X-ray fluorescence analysis of rocks
—using a benchtop X-ray fluorescence spectrometer, Supermini—

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1. Introduction

There are growing demands for mineral resources around the world, and rapid and accurate elemental analysis is required at a satellite laboratory in a mining site for quality check, geological resource survey, etc. One of the Rigakus solutions for such requirements is the compact-size light-weight benchtop wavelength dispersive X-ray fluorescence spectrometer (WDX), Supermini (see Fig. 1).

Although a benchtop energy dispersive X-ray fluorescence spectrometer (EDX) is commonly used for an elemental analysis, WDX, with its superior spectral resolution and light-element sensitivity, is more suitable for the analysis of rocks and minerals, because they usually contain a large number of light- and heavy- element oxide components,

Supermini is equipped with a newly developed high power air cooled 200-W X-ray tube, which has about 4 to 6 times higher sensitivity than that of a former benchtop spectrometer. This enables an XRF analysis of a sample with high precision. This paper reports the results of an XRF analysis of rocks using a Supermini spectrometer.

2. Samples

Geological reference materials (JA-1, JA-2, JA-3, JB-1a, JB-2, JB-3, JG-1a, JG-2, JG-3, JGb-1, JGb-2, JR-1, JR-2, JR-3) from National Institute of Advanced Industrial Science and Technology (AIST) Geological Survey of Japan Geoinformation Center were used to obtain calibration curves for the XRF analysis. Three of the samples (namely, JA-1, JG-1a, JGb-1) were used for repeatability and accuracy tests.

Fig. 1. Benchtop X-ray fluorescence spectrometer, Supermini.

3. Sample preparation

Samples were prepared using the fusion bead method. This method gives accurate results by removing possible inhomogeneity caused by mineralogical and particle size effects presented in a sample.

0.7 g of each sample and 3.5 g of flux, lithium tetra borate (dilution ratio 1 : 5), were mixed thoroughly. The mixed sample was then heated at 1200°C in a platinum crucible to fuse the sample using a desktop fusion machine (Fig. 2). The sample was finally cooled to form a fusion bead.

Since the samples were diluted with flux during the fusion process, the dilution effect reduces the influence of the matrix absorption and enhancement effect of X-rays caused by the coexistent elements.

Since the dilution ratio of 1 : 5 is smaller than the commonly used ratio of 1 : 10, its dilution effect is relatively small. This results in a large matrix effect. However, high-sensitivity analysis of trace elements is possible using a Supermini spectrometer because of its superior spectral resolution.

4. Experimental conditions

A total of 10 elements (namely, Si, Ti, Al, Fe, Ca, Mg, Mn, K, Na and P) were measured in the samples. The experimental conditions used for quantitative analysis of

Fig. 2. Desktop type bead sampler.

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Table 1. Experimental conditions.

Element	Si	Ti	Al	Fe	Ca	Mg	Mn	K	Na	P
X-ray line	Kα	Kα	Kα	Kα	Kα	Kα	Kα	Kα	Kα	Kα
X-ray tube	End-window Pd tube									
kV & mA	50 kV and 4 mA									
Filter	Out	Out	Out	Out	Out	Out	Out	Out	Out	Out
Analysis diameter	30 mm									
Slit	Std.	Std.	Std.	Std.	Std.	Std.	Std.	Std.	Std.	Std.
Analyzing crystal	PET	LiF200	PET	LiF200	PET	RX25*	LiF200	PET	RX25*	PET
Detector	F-PC	SC	F-PC	SC	F-PC	F-PC	SC	F-PC	F-PC	F-PC
PHA	Differential method									
Measurement time (s)	40	100	40	20	40	100	100	40	100	100
X-ray path	Vacuum									

*Synthetic multilayer

Table 2. Theoretical matrix correction coefficients (The de Jongh model, in which the ignition loss is regarded as the balance component, is used).

