X-RAY SPECTROMETRIC ANALYSIS OF MAJOR AND SELECTED MINOR ELEMENTS IN SILICATE ROCKS UTILIZING AN AUTOMATIC FUSION TECHNIQUE

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ABSTRACT

An automatic fusion technique was used to prepare moderate dilution (1:7.33), glass discs of a wide variety of silicate rock types. Lithium tetraborate was used as the flux, lithium nitrate as the oxidant, and HBr as the releasing agent. The fused discs were analyzed with an automated X-ray fluorescence spectrometer system, utilizing appropriate matrix corrections for the common major oxides (SiO_2, Al_2O_3, Fe_2O_3, MgO, CaO, Na_2O, K_2O, TiO_2, P_2O_5, and MnO), selected minor oxides (BaO, Cr_2O_3, NiO, SrO, and ZrO_2), and chlorine.

Standards included 16 internationally recognized silicate rocks ranging in type from granitic to mafic, referenced to an in-house U.S.G.S. glass standard, GSE, spiked with known amounts of minor elements. Volatility corrections were made by referencing the individual sample disc weights to the weight of a disc fused from a sample containing no volatiles, dry flux, and residual lithium oxide and bromine (7.33g). The precision of the method was determined from the analysis of duplicate sets of glass fusion discs for 16 rock samples representing a variety of rock types. Values ranged from 0.14% (SiO_2) - 0.79% (Na_2O). Accuracy was defined as the average absolute relative error between calculated, matrix-corrected XRF concentration values obtained from intensity measurements, and assigned literature values for the international and other rock standards. Average relative error values were determined for both the major and minor element oxides. These values were in good agreement for all elements except for TiO_2, P_2O_5, and NiO. The average relative errors for the major element oxides ranged from 0.55% (SiO_2) - 8.6% (P_2O_5), while the minor element oxides and chlorine exhibited average relative errors ranging from 2 - 7%. Major element analysis of 20 rocks with a broad range of compositions, previously analysed using a single gravimetric analysis, exhibited average relative error values similar in magnitude or up to two fold higher. The lower limit of detection (2σ) varied from approximately 10 ppm for Mn, Ba, and Ni to about 120 ppm for Al and Mg, and 450 ppm for Na.

INTRODUCTION

During the last 25 years, numerous methods and techniques have been advanced involving the use of borate fluxes for the preparation of rocks, minerals, ores, etc. by fusion techniques. The products of these preparations, usually called fusion discs, have then been extensively used for the determination of major and sometimes minor elements by X-ray fluorescence analysis. The experimental parameters in fusion preparation include: the chemical composition of the flux; the dilution ratio of sample to flux; the use of various oxidants; internal standards (heavy absorbers); various crucible types; releasing agents; modes of fusion, including automated procedures; casting techniques; and polishing. The intent of this work has been to develop a fusion method, by extending existing technology, which would produce a high volume of high-quality fusion discs with a minimum of labor. These discs were to be suitable for the determination of both major and minor elements of geochemical interest on the same disc by an automated x-ray spectrometer system with a commmercial software package.

Claisse (1956) reported the use of sodium tetraborate as a flux to prepare rock powders for analysis by x-ray flourescence in the form of solid solutions. The Claisse approach was to obtain a very dilute sample (1:100) so as to eliminate matrix effects, but with a consequent decrease in precision and sensitivity. Andermann and Allen (1961) in contrast adopted a 1:1 sample-to-flux ratio, using lithium tetraborate and obtaining a high degree of accuracy for samples of uniform composition. Such idealized cases are not common, however, and matrix errors may be considerable at this low dilution ratio.

Rose and others (1963) effected a compromise with a 1:8 ratio of sample to $Li_2B_4O_7$ flux, starting with 0.125 g sample, and introducing the use of La_2O_3 as a heavy absorber to reduce matrix effects. La_2O_3 is most effective for elements K through Fe, has a minimal effect for elements Al through P, interferes with Mg, and reduces Na intensities to indeterminable levels. After fusion in graphite crucibles, the resultant glass was ground and pelletized for analysis. Boric acid (later powdered cellulose) was added to bind the sample particles which resulted in a final sample dilution of 1:9.4. The method was successfully applied to silicate, carbonate, and phosphate rocks. Fabbi (1972, 1973) modified this technique for the determination of major elements in rocks, Omitting the heavy absorber, substituting $LiBO_2$ as the flux, and adding cellulose to the crushed fusion bead with a resultant 1:18 dilution of sample. More recently Palme and Jagoutz (1977, 1978) fused 100 mg rock samples in place in Pt-5% Au crucibles with a lithium tetraborate flux and $NaNO_3$ as oxidant, eliminating the heavy absorber and achieving a sample dilution of approximately 1:10. The thin glass discs were analyzed as is, without casting, for both major and minor elements in silicate rocks utilizing fundamental parameters correction methods and thickness corrections.

Another kind of innovation in sample preparation occurred when Kodama and others (1967) crushed and recast their borate glass fusion discs in a graphite mold. They also omitted use of a heavy absorber and were distinctive in their use of synthetic standards and of extensive computer corrections for interelemental absorption and enhancement effects. Norrish and Hutton (1969) utilized a fusion-casting technique involving the pressing of molten fused samples into graphite discs with an aluminum plunger technique. Appropriate matrix corrections were applied for the determination of 10 major elements in a wide range of geologic materials. They used a 1:6 sample-to-flux ratio, lowered the fusion temperature to 1000° C by inclusion of Li_2O in the tetraborate fusion mixture, and used both an oxidant and La_2O_3 as an heavy absorber. Many others have utilized the Norrish and Hutton technique or variations thereof, such as Van Willingen and others (1971), who used platinum disc molds, and Kraeft (1974), and Hattori (1971), who eliminated the casting step altogether. Harvey and others (1973) improved upon the Norrish and Hutton technique by using duralumin mounting plattens rather than graphite discs and by design and use of a mechanical, duralumin plunger assemblage. The duralumin platten were more durable than graphite discs and free of contamination, and the discs had fewer failure rates with better counting precision. Haukka and Thomas (1977, 1978) and Lee and McConchie (1982) both used low-dilution metaborate fusion methods to produce samples suitable for both major and trace elements in an automated XRF system, but the latter researchers eliminated the heavy absorber. Hutton and Elliott (1980) used a similar dilution for the same purpose, fusing in an electric furnace at 1000^o C, followed by a final heating at 1050^o C with an oxypropane flame. Schroeder and others (1980) used a Claisse fluxer to prepare glass discs for the major elements, but used a powder pellet method for the trace elements.

Matocha (1974, 1975) developed an automatic, programmable fusion device, known as PUFF, for the direct analysis of borate, fused-glass discs. The procedure developed by Matocha utilized a specially-designed Pt-5% Au alloy crucible for optimum release of the fused discs, and 48% HBr solution as the releasing agent. The sample dilution was 1:7, the flux $Li_2B_4O_7$, the oxidant NH_4NO_3, and the fusion temperature 1100^o C. A brief grinding step with a 220-mesh diamond abrasive wheel was instituted to provide more uniform disc surfaces for analysis. Loss on fusion (LOF) values were found equivalent to loss on ignition (LOI) values, and provided an adequate correction for the elements being determined.

More recently, Taggart and Wahlberg (1980) developed a unique two-piece Pt-5% Au alloy mold for casting molten samples to produce optically flat discs. The casting molds are placed in a muffle furnace where they are mounted on the bottom of an externally coupled mechanical oscillating device which holds up to seven platinum crucibles. After the molten samples are directly poured into the molds, the whole assemblage is removed from the furnace for cooling to room temperature. Volatiles are removed prior to fusion of the samples by a pre-heating step. This procedure makes possible the production of up to 150 sample discs per day, if the samples are pre-weighed. This production rate is especially desireable for laboratories equipped with a simultaneous, multi-channel X-ray spectrometer.

A novel approach was that of Govindaraju and Montanari (1978) who, after a lithium borate fusion step, dissolved the ground fusion product and adsorbed the cations from the solution on an ion exchange resin. The resin beads were then coated on adhesive paper for analysis, yielding high-quality data without the need for mathematical corrections.

