A REFINED FUSION X-RAY FLUORESCENCE TECHNIQUE, AND DETERMINATION OF MAJOR AND MINOR ELEMENTS IN SILICATE STANDARDS[1,2]

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Abstract

An X-ray fluorescence fusion technique involving 1:18 dilution was used for the determination of SIO_2, Al_2O_3, total Fe as Fe_2O_3, MgO, CaO, K_2O, TiO_2, P_2O_5 and MnO in silicate rocks. Fusion of the sample with $LiBO_2$ followed by grinding and pelletizing the fused bead prior to X-ray irradiation eliminates most of the matrix problems associated with X-ray fluorescence analysis. Values obtained by this method compare favorably with the preferred chemical values for seventeen international silicate rock standards.

Introduction

A fusion technique using the proportions 1:14:3 for sample:flux: binder has been applied to X-ray fluorescence (XRF) analysis of major and minor elements in silicate rocks to reduce matrix effects and eliminate grain size and mineralogical effects. Despite the number of papers that have been published on this subject, no published technique has proven fully satisfactory in our applications. Welday *et al.* (1964) suggested that a moderate (1:2, sample to flux) dilution-fusion technique be used to overcome matrix effects not overcome by the direct pelletizing technique of Volborth (1963). Czamanske *et al.* (1966) found that the moderate dilution-fusion technique is not applicable with good accuracy for many of the elements determined in silicate rocks by XRF.

The technique of Norrish and Chappell (1967) or Norrish and Hutton (1969) requires special expertise on the part of the individual preparing samples (Ingamells, 1970) and is more time consuming than the technique reported here. Also, the presence of lanthanum in all samples interfers in the determination of magnesium, especially when the samples contain low concentrations of magnesium. The lanthanum heavy absorber technique of Rose *et al.* (1963) requires the preparation of standards each time a new lot of samples are to be analysed in order to duplicate conditions of sample preparation,

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owing in part to hygroscopic nature of lanthanum oxide, which can absorb 14 percent of its weight in H_2O.

A dilution ratio of 1:14:3 (Sample to flux to binder) was selected over these and other preparation techniques described in the literature to determine SiO_2, Al_2O_3, total Fe as Fe_2O_3, MgO, CaO, K_2O, TiO_2, P_2O_5, and MnO in seventeen international silicate rock standards. The XRF values are in good agreement with preferred chemical values reported in the literature. Mathematical corrections for the matrix effects of absorption and enhancement are not necessary; the pellets are durable; and the $LiBO_2$, being more alkaline than $Li_2M_4O_7$, is better suited as a fluxing agent to dissolve the refractory rock-forming minerals (Ingamells, 1970).

<center>EXPERIMENTAL</center>

Apparatus

A multichannel polychromator (Applied Research Laboratories, VXQ) having an external standard monitor channel and rhodium target tube was used in determining SiO_2, Al_2O_3, total Fe as Fe_2O_3, MgO, CaO, K_2O, TiO_2, and P_2O_5 simultaneously. The configuration of crystals and detectors in the spectograph has been discussed by Rose *et al.* (1963). During irridation of the sample, pluses from the detector charge a capacitor (integrator) for each channel. Charging of all capacitors stops when the external standard reaches a pre-set fixed charge. Integrated intensity ratios of all elements to the external standard are then recorded.

MnO was determined on a single channel spectograph (General Electric, XRD-6) using the tungsten side of a dual target Cr-W tube. Operating conditions for both spectographs are given in Table 1.

Standards and Samples

Many international rock standards were investigated in the course of this work: U.S. Geological Survey standards—granite G-1, diabase W-1, andesite AGV-1, granite G-2, basalt BCR-1, granodiorite GSP-1, peridotite PCC-1, and dunite DTS-1; Canadian Association of Applied Spectroscopy standard—syenite S-1; Centre de Recherche Petrographique et Geochimiques standards—basalt BR, granite GA, granite GR, granite GH, diorite DR-N, and serpentine UB-N; Leningrad State University standard—nepheline syenite USSR; and Geological Survey of Tanzania—tonalite T-1.

