly. The mixed powder is transfer into a platinum (95%) and gold (5%) alloy crucible. Before melting with the TK-4100, two drops of releasing agent, a lithium bromide solution, are added from a drop bottle. The lithium bromide solution is prepared from lithium bromide hydrate (LiBrH<sub>2</sub>O,

Kanto Kagaku Co.) for dilution with deionized water. The weight of added deionized water is twice of the weight of the lithium bromide hydrate, resulting in the bromine concentration in the solution being 25.4%. The bromine added to the flux-sample mixture is approximately 0.018 g, resulting in a concentration of 3,400 ppm of Br in the glass bead. As the sample is diluted 11 times in the glass bead, i.e., the sample flux ratio is 1:10, this concentration is equivalent to 3.74 wt.% in the sample.

The crucible is placed in the fusion unit of the TK4100 and covered with a platinum lid (Pt-Au alloy). The heating parameters of the TK4100 can be controlled in three steps. Although the temperature of each step can be set separately, the temperature settings of the present protocol are fixed to 1150 °C for all steps. The duration of the initial heating stage is 120 seconds and that of the main fusion stage is 180 seconds. This is followed by 180 seconds of fusion with agitation to make the melt homogeneous without any bubbles. After the third step, an initial cooling cycle of approximately 20 seconds is started. The crucible is then transferred from the heating unit to the quenching station until complete cooling, which requires approximately 3 minutes on the quenching station. After the transferring the crucible from the heating unit to the quenching station, the next sample can be placed in the heating unit for fusion. Thus, the total cycle time, excluding the quenching phase, is approximately 8.5 minutes. The parameters were selected so as to maximize the efficiency of sample preparation and the complete digestion of typical geological samples. The glass beads can be kept in a plastic bag with a seal and are stored in a desiccator until measurement.

The crucible and lid are generally used for a day without cleaning. After work, the platinum ware can be cleaned by leaving it overnight, or longer, in a citric acid solution. The citric acid is sufficient to digest any residual melt stuck to the platinum ware and is safer than a hydrochloric acid solution.

#### 4. Optimization of analytical conditions

Various analytical parameters have to be optimized to perform efficient and accurate analysis with XRF. Table 4 shows the analytical conditions of the present study. The kV and mA settings for Axios Advanced XRF can be adjusted quickly without losing stability, as long as the wattage is maintained unchanged. Tani *et al.* (2002) used a 3 kW X-ray tube at 24 kV and 125 mA for light elements from Na to K, at 30 kV and 100 mA for Ca, at 40 kV and 75 mA for Ti, and at 60 kV and 50 mA for Mn and Fe. It is optimal to use such variable kV and mA settings to obtain the highest count rates from each element. However, a high mA setting may affect the lifetime of the X-ray tube. In the present study, the kV and mA setting for an X-ray tube is fixed to 50 kV and 50 mA. The 50 kV setting is sufficient to effectively generate Fe K $\alpha$ , although such high voltage is not optimum for light elements. A lower

mA setting for light elements requires longer counting times, resulting in a longer analytical time. The increase in analytical time generally does not affect the overall efficiency of research, although the increase may be significant in routine analysis in industry. As the X-ray generator of the Axios Advanced XRF is maintained at 50 kV and 20 mA even when not in use, the increase from 50 kV and 20 mA to 50 kV and 50 mA for measurement does not require a long wait time.

In Bead03, a tube filter is not used. The sample spinner is turned on in order to eliminate any variation in the flatness of the glass disc surface and possible heterogeneity of the disc. A 27 mm collimator mask is used to transfer fluorescence X-rays generated from a glass bead sample with a 32 mm diameter. The collimator for Na and Mg is a 700  $\mu$ m collimator, and the collimator of other elements is a 300  $\mu$ m collimator. Table 4 lists the analysing crystals for each element. The synthetic crystal PX1 is used for Na and Mg. PE(002)-C and Ge(111)-C crystals are used for Al and Si and for P, respectively. Other elements were analyzed using the synthetic PX10. A duplex detector system is used for Mn and Fe, and a flow proportional counter is used for other elements. The pulse height analyzer (PHA) settings of the detectors listed in Table 4 are specific parameter values used in the PANalytical XRF.

