SM1. SUPPLEMENTARY MATERIAL

**Analytical methods – Obtained from GeoAnalytical Lab, Washington State University.**

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**XRF analysis of rocks and minerals for major and trace elements**

Johnson, D.M., Hooper P.R., and Conrey, R.M. (1999). XRF Analysis of Rocks and Minerals for Major and Trace Elements on a Single Low Dilution Li-tetraborate Fused Bead. GeoAnalytical Lab, Washington State University. Advances in X-ray Analysis 41, 843-867.

**Abstract**

The precision and accuracy of a low (2:1) Li-tetraborate fused bead technique by X-ray fluorescence analysis for 27 major and trace elements is demonstrated by comparison to accepted values of standard samples and to values acquired by other techni ques in other laboratories. The increased efficiency of using a single bead for major and trace elements is achieved without loss of precision or accuracy and the beads may be stored for tens of years without degradation.

**Introduction**

Of the many advantages in applying X-ray fluorescence (XRF) to the analysis of rocks and minerals, one of the most obvious is the versatility of the instrumentation. Methods can be developed to satisfy a wide variety of needs. In the GeoAnalytical Laboratory of Washington State University, the method developed over a period of more than 30 years (e. g. Hooper, 1964) was originally designed to distinguish the subtle chemical differences between flows of the Columbia River Basalt Group. To trace these flows over the Columbia Plateau required larger than normal numbers of analyses for the maximum number of elements and the highest possible analytical precision, while retaining the best available absolute accuracy. The approach finally adopted includes three separate components which differ from the more commonly employed methods based primarily on the work of Norrish and Hutton (1969). First, a single low dilution (2:1 diLi-tetraborate: sample) fusion is used for both major and trace elements, providing maximum efficiency without loss of accuracy. Second, a constant voltage on a Rh target is used for all elements to achieve maximum long-term stability and precision, despite this causing less than perfect conditions for a few trace elements. Third, the oxidation state of iron and the volatile content of the rock are ignored. The original major element concentrations are then normalized to 100%, volatile-free, with all the iron expressed as FeO.

**Single bead low-dilution fusion technique**

Sample Preparation

Fresh chips of the sample are handpicked and a standard volume of chips (approximately 28 g) is ground in a swing mill with tungsten carbide surfaces for 2 minutes. Three and a half grams (3.5 g) of the sample powder is weighed into a plastic mixing jar with 7.0 g of spec pure dilithium tetraborate (Li2B4O7) and, assisted by an enclosed plastic ball, mixed for ten minutes. The mixed powders are emptied into graphite crucibles with internal measurements of 34.9 mm diameter by 31.8 mm deep. Twenty-four (24) filled crucibles are placed on a silica tray and loaded into a muffle furnace only large enough to contain the tray. Fusion takes 5 minutes from the time the preheated furnace returns to its normal 1000oC after loading. The silica plate and graphite crucibles are then removed from the oven and allowed to cool. Each bead is reground in the swing mill for 35 seconds, the glass powder then replaced in the graphite crucibles and refused for 5 minutes.

Following the second fusion, the cooled beads are labelled with an engraver, their lower flat surface is ground on 600 silicon carbide grit, finished briefly on a glass plate (600 grit with alcohol) to remove any metal from the grinding wheel, washed in an ultrasonic cleaner, rinsed in alcohol and wiped dry. The glass beads are then ready to be loaded into the XRF spectrometer. Preparation of a single bead takes, on average, 45 minutes.