Procedure

The sample to flux ($LiBO_2$) to binder (chromatographic cellulose, Whatman CF-11) ratio was 1:14:3. $LiBO_2$[1] was dried in batches at 650°C for 30 minutes in a $\frac{1}{3}$ to $\frac{1}{2}$-full platinum evaporating dish covered with a radial ribbed watch glass. Dried $LiBO_2$ was sieved through a 16-mesh screen and the several dried batches homogenized. 0.1000 gram of sample and 1.4000 gram of dried and screened $LiBO_2$ were placed in a 30 ml porcelain crucible, mixed with a spatula, and carefully transferred to a pre-ignited (950°C for 20 minutes) crucible.[2]

[1] $LiBO_2$, Southwestern Analytical Chemicals, Austin, Texas.

[2] Graphite crucibles, Ultra Carbon Co., A2726, grade UF4S, full radius inside bottom.

The mixture was fused in a furnace for 15 minutes at 900°C. Fused beads were cooled and weighed. 0.3 gram of chromatographic cellulose, plus the equivalent weight loss of H_2O, CO_2, etc., was added to bring the weight of the bead and cellulose to 1.8000 grams. Beads were crushed in a hardened tool steel mortar, transferred with grinding ball and cellulose into a grinding vial (polystyrene with tungsten carbide ball and end caps) and ground in a mixer-mill (Spex) for 10 minutes. The ground powder was further ground and mixed by hand in a boron carbide mortar to ensure complete comminution and homogeneity. Pellets are produced at 30,000 psi (Fabbi, 1970).

SiO_2, Al_2O_3, Fe_2O_3, CaO, MgO, K_2O, TiO_2, and P_2O_5 were determined simultaneously using the multichannel polychromator. Pellets were irradiated for 200 seconds, and charges on the capacitors read sequentially in digitized form as integrated intensity ratios of the element lines to the external standard. This procedure was repeated twice for each sample to improve precision of the analysis. Standard BR (preferred because of its spread of all elements) was analysed after every four samples to determine whether drift occurred in any of the channels. When drift was detected, a correction was appiled. MnO was determined on the single channel spectrograph by counting for 10,000 counts at a 2θ setting of 62.97°. An intensity ratio was calculated for each sample (Bertin, 1970). Calibration curves (intensity ratio *vs*. concentration) for each oxide of the nine elements

Table 1. Instrumental Operating Conditions

Element	Crystal	Counter and Voltage	KV	Ma	Path
Si	Eddt	Ne Minitron Fixed	30	50	Vacuum
Al	Eddt	Ne Minitron Fixed	30	50	Vacuum
Fe	LiF	Ar Multitron Fixed	30	50	Air
Mg	ADP	Ne Minitron Fixed	30	50	Vacuum
Ca	LiF	Ne Multitron Fixed	30	50	Vacuum
K	LiF	Ne Multitron Fixed	30	50	Vacuum
Ti	LiF	Ne Multitron Fixed	30	50	Vacuum
Mn	LiF	Flow Proportional 1400 V	40	50	Air
P	Eddt	Ne Minitron Fixed	30	50	Vacuum

were plotted and a least squares regression was fit to the data. Correct P_2O_5 for second-order CaK_{β_1} and K_{β_5} spectral interference in the manner reported in an earlier paper (Fabbi, 1971).

RESULTS AND DISCUSSION

Factors in Sample Preparation

Powders were ground to 20 μ because it is essential in XRF analysis of light elements to reduce grain size of ground powders to below 400 mesh (36 μ) so as to minimize particle size effects (Bertin, 1970). Cleanliness of the glass lenses used to produce smooth mirrolike pellet surfaces in order to avoid contamination cannot be overemphasized. The procedure for cleaning is reported in an earlier paper (Fabbi, 1970).

The addition of chromatographic cellulose to the sample in the grinding process aids in cleaning the vials and acts as a binder to extend pellet life. Pellets prepared as outlined above with chromatographic cellulose (Whatman, CF-11) binder and methyl cellulose (Matheson, MX850) backing are homogeneous, reusable, durable, will not break when dropped, are not easily contaminated by handling, and have smooth plane surfaces and fine grain size. The preparation can be done by semi-skilled personnel.