Wittman and others (1974) developed an automatic device for preparing iron ore samples for XRF. The apparatus consists of two high-frequency induction furnaces for fusing and casting the discs. Halma (1973) developed an induction heating method which eliminates the need for a releasing agent and for resurfacing of the fusion discs, although reshaping of the platinum crucibles is occasionally needed. West (1980) prepared homogeneous discs both in Pt-5% Au alloy and graphite crucibles using a 1:10 sample to $Li_2B_4O_7$ flux ratio. The whole process takes place in a completely automated resistance furnace.

Being equipped with sequential, automated XRF systems, the requirements of our laboratory are best met by a moderately high volume sample preparation system. The PUFF* fusion system was selected because: 1) the fusion temperatures can be accurately established and are reproducible; 2) the air/gas mixtures can be controlled so as to maximize an oxidizing environment; 3) consistently homogeneous discs with minimal cracking problems can be produced; 4) the sum total of heating, mixing, and cooling operations can be automated; 5) the fused discs are ready for analysis with minimal surface grinding (the amount depending on one's analytical requirements); and 6) three or four PUFF units can be operated synchronously. U. S. Geological Survey standards prepared in Matocha's laboratory utilizing the PUFF fusion method and analyzed with our XRF instrumentation gave evidence of good precision and accuracy of results. Alternative fusion devices then available, though lower in cost and capable of a greater capacity, gave less promise of consistent results, reliability, and sample homogeneity under conditions of routine analysis. The large initial cost of induction heating furnaces and their need for attention while in operation was considered a restraint to their use.

A 1:7 sample dilution was chosen as being sufficiently dilute to considerably reduce the matrix effects for the major elements, and yet allow sufficient sensitivity for several of the minor elements of interest.

A major consideration in XRF analysis is the mathematical treatment of the element data to effectively correct for the matrix. In an earlier paper, Fabbi and others (1976) grouped the various approaches into "coefficient methods" and fundamental parameter methods and summarized some of the more important papers. Many papers have since dealt with efforts to evaluate or improve upon the existing coefficient methods, often by use of fundamental parameter methods (Sage and Tertian, 1976, 1977; Sage and others, 1979; Cricius and Wybenga, 1973; Matocha, 1976; Kirchmayer and Ziunikowski, 1978; DiFruscia and others, 1976; Stankiewicz and Sanner, 1979; LaChance, 1979; Plesch, 1979, 1981; and Chamberlain, 1980). Ben-Haim (1980) and Mainardi and others (1981, 1982, 1982) have demonstrated the necessity of developing coefficients derived from binary systems before application to multi-component systems. Keith and Loomis (1978, 1978) stressed the need for accurate measurements of both fluorescence yields and relative intensities and of making scattering corrections in applying the fundamental parameters method. Perhaps the most novel approach is that of Asada and others (1980), who utilized the relationship between the reciprocals of the line intensities of the elements of interest and the element weight fractions to obtain quantitative results for either liquids or fused samples.

The matrix correction software available in our computer used an empirical correction technique; namely, multiple linear regression, requiring a large number of standards. The matrix effects amenable to correction were absorption and enhancement, spectral line interferences and background. There was insufficient computer memory for fundamental paramenters corrections. Element tables were developed for the determination of ten major and five minor elements as their oxides, plus Cl and S.

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* Trade names and company names are for identification purposes only and do not imply endorsement by the U.S. Geological Survey.

EXPERIMENTAL

Selection and Preparation of Standards

Calibration was primarily based on 16 internationally recognized silicate rock standards with compositions ranging from granitic to ultramafic. These were the U.S. Geological Survey Standards: G-1, W-1, AGV-1, G-2, BCR-1, GSP-1, PCC-1, and DTS-1; the French ANRT Standards: BR, GA, GH, DRN, and UBN; the USSR Syenite Standard: NS-1; the Geological Survey of Tanganyika Tonalite Standard: T-1; and the Geological Survey of Canada Syenite Standard: S-1. The USGS in-house Glass Standard, GSE, was used as the instrumental reference standard to correct for short term drift. Seven additional, gravimetrically analyzed, ultramafic rock samples were used as secondary standards to calibrate for Cr and Ni. The ultramafic rocks represented were peridotites, pyroxenites, an eclogite xenolith, and a dunite. All primary standards were prepared in triplicate and the secondary standards in duplicate. The coefficients developed for the primary standards were further validated by the analysis of 20 rocks which had been gravimetrically analyzed at the U.S.G.S. Denver facility for the major element oxides. The GSE glass standard was diluted 9:1 by spiking with a synthetic mixture containing weighed amounts of the minor element oxides of Ba, Sr, Zr, Ni, and Cr, TiO_2, P_2O_5, and salts of S and Cl to enhance their counting precision. The resulting concentrations of Ba, Zr, Sr, Cr, and Ni represented an approximately five-fold increase over their normal concentrations in GSE (Table 8). A separate fused glass standard containing essentially only the alkali metal salts of S and Cl, plus SiO_2, was also utilized for comparison purposes.

The chemical, elemental oxide concentration values adopted for the standards were published or recommended literature values (Flanagan, 1969, 1973; Abbey, 1972, 1973, 1977; Ingamells and Suhr, 1963; Goldich and others, 1967; Ingamells and others, 1971; de la Roche and Govindaraju, 1971, 1973; Loney and others, 1971; and Crock, 1975) with the exception of two Cr values (Huffman). The GSE synthetic standard values (Myers and others, 1976) were appropriately recalculated for the additional amounts of minor or major elements added (Table 1).

Reagents and Apparatus*

Flux: 99.99% $Li_2B_4O_7$ (Spex Industries, Inc.)
Oxidant: 99.9% anhydrous $LiNO_3$ (Research Organic/Inorganic Corp.)
Releasing agent: 48% HBr solution (Angstrom, Inc.)
Platinum crucibles: Pt-5% Au alloy with double thickness domed lids of the same material (Johnson Matthey, Inc.)
Fusion devices: PUFF automatic fusion devices - master and auxilliary units (Angstrom, Inc.)

The computerized XRF system was a Diano Corp. 710 system, consisting of an XRD-6 vacuum spectrometer, a CR-W dual target x-ray tube, a 10-position sample changer, a four-position crystal changer, a flow gas detector using research grade and gravimetrically mixed P-10 gas, and a sealed xenon gas proportional detector. The spectrometer was interfaced with a Digital Equipment Corporation PDP-8/M computer and a LA 36 DECwriter high speed terminal.

Table 1.--Composition of GSE-synthetic reference standard[1]

Oxide	Concentration (Wt %)	Oxide	Concentration (Wt %)
SiO_2	54.85	Na_2O	4.08
Al_2O_3	12.13	K_2O	4.26
Fe_2O_3	5.66	TiO_2	0.64
MgO	3.28	P_2O_5	0.63
CaO	4.75	MnO	0.086

[1] GSE (in-house U.S.G.S. synthetic glass standard) spiked with a synthetic mixture composed of TiO_2, P_2O_5, minor element oxides, and Cl and S salts.

Sample Preparation

Sample preparation began with hand mixing of minus 150 mesh rock powders on Albanene paper. In succession 6.000 g flux, 1.000 g sample, and 1.5 g oxidant were weighed into each Pt-5% Au alloy crucible. After brief mixing with a spatula, two holes were poked 6 mm into the surface with a glass stirring rod, and two drops of the 48% HBr solution added to each hole just prior to fusing the samples. The samples were fused according to the program outlined in Table 2.

After cooling, the resulting glass discs were weighed and the bottom surfaces ground using metal-bonded diamond discs with adhesive backing. The most efficient procedure was to use a 260-mesh particle disc to produce a flat surface of about 38 mm diameter, followed by successive use of 600- and 1200-mesh grinding-polishing discs. Number nine rubber stoppers with an excised central depression served as efficient devices to hold the discs during polishing. Alternatively, plain rubber stoppers or circular plastic discs to which the discs are affixed with double-sided masking tape may be used. The total grinding process, including ultrasonic cleaning with distilled water followed by rinsing with distilled water and alcohol, required 5-6 minutes per disc.

