

Multi-Element Analysis of Fifty-Four Geochemical Reference Samples Using Inductively Coupled Plasma-Atomic Emission Spectrometry

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Inductively Coupled Plasma-Atomic Emission Spectrometry (ICP-AES) has been applied for simultaneous, multielement analysis of a diverse suite of igneous rocks and minerals, metamorphic and sedimentary rocks, coals and soils using a single matrix calibration procedure and a single sample preparation. Analytical results determined on 40 elements in 54 geochemical reference samples are presented. A sample analysis time of about three minutes allows the analyst to run several hundred samples per day, but does not include sample dissolution. The instrumental method described here provides the capability for rapid, simultaneous, multielement determination of the major (except silica), minor, and trace elements in rocks using a single sample preparation technique. Analytical data collected on the Geochemical Reference Samples (GRS) demonstrate the general utility of the method. Analytical results show an excellent agreement with previously published results for the major and minor elements. Of the 28 trace elements studied, 17 can be routinely determined in crustal rocks, but the concentration of several of the others can be determined only if present at concentrations several times above their crustal-abundance level.

Recent developments in the field of analytical chemistry have rendered possible new analytical instrumentation that can be used for rapid determination of major, minor, and many

trace elements in geological samples. This new instrumental method is called the Inductively Coupled Plasma-Atomic Emission Spectroscopy or ICP-AES method (1). ICP instrumentation consists basically of three components:

1. the ICP source or excitation unit,
2. the monochromator or polychromator, and
3. the electronic readout and data reduction system.

At the heart of the ICP-AES analytical method is the excitation source. The ICP is an inductively coupled argon plasma that is sustained by radio frequency (RF) energy induced by a RF generator. Analyte atoms, which are injected into the central, axial region of the plasma as an aerosol, experience high temperatures (>6000K, 2) and a long residence time (1) as they pass through the plasma, resulting in a high degree of disassociation and emission of light quanta. The geometry of the source and the containment of the analyte within the axial region of the plasma result in an optically thin source, largely free from range-limiting self-absorption associated with flames and ionization interference associated with microwave and D.C. plasma excitation methods (e.g., 3-16). Finally, the low background emission, the absence of self-absorption, and the high excitation efficiency of the ICP produce analytical response functions that are essentially linear over four orders of magnitude in concentration above the limit of detection. If adequate curve-fit methods are used (17), the working range of four orders of magnitude can be extended to five or more orders of magnitude above the limit of detection. In terms of the analytical utility of the ICP-AES method for routine analysis of geological samples, the low level of sample matrix effects, the

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wide dynamic range, the high sensitivity, and the specificity of analytical lines make practical the simultaneous multielement determination of major and minor elements and of many trace elements from a single sample preparation. Utilization of a computer-controlled data-collection and sample analysis routine, when used either with a polychromator or a computer-controlled scanning monochromator (18), allows the complete analysis of a single sample in a matter of minutes. Sample analysis time, which includes the data reduction and printout during the analysis cycle, but not the time needed to dissolve the sample, is about three minutes for fixed-array instrumentation. The time required for a scanning instrument is dependent on both the number of elements analyzed as well as the concentration of those elements in solution. Analysis of a hundred samples or more per day for 30-40 elements or more is possible. In order to evaluate the analytical potential and capability of this new method, the author undertook a series of studies using the ICP instrumentation commercially available from Applied Research Laboratories*. The initial report dealt primarily with instrumental features: the choice of analytical lines for the geological matrix, the evaluation of spectral interferences and their use, and sample dissolution and introduction into the ICP (19). Several different polychromator instruments, each having a different secondary array, were used to evaluate the general applicability of the ICP-AES instrumentation to rock analysis. The most revealing feature of the study of the line-selection problem was that the interferences on analytical lines for the geochemical matrix were remarkably constant for a given wavelength regardless of the other lines present in the secondary array or of its spectral order. This generalization means that the primary source of analytical error in the ICP method is the contribution from direct spectral interferences rather than secondary scattering from the grating or other optical surfaces in the secondary array (19). Therefore, good analytical results on geochemical samples are obtainable if the contribution from spectral interferences from all elements are accounted for in the data acquisition process. The test of this thesis is the subject of this paper. A large suite of Geochemical Reference Samples (GRS) were obtained and analyzed on several ICP instruments. The dissolution procedures, spectral interferences used and analytical results obtained are given below. Comparison of these data with the published recommended or preferred values for these reference materials allows the evaluation of the accuracy and precision of the ICP-AES method for geochemical applications, including an evaluation of a matrix calibration scheme for a widely diverse sample suite of igneous rocks and

minerals, glasses and slags, sedimentary rocks of both chemical and detrital origin, coals, and soils.

EXPERIMENTAL

The instrumentation used in this study consisted of the ICPQ model QA 137000 and the more recently developed 34000 ICP manufactured by Applied Research Laboratories. The instrumental parameters of both models are described in Table 1. The secondary arrays of the four instruments used are given in Table 2. The spectral bandpass can be calculated from the reciprocal linear dispersion values given for each spectral order for a given grating and exit slit used in the secondary optics. The instrument is controlled by, and all data reduction is done with, a dedicated PDP-11 minicomputer; results are printed out during the analysis cycle.

In terms of a summary statement of the analytical capability of the ICP-AES method, the data presented in Figure 1 demonstrate the high level of precision and the large dynamic working range that can be routinely achieved. *Limits of detection on single element solutions cannot, however, be translated directly into analytical capability in a geologic matrix.* The analytical limitations caused by the presence of other elements in the solution being analyzed will be discussed later.

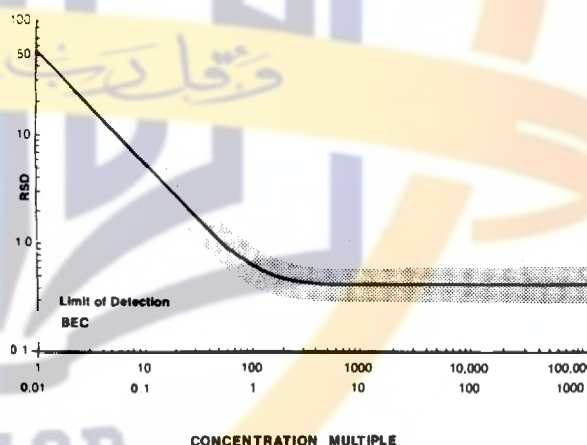


Figure 1. Diagram showing the theoretical analytical precision of the ICP as a function of analyte concentration expressed as multiples of the limit of detection or background equivalent concentration (BEC). Note that five orders of magnitude in concentration can be used and that the relative standard deviation (RSD) above 100 times the limit of detection is less than 1%. The curve shown is the RSD calculated using a ± 1 sigma limit. Ajhar et al. (22) stated that when 80 empirical data points from 25 different elements whose range of concentration uniformly covered the range of concentration given on the X-axis were plotted in this diagram, 67% fell within the ± 1 sigma limit exactly as predicted by elementary measurement statistics. (Reproduced with permission).

