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SILICATE SAMPLE PREPARATION FOR LIGHT-ELEMENT ANALYSES BY X-RAY SPECTROGRAPHY

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Abstract

Specimen preparation methods for light element analyses Na through Fe in silicates, by *x*-ray fluorescence spectrography, have been compared on the bases of precision, applicable ranges of elemental compositions, and ease of making. It is concluded that fusions using 65% $Li_2B_4O_7$ flux provide the highest overall precision for analyses of Na, Mg, Al, Si, K, Ca and Fe from a single preparation. Fusion techniques may not be significantly more difficult and costly than preparations of unfused ground powders if done routinely in batches. Fusion techniques may be required in the analyses of some mineralogically heterogeneous samples where uniform grinding is not possible. In the compositional ranges tested (equivalent to that between leucocratic granite and gabbro) addition of a heavy absorber is unnecessary and causes poorer signal/noise ratios for the lightest of light elements. The details of a moderate dilution fusion technique are presented which has been used routinely for several hundred analyses. The precision and speed of this technique are discussed.

Introduction

For a number of years *x*-ray spectrography has been used routinely for the quantitative determinations of elements in rocks and minerals. Until recently, however, the method has been limited to aluminum and heavier elements, or in cases of relatively high concentration, to magnesium as a lower limit. The development of soft *x*-ray sources by Henke (1962, 1963a) and their applications to commercially available spectrographic equipment has extended the method through sodium for routine rock analysis (Baird *et al.*, 1963a) and now offers the possibility of quantitative results for elements as light as boron, carbon, and oxygen (Henke, 1963b; Baird *et al.*, 1963b).

X-ray spectrography is a universal method applicable to nearly all major and minor elements in silicates. The precision and speed have been shown to be superior to results obtained by wet methods (Baird *et al.*, 1962 and 1963a). An advantage of *x*-ray analysis, usually unobtainable by wet-chemical procedures, is that the precision can be partly controlled by the amount of care used in preparing the specimens for analysis, and thus can be tailored to the requirements of the job to be done. This paper presents the results of a study of commonly used specimen preparation procedures, with the aim of evaluating the relative precision, speed and cost of each. It is limited to silicates in the range of rock composition from gabbro to leucocratic granites.

PREPARATION REQUIREMENTS FOR X-RAY ANALYSIS

All quantitative determinations by x-ray spectrography, regardless of the form of specimen preparation used, have as a basic error the variance produced in counting the random pulses received from the detector. The statistics of such counting procedures are well known (see, for example, Klug and Alexander, 1954; Stanley, 1961), and allow the analyst to choose a counting precision within the limits of his signal to noise ratio and total signal to time allowed for analysis. For example (Fig. 1), to achieve a precision (counting error only) for analysis of SiO_2 equivalent to that of better wet-chemical methods (0.6% relative deviation; Fairbairn *et al.*, 1951) about 32,000 counts would have to be accumulated, assuming a signal to noise ratio of about 30. At a counting rate of 300 cps (typical for tungsten excitation with fused rocks as specimens) this count would require $1\frac{3}{4}$ minutes. Lower total signal and signal to noise ratio obviously increase counting time, and as lighter elements and lower concentrations are considered, the necessary counting time may become unreasonable (or even infinite) in terms of instrument electronic drift and/or cost. The example above deals only with the basic counting error and all higher-order sources of variance introduced in preparing specimens need to be considered in relation to this error.

