

The preparation of fused samples in X-ray fluorescence analysis

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SUMMARY. A rapid fusion technique is described in which the $\text{Li}_2\text{B}_4\text{O}_7$ bead is polished, not crushed. The reliability of the technique is illustrated by a series of precision tests and analyses of standard rocks, using a 2:1 $\text{Li}_2\text{B}_4\text{O}_7$:rock-powder dilution. It is also pointed out that such a low-dilution fusion method may be used for Na_2O and trace element analyses with only a small loss in sensitivity relative to the unfused-powder method. Any fusion method has the advantages of greatly reducing absorption effects and eliminating particle-size effects.

A MAJOR problem in X-ray fluorescence analysis is the dependence of the intensity of a particular radiation upon the composition of the matrix. The most important of the various matrix effects are those due to the absorption and enhancement of the radiation, which can be related directly to the bulk composition of the matrix, and those due to particle size. The wide variation in the chemistry and mineralogy of rocks makes them particularly susceptible to these effects.

Geologists have generally tackled the problem in one of two ways: by choosing standards with a similar matrix to the unknown combined with prolonged grinding, or by fusing the rock powder with a suitable flux. In the unfused method, difficulties arise in several ways: in obtaining the same grain-size distribution in rocks of variable mineralogy; in the initial assumption of the crude composition made in order that the correct set of standards can be used; and in the large number of standards required. The fusion method, on the other hand, involves a loss of sensitivity due to dilution, while the preparation of fused samples has frequently been regarded as difficult and time-consuming.

The choice of method must depend on the nature of a particular problem, but it is the authors' contention that, because of some initial technical difficulties, the fusion method has been neglected by many geologists as a routine approach to rock and mineral analysis. In the course of a prolonged series of experiments aimed at determining the method most applicable to routine work, the authors have concluded that a modification of the method first described by Welday *et al.* (1964) is the most satisfactory. It eliminates particle-size effects and drastically reduces, but does not entirely remove (Czamanske *et al.*, 1966), absorption and enhancement effects, while the loss in sensitivity is much less than might have been expected. Sodium is well within range, even with a 1 kW generator. The lower limit of detection of trace elements for any particular count time is only marginally higher than in an unfused pellet. The sample preparation procedure is simple and appears to be rather less time-consuming than those used to make pellets from unfused powders.

Procedure. Weigh out 3.5 g rock powder, previously ground as for chemical analysis, and 7.0 g lithium tetraborate (Specpure) into a polystyrene mixing phial, mixing for 10 min with lucite balls on a ball mill. Pour the mixture into a graphite crucible and place in a muffle furnace at 1000 °C for 15 minutes. The graphite crucibles suggested by Welday *et al.* (1964) may be obtained from Heyden and Son Ltd., London, with a carrier holding ten crucibles, which may be loaded into the furnace as a single unit.

TABLE I. *Variation in the Fe- $K\alpha_1$ intensity at various levels in two separately prepared beads of Whin Sill dolerite. After grinding to the level stated, each bead was briefly polished with diamond paste*

	Intensity (c/s)		
	Bead A	Bead B	
Whole bead remaining	8352	8568	Standard deviation for eight readings
$\frac{1}{2}$ bead remaining	8396	8412	(s) = 68 c/s
$\frac{1}{3}$ bead remaining	8468	8440	(= 0.1 % Fe_2O_3)
$\frac{1}{4}$ bead remaining	8396	8376	the coefficient of variation (C) = 0.8%

The total weight of sample and flux and the internal diameter of the graphite crucibles are critical. The final beads are designed to fit the standard Philips sample holders. If the quantity of material is too great relative to the diameter of the crucibles, so that the melt is in contact with the sides of the crucibles all the way around, then the beads are likely to shatter on cooling or become stuck in the bottom of the crucible.

After cooling, the glass beads drop out of the crucibles and their flat surfaces are ground on a carborundum wheel and then polished briefly with diamond paste. Total grinding and polishing time is approximately 15 min for each bead. The beads, now ready for analysis, are very tough and do not deteriorate with time. Should the necessity arise the surface may be cleaned with carbon tetrachloride or repolished.

Precision tests. All measurements were carried out on a Philips X-ray spectrograph, model PW 1540, using a 1-kW generator and a Cr target.

