

MULTIELEMENT ANALYSIS OF GEOLOGIC MATERIALS BY
INDUCTIVELY COUPLED PLASMA EMISSION SPECTROSCOPY

Odin D. Christensen and Ruth L. Kroneman

Earth Science Laboratory Division/University of Utah Research Institute

420 Chipeta Way, Suite 120

Salt Lake City, Utah 84108

ABSTRACT

The emphasis in geochemistry on multielement analysis of a variety of natural materials has stimulated interest in the application of inductively coupled plasma emission spectroscopy (ICP) to the analysis of geologic materials. Achievement of the requisite flexibility and capability necessitates that compromise procedures and instrument configuration be used to accommodate the varied requirements. A realistic assessment of the quality of analytical data must consider the entire sample preparation and analytical process and the effects of interelement interaction and interference in the sample matrices actually encountered.

Statistical evaluation of determinations made over one year from replicate samples within and between analytical sessions and from repeated analysis of reference standard rocks has permitted estimation of realistic empirical measures of precision, limits of quantitative determination, and accuracy. The quality of analytical data is generally satisfactory for most multielement geochemical exploration applications and for many petrologic investigations.

INTRODUCTION

In recent years, there has been a growing interest in the use of inductively coupled plasma emission spectroscopy (ICP) for the analysis of geologic materials. The capability of simultaneously determining major, minor, and trace elements in virtually all sample types has been especially attractive. Much of the analytical work at the Earth Science Laboratory Division (ESLD) of the University of Utah Research Institute is performed by ICP (Christensen et al., 1980). Our experience with this technique over more than 30 months has shown that the quality of analytical data obtained by ICP is satisfactory for most multielement geochemical exploration applications and for many petrologic investigations. We have also found, however, that the figures of merit frequently cited, particularly by commercial laboratories and instrument manufacturers, do not accurately represent the quality of analytical data actually obtained.

The types of material frequently analyzed in geologic applications are highly varied, including rocks, minerals, soils, brines, natural waters, and laboratory or process leach solutions (Church, 1977a, b, c, d; Sobel and Ward, 1977; Ward, 1977). The matrices are commonly complex. Potential concentration ranges may be several orders of magnitude. Rock and soil samples are frequently inhomogeneous and consist of a mixture of mineral grains that may include silicate, sulfide, oxide, carbonate, and sulfate minerals as well as organic materials.

The advantages of ICP spectroscopy have been discussed in a number of papers (Dahlquist and Knoll, 1978; Fassel and Kniseley, 1974; Baurman and Bostrum, 1979). These include rapid throughput of samples, simultaneous determination of major, minor and trace element abundances, minimization of

interelement interaction effects, applicability to small samples and acceptable precision and accuracy. The unique characteristics of the plasma configuration that make it a superior excitation source are the high temperatures attained ($>7000^{\circ}\text{K}$), long residence time of the analyte in the plasma and containment of the analyte within the inert axial region of the plasma. These features result in very low detection levels, linear or near-linear calibration curves over concentration ranges of four or more orders of magnitude, and minimization of the interelement effects experienced in other analytical methods.

ICP spectroscopy is ideally suited for many geologic applications where large numbers of samples need to be analyzed for a number of elements at all concentration ranges. To achieve the requisite flexibility and capability requires that compromises be made in procedures and instrument configurations to accommodate all elements, anticipated concentrations, and sample types. The analytical results are thus of variable and generally somewhat lower quality than the optimum possible for each element determined individually. This report describes the procedures and instrumentation employed at ESLD for multielement ICP analysis of geologic materials and assesses the precision and accuracy of resulting analyses and the limits of quantitative determination for the 37 elements in our instrument array. The capabilities and limitations of this method for geological analysis are discussed.

EXPERIMENTAL

Instrumentation

The ICP used at ESLD is an Applied Research Laboratories Model QA-137

consisting of an inductively coupled argon plasma excitation source, a 1080 lines/mm grating, 38 channel direct-reading polychromator, with provision for pneumatic nebulization of liquid samples and direct introduction of the aerosol from the spray chamber into the plasma axial chamber. The instrument is controlled by a PDP 11/05 computer with DECwriter consol. The spectral lines used in the current instrument configuration are listed in Table I. Two Fe channels permit determination of a greater range of sample concentrations.

