Title	Major Element Analysis of Rock Samples by X-ray Fluorescence Spectrometry, using Scandium Anode Tube
Author(s)	Tsuchiya, Nobutaka; Shibata, Tomoyuki; Koide, Yoshiyuki et al.
Citation	北海道大学理学部紀要, 22(3), 489-502
Issue Date	1989-02
Doc URL	https://hdl.handle.net/2115/36761
Type	departmental bulletin paper
File Information	22_3_p489-502.pdf

Jour. Fac. Sci., Hokkaido Univ., Ser. IV
vol. 22, no. 3, Feb., 1989, pp. 489-502.

MAJOR ELEMENT ANALYSIS OF ROCK SAMPLES BY X-RAY FLUORESCENCE SPECTROMETRY, USING SCANDIUM ANODE TUBE

by

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(with 5 text-figures and 6 tables)

Abstract

An X-ray fluorescence spectrometer (Philips PW1404) equipped with a scandium anode tube was tested for major element analysis of rock samples. Rock powder, five times flux ($Li_2B_4O_7$), and 20 to 30mg of $LiBr \cdot H_2O$ were mixed and fused to make a glass bead. The calibration lines were determined from 13 rock standards of GSJ and USGS and 14 synthetic standards by using a software X44 for the PW1404. The synthetic standards were useful in estimating of the matrix correction factors, and adequate calibration lines were provided for a wide range of composition. The analytical errors of the calibration lines were enough small for the purpose of petrological investigations. Using an automatic sample changer PW1500 and a software X44 for XRF, more than 80 rock samples can be automatically analyzed in a day. This method is suitable for the routine work of major element analysis of rock samples.

Introduction

X-ray fluorescence spectrometry (XRF) is one of the most versatile methods for analyzing major and trace elements of rock samples. In major element analysis, anode materials used for X-ray tube are generally chromium (*e.g.* Sugisaki *et al.,* 1977; Matsumoto and Urabe, 1980) and rhodium (Goto, 1976). Recently, a Philips automatic sequential-spectrometer PW1404 equipped with scandium and rhodium anode tubes has been installed at Hokkaido University. The Sc anode tube is suitable for exciting light elements such as Na and Mg, *e.g.* intensities of NaKα and MgKα attain about three times those by the Rh anode tube. X-ray intensities of light elements excited by the Sc anode tube are also higher than those by the Cr anode tube. Hence, the PW1404 equipped with the Sc anode tube is very useful for major element analysis of rock samples.

In this report, we describe the analytical method of major elements in rock samples by XRF using the Sc anode tube.

Sample Preparation

Suitable samples prepared for XRF analysis are pressed powder pellets (Goto and

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Oono, 1981; Goto and Kanaya, 1985) and dissolved glass beads (*e.g.* Ohmori and Ohmori, 1976; Sugisaki *et al.*, 1977; Matsumoto and Urabe, 1980; Nakada *et al.*, 1985). We prepared glass beads because of easy treatment, good preservation, and eliminating the particle-size and mineralogical effect (*e.g.* Norrish and Hutton, 1969; Sugisaki *et al.*, 1977).

About 0.8 to 1g of powdered sample is weighed out in a Pt crucible. It is ignited at 1050° to 1100°C for 1 to 2 hours, and the loss on ignition is measured. Then weigh out about 0.7g of the ignited sample and accurately five times flux of anhydrous lithium tetraborate ($Li_2B_4O_7$). In this case, the loss on ignition of the lithium tetraborate flux should be previously measured, and its expected loss should be added. The loss on ignition of the lithium tetraborate reagent of Merck Co. Ltd. was 1.3 to 2.0 wt%. Finally, about 20 to 30mg of lithium bromide ($LiBr \cdot H_2O$) is added in order to ensure removal of the glass bead from the crucible. The mixture is well ground in an agate mortar, and is put in a crucible of Pt-Au alloy (5 wt% Au). The mixture is melted at 1050°C for about 20 minutes using a Philips PELX' 2 automatic bead sampler. Well stirring during melting and making the flat base of the beads are essential to obtain good glass beads. Volatilization of Na and K from glass bead must be taken into consideration. However, it may be negligible in this case because the heating temperature is not so high and the duration is short (Ohmori, 1980).

It is difficult to weigh out accurately lithium bromide because of its strong deliquescence. Furthermore, Br content remaining in the glass bead varies with ignition conditions. Hence, accurate measurements may not be made for some trace elements such as Rb, because $BrK\beta$ interferes on $RbK\alpha$ (*e.g.* Kobayashi *et al.*, 1981). However, there is no significant problem concerning with major element analysis.

Analytical Procedure

1. Preparation of Standard Samples for Calibration

Various rock standards JR-1, JR-2, JG-1, JG-2, JA-1, JA-2, JB-1, JB-2, JB-3, JGb-1, JP-1, and JF-1 of Geological Survey of Japan and STM-1 of U.S. Geological Survey, and 14 synthetic standards were used as standard samples for calibration. The synthetic standards were prepared from pure chemical reagents listed in Table 1 and the rock standards (JP-1 and JA-1). Table 2 shows the chemical compositions of rock and synthetic standard samples for calibration. They cover a wide compositional range of various igneous rocks such as cumulates, ultramafic rocks, and peralkaline rocks, which enables us to improve the calculation of the matrix correction factors.

In order to reduce error of weighing, a total of about 10g of mixture was taken and stirred with a pestle in an agate mortar for more than 30 minutes.