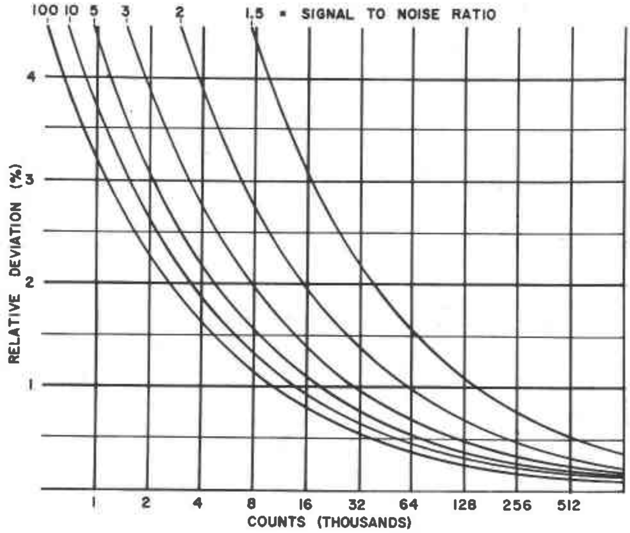

FIG. 1. Statistics of counting random pulses from an x-ray detector. Precision expressed as per cent relative deviation = 100× (standard deviation)/mean, for a given fixed count at a given signal to noise ratio.

At the other extreme of considerations of analytical precision, the spectrographer should be aware of what overall precision is actually required for the job to be done. Because higher precision obviously necessitates more care and expense than lower precision, an attempt should be made to determine the limits. Unfortunately, in many geologic studies this cannot be known "a priori," but must be tested. For example, Table 1 shows analytical precisions (standard deviations) for several elemental determinations in comparison with locality variability; *i.e.* the variability caused by selecting one specimen, rather than another, within a restricted area when there is no basis for making a field judgment on which specimen should be collected. It is clear from Table 1 that for every element except Si and Al, the analytical precision is, in a sense, too good and that too much effort has been expended in analytical techniques. But a single preparation was used for all elements, and therefore the effort expended was required for the adequate determination of Si and Al. This conclusion may not be applicable to other rocks and other petrologic problems.

TABLE 1. ANALYTICAL PRECISION AND FIELD LOCALITY VARIABILITY: BIOTITE QUARTZ MONZONITE, SAN BERNARDINO MTS., CALIFORNIA

Element	Composition	Analytical[1] Precision wt. %	Field locality[2] variability wt. %
Na	2.0	0.02	0.21
Mg	0.25	0.01	0.07
Al	7.9	0.04	0.14
Si	34.0	0.18	0.53
K	3.8	0.03	0.47
Ca	1.0	0.01	0.19
Fe	0.7	0.02	0.49

[1] Standard deviations based on 2 splits from each of 68 rocks. It is assumed that every determination reported will be the mean of two briquettes.

[2] Standard deviations of residuals from highest order significant trend surfaces.

Considering these approaches to problems of analytical precision the following points were evaluated for the various techniques studied:

1) Useful range of elemental compositions handled by preparations
2) Relative precisions of preparations
3) Ease, and therefore cost of preparations

PREPARATION TECHNIQUES STUDIED

Techniques in common usage today are of two general types: 1) direct analysis of ground powders (Chodos and Engel, 1961; Volborth, 1963), with or without dual grinding procedures to assess introduction of grinding-plate contaminants (Volborth, 1964); and 2) analysis of silicate glasses produced by fusion with various fluxes and dilution ratios, and with or without addition of heavy-element absorbers to produce more uniform matrices (Claisse, 1956; Rose *et al.*, 1962).

From these two groups the following modifications of particular techniques were tested:

1) Simple ground powders of silicates
2) Fusions using 70% sodium tetraborate flux

TABLE 2. ELEMENTAL RANGES TESTED AND PRECISIONS OF PREPARATION METHODS

	Element	Na	Mg	Al	Si	K	Ca	Fe
	Composition Range-wt. %	1–7	1–8	2–10	19–46	0.5–12	1–9	2–14
Relative Deviations in %	Unfused Ground Powder	5	7	10	5	10	5	10
	Moderate Dilution	4	7	9	3	3	2	7
	High Dilution $+La_2O_3$	5	6	13	3	8	2	8
	High Dilution	—	11	16	2	4	3	7
	Very High Dilution	—	18	20	5	7	14	23