Sample preparation

Fluid samples require a minimum of sample preparation. Generally samples are filtered to assure the exclusion of particulate matter and acidified 20% by volume with 16 M HNO_3 to match the matrix of synthetic calibration standards. It has been shown by a number of workers (Dahlquist and Knoll, 1978; Ward et al., 1976) that the acid strength of samples can significantly affect solution viscosity and hence sample uptake and nebulization rates. Thus, we have employed the practice of maintaining as nearly as possible a constant acid strength in samples and standards. For the analysis of natural waters, acidification at the time of collection has the further benefit of stabilizing the solution and inhibiting precipitation of solid phases.

All solid samples are dissolved by a four-acid digestion procedure using HF, HClO_4 , HCl and HNO_3 . For rock analyses in which acceptable values for all 37 elements are desired, 2% weight-to-volume solutions are prepared (the actual solution concentration often approximates 1% due to Si loss during HF digestion). For analysis of samples in which some elements may be present in abundances that exceed the calibration range or where major element concentrations are desired and trace elements are not of concern, more dilute

solutions are prepared. Specifics of the digestion procedure are presented by Christensen et al. (1980).

Potentially, the sample preparation and digestion procedure may represent the most critical step in the analytical procedure. Samples must be pulverized sufficiently to assure complete dissolution. Even so, highly resistant phases such as chromite and Ti-oxides are frequently observed to remain undissolved. Uniformly fine comminution of rock samples is thus extremely important for analytical accuracy. Because HF is used to attack the silicate minerals, most Si and some W are lost in vapor, rendering the Si and W analyses of questionable value. B determination in solids is similarly adversely affected by the acid digestion. Although the HF is largely driven off during digestion, some residual fluoride remains and attacks the glass of the instrument nebulizer and spray chamber, introducing spurious B and Si concentrations.

Data acquisition

Data acquisition is controlled by ICP-BLISS, a program providing segmented second-order polynomial calibration functions using four successive data pairs per curve, and second-order interference corrections (Hinthorne et al., 1977). BLISS uses the variance of seven multiple integrations for weighting the calibration measurements in the polynomial regression routine. Six or seven multielement solutions, including an acid digestion blank, are used to define the calibration functions, usually spanning at least 3 orders of magnitude concentration range. The entire calibration data set and analytical curves are stored on disk for immediate application during analysis or for later retrieval and use.

Prior to an analytical session, a normalization or standardization procedure is used to update the calibration information for instrument drift or to reinitiate a calibration file created at an earlier time. The normalization is done with groupings of elements in both high and low concentration solutions.

Samples may be individually introduced manually or automatically introduced through an autosampler. As each sample is run, the analysis program times a preflush interval, reads the integrator offset voltages and times a series of signal integrations. The net intensities for the multiple integrations are averaged, corrected by the normalization factors, and the concentrations calculated from the appropriate calibration function to yield an in-solution concentration value. Interelement correction factors are applied to produce a corrected in-solution concentration and finally the dilution correction is made to yield a corrected in-sample concentration. The elapsed time for the process is approximately 5 minutes.

Data correction

One of the most important factors in the application of any analytical technique is the degree of freedom from interelement interactions or interferences (matrix effects). Interferences by concomitants may be both nonspectral and spectral in nature.

Nonspectral interferences directly affect the emission signal of the analyte and are common in most other spectral methods, particularly in some atomic absorption applications. These result from physical or chemical interferences with the analyte vaporization, dissociation or atomization. It has been shown that the high temperatures, long residence time of the analytes

in the plasma and the nonreactive argon plasma reduce or eliminate most of the interelement effects (Dahlquist and Knoll, 1978; Fassel, 1978; Fassel and Kniseley, 1974; Larson et al., 1975). Because of the high degree of freedom from interelement effects, it is possible to establish a set of calibration curves for analysis in a variety of sample matrices.

Spectral interferences are unavoidable in emission spectroscopy, but adequate corrections can be made. Spectral interference correction coefficients are experimentally derived by relating the combined net measures of residual stray light and spectral overlaps to concentrations of the interfering element using single element solutions. The general unavailability of pure reference samples remains a critical problem for the proper establishment of an adequate correction matrix. A matrix of 180 second-order correction factors is currently in use in our lab. Selection of the element array to be included in the instrument was based in part upon the necessity of analyzing interfering elements for correction purposes whether the actual concentrations in samples were of concern or not. Some adjustment of the empirically calculated values, based upon analysis of standard rock samples, has been necessary to make them generally applicable to the variety of materials encountered within geologic samples.

RESULTS

Approach

The collection, preparation, and analysis of materials involves a sequence of material manipulations, all of which affect the accuracy and precision of the final analysis. It is essential that the integrity and

representative nature of the sample be preserved throughout the entire process. Likewise, a realistic evaluation of the quality of analytical data must consider the entire sample preparation and analytical process.