Boric acid is unsatisfactory as a binder or backing material, for laboratory tests show that combined water in the boric acid is given off under vacuum in the spectrograph, and the intensity of silica, for example, increases by 10-15 percent in 8 hours. Furthermore, pellets made with boric acid as a binder or backing material become inhomogeneous, unreliable, and disintegrate over a period of time. A thorough discussion of the desirability of using $LiBO_2$ as a fluxing agent for XRF analysis is given by Ingamells (1970). Because finely ground $LiBO_2$, as any finely divided substance, can take up water, pellets should be stored in a desiccator cabinet prior to analysis, and if they are to be used as standards or kept for reference work.

Norrish and Chappell (1967) noted that in reducing matrix effects high dilution of samples achieves results similar to heavy absorber addition. With respect to sensitivity, laboratory tests indiacte that P, Ti, K, and Ca have the same intensity using the high dilution method as obtained using lanthanum heavy absorber method of Rose *et al.* (1963). The intensity of Fe is 2.5 times greater and that of Mn 6 times using the high dilution method. But the intensity of Si is 1.15 and that of Al 1.25 times greater using the heavy absorber method. The intensity of Mg is 1.4 times greater using a heavy absorber than

it is using $LiBO_2$ at the high dilution, but the signal is interferred with by La.

Accuracy of the Method

There is very good agreement between XRF values and preferred values for the oxides of all elements in the standard rocks, as indicated in Table 2. Al_2O_3 values obtained by XRF for the mafic rocks PCC-1 and DTS-1 do not agree with the preferred values. However, they do agree with gravimetric values reported by Goldich *et al.* (1967), 0.58 and 0.16 percent Al_2O_3 respectively. Abbey (1970), using atomic absorption, also reports lower Al_2O_3 values, 0.71 and 0.29 percent Al_2O_3, respectively, for PCC-1 and DTS-1. There is agreement between the XRF value and the preferred Al_2O_3 value for another mafic rock, UB-N. This suggests that the preferred values for Al_2O_3 in PCC-1 and DTS-1 are somewhat high.

Values for SiO_2 and total Fe as Fe_2O_3 for the mafic rocks PCC-1, DTS-1 and UB-N showed the most deviation from preferred values. An infinite dilution technique using five standard rocks, AGV-1, W-1, BR, DR-N, and S-1, for calibration purposes was employed at dilution ratios of 1:1, 1:9, 1:18, and 1:36 with replicate preparations to determine SiO_2 and Fe_2O_3 in the three mafic rocks. Results of the infinite dilution technique are given in Table 2. The SiO_2 values are in agreement with the preferred values and are higher than values obtained using the 1:18 technique. Iron values obtained using the infinite dilution technique are slightly higher than the preferred values, but lower than values obtained using the 1:18 dilution technique. It is apparent that the 1:18 dilution technique does not completely overcome matrix effects in the determination of SiO_2 and Fe_2O_3. It is recommended that SiO_2 and Fe_2O_3 in mafic rocks be determined using similar rock standards such as PCC-1, DTS-1, and UB-N for calibration. All other oxides of the elements reported in this work may be determined using silicate rock standards other than mafics.

Some workers (Leake *et al.*, 1969) recommended a calibration technique reliant solely on statistical reasoning and chemical analyses from one laboratory. The approach used here has been to calibrate with well known standards and use the relative deviation from the calibration curve established by the standards to define the accuracy of the technique. This approach gives more insight and reliability to expected accuracy for a wide variety of rock samples.

The XRF determinations were obtained on triplicate pellets of each rock standard. Errors due to pellet inhomogeneity or sampling at the

Table 2. Comparison of XRF and preferred values for major and
minor elements in percent as oxides.