Selection of Instrumental and Analysis Parameters

The procedure for selection of instrumental parameters is essentially the same as reported previously by Fabbi and others (1976). Predetermined, optimized instrumental parameters were entered as element tables into the PDP-8/M computer (Table 3), and elemental intensities were measured in triplicate on the reference and silicate rock standards to increase precision. A multiple linear regression curve with its corresponding correction coefficients was generated for each element from the intensity and concentration data. Intensity data for Si in four of the international standards with a known total water and carbon dioxide content of 2.4 wt% or more; namely, UBN, DRN, BR, and PCC-1, were corrected for loss on volatility before entering their intensities in the Si element table. No further volatility corrections were made for intensities of any other of the elements. Correction for a maximum of four affecting elements was possible with available software and the corrections utilized are shown in Table 4. The sequential measurement of X-ray line intensities for all samples in a given run, one element at a time, was the method of choice, with a resultant gain in precision of a factor of two (due to fewer instrumental manipulations) over the alternative procedure of sequentially analyzing X-ray line intensities for all elements, one sample at a time.

RESULTS and DISCUSSION

Experimental Development

Modifications of certain features of Matocha's procedure (1974, 1974, 1975) were made to extend the capability of the method: 1) the mixing period was extended to insure homogeneity of highly silicic rocks which have a high viscosity; 2) lithium tetraborate was substituted for lithium metaborate as the fluxing agent; 3) the amount of HBr added as a releasing agent was increased; 4) lithium nitrate was substituted for ammonium nitrate as the oxidant.

Table 2.--Fusion procedure

Event	Time (min.)
Low temperature heating (550-600^{0} C max.)	4
High temperature heating (1100^{0} C max.)	8
High temperature mixing (1100^{0} C max.)	20
Static cooling	3
Forced air cooling	4
TOTAL	39

Table 3.--Instrumental parameters for element tables[1,2]

Element	Flow counter (volts)	Xenon counter (volts)	PHS (volts)		Gain	Target	Crystal	Time (sec.)
			Base	Window				
Si	1600	0	0.3	1.5	4	Cr	PET	100
Al	1600	0	.3	1.5	4	Cr	PET	80
Fe	1460	0	.3	1.5	4	W	LiF(220)	20
Mg	1600	0	.6	2.0	8	Cr	TAP	150
Ca	1460	0	.6	1.5	8	W	LiF(200)	40
Na	1600	0	.3	2.0	8	Cr	TAP	100
K	1460	0	.3	1.5	8	Cr	PET	20
Ti	1460	0	.6	1.5	8	Cr	LiF(200)	10
P	1600	0	.3	1.5	4	Cr	PET[4]	30
Mn	1360	0	.3	2.0	16	W	LiF(200)	35
Cl	1460	0	.6	2.0	16	Cr	PET	50
Ba	1460	0	.6	1.5	8	Cr	LiF(200)	30
Zr	0	2280	.6	1.0	16	W	LiF(220)	90
ZrB[3]	0	2280	.6	1.0	16	W	LiF(220)	90
Sr	0	2280	.3	1.5	16	W	LiF(220)	75
SrB[3]	0	2280	.3	1.5	16	W	LiF(220)	75
Ni	1460	0	.3	1.5	4	W	LiF(220)	65
NiB[3]	1460	0	.3	1.5	4	W	LiF(220)	65
Cr	1360	0	.3	1.5	16	W	LiF(220)	100
CrB[3]	1360	0	.3	1.5	16	W	LiF(220)	100

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[1] Samples are under vacuum and rotating at all times. KV = 50 and ma = 50 for all elements.

[2] All 2θ settings correspond to the element $K\alpha$ lines for the indicated crystal, with the exception of the Ba $L\alpha$ line.

[3] Denotes 2θ background analytical parameters.

[4] Ge would have been the crystal of choice, but the limited number of crystal holders precluded its use.

Table 4.--Interfering element corrections[1] for the analysis of silicate rocks

	Element	Interfering elements	Element	Interfering elements
MAJOR	Si	Fe, Ca, Al, Mg	Na	None
	Al	Ca, Si, Mg, Na	K	Fe, Ca, Si, Al
	Fe	Ca, Si, Ti	Ti	None
	Mg	Si	P	Ca[2]
	Ca	Fe, Si, Al, Mg	Mn	Fe, Ca, Mg, Ti
MINOR	Cl	Fe, Al, Mg, P	Ni	Background + Fe, Ca, Mg
	Ba	Ti[2]	Sr	Background
	Cr	Background + Ca, Mg	Zr	Background + Sr[2], Ca

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[1] Absorption/enhancement corrections, except as noted.

[2] Spectral interference correction.

Lithium tetraborate, though more acidic than $LiBO_2$, resists hydration and was generally found to be more satisfactory, particularly for ultramafic rocks which have a tendency to yield fractured discs. The $Li_2B_4O_7$ flux also had a higher powder density than the available $LiBO_2$ flux, which made it more desirable for weighing.

Ultramafic rocks commonly contain trace to minor concentrations of nickel, copper, and chromium. All three elements are strongly reducing and tend to cause fracturing of borate glass discs when present in concentrations of several tenths of a weight percent. Van Willingen (1971) added chloride salts to alleviate a fracturing problem caused by Cu. Bromide salts, which are the halide of choice (Matocha, 1974) as a releasing agent, serve the same function. It was found in this work that the addition of four drops of HBr, rather than two, eliminated the fracturing in the majority of cases, including rocks of high silica content which also tend to fracture. For some rocks containing 0.4 - 0.5 wt % copper or large amounts of pyrite, it was necessary to add as many as eight drops of HBr. The infrequent fracturing of a disc was dealt with by the addition of a few extra drops of HBr to the top of the disc, followed by refusion. The disc was weighed after the initial fusion to ensure proper correccorrection of the XRF intensities.

One negative consequence of the use of bromine is that it interferes spectrally with the element Rb to the degree that it cannot be determined. Extensive investigation disclosed no other significant spectral interferences or matrix effects due to bromine on the elements determined. The potential interference of bromine on silica and aluminum is minimal and was found to be of no significance using our instrumentation and the multiple linear regression method for matrix corrections. Depth profiling, through repeated grinding and subsequent measurement of the XRF intensity of bromine, confirmed a homogeneous distribution of bromine in the glass discs. This fact coupled with observations of greater disc stability and reduced surface tension when additional bromine was added, suggest that residual bromine possibly becomes part of the bonding structure of the disc.

Lithium nitrate is a stronger oxidant than the commonly used ammonium nitrate, and is therefore preferable, particularly in dealing with strongly reducing substances, such as Cr, Ni, and Cu, high concentrations of sulphides, organic material,and ferrous iron. Unlike ammonium nitrate, which is hygroscopic and totally converted to gaseous products, lithium nitrate evokes little or no splattering upon heating. Lithium nitrate yields a quantitative neutral fusion product, Li_2O (1.5 g $LiNO_3$ yields 0.325 g Li_2O), which presents no matrix problems and aids in decomposing more refractory minerals.

In order to validate the homogeneity of the fusion discs, four different rock types were chosen for study; a granite, a gabbro, a diabase, and a peridotite. Duplicate discs were prepared; cut in half, so as to present a cross-section; mounted in plastic; and polished for electron microprobe analysis. Traverses perpendicular to the disc surfaces were made, and intensities were measured at closely spaced intervals for the elements Si, Al, Fe, Mg, Ca, and Na. Intensity variations fell within microprobe statistical limits (1% or better) for each element for all four rock types, confirming that the fusion process yields homogeneous discs for a wide variety of rock types.

Prior to establishing the final procedure, extensive experimentation was made as to the extent of grinding and polishing necessary to achieve optimum reproducibility. The data in Table 5 illustrate the precision of the method and indicate the two-fold improvement achieved by a multi-step grinding procedure which ends with a 1200-mesh (15 micron) diamond disc polishing step. The data were obtained from a suite of 16 gravimetrically analyzed rock samples, from which duplicate discs were prepared, representing a full spectrum of rock types. Further polishing of the glass discs, finishing with a 3 micron diamond paste, did not increase the precision for the eight major elements investigated. A 15 micron ground surface was thus deemed to be satisfactory.