3) Fusions using 60% lithium tetraborate flux
4) Fusions using 85% sodium tetraborate flux
5) Fusions using 95% sodium tetraborate flux
6) Fusions using 66.6% lithium tetraborate and 16.6% lanthanum oxide (83.3% total dilution)

Preparation method 1) will be termed "ground powder" in the text to follow; methods 2) and 3) "moderate dilution"; 4) "high dilution"; 5) "very high dilution"; and 6) "high dilution with heavy absorber." Protions of flux, rock, and lanthanum oxide used in the heavy absorber preparations are those stated by Rose *et al.* (1962). According to these authors (p. 82) the ratios may not be optimum, but have yielded successful results in their laboratory.

In order to include a range of elemental compositions, exceeding that of common igneous rocks, apparently pure mineral species were mixed in varying proportions. Minerals used were quartz, biotite, hornblende, orthoclase and oligoclase. Splits of 25 different mineral mixtures were prepared by the techniques listed above. Though precise knowledge of the chemical composition of each "rock" is not available, relative deviations can still be compared between methods. The approximate ranges of elemental concentrations are given in Table 2. For the ground powder technique, constituent minerals were ground for four minutes in a ball mill. All fusions were prepared by the method outlined at the end of this paper. Both ground powders of "rocks" and reground fusions were pressed into a coherent specimen for spectrographic analysis at 30,000 psi with a bakelite jacket and no internal binder.

TABLE 3. CONDITIONS OF RUNNING PHILIPS VACUUM-PATH *X*-RAY SPECTROGRAPH

Element	Na	Mg	Al	Si	K	Ca	Fe
Excitation	Al K		Ag L		W (Philips FA-60)		
Power	10 kv—150 ma				50 kv-35 ma		35 kv 25 ma
Tube Window	6μ Al foil		25μ Be foil		1500μ Be		
Collimation	4×1×0.500 in.		4×0.6×0.035 in.		4×0.6×0.015 in.		
Analyzing Crystal	Gypsum		EDDT				
2θ	103°	81.1°	142.5°	108.0°	50.3°	44.9°	25.4°
Flow Counter Window	6μ Al foil			6μ Aluminized Mylar			

Note: Center of pulse distribution set at 15v baseline for each element by adjustment of counter voltage, and appropriate baseline and window selected to include 99% of distribution.

X-RAY ANALYSIS OF PREPARATIONS

Running conditions of spectrographic equipment are given in Table 3. Explanations of excitation, windows, crystals, collimation, etc., have been previously published (Baird *et al.*, 1963a). All prepared samples were run in elemental batches with two readings of each taken symmetrically about a mid-point of running time to avoid any effects of instrumental drift. In order to complete all readings on one element within one instru-

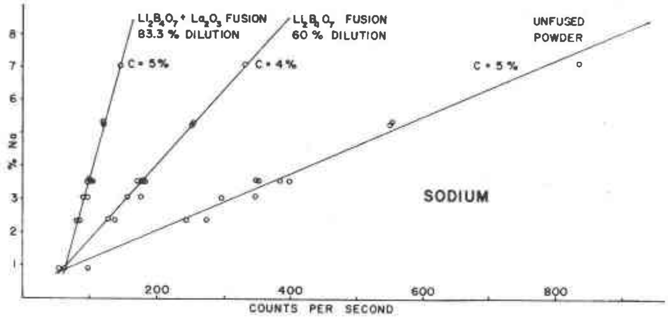

FIG. 2. Calibration curves for sodium analyses by preparation techniques indicated. C = per cent relative deviation of weight per cent sodium.

ment run it was necessary to restrict the total time of fixed-counting on individual specimens. This resulted in different values of precision for counting dependent on total signal. The effect of varying counting precision is analyzed below. For ground powder 64,000 to 128,000 fixed counts were accumulated; for moderate and high dilutions and for high dilutions with heavy absorber 16,000 to 64,000; and for very high dilutions 4,000 to 32,000. Even with these restrictions, time intervals exceeding 1,000 seconds of fixed counting per specimen occurred in preparations of very high dilution and low elemental concentration.

