X-ray Fluorescence Analysis for Major Elements in Granitic Rocks by Fused Glass Disk Method

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Abstract

Chemical analysis of major elements has been carried out by XRF method, using fused glass disks prepared with 1 : 10 proportion of sample : flux. Standard samples of the Geological Survey of Japan were employed to draw the calibration curves for the following oxides : SiO_2, TiO_2, Al_2O_3, Fe_2O_3, MnO, CaO, MgO, P_2O_5 and K_2O. On the basis of these curves, total analysis was performed on 6 unknown samples of granite. Contents of Na_2O were determined separately by flame photometry and the results were discussed with special emphasis to silica determination.

1. Introduction

Quantitative chemical analysis by X-ray fluorescence gives rapid results compared with conventional wet method. However, resulting values are not always in high accuracy, when pressed brickets of powdered samples are used because of inhomogeneity of forming pressure, mineral effect, matrix effect and so on. On the other hand fused glass disk method generally gives more accurate results because of reducing these bad effects, although the cost of disk preparation is rather high including crucibles and other surrounding equipments. The fused glass disk method has been carried out in order to check the reliability of analysis and this paper may provide a note of guide to XRF.

2. Experimental

Five standard samples in powder supplied from Geological Survey of Japan, JR-2 (rhyolite), JG-1a (granodiorite), JA-1 (andesite), JB-1a(basalt) and JGb-1 (gabbro), and six granitic samples from Argentina, CH-97, CH-122, CH-124, CH-126, CH-127 and CH-150 were collected. Rock samples were finely pulverized by a vibrational mill for two minutes and homogenized in sample bottles by shaking. These rock samples as well as the standard samples were calcined beforehand at 900℃ for 2 hours in air to eliminate unstable volatile components, mainly hydroxyl and water. By this treatment FeO and MnO components convert to Fe_2O_3 and Mn_3O_4 respectively[1,2] as shown in Table 3. Six grams of lithium borate, $Li_2B_4O_7$, and 0.6 gram of the heat treated

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samples were weighed and dry-mixed in an agate mortar with a slight addition of 0.03 gram of lithium bromide, LiBr, as debbubling agent.* Fusion of mixes was performed at 1100℃ employing an electric furnace and an 80 gram platinum crucible** of flat bottom dissolving 5 percent gold which facilitates easy demolding of glass disks from the crucible. The mixes were transferred throughly to the crucible and then inserted directly to the furnace, using a pair of tongue with tips of platinum cover after the temperature of the furnace reached 1100℃. Then the crucible was taken out of the furnace after 3 to 5 minute ignition and stirred manually with horizontal and circular

Table 1 Measurement conditions for present fused glass disk method.

Component	SiO_2	TiO_2	Al_2O_3	Fe_2O_3	MnO	CaO	MgO	P_2O_5	K_2O
Spectrum	← Ka →								
Generator									
Target	← Cr →								
KV	← 50 →								
mA	← 30 →								
Spectrometer									
Crystal	EDDT	LiF	EDDT	LiF	LiF	LiF	ADP	Ge	Ge
Detector	PC	SC	PC	SC	SC	SC	PC	PC	PC
2θ for peak	108.07	86.18	142.73	57.55	62.97	113.15	136.73	141.08	69.98
2θ for Bg1	105.00	84.00	···†	56.00	60.00	110.50	135.00	137.50	67.00
2θ for Bg2	111.50	89.00	146.00	59.50	···†	114.75	139.50	145.00	73.00
X-ray path	← vacuum →								
Sample spin	← on →								
P.H.A.									
Mode	← Dif. x1 →								
Coarse gain	← 5 →								
Base line	280	380	280	360	380	360	300	300	300
Window	120	220	140	220	160	260	100	90	90
Linking	← on →								
Recorder									
Ratemeter (cps)	8,000	4,000	200	8,000	10,000	20,000	100	200	40,000
Time const. (sec)	← 0.5 →								
Chart speed (mm/min)	← 20 →								
Count									
Fixed time (sec)	40	20	40	20	40	20	40	40	20
Others									
Slit	← 3S →								
PC HV(V)	← 1,850 →								
SC HV(V)	← 750 →								

† Interference from other peaks.

*Merk analytical grade, melting point of the lithium bromide, 920℃.

