ATOMIC ABSORPTION MAJOR ELEMENT ANALYSIS USING A
LITHIUM METABORATE FUSION TECHNIQUE AND SOME
POSSIBLE APPLICATIONS TO ORE FINDING [1]/

By

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INTRODUCTION

A lithium metaborate fusion technique for the analysis
of silicate rocks has been adapted to atomic absorption spectro-
scopy by Medlin et al (1969). Some trace and all major elements
can be easily determined, and the method has also been applied
successfully to analyses of such diverse materials as massive
sulfide ore, alumina refractories, portland cement, and silica
brick (Medlin et al, 1969; Slavin, 1968). This paper presents
some comments on details of the laboratory technique not dis-
cussed by Medlin et al, and represents a portion of a disser-
tation by the author in the Department of Geosciences of the
University of Arizona.

ANALYTICAL TECHNIQUE

Fusion Procedure

To prepare the solution 0.100 gm of sample is mixed
with 0.500 gm of lithium metaborate on a weighing paper. The
sample is gently transferred to a pre-ignited graphite fusion
crucible, and fused in a muffle furnace for 15 minutes at about
$1000^{\circ}C$. Forty ml of 3 percent HNO_3 (v/v) are pipeted into a 250
ml Nalgene beaker, containing a teflon-coated stirring bar, then
placed on a magnetic stirring unit. The crucible is then removed

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from the furnace, swirled gently to gather any uncoalesced beads
of melt and the molten bead is immediately poured into the beaker.
The beaker is quickly covered with a glass plate to limit steam
loss and the acid-bead mixture is stirred gently without heating
until solution is complete (about 15 minutes). The solution is
then transferred to a clean bottle with a tightly fitting cap.

Medlin et al (1969), Yule and Swanson (1969), and others
specify that the sample should be ground to -200 mesh to speed
up the fusion. The minerals fused in this investigation were
all in the range -65+100 mesh and some contained over 50 percent
quartz. To test the importance of grind size on completion of
fusion, duplicate fusions were made on numerous feldspars and
micas in two size ranges, -65+100 and -200 mesh. A 15 minute
fusion time on samples of both size ranges resulted in no dif-
ference in either the speed of subsequent solution of the bead
or the reproducibility of the resulting analyses. Consequently,
it was concluded that in 15 minutes any mineral under -65 mesh
size will fuse completely. It is important that the sample and
flux be well mixed. Otherwise locally high concentrations of
silica form in the molten bead, and solution may be incomplete
even after several hours stirring.

All crucibles (Ultra Carbon A-2260, YU-40) were pre-
ignited at 700°C for 10 to 15 minutes. Failure to do so invari-
ably resulted in some of the bead sticking to the bottom of the
crucible during the first fusion. Crucibles can be reused 6 or
7 times before they deteriorate excessively. During the fusion
small amounts of a sublimate form part way up the inside of the
crucible. The sublimate does not appear to affect the analyses
and can be wiped off, along with the carbon powder which collects
on the surface, with a soft tissue. If excessive carbon parti-
cles occur in the solution, they can be removed by filtering.

The loss of solvent through boiling during the pour
appears to be minor. The molten bead does not damage the beaker
due to the formation of a layer of steam between it and the
beaker walls, according to Koutz (1969). Care must be taken to
prevent loss of the solution by operating the stirrer too rapidly.
The time for complete solution varies from about seven to ten
minutes, with samples containing higher silica and alumina re-
quiring more time to dissolve.

The resulting solution may be stored for several days.
Good reproducibility was obtained for K and Na analyses in a
high silica matrix from samples which had been stored for five
days. Some erratic results were noted, however, particularly
with Ca, and the samples analyzed for Ca should be run as soon
as possible. If storage is necessary, standards and unknowns
should be fused at the same time to minimize the effects of time.
The stability of the solutions increases rapidly as the complexity
of the matrix decreases.