2. Instrumental Condition

Table 3 shows instrumental conditions for each element. Analyzing crystals, collimators, and detectors were selected at the maximum intensity of X-ray. In the case of $CaK\alpha$, the maximum intensity can be obtained by the use of analyzing crystal of

Table 1 Chemical reagents and their heating temperature for synthetic standards

Reagents	Heating Temperature	
SiO_2	1100°C	N
TiO_2	1100	K
Al_2O_2	1100	K
Fe_2O_3	600	K
MnO	110	K
MgO	1100	K
$CaCO_3$	100	K
Na_2CO_3	300	K
K_2CO_3	300	K
Na_2HPO_4	110	K

N: Nakai Chemicals LTD.
K: Kishida Chemical Co. LTD.

LiF200. Although the intensity of CaKα by Ge is slightly lower than that by LiF200, we selected the analyzing crystal of Ge, because count rates of samples with high Ca content exceed the capacity of the PW1404. Lower and upper levels of the pulse height discriminator can be easily determined by using the software X44. Text-fig. 1 shows a pulse height distribution output for SiKα and FeKα on a graphics terminal. If escape peaks are present, they are completely included or excluded in the pulse height discriminator.

The intensity measurements should be corrected for dead-time, which is automatically made by a dead-time correction circuit in the PW1404. Text-fig. 2 shows FeKα/FeKβ versus FeKα relations at various tube currents and voltages. The FeKα/FeKβ ratios remained almost constant, indicating that the dead-time correction by the PW1404 is satisfactory.

The net count rate of each element should be corrected for background. The measuring positions of background are determined by qualitative scans around the peaks by using the automatic qualitative analysis program of the software X44. Text-fig. 3 shows the scan profiles of X-ray spectra. Background measurements were normally made on either sides of the peak, but they were made on one side in some cases. For example, the strong spectral line of ScKβ from the X-ray tube exists at higher angles nearby the peak of TiKα. Therefore, the background measurement of TiKα was set on the side of lower angle of the peak. In this case, the background correction factor was determined by measuring the intensity of fluorescent radiation at the peak and background positions for several pure reagents free from Ti, using the slope factor obtained after Ogasawara (1987).

Table 4 shows the count rates of X-ray of each element by the use of the Sc and Rh anode tubes. The X-ray intensities by using the Sc anode tube are higher than those by the Rh anode tube except Ti, Mn, and Fe. This tendency is clearly shown in the case

Table 2 Chemical compositions of the standard samples for calibration.

	JG-1	JG-2	JR-1	JR-2	JA-1	JA-2	JB-1	JB-2	JB-3
SiO_2	72.80	77.35	76.37	76.76	64.62	57.57	52.88	52.82	50.84
TiO_2	0.26	0.04	0.10	0.09	0.88	0.69	1.36	1.18	1.44
Al_2O_3	14.30	12.47	13.05	13.01	15.11	15.70	14.73	14.57	16.82
Fe_2O_3	2.15	0.92	0.97	0.87	7.01	6.29	9.09	14.24	11.83
MnO	0.06_3	0.01_5	0.01	0.11	0.15	0.11	0.16	0.20	0.16
MgO	0.75	0.04	0.09	0.05	1.62	7.87	7.83	4.63	5.18
CaO	2.19	0.80	0.64	0.46	5.73	6.64	9.42	9.82	9.82
Na_2O	3.41	3.57	4.15	4.09	3.89	3.16	2.83	2.02	2.81
K_2O	3.98	4.78	4.50	4.55	0.83	1.82	1.44	0.43	0.80
P_2O_5	0.09_8	0.00_2	0.02	0.01	0.16	0.15	0.26	0.10	0.29

	JGb-1	JP-1	JF-1	STM-1	JA1SI	JP1SI1	JP1SI2	JP1SI3	JP1SI4
SiO_2	43.70	43.80	66.95	60.54	82.30	50.53	62.49	71.93	85.99
TiO_2	1.63	<0.01	0.00_5	0.13	0.44	0.00	0.00	0.00	0.00
Al_2O_3	17.77	0.64	18.07	18.90	7.56	0.58	0.43	0.32	0.16
Fe_2O_3	15.25	8.62	0.08	5.27	3.51	7.76	5.75	4.31	2.15
MnO	0.17	0.12	0.00	0.23	0.08	0.11	0.08	0.06	0.03
MgO	7.88	46.21	0.00_6	0.10	0.81	41.58	30.84	32.08	11.52
CaO	12.05	0.58	1.05	1.18	2.87	0.52	0.39	0.29	0.14
Na_2O	1.24	0.02_2	3.56	9.15	1.95	0.02	0.01_5	0.01	0.00
K_2O	0.26	0.00_3	10.10	4.34	0.41_4	0.00	0.00	0.00	0.00
P_2O_5	0.05	0.00	0.00_9	0.16	0.08	0.00	0.00	0.00	0.00

