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DOE/ID/12079-2

**MULTIELEMENT ANALYSIS OF GEOLOGIC
MATERIALS BY INDUCTIVELY COUPLED
PLASMA—ATOMIC EMISSION SPECTROSCOPY**

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D154-195
NT13-25

March 1980

Work Performed Under Contract No. AC07-79ID12079

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Earth Science Laboratory
University of Utah Research Institute
Salt Lake City, Utah

U. S. DEPARTMENT OF ENERGY
Geothermal Energy

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ABSTRACT

Much of the chemical analytic work at the Earth Science Laboratory of the University of Utah Research Institute is performed by atomic emission spectroscopy using an inductively coupled plasma (ICP) source. This method permits the rapid acquisition of multielement geochemical data from a wide variety of geologic materials. Rocks or other solid samples are taken into solution with a four acid digestion procedure and introduced directly into the plasma; fluid samples are acidified or analyzed directly. The entire process is computer-controlled, fully-automated, and requires less than five minutes per sample for quantitative determination of 37 elements.

This paper describes the procedures and instrumentation employed at the ESL for multielement ICP analysis of geologic materials and is intended as a guide for evaluating analytic results reported from this laboratory. The quality of geochemical data can be characterized by precision, limits of quantitative determination, and accuracy. Precision values are a measure of the repeatability of analyses. In general, major element analyses have precision of better than 5% and trace elements of better than 10% of the amount present. Limits of quantitative determination represent lowest meaningful analytic values considering the variance present in the entire analytic procedure and are defined as values at which precision is equal to 1.0 at the 95% confidence level. Accuracy varies between elements and with concentration but is, in general, satisfactory for most elements at concentrations significantly above limits of quantitative determination.

As a technique for simultaneous multielement determination for a wide

variety of material types in a short time, ICP spectroscopy has unparalleled potential. In general, the quality of analytic data is satisfactory for most multielement geochemical exploration applications and for many petrologic investigations.

INTRODUCTION

The methods employed for the chemical analysis of geologic materials are numerous and varied. Each has advantages and limitations rendering it more suitable for certain applications than for others. The selection of any one analytic method for a particular application requires choices among the various attributes of accuracy, precision, limits and ranges of detection, rate of sample throughput, and initial and per-analysis cost. Much of the analytic work at the Earth Science Laboratory (ESL) of the University of Utah Research Institute is performed by atomic emission spectroscopy (AES) using an inductively coupled argon plasma (ICP) source. This method permits the rapid acquisition of multielement data of acceptable precision and accuracy for routine studies from a wide variety of geologic materials.

The inductively coupled plasma quantometer (ICPQ) used at ESL has a direct-reading 38 channel polychromator allowing simultaneous quantitative determination of 37 elements. Rocks or other solid samples are taken into solution with a single digestion procedure and introduced directly into the plasma. The entire analytic procedure is computer-controlled, fully-automated and requires less than 5 minutes per sample. Hence, the technique is ideally suited for applications where large numbers of samples need to be analyzed for a number of elements at all concentration levels. To achieve this flexibility and capability, however, requires that compromises be made in procedures and instrument configuration to accomodate all elements, anticipated concentrations, and sample types. The analytic results are thus of variable quality and generally somewhat less than the optimum possible for each element individually by this method.

This paper describes the procedures and instrumentation employed at ESL for multielement ICP-AES analysis of geologic materials and is intended as a guide for evaluating the quality of analytic results reported from this lab. Since ICP-AES is a relatively newly developed technology, continuing advancements make future modification of the instrument likely. Sample preparation techniques are also in the developmental stage and changes may be anticipated. Thus, this report should be considered a progress report documenting the current capabilities and limitations of the ICP-AES methodology and instrumentation used at ESL; periodic revision of tabulated performance values is anticipated as analytic techniques and hardware are refined.