Dilutions

Once the sample has been taken into solution it is
necessary to dilute portions to lower concentrations. The opti-
mum concentration for analyses of most elements is below about
40 ppm, and for samples containing 10 percent of an element to
be determined (equivalent to 250 ppm in the fusion solution),
considerable dilution is necessary. For analysis of K and Na
an aliquot of the fusion solution is diluted with water. For

analysis of Fe, Mg, Ca, Al, Si, and Mn an aliquot of the fusion solution is diluted with a one percent solution of La (as $LaNO_3$). Trace elements, including Ti, Cu, and Zn are determined directly from the fusion solution. The dilutions used here are listed on Table 1, and are mostly those recommended by Medlin et al (1969).

A La stock solution is prepared by dissolving 100 grams of $LaNO_3$ in one liter of water and filtering through a tight filter paper. From the filtered solution a one percent La solution is prepared by diluting 250 ml of the storage solution to one liter. Lanthanum acts as a releasing agent (Dinnin, 1960), and prevents the formation of refractory substances in the flame. Refractories are not easily reduced to the atomic state, and this state is essential to the success of the atomic absorption method. The formation of refractories results in readings lower than that amount actually present.

In most cases the dilutions mentioned above were sufficient. Where concentrations are too high additional dilutions can be made over those noted on Table 1. Suhr (personal communication, November 1970) suggests that, alternatively, a less sensitive portion of the flame can be used, or a smaller quantity of the sample can be fused.

Standards

It is a generally recommended procedure in atomic absorption work to match standards and unknowns with respect to the major components in solution. This tends to reduce errors due to different physical characteristics of the solutions such as viscosity, specific heat, density, and surface tension, collectively referred to as matrix effects. Failure to match matrices does not affect the precision of the analysis, but results in uniformly low, and thus inaccurate, results being reported. Matrix matching is less important at high dilutions.

The ideal standards would be a set of natural rocks which had been crushed, homogenized, and accurately analyzed, and which were plentiful enough to use as working standards. Although acceptable in all respects the U.S.G.S. standards are only available in limited quantities. Alternative approaches involve collecting natural rock samples and analyzing them by other methods, or preparation of artificial standards from various oxides and salts of the elements. Blank standards containing all major elements present in the mineral except the one being determined are necessary for zeroing the instrument and generally have to be prepared artificially.

Instrumentation

All analyses were preformed on a Perkin-Elmer Model 290 atomic absorption spectrophotometer equipped to read in direct concentration units. The readings are displayed on a meter marked from 0 to 100 units and generally provide linear working curves up to at least 50 units absorbance. The light sources used were either single or multiple element hollow cathode lamps, and were usually found to provide more noisefree and precise analyses when given 10 to 15 minutes warmup. A premix burner was used for all determinations involving an air-acetylene flame. A nitrous oxide-acetylene flame was used for Al and Ti. Other instrumental parameters are given in Table 1.

TABLE 1

INSTRUMENTAL AND ANALYTICAL CONDITIONS

Element	Wavelength (Å)	Flame	Burner Position	Dilution (Sample : Dilutent)
Al	3093	$N_2O-C_2H_2$	Parallel	1:6 La
Fe	2483	$Air-C_2H_2$	Parallel and Perpendicular	1:6, 1:11 La
Mg	2852	$Air-C_2H_2$	Perpendicular	1:6, 1:11 La
Ca	4227	$Air-C_2H_2$	Parallel	1:6, 1:11 La
Na	5890, 5896	$Air-C_2H_2$	Parallel	1:40 H_2O
K	7699	$Air-C_2H_2$	Parallel	1:40 H_2O
Mn	2795, 2798, 2801	$Air-C_2H_2$	Parallel	1:6 La
Ti	3643	$N_2O-C_2H_2$	Parallel	none
Cu	3247	$Air-C_2H_2$	Parallel	none
Zn	2138	$Air-C_2H_2$	Parallel	none

Drift in the instrument was noticeable for Al and Ti. This was continually monitored and corrected by running standards along with the unknowns after the standard curve had been defined. Burner clogging was occasionally a problem using the N_2O burner, and it had to be cleaned several times during each period of operation.