In order to evaluate the reliability of analytical data generated by the ICP, several approaches were employed. These included, (1) performing multiple analyses of selected samples over a period of several months, (2) systematically performing duplicate analyses of samples within and between analytical sessions, (3) repeatedly analyzing reference standard materials, and (4) statistically evaluating the performance of each analytical channel. In general, the resulting estimates of analytical reproducibility and accuracy are conservative since these approaches tend to detect the greatest variation possible and evaluate the precision of sample preparation as well as sample analysis.

Factors affecting accuracy

A number of factors influence the accuracy of the analytical procedure. Sample preparation is critical. Inadequate comminution leaves unacceptably large mineral fragments, which may result in incomplete dissolution and deficient analyses. The method of digestion employed uses HF to attack silicate minerals, resulting in the loss of Si and W; these values are of doubtful reliability in our routine rock analyses. Occasionally, phases are encountered which are not rendered sufficiently soluble, such as Ti-oxides, zircon, and chromite, or insoluble phases such as $KClO_4$ may form and precipitate from solution. These effects are evident in the analytical results for the United States Geological Survey (USGS) standard rocks (Figure 1). It is emphasized that these are uncertainties introduced during samples

preparation; they similarly affect other analytical methods and are not unique to the ICP. In most cases if the problem is recognized and considered critical, the sample preparation procedure may be modified to alleviate the difficulty.

Because samples are introduced into the plasma by nebulization of a solution, the analytical results are critically dependent upon the physical characteristics of the solution. It has been shown that the effects of differing acid matrices can be significant (Dahlquist and Knoll, 1978; Ward et al., 1976). Fortunately, this deficiency may be largely overcome by following the practice of maintaining, as much as possible, constant acid matrix for sample and reference solutions.

Detection Limits

Measures of analytical limits vary between analytical techniques and investigators. The term "detection limit" in ICP investigations has been most commonly used to represent concentrations required to produce a line signal twice as great as the standard deviation of the background scatter (Church, 1977d; Ward, 1977; Dahlquist and Knoll, 1978; Fassel and Kniseley, 1974), although it has also been used to represent concentrations of three times the background standard deviation (Fassel, 1978) or six times the background standard deviation (Souillart and Robin, 1972). "Limits of quantitative determination" (LQD) or "minimum reportable quantities" are most commonly established at five times the detection limits, or ten to fifteen times the background standard deviation (Ward, 1977; Dahlquist and Knoll, 1978; Fassel, 1978; Fassel and Kniseley, 1974). As established, these are measures of the analytical limits of the instruments under ideal conditions.

Realistically, a measure of technique precision should consider the analytical scatter introduced by the normalization procedure, interference corrections, and blank subtraction as well as the inherent instrument noise. Several criteria were evaluated in establishing the limits of quantitative determination for our ICP. Instrument background signal variation was measured for eleven successive measurements of a deionized distilled water blank to establish "detection limits" as defined by other investigators. Variation in background levels due to instrument drift and variation in successive normalizations were evaluated through comparison of acid digestion blanks run periodically within and between analytical sessions over a period of several months. Similarly, reference standard materials (including USGS standard rocks) were repeatedly analyzed to establish variation at greater concentration levels in material with geochemically realistic matrices. Finally, estimates of variation at zero concentration and of precision for a range of concentrations were calculated by the method of Thompson and Howarth (1976) using duplicate analyses of actual samples repeatedly analyzed within and between analytical sessions. Using this suite of information, limits of quantitative determination (LQDs) were established for the ESLD instrument (Table I). These represent lowest meaningful analytical values for each element, considering uncertainties of the entire analytical process. Precision at the LQD is approximately $\pm 100\%$ of the given value with a confidence level of 95%. As established, the LQD values presented are quite conservative. These will change somewhat as the instrument, operating conditions, and sample preparation change.

Precision

As with the LQDs, precision has been established from replicate analyses

of standard and routine analytical samples. The values presented thus reflect the precision of the overall laboratory procedure.