EXPERIMENTAL FACILITIES AND PROCEDURES

Instrumentation

The ICPQ used at ESL is an Applied Research Laboratories Model QA-137 (Fig. 1), consisting of an ICP excitation source, 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 advantages of ICP-AES have been discussed in a number of papers (Dahlquist and Knoll, 1978; Fassel and Kniseley, 1974; Fassel, 1978; Church, 1977, a, b, c, d). These include rapid throughput of samples, simultaneous determination of major and trace element abundances, minimization of interelement interaction effects, applicability to microgram samples, and acceptable precision and accuracy. The unique characteristics of the plasma

Figure 1. Schematic diagram of ICPQ analytic system. Modified after Applied Research Laboratories sales brochures.

configuration which 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 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 analytic methods.

Sample Preparation

Fluid samples require a minimum of sample preparation, or may be analyzed without further preparation. Generally, samples are filtered to assure the exclusion of particulate matter and acidified 20% by volume (v/v) with 16M HNO_3 to more closely match the matrix of the synthetic calibration standards. It has been shown by a number of workers (Ward, Sobel, and Crawford, 1976; Dahlquist and Knoll, 1978) 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 fluids, 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. For rock analyses in which acceptable values for all 37 elements are desired, 2% weight to volume (w/v) solutions are prepared (the actual solution concentration approximates 1% due to Si loss during digestion). For analysis of samples in which some elements may be present in abundances that exceed the calibration range (such as heavy mineral concentrate samples) or where major

element concentrations are desired and trace element concentrations are not of concern, 1% W/v solutions are prepared. Specifics of the digestion procedure are outlined in the appendix.

Potentially, the sample preparation and digestion procedure may represent the most critical step in the analytic procedure. Samples must be pulverized sufficiently to assure complete dissolution. Even so, highly resistant phases such as chromite and Ti-oxides frequently are observed to remain as an undissolved residue. Uniformly fine comminution of samples is thus extremely important for analytic accuracy. Because HF is used to attack the silicate minerals, most Si and some W are lost in the vapor, rendering the Si and W analyses of questionable value. B determination is similarly adversely affected by the use of HF. Although the HF is largely driven off during the digestion, some residual fluoride remains and attacks the borosilicate glass of the instrument spray chamber, introducing spurious B concentrations. Should quality analytic values be desired for these three elements, other analytic techniques must be employed or alternative digestion procedures followed to take the sample into solution for ICPQ analysis.

Data Acquisition

Data acquisition by the ICPQ is controlled by ICP-BLISS, a program providing segmented second-order polynomial analytic calibration functions using four successive data pairs per curve and second-order interference corrections. The BLISS program employs 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 spanning up to 3

orders of magnitude concentration range. The entire calibration data set and analytic curves are stored on disk for immediate application during analysis or for later retrieval and use. The calibration ranges currently employed are shown in Table 1.

Prior to an analytic session, a normalization or standardization procedure is used to update the calibration information for electronic drift or to reinitiate a calibration file created at an earlier time. Because of the incompatibilities of some elements in solution, the normalization is done with groupings of elements in solution. Each group of elements is run in a low concentration and a high concentration solution.

Samples for analysis may be individually introduced manually or automatically introduced through the autosampler. As each sample is run, the analysis program times a preflush interval, reads the integrator offset voltages, and times a series of three signal integrations. The net intensities for the three multiple integrations are averaged, corrected by the normalization factors, and the concentration 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 entire process, including printing and storing of data, is approximately 5 minutes. Approximately 5 ml of solution are consumed.

Data generated by the ICPQ are listed on the DECwriter, permitting immediate and continuous monitoring of the analytic procedure and of

instrument performance by the operator. Print options include channel intensities, in-solution apparent concentrations, corrected concentrations, in-sample concentrations, and relative standard deviations for the three integrations. In-solution corrected concentration and dilution factors are also stored on disk for later retrieval. At ESL, these data may be directly transferred by tape to the DRILL and PLANMAP computer graphics programs for display of drill hole or map data sets respectively (Killpack, 1979; Withrow, 1979). Other reporting format programs, which convert major element concentrations to oxide percentages, delete analytic values below meaningful detection levels, and round off data to a meaningful number of significant figures are similarly available for direct presentation of disk-stored data.