	JP1SI5	60	61	62	63	64	65	66	67
SiO_2	92.87	34.71	37.96	32.86	33.31	33.55	28.94	34.35	46.99
TiO_2	0.00	3.05	2.53	2.09	1.89	1.70	1.01	2.70	0.53_4
Al_2O_3	0.08	11.97	3.97	4.54	22.80	2.00	7.97	25.01	10.50
Fe_2O_3	1.09	7.99	17.00	24.95	19.85	3.00	1.05	29.91	10.50
MnO	0.02	0.79_6	0.61_5	0.52	0.40	0.31	0.71	0.59_4	0.00
MgO	5.86	15.08	19.92	3.00	3.99	30.04	39.97	2.02	24.96
CaO	0.07	10.99	3.68	19.92	7.92	24.96	15.97	1.97	0.00
Na_2O	0.00	7.00	5.81	8.08	6.28	2.02	1.02	2.05	0.52_4
K_2O	0.00	6.92	7.95	3.28	2.71	2.01	3.07	3.97	5.99
P_2O_5	0.00	1.49	1.20	0.75_3	0.84	0.41_4	0.30	2.06	0.00

The compositions of the rock standards of GSJ (Nos. JG-1 to JF-1; Ando *et al.*, 1988) and USGS (No. STM-1; Flanagan, 1976) are recalculated to 100% without H_2O. Nos. JA1SI to JP1SI5 are synthesized using the chemical reagents listed in Table 1 and the rock standards of GSJ (JA1 and JP1). Nos. 60 to 67 are prepared from the chemical reagents.

Table 3 Instrumental conditions for each elements

Element	Collimator	Crystal	Peak (2θ)	Background				Counting time (sec)	Discriminator level (%)	
				off set (2θ)		correction factor				
				(+)	(−)	(+)	(−)		lower	upper
Si	Coarse	PE	109.095	3.000	3.000	0.500	0.500	30	22	80
Ti	Fine	LiF200	86.175	—	1.000	—	2.323	40	13	70
Al	Coarse	PE	144.850	—	4.500	—	1.000	30	19	80
Fe	Fine	LiF200	57.525	1.500	1.500	0.500	0.500	20	20	70
Mn	Fine	LiF200	62.990	0.500	—	1.515	—	40	20	70
Mg	Coarse	PX1	21.835	2.500	—	1.761	—	60	20	82
Ca	Coarse	Ge	61.965	—	2.000	—	1.000	20	25	75
Na	Coarse	PX1	26.400	2.000	—	1.620	—	60	20	80
K	Coarse	LiF200	136.775	2.500	5.000	0.667	0.333	20	28	75
P	Coarse	Ge	141.070	—	1.200	—	1.038	40	20	80

Sc anode tube (side window, Be window thickness = 0.3mm), 50kV 60mA, 2d of crystals (nm): PE = 0.8742, LiF200 = 0.4021, PX1 = 5.1200, and Ge = 0.6532
Detector = flow gas counter, Sample spin ON, Sample holder = aluminum, Holder mask = copper

of light elements whose X-ray intensities are low. Accordingly, the Sc anode tube is very effective for the major element analysis of rock samples.

3. Setting Up of Calibration Lines

On setting up of calibration lines, net count rates of X-ray of the standard samples should be corrected for spectral effects (line overlaps) and inter-element effects (matrix effects). Concerning the major element analysis of rock samples, the line overlaps can be neglected.

The matrix correction is essentially needed for XRF analysis. The matrix effects can be reduced to some extent by dilution, but they are not completely removed at the degree of six times dilution (*e.g.* Norrish and Chappell, 1977; Sugisaki *et al.*, 1977). In the software X44 for PW1404, various methods for matrix correction can be selected. We adopt the de Jongh model (de Jongh, 1973), and it is simplified as follows:

$$C_i = D_i + E_i \times R_i \times (1 + \sum_j \alpha(i, j) \times C_j/100)$$

where:

i; an interest element,

j; an element using matrix correction on the element "i",

C; concentration (wt %),

D; correction for fixed background which represents

$$D = \frac{\text{(Y-axis intercept of the calibration line)}}{\text{(the slope of the calibration line)}}$$

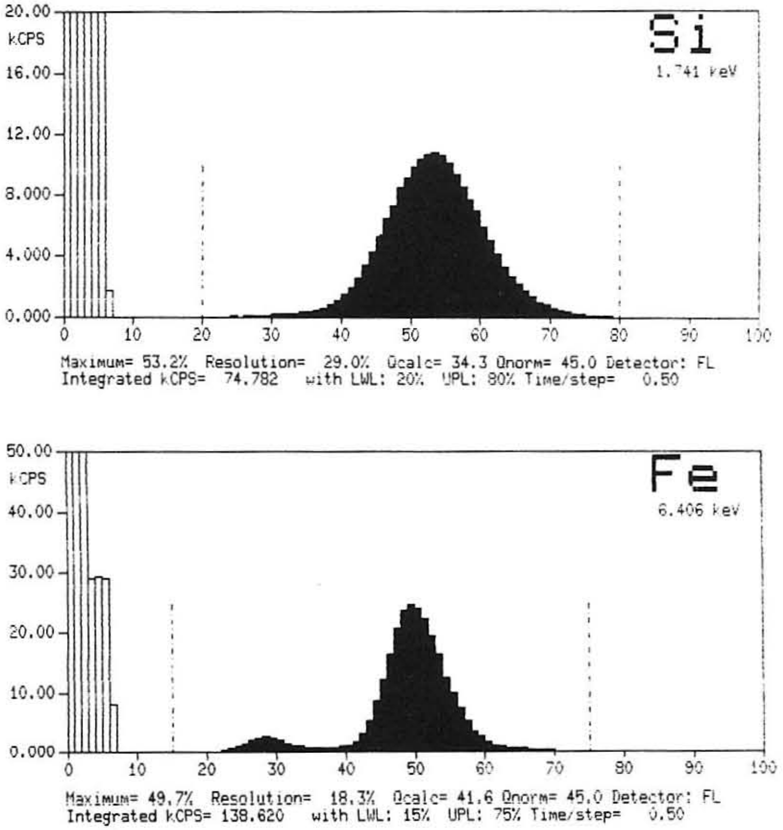
E; calibration constant representing the inverse slope of the calibration line,

R; net count rate, and

$\alpha(i, j)$; constant representing matrix correction for the element "j" on the element "i".