A number of practical points in this process need emphasis. Hand picking of fresh chips after the use of steel hammers, hydraulic press, and steel jaw crusher should prevent significant iron, chromium or nickel contamination, which resides mainly i n the finer dust. It has long been recognized that tungsten carbide mills cause contamination with tungsten and cobalt and these elements are not analyzed. Niobium contamination has also been reported from tungsten carbide mills (Joron et al., 1980; Hicks on and Juras, 1986) and tests using pure vein quartz suggest that different mills cause variable degrees of Nb contamination, which is typically of the same order of magnitude (2%) as the precision of the method (one standard deviation 1.0 ppm). Tantalum contamination is apparent. Alumina ceramic mills can be substituted for tungsten carbide but are brittle and therefore costly and only achieve the fine and even-grained powder required over a much longer period. fine and even grinding is surprisingly important. coarse powders result in separation of mineral phases during fusion (even double fusion) and can be a cause of high totals.

Analytical Procedure

The concentrations of 27 elements in the unknown samples are measured by comparing the X-ray intensity for each element with the intensity for two beads each of nine USGS standard samples (PCC-1, BCR-1, BIR-1, DNC-1, W-2, AGV-1, GSP-1, G-2, and STM -1, using the values recommended by Govindaraju, 1994) and two beads of pure vein quartz used as blanks for all elements except Si. The 20 standard beads are run and used for recalibration approximately once every three weeks or after the analysis of about 300 unknowns. The intensities for all elements are corrected automatically for line interference and absorption effects due to all the other elements using the fundamental parameter method.

Precision

Two standard beads (BCR-P and GSP-1) are used as internal standards. Kept in the same position in the automatic loader, they are run between every 28 unknown samples and so provide a continuing check on instrumental performance. They also provide a measure of instrumental precision within a single run and between runs over much longer periods.

The other critical aspect of analytical precision is the ability to reproduce the same concentration values in many separate beads prepared from the same rock or mineral sample. The important factors here are the homogeneity of the original sample and the ability to make a homogeneous bead. Clearly, coarse grained rock samples need to be homogenized adequately before mixing with the tetraborate flux. Assuming that the sample powder is perfectly homogenous, then the analysis of multiple beads prepared from that powder should provide a realistic measure of the overall precision of the technique. A quick visual illustration of the variation in elemental concentrations between two beads made from the same powder is provided in the vertical discrepancies between each of the two beads made from the ten standard samples used to create the calibration curves.

In a laboratory dedicated to the analyses of up to one hundred samples a week, every week of the year, one of the most acute concerns is the possibility of mixing samples. This can occur at any stage, but in the preparation procedure used here the most obvious step in which samples may get mixed is the placing of the 20 samples in unmarkable carbon crucibles in the furnace for fusion. As a precaution against mixing at this stage the plate on which the samples are loaded is notched and sample numbers recorded on a paper template. In addition, a second bead is made from one, randomly chosen, sample from each tray and reported as a “repeat” analysis. Such repeat beads also provide the user with an immediate measure of the precision of the analyses and whether small variations in the composition of two samples are analytically significant or not.

Accuracy

Unlike precision, a definitive measure of the accuracy of geologic samples is not possible. We can best estimate accuracy by comparing our results to the “given” values of standard (reference) samples, compiled from numerous analyses by different workers in different laboratories using a variety of techniques. Reliance on oxide totals approximating to 100% as a measure of accuracy is of limited value. While the use of totals as a test of accuracy was the only such check available to the classical wet chemical analyst, it should only be used in instrumental analysis as a rough guide to locate gross errors, as in the weighing of sample and flux. This is particularly true if, as in the methods outlined here, the volatile content and oxidation state of iron are ignored. The modern instrumental analyst has better methods of estimating accuracy. In the WSU GeoAnalytical Laboratory we estimate the accuracy of our analyses in two ways: First, by the scatter of the standard samples around the calibration curve for each element; and second, by comparing our values to those of the same samples analyzed by other workers in different laboratories and using different techniques.

(1) Accuracy estimated by use of standard samples:

By treating the ten calibration standards as unknowns and comparing the values so obtained to the “given” values (that is, other peoples’ best estimates) we gain an immediate visual impression of accuracy. In essence this is the amount of scatter of any one sample from the calculated calibration curve drawn through all 20 analyzed standard beads. These results are quantified, where the observed WSU XRF values are compared to the best or “given” values compiled by Govindaraju (1994), normalized to 100% on a volatile-free basis.