The K $\alpha$  lines of the major elements are analyzed in Bead03. In addition to the major element K $\alpha$  lines, Br L $\alpha$  is analyzed to calculate Br L $\alpha$  interference on Al K $\alpha$ . The background measurement angles, counting times, and data reduction for overlapping and matrix collections, and the final calibration are the most important parameters to consider. Fig. 1 shows X-ray scans for the major elements. As the background is curved for the Mg and Na K $\alpha$  regions (Figs. 1a, b), a curve fitting of the background with a Lagrange interpolation by four background measurements is applied. The same background measurement data are used to calculate each background for Na and Mg. The background counts of the Si K $\alpha$  and Al K $\alpha$  are small relative to the peak counts, and the background curves are flat (Fig. 1c). Kusano *et al.* (2015) did not measure backgrounds for Mg K $\alpha$ , Si K $\alpha$ , K K $\alpha$ , Ca K $\alpha$ , and Fe K $\alpha$  as peak-to-background X-ray count ratios are large. For the high-dilution glass beads, the backgrounds are largely a result of the Rayleigh scatter of continuous X-rays with flux. Therefore, the variation of background counts among the different sample compositions is relatively small. The concentration can be calculated by subtracting constant values as background values. However, it is still better to subtract measured backgrounds for elements with large count rates (Fig. 1c, e, f), reducing any small variation in the background value resulted from the variation of the sample composition. Bead03 measured only one background each for Si K $\alpha$  and Al K $\alpha$ . Furthermore, it is difficult to select a background position on the higher-angle side of Al K $\alpha$  (Fig. 1c) due to the Br L $\alpha$  peak and the limit of the goniometer. As the background profiles for Ti, Ca, K, Fe, and Mn show a slight slope, two background

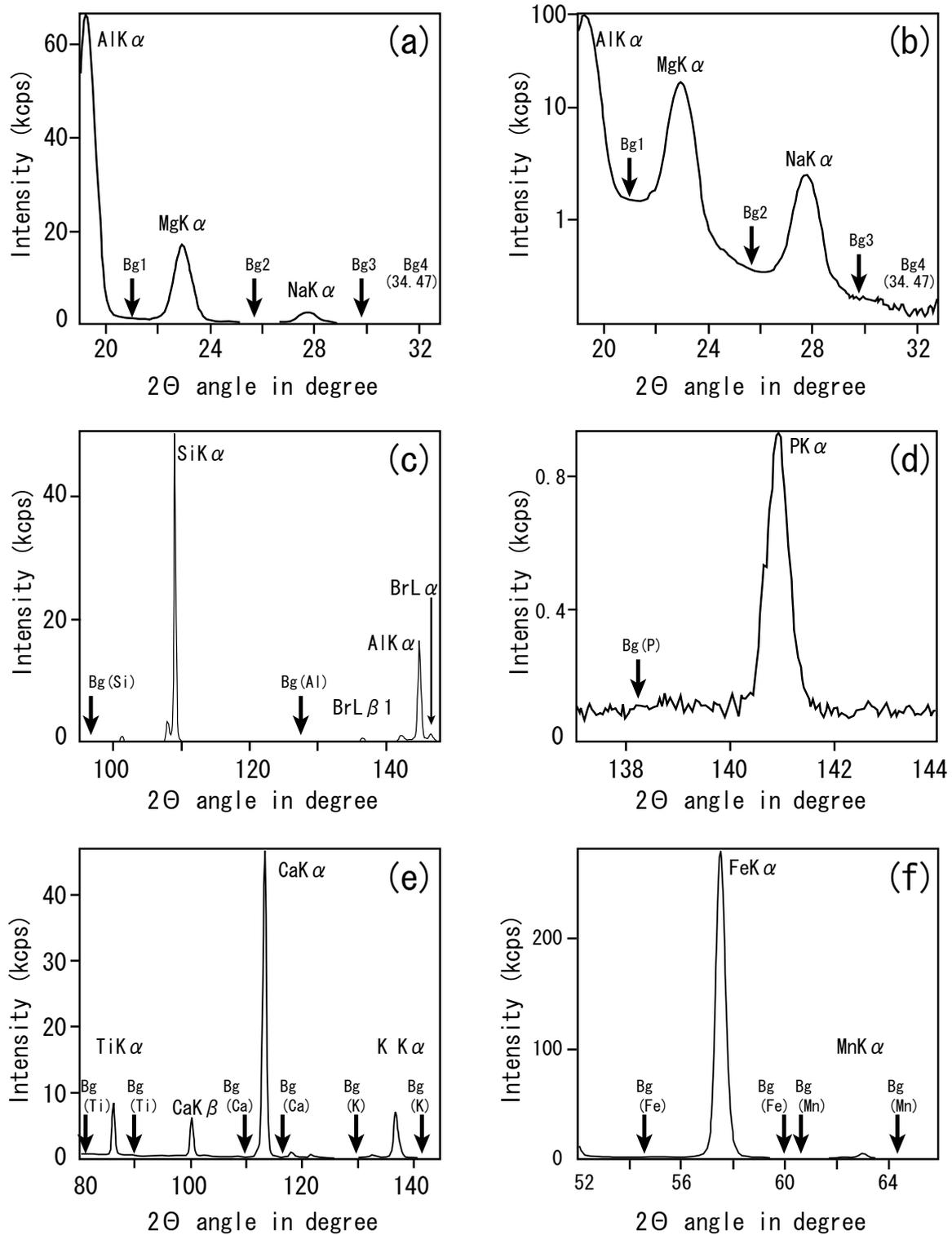


Fig. 1 X-ray scan profiles showing the peak and background positions.

The scan profiles are obtained on a glass bead of JB-1a.

(a) and (b): Na and Mg using PX1 analysis crystal. The X-ray intensity plotted (a) on a normal scale and (b) on a log scale. The position of background 4 is outside the range of this figure.

(c): Si and Al using PE (002)-C analysing crystal.