Data Correction

One of the most important factors in the application of any analytic technique is the degree of freedom from interelement interactions or interferences (matrix effects). Interferences by concomitants (constituents in the sample other than the analyte) 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 chemical or physical 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 (Fassel, 1978; Fassel and Kniseley, 1974; Dahlquist and Knoll, 1978; Larson et al., 1975). Because of the high degree of freedom

from interelement effects, it is possible to establish a single set of calibration curves for analysis in a variety of sample matrices.

Spectral interferences are unavoidable in AES, 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 problem for the proper establishment of an adequate correction matrix. Raw intensity data gathered by the ICPQ are reduced by the BASIC software to generate a matrix of second-order correction factors for use by the analysis program. Some adjustment of these values, based upon analysis of standards, has been necessary to make them generally applicable to the variety of materials encountered within geologic samples.

RELIABILITY OF 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 analytic data must consider the entire sample preparation and analytic process.

In order to evaluate the reliability of analytic data generated by the ESL ICPQ, several approaches were employed. These included performing multiple analyses of selected samples over a period of several months, systematically performing duplicate analyses of samples within and between analytic sessions, repeatedly analyzing reference standard materials, and statistically evaluating the performance of each analytic channel. In general, the resulting estimates of analytic 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

As stated earlier, a number of factors influence the accuracy of the analytic procedure. Sample preparation is critical. Inadequate comminution leaves unacceptably large mineral fragments, which 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 ICPQ rock analyses. Occasionally, phases are encountered which are not rendered sufficiently soluble, such as Ti-oxides, zircon, and chromite, or insoluble phases may form and precipitate from solution, such as $KClO_4$ from potassium-rich rock solutions. These effects are evident in the analytic results for the USGS standard rocks (Table 2). It is emphasized that these are uncertainties introduced during sample preparation; they similarly affect other analytic methods and are not unique to the ICPQ. 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 analytic results are critically dependent upon the physical characteristics of the solution. It has been shown by Dahlquist and Knoll (1978), Ward, Sobel and Crawford (1976), and others that the effects of differing acid matrices can be significant. Fortunately, this deficiency may be largely overcome by following the practice of maintaining, as much as possible, constant acid strength for sample and reference solutions.

Detection Limits

Measures of analytic limits vary between analytic techniques and investigators. The term "detection limit" in ICP-AES 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 (Fassel and Kniseley, 1974; Church, 1977a; Ward, 1977a, b; Dahlquist and Knoll, 1978), 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 (Souilliant 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 (Fassel and Kniseley, 1974; Fassel, 1978; Ward 1977a, b; Dahlquist and Knoll, 1978). As established, these are measures of the analytic limits of the instrument under ideal conditions.

Realistically, a measure of technique precision should consider the analytic 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 the ESL ICPQ. 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 analytic 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, 1978) using duplicate analyses of actual samples repeatedly analyzed within and between analytic sessions. Using this suite of information, limits of quantitative determination (LQDs) were established for the ESL instrument

(Table 1). These represent lowest meaningful analytic values for each element, considering uncertainties of the entire analytic 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 analytic 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, 1978), 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

$$p_c = 2s_c/c.$$

TABLE 1
Limits of quantitative determination, calibration
ranges, and precision values for the ESL ICPQ.