The standard deviation of a determination within a system tends to vary with concentration of the analyte. Following Thompson and Howarth (1976), we may express the standard deviation of a determination (s_c) as a function of concentration (c) and the standard deviation at zero concentration (s_0), thus:

$$s_c = s_0 + kc, \text{ where } k \text{ is a constant.}$$

The parameters s_0 and k can be used to quantify the precision, p_c , at concentration c by means of the definition of precision

$$p_c = 2s_c/c.$$

This gives then

$$p_c = 2s_0/c + 2k$$

where k corresponds to the precision observed at concentrations well above the LQD. The concentration of the LQD is defined by letting $p_c = 1.0$ (100% relative variation at 95% confidence level) yielding the expression

$$\text{LQD} = 2s_0/(1-2k).$$

In these equations, it is seen that the precision approaches k asymptotically at high concentrations, sufficiently greater than the LQD. In general, the precision approaches to within 10% of its asymptotic value only above concentrations (c) where $c/\text{LQD} = 10/k$. It is, therefore, not safe to assume that the precision will attain a steady value at concentrations less than two orders of magnitude greater than the established limits of quantitative determination (Thompson and Howarth, 1976).

Values for percent precision are presented in Table I. Because samples

and standards with adequate ranges of concentration were not available for all elements, precision values have not been established for all channels. In general, precision for major elements is better than approximately 5%, and for minor and trace elements is better than approximately 10%.

Accuracy

The accuracy of analytical values has been evaluated through analysis of standard reference materials including 13 USGS rock standards (Flanagan, 1976). Representative results are presented in Figure 2; complete results have been reported elsewhere (Christensen et al., 1980). When evaluating these data, the reader is encouraged to consult Flanagan (1976) to learn the extent of variation found by other analysts. The determined concentrations of some elements vary greatly depending upon the analytical method employed and especially upon whether digestion and dissolution are required. Variance is observed, especially in trace elements, between samples as a result of sample inhomogeneity. The "recommended" values presented for many elements (Flanagan, 1976) are the best estimates and not necessarily representative of the true composition of the sample analyzed at ESLD.

The results shown in Figure 2A are representative of major element analyses which are, in general, quite good. The low ICP values for high K concentrations probably result from precipitation of $KClO_4$ during sample digestion. The results presented in Figure 2B are illustrative of trace element analyses. Accuracy is acceptable for most geological applications despite minor biases. Figures 2C and 2D illustrate the accuracy for seven trace metals of geologic interest. Mn and Cu are quite acceptable. Cr, Co and Ni all display low biases and low precision. For Cr and probably as well

for Co and Ni, dissolution problems may contribute to the inaccuracy. Chromite especially is difficult to bring into solution. Again, the reader is encouraged to consult Flanagan (1976) for an assessment of the accuracy of the accepted values and of the variation between splits of the reference standards. The variation reported by other analysts for these elements is as great as that found here; the "recommended" values reported are averages of the various laboratories. In general then, ICP determinations for these elements are of comparable accuracy to determinations made by other methods commonly employed for geochemical analysis. The precision of the chemical determinations is in most cases better than the precision between splits of the standard reference samples.

DISCUSSION

One of the dangers inherent in the utilization of highly-automated, technologically sophisticated instrumentation such as an ICP is the temptation to accept the multidigit results uncritically. The values for LQDs, precision, and accuracy presented here represent best estimates of the quality of chemical data currently being collected at ESLD. These estimates have been determined through evaluation of actual analyses of geologic materials performed over a period of about one year and thus reflect an evaluation of the complete analytical procedure. Values for LQDs, although significantly greater than "detection limits" frequently presented by other analysts, are more realistic estimates of actual analytical capabilities.

Because the sample preparation for ICP analysis attempts to process all materials for all purposes in a uniform manner, it is necessarily a compromise

procedure. In general, it accomplishes the purposes well, although certain sacrifices, such as inaccurate values for Si and W concentrations, are unavoidable. The instrument of course does not require that a particular methodology be employed to take samples into solution. Other procedures may be used provided total dissolved solids content remains less than about 2%.

For the analysis of natural solutions, sample preparation is minimal. Solutions are acidified to approximately the acid strength of the analytical standards and analyzed directly. As a result of this minimal preparation and the fact that interelement interferences are markedly reduced because of the low concentrations of interfering elements, the LQD values are consequently lower than for rock digestion solutions.

Three sets of parameters are presented that characterize the quality of ICP-generated analytical data. Limits of quantitative determination (LQDs) represent lowest meaningful analytical values considering the variance present in the entire analytical system, or, more specifically, are those analytical values at which precision is equal to 1.0 at the 95% confidence level. The precision values presented are a measure of the repeatability of analyses or the dispersion of replicate analyses, again considering the effects of the entire analytic system. In general, major element analyses have precision of better than 5% and trace elements of better than 10%. The accuracy varies significantly between elements and with concentration. In general, the accuracy appears to be satisfactory for most elements at concentration ranges significantly above the LQD concentrations. The greatest source of disagreement between the ICP analyses and the recommended values for the standards appears to be related to solution problems and sample inhomogeneity.