(d): P using Ge (111)-C analysing crystal.

(e): K, Ca, and Ti using PX10 analysing crystal.

(f): Mn and Fe using PX10 analysing crystal.

Table 4 Analytical conditions

Element	Line	Analyzing Crystal	Peak Angles (2θ°)	Background off set from peak (2θ°)				Collimator	Detector	PHA	Counting time (sec)	
				BG1	BG2	BG3	BG4				Peak	BG
Si	Kα	PE	109.0476	-12.9130				300μm	FPC	24-78	62	2
Ti	Kα	PX10	86.1732	-3.0290	4.1336			300μm	FPC	22-71	10	2
Al	Kα	PE	144.8556	-17.8686				300μm	FPC	22-81	20	20
Fe	Kα	PX10	57.5188	-2.6482	2.5000			300μm	Duplex	11-72	4	2
Mn	Kα	PX10	62.9826	-2.0874	1.4404			300μm	Duplex	11-70	8	2
Mg	Kα	PX1	22.9506	-2.0920	2.8790	6.8346	11.5206	700μm	FPC	23-83	60	8,10,4,2
Ca	Kα	PX10	113.1346	-3.7138	3.1282			300μm	FPC	27-73	10	2
Na	Kα	PX1	27.7374					700μm	FPC	27-80	60	
K	Kα	PX10	136.7228	-7.6928	6.1002			300μm	FPC	25-75	16	4
P	Kα	Ge	140.8998	-2.6934				300μm	FPC	32-70	16	4
Br	La	PE	146.4460					300μm	FPC	22-78	10	

PE: PET (002)-C

PX10: Synthetic crystal replacing LiF200 produced by PANalytical

Ge: Ge (111)-C

FPC: Flow proportional counter

PHA: Pulse height analyser setting

Table 5 Sensitivity and precision of calibration

	JB-1a					Calib. Cor.	Calib. Intercept D	Relative range of matrix correction values (%)	
	NetCount (kcps)	Background (kcps)	Sensitivity (kcps/%)	BEC (ppm)	LLD (ppm)			15 stds	13 stds
SiO <sub>2</sub>	51.05	0.021	0.974	221	131	0.99990	-0.0115	4.39	2.90
TiO <sub>2</sub>	7.93	0.568	6.193	917	52	0.99984	0.0038	10.91	5.43
Al <sub>2</sub> O <sub>3</sub>	16.11	0.041	1.115	365	83	0.99991	0.1609	7.07	3.59
Fe <sub>2</sub> O <sub>3</sub> *	294.02	2.893	32.488	891	23	0.99988	-0.0029	12.46	9.66
MnO	4.06	1.900	27.415	693	23	0.99944	-0.0006	12.15	8.46
MgO	16.24	0.982	2.075	4735	77	0.99998	0.1020	1.79	1.60
CaO	47.26	0.308	5.077	606	54	0.99998	-0.0133	8.51	5.08
Na <sub>2</sub> O	2.18	0.325	0.798	4080	122	0.99924	0.0537	2.04	2.04
K <sub>2</sub> O	6.91	0.171	4.933	347	30	0.99997	-0.0086	3.44	3.44
P <sub>2</sub> O <sub>5</sub>	0.80	0.056	3.084	180	34	0.99913	0.0012	2.59	2.59

BEC: Background equivalent concentration

LLD: Lower limit of detection

Calib. Cor. : Calibration correlation coefficient

Calib. Intercept D: Intercept (D) value of calibration equation

Relative range of matrix values (%): Relative range of matrix correction values.

15 stds: Relative range of matrix correction values for all 15 standards used for calibration.

13 stds: Relative range of matrix correction values for 13 standards, excluding JP-1 and JF-1.

Fe<sub>2</sub>O<sub>3</sub>\*: Total Fe as Fe<sub>2</sub>O<sub>3</sub>

measurements were used to obtain background counts. Background positions of other elements are shown in Table 4 and Fig. 1.

The performance of the analytical program was evaluated using various parameters. The sensitivities for the analyzed elements are shown in Table 5 and Fig. 2a. The sensitivities are expressed as counts per seconds for 1% of oxides of the elements that are present. The primary analytical conditions, i.e., the types of collimator,

analysing crystal, and detector, are shown in Fig. 2a. The sensitivities basically increase from 0.8 kcps/% of Na<sub>2</sub>O to 32 kcps/% of Fe<sub>2</sub>O<sub>3</sub> (Table 5). With the same analytical settings, the sensitivities are basically a function of the excitation efficiency of the fluorescence X-rays at the given kV and mA setting of the X-ray tube; i.e., Fe Kα is more effectively generated from the sample than Mn Kα under the same analytical condition (Fig. 2a). Even for an Fe<sub>2</sub>O<sub>3</sub> concentration of 15%, which is approximately