Experimental Results

The percent relative standard deviation values displayed in the 3rd and 6th columns of Table 5 represent a measure of the precision of the method, as regards sample preparation and instrumentation errors, including counting errors.

Table 6 compares the matrix-corrected XRF data obtained from the international reference standards, utilizing a multiple linear regression program (MLRP), with the recommended chemical values (Flanagan, 1969, 1973; Abbey, 1972, 1973, 1977; Ingamells and Suhr, 1963; Goldich and others, 1967; Ingamells and others, 1971; de la Roche and Govindaraju, 1971, 1973; Loney and others, 1971; Crock, 1975; Huffman, pre-1976; Myers and others, 1976) for the major element oxides of the calibration standards. The upper limits of the working concentration ranges for certain of the elements have since been extended upward as follows: SiO_2: 90%; TiO_2: 3.5%; MnO: 1.5%; and P_2O_5: 2.0%. Accuracy for these primary standards was measured as the average absolute relative error or difference between the matrix-corrected XRF intensity values of the various elements analysed for, translated into concentrations, and "best value" literature concentration values. The formula for the average % relative error may be expressed as:

$$\%\ \text{R.E.} = \left(\sum^{N} \frac{|Ev - Lv|}{Lv}\, 100 \right) \Big/ N \ ;$$

where R.E. = relative error, Ev= experimental value, Lv = literature value, and N = number of standards (Leoni and others, 1982). This approach was identical to that employed by Fabbi (1972) for major element analysis of powder pellets prepared from fused rock samples. For purposes of comparison the relative error values for that earlier work, which were obtained without benefit of matrix corrections, have been included in Table 6.

The average relative errors for the XRF analyses of the international standards run as unknowns compare quite favorably with the average relative errors for the computer-generated concentration values shown in Table 6. Least squares linear regression calculations for both sets of data exhibit good correlation coefficients with three to four "nines" to the right of the decimal. Their standard errors of estimate are compatible, as well, ranging from 0.003 for MnO to 0.2 - 0.3 for SiO_2. This illustrates the effectiveness of the matrix corrections used in the program and their applicability to the accurate analysis of a broad range of silicate rocks using a single calibration curve.

A verification of the longevity of the matrix-correction program may be seen in Table 7. Certain standards were used as check standards with each run. The average relative error obtained for each elemental oxide of these selected standards is compared with the original calculated relative error.

Table 5.--The effect of grinding on relative standard deviation (RSD) for 1:7.33 glass fusion discs

Element oxide	Sample preparation and instrumental RSD (%)		Element oxide	Sample preparation and instrumental RSD (%)	
	Unground discs	Ground discs (600M & 1200M)		Unground discs	Ground discs (600M & 1200M)
SiO_2	0.35	0.14	CaO	0.28	0.20
Al_2O_3	1.00	.29	Na_2O	1.81	.79
Fe_2O_3	.63	.30	K_2O	1.13	.43
MgO	.83	.31	TiO_2	.69	.54

Table 6.--Comparison of XRF determined values (MLRP) vs. preferred chemical values (Wt %) for the Major element oxides of selected international silicate rock standards

Std.	Value	SiO_2	Al_2O_3	Fe_2O_3	MgO	CaO	Na_2O	K_2O	TiO_2	P_2O_5	MnO
G-1	Chemical	72.52	14.04	1.94	0.38	1.32	3.32	5.48	0.26	0.09	0.030
	XRF	72.36	14.10	1.94	0.33	1.28	3.39	5.50	0.26	0.08	0.030
W-1	Chemical	52.58	14.85	11.09	6.62	10.92	2.15	0.64	1.07	0.14	0.17
	XRF	52.24	15.05	11.10	6.65	10.90	2.29	0.63	1.06	0.13	0.17
AGV-1	Chemical	59.09	17.01	6.76	1.54	4.94	4.21	2.89	1.05	0.50	0.097
	XRF	59.26	16.88	6.79	1.56	5.00	4.18	2.92	1.08	0.49	0.100
G-2	Chemical	69.11	15.33	2.72	0.76	1.94	4.06	4.50	0.50	0.14	0.034
	XRF	69.00	15.22	2.74	0.72	1.94	4.12	4.48	0.50	0.13	0.037
BCR-1	Chemical	54.36	13.41	13.40	3.46	6.92	3.26	1.68	2.21	0.36	0.180
	XRF	54.12	13.36	13.41	3.47	6.95	3.22	1.69	2.25	0.36	0.178
GSP-1	Chemical	67.27	15.00	4.33	0.96	2.02	2.78	5.50	0.66	0.28	0.042
	XRF	67.34	14.95	4.30	0.95	2.00	2.68	5.48	0.68	0.28	0.044
PCC-1	Chemical	41.90	0.73	8.23	43.37	0.51	0.010	0.00	0.01	0.002	0.120
	XRF	41.76	0.75	8.27	43.32	0.50	0.06	0.006	0.02	0.01	0.115
DTS-1	Chemical	40.50	0.29	8.59	49.81	0.15	0.010	0.00	0.01	0.002	0.120
	XRF	40.30	0.28	8.49	49.48	0.11	0.06	0.005	0.02	0.01	0.119
BR	Chemical	38.20	10.20	12.92	13.28	13.80	3.05	1.40	2.60	1.07	0.20
	XRF	38.11	9.94	12.93	13.37	13.80	2.99	1.39	2.58	1.07	0.201
GA	Chemical	70.01	14.54	2.85	0.95	2.45	3.55	4.05	0.38	0.12	0.090
	XRF	70.08	14.66	2.85	0.88	2.48	3.46	4.08	0.37	0.13	0.088
GH	Chemical	75.80	12.50	1.37	0.03	0.69	3.85	4.81	0.08	0.02	0.050
	XRF	75.72	12.45	1.40	0.02	0.71	3.77	4.80	0.08	0.02	0.049
DRN	Chemical	52.75	17.52	9.67	4.46	7.08	3.00	1.70	1.10	0.25	0.210
	XRF	53.03	17.62	9.61	4.33	7.05	2.92	1.70	1.07	0.22	0.211
UBN	Chemical	39.47	2.99	8.35	35.00	1.17	0.10	0.02	0.12	0.03	0.120
	XRF	39.98	3.06	8.44	35.49	1.21	0.15	0.02	0.12	0.02	0.128
T-1	Chemical	63.08	16.57	5.94	1.86	5.19	4.40	1.23	0.59	0.14	0.110
	XRF	63.43	16.45	6.04	1.85	5.21	4.43	1.21	0.59	0.16	0.105
NS-1	Chemical	53.24	21.27	4.03	0.63	1.67	9.85	6.50	1.06	0.28	0.180
	XRF	53.14	21.33	3.93	0.63	1.64	9.88	6.50	1.05	0.28	0.181
S-1	Chemical	59.78	9.6	8.21	4.20	10.09	3.38	2.60	0.49	0.23	0.40
	XRF	59.91	9.71	8.16	4.27	10.06	3.43	2.59	0.47	0.25	0.40
GSE	Chemical	54.85	12.13	5.66	3.28	4.75	4.08	4.26	0.64	0.63	0.086
	XRF	54.84	12.16	5.66	3.30	4.76	4.12	4.27	0.63	0.63	0.084

Standard	SiO_2	Al_2O_3	Fe_2O_3	MgO	CaO	Na_2O	K_2O	TiO_2	P_2O_5	MnO
2σ Detection limit (ppm)	125	200	27	205	28	640	10	50	10	23
Working range(%)	35-80	0.7-22	1.3-14	0.4-50	0.5-14	2.1-10	0.02-7	0.02-2.6	0.02-1.1	0.03-0.4
Relative error 1:7.33 Fusions (%)	.36	.98	.74	2.58	1.15	2.02	.58	1.42	5.05	2.48
Relative error 1:18 Fusions (%)[1]	.38	1.39	1.53	2.22	1.74	3.0[2]	2.37	2.24	7.92	7.13

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[1] Fabbi (1972, p. 237-245).