* Any trade names used in this paper are for descriptive purposes only and do not constitute an endorsement by the U.S. Geological Survey.

Table 1. ICP source conditions and operating parameters

| ICPQ | | 34000 ICP |
|------------------------|--|--|
| RF Generator: | Air-cooled, 3-KW continuous-rating generator operated at 27.12 MHz, crystal-controlled. | Air-cooled, 2.5-KW continuous-rating generator operated at 27.12 MHz, crystal-controlled. |
| Forward Power: | 1600 \pm 50 watts. Regulated to <1% using a π -impedance matching network. | SAME |
| Induction Coil: | Two-turn, 4.7-mm-O.D., silver-plated copper tube coiled on a 28.7-mm-diameter form, water-cooled. | Two-turn, 4.7-mm-O.D., gold-over-silver-plated copper tube coiled on a 28.7-mm-diameter form, water-cooled. ¹ |
| Plasma Torch: | Integrated, three-concentric-tube configuration, (18-mm-O.D.) utilizing 2.0-mm capillary injector tube. | SAME |
| Nebulizer: | Permanently aligned glass, co-axial pneumatic nebulizer. All nebulizers used in this study had an uptake rate of 1.8-2.4 mL/minute. Water-saturated argon was used as the carrier gas, and the system utilized a tip washer, under computer control, to insure that there was no salt build-up on the nebulizer. | SAME |
| Spray Chamber: | "Scott" co-axial spray used in early studies on instrument #1. Conical spray chamber with impact ball used thereafter. | Conical spray chamber with impact ball. |
| Gas: | Welding-grade Argon | SAME. |
| | Coolant: 10.5 L/min. Plasma: 1.5 L/min. Carrier: 1.0 L/min. | SAME |
| Gas-Flow Regulation: | Three stages: two gas-flow regulators in series followed by capillary restrictors which control the ratio of the gas flow of the coolant:plasma gases. | Three stages: gas-flow regulators in series, followed by restrictors; flow rates of the coolant gas and plasma gas can be independently varied. |
| Primary Optics: | A 4-mm vertical segment of the axial channel of the plasma is focused on the primary slit (12 μ m) with 0.7 demagnification. The primary lens is fused quartz with a focal length of 15 cm (#587 nm). | A 4-mm vertical segment of the axial channel of the plasma is focused on the primary slit (20 μ m) with 1.8 magnification. The primary lens is fused quartz with a focal length of 15 cm (#587 nm). An Argon flush path (1 L/min) is used on vacuum systems to provide a transmitting light path for the vacuum UV radiation. |
| Height of Observation: | 17-mm above the RF coil. Observation zone is 15-19 mm. | SAME |
| Spectrometer: | 1.0-m Paschen-Runge mount, f/30; air path only. | 1.0-m Paschen-Runge mount, f/30. A 1/4" steel-plate weldment provides vacuum-path capability. Spectrometer temperature maintained at 38° \pm 0.2°C in a thermally controlled cabinet. |
| Gratings: | 1920 g/mm: interferometrically-ruled quartz-blank replica blazed at 270 nm; reciprocal linear dispersion: 0.48-0.52 nm/mm, first order; spectral range 180-460 nm. 1080 g/mm: See description under 34000 ICP. | 1080 g/mm: interferometrically-ruled quartz-blank replica blazed at 600 nm; reciprocal linear dispersion: 0.926 nm/mm, first order; 0.463 nm/mm, second order; 0.309 nm/mm, third order; spectral range: 175-820 nm. |
| Secondary Optics: | 50- μ m exit slits, concave secondary mirrors collect and refocus light on PMT's. 40-nm-bandpass filters (Acton Research) used on all lines below 230 nm. | 35- and 50- μ m exit slits, concave secondary mirrors installed at 45° refocus light on the PMT's which are located above (and below) the optical plane. 40-nm-bandpass filters (Acton Research) and color filters (Corning) used for order sorting. |

¹ Instrument #4 (see Table 2) had a three-turn experimental coil.

Dissolution of silicate materials for analysis in the plasma can be achieved either by fusion methods or by digestion with HF. Because of the large dilutions required to dissolve the fused sample, dissolution of silicates with HF was judged to provide the best method of sample dissolution for trace element analysis of geological samples using the ICP-AES analytical technique. Several techniques of sample dissolution were used depending on the mineralogy of the sample. These methods and their limitations will be discussed. All samples were processed in a clean laboratory environment in a class-100 laminar-flow hood. Acid blanks were routinely run with the samples. Reagent-grade acids were found to be adequate for the analytical task and were used throughout the study. The water used for sample dilution was purified by passing it through two anion-cation mixed bed resin columns followed by an organic stripper column.

Most samples studied are silicate materials and were dissolved in the following manner: approximately 1 g of powdered sample (0.8-1.2 g)

was weighed into a 50 mL FEP Teflon beaker. One to two mL of concentrated HNO₃ acid was carefully added to the beaker and the sample was swirled until completely wetted. The beaker was placed in a steam bath and the sample covered with a Teflon beaker cover and allowed to react for 20-30 minutes. Care was taken to be sure that the reaction was totally contained within the beaker and that the sample was still covered with acid after the reaction subsided. Following the nitric acid pretreatment, a mixture of 10 mL HF, 3 mL HClO₄, and 2 mL HNO₃/g of sample was added and allowed to react overnight. The following morning, the Teflon beaker covers were removed and the HF driven off by heating for 4-6 hours. The sample residue was transferred to a 200 mL, tall-form quartz beaker and gently taken to dryness to drive off the HClO₄. About 5 mL of concentrated HCl was added to the sample residue and the sample was again taken to dryness. Forty mL of 6.2 M HCl was added to the sample and gently heated until a clear solution was obtained. The sample was removed from the hot plate and the solution allowed to cool in the quartz