Presentation of Analytical Results

Counting rates, corrected for any instrumental drift, were combined with composition values and calibration curves were fitted by the least-squares method. A measure of the total scatter from the calibration line is provided by the relative deviation, "C," in per cent. Values of C% con-

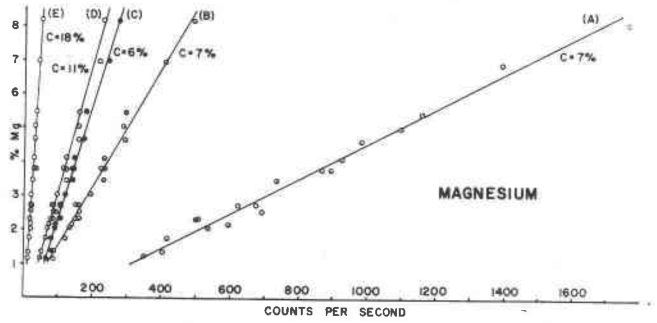

FIG. 3. Calibration curves for magnesium. (A) = ground powder; (B) = moderate dilution; (C) = high dilution with heavy absorber; (D) = high dilution; and (E) = very high dilution. C = per cent relative deviation of weight per cent magnesium.

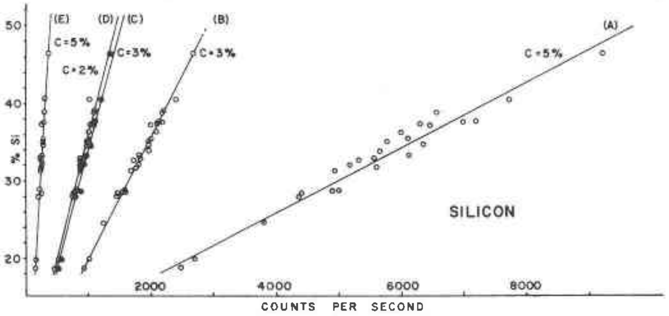

Fig. 4. Calibration curves for silicon. (A) = ground powder; (B) = moderate dilution; (C) = high dilution with heavy absorber; (D) = high dilution; and (E) = very high dilution. C = per cent relative deviation of weight per cent silicon.

verted from cps to weight per cent for Na, Mg, Al, Si, K, Ca and Fe are shown in Table 2, and representative calibration curves are given in Figs. 2 through 5, with each preparation method indicated. Curves for Al are similar to those for Si and curves for Ca and Fe are similar to K. Separate values are not shown for moderate dilutions using lithium borate because no significant improvement in relative deviation was detected. As noted below, however, lithium borate is to be preferred to sodium borate due to improved total signal. The curves for Na differ from those of the other elements because sodium borate is not appropriate as a flux. For moderate dilution the lithium borate curve is substituted on the Na diagram. Values of relative deviation presented on all curves and in Table 2 are rounded to the nearest whole per cent. It should be noted that the plotted points on all curves of very high dilution always *appear* to be a better fit than those of lower dilution or no dilution. This apparently good fit is,

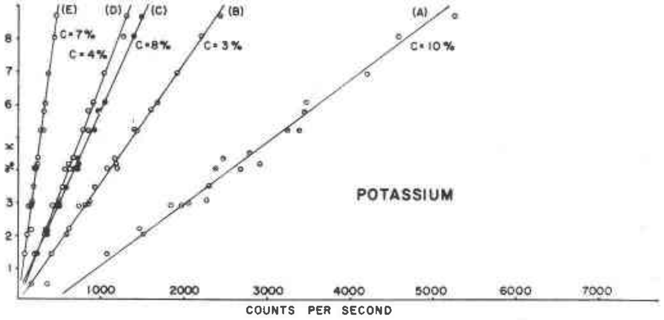

Fig. 5. Calibration curves for potassium. (A) = ground powder; (B) = moderate dilution; (C) = high dilution with heavy absorber; and (D) = high dilution; and (E) = very high dilution. C = per cent relative deviation of weight per cent potassium.

however, merely a reflection of the steep slope of these calibration curves and in all cases results in lower precision when equated to weight per cent of the element.