[2] Fabbi (1973, p. 15-17).

Table 7.--Reproducibility of XRF check standard data

Standard	SiO_2	Al_2O_3	Fe_2O_3	MgO	CaO	Na_2O	K_2O	TiO_2	P_2O_5	MnO
All										
Relative error (%)	0.36	0.98	0.74	2.58	1.15	2.02	0.58	1.42	5.05	2.48
DRN										
Relative error (%)										
MLRP	.53	.57	.62	2.91	.42	2.67	.00	2.72	12.00	.48
$\overline{x}$= 60	.51	.80	.41	1.57	.00	2.33	.59	4.54	8.00	1.90
$\overline{x}$= 164	.49	.91	.31	1.79	.14	3.33	.59	4.54	7.6	1.90
GH										
Relative error (%)										
MLRP	.10	.40	2.19	----	2.90	2.08	.21	.00	.00	2.00
$\overline{x}$= 51	.70	.72	2.92	----	2.90	.26	.42	5.00	5.00	2.00
PCC-1										
Relative error (%)										
MLRP	.33	2.74	.49	.12	2.00	----	----	----	----	4.17
$\overline{x}$= 12	.19	15.1	.73	1.31	2.00	----	----	----	----	4.17

In nearly all cases the mean relative errors are comparable to the original relative error values taken from the calibration curve. In the case of Al_2O_3 for PCC-1, one must take into account that the relative error of 15.1% is based on an absolute difference of 0.13%, which compares to an average standard error of estimate for that element of 0.14%.

A major purpose of this study was the determination of certain minor element oxides of geochemical interest in the same sample discs used for the demination of the major element oxides. Barium, zirconium, and strontium were determined utilizing the 16 international standards and GSE. Nickel and chromium were determined using some of these standards plus seven gravimetrically analyzed rock samples as secondary standards. Table 8 compares the matrix-corrected XRF data obtained from the standards, utilizing a multiple linear regression program, with the literature values. The detection limits indicated were the working detection limits, except for Cr, which was lowered to 15 ppm after installation of a new x-ray tube. In general, with the exception of lower limits for Cr, the detection limits for the fusion discs are only 3-5 times less sensitive than those for 85:15 cellulose powder pellets as reported by King and others, (1978). The average relative errors obtained for 1:7.33 fusion discs are equivalent to or less than those reported for the 85:15 pellets for the elements Zr, Sr, Ni, and Cr, but greater than the relative error reported for Ba.

Figures 1 and 2 illustrate how effectively multiple linear regression techniques correct for complex matrix effects. Figure 1 illustrates the magnitude of Ti spectral interference on the determination of barium. Figure 2 indicates the nature and magnitude of the combined matrix effects of Sr, Ca, and background on the Zr signal.

Precision studies on a group of 18 basalts yielded the following average relative standard deviations over the indicated ranges for the minor element oxides: BaO, 0.74%, 580-785 ppm; ZrO_2, 1.3%, 880-1100 ppm; SrO, 2.3%, 250-450 25ppm; NiO, 13.5%, 6.5-16 ppm; and Cr_2O_3, 23.5%, 22-68 ppm.

Table 9 lists multiple linear regression values for chlorine based on XRF intensity data on 1:7.33 glass fusion discs made from the 16 international standards and GSE. A comparison is made with neutron activation data by Johansen and Steinnes (1969) and XRF data on 1:1 powder pellets by Fabbi and Espos (1972). The average relative error(%) was calculated versus NAA values, where available, and against the XRF values in the remainder of cases.

With every suite of samples analyzed, it was customary to run a check standard to monitor the precision of the XRF analysis system. The French ANRT standard diorite, DRN, is a good choice for this purpose because of its mid-range composition for most major elements. Where samples of relatively high or low silica content were analyzed, a granite such as GH or a basalt such as BR or BCR-1 were used, respectively, as a check standard. A measure of the instrumental precision obtainable for 60 determinations for the same DRN fusion disc over a period of several months without resurfacing is shown in Table 10.

Le Maitre and Haukka (1973) reported anomalies in the stability of count rates for lithium tetraborate glass discs when exposed to prolonged x-ray radiation. They reported that Na and Mg count rates decrease, while those of Si, Al, and P increase. They rectified this problem by periodically grinding away a thin layer of the disc surface. We encountered the same anomalies and corrected them in similar fashion.