For most major elements the variation between the two standard sample beads is of the same order as their variation from the given value, with the inference that imprecision resulting from the preparation of the beads (as recorded in the overall precision) is equal to or greater than inaccuracies caused by inadequate matrix and interference corrections. With the exception of Na, the total discrepancies from the “given” values are less than might reasonably be expected between two random samples collected in the field from the same rock unit - lava flow, igneous intrusion, etc. Hence, this degree of inaccuracy may be regarded as insignificant for most purposes of geologic correlations or petrogenetic modelling

Among the trace elements the precision, and therefore the accuracy, of Ni, Cr, SC, V, and Ba is significantly less than for Rb, Sr, Zr, Nb, Y, Ga, Cu, and Zn. This correlates in part with the lower count rates (cts/sec/ppm) for SC, V, and Ba using a Rh target. Ni, Cr, SC, V, and Ba are regarded as only semiquantitative below the 30 ppm level. Rb, Sr, Zr, Nb, Y, Pb, and Th have satisfactory precision and accuracy down to 1 to 3 ppm. La and Ce concentrations are qualitative only.

Precision and accuracy of SC, V, Ba, and Nb in particular, could be improved by changing the X-ray tube target and operating conditions, but only at a loss of some long term reproducibility for all elements. The WSU GeoAnalytical Laboratory has an ICP/MS facility which measures SC, Ba, Pb, Nb and La and Ce with the other rare earth elements much more accurately than XRF, so attempts to perfect the XRF system for these elements have not been pursued.

(2) Accuracy estimated from inter-laboratory comparisons:

*Major and Minor Elements.* For each element a comparison of analyses of the same powders by another laboratory has been attempted using, where possible, the most appropriate technique.

For major and minor elements other XRF laboratories have been used. Comparisons are available from Los Alamos, the USGS (Denver), Rhodes University (South Africa), and from XRAL (Canada). In addition, comparisons of Fe and Na data by INAA are available from Washington State University, Oregon State University, and the University of Oregon. Na data have also been compared to ICP data from London.

Of these various comparative data sets, that of 158 samples from the Cascade Range supplied by Dr. Dave Sherrod, USGS, (Sherrod, 1986) and run in Los Alamos have the widest concentration range. In general, the correlations are tight and within the limits set by the precision measurements. Slight biases between the WSU values and other XRF laboratories have been noted previously (Hooper et al., 1993) and are not yet fully understood. The WSU data sets appear to have consistently lower Fe (0.3% FeO) and higher Si (0.45% Si02) than other XRF laboratories. We suspect this reflects differences in the Fe measurements which are then reflected in Si02 by the normalization procedure used. However, no such bias is apparent between the WSU XRF data and WSU INAA data for Fe from WSU (185 Cascade Range samples (Conrey, 1991)), nor between WSU XRF and INAA data from Oregon State University (Hill, 1992). In all cases the biases are well within the natural variation between two samples from the most homogeneous flow from the Columbia Plateau and are therefore unlikely to prove significant in petrologic studies. The Na data, while less precise than that for other major elements, nevertheless compares well with the Los Alamos XRF data and with INAA (WSU) and ICP (London) data.

*Trace Elements.* Ni has been compared to XRF data from Rhodes University, South Africa (J. S. Marsh, 1993, unpublished data), XRAL, and six samples from the USGS-Menlo Park (Gardner, 1994). There is a fair scatter and the WSU data is consistently 10 to 15 ppm lower than the Rhodes values but similar or slightly higher than the USGS and XRAL values. The Rhodes data may not have been corrected for enhancement by Fe.

