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Evaluation of major and trace element XRF analyses using a flux to sample ratio of two to one glass beads

Jun-ichi KIMURA* and Yasujiro YAMADA**

**Regional Sciences Laboratory, Faculty of Education, Fukushima University*
Matsukawa, Fukushima 960-12, Japan
***Rigaku Industrial Corporation*
Akaoji 14-4, Takatuki, Osaka 569, Japan

A high concentrated glass bead, with a flux to sample ratio of two to one, was prepared to evaluate the potential for major and trace element analyses of various silicate rocks by X-ray fluorescence spectrometry. Careful instrument set up, matrix effect and peak overlap corrections allowed enhanced accuracy of analysis. The accuracy reached a level comparable to that of using five to one glass beads for major elements and pressed powder pellets for trace elements. Using this method, major and trace element analyses were possible using one single glass bead.

Keywords: XRF spectrometry, Glass bead, Major element, Trace element

I. Introduction

If a powdered specimen is exposed to X-rays, the fluorescent X-ray intensities will depend in a complex way on the inhomogeneity of the powders and the particle size distribution of each of the mineral components (Claisse and Samson, 1962; Bernstein, 1963; Czamanske *et al.*, 1966; Goto and Oono, 1981). For sample preparation of X-ray fluorescent spectrometry, the use of fused glass beads is recommended. Various sample-flux mixing rates and various types of alkali flux have been tested for the method. The mixing rate varies from 100 : 1 (Claisse, 1956) to 1 : 1 (Andermann and Allen, 1961) as a flux to sample ratio. Norrish and Hutton (1969) proposed the use of Lithium tetraborate as a flux with a flux to sample ratio of 5 : 1. This ratio seems to be widely accepted for major element analysis, as while the matrix effect is not so serious, the fluorescent X-ray intensity is sufficient. However, many laboratories use pressed powder pellet specimens, besides the glass beads, for trace element analysis in order to gain greater fluorescent intensitiy.

Recently, the development of a high powered X-ray tube with improved fluorescent X-ray intensity, has made possible the use of glass beads for trace element analysis. Yamada *et al.* (1995) carried out analysis using glass beads with a flux to sample ratio of two to one (2 : 1 glass bead, here after). They reported that careful matrix correction can provide sufficient accuracy for major element analysis, and they also showed that glass beads can be used for trace element analysis of silicate rocks. The authors have examined the 2 : 1 glass bead method for major and trace element analyses of various igneous rocks. The technique for preparing glass beads was also examined. The accuracy of this method is investigated through a comparison with pressed powder pelettes. The standard addition method for trace ele-

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Table 1. Instrumental settings of X-ray fluorescent spectrometer

Element (Major)	Line	Angle (2θ) peak	BG.*1	BG.*2	Counting time(s) peak	BG.*	Analyzing crystal	Detector	Collimator
Si	Kα	109.06	106.54	111.04	40	20 x 2	PET	PC	Coarse
Ti	Kα	86.12	85.00	78.62	40	20 x 2	LiF(200)	SC	Coarse
Al	Kα	144.80	140.70	147.00	40	20 x 2	PET	PC	Coarse
Fe	Kα	57.50	56.02	59.02	40	20 x 2	LiF(200)	SC	Coarse
Mn	Kα	62.96	61.48	64.48	40	20 x 2	LiF(200)	SC	Coarse
Mg	Kα	45.25	42.75	47.75	40	20 x 2	TAP	PC	Coarse
Ca	Kα	61.95	59.60	64.95	40	20 x 2	Ge	PC	Coarse
Na	Kα	55.20	53.15	57.15	40	20 x 2	TAP	PC	Coarse
K	Kα	69.70	67.30	72.60	40	20 x 2	Ge	PC	Coarse
P	Kα	141.10	138.20	143.20	40	20 x 2	Ge	PC	Coarse
(Trace)									
Ba	Lα	87.135	84.950	-	1000	1000	LiF(200)	SC	Coarse
Ce	Lβ	71.600	71.000	72.800	1000	500 x 2	LiF(200)	SC	Coarse
Co	Kα	52.775	54.000	-	400	400	LiF(200)	SC	Fine
Cr	Kα	69.325	68.500	70.510	200	100 x 2	LiF(200)	SC	Coarse
Ga	Kα	38.880	38.550	39.500	400	200 x 2	LiF(200)	SC	Coarse
Nb	Kα	21.385	21.050	21.700	500	250 x 2	LiF(200)	SC	Fine
Ni	Lα	48.640	48.000	49.300	200	100 x 2	LiF(200)	SC	Coarse
Pb	Kα	28.240	27.840	28.640	200	100 x 2	LiF(200)	SC	Coarse
Rb	Kα	26.595	26.300	27.100	200	100 x 2	LiF(200)	SC	Fine
Sr	Kα	25.130	24.630	25.630	200	100 x 2	LiF(200)	SC	Fine
Th	Kα	27.455	27.100	27.780	400	200 x 2	LiF(200)	SC	Coarse
V	Kα	76.910	76.310	77.510	200	100 x 2	LiF(200)	SC	Fine
Y	Kα	23.745	23.180	24.530	200	100 x 2	LiF(200)	SC	Fine
Zr	Kα	22.495	22.200	23.100	200	100 x 2	LiF(200)	SC	Fine

ment analysis can also be used with this method.

II. Analytical procedure

1. Sample preparation

The samples used in this study were igneous rock and mineral standard samples provided by Geological Survey of Japan (GSJ): JB-1, JB-1a, JB-2, JB-3 basalts, JA-1, JA-2, JA-3 andesites, JR-1, JR-2 rhyolites, JP-1 peridotite, JGb-1 gabbro, and JG-1, JG-1a, JG-2, JG-3 granitoids, and JF-1 feldspar. For a test of actual analyte, JGb-2 gabbro and JR-3 rhyolite (GSJ), and KT-1 tephroite (Korean Institute of Energy and Resources) were used.