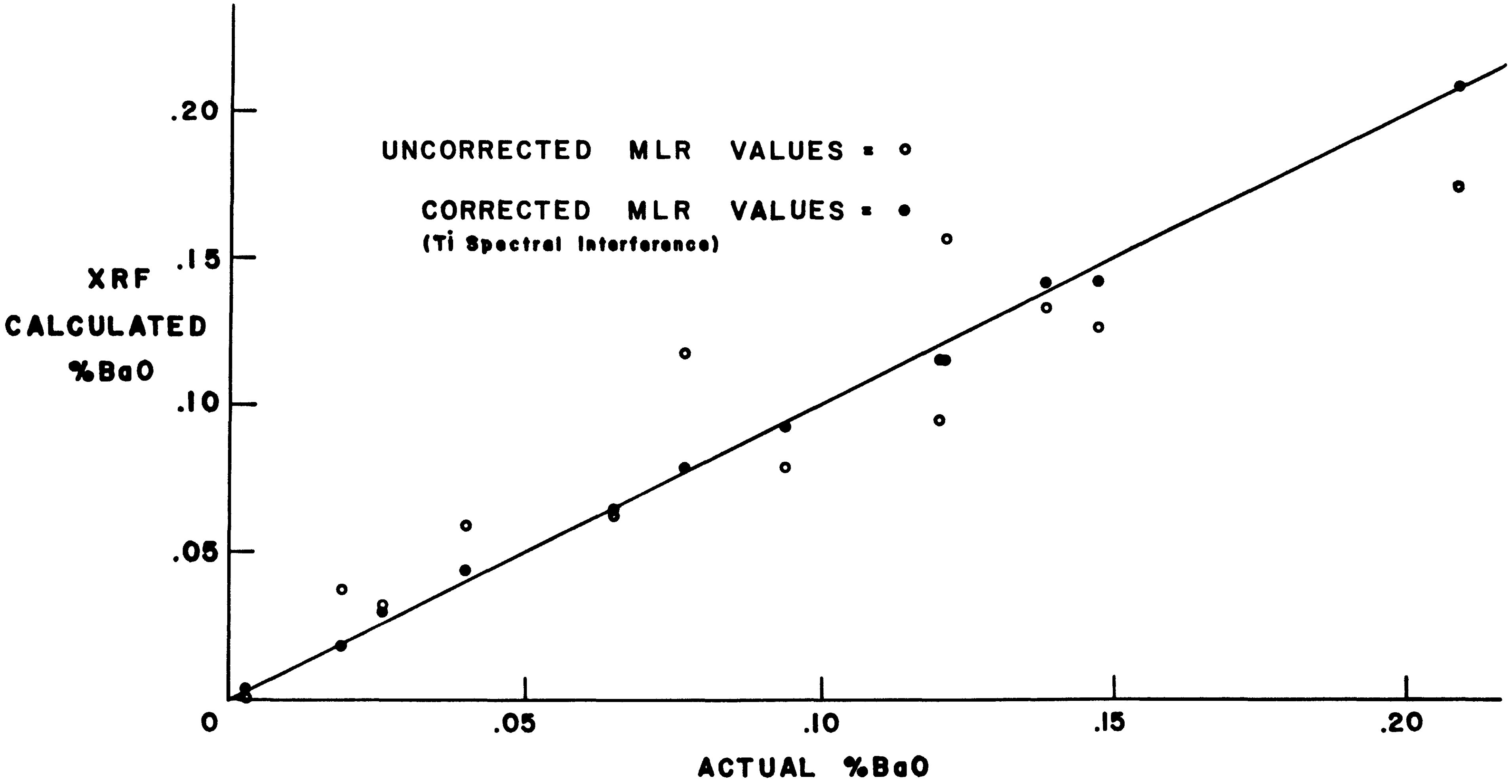

Figure 1. XRF Determination of BaO in 1:7 glass fusion discs

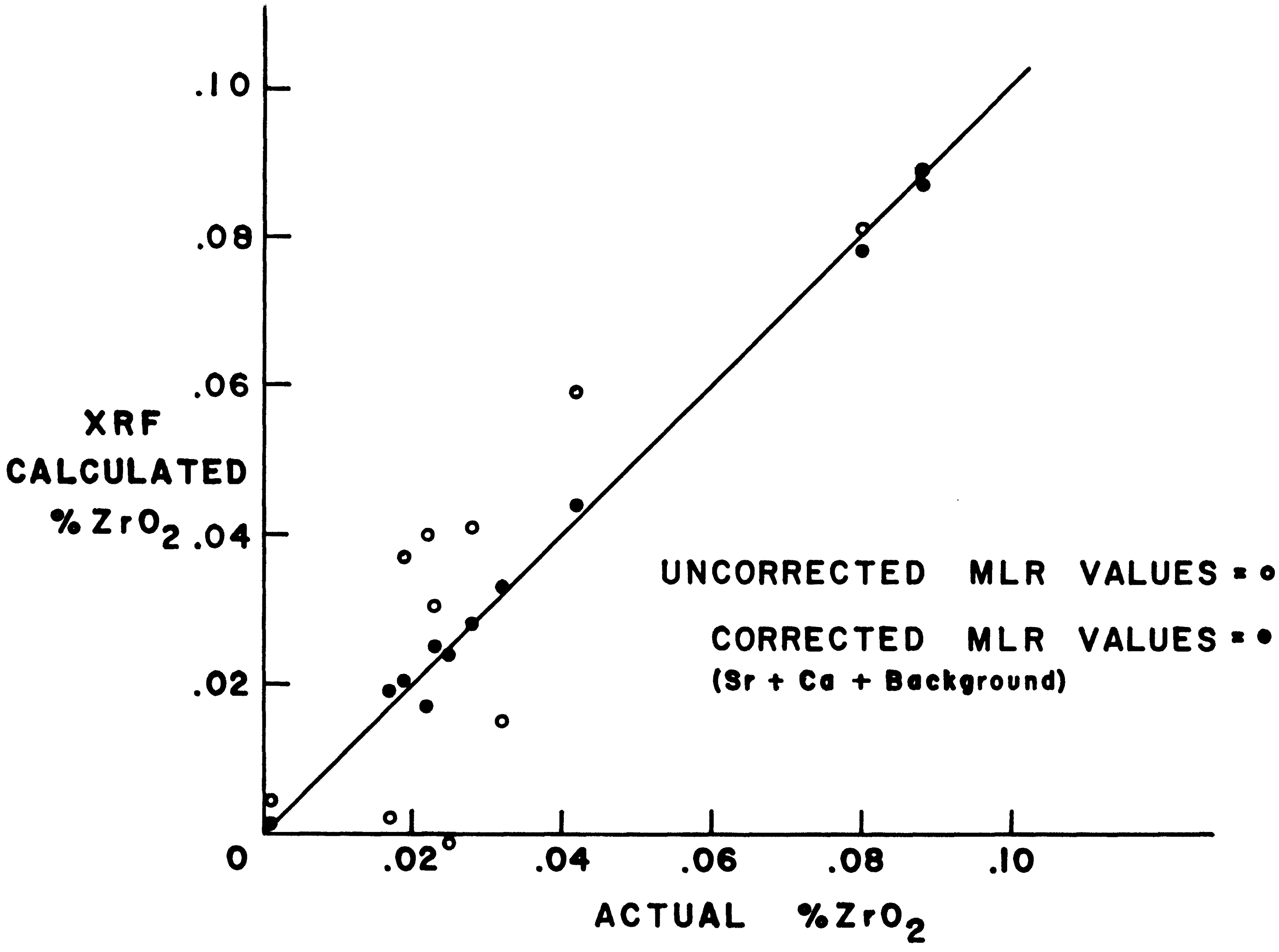

Figure 2. XRF Determination of ZrO_2 in 1:7 glass fusion discs

Table 8.--Comparison of XRF determined values vs. preferred chemical values (Wt %) for BaO, ZrO, SrO, NiO, and Cr_2O_3 for selected standards and gravimetrically analyzed samples

Std.	Value	BaO	ZrO_2	SrO	NiO	Cr_2O_3	Std.	Value	BaO	ZrO_2	SrO	NiO	Cr_2O_3
G-1	Chemical	0.120	0.028	0.031	---	---	UBN	Chemical	0.003	0.000	0.001	0.254	0.326
	XRF	.116	.028	.031	---	---		XRF	.004	.002	ä.002	.266	.361
W-1	Chemical	.019	.014	.023	.010	.018	T-1	Chemical	.065	.023	.045	.002	---
	XRF	.018	.009	.023	.010	.019		XRF	.065	.025	.047	.002	---
AGV-1	Chemical	.138	.030	.080	.002	---	NS-1	Chemical	.138	.088	.198	---	---
	XRF	.137	.032	.084	.002	---		XRF	.142	.087	.199	---	---
G-2	Chemical	.208	.042	.056	---	---	S-1	Chemical	.026	.425	.022	.006	---
	XRF	.210	.044	.057	---	---		XRF	.030	.425	.025	.006	---
BCR-1	Chemical	.077	.025	.040	.002	---	GSE	Chemical	.276	.254	.281	.260	.260
	XRF	.079	.024	.040	.002	---		XRF	.277	.258	.281	.257	.253
GSP-1	Chemical	.147	.080	.029	.002	---	M101231	Chemical	---	---	---	.12	.64
	XRF	.143	.078	.029	.002	---	Orthopyrox.	XRF	---	---	---	.121	.610
PCC-1	Chemical	.0007	.0009	.000	.318	.418	M101234	Chemical	---	---	---	.31	.41
	XRF	.001	.002	.002	.311	.412	Harzburg.	XRF	---	---	---	.316	.412
DTS-1	Chemical	.0007	.0004	.0001	.310	.625	D102698	Chemical	---	---	---	.07	1.24
	XRF	.001	ä.002	.002	.302	.605	Websterite	XRF	---	---	---	.067	1.234
BR	Chemical	.121	.032	.160	.034	.061	D103702	Chemical	---	---	---	.27	.24
	XRF	.116	.023	.156	.032	.054	Dunite	XRF	---	---	---	.269	.252
GA	Chemical	.094	.019	.036	---	---	D103703	Chemical	---	---	---	.06	.13
	XRF	.093	.020	.033	---	---	Griquaite	XRF	---	---	---	.060	.126
GH	Chemical	.002	.022	.001	---	---	D103704	Chemical	---	---	---	.18	.86
	XRF	.001	.017	.002	---	---	Lherzolite	XRF	---	---	---	.186	.881
DRN	Chemical	.040	.017	.047	.003	.007	D103707	Chemical	---	---	---	.08	.44
	XRF	.044	.019	.047	.002	.003	Websterite	XRF	---	---	---	.082	.449
Relative error (%)													
1.7.33 Fusion disc		6.3	4.2	2.8	5.8	5.0							
85:15 Powder pellet		2.5	3.7	4.9	3.3	9.0							
2σ Detection limit (ppm)		11	21	21	6	32							

Table 9.--Comparison of XRF with neutron activation values for chlorine (Wt %)

Standard	NAA[1]	XRF[2]	XRF[3]	Standard	NAA[1]	XRF[2]	XRF[3]
G-1	--	0.0075	0.007	GA	--	0.0213	0.022
W-1	0.0206	.0219	.020	GH	--	.0072	.006
AGV-1	.0115	.0108	.011	DRN	--	.0400	.040
G-2	.0053	.0054	.004	UBN	--	.0900	.090
BCR-1	.0058	.0064	.005	T-1	--	.0159	.018
GSP-1	.0311	.0305	.031	NS-1	--	.0520	.052
PCC-1	.0066	.0059	.006	S-1	--	.0174	.020
DTS-1	.00094	.0011	.002	GSE	--	1.21	1.21
BR	--	.0385	.039				

Relative error (%): 6.91 2 Detection limit (ppm): 15

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[1] Johansen and Steinnes (1967, p. 1107-1109).