**Commercially sold from Tokyo-Kagaku Co., model CS-2.

motion to eliminate the bubbles and to get a homogeneous melt. If droplets of melt are found on the wall of the crucible, they should be included to the host melt through this stirring. This fusion and stir procedure should be repeated several times, usually 3 to 4 times. Duration of fusion did not exceed a total of 20 minutes in this study*. After this treatment the crucible was cooled to room temperature, placing it on a marble plate for 5 to 10 minutes. Then a transparent glass disk with surface diameter of 30 mm and bottom diameter of 28 mm was obtained easily by up side down the crucible. The bottom surface was faced to X-ray.

Operating conditions of the X-ray fluorescence apparatus, Rigaku KG-X, are given in Table 1. A chromium tube was installed and operated at 50 KV and 30 mA. Prior to measurements blanc test of X-ray radiation from sample holder made of aluminum metal was performed in order to detect the effect of the aluminum itself on measurements, indicating the trace presence of impurities, Si, S, Cl, Ca, Mn, Fe, Ni, Cu, Zn, Ga? and Sb other than dominant presence of Al and minor presence of Ti. Then disks of lithium borate as heavy as 5.53 grams and 6.63 grams were mounted on the sample holder separately as dummies. Insufficient screening was found in the case of the former, but sufficient screening was attained in the case of the latter for present operating conditions of the target, 50 KV and 30 mA**. Therefore, present disks consisting of 6 gram flux and 0.6 gram sample together with 0.03 gram debubbling agent may screen enough the radiations from the bottom. Measurements of peak top and back ground on both sides were repeated five times to get mean values. Recommended chemical compositions of the standard samples by wet method and

Table 2 Chemical compositions of the standard samples by wet method.

	JGb−1	JB−1a	JA−1	JG−1a	JR−2
SiO_2	43.44	52.16	64.06	72.19	75.65
TiO_2	1.62	1.30	0.87	0.25	0.09
Al_2O_3	17.66	14.51	14.98	14.22	12.82
Fe_2O_3	4.89	2.52	2.42	0.43	0.38
FeO	9.24	5.92	4.08	1.46	0.43
MnO	0.16	0.15	0.15	0.06	0.11
CaO	11.98	9.23	5.68	2.13	0.45
MgO	7.83	7.75	1.61	0.69	0.05
P_2O_5	0.05	0.26	0.16	0.08	0.01
K_2O	0.26	1.46	0.82	4.04	4.48
Na_2O	1.23	2.74	3.86	3.41	4.03
H_2O+	1.23	1.10	0.80	0.59	1.28
H_2O-	0.04	0.86	0.26	0.09	0.14
Total	99.63	99.96	99.75	99.64	99.92

*According to Nakada et al.[3] no appreciable depletion of volatile elements such as sodium occurs at 1050℃, even if the duration of fusion is prolonged up to one hour.

**According to Nakada et al.[3] combination use of plastic and copper plates are helpful to this screening purpose at higher power of X-ray.

Table 3 Chemical compositions of the standard samples normalized to one hundred after the calcination.

	JGb−1	JB−1a	JA−1	JG−1a	JR−2
SiO_2	43.70	52.87	64.61	72.83	76.76
TiO_2	1.63	1.32	0.88	0.25	0.09
Al_2O_3	17.77	14.71	15.11	14.34	13.00
Fe_2O_3	15.25	9.22	7.01	2.07	0.87
Mn_3O_4	0.17	0.16	0.16	0.06	0.12
CaO	12.05	9.35	5.73	2.15	0.46
MgO	7.88	7.85	1.62	0.70	0.05
P_2O_5	0.05	0.26	0.16	0.08	0.01
K_2O	0.26	1.48	0.83	4.08	4.55
Ka_2O	1.24	2.78	3.89	3.44	4.09

Table 4 Calibration curves obtained from the standard samples by regression analysis.

Component	Formula	σ
SiO_2	$Y=-9.554+102.772X-21.276X^2$	0.490
	$Y=2.449+70.220X$*	0.215
TiO_2	$Y=0.014+0.244X$	0.011
Al_2O_3	$Y=-2.567+16.743X$	0.134
Fe_2O_3	$Y=-0.111+2.134X$	0.174
MnO**	$Y=-0.639+0.698X$	0.035
CaO	$Y=-0.090+2.183X$	0.038
MgO	$Y=-0.012+0.737X$	0.019
P_2O_5	$Y=-0.001+0.081X$	0.004
K_2O	$Y=-0.059+4.132X$	0.024

Y : Chemical composition, X : Counting ratio to host sampl, JG−1a.
* : Excluding JR−2 ** Recalculated from Mn_3O_4.

recalculated chemical compositions after the calcination are given in Tables 2 and 3, respectively.