The alkali flux used was a mixture of Lithium tetraborate ($Li_2B_4O_7$: MERCK) and Lithium metaborate ($LiBO_2$: MERCK) with a mixing rate of 8 : 2. The addition of $LiBO_2$ decreases the melting point of Lithium tetraborate (Sastry and Hummel, 1959), and increases alkalinity resulting in a decrease in melt viscosity decrease (Norrish and Hutton, 1969). The two alkali fluxes were ignited to ~500°C prior to weighing, cooled down in a desiccater box, and then ground by an agate motor for ten minutes. The mixed powder was kept in a polyethylene bottle in the desiccater box.

Table 2. Results of reproducibility tests for major and trace elements

Element	Average	1σ error	C.V.max	Element	Average	1σ error	C.V.max
Major	(wt.%)	(wt.%)	(%)	Trace	(ppm)	(ppm)	(%)
SiO_2	52.92	0.016	0.052	Ba	308.4	7.3	3.6
TiO_2	0.66	0.002	0.467	Ce	32.5	1.9	4.4
Al_2O_3	12.88	0.009	0.121	Co	33.1	0.7	4.9
Fe_2O_3	7.03	0.007	0.131	Cr	492.1	9.4	3.8
MnO	0.14	0.001	0.801	Ga	16.7	0.3	2.7
MgO	3.68	0.007	0.420	Nb	9.6	0.1	2.3
CaO	12.90	0.008	0.111	Ni	146.0	1.1	1.1
Na_2O	7.98	0.016	0.379	Pb	19.8	0.6	6.5
K_2O	1.52	0.001	0.140	Rb	70.4	0.2	0.5
P_2O_5	0.28	0.001	0.645	Sr	249.3	0.8	0.7
Total	100.00			Th	4.9	0.3	9.9
				V	130.5	3.8	6.0
				Y	16.2	0.2	1.6
				Zr	116.6	0.8	2.0

Statistical results are shown as one sigma errors and the maximum coefficient of variations (C.V. max.). The analyzed sample is JA-2.

The rock specimens were ground using an agate motor, and then ignited in a muffle furnace for two hours over 1000°C. Specimens for analysis were prepared by mixing 3.6 g of the mixed flux and 1.8 g of the powdered rock sample. No other reagents were added in order to prevent contamination of trace elements. The mixture was put into a platinum crucible (alloy of Pt with 5% Au).

An automated high frequency bead sampler (NT-2100: Tokyo Kagaku Co.) was used for heating and mixing the specimens. Each specimen was heated to 1200°C for 3 minutes until totally dissolved. The melt was stirred and swirled automatically for a further 6 minutes. The heated specimen was naturally cooled within the heater mantle until the surface color turned dark red (~600°C), and then moved to a fan cooler site facilitated by the bead sampler.

In cases where strong alkali rocks or alkali-rich minerals, such as feldspar and a Fe-rich basalt specimen, were fused, removing the glass beads was difficult. A small amount (~100 μl) of HCl was added to the specimen, and was fused and stirred again for about 3 minutes. The addition of HCl did not interfere with the X-ray fluorescence of the elements of

Table 3. Matrix correction factors for major elements

Element	SiO_2	TiO_2	Al_2O_3	Fe_2O_3	MnO	MgO	CaO	Na_2O	K_2O	P_2O_5	Error	Error*
Line	SiKα	TiKα	AlKα	FeKα	MnKα	MgKα	CaKα	NaKα	KKα	PKα	(wt.%)	(wt.%)
Correction factor for 5:1 glass bead												
SiO_2	-	0.00072	0.00457	0.00113	0.00645	0.00031	-0.00137	0.00242	-0.00249	-0.00082	0.322	0.374
TiO_2	-0.00438	-	0.00434	0.02325	0.02254	0.00507	-0.00518	0.00558	-0.00531	-0.00473	0.010	0.017
Al_2O_3	0.00166	-0.00113	-	-0.00125	-0.00123	-0.00090	-0.00104	-0.00092	-0.00098	-0.00064	0.177	0.182
Fe_2O_3	-0.00145	-0.00472	0.01168	-	0.00307	0.01239	-0.00397	0.01271	-0.00363	-0.00189	0.057	0.115
MnO	-0.00199	-0.00490	0.00103	0.00619	-	0.01095	-0.00452	0.01126	-0.00423	-0.00246	0.008	0.015
MgO	-0.00091	-0.00176	0.01429	-0.00196	-0.00192	-	-0.00164	-0.00211	-0.00157	-0.00123	0.227	0.211
CaO	-0.00509	0.02135	0.00270	0.02362	0.02310	0.00338	-	0.00389	-0.00465	-0.00539	0.069	0.098
Na_2O	-0.00156	-0.00270	0.01192	-0.00296	-0.00291	0.01292	-0.00253	-	-0.00243	-0.00193	0.036	0.091
K_2O	-0.00570	0.02048	0.00129	0.02330	0.02268	0.00187	0.01877	0.00229	-	-0.00594	0.026	0.098
P_2O_5	-0.00559	0.00073	0.00076	0.00090	0.00087	0.00080	0.00063	0.00086	0.00056	-	0.004	0.023
Correction factor for 2:1 glass bead												
SiO_2	-	0.00139	0.00673	0.00182	0.00789	0.00239	-0.00221	0.00410	-0.00312	-0.00147	0.217	0.374
TiO_2	-0.00437	-	0.00436	0.02325	0.02254	0.00509	-0.00516	0.00560	-0.00528	-0.00472	0.010	0.017
Al_2O_3	0.00000	-0.00113	-	-0.00125	-0.00123	-0.00088	-0.00104	-0.00090	-0.00098	-0.00064	0.153	0.182
Fe_2O_3	-0.00144	-0.00469	0.01170	-	0.00306	0.01243	-0.00393	0.01274	-0.00357	-0.00188	0.077	0.115
MnO	-0.00198	-0.00491	0.01028	0.00618	-	0.01099	-0.00447	0.01128	-0.00417	-0.00245	0.007	0.015
MgO	-0.00091	-0.00176	0.01431	-0.00196	-0.00192	-	-0.00164	-0.00208	-0.00157	-0.00123	0.217	0.211
CaO	-0.00508	0.02135	0.00271	0.02362	0.02310	0.00340	-	0.00391	-0.00463	-0.00539	0.080	0.098
Na_2O	-0.00156	-0.00270	0.01194	-0.00296	-0.00291	0.01295	-0.00253	-	-0.00243	-0.00193	0.048	0.091
K_2O	-0.00569	0.02048	0.00131	0.02330	0.02268	0.00189	0.01877	0.00231	-	-0.00594	0.021	0.098
P_2O_5	-0.00558	0.00073	0.00077	0.00090	0.00087	0.00081	0.00063	0.00087	0.00056	-	0.004	0.023