These correction factors can be obtained by using an iterative calculation with the software X44.

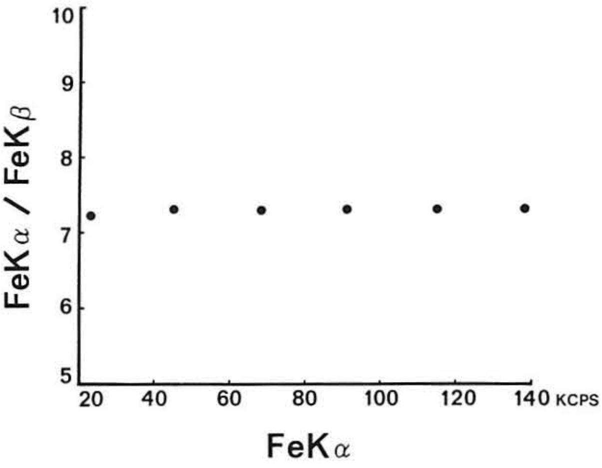
However, the above matrix correction is valid only in the case that there is no corre-



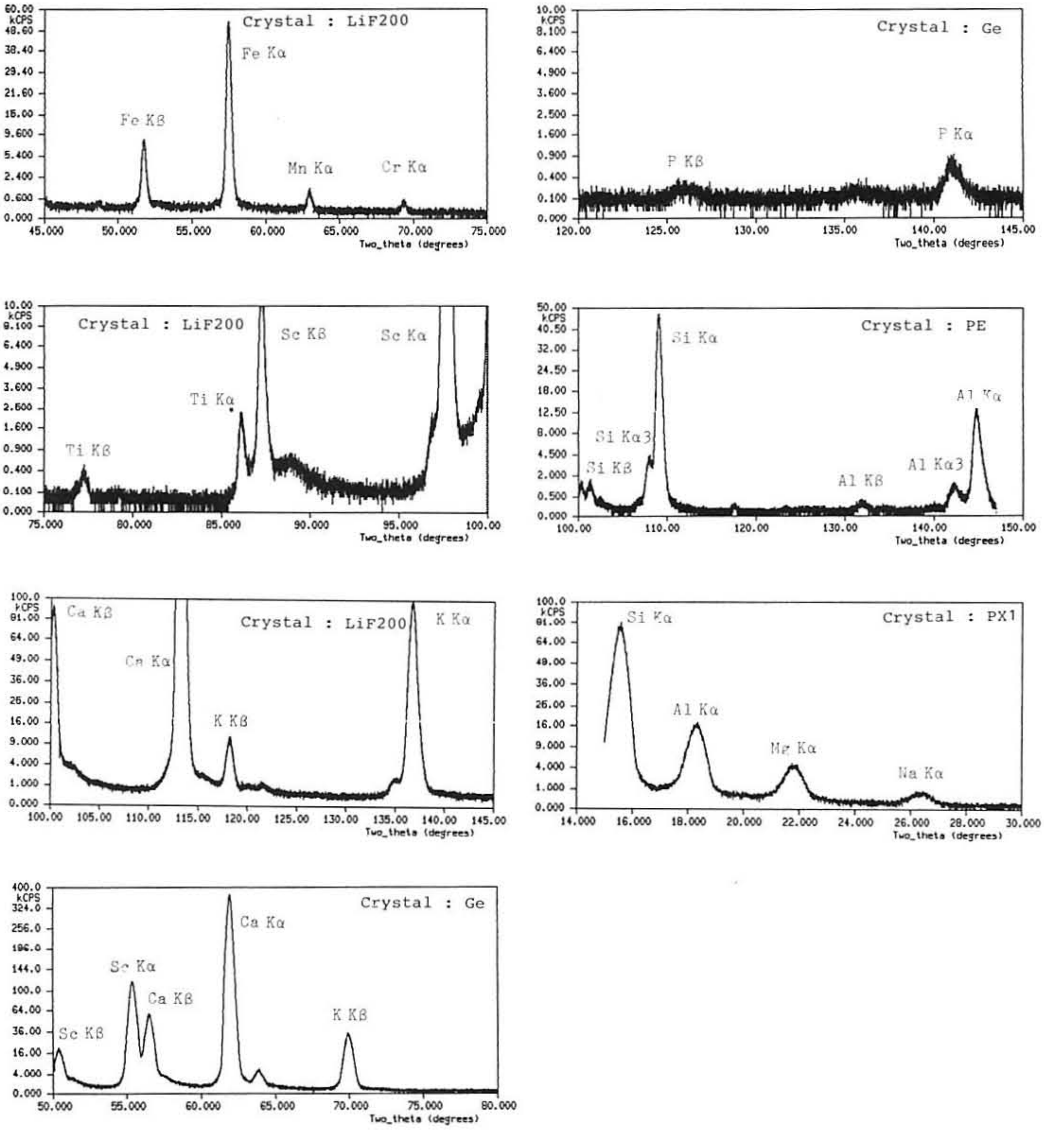
```
Maximum= 53.2%  Resolution=  29.0%  Qcalc= 34.3 Qnorm= 45.0 Detector: FL
Integrated kCPS=  74.782   with LWL: 20%  UPL: 80% Time/step=   0.50
```

```
Maximum= 49.7%  Resolution=  18.3%  Qcalc= 41.6 Qnorm= 45.0 Detector: FL
Integrated kCPS= 138.620   with LWL: 15%  UPL: 75% Time/step=   0.50
```

Text-fig. 1 Pulse height distribution output for SiKα and FeKα on a graphics terminal. Broken lines indicate lower and upper levels of the pulse height discriminator.