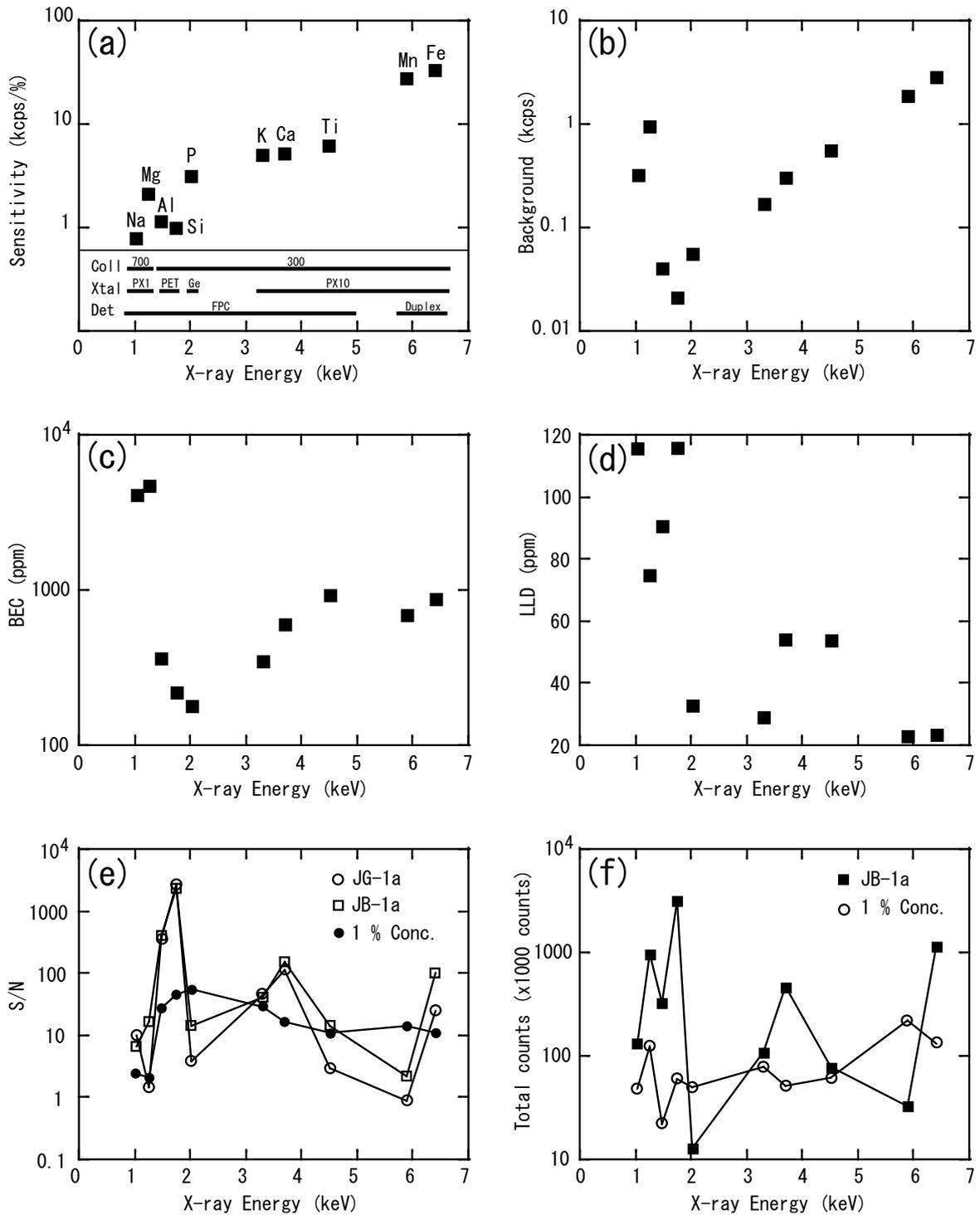


Fig. 2 Sensitivity and background equivalent concentration (BEC) and other parameters to optimize analytical conditions. Data are plotted with the X-ray energy of the respective elements. Names of elements are shown in (a).

- (a) Sensitivity. The sensitivity is expressed as counts per second for 1% of oxide of element present.
- (b) Background. Unit is count per second for a standard sample JB-1a.
- (c) Background equivalent concentration (BEC).
- (d) Lower limit of detection (LLD).
- (e) Signal noise ratio (S/N) = signal background ratio.
- (f) Total counts with the counting time of Bead03 for 1% oxide and JB-1a.

the maximum value in geological samples, the count rate does not exceed the maximum limit of the detector. This indicates that the 50 kV and 50 mA setting of the X-ray generator is appropriate. The background counts are low for Al and Si (Fig. 2b). Background equivalent concentrations (BEC) are calculated from the sensitivity and the background count rates; i.e., the background count rate is divided by the sensitivity (Fig. 2c). The BEC values range from 180 ppm to 920 ppm, with high values for Na<sub>2</sub>O and MgO of 4,100 ppm and 4,700 ppm, respectively (Table 5). The lower limit of detection (LLD) values range from 17 to 88 ppm (Table 5 and Fig. 2d). These values are sufficient for major element analysis. The signal/background ratios (S/B = S/N: signal/noise) for JG-1a, JB-1a, and 1% oxides are shown in Fig. 2(e). The 1% oxide values are obtained in order to indicate the S/N ratios independent of the concentrations of elements in the samples and are calculated from the signal intensities at the 1% concentration of each element. The 1% oxide S/N ratios range from 2.1 to 55 (Fig. 2e), indicating that the analytical parameters are appropriately selected for all elements measured. As natural geological samples, e.g., JG-1a and JB-1a, have high concentrations of SiO<sub>2</sub> and Al<sub>2</sub>O<sub>3</sub> (Fig. 2e), the S/B ratios of these elements are extremely high.