3. Results and Discussion

Calibration curves obtained by regression analysis for each component are listed in Table 4 in the form of equations with X and Y, which denote counting ratios to the host rock (present investigation JG-1a) and contents of component to be determined, respectively. Analytical results are summarized in Table 5. Generally speaking, acceptable results have been obtained, judging from the total values in each sample. However, it should be better to discuss more about silica determination. It has been pointed out hitherto by many authors that silica contents can well be determined by square functions and this approximation was followed this time, since the samples are

Table 5 Analytical results of the granitic rocks.

	CH−97	CH−122	CH−124	CH−126	CH−127	CH−150
SiO_2	75.94	76.05	76.57	76.91	77.19	71.70
TiO_2	0.08	0.12	0.11	0.12	0.12	0.31
Al_2O_3	14.28	12.94	13.18	13.23	12.43	14.30
Fe_2O_3	1.16	1.39	1.29	0.93	1.35	3.36
MnO	0.03	0.06	0.05	0.04	0.05	0.08
CaO	0.44	0.64	0.56	0.57	0.68	1.33
MgO	0.07	0.13	0.05	0.05	0.04	0.37
P_2O_5	0.01	0.01	0.01	0.02	0.02	0.08
K_2O	4.88	4.85	5.08	4.99	4.85	5.31
Na_2O*	3.16	3.65	3.31	3.44	3.41	3.65
Total	100.05	99.84	100.21	100.30	100.14	100.49

*Analized by flame photometry.

silica rich rocks and their counting ratios are expected to deviate from linear functions. However, it seems that approximation by the linear function is suitable in the range between X=0.62 and 0.91 corresponding to 46 and 66 percent SiO_2 as shown in Fig. 1, judging from the standard deviations calculated. In the ranges higher than 0. 91 and lower than 0.62 the difference between the two functions increases gradunally. Therefore, caution should be paied on the analysis of silica poor samples such as ultrabasic rocks as well as silica poor basaltic rocks, when the square function is applied. The difference between the two functions is represented in Table 6 for reference.

According to Nakada et al.[3], square function is applicable for ferric determination. However, in the present investigation no difficulty was found in applying the linear function.

There are several methods for dilution of samples with lithium borate, e. g., 1 : 4[4], 1 : 5[3] and 1 : 10[5]. In order to reduce the matrix effect more dilution is convenient. In this respect the present investigation was carried out by the 1 : 10 method.

According to the eqations determined by the 1 : 5 method[3], matrix effects are very strong for P_2O_5, strong for K_2O and weak for Al_2O_3 and weak for SiO_2. The secondary exciting elements are silicon for P_2O_5, K_2O and Al_2O_3 and calcium for SiO_2. In this study no correction was made on these matrix effects due to the large dilution of samples. Besides the matrix effects would be compensated by using similar rock samples as standard. However, as mentioned above the silicon effect is stronger for P_2O_5 and K_2O and caution should be paid on the analysis of these components, if they are included much more. In such cases colorimetry and flame photometry would be better.

The most modern apparatus, eg., Rigaku 3070 etc., are equipped with automatic calbration system together with the correction of matrix effect by the aid of the installed personal computer. Besides, these apparatus are equipped with an analizing crystal of TAP (100) which facilitates the analysis of sodium and hence total analysis