No significant difference has seen between 1 : 5 (upper) and 1 : 2 (lower) glass beads. Error shows the accuracy of calibration lines calculated by Error=$\sqrt{\Sigma(Cm-Cr)^2/(n-2)}$, where Cm=measured value, Cr=recommended value, and n=number of samples. Error* indicates the accuracy of calibration lines obtained from the pressed powder pellet method by Tsuchiya *et al.* (1989) shown for comparison.

interest. The amount of HCl added was the equivalent of ~0.1 wt.% of bulk rock composition, which did not significantly change the matrix. The additional heating had no effect on the element concentration ratios, including alkalis.

2. Standard addition

One of the advantages of the glass bead method is that it is easy to prepare homogenized specimens. This allows the application of the following techniques to XRF analysis: addition of trace element(s) to a standard rocks producing qualified synthetic standards, direct determination of interference coefficients for peak overlap corrections by the incremental addition of an interfering element, and the standard addition technique for trace element analysis of an unknown sample.

There is a problem with this method in the case of a solid standard material due to the difficulty of accurately weighing a trace amount. Thus, standard solutions of 1000 ppm (Wako Chemicals Co.) were used for the addition of standard materials. An appropriate amount of standard solution was pipetted by a micro-syringe onto the surface of the sample-flux mixture in a Pt crucible. The specimen was dried at 110°C in a drying oven for about 1 hour. The samples were fused by a bead sampler according to the above procedure.

3. Instrument conditions

The X-ray fluorescence spectrometer used was a Rigaku RIX 2000 at the Department of Geology, Faculty of Education, Fukushima University. An end-window type Rh anode X-ray tube (TOSHIBA Electronic Co.) was fitted in the spectrometer. The accelerating voltage and tube current were set at 50 kV and 50 mA, respectively.

An automated wavelength-range scan program of the RIX 2000 was used to determine the analyzer crystals, the wavelength positions at

Table 4. Comparison of signal intensities of JB-1 using various specimens

a) Major elements (net kcps)				b) Trace elements (net kcps)				c) Trace elements (Ip/Ib)			
Element	2:1 bead	5:1 bead	R.I.*	Element	2:1 bead	powder	R.I.*	Element	2:1 bead	powder	R.I.*
SiO_2	164.675	93.429	1.76	Ba	0.0905	0.1241	0.73	Ba	0.8586	1.6591	0.52
TiO_2	3.763	2.629	1.43	Ce	0.0144	0.021	0.69	Ce	0.0784	0.1464	0.54
Al_2O_3	55.441	29.669	1.87	Co	0.2163	0.2498	0.87	Co	0.7692	1.2021	0.64
Fe_2O_3	213.047	155.505	1.37	Cr	0.3224	0.3576	0.90	Cr	4.3745	6.1762	0.71
MnO	2.629	1.875	1.40	Ga	0.1692	-	-	Ga	0.0924	-	-
MgO	10.026	5.224	1.92	Nb	0.8781	0.975	0.90	Nb	0.1936	0.4461	0.43
CaO	103.836	68.406	1.52	Ni	0.4816	0.4792	1.01	Ni	1.5031	2.4399	0.62
Na_2O	1.282	0.672	1.91	Pb	0.0588	0.0649	0.91	Pb	0.0120	0.0256	0.47
K_2O	11.974	7.667	1.56	Rb	0.6877	0.7425	0.93	Rb	0.2983	0.6291	0.47
P_2O_5	1.823	1.175	1.55	Sr	7.8239	9.5505	0.82	Sr	2.7872	6.7514	0.41
				Th	0.8469	0.0662	12.79	Th	0.1823	0.0621	2.93
				V	0.0783	0.0927	0.84	V	0.8671	1.1142	0.78
				Y	0.5619	0.7041	0.80	Y	0.1683	0.4268	0.39
				Zr	4.0248	4.8968	0.82	Zr	1.0084	2.4421	0.41

a) Major element net intensities of 1 : 5 and 1 : 2 glass beads with relative intensities (R.I.*), b) Trace element net intensities of 1 : 2 glass bead and powder pellet specimens with relative intensities (R.I.), c) Ip/Ib ratio values of trace elements from 1 : 2 glass bead and powder pellet specimens, with relative intensities.

peaks and backgrounds of analyzed spectra, and the setting up of the energy path range of the pulse height analyzer. The analyzed elements were SiO_2, TiO_2, Al_2O_3, Fe_2O_3, MnO, MgO, CaO, Na_2O, K_2O, and P_2O_5 for major elements, and Ba, Ce, Co, Cr, Ga, Nb, Ni, Pb, Rb, Sr, Th, V, Y, and Zr for trace elements. Standard addition samples were used for trace element setting. Table 1 shows the instrument setting. A series of 10-times reproducibility tests were performed to determine the counting times until the statistical errors reached a required minimum (Table 2).

4. Setting up of calibration lines for major elements

Matrix correction is necessary for XRF analysis (Czamanske *et al.*, 1966, and others). Even with a dilution factor of 10 times, the X-ray fluorescent intensity of an element is affected by the enhancement or suppression from coexisting matrices (Norrish and Chapel, 1977; Sugisaki *et al.*, 1977; Nakada *et al.*, 1985, Tsuchiya *et al.*, 1989, and others). Matrix correction factors were determined by using the sixteen GSJ samples. A computer program in the RIX 2000 system has an automated calculation sequence for the correction. A series of convergent calculations are made based on measured X-ray intensities of elements and the fundamental parameters (RIGAKU Denki Co., 1982; Kohno *et al.*, 1988; Murata *et al.*, 1988; Murata, 1993). For a detailed explanation of the calculation process, see the relevant reports.