The counting times on peaks and backgrounds are given in Table 4. These times were optimized considering the sensitivity and other parameters. The total counts for 1% oxide contents and JB-1a are presented in Fig. 2f. The total counts for 1% oxide contents indicate the total counts independent of the concentrations of elements in the samples and are calculated from the total count of each element for JB-1a divided by the respective concentrations of the respective elements. Setting the counting time to have similar total counts for all of the analyzed elements is optimal. The total counts for most of elements of 1% concentration are approximately 100,000, indicating that all of the elements have similar precision. As the P<sub>2</sub>O<sub>5</sub> concentration of JB-1a is low at 0.24%, the total count of P<sub>2</sub>O<sub>5</sub> is somewhat low at 13,000. Using the above examination, the analytical conditions of Bead03 have been optimized.

## 5. Calibration

Calibration was made using 15 standard reference samples issued by the Geological Survey of Japan. The standards used are JA-1, JA-2, JA-3, JB-1a, JB-2, JB-3, JF-1, JG-1a, JG-2, JG-3, JGb-1, JGb-2, JH-1, JP-1, and JR-1. Before calculation of the calibration lines, background and line overlapping corrections are applied. A lower-angle-side tail of Br L $\alpha$  interferes with Al K $\alpha$ . In Bead03, this Br L $\alpha$  interference with Al K $\alpha$  is corrected using measured Br L $\alpha$  data. Because Al K $\alpha$  also interfere with Br L $\alpha$ , it may be better to use Br K $\beta$  for correction of this interference.

The calibration lines were prepared with full matrix

correction using classic theoretical alpha values. The theoretical alpha values were obtained using the SuperQ software program (PANalytical Co.). The alpha values were calculated using the composition of JA-1 as a typical compositional value among standards. SiO<sub>2</sub> was designated as the base component and was eliminated in order to obtain the alpha values using SuperQ.

The calibration was established by the following equation:

$$C_i = D_i + E_i \times R_i \times M_i \text{ -----(1)}$$

where

C<sub>i</sub>: concentration of component i

D<sub>i</sub>: intercept of component i

E<sub>i</sub>: slope of component i

R<sub>i</sub>: count rate of component i

M<sub>i</sub>: matrix correction value of component i.

The intercept is the point at which the calibration line intercepts the Y axis (Table 5), when data are plotted on a diagram with the count rate (X axis) and the concentration (Y axis).

The matrix correction values are calculated using the following equation:

$$M_i = 1 + \sum_{aj} \alpha_{ij} \times C_j \text{ -----(2)}$$

where

$\alpha_{ij}$ : theoretical alpha value of component i in the matrix of component j

C<sub>j</sub>: concentration of component j.

In the case of the calculation of unknown samples, nominal concentrations of components are derived without matrix correction, and further calculations are then performed using the nominal concentrations until the differences between the new and previous calculations become less than 0.01% or until the maximum number of iterations, 20, is reached in Bead03.

The calibration lines are shown in Fig. 3. The quality of calibration is expressed with the correlation coefficient (R) between the reference and calculated values. The correlation coefficients of all of the elements are better than 0.999, indicating that excellent calibration lines have been established. All of the standards are used to establish calibration lines, with the exception of Na<sub>2</sub>O of JP-1. The high MgO content of JP-1 slightly increases the background of Na<sub>2</sub>O. As the low Na<sub>2</sub>O concentration in the JP-1 was affected by this, the Na<sub>2</sub>O value of JP-1 was rejected from the calculation of the calibration line.

As the full matrix corrections with theoretical alpha were applied, the calibrations will work even slightly beyond the compositional ranges of standards used to establish the calibration. The effectiveness of matrix correction is examined with matrix correction values for standard samples. The relative ranges of matrix correction values (Table 5) among the standard samples used to establish the calibration lines are shown in Fig. 4a. The figure indicates that a maximum difference of 12% will result without the matrix correction. The relative ranges of matrix correction values are high for the heavy elements and low for the light elements. The small variation of the matrix effect on light