ELEMENT	LIMITS OF QUANTITATIVE DETERMINATION		CALIBRATION RANGES		% PRECISION**
	Solutions*	Sample (2%)*	Solutions*	Sample (2%)*	
Na	3	100	3-3000	150-15%	4
K	3	100	2-2000	100-10%	5
Ca	2	100	2.5-2500	125-12.5%	2.5
Mg	2	100	2-2000	100-10%	4.5
Fe (high conc.)	---	100	1-5000	50-25%	2
Fe (low conc.)	.02	---	.02-100	.1-0.5%	***
Al	.5	100	.4-2000	20-10%	3
Si	1	---	.93-468	47-2.3%	***
Ti	.1	5	.1-500	5-2.5%	3
P	.5	25	.5-500	25-2.5%	3
Sr	.02	1	.02-20	1-1000	3
Ba	.5	25	.5-500	25-2.5%	5
V	1	150	1-1000	50-5%	***
Cr	.04	2	.2-200	10-1%	2
Mn	.2	10	2-2000	100-10%	5
Co	.02	1	.1-100	5-.5%	10
Ni	.1	5	.2-200	10-1%	5
Cu	.1	5	.06-300	3-1.5%	10
Mo	1	50	.5-500	25-2.5%	***
Pb	.2	10	.3-300	15-1.5%	5
Zn	.1	5	.04-200	2-1%	10
Cd	.1	5	.02-100	.1-.5%	***
Ag	.04	2	.04-200	2-1%	***
Au	.08	4	.05-50	2.5-2500	***
As	.5	25	.4-400	20-2%	***
Sb	.6	30	.6-600	30-3%	***
Bi	2	100	2-2000	100-10%	***
U	5	2000	1-1000	50-5%	***
Te	1	50	.5-500	25-2.5%	***
Sn	.1	5	.2-200	10-1%	***
W	.2	10	.2-100	10-0.5%	***
Li	.04	2	.04-200	2-1%	5
Be	.004	.5	.004-2	.2-100	10
B	.1	400	.1-100	5-5000	***
Zr	.1	5	.1-100	5-5000	5
La	.1	5	.1-500	5-2.5%	10
Ce	.2	10	.4-400	20-2%	12
Th	3	150	1-1000	50-5%	***

* All values in mg/l unless otherwise noted.

** Relative precision at greater than 10 times LQD.

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

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 1. 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 analytic values has been evaluated through analysis of standard reference materials including 13 USGS rock standards (Flanagan 1976). Results are presented in Table 2 and Figures 2-8. When evaluating these data, the reader is encouraged to consult Flanagan (1976) to learn the extent of

TABLE 2. Experimental determinations of element abundances and recommended values for standard samples

ELEMENT	AGV-1		BHVD-1		G-2		GSP-1		MAG-1		PPC-1		QLO-1	
	Given	ICP	Given	ICP	Given	ICP	Given	ICP	Given	ICP	Given	ICP	Given	ICP
Na%	3.16	3.32	1.63	1.81	3.02	2.99	2.08	2.01	2.89	2.89	<100 ppm	<100 ppm	3.15	3.14
K%	2.40	2.37	.44	.41	3.74	3.48	4.59	4.48	2.99	2.96	<100 ppm	<100 ppm	2.99	2.98
Ca%	3.50	3.46	8.16	8.12	1.39	1.30	1.44	1.37	1.07	.96	.36	.33	2.30	2.23
Mg%	.92	.77	4.43	3.85	.46	.39	.58	.51	1.80	1.77	26.04	25.35	.62	.54
Fe%	4.75	4.16	8.35	7.70	1.88	1.65	3.03	2.71	4.68	4.58	6.07	5.18	3.01	2.74
Al%	9.13	9.03	7.36	7.10	8.16	7.51	8.07	7.43	8.72	8.33	.39	.20	8.65	8.13
Ti	6190	5800	15900	15600	2780	2432	3990	3460	4190	3579	70	28	3570	3373
P	2140	1960	1220	1040	610	510	1220	1150	1390	649	9	<25	1090	1029
Sr	657	649	473	356	479	463	233	219	158	128	<1	<1	340	318
Ba	1210	1080	132	118	1870	1723	1300	1190	493	420	1	37	1401	1260
V	125	<150	296	236	35	<150	53	<150	132	<150	30	<150	61	<150
Cr	12	6	317	241	7	5	13	8	121	87	2730	521	2	<2
Mn	763	712	1250	1170	260	240	331	286	713	715	959	661	643	666
Co	14	12	45	57	6	4	6	6	18	19	112	89	7	6
Ni	19	14	114	99	5	<5	13	9	51	46	2340	2063	2	6
Cu	60	63	133	143	12	10	33	34	49	29	11	10	31	28
Mo	2	<50	<1	<50	<1	<50	<1	<50	3	<50	<1	<50	4	<50
Pb	35	39	6	12	31	35	51	63	20	35	13	13	20	28
Zn	84	79	102	79	85	191	98	93	138	121	36	31	66	62
Cd	<1	<5	---	<5	<1	<5	<1	<5	---	<5	<1	<5	---	<5
Ag	<1	<2	<1	<2	<1	<2	<1	3	<1	<2	<1	<2	<1	<2
Au	<1	<4	2	<4	<1	<4	2	4	<1	<4	2	5	<1	<4
As	<1	<25	<5	<25	<1	<25	<1	<25	<5	27	<1	<25	<5	<25
Sb	5	31	<1	<30	<1	<30	3	32	1	<30	1	<30	3	<30
Bi	<1	<100	<1	<100	<1	<100	<1	<100	<1	<100	<1	<100	<1	<100
U	2	<2000	<1	<2000	2	<2000	2	<2000	3	<2000	<1	<2000	2	<2000
Te	<1	<50	---	<50	<1	<50	<1	<50	---	<50	<1	<50	---	<50
Sn	4	6	<3	<5	2	<5	6	9	6	<5	1	54	4	6
W	1	<10	---	<10	<1	<10	<1	<10	---	<10	<1	<10	---	<10
Li	12	11	4	3	35	34	32	30	72	86	2	<2	23	26
Be	3	2.6	1	1.7	2.6	2.6	1.5	1.6	2.7	3.6	---	.7	2	2.1
B	5	<400	<10	<400	2	<400	<3	<400	130	<400	6	<400	38	<400
Zr	225	208	145	153	300	51	500	30	128	89	7	<5	162	28
La	35	45	18	16	96	89	191	131	50	36	<1	<5	36	45
Ce	63	67	33	37	150	138	394	283	104	72	<1	<10	76	17
Th	6	<150	<1	<150	24	<150	104	<150	12	<150	<1	<150	3	<150