Cost of the Method

Using the technique described above approximately 20 rocks were analyzed for eight major elements and selected trace elements in two days by one man, representing a minimum average production of about 80 analyses per day per analyst. This is comparable to the commercial production rate for trace element determinations. The speed and simplicity of the method indicate that the cost per analysis for major element determinations would not exceed that for trace elements. The atomic absorption units necessary for the work are currently owned by most mining and commercial laboratories. The only additional costs to these laboratories would be for more glassware and training of the analyst, and these costs would be minimal.

Precision and Accuracy

Precision was not reported by Medlin et al (1969). In the present work the relative average deviation was generally less than one percent. The precision for the trace elements Mn, Cu, and Zn using the lithium metaborate fusion technique and the Perkin-Elmer Model 290, although good, is generally less than for the major rock-forming elements. Superior precision would undoubtedly be possible with the more sophisticated instruments currently available.

A measure of the accuracy obtainable by using artificial standards is shown in Table 2. The inconsistencies present, such as too little FeO and Al_2O_3, and too much MgO and CaO, are in part attributable to the use of artificial mineral standards rather than rock standards. Thus the concentrations of many of the elements in the standards were far above the concentrations found in the rocks. Since major element concentrations in the rocks fell outside the range of the standards, projection of the curves to lower ranges was necessary, and probably contributed to the errors present. The data presented here and by Medlin et al (1969) clearly establish that the accuracy of the lithium metaborate fusion method is equal to that of the more laborious conventional wet analytical methods.

POSSIBLE APPLICATIONS TO EXPLORATION GEOLOGY

Essentially all whole rock analytical work used by exploration geologists is concerned with the trace elements commonly associated with hydrothermal mineralization. Such work is widely applied in the search for mineralized areas and defining drill targets. It is noteworthy that in magmatically related deposits, changes in the concentration of major rock forming elements also occur in the process leading up to and including ore deposition. Geochemical studies of these changes may provide an additional tool for the evaluation of potentially mineralized areas.

TABLE 2

ANALYTICAL DATA ON STANDARD ROCKS

	Granite, G-2[1]		Andesite, AGV-1[1]		Basalt, BCR-1[1]		Orthoclase, SRM-70a[2]	
	Found	Present	Found	Present	Found	Present	Found	Present
Al_2O_3	15.4	15.14	17.2	16.90	13.6	13.41	17.9	17.9
FeO	2.3	2.42	6.0	6.01	12.5	11.98	-	-
MgO	0.9	0.75	1.7	1.46	3.9	3.41	-	-
CaO	1.94	2.03	4.77	4.92	6.65	6.98	0.12	0.11
Na_2O	4.04	4.05	4.18	4.21	3.18	3.23	2.32	2.5
K_2O	4.6	4.50	2.9	2.89	1.7	1.68	12.2	11.8
MnO	0.025	0.03	0.102	0.10	0.191	0.19	-	-
TiO_2	0.33	0.47	0.92	1.04	2.16	2.23	-	-
Cu	13	11	68	69	8	27	-	-
Zn	70	88	80	118	127	130	-	-

Note: Values were reported to one decimal place for those elements where no standards were available in that range and a curve had to be extrapolated, or the range between standards was too great to plot a curve more accurately.

References: 1) Medlin et al (1969), and 2) National Bureau of Standards Certificate of Analysis, March 26, 1965.