The parameters presented in this paper demonstrate the capabilities of

the ICP to geochemical applications. Each instrument is, of course, unique in its elemental array, line selection and precise alignment. Consequently, the specific parameters presented here are directly applicable only to our instrument. We have in this discussion presented procedures by which the capabilities and limitations of other instruments might be ascertained, as well as some general observations concerning the utility of ICP analysis for geological applications.

As an instrument that can make simultaneous multielement determinations for a wide variety of material types in a short time, the ICP has unparalleled potential. In general, the quality of the analytical data is satisfactory for most multielement geochemical exploration applications and for many petrologic investigations. The rapid throughput of samples prepared by one digestion for both major and trace element analysis makes the technique extremely cost-effective, especially in studies of geochemical dispersion where such a spectrum of data may be valuable but the cost and time necessary for separate analysis of each individual element might be prohibitive. As ICP instrumentation is improved and as procedures for sample and standard preparation are refined, the quality of ICP data will likely improve as well.

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TABLE CAPTION

Table 1. Limits of quantitative determination for rock and water samples, calibration ranges and precision estimates for the Earth Science Laboratory ICP.

TABLE 1

Element	Line, Å	LQD, solution*		Calibration Ranges		% Precision**
		Water	Rock	Solution	Samples (2%)	
Na	5890	1	3	3-3000	150-15%	4
K	7664	2	3	2-2000	100-10%	5
Ca	3179.3	.2	2	2.5-2500	125-12.5%	2.5
Mg	2790.8	.4	2	2-2000	100-10%	4.5
Fe	2714.4	-	2	1-5000	50-25%	2
Fe	2599.4	.02	-	.02-100	.1-.5%	***
Al	3082.2	.5	2	.4-2000	20-10%	3
Si	2881.6	.2	1	.93-468	47-2.3%	***
Ti	3372.8	.1	.2	.1-500	5-2.5%	3
P	2136.2	.5	.5	.5-500	25-2.5%	3
Sr	4077.7	.01	.02	.02-20	1-1000	3
Ba	3891.8	.5	.5	.5-500	25-2.5%	5
V	4379.2	1	1	1-1000	50-5%	***
Cr	2677.2	.04	.04	.2-200	10-1%	2
Mn	2576.1	.2	.2	2-2000	100-10%	5
Co	2286.2	.02	.02	.1-100	5-.5%	10
Ni	2316	.1	.1	.2-200	10-1%	5
Cu	3247.5	.05	.1	.06-300	3-1.5%	10
Mo	3132.6	1	1	.5-500	25-2.5%	***
Pb	2203.5	.2	.2	.3-300	15-1.5%	5
Zn	2025.5	.1	.1	.04-200	2-1%	10
Cd	2265	.05	.1	.02-100	.1-.5%	***
Ag	3280.7	.04	.04	.04-200	2-1%	***
Au	2427.9	.08	.08	.05-50	2.5-2500	***
As	1937.7	.5	.5	.4-400	20-2%	***
Sb	2068.4	.6	.6	.6-600	30-3%	***
Bi	3067.7	2	2	2-2000	100-10%	***
U	3859.6	5	5	1-1000	50-5%	***
Te	2142.8	1	1	.5-500	25-2.5%	***
Sn	1899.9	.1	.1	.2-200	10-1%	***
W	2397.1	.1	.2	.2-100	10-0.5%	***
Li	6707.8	.04	.04	.04-200	2-1%	5
Be	2348.6	.004	.004	.004-20	.2-1000	10
B	2497.7	.1	.1	.1-100	5-5000	***
Zr	3392	.1	.1	.1-100	5-5000	5
La	3988.5	.1	.1	.1-500	5-2.5%	10
Ce	4186.6	.2	.2	.4-400	20-2%	12
Th	3539.6	2	3	1-1000	50-5%	***

* All values in mg/L.

** Relative precision at greater than 10 times LQD determined on solid samples.

*** Element was not present in sufficient concentration in standards to calculate precision.

FIGURE CAPTIONS

Figure 1. Schematic diagram of ICP analytical system (modified after ARL sales brochures).

Figure 2. Comparison of experimentally determined concentrations with recommended values for standard samples (A) Na, K, Ca and Mg. Values are percentages. (B) Li, Be, Sr and Ba values in mg/kg. (C) Cr, Mn, Co and Ni values in mg/kg (D) Cu, Zn and Pb values in mg/kg.