Table 2. Secondary arrays, detection limits and spectral-interference corrections for the instruments used in this study

| Element | Wavelength (nm) | Spectral Order | Measured D.L. (ppm) | Expected ¹ D.L. (ppm) | Instrument | Interferences (ppm interference/ppm concomitant) | | | | | |
|---------|--------------------|-------------------|---------------------------|--|------------|--|---------|---------|----------|---------|--|
| | | | | | | Mg | Ca | Fe | Al | Ti | Other concomitants |
| Na | 588.99 | 1 | 0.026 | (0.02) | 3 | | | | | | |
| | 589.59 | 1 | 0.04 | (0.02) | 2, 4 | | | | | | |
| K | 766.49 | 1 | 0.15 | (0.10) | 2, 3, 4 | | | | | | |
| Mg | 279.08 | 1 | 0.024 | 0.030 | 1 | | | | | | |
| | 279.08 | 2 | 0.026 | | 2, 3, 4 | | | | | | |
| Ca | 422.67 | 1 | 0.016 | 0.010 | 1 | | | | | | |
| | 317.93 | 2 | 0.004 | 0.010 | 2, 3, 4 | | | | | | |
| Fe | 259.94 | 1 | 0.003 | 0.0062 | 1 | | | | | | |
| | 259.94 | 3 | 0.002 | | 2, 3 | | | | | | |
| | 263.11 | 3 | 0.020 | 0.015 | 4 | | | | | | |
| Al | 309.27 | 1 | 0.040 | 0.023 | 1 | 0.00604 | | | | | V-0.087, Be-0.0165 |
| | 309.27 | 2 | 0.026 | | 2 | | | | | | V-0.083 |
| | 308.22 | 2 | | 0.045 | 3 | | | | | | V-0.0215 |
| | 237.31 | 3 | 0.062 | 0.030 | 4 | 0.0023 | 0.0004 | 0.0027 | | | Mn-0.0049 |
| Ti | 334.94 | 1 | 0.001 | 0.0038 | 1 | | | | | | Cu-0.000016 |
| | 334.94 | 2 | 0.003 | | 2 | | | | | | |
| | 368.52 | 2 | 0.005 | 0.0011 | 3 | | | | | | Mn-0.0008 |
| | 368.52 | 1 | 0.008 | | 4 | | | | | | |
| P | 213.62 | 1 | 0.095 | 0.076 | 1 | | | | | | Cu-0.310, Zn-0.103, V-0.00022 |
| | 213.62 | 3 | 0.083 | (0.10) ² | 2 | | | | | | Cu-0.108 |
| | 178.292 | 3 | 0.050, 0.035 | | 3, 4 | | | | | | |
| Li | 670.78 | 1 | 0.005 | (0.003) | 3 | | | | | | |
| Be | 313.04 | 1 | 0.00008 | 0.00027 | 1 | | | | | | |
| Sr | 407.77 | 1 | 0.00005 | 0.00041 | 1 | | | | | | |
| Ba | 455.40 | 1 | 0.00002 | 0.0013 | 1 | | | | | | |
| | 493.41 | 1 | 0.001 | 0.0023 | 4 | | | | | | |
| La | 398.85 | 1 | 0.005 | 0.011 | 1 | | | | | | |
| | 379.48 | 1 | 0.011 | 0.010 | 4 | | | | | | |
| Ce | 394.28 | 1 | 0.050 | 0.068 | 1 | | | | | | |
| | 413.77 | 1 | 0.066 | 0.048 | 4 | 0.00036 | 0.00029 | 0.00008 | | | V-0.0033, Ba-0.0007, Mn-0.0006 |
| | | | | | | | 0.00015 | 0.00025 | 0.000025 | | V-0.0025, Eu-0.12, Sm-0.028, Gd-0.01, Nd-0.028, Mn-0.005 |
| | | | | | | | 0.011 | 0.00022 | 0.00011 | 0.00025 | V-0.0017, Cu-0.0004, Cr-0.0005, Ba-0.0005, Mn-0.0008 |
| Nd | 417.73 | 1 | 0.060 | 0.136 | 1 | | | | | | Ce-0.00005, Eu-0.026, Y-0.90 ³ |
| Sm | 443.43 | 1 | 0.020 | 0.083 | 1 | | | | | | |
| Eu | 381.97 | 1 | 0.002 | 0.0027 | 1 | | | | | | V-0.001, Ce-0.013, Nd-0.018 |
| Gd | 376.84 | 1 | 0.007 | 0.025 | 1 | | | | | | |
| Yb | 369.42 | 1 | 0.0006 | 0.0030 | 1 | | | | | | |
| Zr | 343.82 | 1 | 0.003-0.006 | 0.0071 | 1, 3, 4 | | | | | | |
| U | 409.01 | 1 | 0.40 | 0.337 | 2 | | | | | | |
| | 385.96 | 2 | 0.065 | 0.250 | 4 | 0.0002 | 0.0012 | 0.003 | 0.0003 | 0.0024 | Mn-0.003 |
| Th | 353.96 | 2 | 0.110 | 0.100 | 4 | 0.0004 | 0.0003 | 0.0002 | | | Mn-0.004, V-0.004, Zr-0.001, Ce-0.094. |