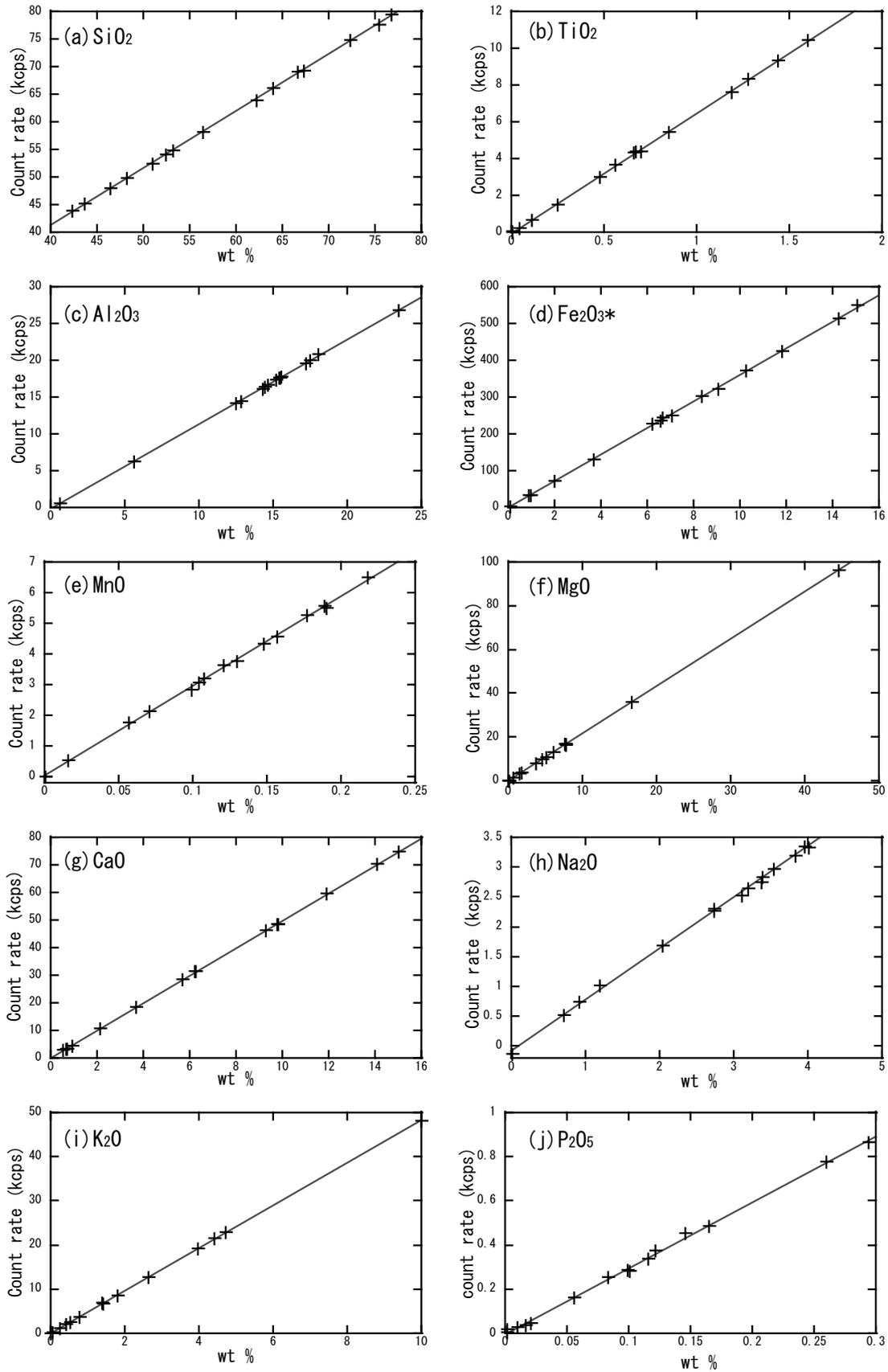


Fig. 3 Calibration lines, recommended value of standard samples vs. corrected count rate. The calibration lines are indicated.