TABLE 2 (continued)

ELEMENT	RGM-1		SCo-1		SDC-1		SGR-1		STM-1		GRLD-102		GRLD-105		BSWJ-26	
	Given	ICP	Given	ICP	Given	ICP	Given	ICP	Given	ICP	Given	ICP	Given	ICP	Given	ICP
Na%	3.10	3.15	.72	.68	1.56	1.49	1.97	2.28	6.66	6.56	1.16	1.07	.64	.67	---	---
K%	3.60	3.55	2.32	2.31	2.66	2.65	1.42	1.30	3.53	3.41	7.20	4.37	4.72	4.08	---	---
Ca%	.84	.81	1.92	1.82	.93	.96	6.34	6.15	.82	.76	.36	.31	.92	.85	---	---
Mg%	.18	.14	1.62	1.53	.96	.92	2.71	2.58	.06	.05	1.16	1.08	1.67	1.57	---	---
Fe%	1.31	1.15	3.57	3.39	4.91	4.44	2.24	1.83	3.61	3.32	.92	.70	2.90	2.57	42.2	42.9
Al%	7.27	6.81	7.10	7.11	8.63	7.86	3.84	3.27	9.85	9.05	7.94	7.05	6.19	5.56	---	---
Ti	1630	1460	4970	3090	5870	5390	1740	1250	948	729	4100	1390	3900	1770	---	---
P	220	186	1920	827	785	547	1300	1080	700	606	600	870	750	1220	--	---
Sr	104	101	200	162	176	172	425	369	695	691	---	---	267	245	---	---
Ba	822	785	570	538	641	580	328	251	584	526	---	---	1560	1030	---	---
V	13	<150	100	<150	62	<150	134	<150	<10	<150	---	---	---	---	---	---
Cr	3	3	70	59	70	53	33	29	2	<2	65	41	137	56	---	---
Mn	287	268	411	377	928	831	297	222	1600	1611	36	40	106	102	500	468
Co	2	3	10	10	20	14	10	10	<1	<1	10	2	24	12	20	9
Ni	6	5	30	24	50	28	39	26	2	<5	30	25	44	34	60	30
Cu	10	13	30	29	30	30	62	62	3	8	9320	9010	7260	7080	420	438
Mo	3	<50	3	<50	2	<50	---	<50	6	<50	301	305	344	316	10	<50
Pb	21	37	15	38	25	28	41	36	16	28	32	39	37	37	6000	4660
Zn	39	28	115	89	106	85	83	59	243	207	18	31	48	65	2800	2570
Cd	---	<5	---	<5	---	<5	---	<5	---	<5	<1	<5	1	<5	---	---
Ag	<1	3	<1	<2	<1	<2	<1	<2	<1	<2	7	6	3	3	15	12
Au	<1	5	<1	<4	2	<4	<1	<4	<1	<4	1	<4	<1	<4	<2	<4
As	<5	27	11	<25	<5	<25	75	48	<5	<25	47	60	26	34	250	304
Sb	2	<30	3	<30	<1	<30	3	<30	2	<30	<1	<30	---	---	---	---
Rt	<1	<100	<1	<100	<1	<100	<1	<100	<1	<100	18	<100	8	<100	28	<100
U	6	<2000	3	<2000	3	<2000	6	<2000	9	<2000	---	---	---	---	---	---
Te	---	<50	---	<50	---	<50	---	<50	---	<50	<1	<50	<1	<50	20	<50
Sn	4	5	5	<5	3	<5	<3	5	12	5	---	---	---	---	7	5
W	---	<10	---	<10	---	<10	---	<10	---	<10	15	<10	45	<10	15	15
Li	56	64	42	50	32	38	123	141	32	38	---	---	---	---	---	---
Be	2.8	2.6	1.6	2.2	3	3.3	.9	1.3	9	9.4	---	---	---	---	---	---
B	33	<400	70	<400	30	<400	30	<400	---	---	---	---	---	---	---	---
Zr	205	222	150	94	219	37	59	30	1230	1401	---	---	213	26	---	---
La	27	29	50	30	150	38	32	18	188	148	---	---	62	43	---	---
Ce	60	60	100	50	76	66	59	20	530	248	---	---	---	---	---	---
Th	13	<150	10	<150	11	<150	8	<150	27	<150	---	---	---	---	---	---