The matrix factors were determined for both the 2 : 1 and 5 : 1 glass beads (Table 3). There were slight differences observed between the matrix correction factors for 5 : 1 and 2 : 1 glass beads under the same instrument conditions. Table 3 shows the errors of the calibration lines (in wt.%) for 2 : 1 and for 5 : 1 glass beads. Generally, 5 : 1 glass beads gave smaller errors than 2 : 1 glass beads. The accuracy of 2 : 1 glass beads method was better than that of previous reports (Sugisaki *et al.*, 1977; Matsumoto and Urabe, 1980; Nakada *et al.*, 1985; Tsuchiya *et al.*, 1989). It is notable that the analytical accuracy of elements that have lower concentrations in rocks, such as TiO_2, MnO, and P_2O_5, have improved by one order of magnitude. This may due to the increase of fluorescent X-ray intensities by using high concentration glass beads (Table 4a).

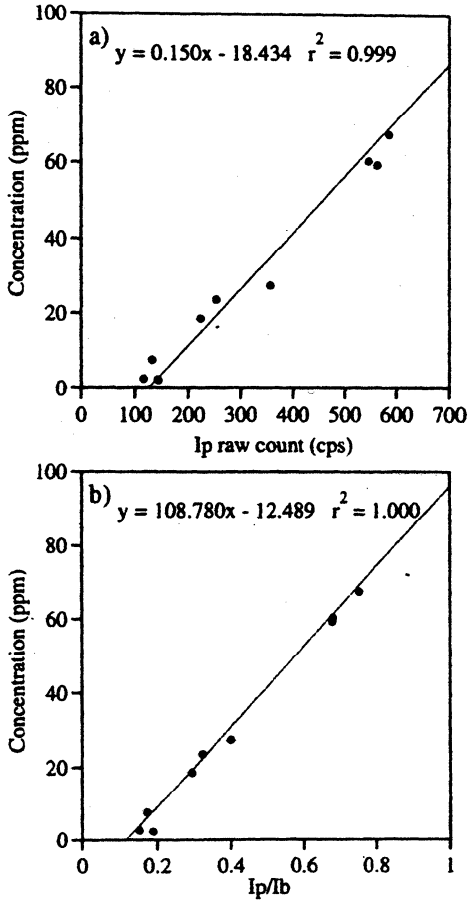

Fig. 1. Comparison of calibration lines and statistical values in Chromium
Staistical value (r^2) is improved from a) using Ip raw count data set to b) after making Ip/Ib matrix correction.

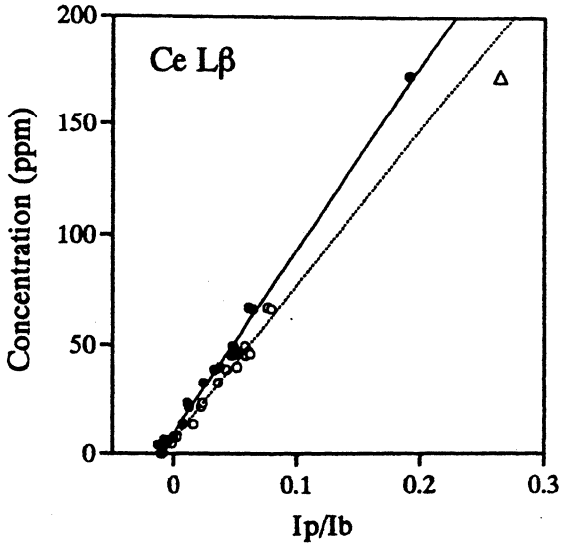

Fig. 2. Comparison of Ce Lβ calibration lines with or without Zr overlap correction.
Ce Lβ is affected by the Zr Kα2 line, and the measured Ip/Ib of KT-1 (open triangle) is identically differ from calibration line (dotted line) made by GSJ standards (open circles) without peak overlap correction. Solid circles are results after peak overlap correction.

5. Setting up of calibration lines for trace elements

Goto (1976) compared the intensities of fluorescent X-rays of powdered pellet specimens with those of 10 : 1 glass bead, and found that the glass bead showed higher intensities in some of the elements. Nakada (1985) proposed that the use of alkali flux decreases the mass absorption effect in a glass bead resulting in an increase of fluorescent X-rays. The Ip (net) values measured by 2 : 1 glass bead surpassed those of powder pellets in Ni and Th, were approximately 80% for other elements (Table 4b). For trace element measurement, Ip/Ib (net over background intensity, or S/N) ratios are more important. The Ip/Ib values of 2 : 1 glass beads range from one third to three times of the magnitude of values from powder pellets, and were usually approximately 60% (Table 4c). This indicates that glass beads have a higher background as well as peaks. The Ni Lα line is affected by the irradiated Ni Lα emission from the impurity contained in the X-ray tube, resulting in the apparent higher count rate. The reason of higher count rate found in Th Kα is unknown. The integration counting times for trace elements were determined by a series of 10-times reproducibility tests (Table 1).

There are three types of matrix correction methods that are applicable to trace element analysis. One method uses the Compton scatter as an estimation of bulk mass absorption coefficient (Reynols, 1963; Nesbitt *et al.*, 1976, and others). The coefficient can also be calculated from major element compositions, if these have been measured before. Another method involves calculating the matrix correction fac-

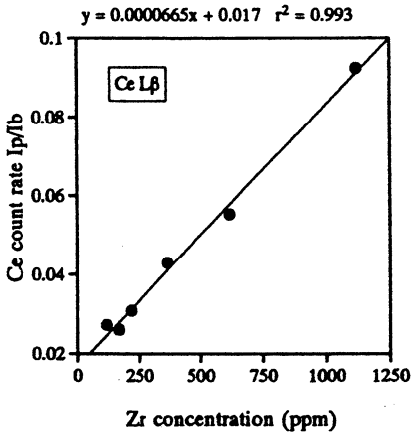

Fig. 3. Increment of Ce Lβ count rate by the addition of Zr standard.
The addition of Zr clearly affects the count rate of Ce Kβ.