Sample	Source	SiO_2	Al_2O_3	Total Fe as Fe_2O_3	MgO	CaO	K_2O	TiO_2	P_2O_5	MnO
Granite	USGS[a]	72.64	14.04	1.94	0.38	1.39	5.48	0.26	0.09	0.03
G-1	XRF	72.85	14.35	1.88	0.37	1.33	5.46	0.25	0.09	0.026
Diabase	USGS[a]	52.64	14.85	11.09	6.62	10.96	0.64	1.07	0.14	0.17
W-1	XRF	52.90	14.91	11.09	6.61	10.94	0.61	1.06	0.14	0.167
Andesite	USGS[b]	59.00	17.01	6.80	1.49	4.98	2.90	1.08	0.49	0.098
AGV-1	XRF	59.05	17.06	6.98	1.57	5.01	2.93	1.08	0.49	0.094
Granite	USGS[b]	69.19	15.35	2.77	0.78	1.99	4.51	0.53	0.14	0.037
G-2	XRF	69.36	14.95	2.76	0.81	1.97	4.38	0.50	0.12	0.034
Basalt	USGS[b]	54.49	13.66	13.51	3.28	6.95	1.68	2.23	0.36	0.176
BCR-1	XRF	54.55	13.32	13.50	3.48	6.98	1.70	2.25	0.36	0.185
Granodiorite	USGS[b]	67.28	15.12	4.33	0.96	2.03	5.49	0.70	0.29	0.044
GSP-1	XRF	67.44	15.02	4.37	0.98	2.01	5.46	0.67	0.29	0.040
Peridotite	USGS[b]	41.87[h]	0.86	8.54[h]	43.56	0.53	0.02	0.02	0.01	0.122
PCC-1	XRF	41.55[h]	0.58	8.56[h]	43.15	0.53	0.00	0.02	0.03	0.135
Dunite	USGS[b]	40.46[h]	0.55	8.85[h]	49.81	0.16	0.02	0.02	0.01	0.126
DTS-1	XRF	40.35[h]	0.16	9.13[h]	50.03	0.16	0.00	0.02	0.02	0.145
Syenite	SSC[c]	59.5	9.6	8.3	4.2	10.2	2.67	0.49	0.22	0.40
S-1	XRF	59.66	9.14	8.29	4.22	10.04	2.61	0.48	0.23	0.390
Basalt	France[d]	38.20	10.20	12.93	13.28	13.74	1.40	2.62	1.04	0.21
BR	XRF	38.89	10.28	12.71	13.29	13.84	1.41	2.62	1.11	0.190
Granite	France[d]	65.90	14.75	4.05	2.40	2.50	4.50	0.65	0.28	0.06
GR	XRF	66.05	14.53	4.06	2.42	2.35	4.52	0.65	0.27	0.053
Granite	France[d]	69.90	14.50	2.86	0.95	2.45	4.03	0.38	0.12	0.09
GA	XRF	69.51	14.69	2.74	0.95	2.41	4.12	0.35	0.16	0.084
Granite	France[d]	75.80	12.50	1.33	0.03	0.65	4.78	0.09	0.01	0.05
GH	XRF	75.60	12.87	1.35	0.07	0.64	4.92	0.08	0.03	0.046
Diorite	France[e]	52.65	17.42	9.91	4.50	7.08	1.70	1.11	0.27	0.21
DR-N	XRF	52.19	17.51	9.92	4.46	7.05	1.78	1.11	0.30	0.216
Serpentine	France[e]	39.40[h]	2.99	8.52[h]	35.00	1.12	0.02	0.12	0.03	0.12
UB-N	XRF	39.20[h]	2.79	8.61[h]	35.44	1.12	0.02	0.12	0.07	0.140
Syenite	USSR[f]	53.22	21.26	4.35	0.65	1.80	6.52	1.05	0.29	0.18
USSR	XRF	52.78	21.08	4.12	0.66	1.65	6.50	1.06	0.27	0.182
Tonalite	DES[g]	62.65	16.52	6.03	1.89	5.19	1.23	0.59	0.14	0.11
T-1	XRF	62.80	16.30	6.12	1.67	5.11	1.20	0.58	0.17	0.101