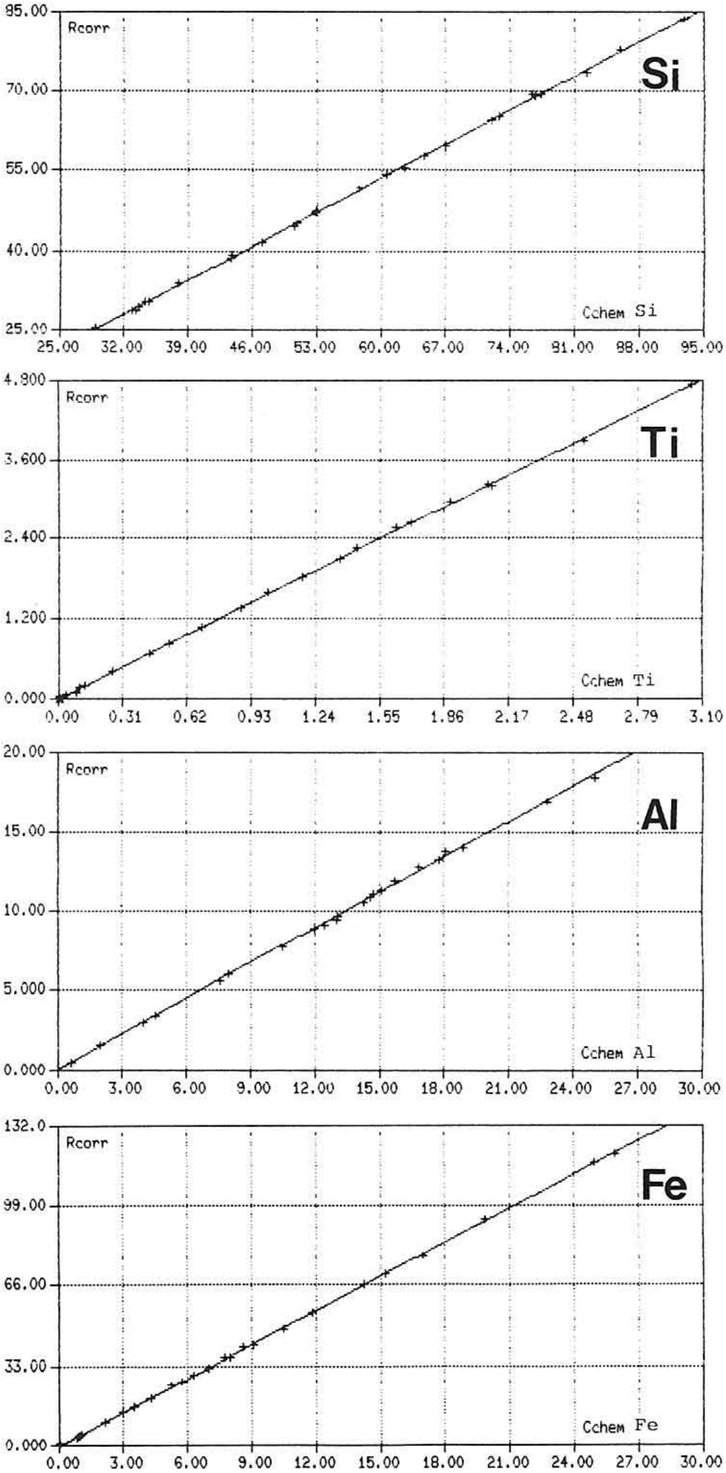


Text-fig. 2 FeKα/FeKβ versus FeKα relations at various tube currents and voltages. Dead-time correction was automatically made by the PW1404.