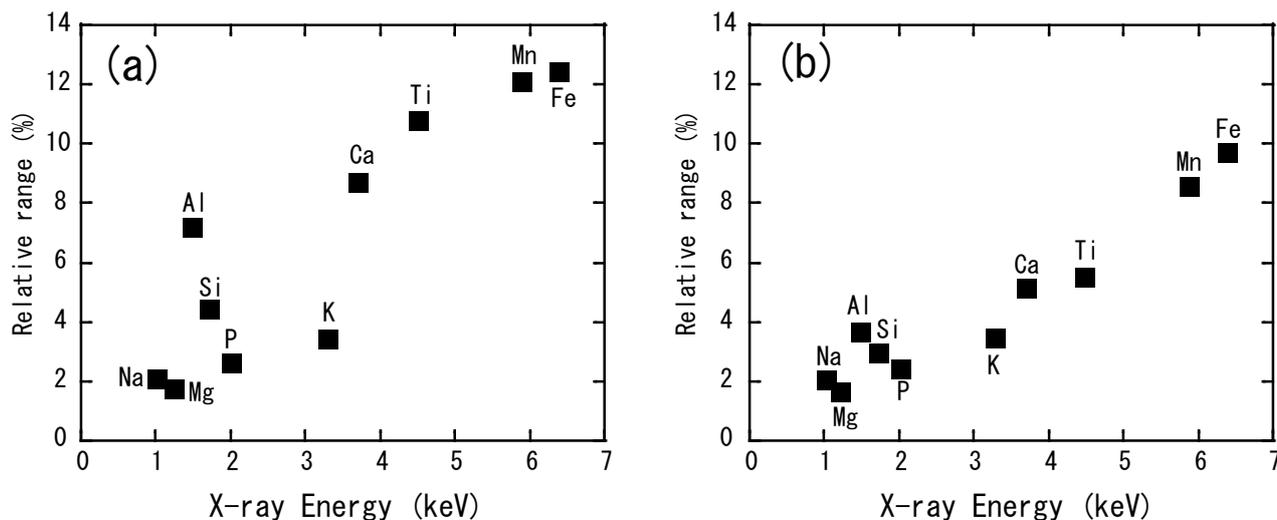


Fig. 4 Relative ranges of matrix correction values among standard samples plotted against the X-ray energy of each element.  
 (a) 15 standard samples used to prepare calibration lines.  
 (b) 13 standard samples without JP-1 and JF-1.

elements, such as Na and Mg, should be largely controlled by abundant oxygen and boron in glass beads. As oxygen and boron are major elements in lithium tetraborate flux, the variations of oxygen and boron abundances among samples are small, resulting in a small matrix effect among the samples. Fig. 4b shows the relative ranges of matrix correction values among the standard samples, excluding JP-1 and JF-1, and the high MgO and high K<sub>2</sub>O samples, respectively. The maximum relative ranges are reduced to less than 10%. The matrix correction values of Al and Si for JP-1 are large, thus the relative ranges of the Al and Si are reduced to less than 4% (Fig. 4b). Similarly, excluding the high K<sub>2</sub>O standard of JF-1 reduced the relative ranges of the matrix correction values of Ca, as the variation of matrix K<sub>2</sub>O content significantly influence Ca K $\alpha$ . Fig. 4b indicates that analytical results will be inaccurate to several percent without the matrix corrections.

## 6. Analytical precision

Precision (reproducibility) of analysis was evaluated with 10 repeated analyses of glass bead of JB-1a (Table 6). JB-1a is one of the 15 standards that can be used to establish the calibration lines. Thus, the analytical results should be the same as the reference values used for the calibration. The mean values of the ten analyses are approximately the same as those of the reference values. The standard deviations for each major element are low (less than 0.028). SiO<sub>2</sub> and Al<sub>2</sub>O<sub>3</sub> show slightly high standard deviations due to the high abundance of these elements in JB-1a. Excluding SiO<sub>2</sub> and Al<sub>2</sub>O<sub>3</sub>, these standard deviations are less than 0.013. The relative standard deviations are less than 1% for all elements. MnO and P<sub>2</sub>O<sub>5</sub>, which have abundances of less than 1%, have slightly high relative standard deviations of 0.91%

and 0.99%, respectively. For elements with concentrations between 1 and 3 wt.%, the relative standard deviations are between 0.35% and 0.39%. Elements with concentrations greater than 3 wt.% have relative standard deviations of less than 0.18%. The precision of the analysis of the present study is similar to those of Yamasaki (2014) and Kusano *et al.* (2015).

## 7. Discussion on the further improvement of analytical protocol

The objectives of the present report are the optimization of the XRF analysis of silicate rocks and the presentation of a detailed analytical method for use on Bead03. Although the program has been successfully used for the last 8 years, it is possible to further improve the program on several points, as discussed in the following.

### 7.1 Sensitivity of Na and Mg

The sensitivities of light elements, including Na, Mg, Al, and Si, are slightly low, especially Na, as compared to the other elements (Fig. 2a). Bead03 uses a tube setting of 50 kV and 50 mA. The optimal kV setting of the X-ray tube is considered to be three to four times the X-ray energy of the analyzed element. As the X-ray energy of Fe K $\alpha$  is 6.40 keV, a setting of 25 kV should be sufficient to generate Fe K $\alpha$  from the samples. It is empirically known that setting the kV value to be larger than the mA value is better for maintaining the lifetime of the X-ray tube. This is one reason for selecting the 50 kV and 50 mA setting. X-rays of any of the major elements from the silicate rocks do not saturate the detectors at this setting. For example, the count rate of Fe K $\alpha$  is still less than 1 million counts/second. Thus, the setting of 40 kV and 60 mA instead of 50 kV and 50 mA may be applied. Furthermore, evaluation

Table 6 Precision of analysis obtained based on the results of 10 measurements of a glass bead of JB-1a

(wt.%)	Rec.	Mean	StdDev	R.StdD(%)
SiO <sub>2</sub>	52.41	52.37	0.028	0.053
TiO <sub>2</sub>	1.28	1.29	0.005	0.388
Al <sub>2</sub> O <sub>3</sub>	14.45	14.31	0.026	0.183
Fe <sub>2</sub> O <sub>3</sub> *	9.05	8.97	0.008	0.092
MnO	0.15	0.15	0.001	0.907
MgO	7.83	7.70	0.011	0.137
CaO	9.31	9.31	0.013	0.143
Na <sub>2</sub> O	2.73	2.80	0.010	0.356
K <sub>2</sub> O	1.40	1.41	0.005	0.350
P <sub>2</sub> O <sub>5</sub>	0.26	0.26	0.003	0.992
Sum		98.58		

Rec: Recommended value of Imai *et al.* (1995)

StdDev: Standard deviation

R.StdD: Relative standard deviation

Fe<sub>2</sub>O<sub>3</sub>\*: Total Fe as Fe<sub>2</sub>O<sub>3</sub>

of the lifetime of the X-ray tube with frequently changing kV and mA settings during analysis is difficult, and a fixed setting of 40 kV and 60 mA may be optimal for major element analysis of geological samples.