| Element | Wavelength (nm) | Spectral Order | Measured D.L. (ppm) | Expected ¹ D.L. (ppm) | Instrument | Interferences (ppm interference/ppm concomitant) | | | | | | Other concomitants |
|---------|---------------------|-------------------|---------------------------|--|------------|--|----------|----------|----------|---------|--|--------------------|
| | | | | | | Mg | Ca | Fe | Al | Ti | | |
| V | 311.07 | 1 | 0.003 | 0.010 | 1 | | | | | 0.012 | Mn-0.0003, Cr-0.0001, Zr-0.004 | |
| | 268.80 | 3 | 0.004 | 0.010 | 3 | | | | | | Cr-0.0021 | |
| | 292.40 | 2 | 0.003 | 0.0075 | 4 | | | 0.00008 | | 0.0012 | Mn-0.0003, La-0.0013 | |
| Cr | 283.56 | 1 | 0.007 | 0.0071 | 1 | 0.00007 | | 0.00125 | | 0.0001 | V-0.00011 | |
| | 267.72 | 2 | 0.004 | 0.0071 | 2 | | | | | | Mn-0.0002, Mo-0.0001, U-0.002 | |
| | 205.55 | 2 | 0.010 | 0.0061 | 4 | | | | 0.0003 | | Mn-0.0006 | |
| | 257.61 | 1 | 0.0007 | 0.0014 | 1 | | | | | | W-0.0004 | |
| Mn | 257.61 | 2 | 0.0009 | | 2, 3, 4 | | | | | | | |
| | 238.89 | 1 | 0.007 | 0.006 | 1 | | | 0.0026 | | 0.00002 | V-0.00012 | |
| | 228.62 | 2 | 0.006 | 0.007 | 2 | | | | | 0.0018 | W-0.0003, W-0.001 | |
| Co | 228.62 | 3 | 0.002 | | 4 | | | 0.00008 | | 0.0016 | V-0.0003 | |
| | 231.61 | 1 | 0.015 | 0.015 | 1 | | | | | | | |
| | 231.61 | 2 | 0.013, 0.010 | | 2, 4 | | | | | | | |
| Cu | 324.75 | 1 | 0.003 | 0.0054 | 1 | | | 0.00012 | | 0.00012 | Be-0.0013 | |
| | 324.75 | 2 | 0.005 | | 2 | | | 0.00012 | | | | |
| | 224.75 | 2 | 0.020 | 0.0077 | 4 | | | 0.0017 | | | Pb-0.0027 | |
| Zn | 202.55 | 1 | 0.002 | 0.004 | 1 | 0.00014 | | | 0.00011 | | Cu-0.006 | |
| | 202.55 | 2 | 0.003 | | 2 | 0.00012 | | | | | Cu-0.005, W-0.0001 | |
| | 202.55 | 3 | 0.003 | | 3 | 0.00007 | | | | | | |
| | 213.86 | 2' | 0.005 | 0.0018 | 4 | 0.00002 | | 0.00002 | 0.000085 | | | |
| | | | | | | | | | | | | |
| Mo | 313.62 | 2 | 0.050 | (0.02) | 2 | | | 0.0008 | | | Cr-0.0045, W-0.002, Zr-0.002 | |
| | 202.03 | 3 | 0.014 | 0.0079 | 4 | | 0.000012 | 0.000068 | 0.00022 | | As-0.0001 | |
| | | | | | | | | 0.00069 | 0.000024 | | | |
| W | 239.70 | 3 | 0.030 | 0.055 | 2 | | | | | | | |
| | | | | | | | | | | | | |
| Ag | 328.07 | 1 | 0.003 | 0.007 | 1 | | 0.000016 | 0.000014 | 0.000017 | 0.0002 | Zr-0.01 | |
| | 328.07 | 2 | 0.007 | | 2 | 0.000022 | | 0.000011 | 0.000007 | 0.0002 | Zr-0.004 | |
| Au | 242.80 | 1 | 0.007 | 0.017 | 1 | | | 0.00038 | | | Mn-0.011, V-0.0001, Sr-0.00055 | |
| | 242.80 | 3 | 0.014 | | 2 | | | 0.00016 | | | Mn-0.011 | |
| Cd | 226.50 | 1 | 0.002 | 0.0034 | 1 | | | 0.00011 | | 0.00004 | Ni-0.0003 | |
| | 226.50 | 2 | 0.002 | | 2 | | | 0.00008 | | | | |
| | 226.50 | 3 | 0.003 | | 4 | | | 0.00007 | 0.000003 | 0.00014 | | |
| Sn | 189.99 ² | 3 | 0.027, 0.008 | 0.025 | 2, 4 | 0.0005 | 0.000063 | | 0.00026 | | V-0.0001, Zr-0.0008, As-0.0035 | |
| | | | | | | | | | | | | |
| Pb | 220.35 | 1 | 0.048 | 0.042 | 1 | | | 0.0003 | 0.0014 | | | |
| | 220.35 | 3 | 0.027, 0.034 | | 2, 4 | 0.000053 | | 0.00017 | 0.0013 | 0.0004 | V-0.0006, As-0.0001, La-0.0005, Zn-0.002 | |
| Bi | 223.06 | 2 | 0.260, 0.105 | 0.034 | 2, 4 | 0.0001 | 0.0002 | 0.00039 | 0.0003 | 0.0049 | V-0.0014, Cr-0.0014, La-0.0013, Ni-0.002 | |
| | | | | | | | | | | | | |
| As | 193.76 | 1 | 0.130 | 0.053 | 1 | 0.00026 | | 0.00027 | 0.0085 | | V-0.010, Cr-0.0007, Zr-0.0005 | |
| | 193.76 | 3 | 0.047 | | 2 | | | | 0.005 | | V-0.014, Cr-0.0015 | |
| | 189.04 ² | 3 | 0.023 | (0.136) ² | 4 | 0.0001 | 0.00006 | 0.00009 | 0.0006 | 0.0003 | V-0.0005, Cr-0.0027, La-0.043 | |
| | | | | | | | | | | | | |
| Sb | 206.84 | 2 | 0.120 | 0.032 | 2 | | | 0.00012 | 0.0024 | 0.0014 | Cr-0.007, Zn-0.001 | |
| | 206.84 | 3 | 0.045 | | 4 | 0.00005 | 0.0004 | 0.00013 | 0.0016 | 0.0012 | V-0.0022, Cr-0.022 | |
| | | | | | | | | | | | | |
| Se | 196.09 | 1 | 0.095 | 0.075 | 1 | | | 0.00035 | 0.0019 | | Mn-0.002, V-0.0011 | |
| | | | | | | | | | | | | |

1 Data used from Vinje et al. (20). Data in parenthesis from Applied Research Laboratories.

2 Vacuum path recommended or required.

3 No Y line was present in the instrument. Therefore, a correction was made on the basis of the measured abundance of Yb and using a Y/Yb ratio of 10 (21).

PUACP

beaker. The volume of the sample solution was measured and enough 6.2 M HCl added to bring the solution back to a volume of 40 mL. This step is essential in that the response function of the ICP for a given element is dependent on the acid content (5,19). Control of the final acidity of the solution can only be achieved if one works at the azeotrope of the acid-water binary system being used for sample dissolution and if the volume of constant boiling acid is carefully monitored following dissolution. The sample was then transferred to 100 mL (class B) volumetric flasks and diluted to a volume of about 90 mL with deionized water. Five mL of HClO_4 was added to the sample; the solutions were mixed and then diluted to final volume (100 mL). The sample solutions were transferred to pre-cleaned, 125 mL polypropylene bottles for storage until the samples could be analyzed. The final acid solution achieved using this sample preparation procedure is 20% HCl - 5% HClO_4 (V-V).