($\times 10^{-3}$)

		Analyzing oxide components									
		SiO_2	TiO_2	Al_2O_3	T-Fe_2O_3	CaO	MgO	MnO	K_2O	Na_2O	P_2O_5
Component to apply correction	SiO_2	2.63067	8.32648	2.24037	8.83817	7.66251	2.07262	8.74517	7.48860	1.95555	6.70749
	TiO_2	3.32931	8.04665	3.27340	29.3818	3.63445	.3.20699	28.4337	3.40173	3.13119	3.38402
	Al_2O_3	5.89495	7.38258	2.17161	7.73531	6.84241	1.88899	7.67308	6.72149	1.77394	6.12329
	T-Fe_2O_3	5.08775	4.16587	4.94681	14.9180	4.30761	4.77664	11.4384	4.46715	4.57535	5.21112
	CaO	2.92832	2.61327	2.88601	29.7106	6.95320	2.83816	28.9270	3.67402	2.78859	2.96961
	MgO	5.79771	6.85846	5.60121	7.10738	6.47934	1.78125	7.07105	6.39179	1.58388	5.96095
	MnO	4.74169	3.97533	4.62285	14.2443	3.92944	4.47315	14.1285	4.05343	4.28834	4.84366
	K_2O	2.65099	25.4027	2.60242	29.4233	24.6280	2.54297	28.5590	6.42215	2.46941	2.69666
	Na_2O	5.14022	6.07817	5.03889	6.21994	5.61787	4.91761	6.20548	5.54395	1.21709	5.23442
	P_2O_5	2.60556	8.92780	2.37759	9.63647	8.40969	2.21184	9.50222	8.20914	2.10235	3.14150

the 10 elements using a Supermini spectrometer are listed in Table 1.

5. Data analysis and results

5.1. Theoretical matrix correction coefficients

A computer program was used in Supermini for the calculation of the theoretical matrix correction coefficients caused by the absorption and enhancement of X-rays due to the coexistence of oxide components in a sample.

This program uses the fundamental parameter (FP) method to calculate theoretical X-ray intensities by automatically changing the concentrations of all elements presented in a sample, and then the theoretically calculated intensities are used to obtain the matrix correction coefficients. The FP method can obtain the correction coefficients using typical composition of major elements without the need to use reference standard samples, and therefore no cumbersome measurements of standard samples are needed. The FP program has been installed in Rigaku's X-ray fluorescence spectrometers for more than 20 years, and widely used for quantitative elemental analysis. Table 2 lists the theoretical matrix correction coefficients for all components presented in the samples.

5.2. Calibration curves

The corrected calibration curves with uncorrected data plot for SiO_2, TiO_2, Al_2O_3 and T-Fe_2O_3 (total iron oxide) plotted in Figs. 3 to 6 show that the corrected concentrations are significantly different from those of the uncorrected concentrations, indicating theoretical matrix corrections are important to obtain XRF results with high accuracies.

The accuracy (σ_d) of a calibration curve can be estimated using the by the following the root-mean-square equation:

$$\sigma_d = \sqrt{\frac{\sum_i (Ci - \hat{W}i)^2}{n - m}} \text{ (mass\%)}$$

Where Ci is the standard concentration of the sample i, $\hat{W}i$ the measured X-ray concentration, n the number of samples, $m=2$ for a linear equation or $m=3$ for a qua-

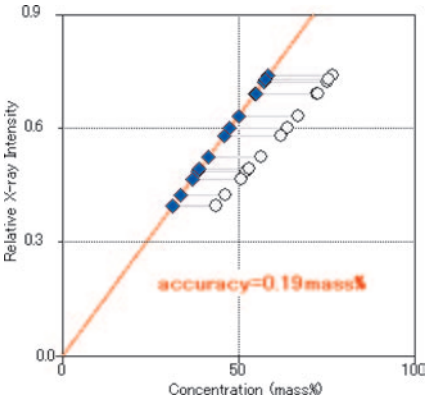

Fig. 3.1. Corrected calibration curve for SiO_2.

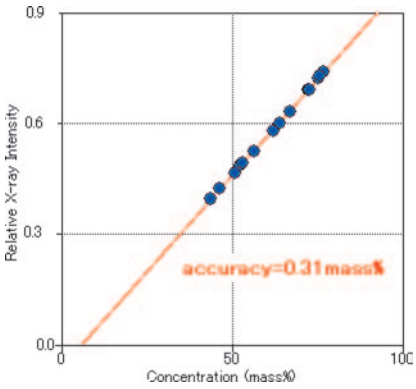

Fig. 3.2. Uncorrected calibration curve for SiO_2.