variation found by other analysts. The determined concentrations of some elements vary greatly depending upon the analytic 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 are thus best estimates, or averages, and not necessarily representative of the true composition of the sample analyzed at ESL. Several elements are not present in the standard rocks in concentrations within the analytic range of the ICPQ, and their accuracy has not been determined here.

The accuracy of Na, K, Ca, and Mg are acceptable, although Mg seems to have a slightly low bias over its lower and middle concentration ranges (Fig. 2). The unusually low ICP-AES values observed at high K concentrations may be a result of precipitation of $KClO_4$ during digestion with $HClO_4$. Greater dilution of potassium-rich samples can alleviate the problem.

Fe, Al, and Ti all are systematically low whereas data for P are characterized by a large variance (Fig. 3). For Ti, and perhaps for P and Al as well, the low bias is undoubtedly due in part to solution problems: Ti-oxides are especially difficult to take into solution, particularly if not finely pulverized. It should be noted that all of the P values are less than two orders of magnitude greater than the LQD (25 ppm), hence some greater variance is expected.

Li, Be, Sr, and Ba all can be determined with acceptable accuracy, despite apparent minor high and low biases (Fig. 4).

Figure 2. Comparison of experimentally determined Na, K, Ca, and Mg concentrations with recommended values for standard samples. Complete analyses are tabulated in Table 2. All values are percentages.

Figure 3. Comparison of experimentally determined Fe, Al, Ti, and P concentrations with recommended values for standard samples. Complete analyses are tabulated in Table 2. Fe and Al values are percentages, Ti and P values are in mg/kg.

Figure 4. Comparison of experimentally determined Li, Be, Sr, and Ba concentrations with recommended values for standard samples. Complete analyses are tabulated in Table 2. All values are in mg/kg.

Figure 5. Comparison of experimentally determined Cr, Mn, Co, and Ni concentrations with recommended values for standard samples. Complete analyses are tabulated in Table 2. All values are in mg/kg.

Figure 6. Comparison of experimentally determined Cu, Zn, and Pb concentrations with recommended values for standard samples. Complete analyses are tabulated in Table 2. All values are in mg/kg.

Figure 7. Comparison of experimentally determined Ag, As, and Sn concentrations with recommended values for standard samples. Complete analyses are tabulated in Table 2. All values are in mg/kg.