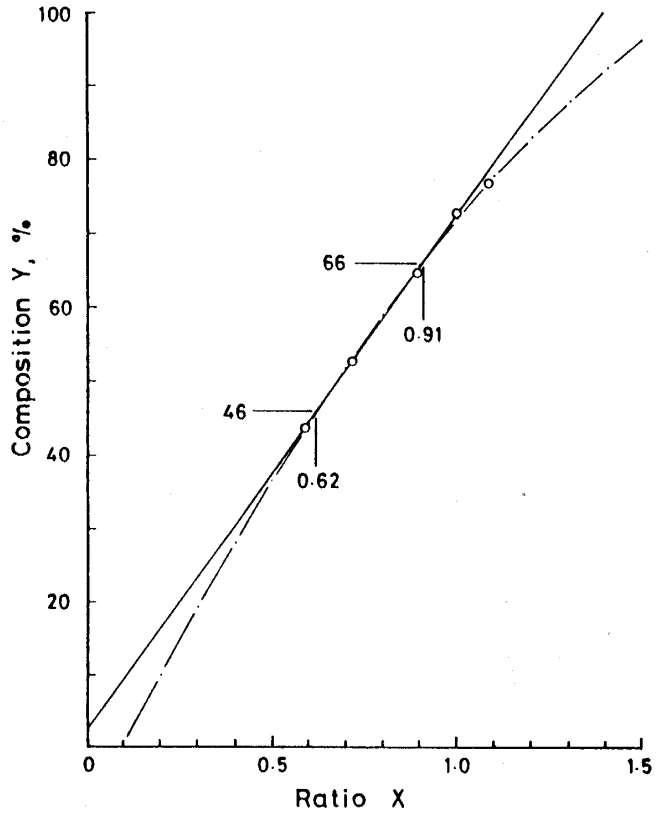

Fig. 1 Calibration curves for silica.

can be done without doing flame photometry on sodium.

4. Summary and Conclusion

X-ray fluorescence analysis has been carried out on 6 granitic samples by using fused glass disk method of 1 : 10 dilution with lithium borate. Determinative curves were obtained by regression analysis, employing 5 standard samples supplied from the Geological Survey of Japan. Acceptable results were obtained without correction of matrix effect. Differences between square function and linear function were discussed on silica determination. Square function is applicable to silica rich samples, but caution should be paied on silica poor samples.

Nakada et al.[3] found serious counting errors of fluorescent X-ray caused by mismount of samples. In some cases we also encountered very bad results probably due to the mismount of the sample. Same mount position of height level and center should be maintained throughout measurements. In this respect it is desired to develop an improved mounting device for fused glass disks. Fused glass disks are not hygroscopic and have a convenience of easy storage and transportation.

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Table 6 Difference between present square funtion and linear function. Minus values of delta indicate exceeding linear function.

X	DELTA(Y)	X	DELTA(Y)
0.310	−3.957	0.760	0.448
0.320	−3.765	0.770	0.447
0.330	−3.578	0.780	0.443
0.340	−3.395	0.790	0.435
0.350	−3.216	0.800	0.422
0.360	−3.042	0.810	0.405
0.370	−2.871	0.820	0.384
0.380	−2.705	0.830	0.358
0.390	−2.544	0.840	0.328
0.400	−2.386	0.850	0.294
0.410	−2.233	0.860	0.256
0.420	−2.084	0.870	0.213
0.430	−1.940	0.880	0.167
0.440	−1.799	0.890	0.116
0.450	−1.663	0.900	0.060
0.460	−1.531	0.910	0.001
0.470	−1.403	0.920	−0.063
0.480	−1.280	0.930	−0.131
0.490	−1.161	0.940	−0.204
0.500	−1.046	0.950	−0.280
0.510	−0.935	0.960	−0.361
0.520	−0.829	0.970	−0.446
0.530	−0.727	0.980	−0.536
0.540	−0.629	0.990	−0.629
0.550	−0.535	1.000	−0.727
0.560	−0.446	1.010	−0.829
0.570	−0.361	1.020	−0.936
0.580	−0.280	1.030	−1.046
0.590	−0.203	1.040	−1.161
0.600	−0.131	1.050	−1.280
0.610	−0.063	1.060	−1.404
0.620	0.001	1.070	−1.531
0.630	0.060	1.080	−1.663
0.640	0.116	1.090	−1.799
0.650	0.167	1.100	−1.940
0.660	0.213	1.110	−2.084
0.670	0.256	1.120	−2.233
0.680	0.294	1.130	−2.387
0.690	0.328	1.140	−2.544
0.700	0.358	1.150	−2.706
0.710	0.384	1.160	−2.872
0.720	0.405	1.170	−3.042
0.730	0.422	1.180	−3.216
0.740	0.435	1.190	−3.395
0.750	0.443	1.200	−3.578

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P.S. Mounting covers of smaller opening diameters are available from makers for the fused glass disk method.