Thus one approach to the definition of potentially favorable mineralized areas would be to study the various major element contents and ratios in rocks. Such an investigation would be based on the concept that magmatically related ore deposits are a result of differentiation trends which are reflected in the chemistry of the rock. As an example of this type of approach, the suggestion made by Anderson (1966) is noteworthy. He demonstrated that unaltered porphyry copper-related intrusions tend to have Niggli k values (molecular proportion $K_2O/K_2O + Na_2O$) of between 0.3 and 0.4. It has not yet been demonstrated that this characteristic is peculiar to porphyry copper-related intrusions or to all Laramide intrusions in general, although such information would clearly have a bearing on further exploration in the Southwestern United States. Extension of this approach to intrusions in British Columbia, South America, and the Southwest Pacific may also yield significant and useable information.

Knowledge of major element variation in minerals and rocks in altered zones might also be useful for defining drill targets. As an example two whole rock analyses from the Four Metals area in the Patagonia Mountains in southeast Arizona are cited. The unaltered granodiorite adjacent to the Four Metals breccia pipe has a K_2O/Na_2O ratio of 0.98, while the altered granodiorite in the mineralized portion of the pipe has a ratio of 10.89. The recognition of similar changes in the major element composition of altered rocks could assist with the interpretation of weak trace element anomalies.

Major element analyses of minerals can be equally useful in exploration. Kuellemer (1960) used an X-ray technique to determine the albite (and thus the Na_2O) content of orthoclase in the Schultze granite in the Globe-Miami district. His work indicated that the albite (or Na_2O) content of orthoclase decreased adjacent to the Castle Dome and Inspiration deposits.

Variations in Fe and Mg contents in biotite can also be useful. Wones and Eugster (1965) demonstrated experimentally that where oxygen pressure in a magma increases, iron is removed from early biotite and combines with the oxygen to form magnetite and a new biotite with a lower Fe/Mg ratio than early-formed biotites. In those parts of a system where water contents are increasing, oxygen pressures will increase due to the dissociation of water to form oxygen and hydrogen (hydrogen being lost by outward diffusion). Thus in a magma where water content is increasing (and a potential hydrothermal solution is being developed) a progressive decrease in Fe/Mg ratios of biotite will occur in the later crystallized rock. The trend of decreasing Fe/Mg ratio is opposite to that normally observed in dry, cooling intrusions and might be used as a guide to potentially productive areas within a given pluton. Such "productive" trends have been recognized by this writer in the Four Metals area in the Patagonia Mountains, Arizona, where the trends are positively correlated with hydrothermal alteration and sulfide mineralization.

The use of major element analyses in mineral exploration is not restricted to the search for porphyry copper-type deposits. For instance, Gallagher (1941) has pointed out that some gold deposits (silver absent) are associated with albite (Na_2O)-rich granites. In another study Roscoe (1965) stated that volcanic and intrusive rocks in the Noranda area, Quebec are characterized by high Na_2O contents. He also found that the silica contents of volcanics tend to rise very abruptly near the stratigraphic level at which most of the massive sulfide deposits in the area

occur. He suggests that rock analyses would assist in strati-
graphic mapping of critical zones in the Noranda area. Another
environment where whole rock analyses might be of value is that
of the limestone replacement deposits. Radtke and Scheiner (1970)
found that carbonate was removed from and silica added to carbonate
rocks adjacent to the Carlin gold deposit in Nevada. In areas
where widespread dolomitization is present, such as the Gilman or
Mississippi Valley type deposit, Ca and Mg analyses could provide
guides to the location of mineralization.

<div align="center">CONCLUSION</div>

The lithium metaborate fusion technique using atomic
absorption instrumentation is a simple, rapid, and precise method
for obtaining whole rock analyses. This analytical method pro-
vides the exploration geologist with an additional inexpensive
technique which has considerable potential application to ore-
finding. There is currently a general absence of published
applications of major element analyses to orefinding. The indi-
cated lack of work may be mostly attributed to the high cost of
conventional analytical procedures. The availability of low cost
whole rock analyses, through use of the lithium metaborate fusion
technique, should provide considerable incentive for exploration
groups to research the application of major element analyses to
orefinding.

<div align="center">REFERENCES</div>

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