Figure 8. Comparison of experimentally determined Zr, La, and Ce concentrations with recommended values for standard samples. Complete analyses are tabulated in Table 2. All values are in mg/kg.

The analytic results for Mn are acceptable. Cr, Co, and Ni all display low biases and low precision (Fig. 5). For Cr, and perhaps as well for Co and Ni, dissolution problems may again contribute to the inaccuracy. Chromite especially is difficult to bring into solution by the routine digestion procedure. Again, the reader is encouraged to consult Flanagan (1976). The variation reported by other analysts for these elements is as great as that found here; the values reported are "averages" of the various laboratories.

Cu, Zn, and Pb are also acceptably accurate, considering again the magnitude of results relative to LOD values, and the variation in the values reported by Flanagan (1976), (Fig. 6).

The few determinations made of Ag, As, and Sn appear to be of acceptable accuracy (Fig. 7).

A low bias and high variance characterize Zr, La, and Ce determinations (Fig. 8). Again, solution problems (especially of zircon), low concentration levels relative to the LOD concentrations, and sample inhomogeneity may explain the poor accuracy.

DISCUSSION

One of the dangers inherent in the utilization of highly-automated, technologically-sophisticated instrumentation such as an ICPQ is the temptation to accept the multidigit results uncritically. The values for LODs, precision, and accuracy presented here represent best estimates of the quality of chemical data currently being collected at ESL. 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 analytic procedure. Values for LQDs, although significantly greater than "detection limits" frequently presented by other analysts, are more realistic estimates of actual analytic capabilities.

Because the sample preparation for ICPQ 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 if desired.

For the analysis of natural solutions, sample preparation is minimal. Solutions are acidified to approximately the acid strength of the analytic 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 which characterized the quality of ICPQ-generated analytical data. Limits of quantitative determination (LQDs) represent lowest meaningful analytic values considering the variance present in the entire analytic system, or, more specifically, are those analytic 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 ICPQ 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-AES technique to geochemical applications. As an instrument that can make simultaneous multielement determinations for a wide variety of material types in a very short time, the ICPQ has unparalleled potential. In general, the quality of the analytic 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 ICPQ instrumentation is improved and as procedures for sample and standard preparation are refined, the quality of ICP-AES data will likely improve as well.

ACKNOWLEDGEMENTS

The development of geochemical laboratory facilities and procedures at the Earth Science Laboratory has been managed by Robert Bamford and Joe Moore. Their contributions to the present operating system are gratefully acknowledged. We wish to extend our thanks to Tina Cerling who assisted with data compilation. Critical reviews of the manuscript by Duncan Foley, Joe Moore, and Jim Stringfellow are appreciated.

Funding was provided by the United States Department of Energy, Division of Geothermal Energy to the Earth Science Laboratory under contract no. DE-AC07-80ID12079.

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APPENDIX

Four Acid Sample Digestion Procedure

Whole Rock (2% w/v) solutions

1. Weigh $1.000 \pm .001$ grams of sample, dried for at least 2 hours at $105^{\circ}\text{--}110^{\circ}\text{C}$ into a teflon (TFE) beaker.
2. Add 12-15 ml HF and heat to dryness in hood.
3. Add 5 ml HClO_4 , 10 ml HCl , 10 ml HNO_3 ; cover and heat 2-3 hours; remove cover, raise temperature, and heat to perchloric fumes.
4. Add a few drops of HF and heat to dense perchloric fumes (volume approximately 2.5 ml).
5. Add 20-30 ml demineralized water, cover, bring to a boil.
6. Cool; add 5 ml HNO_3 ; dilute to 50 ml.

Final acid concentration: 5% HClO_4 , 10% HNO_3

Final concentration is approximately 1% total dissolved solids due to Si loss during digestion.

Heavy mineral concentrate (1% w/v) solutions

1. Proceed as above using

0.100 g sample (step 1)

5 ml HF (step 2)

1 ml HClO_4
6 ml HCl (step 3)
10 ml HNO_3

1 ml HNO_3 (step 6)
.5 ml HClO_4