A number of rock-forming minerals will not be completely attacked by this dissolution procedure: the mineral zircon and some members of the spinel series, namely chromite (FeCr_2O_4) and spinel (MgAl_2O_4), will not be completely dissolved. Other minerals such as cassiterite, some garnets, alumina (corundum), kyanite, and several other minerals found in metamorphic terrains will not be dissolved. Some secondary minerals, particularly barite, will not be dissolved as well. Some of these minerals (zircon, beryl, garnet, spinel) can be completely dissolved by decomposition in an acid digestion bomb, but the advantages were not judged to be worth the additional effort and expense involved for the purposes of this study.

In the final part of this study, a special digestion procedure was used for the dissolution of chromite residues found in the ultramafic samples. Following the silicate dissolution procedure described above, the residual chromite was attacked in a quartz beaker using 2 mL of H_3PO_4 . The chromites were completely dissolved and these samples were analyzed for trace elements in a final solution of 2% H_3PO_4 -20% HCl (V/V). The low recoveries for chrome reported by Floyd et al. (18) are probably the result of incomplete digestion rather than poor analytical capability.

Sedimentary samples which had a high carbonate or phosphate content were decomposed by a different approach. The sample was placed in a 200 mL, tall-form quartz beaker and the sample covered with about 10 mL of deionized water. Dilute HCl was slowly added to the sample in order to contain the reaction in the beaker. Following complete dissolution of either the carbonate or phosphate minerals present, the residue was transferred to a teflon beaker and the silicates decomposed by the HF dissolution procedure described above. About 5 mL of the HF/ HClO_4 / HNO_3 acid mixture was used in these cases.

The sediment sample SGR-1 was not analyzed because the author understood its intent was to

serve as an organic standard rather than an elemental standard. In hind sight, this decision appears to have been unfortunate because several workers have reported elemental contents in this GRS.

Dissolution of the NBS Coal (SRM-1632) residue (following ashing) and NBS flyash sample (SRM-1633) was done using the HF/ HClO_4 / HNO_3 method. The samples were prepared by Mr. D. Heinrich of Radian Corp., Austin, Texas. The final solution was 5% HClO_4 -20% HCl (V/V). Barium was not determined because of the precipitation of BaSO_4 , and the samples had to be centrifuged before analysis to avoid clogging the nebulizer.

Instrument calibration was achieved using gravimetric standards made from commercially available, single-element solutions. A matrix matching method was found to give the best results. The major element variations in these standards were made up to approximate the sympathetic variation of mafic and sialic elements as seen in the igneous rock series. The standards were prepared in 20% HCl-5% HClO_4 (V/V). An example of the matrix-matching approach found to be most effective is given in Table 3. Note that, with the exceptions of the acid blank and the standard containing the elements Ag and Bi which were prepared in 25% HNO_3 , all standards are made up to approximate the cation content of 2500-3000 ppm, or about the equivalent of 1 g of rock diluted to 100 mL (excluding silica). Using a sliding weight scale as a function of the estimated silica content, if the analyst dissolves approximately 1.2 g of granite or 0.9 g of basaltic rock, the cation content of the final solution diluted to 100 mL will lie in the 2500 ± 400 ppm range. For ultrabasic rocks and sediments, lesser amounts of sample were used. This matrix-calibration approach utilizes the linear portion of the analytical curves for both the trace and minor elements. However, the response function of the major elements lies in the nonlinear region, and second-order and third-order polynomial equations are necessary to define the shape of the response function for each of the major elements; in the curve-fit calculations, the data for each point were weighted by the variance of the determination (17). The root-mean-square error for these response functions was routinely less than $\pm 2\%$ and was generally in the ± 0.5 - $\pm 1\%$ range.

EVALUATION OF INTERFERENCES

The most important source of error in the analytical procedure described in this paper is the effect of unwanted spectral light emitted by concomitant elements on the analytical channels of the instrument. Because of the complexity of the spectra emitted by the ICP, it is extremely important that these spectral interferences be carefully evaluated. These interferences are manifest as direct spectral interferences, spectral wings, and broadband spectral shifts. Detailed studies were made of the interferences observed for each secondary array (Table 2). These data were generated using the measured

Table 3. Example of a matrix-matching-calibration scheme used in the determination of the major, minor, and trace elements in rocks and soils