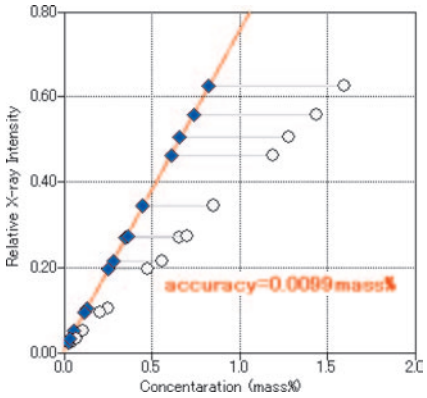

Fig. 4.1. Corrected calibration curve for TiO_2.

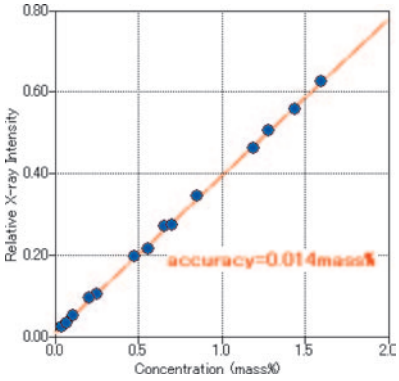

Fig. 4.2. Uncorrected calibration curve for TiO_2.

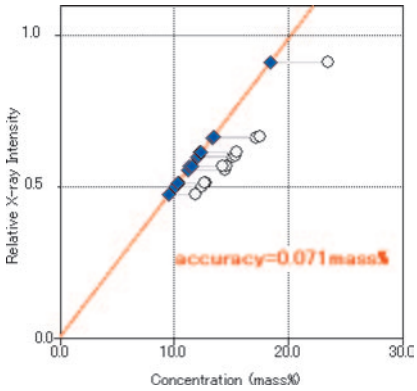

Fig. 5.1. Corrected calibration curve for Al_2O_3.

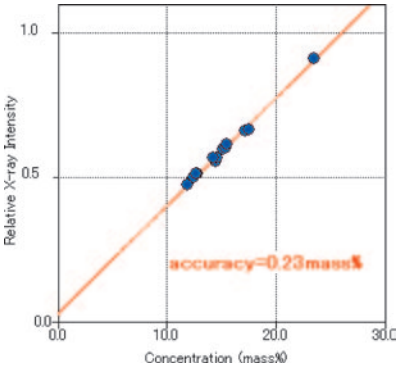

Fig. 5.2. Uncorrected calibration curve for Al_2O_3.

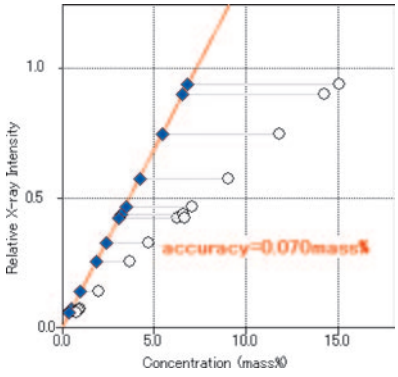

Fig. 6.1. Corrected calibration curve for T-Fe_2O_3.

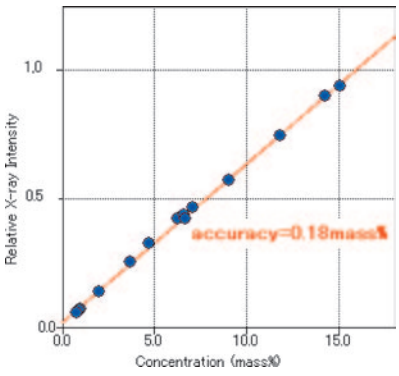

Fig. 6.2. Uncorrected calibration curve for T-Fe_2O_3.

Table 3. Results of the regression calculation.