Table 5. Calculated results of calibration lines for trace elements with overlap correction factors and errors

Element	Slope a	Intercept b	overlap coefficient	overlap element	Error (ppm)	1σ error (ppm)	Error* (ppm)	1σ error* (ppm)
Ba	804.02	-131.41	-48	TiO_2 (wt.%)	12.6	10.1	16.6	7.4
Ce	849.78	9.60	-0.12	Zr (ppm)	2.5	2.2	5.6	2.0
Co	102.98	-15.42	-75	Fe_2O_3 (wt.%)	2.8	1.0	3.5	0.7
Cr	108.93	-14.32	-0.1	V (ppm)	5.8	3.9	9.0	9.8
Ga	169.86	2.11	-	-	0.6	0.3	-	-
Nb	177.90	0.41	2.0	Y (ppm)	0.8	0.3	0.4	0.1
Ni	120.88	-38.32	-	-	2.3	2.4	5.8	1.2
Pb	648.84	-0.50	-	-	1.1	0.9	1.1	0.6
Rb	152.13	-5.35	-	-	2.5	0.6	3.0	0.2
Sr	157.02	-0.30	-	-	2.3	1.3	5.8	0.8
Th	344.39	-55.26	-	-	0.7	0.4	0.9	0.3
V	247.27	0.89	-	-	7.1	4.4	15.1	3.6
Y	170.91	2.32	-54.6	Rb (ppm)	1.8	0.4	2.8	0.2
Zr	186.79	-2.20	-17.9	Sr (ppm)	3.7	0.5	5.2	0.9

Values of slope (=a) and intercept (=b) are given as Y (conc.) = a X (Ip/Ib) + b. Overlap coefficients (=c) are Ip (corrected) = Ip (measured) - cX, where X is the calculated concentration of interfere elements by wt.% or ppm. Error and 1σ error indicate errors of calibration lines and one sigma deviations of ten times reproducibility test. Error* and 1σ error* show the results by the powder pellet method, in the same manner, and measured under the same instrumental conditions.

tors using the same procedure as for the major elements. The third method is the same as that of Murata (Murata, 1993), which is the so called Ip/Ib method, and is based on the assumption that the wavelengths of the peak and backgrounds of an element are situated close to each other. These would be affected by a bulk mass absorption effect at nearly the same amount (Anderman and Kemp, 1958; Murata, 1993). Fig. 1 shows an example of the effect of matrix correction by this method for chromium.

For trace element analysis, peak overlaps from coexisting elements are a problem. Fig. 2 shows an example of CeLβ interfered by ZrKα2. Analyzed tephroite, KT-1 contains high Zr and Ce. Without an overlap correction, the CeLβ calibration line (right) is drawn identically off from the actual concentration (175 ppm) of KT-1. The overlap from ZrKα2 leads an overestimation of the concentration (192 ppm, +9.7% from a reference value by Murata, 1993). The most straightforward technique involves the addition of a certain amount of an interfering element to a specimen and determination of the correction factor. Fig. 3 shows that the increment of the count rate of CeLβ by the addition of Zr. Other overlap correction coefficients are also determined by this method. The GSJ standard and their recommended values (Ando *et al.*, 1987 and Itoh *et al.*, 1992) were used to determine the overlap coefficients from major elements for BaLα, CoKα, and VKα. Table 5 shows the overlap correction coefficients with calibration line errors.

All the calibration lines were calculated by linear least square regression (Fig. 4). The curves include both the results from GSJ standard samples and from the addition of standard samples. The two sets of calibration lines do not differ greatly. Calibration lines are extendible over 1000 ppm by a standard addition. This is valuable for measuring rocks that have naturally high trace element concentrations.