[2] Fabbi and Espos (1972, p. 293-295).

[3] This work.

Table 10.--Instrumental precision[1] for 1:7.33 glass fusions with a DRN[2] disc as a check standard

Oxide	$\bar{x}$	SD	RSD (%)	Oxide	$\bar{x}$	SD	RSD (%)
SiO_2	53.02	0.115	0.22	Na_2O	2.93	0.066	2.2
Al_2O_3	17.38	.066	.38	K_2O	1.69	.0028	.17
Fe_2O_3	9.63	.027	.28	TiO_2	1.05	.0052	.50
MgO	4.35	.034	.78	P_2O_5	.23	.011	4.8
CaO	7.08	.011	.16	MnO	.214	.0014	.65

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[1] 60 determinations.

[2] French ANRT standard diorite.

Applications

The reported automated XRF fusion method has been applied to a large number and variety of rock samples to date. Thousands have been analyzed whose constituents have summed to 99.2% - 100.5% via this technique. Table 11 illustrates some of this data with the reported chemical values being obtained by a single, accurate gravimetric analysis. The average relative error (%) values for each element are either similar or within a factor of two higher than those for the primary calibration standards (Table 6). Least squares linear regression calculations using this data exhibited similar or at most a loss of one "nine" in the correlation coefficient when compared with the primary standards data. The standard error of estimate values followed the same trends as the relative error values when compared to the international standards.

Nine plagioclase mineral separates were analyzed for barium using both 1:7.33 glass fusion discs and 85:15 cellulose pellets. Table 12 compares the results, which display a relative difference (%) for the 1:7 fusion discs similar to that obtained for the calibration standards (Table 8).

Table 13 illustrates good correlation with a low average relative error (%) when the fusion method was applied to the determination of Cr_2O_3 in ultramafic rocks. These had been previously analyzed gravimetrically.

Table 14 compares chlorine determinations on 1:7.33 glass fusion discs prepared from six marine clays to data obtained from 85:15 powder pellets (Elsheimer and Espos, 1978), referenced to a common separate fused glass chloride standard. The correlation between data sets was obtained by a least squares calibration plot of fused disc data vs. powder pellet data. The data indicate that at concentrations below 2.5 wt % Cl the results are reproducible for duplicate samples. Above that concentration, the uncertainty between duplicates markedly increases, indicating the need for more oxidant. This problem is much more severe in the case of sulfur. The data show that sulfur in excess of 0.3 wt % was not quantitatively oxidized. The problem may be circumvented by use of a lower fusion temperature, i.e. 1000° C rather than 1100° C as, reported by Baker (1981). He used essentially the same flux and oxidant as this work with a similar dilution ratio of sample to flux. For the complete oxidation of sulfur species it is essential to have an effective oxidant and a large oxidant to sample ratio (Elsheimer and Fabbi, 1974).

Preliminary work has indicated that other minor elements of geochemical interest, such as V, Nb, Cu, and Zn, should be capable of determination with comparable accuracy and precision in 1:7.33 fusion discs.

Data Corrections and Handling

Rock types with extreme concentrations of particular elements may require specific corrections or unique calibration curves for their accurate analysis. This was illustrated in the case of alkalic mafic rocks where summations were generally 1 - 2% low by weight. Rocks of this type often have relatively low silica and alumina contents, a high alkaline earth content (particularly CaO), and a high TiO_2 content (2.7 - 3.7 wt %). Consequently, King, (1978) developed a special set of element tables applicable to this and related rock types.

Table 11.--Comparison of XRF determined values vs reported chemical values (Wt %) for the major element oxides of gravimetrically analyzed silicate rocks[1,2]

Rock type	Value	SiO_2	Al_2O_3	Fe_2O_3	MgO	CaO	Na_2O	K_2O	TiO_2	P_2O_5	MnO
Quartz	Chemical	77.63	12.07	1.14	0.14	0.86	5.82	1.00	0.11	0.01	0.02
Rhyodacite	XRF	77.05	12.32	1.28	0.14	0.90	5.89	1.04	0.13	0.02	0.021
Granite	Chemical	81.12	10.03	2.35	0.07	0.56	0.57	3.43	0.02	0.01	0.040
	XRF	80.62	9.78	2.53	0.06	0.61	0.64	3.40	0.04	0.02	0.046
Rhyolite	Chemical	69.56	12.74	3.56	0.44	1.41	2.61	5.49	0.52	0.08	0.050
	XRF	69.22	12.71	3.62	0.44	1.39	2.69	5.45	0.51	0.10	0.054
Quartz	Chemical	51.44	17.07	11.00	4.78	8.07	3.11	1.69	1.43	0.57	0.140
Diorite	XRF	51.47	16.62	11.06	4.85	8.08	3.18	1.70	1.41	0.56	0.138
Diorite	Chemical	56.81	16.62	7.69	4.88	5.96	3.67	2.03	0.89	0.34	0.100
	XRF	56.70	16.55	7.80	4.87	5.96	3.67	2.04	0.92	0.34	0.104
Granodiorite	Chemical	60.44	17.32	6.23	1.93	5.81	3.46	2.79	0.74	0.40	0.180
	XRF	60.67	17.26	6.35	2.00	5.71	3.53	2.77	0.74	0.38	0.174
Andesite	Chemical	59.52	15.99	6.05	3.90	5.84	3.81	2.41	0.85	0.53	0.100
	XRF	59.57	15.59	6.25	3.90	5.87	3.94	2.39	0.86	0.39	0.103
Granodiorite	Chemical	72.79	13.41	5.02	0.23	1.40	0.46	2.81	0.21	0.01	0.110
Gneiss	XRF	73.11	13.30	5.22	0.25	1.43	0.39	2.82	0.23	0.04	0.106
Gneiss	Chemical	61.83	14.03	5.65	2.29	6.09	3.65	4.47	0.40	0.03	0.41
	XRF	61.15	13.66	5.64	2.30	6.03	3.58	4.40	0.40	0.08	0.40
Gabbro	Chemical	48.92	13.91	10.46	10.87	10.00	2.02	0.74	1.41	0.09	0.14
	XRF	48.32	13.25	10.59	10.88	10.04	2.19	0.77	1.39	0.06	0.14
Basalt	Chemical	41.82	10.77	9.47	9.14	11.26	4.07	2.82	1.66	0.63	0.170
	XRF	41.45	10.77[3]	9.53	9.42	11.35	4.08	2.91	1.54	0.66	0.168
Basalt	Chemical	46.30	16.58	13.92	5.55	8.73	3.17	1.10	3.47	0.62	0.20
	XRF	46.09	16.46[3]	14.12	5.67	8.72	3.22	1.12	3.50	0.62	0.18
Basalt	Chemical	48.25	17.02	11.00	7.85	10.58	2.61	0.41	1.24	0.25	0.19
	XRF	48.22	17.10[3]	11.16	8.07	10.68	2.67	0.40	1.19	0.17	0.18
Diabase	Chemical	40.25	12.30	12.90	8.49	14.23	2.45	1.54	2.29	1.01	0.24
	XRF	40.08	12.05	12.73	8.75	14.12	2.53	1.59	2.09	1.02	0.23
Obsidian	Chemical	76.39	12.30	1.36	0.06	0.34	3.79	4.88	0.09	0.01	0.030
	XRF	76.33	12.07	1.47	0.11	0.49	3.83	4.88	0.10	0.02	0.032
Tuff	Chemical	69.57	14.94	2.84	0.75	1.03	3.86	4.46	0.32	0.07	0.050
	XRF	69.63	14.90	2.93	0.77	1.00	3.97	4.52	0.34	0.08	0.056
Peridotite	Chemical	44.65	3.98	10.05	37.43	3.27	0.32	0.02	0.20	0.01	0.15
	XRF	44.28	3.88	9.92	37.43	3.03	0.45	0.05	0.22	0.03	0.14
Dunite	Chemical	38.15	0.23	7.18	47.73	0.00	0.01	0.00	0.01	0.00	0.10
	XRF	37.96	0.16	7.28	47.39	0.09	0.19	0.005	0.03	0.02	0.098
Dunite	Chemical	37.57	1.23	8.90	46.26	0.00	0.00	0.0002	0.01	0.00	0.12
	XRF	37.56	1.20	8.77	46.37	0.14	0.15	0.004	0.03	0.03	0.124
Serpentenite	Chemical	37.83	1.39	4.60	41.79	0.00	0.01	0.01	0.01	0.00	0.10
	XRF	37.96	1.25	4.88	41.80	0.01	0.15	0.01	0.04	0.02	0.112
Relative error (%)		0.45	1.69	2.54	2.00	2.12	3.80	1.64	4.47	13.05	2.41

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[1] XRF results corrected for loss on fusion.