	SiO_2	TiO_2	Al_2O_3	T-Fe_2O_3	CaO	MgO	MnO	K_2O	Na_2O	P_2O_5
Conc. .range Max.	76.83	1.6	23.48	15.06	14.1	7.85	0.218	4.71	4.96	0.294
Min.	43.66	0.07	11..9	0.77	0.093	0.005	0.016	0.059	0.92	0.002
Accuracy without correction	0.31	0.0145	0.23	0.18	0.0493	0.0814	0.0043	0.0235	0.0331	0.0045
Accuracy with correction	0.19	0.0099	0.07	0.07	0.0424	0.0505	0.0035	0.0229	0.0331	0.0042

Table 4.1. Repeat measurement results for sample JA-1. (Unit: mass%)

	SiO_2	TiO_2	Al_2O_3	T-Fe_2O_3	CaO	MgO	MnO	K_2O	Na_2O	P_2O_5
Standard value	64.06	0.87	14.98	6.95	5.68	1.61	0.15	0.78	3.86	0.16
Average value	64.18	0.85	15.19	6.96	5.69	1.53	0.16	0.77	3.88	0.16
Standard deviation	0.0809	0.0059	0.0348	0.0113	0.0126	0.0146	0.0101	0.0060	0.0448	0.0010
R.S.D. (%)	0.13	0.69	0.23	0.16	0.22	0.95	0.69	0.78	1.15	0.60

Table 4.2. Repeat measurement results for sample JG-1a. (Unit: mass%)

	SiO_2	TiO_2	Al_2O_3	T-Fe_2O_3	CaO	MgO	MnO	K_2O	Na_2O	P_2O_5
Standard value	72.19	0.25	14.22	2.05	2.13	0.69	0.06	4.01	3.41	0.08
Average value	72.38	0.25	14.24	2.01	2.12	0.69	0.060	4.02	3.40	0.082
Standard deviation	0.1084	0.0034	0.0386	0.0062	0.0110	0.0120	0.0007	0.0117	0.0400	0.0014
R.S.D. (%)	0.15	1.38	0.27	0.27	0.52	1.74	1.23	0.29	1.18	1.67

Table 4.3. Repeat measurement results for sample JGb-1. (Unit: mass%)

	SiO_2	TiO_2	Al_2O_3	T-Fe_2O_3	CaO	MgO	MnO	K_2O	Na_2O	P_2O_5
Standard value	43.44	1.62	17.66	15.16	11.98	7.83	0.12	0.24	1.23	0.05
Average value	43.61	1.60	17.51	15.1	11.9	7.86	0.19	0.25	1.23	0.059
Standard deviation	0.0724	0.0064	0.0473	0.0322	0.0263	0.0292	0.0015	0.0031	0.0215	0.0011
R.S.D. (%)	0.17	0.40	0.27	0.21	0.37	0.37	0.79	1.26	1.75	1.81

dratic equation. The smaller the value of σ_d, the higher the accuracy. The concentration ranges and values of the accuracy for the corrected and uncorrected calibration curves for all ten oxide components determined by regression calculations are listed in Table 3. An improvement in accuracy for the corrected calibration curve over the uncorrected curve was obtained for each of the oxide components, and drastic improvements in accuracy by about 2 to 3 times were obtained for the corrected calibration cures of 4 oxide components, namely SiO_2, TiO_2, Al_2O_3 and T-Fe_2O_3 (see also Figs. 3 to 6).

5.3. Repeat measurement results

The measurements on three standard samples (namely, JA-1, JG-1a and JGb-1) were repeated 10 times to determine the accuracy and precision of the analysis.

Tables 4.1 to 4.3 list the analysis results. The average analysis results are very close to the standard values, and the results of the repeat measurements are also very good.

6. Concluding remarks

A Supermini XRF spectrometer was used to analyze major and minor oxide components in rock samples prepared by the fusion bead method. The XRF results on the analysis of the major oxide components in rock samples were highly accurate and precise. The results on analyzing relatively low-concentration oxide components such as P_2O_5 and MnO were also successful.

Supermini, a compact-size light-weight spectrometer, can easily be installed in a small laboratory with a limited space. The results reported in this note again confirm that Supermini gives high intensities and has high resolution. A Supermin XRF spectrometer is most suitable to be used for the XRF analysis of rock samples at a satellite laboratory of a geological resource survey, a mining company, etc.