Cr XRF values from WSU have been compared to XRF values from the USGS, XRAL, and Rhodes University, and to INAA data from WSU and from Oregon State University (OSU). The correlation is fairly tight, but the WSU values appear lower, the discrepancy increasing at higher concentrations (>100 ppm).

Sc values have been compared to INAA values (WSU and OSU), ICP (London), and ICP/MS (WSU). INAA should provide excellent Sc. ICP and ICP/MS comparisons are less tight, indicating these techniques are somewhat less suitable for Sc analysis. The main problem with the WSU XRF data for Sc is the poor precision, a result of the low count rate caused by the combination of the Rh target and 50 kV/50 mA settings used.

Duplicate analyses for V are available by XRF from Rhodes University, by ICP (London, Texas Tech. U.). Precision is again relatively poor because of the set operating conditions, but no obvious bias is apparent.

Ba values are compared with ICP/MS (WSU) and ICP (King’s College and Texas Tech. U.) values. There is no discernible bias over a large range in concentration, but again with a fair scatter due to relatively poor precision.

Rb and Sr values indicate both high precision and accuracy for these two elements. This is well illustrated by a large data set for samples from Greenland for which Dr. John Duke (University of Alberta, Edmonton) obtained duplicate analyses by isotope dilution (Duke, 1993). Correlation with ICP/MS values is almost as tight. The exceptionally close correlations demonstrated in these plots is particularly significant because it implies that the reproducibility of the sample preparation technique must be at least that good. And this, of course, is applicable to all other elements, so long as the original powder was homogeneous.

Duplicate Zr values are available by XRF (Rhodes University and U. S. G. S., Menlo Park) and by ICP (London). No bias is apparent but while very adequate, the scatter on these plots is slightly greater than expected, given a precision which is theoretically as high as that for Rb and Sr. The answer may lie in the dispersed nature of the principal Zr bearing phase, zircon; the powders may not be entirely homogeneous with respect to this phase and element.

Duplicate analyses for Y are available by XRF (USGS, Menlo Park, Rhodes University, and XRAL), by ICP (London) and by ICP/MS (WSU). The ICP/MS data correlates well with the WSU XRF data although the two separate runs differ in that in one case the XRF is slightly higher and in the other the XRF data is slightly lower than the ICP/MS data. It is virtually impossible for this type of variation to be due to the XRF in which the conditions are rigidly constant, so these differences are believed to reflect small differences between the two ICP/MS runs.

Nb values have been compared with XRF data (USGS, Menlo Park, XRAL, Rhodes University), ICP data (London), and ICP/MS data (WSU). The results are scattered, suggesting many laboratories have problems in obtaining good Nb values. The tightest correlations of the XRF data are with the ICP/MS values, but there is a slight bias which increases with concentration suggesting the XRF values are high. As for Y, this bias differs significantly between the two runs suggesting that at least a part of this problem lies with the ICP/MS values.

No comparative data is available for Ga and duplicate Cu analyses are only available from one XRF run (Rhodes University) which demonstrates adequate correlation. Duplicate values on Zn by XRF (USGS, Menlo Park and Rhodes University) and by ICP (London) are again somewhat scattered but the relatively good correlation with the ICP data, while implying a small bias between the two data sets, suggests the WSU XRF data are adequate. Clearly, more duplicate analyses are required for Ga, Cu, and Zn to provide a better estimate of the accuracy of the WSU XRF values.

XRF values for La and Ce are only quoted by the WSU GeoAnalytical Laboratory because of special requests. They demonstrate poor precision and are regarded as qualitative only.

Recent XRF runs have been expanded to include Pb and Th. Adequate comparisons are only available from the ICP/MS (WSU). The Pb and Th values show adequate correlation and suggest the limiting factor in the accuracy of the values for both elements is the precision of the XRF data.