Use of uncrushed beads raises the possibility of a lack of homogeneity. This was checked by grinding beads to successive levels and measuring the intensity after each grinding. The results for the Fe- $K\alpha_1$ radiation is given in table I. The over-all precision resulting from this preparation technique, including an artificially large variation in the length of the fusions, is given in table II. It is appreciated that the measurements are too few to give a statistically reliable standard deviation (s), yet the order of the likely error is clear. The precision indicated is poor relative to the expected instrumental precision, but probably well within the overall precision of most analytical laboratories.

Loss of volatiles. Inherent in any fusion technique is the loss of the volatile constituents and it is necessary to measure the volatile content separately. While it is possible to use rock powder from which the volatiles have already been removed

before mixing with the tetraborate (Welday *et al.*, 1964), it is simpler to weigh out the rock powder with its normal volatile content. The removal of the volatiles during fusion involves an increase in the concentration of the other ions of the rock powder to the extent of $\frac{1}{3}$ of the volatile content if a 2:1 dilution is employed. This will result in the summation of the analysis adding up to $100 + \frac{1}{3}$ of the volatile percentage and the total of each oxide must be corrected accordingly.

TABLE II. Variation in the intensity (c/s) of the $K\alpha_1$ line of some major elements in separately prepared beads of the Whin Sill dolerite and an aplite vein. A, fused for 15 min; B, fused for 30 min in muffle furnace. The standard deviation (s) as % oxide and the coefficient of variation (C) are given for each group of four measurements

	Whin Sill						Aplite vein					
	A ₁	A ₂	B ₁	B ₂	s	C	A ₁	A ₂	B ₁	B ₂	s	C
Ca	3628	3632	3616	3652	0.04	0.4	1124	1164	1155	1143	0.03	1.5
Ti	3548	3296	3308	3468	0.08	3.6	460	463	458	452	0.002	1.0
K	335	336	336	327	0.01	1.3	64	63	62	64	0.09	2.7
Si	2264	2238	2214	2248	0.46	0.9	—	—	—	—	—	—
Mg	125	123	122	123	0.07	1.4	—	—	—	—	—	—
Mn	437	439	434	432	0.004	2.1	486	492	483	475	0.002	1.4
Fe	5352	5376	5430	5540	0.20	1.5	1657	1652	1637	1644	0.01	0.5

Absorption effects, although greatly reduced, are still apparent at the 2:1 dilution level (Czamanske *et al.*, 1966) and are particularly noticeable for SiO₂ and Al₂O₃. The effect may be minimized by using calibration curves derived from a series of semi-standards analysed by some other technique. Column A in table III gives the values for a number of international standard rocks calculated in this way. The semi-standards used to derive the calibration curves were mainly igneous rocks and shales analysed more than once by different chemical techniques. Synthetic standards were used in the case of MgO. While the results are generally less satisfactory than the values corrected for fluorescent absorption, shown in column C, they nevertheless show a very fair correspondence with values published for these rocks (Flanagan, 1967; Roubault *et al.*, 1966). SiO₂ is the least satisfactory while Al₂O₃ values are persistently high. The two ultrabasic rocks, with their extreme compositions, are somewhat less satisfactory than the others, as might be expected from the calibration procedure used. By employing standards more similar in composition to the unknowns these results would be improved, just as they are in unfused-powder techniques.

By neglecting absorption corrections it is possible to analyse an element independent of others, a procedure particularly desirable on non-automatic instruments.

The values in column C of table III have been found by first correcting the intensity values for the fluorescent absorption, then using one of them and a blank as standards to draw a straight-line calibration curve (Gunn, 1967). Exceptions to this were made in the case of SiO₂ for which two of the standard rocks were used (without a blank), and of MgO where three synthetic standards were used to construct the calibration curve. Corrections for MnO and P₂O₅ were not applied.

TABLE III. Analyses of the major elements of standard rocks. A, uncorrected X.R.F. analyses using calibration curves derived from a series of chemically analysed rocks. B, average analyses published by the Geological Survey of America (Flanagan, 1967) and Roubault et al. (1966). C, the same analyses as in A but with the intensity corrected for fluorescent absorption. Calibration of the corrected intensities was achieved by accepting two of the rocks as standards (st.) in the case of SiO₂, by using three synthetic standards for MgO and by using one and a blank as standards for the other oxides. The corrections for MnO and P₂O₅ were insignificant and are not included