## 7.2 Backgrounds for Na and Mg

Backgrounds for Na and Mg were calculated with curve fitting of four background measurements (Table 4). The curve fitting of the background for the Na and Mg is considered to be better than that of the two background measurements. Based on a detailed evaluation of the background data, the Al K $\alpha$  overlaps the lower 2 $\theta$  angle side of the Mg background and the Mg K $\alpha$  peak (Fig. 1b). The Mg K $\alpha$  peak also overlaps the background position between Mg K $\alpha$  and Na K $\alpha$ . The overlap of Mg will cause a small problem regarding the measurement of low concentration of Na<sub>2</sub>O with a high concentration of MgO, such as ultramafic rocks, as discussed previously. It may be possible to reduce these overlapping effects using a fine collimator of 150  $\mu$ m, although the sensitivity will be reduced by the fine collimator. Another possibility is to use the PX-8 analysing crystal, which has a slightly shorter d spacing, providing larger dispersion. As the lower 2 $\theta$  angle sides of the Mg K $\alpha$  peak and Na K $\alpha$  have been affected by Al K $\alpha$  and Mg K $\alpha$ , respectively, the background may be calculated by one background measurement with fixed slope factors, which are independently obtained samples without Al<sub>2</sub>O<sub>3</sub> and MgO.

## 7.3 Optimization of counting times on peak and background

The estimated total count for the 1% concentration of each element (Fig. 2f) is above 48,000, except for Al K $\alpha$ , which is 22,000. Thus, the counting time of the Al K $\alpha$  peak can be increased from 20 seconds to 60 seconds, similar

to that of the Si K $\alpha$ . The total count of P K $\alpha$  on JB-1a is low (Fig. 2f), as the concentration of P<sub>2</sub>O<sub>5</sub> in JB-1a is low. The concentrations of P<sub>2</sub>O<sub>5</sub> in typical silicate rocks are low, thus the counting time may be increased from 16 seconds to 30 or 40 seconds in order to provide better analytical precision. In the present analytical condition, the analysis of a sample takes approximately 8 minutes. As the Axios Advanced XRF accommodates 96 glass beads on the sample changer, it takes approximately 13 hours to complete all 96 samples. The total analytical time is effective for automatic overnight measurements. The small increase in measurement time may not affect the efficiency and can be evaluated.

## 8. Conclusion

Major element analysis with Bead03 program using glass bead has been prepared by the optimization of analytical parameters. The analysis has been successfully performed at the shared facility of the GSJ laboratory. The detailed analytical protocol of Bead03 has also been described. Optimization of the analytical condition that is suitable for geological samples was performed considering sensitivity, precision, and the lower limit of detection. Bead03 is generally used without frequent calibration. The user can make analysis with a minimum number of steps and through simple operation. High throughput analysis is also an important characteristic of this protocol. Bead03 has also allows 1) the overlapping correction of Br L $\alpha$  on Al K $\alpha$ , eliminating the effect from the releasing agent, LiBr, and 2) the curve fitting of backgrounds for Na K $\alpha$  and Mg K $\alpha$ . The present report also describes the quality of calibration lines for silicate rock samples and the analytical precision.

## Acknowledgement

The authors acknowledge the members of PANalytical Japan of SPECTRO Co. Ltd. for providing technical advice on XRF, and the late Mr. S. Ohta of Tokyo Kagaku Co. and Mr. M. Itoh of Amena Tech Co. for providing technical advice on the bead sampler equipment. We would also like to thank Dr. Y. Kon and the anonymous reviewers for their various constructive comments.

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Received December 20, 2016  
Accepted May 11, 2018

## ガラスビードを用いた蛍光 X 線分析 (XRF) による地質試料の主成分分析条件の最適化

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### 要 旨

ガラスビードを用いた蛍光 X 線分析 (XRF) による地質試料の主成分分析プログラム "Bead03" が作成され、地質調査総合センター共同利用実験室において多くの分析に用いられている。本分析プログラムは地質試料の分析において必要とされる感度や精度を考慮しつつ、シンプルな操作による分析を可能としている。本プログラムの詳細を示し、また分析条件の最適化のための検討結果を報告する。ガラスビードは分析試料の重量の10倍の融剤(四ホウ酸リチウム)を使用して作成し、また溶融用るつぼからガラスビードの剥離を図るため、臭化リチウムを使用した。XRF分析ではバックグラウンドの測定について詳細な検討を行った。理論アルファ値によるマトリックス補正を行い、その効果についても検討した。また本プログラムによる分析結果の精度の評価結果をまとめた。