Summarizing, it is apparent that for the 17 trace elements analyzed on the WSU XRF system, the accuracy imposed is that of the precision, the limits of which are noted earlier. Small biases may be present in some cases (e. g. Cr, N b) but few are significant, and none appear critical. The precision limits are, however, important. These comparative plots serve to remind us of the high reproducibility of XRF analyses in general but also that the XRF technique loses precision at low concentrations (below 10 ppm and, for some elements, below 30 ppm). At these lower concentrations other techniques, isotope dilution and ICP/MS in particular, are preferable.

**Stable Operating Conditions**

The GeoAnalytical Laboratory uses only a Rhodium target which is run at 50 kV and 50 mA with full vacuum and a 25 mm mask for all elements and all samples. The advantages for retaining the same conditions for all elements, in addition to efficiency, is the greater stability and consequent ability to reproduce the same intensities for the same sample over long periods of time. This can be demonstrated for this laboratory over a 10-year period. In addition, the 2:1 tetraborate beads can be stored for a demonstrable 30 years without significant deterioration and can be re-run if and when the basic equipment, standards, or running conditions are modified. This level of precision has been critical to the tracing of the subtle differences between the many flows sampled from the Columbia Plateau over that period.

The disadvantages of using such constant operating conditions are loss of precision and accuracy for some elements, notably Sc, V, Nb and Ba, for which these conditions are not ideal.

**Oxidation State and Volatile Content – LOI**

The WSU GeoAnalytical Laboratory normally ignores the oxidation state of iron in whole rock samples, quoting all the iron as FeO and normalizing to 100% without measuring the volatile content. LOI and oxidation state are measured only for particular purposes or on special request.

In general, we regard the volatile content and oxidation state of igneous rocks as a distraction for most petrogenetic work. Both are products of post eruptive processes (alteration) in large part and serve to distort the composition immediately prior to eruption which is our principal concern. When data on the volatile content and oxidation state are lacking, it follows that original totals can be used only as a rough check for major errors in weighing, smaller variations in the totals will reflect variable oxidation states and volatile contents. The use of normalized values has caused some concern amongst our colleagues, especially those introduced to geochemistry through wet chemical analysis in which the total, including volatile content, was the obvious check on the accuracy of the analysis. As discussed above, there are now much better ways of measuring precision and estimating accuracy. Incorporation of oxidation states and volatile content so distort analyses of Columbia River basalt, to us e but one example, that their use on the Columbia Plateau significantly reduces our ability to correlate flows. Had this approach been adopted our present knowledge of Columbia River basalt flow stratigraphy would be much less precise.

Two other factors are involved. The analysis of volatiles and the oxidation state of iron tends to be labor-intensive, creating an unjustified cost except in particular circumstances. Both, of course, are independent of the X-ray analysis and can be added or discarded any time, so long as the totals are not relied upon as a measure of accuracy for the whole analysis. Finally, this laboratory would argue that in analytical comparisons inclusion of the oxidation state of iron and the volatile content distorts the results and makes the comparisons of little value (Govindaraju, 1994). To determine genuine bias and analytical differences between laboratories it is essential to calculate the iron in a single oxidation state, eliminate the volatile (LOI) content, and normalize to 100. This is because the methods of measuring the LOI are so variable that differences in these values between laboratories distort the abundances of all other elements (again, see Govindaraju, 1994).

**Conclusions**

We argue that the single low-dilution fusion technique is superior to the more traditional high dilution fusion and pressed powder technique in its much greater efficiency which is achieved without measurable loss of either precision or accuracy.

There are advantages and disadvantages in using stable operating conditions, in which neither the target nor the voltage are changed between elements. The adoption of such a procedure is likely to depend on the specific aims of any one research program. Finally, the measurement of the oxidation state of iron and the volatile content should not be used to distort otherwise excellent XRF analyses.