	SiO ₂			Total Iron as Al ₂ O ₃			Fe ₂ O ₃			MgO			MnO	
	A	B	C	A	B	C	A	B	C	A	B	C	A	B
	G2	68.2	69.14	66.80	16.4	15.55	st.	2.70	2.68	2.58	0.82	0.73	0.80	0.03
GSP-I	67.5	67.23	65.10	16.3	15.42	15.50	4.50	4.33	4.34	0.79	0.95	1.00	0.04	0.05
AGV-I	59.7	59.07	59.25	17.9	17.26	17.57	6.90	6.75	6.77	1.55	1.50	1.82	0.10	0.10
BCR-I	55.2	54.15	54.30	13.9	13.87	14.23	13.00	13.21	st.	3.55	3.53	3.52	0.19	0.19
PCC-I	41.8	42.20	42.45	1.2	0.71	1.10	10.20	8.11	8.42	43.28	43.17	43.50	0.15	0.12
DTS-I	40.0	41.02	40.80	0.6	0.28	0.40	10.30	8.59	9.10	46.84	49.65	48.60	0.16	0.12
G.A.	69.2	69.71	67.10	15.5	14.61	14.37	2.80	2.81	2.65	1.20	0.97	1.20	0.10	0.09
G.H.	76.1	75.58	st.	13.7	12.63	12.95	1.30	1.31	1.17	0.23	0.07	0.20	0.05	0.05
B.R.	40.8	38.60	st.	9.7	10.40	10.50	11.5	12.91	12.70	11.98	12.60	13.20	0.20	0.21

	CaO			K ₂ O			TiO ₂			Na ₂ O			P ₂ O ₅	
	A	B	C	A	B	C	A	B	C	A	B	C	A	B
G2	1.80	1.93	1.91	4.43	4.50	4.71	0.48	0.48	0.48	4.1	4.02	st.	0.10	0.14
GSP-I	1.88	2.03	2.01	5.40	5.52	st.	0.66	0.66	0.66	3.2	2.78	3.18	0.28	0.30
AGV-I	4.83	4.82	4.83	2.96	2.83	2.97	1.08	1.05	1.05	4.6	4.22	4.68	0.52	0.51
BCR-I	7.12	6.85	st.	1.71	1.65	1.72	2.17	2.24	st.	3.7	3.26	4.05	0.39	0.40
PCC-I	0.51	0.45	0.51	0.02	0.01	0.02	0.01	0.01	0.01	0.0	0.01	0.00	0.01	0.03
DTS-I	0.10	0.05	0.11	0.00	0.01	0.03	0.01	0.00	0.00	0.0	0.05	0.60	0.03	0.02
G.A.	2.25	2.48	2.42	4.13	4.03	4.28	0.35	0.37	0.36	4.9	3.57	3.54	0.12	0.12
G.H.	0.57	0.68	0.65	4.77	4.78	4.65	0.05	0.08	0.08	4.6	3.83	3.42	0.01	0.01
B.R.	14.40	13.80	13.15	1.45	1.45	1.38	2.44	2.70	2.65	3.6	3.05	2.90	1.20	1.03

TABLE IV. A comparison of count rate and sensitivity of a 2:1 Li₂B₄O₇ fused bead (A) to an unfused powder pellet (B) for the elements Sr and Zr. C, concentration. P, peak + background. B, background. L, lower limit of detection for 112 sec count

	Sr					Zr				
	C	P	B	c/s	L	C	P	B	c/s	L
	ppm	c/s	c/s	ppm	ppm	ppm	c/s	c/s	ppm	ppm
A	425	503	302	0.470	10	210	516	395	0.590	10
B	130	267	187	0.630	6	400	530	238	0.876	5

With the important exception of SiO₂, the absorption corrections improve the results significantly. For the basic and ultrabasic rocks the SiO₂ results are also improved, but the three most silicic rocks show values up to nearly 3% too low. Because of the calibration method used this is primarily a discrepancy between Granite GH and the other three. The values are reproducible on the same sample, but lack of material has prevented the preparation of other samples. Clearly more work is needed to determine the cause of this divergence.

Sensitivity. It has frequently been remarked to the authors that a fusion method must rule out the measurement of sodium and the trace elements. Our results show that sensitivity is certainly reduced, but that the effect is much less than might have been supposed. Values for Na_2O are recorded in table III. Table IV compares the count rate and lower limit of detection for a specific counting time for a 2:1 fusion and a pelleted unfused powder for the elements Zr and Sr. The implication of these results is that, while in specific problems of trace analysis it might be essential to use unfused powders, in the great majority of cases the 2:1 fused samples show a satisfactory sensitivity and an error that might well be less than that obtained when using a pure-powder technique because the absorption problems are greatly reduced.

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