In evaluating Table 2 and Figs. 2–5, it should be remembered that the total number of fixed counts taken was not constant. Therefore, it is to be expected that larger relative deviations will occur for very high dilutions compared to moderate dilutions and ground powder, for a given elemental concentration, due solely to counting statistics. For example, Fig. 6, based on Si, shows (by shading) that portion of the total relative deviation due to this error. It might be argued that this invalidates the tests between methods, but analytical time is of the utmost importance in practice.

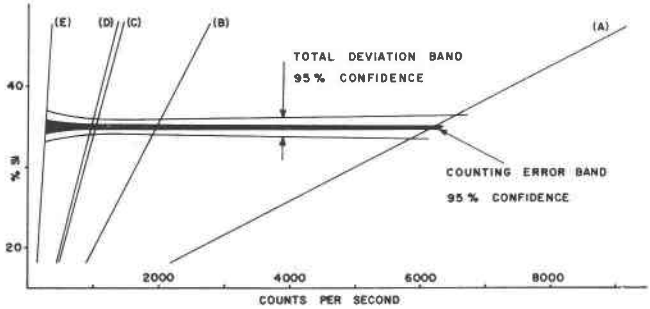

FIG. 6. Relationships between counting statistics error, total error, and preparation technique. See text for discussion.

EVALUATION OF METHODS

Useful elemental ranges of the preparation techniques. Within the element compositional ranges considered, all forms of preparation yielded linear calibration curves; that is, the sensitivities of the tests were inadequate to detect non-linear conditions if present. This result may cease to follow for mineralogical samples including such diverse compounds as carbonates and sulfides on single calibration lines.

Precision

(a) Fusion methods *vs.* ground powders

Fusion techniques were first proposed (Claisse, 1956) as an attempt to overcome the problems of matrix absorption or enhancement of fluorescent *x*-rays used for analysis, as well as to avoid chemical inhomogeneities in heterogeneous mixtures of particles. The results of this test indicate that matrix problems with ground powders are not causing non-linear calibration curves over the elemental ranges considered. However, the total relative deviation from calibration lines is shown to be larger with ground powders than with moderate dilution fusions despite the favorably high counting rates obtained with powders. Figure 6, based on Si, shows this relationship and can be extended to other elements studied, except Mg. Only the Mg run showed no statistically significant improvement after fusion.

TABLE 4. EFFECT OF GRINDING FUSED AND UNFUSED BIOTITE-BEARING ROCK POWDERS

Element	Grinding Time (Min)	Fused Powders		Unfused Powders	
		Wt. %[1]	Std. Dev. Wt. %	Wt. %[1]	Std. Dev. Wt. %
Fe	$\frac{1}{4}$	2.43	0.02	2.01	0.09
	1	2.45	0.01	2.09	0.02
	4	2.46	0.01	2.44	0.03
	16	2.43	0.01	2.66	0.01
	32	2.44	0.01	2.90	0.01
K	$\frac{1}{4}$	2.94	0.01	2.95	0.03
	1	2.93	<0.01	2.86	<0.01
	4	2.93	<0.01	2.96	0.01
	16	2.91	<0.01	2.87	<0.01
	32	2.94	0.01	2.85	<0.01
Al	$\frac{1}{4}$	7.92	0.07	7.13	0.15
	1	8.02	0.04	7.76	0.07
	4	8.01	0.01	8.10	0.02
	16	8.04	0.01	8.21	0.01
	32	8.11	0.04	8.27	0.01
Si	$\frac{1}{4}$	30.73	0.25	29.70	0.20
	1	31.21	0.10	30.58	0.04
	4	31.41	0.06	31.53	0.12
	16	31.57	0.05	31.82	0.09
	32	32.06	0.12	31.49	0.05

[1] Mean of 4 preparations for each grinding time. Fusions prepared by the moderate dilution technique using $Li_2B_4O_7$ flux.