| Element | Std #1 Acid Blank | Std #2 25% HNO ₃ | Std #3 20% HCl -5% HClO ₄ | Std #4 20% HCl -5% HClO ₄ | Std #5 20% HCl -5% HClO ₄ | Std #6 20% HCl -5% HClO ₄ | Std #7 20% HCl -5% HClO ₄ | Std #8 20% HCl -5% HClO ₄ | Std #9 20% HCl -5% HClO ₄ | Std #10 20% HCl -5% HClO ₄ | Std #11 20% HCl -5% HClO ₄ | Std #12 20% HCl -5% HClO ₄ | Std #13 20% HCl -5% HClO ₄ | Std #14 20% HCl -5% HClO ₄ |
|---------|-------------------------|-----------------------------------|--|--|--|--|--|--|--|---|---|---|---|---|
| Na | 0.050 | | 500.0 | 1500. | 1000. | 250.0 | 50.00 | 100.0 | 10.00 | | | | | |
| K | 0.200 | | 1500.0 | 1000. | 500.0 | 250.0 | 50.00 | 100.0 | 10.00 | | | | | |
| Mg | 0.020 | | 50.06 | 10.00 | | 300.0 | | 1000. | | 1500. | | | 2500. | |
| Ca | 0.010 | | 50.01 | 10.00 | 500.2 | 1500. | 1000. | 250.0 | 100.3 | | 2500. | | | |
| Fe | 0.200 | | 50.00 | 10.00 | 1000 | 500.0 | 1000. | 250.0 | 1500. | 100.0 | | | | 3600. |
| Al | 0.040 | | 50.51 | 10.10 | 102.9 | 251.9 | 1502. | | 1005. | | 501.0 | 3000. | | |
| Ti | 0.000 | | 200.0 | | | | | | | | | | | |
| P | 0.000 | | | | | | | | | 326.0 | | | | |
| Ba | 0.000 | | 50.00 | | | | | | | | | | | |
| La | 0.000 | | 50.16 | | | | | | | | | | | |
| Ce | 0.000 | | 50.10 | | | | | | | | | | | |
| Zr | 0.000 | | 50.00 | | | | | | | | | | | |
| U | 0.000 | | | 50.06 | | | | | | | | | | |
| Th | 0.000 | | | 50.02 | | | | | | | | | | |
| V | 0.000 | | 50.16 | | | | | | | | | | | |
| Cr | 0.000 | | 50.07 | | | | | | | | | | | |
| Mn | 0.000 | | 50.00 | 10.00 | | 100.0 | 1000. | 250.0 | 500.0 | | | | | |
| Co | 0.000 | | 50.32 | | | | | | | | | | | |
| Ni | 0.000 | | 50.00 | | | | | | | | | | | |
| Cu | 0.000 | | 50.03 | | | | | | | | | | | |
| Zn | 0.000 | | 50.01 | | | | | | | | | | | |
| Mo | 0.000 | | | | | | | | | 50.00 | | | | |
| Ag | 0.000 | 10.00 | | | | | | | | | | | | |
| Cd | 0.000 | | 10.00 | | | | | | | | | | | |
| Sn | 0.000 | | 50.00 | | | | | | | | | | | |
| Pb | 0.000 | | 50.02 | | | | | | | | | | | |
| Bi | 0.000 | 10.00 | | | | | | | | | | | | |
| As | 0.000 | | 50.01 | | | | | | | | | | | |
| Sb | 0.000 | | 50.02 | | | | | | | | | | | |
| Σ | --- | 20.00 | 2900 | 2850 | 3100 | 2750 | 3000 | 2700 | 2870 | (2888) ¹ | 3000 | 3000 | 2500 | 3600 |

¹ The sum includes the K present in the potassium monobasic used as the reagent for P in this standard.

spectral response observed on each analytical channel, when single-element solutions of known concentrations were aspirated into the plasma. The nature of the spectral response and the response arising from contamination present in the single element solution were then determined from independent observations. This discrimination is made using the wavelength spectra generated by moving the scanning primary slit a distance equivalent to ± 0.2 nanometers along the secondary array while aspirating the single element solution into the plasma and recording the response for each channel. Comparison of the empirical wavelength spectra generated with those reported in the MIT wavelength tables (23) for specific elements and the table of prominent spectral lines emitted by the ICP (19) provides the basis for the identification of observed spectral responses that result from elemental contamination of the single element solutions. The spectral response arising from contamination of the single element solutions must be removed from the spectral interference data base before accurate spectral interference coefficients can be calculated. In Table 2, the interference observed for each analytical channel present in the secondary arrays used in this study is expressed as the slope term of the spectral interference coefficients. These slope terms, however, also contain a component of random or statistical error which is due to measurement statistics. On the basis of replicate determinations, the magnitude of this component of error is generally found to be $\pm 5\%$ of the slope term of the spectral interference coefficient. This error can contribute in a major way to the analytical uncertainty of an elemental determination. This statistical uncertainty will be discussed in the next section.

ANALYTICAL UNCERTAINTY

The accuracy of a determination of the concentration of a given element present in a sample of unknown composition is affected by several components of error. Two of those components, namely the geologic heterogeneity of the sample and the uncertainty introduced by the sample digestion technique, have not been evaluated in this study because all determinations were made from a single digestion. The remaining sources of analytical uncertainty include the error in the calibration standards ($<1.2\%$) and the error of the curve fit itself (the root-mean-square term of the curve-fit calculation described above). Measurement statistics, which vary as a function of the limit of detection, are demonstrated by the data in Figure 1. The maximum analytical error associated with the determination for the major elements is $\pm 3.6\%$. However, analytical errors associated with the trace-element determinations must also include the errors introduced by the correction for spectral interferences. Furthermore, in order that all spectral corrections may be applied, the computer must have adequate capability to handle a minimum of 200 spectral correction coefficients needed for routine geochemical work. The analytical uncer-

tainty on the trace element determinations therefore includes measurement error as well as the uncertainty of the spectral correction coefficients. This component of error is the statistical uncertainty of the slope term of the spectral-interference coefficient, which may be significant if the correction applied is large. A good example of this type of analytical uncertainty would be the effect of the aluminium recombination-spectra on the analytical lines in the UV portion of the wavelength spectrum. Figure 2A is a nomogram showing the relationship between