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**Trace Element Analyses of Rocks and Minerals by ICP-MS**

**Introduction**

Inductively coupled plasma-mass spectrometry (ICP-MS) is well established as a rapid and precise method for the determination of the rare earth elements (REEs) and trace elements in geologic samples – Lichte et al., (1987), Jarvis (1988), Longerich et al., (1990). However, complete sample digestion is required for accurate results. Mixed acid open-vial digestions on a hotplate work well for basaltic and most ultramafic samples, but may fail to completely decompose many trace mineral phases found in more silicic samples. These resistant phases, such as zircon, garnet, and tourmaline, may contain a significant percentage of the total trace elements in a given sample. High-pressure bombs are effective at achieving complete digestion, but are cumbersome, slow, and labor intensive. Fusion with a flux may require large dilutions to avoid unacceptably high levels of total dissolved solids. We have developed a combination fusion-dissolution method that effectively decomposes refractory mineral phases and removes the bulk of unwanted matrix elements. The procedure consists of a low-dilution fusion with di-Lithium tetraborate followed by an open-vial mixed acid digestion. This method allows us to analyze 14 REEs and 13 additional trace elements in a wide range of geologic samples without having to make assumptions as to the presence or absence of resistant mineral phases. The dissolution with HF after the Lithium-tetraborate fusion quantitatively removes silica and more than 90% of the flux as gaseous fluorides, leaving clear, stable solutions for analysis on the ICP-MS.

**Experimental**

The Flux used for the fusion is di-Lithium-tetraborate (Spectromelt® A-10, EM Science, Gibbstown, NJ). Reagents are HNO3 69-70% (Fisher ACS plus grade), HF 48-52% (Baker ACS reagent grade), HClO4 67-71% (Fisher Trace Metal Grade), and H2O2 (Baker ACS Reagent). The HF is further purified before use by sub-boiling distillation in a teflon still. All water used is >18 M deionized water from a Nanopure analytical grade water system (Barnstead/Thermolyne).

Powdered samples are mixed with an equal amount of lithium tetraborate flux (typically 2g), placed in a carbon crucible and fused at 1000° C in a muffle furnace for 30 minutes. After cooling, the resultant fusion bead is briefly ground in a carbon-steel ring mill and a 250 mg portion is weighed into a 30 ml, screw-top Teflon PFA vial for dissolution. The acid dissolution consists of a first evaporation with HNO3 (2ml), HF (6 ml), and HClO4 (2 ml) at 110° C. After evaporating to dryness, the sample is wetted and the sides of the vial are rinsed with a small amount of water before a second evaporation with HClO4 (2 ml) at 160° C. After the second evaporation, samples are brought into solution by adding approximately 10 ml of water, 3 ml HNO3, 5 drops H2O2, 2 drops of HF and warmed on a hot plate until a clear solution is obtained. The sample is then transferred to a clean 60 ml HDPE bottle diluted up to a final weight of 60g with de-ionized water.

Solutions are analyzed on an Agilent model 4500 ICP-MS and are diluted an additional 10X at the time of analysis using Agilent’s Integrated Sample Introduction System (ISIS). This yields a final dilution factor of 1:4800 relative to the amount of sample fused. Instrumental drift is corrected using Ru, In, and Re as internal standards. Internal standardization for the REEs uses a linear interpolation between In and Re after Doherty (1989) to compensate for mass-dependant differences in the rate and degree of instrumental drift. Isobaric interference of light rare earth oxides on the mid- heavy REEs can be a significant source of error in ICP-MS analysis, so tuning is optimized to keep the CeO/Ce ratio below 0.5%. Correction factors used to compensate for the remaining oxide interferences are estimated using two mixed-element solutions. The first contains Ba, Pr, and Nd, and the second Tb, Sm, Eu, and Gd. Standardization is accomplished by processing duplicates of three in-house rock standards interspersed within each batch of 18 unknowns. Concentrations, oxide- and drift corrections are then calculated offline using a spreadsheet.

**Results**

Long term precision for the method is typically better than 5% (RSD) for the REEs and 10% for the remaining trace elements. Analyses of USGS and international rock standards show good agreement with consensus values.

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