It is apparent that the major advantage of the fusion technique lies in reducing the problem of a non-homogeneous specimen in analyses for some of the light elements in rocks containing minerals of heterogeneous physical properties. Evidence from tests of grinding fused and unfused powders supports this statement (Table 4). The rock used contains 75%

feldspar (microcline and oligoclase), 20% quartz, and only 5% biotite. Analytical results for several major constituents were compared for mean weight per cent versus grinding time in a Pica mill (tool steel vials with 3 balls). The results show that after a $\frac{1}{4}$-minute of grinding, compositions determined from fusions become independent of grinding time (except possibly for Si); whereas, compositions determined from rock powders for Fe, Al, and Si continue to increase up to the time limit (32 minutes) used in the tests. Furthermore, lower and more nearly constant standard deviations are achieved with fusions. The tendency for reduction in standard deviations with increased grinding time in unfused powders suggests that times in excess of 32 minutes may be required for the best results.

(b) Lithium tetraborate *vs.* sodium tetraborate flux

Lithium tetraborate has two advantages over sodium tetraborate used as a flux in the same dilution ratio: 1) it allows a single prepared specimen to be used for analyses Na through Fe; and 2) it yields a higher total signal apparently because of decreased matrix absorption which seems to vary inversely with atomic number. For example, in Al analyses the signal is 28% higher than preparations with borax flux.

(c) Moderate and high dilutions *vs.* very high dilutions

Figure 6 shows that differences in relative deviations between all fusion techniques are due largely to counting statistics. In comparing fusions with ground powders it was noted that absorption-enhancement effects can be neglected and therefore there appears to be no advantage in increasing the flux to specimen ratio. Rather, to achieve the best counting statistics, and still avoid mineral grain inhomogeneities, fusion with as low a flux to specimen ratio as possible seems desirable. Practical limits to this ratio, however, are discussed under ease of preparation.

(d) Dilution methods *vs.* dilutions with heavy absorber

Over the elemental ranges considered, the addition of a heavy absorber produced no significant improvement in precision over plain fluxes with similar dilution ratios. In order to use the technique, the total dilution necessarily becomes high; and as noted above, high dilutions seem less desirable because of poorer counting statistics. For the lightest elements Na and Mg, addition of a heavy absorber resulted in much poorer counting statistics than would be expected merely from the higher total dilution. This is shown in Table 5 where it can be noted that noise levels are more than 100% higher than those of simple fusions of similar dilution. Because the total signal is lower and the noise higher, the time that would be required for fixed-counting to the same precision as with simple fusions is increased more than 500%.

Ease of preparation. Plain ground rock powders can be prepared faster and easier than any fusion technique and have the advantage of eliminating possible weighing errors. For monomineralic specimens, and for very light element (below Si) determinations in rocks, this approach may be the least costly. However, some of the advantage of speed may be lost when dealing with mineralogically heterogeneous samples where longer and more precisely timed grindings are necessary for the best precision. For heterogeneous samples, even if highest analytical precision is not needed, compacting or pressing the rock powders into a coherent specimen for use in a vacuum spectrograph may be difficult. Our experience with tuffs and rhyolites has shown a high proportion of breakage compared with ground powders of fused samples of the same rocks.

TABLE 5. COMPARISON OF FUSION TECHNIQUES WITH AND WITHOUT ADDITION OF HEAVY ABSORBER FOR NA AND MG ANALYSES

Preparation		$Li_2B_4O_7+La_2O_3$	$Li_2B_4O_7$ only
Na	Signal	127 cps	240 cps
	Noise	52 cps	19 cps
	Signal/noise	2.5/1	12/1
	Counting time[1]	370 sec	61 sec
Mg	Signal	128 cps	230 cps
	Noise	54 cps	22 cps
	Signal/noise	2.4/1	10/1
	Counting time[1]	370 sec	64 sec

[1] Time required for fixed count necessary to achieve 1% relative deviation (see figure 1).