[2] Analyzed by U.S. Geological Survey, Conventional Rock Lab, Denver, CO.

[3] Fe absorption correction for basalts.

Table 12.--Comparison of XRF BaO determinations for 1:7.33 glass fusion discs vs 85:15 powder pellets for nine plagioclase samples (Wt %).

Sample	85:15	1:7
508	0.0179	0.0188
509	.0145	.0140
510	.0113	.0128
511	.0067	.0063
512	.0112	.0112
513	.0100	.0108
514	.0045	.0040
515	.0234	.0255
516	.0313	.0326

Relative difference (%): 5.1

Table 13.--Comparison of XRF and reported chemical values for Cr_2O_3 for seven analyzed samples (Wt %)

Sample	Chemical[1]	XRF
699	0.85	0.83
700	.94	1.00
706	.42	.42
709	.42	.43
713	.35	.36
232	.55	.56
233	.85	.92

Relative error (%): 3.4

[1] Analyzed by U.S. Geological Survey Conventional Rock Lab, Denver, CO.

Analysts: E. Engleman, V. C. Smith, and E. L. Munson

Table 14.--Comparison of XRF chlorine determinations for 1:7.33 glass fusion discs vs. 85:15 powdered pellets for six marine clay samples (Wt %)

Sample	85:15	1:7.33
137	2.24	2.26
139	2.16	2.17
148	3.81	3.82
151	2.62	2.56
153	1.80	1.77
154	2.10	2.16

Relative difference (%): 1.47

A group of anorthosite rocks containing as much as 34 wt % Al_2O_3 was successfully analyzed using an analytical curve linear through 48 wt % Al_2O_3. The curve was constructed from standards consisting of mixtures of USGS Standard BCR-1 and French ANRT Standard DTN (disthene or kyanite). Clay samples containing as much as 20 wt % CaO required an additional correction for CaO based on a least squares calibration curve derived from secondary standard data from similar rock types.

The determination of alumina in basalts required an interactive solution. A negative bias of up to 1 wt % Al_2O_3 was found, due to absorption of the aluminum K-alpha X-rays by iron. Suitable corrections were derived for Al_2O_3 using previously well-characterized basalt standards representing a range of compositions. The empirically derived correction equation is:

$$\text{corr.\% } Al_2O_3 = \text{xrf\% } Al_2O_3 + [\text{xrf\% } Al_2O_3 \times 0.007 \times (\text{xrf \% } Fe_2O_3 - 7\% \; Fe_2O_3)]$$

where, corr.% Al_2O_3 = the empirically corrected xrf% Al_2O_3;
xrf% Al_2O_3 = the instrumentally determined % Al_2O_3;
xrf% Fe_2O_3 = the instrumentally determined % Fe_2O_3;
0.007 Fe_2O_3 = an empirically derived factor based on application to nine gravimetrically analyzed basalts;
7% Fe_2O_3 = the empirically chosen base level of Fe_2O_3, above which significant absorption of Al intensity occurs.

Table 15 depicts the magnitude of the corrections for various iron and aluminum concentrations.

Two other means of improving the accuracy of aluminum determinations in basalt would have been either to include more affecting elements in the matrix corrections, or, to construct a calibration curve based on basalt standards only. The first was precluded by the system software, while the second would have violated the aim of this work, namely, to construct calibration curves based primarily on international standards of a wide compositional spectrum appropriate for most geochemical investigations. Nevertheless, a minor effort was expended to construct a calibration curve for aluminum unique to basalts using five analyzed basalt standards. The standard error of estimate for Al was reduced by a factor of 700, which indicates the possibilities for such efforts.

Volatility Corrections

Corrections for volatile components which are lost from the sample and flux mixture during fusion are made by factoring the XRF matrix-corrected results times the mean disc weight for the sample pair divided by the theoretical after-fusion weight of the sum of sample (no volatiles), $Li_2B_4O_7$, Li_2O, and Br; this value is 7.33. If the pair of fusion discs for a given sample have a weight difference greater than 10 mg, the heavier disc weight is generally selected, or an additional sample is fused. The selection is based on the assumption that splattering may have occurred; which in practice occurs infrequently, and is primarily a function of sample viscosity and the smoothness of mechanical operation of the fusion device.

The iron corrections for aluminum in basalts and the volatility corrections calculated from Loss-on-Fusion data reported by King and Mossotti (1982), are computed off-line and the results displayed on a computer terminal. A chemical summation of the major constituents plus the volatiles content is also displayed.

Table 15.--Fe absorption corrections for XRF Al_2O_3 values for 1:7.33 fusion discs of basalt samples and their comparison with reported chemical values (Wt %)

Sample	XRF Al_2O_3	Net XRF Fe_2O_3	Corr. Al_2O_3	Chem. Al_2O_3
009	15.70	7.0	16.47	16.58
104B	11.27	12.0	12.22	12.33
106B	14.33	4.7	14.80	15.01
125B	13.15	6.9	13.79	13.66
608	16.65	4.0	17.12	17.02
2654	12.12	5.9	12.62	12.30
257	16.66	4.0	17.13	17.07
250	13.30	6.5	13.91	13.91
713	3.88	3.0	3.96	3.98

If a chemical value for FeO is known, the xrf% Fe_2O_3 value is corrected accordingly. If values for CO_2, water of hydration, and water of adsorption are known, the sum of these is included in the total summation in lieu of the Loss-on-Fusion results. In general, these two sets of values should show agreement within several tenths of a percent absolute.

Experience with rocks having more than 10 wt % volatiles showed evidence of deviations from linearity for major element determinations. Work by King and Mossotti (1979) has verified such deviations for silicate rock mixtures, particularly for the major elements with K-alpha line intensities greater than 3.3 KEV, i.e. K, Ca, Fe, Ti, and Mn. With the exception of Si, elements with lower energy lines do not appear to deviate from linearity. A polynomial expression was developed by King to correct for the deviations from linearity caused by volatility. It is postulated that the deviations from linearity occur because the elemental oxides are more concentrated in the volatile-depleted fusion matrix. XRF radiation for the heavy elements, being more energetic, is generated at greater depth in the disc and is more subject to absorption/enhancement effects (Bertin, 1975). By contrast, radiation for the lighter elements is less energetic, is generated near the surface of the sample disc, and is less subject to absorption/enhancement effects.

These observations contrast with those of Haukka and Thomas (1977), who claim that no LOF corrections are necessary and that the same matrix correction parameters may be used over a wide range of dilutions.

CONCLUSIONS

The XRF fusion technique described here is amenable to the accurate, precise, and rapid analysis of a wide variety of silicate rocks and minerals on a routine basis. Specific applications to silicate rocks with unique properties or extreme concentrations are also possible. Utilization of multiple fusion units, operated simultaneously, enables preparation of sufficient samples to supply an automated sequential X-ray spectrometer system. The 1:7.33 sample dilution is a good compromise for analyzing both major and minor elements without greatly sacrificing sensitivity for the latter.

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