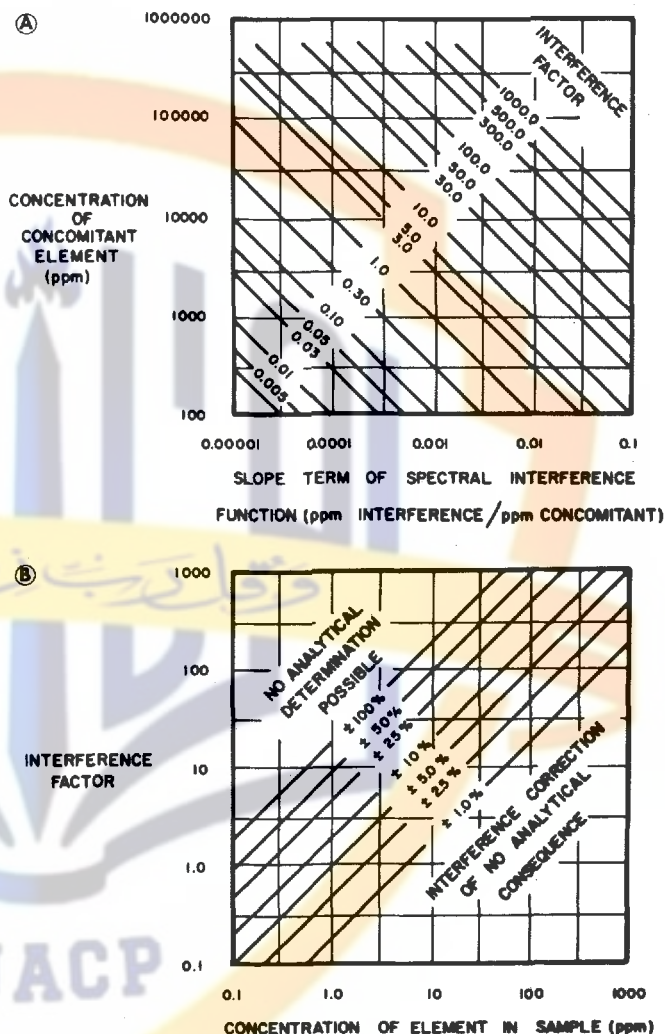


Figure 2. Two nomograms showing the relationship between the interference caused by the presence of a concomitant and the magnitude of the slope term of the spectral interference coefficients. The interference factor is first obtained from the nomogram in Figure 2A, and the analytical uncertainty for a particular determination can then be easily obtained from Figure 2B for which a $\pm 5\%$ statistical uncertainty is assumed for the accuracy of the slope term of the spectral interference correction (from Table 2). This component of analytical uncertainty is expressed in percent as a function of the residual concentration of the analyte element present.

the slope term of the interference coefficient (Table 2) and the concentration of the concomitant element. Once the interference factor has been obtained from this diagram, the analytical uncertainty (in percent) of the determination can be obtained from the nomogram in Figure 2B as a function of the measured concentration of the analyte. All of the components of error are assumed to be additive.

ANALYTICAL RESULTS

The suite of Geochemical Reference Samples analyzed in this study is given in Table 4. Analytical results reported are those obtained from the best analytical line of the four ICP instruments studied. Four samples, G-2, GSP-1,

AGV-1, and BCR-1, were run at the beginning and the end of the data set as control samples. Analytical results for these control samples are plotted by element in Figure 3. Corrections for instrumental drift observed were made assuming a linear change as a function of time. The parameters used are given in Figure 3 as a correction for calibration bias (C) and a change with time (ΔT), or instrumental drift as a function of time over the period of the analysis (4 hrs). No corrections were made to the data for P or the other minor and trace elements reported. The average change over the four hour period was about 3%. This magnitude of change is approximately equivalent to the mean error of the determinations for the major elements, and one could argue that these corrections are unwar-

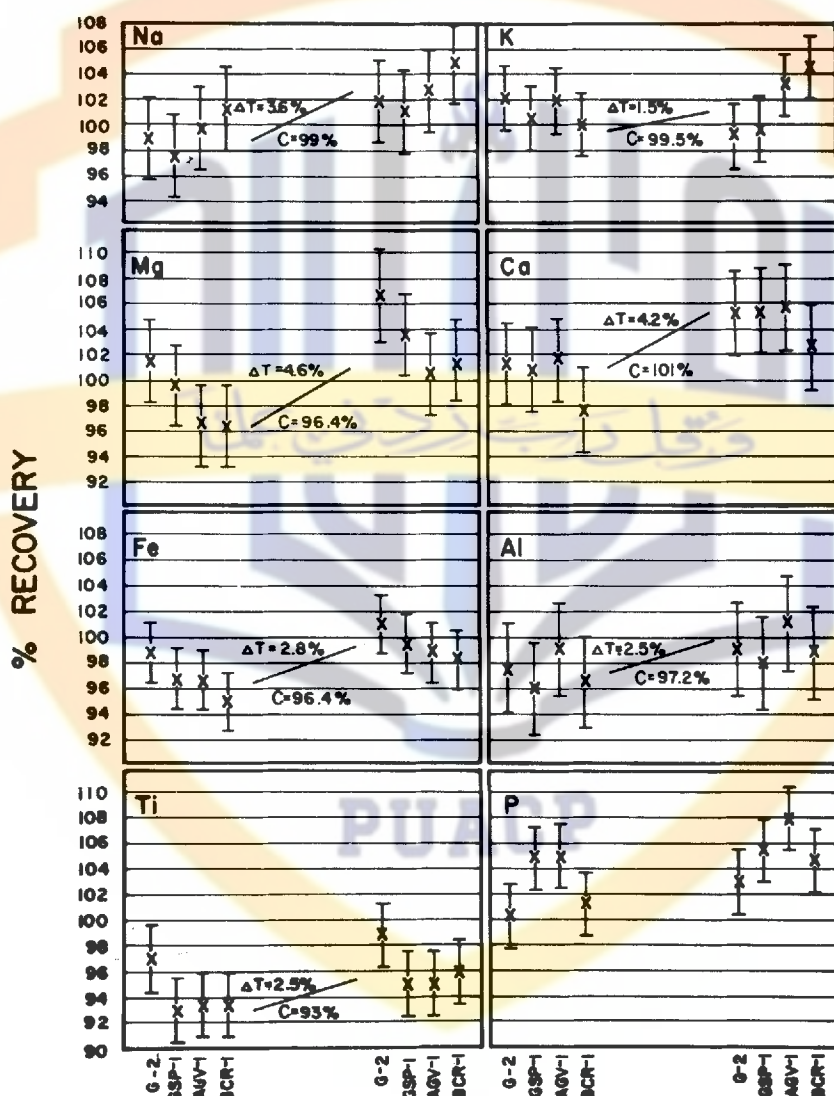


Figure 3. Diagrams of the major elements showing the percent recovery as a function of time for the four control samples analyzed during the data cycle (see Table 4). The time lapse between observations is approximately four hours. Corrections for calibration bias (C) and instrumental drift (ΔT) have been made as a linear function of time to all the major element data reported in Tables 5-14. Error bars shown are calculated from the precision, the RMS error of the curve fit routine, and the dilution errors in the initial chemistry.

Table 4. Sequence and identity of samples analyzed.

| | | | | |
|--------|-------|-------|----------|-------|
| W-1 | MRG-1 | NIM-G | Fe-Mica | B-382 |
| G-2 | SY-2 | NIM-S | Mg-Mica | DTS-1 |
| GSP-1 | SY-3 | NIM-L | B-368 | PCC-1 |
| AGV-1 | SO-1 | NIM-N | B-319 | NIM-D |
| BCR-1 | SO-2 | GA | NBS-88a | NIM-P |
| DTS-1 | SO-3 | GH | NBS-1B | BE-N |
| BHVO-1 | SO-4 | GS-N | UB-N | MA-N |
| MAG-1 | GX-1 | DR-N | NBS-120B | AN-G |
| QLO-1 | GX-2 | BR | B-395 | G-2 |
| RGM-1 | GX-3 | VS-N | L-375 | GSP-1 |
| SCo-1 | GX-4 | B-375 | L-90 | AGV-1 |
| SDC-1 | GX-5 | B-376 | B-367 | BCR-1 |
| STM-1 | GX-6 | FK-N | B-381 | DTS-1 |

ranted. The primary purpose of this diagram, however, is to show that the accuracy of the analytical data over the period of the analyses varied systematically and that the routine analysis of check standards should be used to monitor this process. In routine analytical situations, these corrections would not be applied to the data set; rather, the analytical curves would be redefined using the normalization function present in the software (17).