All fusion techniques present about the same difficulties of preparation, except for the heavy absorber method where an additional weighing is required. Additional steps needed in all fusions are drying, weighing, fusing, and regrinding. For a single specimen, these steps are tedious, but for larger batches they can be performed quickly. Using modern top-loading balances, equipped with taring devices, weighings can be made rapidly. Fusions can be done in graphite crucibles in a large-capacity muffle furnace in groups of ten or more. If large-size crucibles (relative to the total specimen size) are used, the fusion will bead-up on the bottom of the crucible, not wetting the sides, and fall free when cool. No crucible cleaning is required. In our experience the most time consuming phase of preparation cannot be avoided by any technique tested: that is, the cleaning of crushing, pulverizing, grinding and pressing equipment. The additional time required for fusion seems justified in terms of improved precision and ease of handling of the resulting powder.

It was noted above that the moderate dilution method achieves the desired effect of eliminating mineralogical inhomogeneity and also provides higher total signal than high or very high dilutions. Ideally, the lower the flux to rock ratio, the higher the signal will be and, therefore, instrument running time will be shorter for an adequate period of fixed-counting. In practice, however, fusions with more than 40–45% rock are difficult to make, requiring both rock and flux to be very finely ground and thoroughly mixed. Higher furnace temperatures and longer fusion times are also required.

CONCLUSIONS AND A RECOMMENDED PREPARATION TECHNIQUE

For the analysis of common rocks, consisting of heterogeneous mixtures of minerals, a moderate dilution fusion method produces the best overall precision for elements Na through Fe in a single preparation. This method is only slightly more time-consuming to use than plain ground rock powders and avoids both the grinding problems and briquette-pressing problems associated with mineral mixtures having diverse physical properties. Addition of a heavy absorber reduces both signal and signal to noise ratio, without significant improvement in analytical precision. For very light element analyses, using soft *x*-ray excitation, the heavy absorber produces much higher noise levels.

Considering the results of these tests, a moderate dilution technique has been devised for highest overall precision and the details are presented below. This technique has been used routinely for the analyses of several hundred specimens including diverse rock types such as granite, amphibolite and mica schist. The particular method is designed for batch analysis, in groups of 30 or more. For maximum efficiency at least two persons should prepare the specimens, and there should be a third person to operate the spectrograph. A balance with relatively low sensitivity (0.01 gms), such as the top-loading Mettler K, is used to speed routine weighings. Because of the relatively large sample size (8 gm) in comparison to balance sensitivity the weighing error is less than that normally introduced by the counting statistics. All specimens are replicated from the stage of fine grinding. A computer program is used to determine least-squares calibration curves from several standards (prepared in the same manner and with the same flux dilution as the unknowns) and thus to calculate compositions of replicate unknowns. The two calculated values of per cent element are used to check gross error in preparation; their mean is taken to improve the overall precision of the analysis. Replicates with differences exceeding a pre-set amount are automatically marked in the computer output and the specimens remade. Steps in the preparation are:

1) Crush rock in jaw crusher.
2) Grind in pulverizer to approximately 30 mesh (a Bico model UA is used).
3) Split down to a sample of 40 gm. This size is determined by the capacity of the fine-grind ball-mill used (a Pitchford Scientific Instruments Pica blender mill, model 3800).
4) Fine-grind 4 min. in a Pica ball mill. Split in half, with each half carried through remaining steps independently. (Splits taken from the coarser pulverizer step result in significantly greater splitting errors and are more difficult to fuse.)
5) Dry in vacuum oven at >20″ vacuum and 100° C. for 10–15 min. Cool in vacuum desiccator.