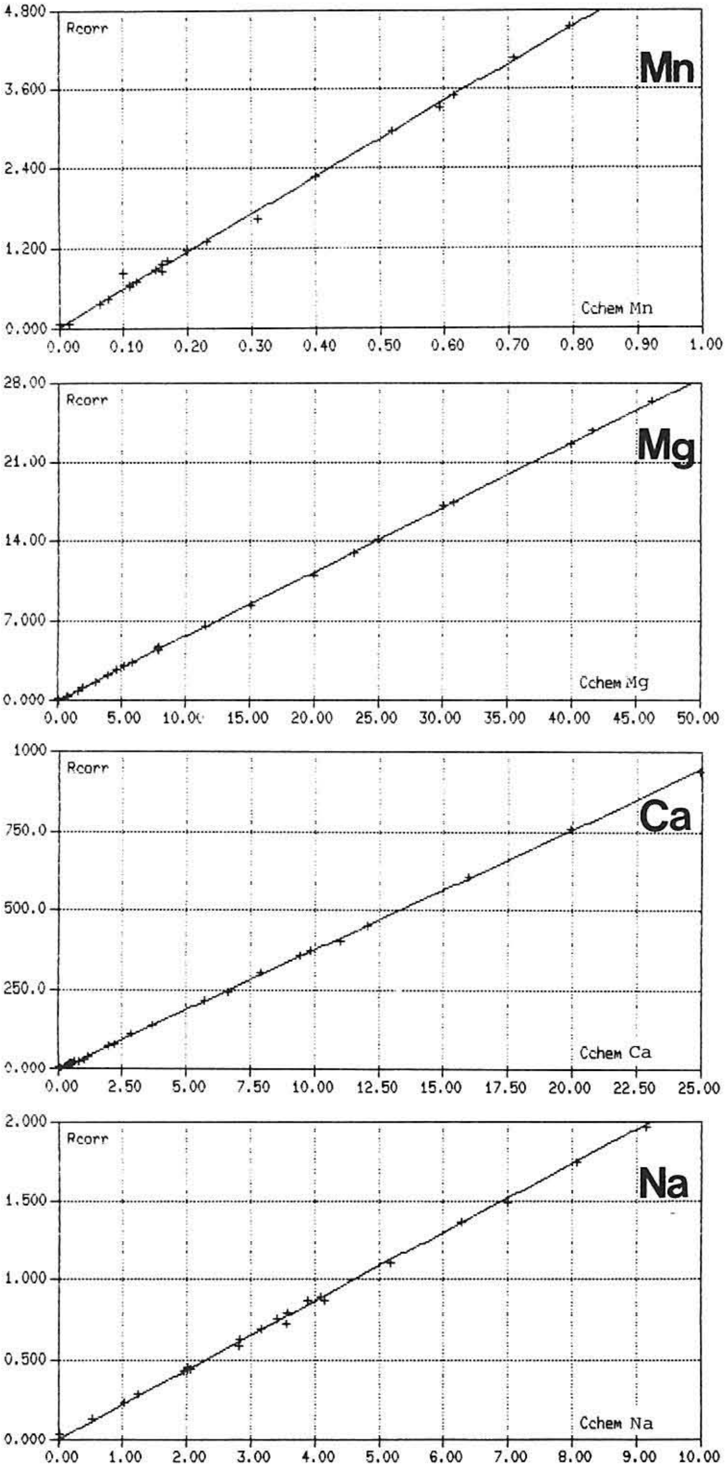


Text-fig. 3 Scan profiles of X-ray spectra for JB-1.
X-ray intensities are drawn on a logarithmic scale.

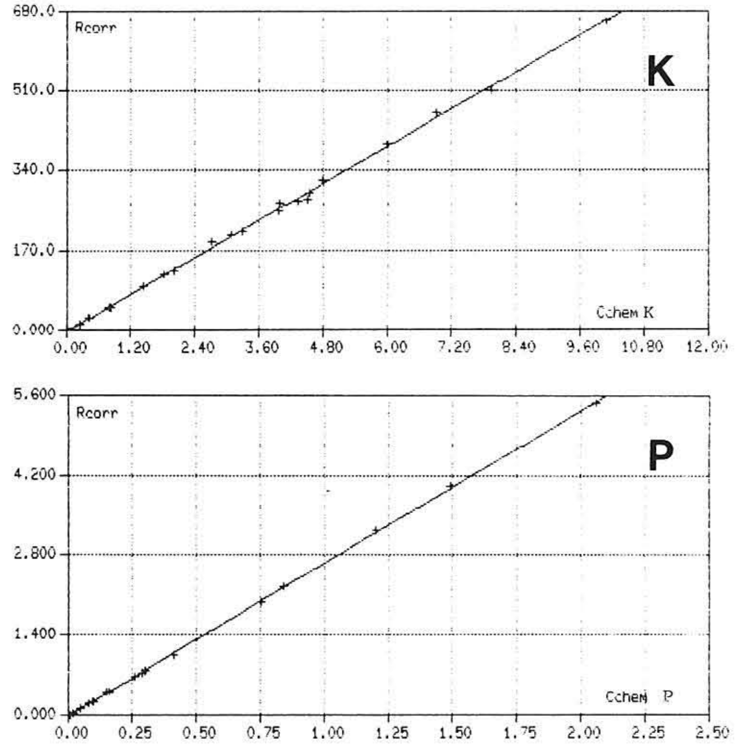
lation among the elements. Since natural rocks have strong correlation among the major element constituents, meaningless solutions of matrix correction factors are occasionally calculated. The synthetic standards are useful in the calculation of matrix correction factors because of their wide compositional range and little or no correlation among major element constituents.



Text-fig. 4 (a) Calibration lines for Si, Ti, Al and Fe.
Rcorr: count rates in kcps corrected for matrix effect.
Cchem: chemical concentrations in wt%.



Text-fig. 4 (b) Calibration lines for Mn, Mg, Ca and Na. Abbreviations as in Text-fig. 4 (a).



Text-fig. 4 (c) Calibration lines for K and P. Abbreviations as in Text-fig. 4 (a).

Table 4 Comparison of X-ray count rates by the use of Sc and Rh anode tubes.

	Sc anode tube (50kV, 60mA)	Rh anode tube (50kV, 60mA)
SiO_2	0.8436	0.2641
TiO_2	1.4236	2.6178
Al_2O_2	0.8428	0.2610
Fe_2O_3	5.8246	12.5507
MnO	4.8025	12.4696
MgO	0.5398	0.1786
CaO	39.5665	6.9554
Na_2O	0.1998	0.0699
K_2O	67.6374	6.6292
P_2O_5	2.0915	0.8815

(kcps/wt %)

Count rate is shown by kcps per wt % of each oxide in JB-1.