III. Analytical results and potential of XRF analysis using 2 : 1 glass beads

1. Accuracy and precision

Table 5 shows the results of reproducibility

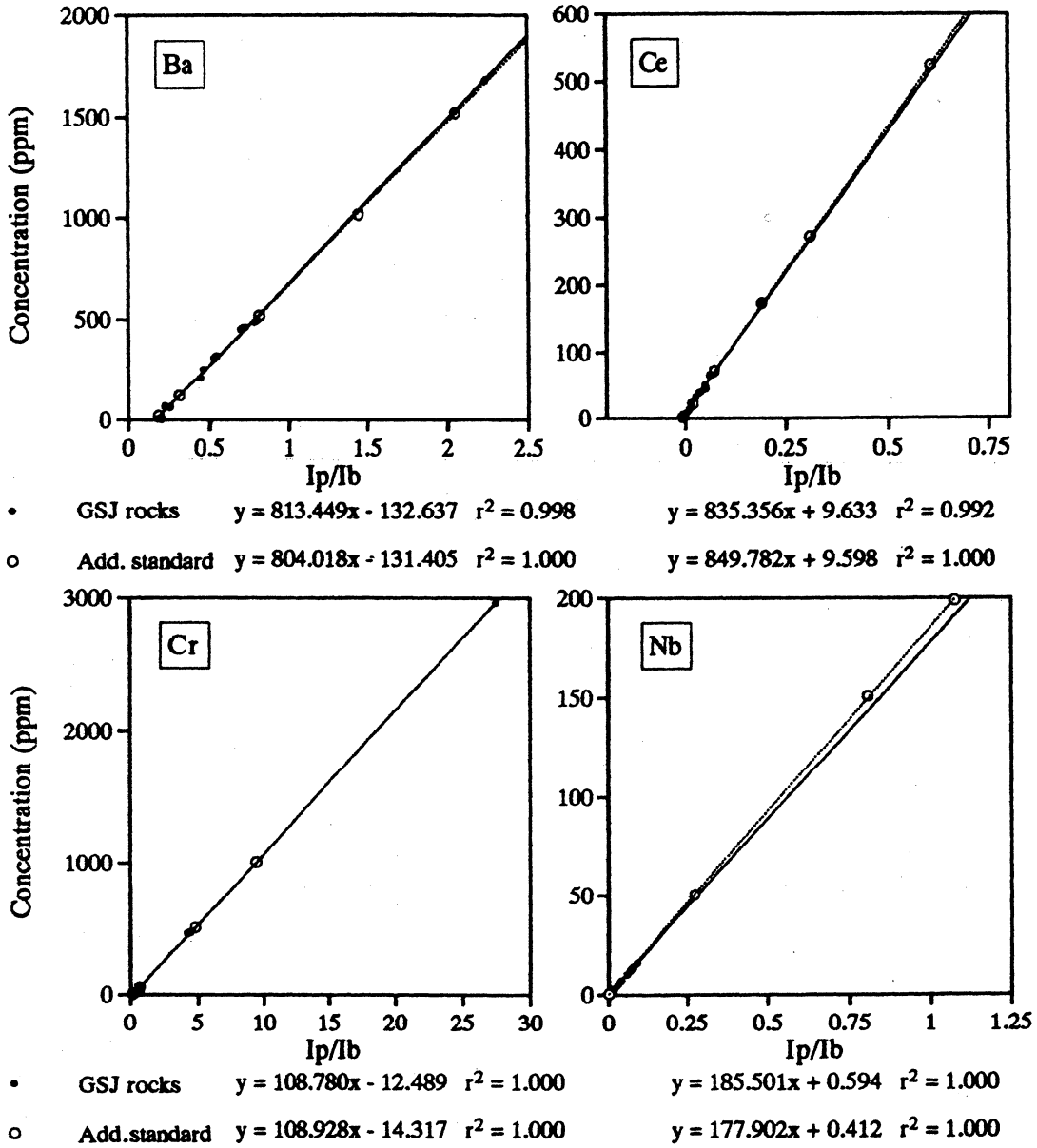

Fig. 4. Comparison of calibration lines obtained from GSJ geostandard samples and synthetic addition standard samples.
The solid line is the linear regression curve from GSJ standard samples (solid circles), and the dotted line is that from the addition standard specimen. Both the curves are very similar, indicating that the standard addition works well and extends the calibration lines.

tests and errors of the calibration lines of 2 : 1 glass beads and powder pellets measured under the same instrument conditions. The precision, indicated as 1σ error in ppm, shows that the glass bead method is a slightly inferior to the method using pressed powder pellets. However, despite the slightly lower degree of precision, the error of the glass bead method performed with better accuracy for most of the elements. Glass bead sampling can overcome dissimilarities in mineral grinding properties (Claisse and Samson, 1962; Bernstein, 1963; Welday *et al.*, 1964; Czamanske *et al.*, 1966; Goto and Oono, 1981), and particularly the "biotite effect" (Volborth, 1963) in acid rocks. Table 6 shows the analytical results of the major and trace elements of GSJ standard samples by the 2 : 1 glass bead method. The

Table 6. Determined concentrations of major and trace elements in GSJ geostandard samples

Element		JA-1		JA-2		JA-3		JB-1		JB-1a		JB-2		JB-3		JF-1		JG-1	
(wt.%)	Ref*	XRF	R.V.	XRF	R.V.	XRF	R.V.	XRF	R.V.	XRF	R.V.	XRF	R.V.	XRF	R.V.	XRF	R.V.	XRF	R.V.
SiO_2	1	64.23	64.64	57.36	57.59	62.29	62.40	52.63	52.92	52.55	52.89	52.54	52.81	50.71	50.90	n.e.	n.e.	72.75	72.75
TiO_2	1	0.87	0.88	0.70	0.69	0.69	0.68	1.35	1.36	1.34	1.32	1.18	1.18	1.45	1.45	n.e.	n.e.	0.27	0.26
Al_2O_3	1	15.26	15.12	15.94	15.70	15.83	15.61	14.71	14.74	14.65	14.71	14.53	14.56	17.14	16.84	n.e.	n.e.	14.31	14.29
Fe_2O_3	1	7.04	7.01	6.55	6.24	6.75	6.55	9.16	9.01	9.16	9.23	14.21	14.12	11.86	11.76	n.e.	n.e.	2.15	2.20
MnO	1	0.15	0.15	0.11	0.11	0.11	0.11	0.15	0.16	0.14	0.15	0.21	0.20	0.17	0.16	n.e.	n.e.	0.07	0.06
MgO	1	1.53	1.62	7.93	7.87	3.75	3.66	7.94	7.84	8.02	7.86	4.69	4.63	5.24	5.19	n.e.	n.e.	0.69	0.74
CaO	1	5.72	5.73	6.54	6.64	6.36	6.29	9.53	9.42	9.57	9.36	9.76	9.82	9.84	9.83	n.e.	n.e.	2.20	2.19
Na_2O	1	3.94	3.90	3.14	3.16	3.25	3.18	2.81	2.83	2.80	2.78	2.07	2.17	2.81	2.81	n.e.	n.e.	3.40	3.41
K_2O	1	0.77	0.79	1.85	1.84	1.42	1.41	1.46	1.45	1.37	1.44	0.42	0.42	0.78	0.78	n.e.	n.e.	4.04	4.00
P_2O_5	1	0.16	0.16	0.16	0.15	0.11	0.11	0.26	0.26	0.24	0.26	0.09	0.10	0.29	0.29	n.e.	n.e.	0.09	0.10
Total		99.66	100.00	100.27	100.00	100.56	100.00	100.01	100.00	99.83	100.00	99.69	100.00	100.27	100.00	n.e.	n.e.	99.95	100.00
(ppm)	Ref*	XRF	R.V.	XRF	R.V.	XRF	R.V.	XRF	R.V.	XRF	R.V.	XRF	R.V.	XRF	R.V.	XRF	R.V.	XRF	R.V.
Ba	1	313	307	319	317	326	318	496	509.6	519	497	223	208	236	251	1677	1680	482	475
Ce	2	12	13.5	35	32.7	24	23.3	65	66.7	66	66.1	6	6.8	20	21.5	2	4.3	53	46.6
Co	1	19	11.8	36	30	24	21	40	38.7	41	39.5	39	39.8	36	36.3	nd.	0.2	4	4
Cr	1	10	7.3	456	465	69	67.5	467	469	413	415	29	27.4	60	60.4	6	5.8	73	64.6
Ga	1	17.5	17.3	16.4	16.4	16.8	17	18.1	18.1	17.5	18	17	17.1	19.6	20.3	18.6	18.1	17.9	17
Nb	1	1.9	1.7	8.5	9.8	3.1	3.0	35.0	34.5	26.5	27.0	0.5	0.8	2.2	2.3	0.4	0.5	11.1	12.6
Ni	1	6	1.8	143	142	35	35.5	141	139	139	140	19	13.3	40	38.8	1	0.4	6	6
Pb	1	6	5.8	19	19.3	7	6.7	7	7.1	8	7.2	5	5.4	4	5.5	37	33.4	27	26.2
Rb	1	12	11.8	69	68	36	36	40	41.2	40	41	6	6.2	13	13	260	264	181	181
Sr	1	262	266	249	252	287	287	431	435	443	443	173	170	389	393	165	163	184	184
Th	1	1.2	0.8	4.7	4.7	3.2	3.4	8.4	9.2	8.8	8.8	nd.	0.3	1.3	1.3	nd.	1.3	14.0	13.5
V	1	117	105	135	130	188	172	211	212	210	220	585	578	376	383	nd.	-	22	25
Y	2	29.0	30.6	15.9	18.1	19.3	21.3	20.8	24.4	20.6	24	23.8	24.9	25.3	27	4.3	4	29.8	28.5
Zr	2	86	88.3	115	119	118	119	139	143	140	146	42	51.4	95	98.3	12	41	122	114