Steps 6 through 9 apply only when fusion loss or gain is to be determined.

6) Weigh on analytical balance in porcelain crucibles.
7) Heat in muffle furnace for 10 min. at 850° C.
8) Cool in vacuum desiccator.
9) Reweigh and determine fusion loss or gain.
10) Using top-loading balance (such as Mettler K) tare graphite crucible (YU-40 grade graphite, crucible A-2726, Ultra Carbon Corp.). Add 5.2 gms $Li_2B_4O_7$ (*x*-ray spectrographic grade, Allied Chemical Corp.). Add 2.8 gms specimen powder from fine-grind split.
11) Stir thoroughly, to assure complete fluxing.
12) Fuse 20 min. at approximately 1050° C. Ten crucibles are set on a graphite carrier (available from Ultra Carbon Corp.) and this carrier is placed in a furnace preheated to 1100° C. Fusion time-count is begun when furnace temperature begins to rise after insertion of cold crucibles. Final temperature is about 1100° C., rising throughout the fusion period.
13) Air cooled fusion beads are reweighed. Weight should be 8.00 gms less fusion loss. (Manufacturer's guaranteed maximum loss of flux at 900° C. is 0.4%. Losses of flux determined in our laboratory have never exceeded 0.1%.) If significantly different an original weighing error is probable and the specimen is remade.
14) Fusion bead is crushed or broken to $\frac{1}{4}''$ chips.
15) Fine-grind fusion for 4 min. in Pica Mill.
16) Final powder pressed into coherent specimen at 30,000 psi with a bakelite backing and rim. No internal binder. (See Baird, 1961, for details of pressing procedure and equipment.)

A typical application of these procedures is represented by the analyses of a batch of 68 individual granitic rock specimens from a single plutonic body. Each was analyzed for Na, Mg, Al, Si, K, Ca and Fe, a total of 136 preparations and 952 spectrographic determinations. With two people in the laboratory, preparation time was 10 days, followed by 7 days of instrument running. This is an average of four rock analyses per day, and the rate could be approximately doubled by simultaneous preparation and running of the spectrograph. An adequately staffed laboratory should, therefore, be able to perform complete silicate analyses at the rate of 40 per week. Precisions of these analyses are shown in Table 1.

COMMENTS ON THE "ACCURACY" OF THE X-RAY METHOD OF ANALYSIS

In this study the relative precisions of several techniques of specimen preparation have been tested. The relative accuracies are more difficult to determine, partly because of uncertainties in the compositions of the original minerals used. Usually the *x*-ray method relies on calibration curves derived from a few standards that have been analyzed repeatedly by wet chemistry. Thus the *x*-ray method of analysis is comparative, dependent upon other methods for absolute values, and cannot be more accurate than the standards permit. In relation to absolute methods, *x*-ray determinations can be more precise, and the combination of relatively imprecise but accurate wet methods with very precise and rapid *x*-ray techniques becomes a powerful tool for silicate analyses.

Unfortunately, well analyzed standards for use in rock analysis are rare; the prime examples are G-1 and W-1. The assumption of a linear *x*-ray emission response with change in weight per cent between two standards is not always justified. Techniques of specimen preparation are designed not only to give the best possible reproducibility of *x*-ray intensities from replicates of one rock, but also to achieve the closest approach possible to linear calibrations amongst several rocks. In all the tests reported here there were no demonstrably non-linear calibrations. However, in routine runs, such as listed in Table I, slightly but significantly quadratic calibrations have occasionally been found by using several standards. For this reason it is desirable to use many standards even if their elemental values are not as well known as those of G-1 and W-1; a least squares regression, weighting G-1 and W-1, gives a measure of the departures (if any) from linearity. If calibrations are non-linear it suggests that the preparation technique being used may not be correcting completely for inter-element enhancement or absorption.

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script. However, the authors alone are responsible for any errors and for conclusions reached.

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