Table 5 Regression functions and analytical errors of the calibration lines for each element

Oxides	Di	Ei	Matrix Factor	Error (in wt %)
SiO_2	1.04325	1.09826	$-0.05182 \cdot C_{SiO_2} + 0.15154 \cdot C_{Al_2O_3} + 0.19184 \cdot C_{Fe_2O_3} + 0.20301 \cdot C_{MgO} - 0.10365 \cdot C_{CaO}$	0.374
TiO_2	−0.00017	0.64337	$1.62614 \cdot C_{TiO_2} - 0.25929 \cdot C_{Fe_2O_3} + 0.8959 \cdot C_{CaO}$	0.017
Al_2O_2	−0.11259	1.40389	$-0.19695 \cdot C_{SiO_2} - 0.20761 \cdot C_{Al_2O_3}$	0.182
Fe_2O_3	−0.00474	0.21300	$-0.31222 \cdot C_{SiO_2} - 0.36129 \cdot C_{Al_2O_3} + 0.01643 \cdot C_{Fe_2O_3} - 0.33156 \cdot C_{MgO} + 0.39772 \cdot C_{CaO}$	0.115
MnO	−0.00577	0.19966	$-0.14523 \cdot C_{Al_2O_3} - 0.17995 \cdot C_{Fe_2O_3} + 0.60683 \cdot C_{CaO}$	0.015
MgO	−0.01914	1.81479	$-0.01591 \cdot C_{SiO_2} + 0.27941 \cdot C_{Fe_2O_3}$	0.211
CaO	−0.03049	0.02630	$-0.19880 \cdot C_{Al_2O_3}$	0.098
Na_2O	−0.05247	5.08491	$0.07890 \cdot C_{Fe_2O_3} + 0.17023 \cdot C_{CaO}$	0.091
K_2O	0.00122	0.01536	$-0.307595 \cdot C_{Fe_2O_3} - 0.23123 \cdot C_{K_2O}$	0.098
P_2O_5	0.00507	0.46226	0	0.023

Error: $\sqrt{\frac{\Sigma (C_1 - C_2)^2}{n}}$ (C_1 and C_2 are calculated and original values, respectively)

Choosing elements for the matrix correction on an interest element, the calculated results are immediately displayed on the graphics terminal. We can select a combination showing the least analytical error of the calibration line by trial and error. In this case, we must choose the elements which strongly interfere with an interest element, *i.e.* those have large mass absorption coefficient and high concentration in rock samples.

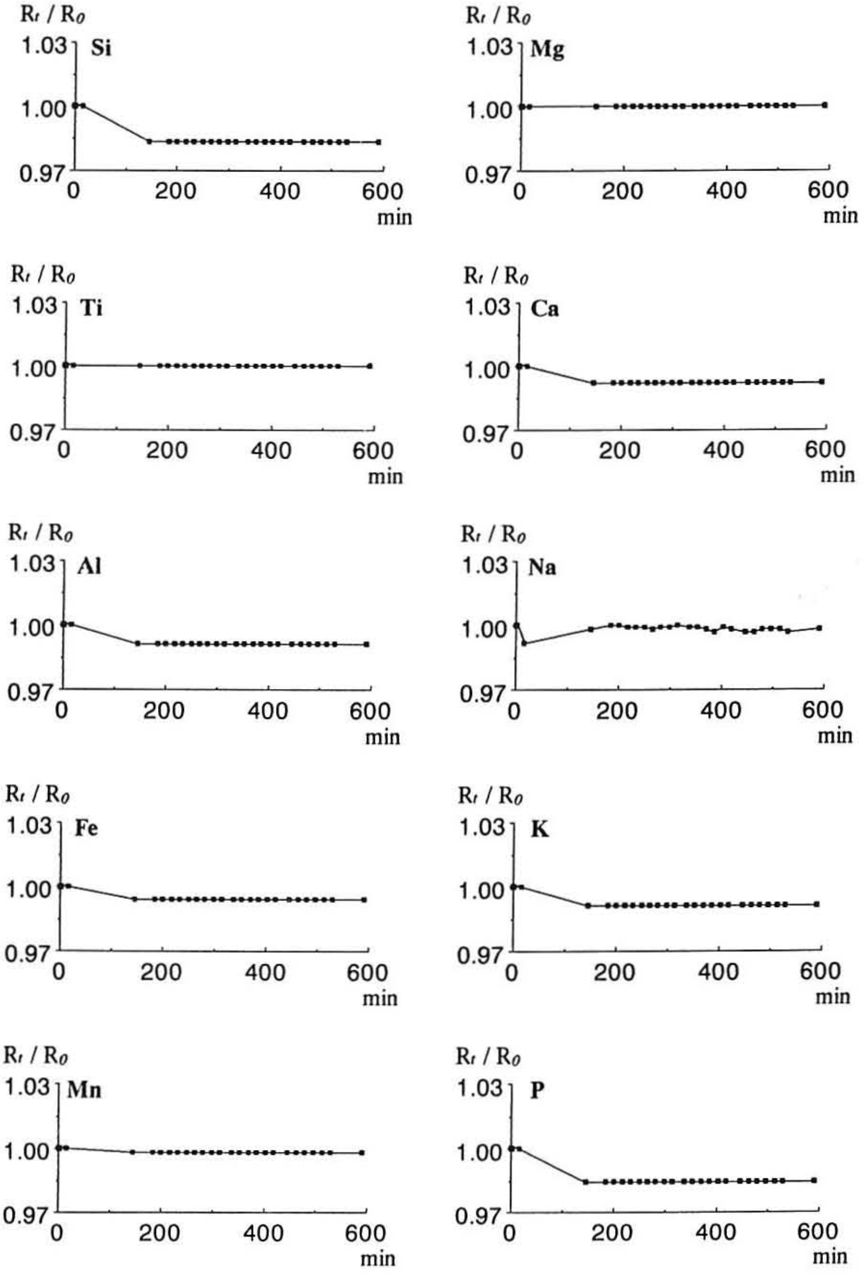
Text-figs. 4(a), 4(b) and 4(c) show the calibration lines and Table 5 lists their correction parameters. The compositional range of the calibration lines for each element is enough wide to apply to most of natural rocks. The analytical errors of the calibration lines (in wt%) are also shown in Table 5. These errors are smaller than or similar to the previous results (*e.g.* Sugisaki *et al.*, 1977; Matsumoto and Urabe, 1980; Nakada *et al.*, 1985), which indicates that this analytical method is satisfactory for the use of petrological investigations.