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[f]A. A. Kukharenko and others, Vses. Mineralog. Obshchest. Zapiski. 97, 133 (1968)

[g]Geol. Surv. Tanzania, Dar es Salaam, Msusule Tonalite Supp., No. 1 (1963)

[h]XRF determination by infinite dilution

100 mg level are minimized, but are additive to any other combined XRF technique errors, *i.e.*, instrumental, counting, pellet placement, pellet surface, particle size, etc. Table 3 illustrates the lowering of average relative error when one, two, or three replicate pellets are analysed. It appears that neither accuracy nor precision is greatly increased if three rather than two replicates of any given sample are analysed. Indeed, for some oxides the error increases with three replicates. Three factors can account for such increases: (1) sample preparation errors, (2) instrumental precision as illustrated by SiO_2 and Al_2O_3, and (3) disagreement with average preferred values, but agreement with gravimetric values in the literature, for example, CaO and Al_2O_3 in samples nepheline syenite USSR and syenite S-1. The XRF value of 1.65 percent CaO does agree with the gravimetric value of 1.67 percent CaO reported by Ingamells (Kukharenko *et al.*, 1968) for sample USSR. The XRF values of 10.04 percent CaO and 9.14 percent Al_2O_3 do agree with the gravimetric values, 10.09 percent CaO and 9.01 percent Al_2O_3 for S-1, reported by Ingamells and Suhr (1963).

Alternative Methods of Sample Preparation

The high dilution-fusion method of XRF analysis suggested in this work overcomes most matrix effects at the 100 mg sampling level. Splits of all samples were taken on an "as received" basis. Consequently, splitting or sampling errors would be greater for samples having coarser grain fractions.

It may be possible to further improve the accuracy of the proposed fusion method by: grinding samples to minus 200 mesh to insure homogeneity before splitting out 100 mg for analysis; taking larger

Table 3. Average relative error in percent for replicate
pellet preparations

Oxide	1 Pellet	2 Pellets	3 Pellets	Concentration Range %
SiO_2	0.88	0.35	0.38	35 – 77
Al_2O_3	2.55	1.27	1.39	2.0 – 21
Total Fe as Fe_2O_3	2.33	2.01	1.53	1.3 – 14
MgO	4.59	2.50	2.22	0.65 – 50
CaO	2.80	1.38	1.74	0.16 – 14
K_2O	3.60	2.72	2.37	0.02 – 7
TiO_2	2.02	2.63	2.24	0.02 – 2.6
P_2O_5	6.70	7.77	7.92	0.10 – 1
MnO	7.16	6.91	7.13	0.03 – 0.40

splits of the sample without grinding and increasing the amount of flux and binder proportionally; or a combination of both grinding and taking larger splits.

Time Required for Analysis

The maximum number of samples that can be handled by the instruments is 10 samples (20 pellets) daily. Thirty samples could be analysed per week for nine elements by three persons; this would include all facets of the analysis, *i.e.*, sample preparation, instrumental analysis, computations, and filing of reports. This is a more realistic estimate of total analytical time expenditure than that of authors who report many samples prepared for analysis per day but neglect time required for mixing samples, cleaning crucibles, computations, report filing, etc. The XRF technique as currently employed with two people performing the analysis (15 samples per week) is 4 to 7 times faster than conventional gravimetric methods. Should the relative error of one pellet preparation give sufficient accuracy for a particular geologic problem, productivity would be doubled.

CONCLUSIONS

The 1:18 dilution fusion technique using $LiBO_2$ as a fluxing agent has reduced or eliminated matrix effects and eliminated mineralogical and grain-size effects. Many samples can be analysed rapidly and routinely. The analyst is not limited by the requirement that standards match closely the composition of samples in the XRF determination. With the exception of phosphorus, mathematical corrections for matrix effects are unnecessary. It is possible to determine Mg accurately in low concentrations. Silicate rocks varying widely in composition can be accurately analysed for SiO_2, Al_2O_3, total Fe as Fe_2O_3, MgO, CaO, K_2O, TiO_2, P_2O_5, and MnO much faster than by conventional gravimetric methods.

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