Element		JG-1a		JG-2		JG-3		JGb-1		JP-1		JR-1		JR-2		JGb-2		JR-3	
(wt.%)	Ref*	XRF	R.V.	XRF	R.V.	XRF	R.V.	XRF	R.V.	XRF	R.V.	XRF	R.V.	XRF	R.V.	XRF	R.V.	XRF	R.V.
SiO_2	1	73.08	71.99	77.39	77.37	67.79	67.63	44.23	43.76	43.72	43.83	76.36	76.40	76.86	76.79	46.85	n.a.	73.65	n.a.
TiO_2	1	0.25	0.25	0.05	0.04	0.48	0.48	1.64	1.63	0.00	-	0.11	0.10	0.07	0.09	0.60	n.a.	0.22	n.a.
Al_2O_3	1	14.30	14.18	12.60	12.48	15.64	15.64	17.55	17.78	0.66	0.64	13.02	13.06	12.90	13.01	23.72	n.a.	11.70	n.a.
Fe_2O_3	1	2.04	2.50	0.93	0.94	3.81	3.74	15.09	15.16	8.02	8.55	0.87	0.96	0.73	0.87	7.07	n.a.	4.64	n.a.
MnO	1	0.06	0.06	0.02	0.02	0.07	0.07	0.18	0.17	0.11	0.12	0.11	0.10	0.12	0.11	0.14	n.a.	0.08	n.a.
MgO	1	0.63	0.69	0.01	0.04	1.75	1.80	8.11	7.89	46.41	46.24	0.09	0.09	0.01	0.05	6.23	n.a.	0.01	n.a.
CaO	1	2.18	2.12	0.69	0.80	3.80	3.79	12.08	12.07	0.55	0.58	0.71	0.64	0.51	0.46	14.53	n.a.	0.06	n.a.
Na_2O	1	3.43	3.40	3.59	3.57	4.07	4.06	1.26	1.24	0.01	0.02	4.10	4.15	4.10	4.09	0.92	n.a.	4.83	n.a.
K_2O	1	4.02	4.00	4.72	4.75	2.66	2.65	0.25	0.25	0.01	0.00	4.50	4.47	4.54	4.52	0.08	n.a.	4.28	n.a.
P_2O_5	1	0.81	0.80	0.00	0.00	0.12	0.12	0.05	0.05	0.00	-	0.02	0.02	0.01	0.01	0.01	n.a.	0.01	n.a.
Total		100.80	100.00	100.00	100.00	100.19	100.00	100.44	100.00	99.49	100.00	99.87	100.00	99.84	100.00	100.15	(0.12)	99.48	(0.48)
(ppm)	Ref*	XRF	R.V.	XRF	R.V.	XRF	R.V.	XRF	R.V.	XRF	R.V.	XRF	R.V.	XRF	R.V.	XRF	ICPM*	XRF	ICPM*
Ba	1	443	458	67	67	471	453	71	63	nd.	17	46	40	37	39	19	34.3	89	58
Ce	2	48	45.9	51	49.5	40	40.1	7	7.9	nd.	-	51	47.1	38	38.8	5	3.1	328	322
Co	1	6	5.7	3	4.3	14	11.4	60	61.6	119	116	nd.	0.65	nd.	-	29	29.5	7	6.3
Cr	1	20	18.6	6	7.6	25	23.6	62	59.3	2953	2970	4	2.3	6	2.6	125	125	7	1.8
Ga	1	17.4	17	19.1	19	16.3	17	18.0	18.9	1.1	0.5	17.2	17.6	18.5	18.2	16.4	16.8	30.2	31.8
Nb	1	11.7	12.0	14.1	15.0	5.7	5.6	2.2	2.8	nd.	1.2	15.1	15.5	17.9	19.2	0.9	1.1	505	491
Ni	1	6	6.4	2	2.1	15	13	26	25.4	2464	2460	1	0.7	nd.	0.8	16	8.5	nd.	nd.
Pb	1	27	27	32	32.8	13	12.3	1	1.9	2	0.1	19	19.1	22	21.9	3	1.0	27	37.0
Rb	1	179	180	297	297	69	66	6	4	1	0.5	256	257	304	297	2	4.3	460	456
Sr	1	186	188	15.7	15.8	373	374	312	310	nd.	-	28	28.2	6	5.8	447	434	8.7	9.3
Th	1	13.1	12.1	30.2	29.7	8.5	8	0.7	0.5	1.7	0.2	25.9	26.5	32.4	32.2	nd.	0.4	111	115
V	1	18	23	nd.	3	71	73	635	640	31	29	3	-	2	-	196	217	1	3.7
Y	2	31.5	31.6	87.4	88.2	17.1	17.2	10.6	10.8	1.7	1	44.1	45.4	52.5	51.3	5.6	3.2	152	166
Zr	2	124	121	111	101	170	137	31	33.5	3	6.3	98	101	94	97.2	23	-	1552	1573

R.V.: recommended values by Ref*1: Ando *et al.* (1987), and by Ref*2: Itoh *et al.* (1992; Ref*2), Ref*: reference. ICPM*: determined values by ICP-MS, n.e.: not examined, nd. not detected, n.a.; not available. The results for JGb-2 and JR-3 are listed with total concentrations of trace elements (shown in brackets at the right of the total). The relatively low total for JR-3 is due to a higher concentration of trace elements (0.48 wt.% as total). The trace element values by ICP-MS have been measured by Takaku *et al.* (1995).