4. Measurements of Unknown Samples

There may be a minimal amount of drift on the PW1404, despite its stability. Therefore, the drift correction should be made before measurements of unknown samples. The drift correction factors can be determined using the count rates of a monitor sample.

Text-fig. 5 shows the short-time drift of the count rates of the monitor sample. The results indicate well stability of PW1404, particularly in short duration. It also shows that the necessity of warming up about 200 minutes after start up of spectrometer. The software X44 for PW1404 cannot correct the drift of the count rates of backgrounds, but substitutes the correction factor at the peak for that of background. However, no problem has arisen so far because of its well stability.

The measuring accuracy was checked using three standard samples of Geological Survey of Japan which were not used for the calibration (Table 6). The results agreed well with the recommended values of Ando *et al.* (1988). K_2O content of JF-2, which exceeds the compositional range of calibration, is rather lower than the recommended value.



Text-fig. 5 Drift of X-ray intensity of a monitor sample in 600 minutes.
Rt: count rate at certain time.
R_0: count rate at 0 minute.

Table 6 Analytical results of three rock standards of GSJ.

Oxides	JG-3 Recommended value	JG-3 This work	JA-3 Recommended value	JA-3 This work	JF-2 Recommended value	JF-2 This work
SiO_2	67.62	67.25	62.36	61.79	65.63	65.58
TiO_2	0.48	0.47	0.68	0.68	0.004	0.00
Al_2O_3	15.64	15.57	15.59	15.64	18.55	18.87
Fe_2O_3	3.40	3.70	6.60	6.60	0.06	0.06
MnO	0.073	0.07	0.106	0.11	0.004	0.00
MgO	1.80	1.82	3.66	3.71	0.003	0.00
CaO	3.79	3.74	6.29	6.35	0.09	0.09
Na_2O	4.06	4.03	3.13	3.14	2.48	2.44
K_2O	2.65	2.68	1.43	1.45	13.20	12.48
P_2O_5	0.12	0.12	0.11	0.11	0.002	0.00
Total	100.00	99.45	99.99	99.58	100.01	99.52

Recommended values of the standards are recalculated to 100% without H_2O from Ando *et al.* (1988).

Concluding remarks

The Philips PW1404 equipped with the Sc anode tube gives us great value in the major element analysis of rock samples. Adequate calibration lines were provided for a wide range of composition by the use of 13 rock standards of GSJ and USGS and 14 synthetic standards. The measuring accuracy of this method is satisfactory for the purpose of the petrological investigations. In addition, the PW1404 with software X44 and sample changer PW1500 can automatically make adjustment of a goniometer, drift correction, measurement of net count rates of unknown samples, calculation of matrix correction, and changing of samples. It can be automated to analyze more than 80 rock samples in a day. Its easy operation, sufficient accuracy, and rapid measurement are suitable for the routine work of major element analysis of rock samples.

In the case of equipped with the Rh anode tube, the PW1404 can be also used for the major element analysis of rock samples by the same method described in this report. Compared with the Sc anode tube, the Rh anode tube is suitable for exciting heavier elements, *i.e.* some trace elements such as Cr, Ni, Rb, Sr, Ba, Y, Zr, Nb, *etc.* The method of trace element analysis using the Rh anode tube will be reported in a separate paper.

Acknowledgements

We wish to thanks Dr. Atsushi Ando of Geological Survey of Japan and Dr. F.J. Flanagan of U.S. Geological Survey for providing the rock standards. We are grateful to Dr. Yasuhito Osanai of Fukuoka University of Education, Mr. Kenji Kizaki of Niigata University, and Miss Norie Fujibayashi of Hokkaido University for their help in this work. Sincere thanks are extended to Dr. Hitoshi Hattori of Geological Survey of Japan who gave us valuable information on analytical method. Thanks are due to Prof. Yoshio Katsui, Dr. Teruo Watanabe, and Dr. Kiyoaki Niida of Hokkaido University for valuable suggestions and critical reading of the manuscript.

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(Manuscript received on Nov. 17, 1988; and accepted on Nov. 30, 1988)