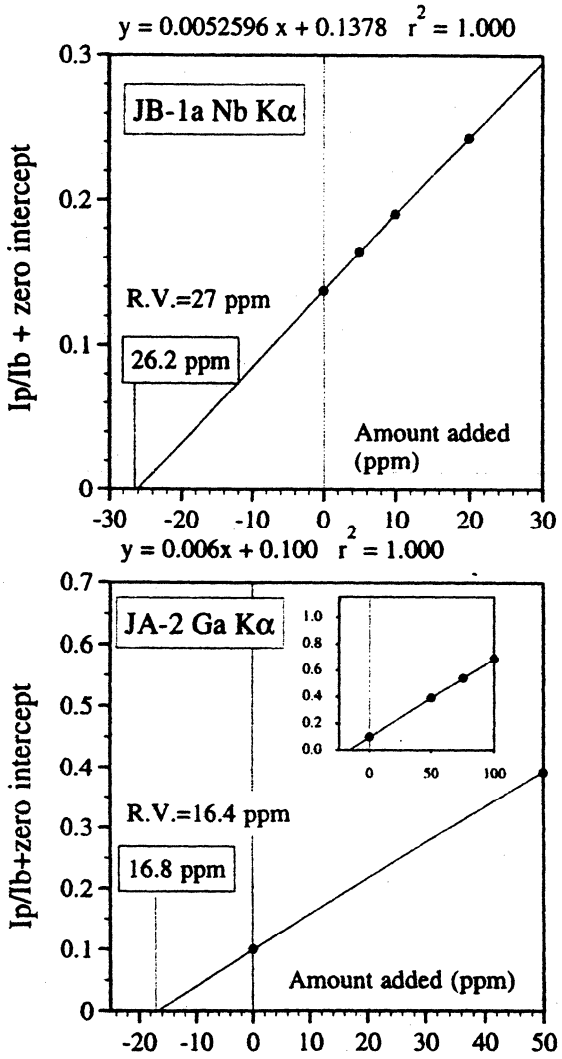

Fig. 5. Preliminary results of trace element analysis by the standard addition method. Analytical errors are within 3%R.D. calculated from recommended values.

analytical results of JGb-2 and JR-3 by ICP-MS and LA-ICP-MS (Takaku *et al.*, 1995; Yoshida *et al.*, 1995; Kimura *et al.*, 1995) are also shown.

2. Application of the standard addition method to XRF trace element analysis

A preliminary study of standard addition measurement for trace elements was carried out on Ga in JA-2 andesite and Nb in JB-1a basalt. The zero intercept values of Ip/Ib ratios were deduced from the calibration lines determined by the GSJ standard rocks. The obtained concentrations were 16.9 (16.4 at recommended value) ppm in Ga for JA-2 and 26.2 (27) ppm in Nb for JB-1a. The C.V.s were 3% in both Ga and also Nb (Fig. 4).

Although Ip/Ib matrix correction is necessary in all cases, the standard addition measurement is internally free from the matrix effect. Small amount of a standard addition do not change the matrix significantly. This method can reduce the statistical counting error of fluorescent X-ray and sampling error of a rock powder by measuring several glass beads. Trace element determination without geostandard rocks is possible by this method.

IV. Summary and conclusions

Sample preparation procedures, analytical methods, and the potential of 2 : 1 glass beads for major and trace elements analyses of geological samples by XRF were examined. By using mixed alkali flux ($Li_2B_4O_7$: $LiBO_2$ = 8 : 2) and fusion conditions at a temperature of 1200 °C for 9 minutes, a flux to sample ratio of 2 : 1 glass beads can be produced. By a least square regression convergent calculation the matrix effect can be corrected satisfactorily for the major elements. Careful examination of measuring conditions, the use of Ip/Ib matrix correction, and peak overlap corrections by a standard addition combined to enable a trace element analysis of fourteen elements. Although the precision by the glass bead method is slightly inferior to that of the powder pellet method under the same measuring conditions, the accuracy is higher in the glass bead method than in the powder pellet method. The standard addition method can be applied to extend the calibration curve to a higher concentration level, and for trace element analysis. The use of the 2 : 1 glass bead method for XRF analysis has a high potential for quantitative element analysis. The simple procedure of this method can reduce the time for sample preparation.

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試料 — 希釈剤比1対2ガラス円盤を用いた主成分・微量成分蛍光X線元素分析法の検討

木村　純一・山田康治郎

1対2希釈ガラス円盤による岩石の主成分・微量成分蛍光X線分析法を検討した。ガラス円盤は試料1.8 g，融剤3.6 gとし，1200°C, 9分間で溶融した。主成分分析には多成分重回帰計算で補正計数を決定し，1対5希釈と同程度の正確度を得た。同じガラス円盤を用い，14微量成分を測定した。検量線は地質調査所標準岩石と，それに標準溶液添加した試料で作成した。両者の検量線は一致している。標準添加した試料を用いて元素間の重なり補正を行った。蛍光X線のS/N比が悪いので，測定時間は粉末法の2-10倍必要だった。同一の測定時間，機器条件で粉末法とガラス円盤法の比較を行った。ガラス円盤法は測定再現性にやや劣るが，正確度は優れている。粉末法には粒度効果や鉱物効果があり，測定時間が長くても精度が上がらないためである。さらに標準添加法を用いた微量成分分析を試みた結果，より精度高い分析ができた。