Analytical results obtained on major, minor, and trace elements present in the Geochemical Reference Samples are given in Tables 5-14. The major elements (except silica) are reported as weight percent oxide, with total iron expressed as Fe_2O_3 . All other element concentrations are given in parts per million. Elemental concentrations not determined are indicated by a dashed line; errors are not assigned where limited values are given. Data in parentheses are subject to large errors and are discussed in the text. The results for igneous GRS materials are grouped by distributing agency: U.S. Geological Survey, Tables 5 and 6; Canadian Geological Survey, Table 7; the Association Nationale de la Recherche Technique, Table 8; the Centre de Recherches Petrographiques et Geochimiques, Table 9; and the South African Bureau of Standards, Table 10. The results on igneous reference minerals are given in Table 11. The results on the synthetic glass VS-N and on three slags are given in Table 12.

Several sedimentary reference rocks have also been analyzed and the results are given in Tables 13 and 14. The results given for the samples in Table 13 are generally more complete than those available from the distributing agency.

In a comparison of analytical methods, discussion unfortunately tends to focus on the differences between methods rather than the agreement achieved. For the vast majority of the determinations reported here, the agreement with recommended values is within the ± 5 -10 % envelop for the trace and minor elements and within ± 2.5 -3 % for the major-element values. A detailed comparison with reference values is left to the reader.

Igneous Rocks

The results presented in Tables 5-10 demonstrate the excellent agreement with published reference values (24-54) that can be obtained using the ICP-AES method. Agreement within the quoted error envelop is achieved for most major elements except for those samples that contain high K_2O (GSP-1, RGM-1, GS-N, GA, GH, NIM-S) and for those that contain high iron (MRG-1, BR, NIM-N, NIM-P). Exceptions are also noted for the determination of the alkali elements in ultrabasic rocks because the concentration of these elements in solutions is less than the limit of determination (3 X the limit of detection). The Al_2O_3 values in NIM-P and NIM-D are overcorrected for the spectral interference of Mg present on Al 237.31 nm. Values for Al_2O_3 in DTS-1 and PCC-1 were determined using different instruments having either Al 309.27 nm or 308.22 nm and are not in error because of this uncertainty. Values of P_2O_5 are generally less than the recommended values. Because of the sensitivity of the ICP-AES method for P and the lack of interferences present on the P lines used (see Table 2), the values given here are probably more accurate than the reference values. Results obtained for MgO show a distinct bias when the sample weight is not adequately controlled. This bias is discussed in a later section entitled evaluation of the instrumental method.

Sufficient data were not available for the USGS-III rocks and the newly issued GRS materials AN-G, BE-N, and MA-N; thus, any valid comparison of the results presented here relative to recommended or preferred values will not be made.

Results reported for the REE (rare-earth elements) agree well with values determined using neutron activation techniques recently reported (38, 39, 49-54). In general, excellent agreement was achieved with these data for La, Ce, Sm, Eu, Gd, and Yb. At low concentrations, the values for Eu and Yb appeared somewhat high. A large uncertainty exists for the data on Nd because of a large interference from Y (19). The value for Gd in SY-3 is in error based on data reported by others (53, 54) and on REE distribution plots. The source of the spectral interference on Gd 376.84 nm has not been identified (19).

Results obtained for Zr agree well with published values in samples where zircon does not appear on the liquidous. Zirconium concentrations in granitic rocks show low recoveries (data in parentheses, Tables 5-10). Values measured in volcanic or basic rocks, ranging from less than 10 to 11,600 ppm (NIM-L), are all slightly high (± 5 -10%) with respect to reference values and may reflect a calibration bias. Special care is required with the use of Zr reference solutions as they often contain HF, even though they may be labeled "in 4M HCl". The HF attacks the concentric glass nebulizer and may cause an error in the calibration of the instrument for that element. Values measured for Zr in the ultramafic standards do not show good agreement with the values recommended by Flanagan (27); however, no known spectral interference can account for the error seen. Unless there is a dissolution problem, Zr concentrations in these samples do not appear as high as those proposed by Abbey (29, 30).

Analysis of U and Th was also carried out for all samples. However, because of the low crustal abundance of these elements and their relatively poor sensitivity (50-200 ppb), values for U were measured only in SY-2 and SY-3. The value measured for U is low for SY-2 (265:290) and high for SY-3 (760:640) with respect to the values recommended by Abbey (29). Values measured for Th compare favorably with the recommended values (29) for both SY-2 (355:370) and SY-3 (940:980); however, the values for Th measured in GSP-1, GS-N, GH, NIM-G, and NIM-L are generally somewhat low when compared with the recommended values (27, 34, 37) as well as the more recently reported data (38, 49-51, 53, 54).

Results for the first-series transition metals (V, Cr, Mn, Co, Ni, Cu, Zn) demonstrate an excellent correlation with recommended values for all elements above the limit of determination (1-10 ppm depending on the sensitivity of the analytical lines used). An H_3PO_4 digestion was used to attack the residual spinels present in the ultrabasic rocks (18).

The determination of a number of other trace elements (Mo, W, Ag, Au, Cd, Sn, Pb, Bi, As, Sb, Se) were attempted. Because of the low crustal abundance of these elements, no values were determined for W, Ag, Au, Cd, Bi, Sb or Se in any of the igneous rock samples. As was determined in samples

Table 5. ICP data on major, minor and trace elements : GRS from USGS' (G-2, GSP-1, AGV-1, BCR-1, W-1, DTS-1, PCC-1)

| Element ² or Oxide | G-2 | GSP-1 | AGV-1 | BCR-1 | W-1 | DTS-1 | PCC-1 |
|-------------------------------------|-------|-------|-------|-------|-------|--------|--------|
| Na ₂ O | 4.06 | 2.75 | 4.28 | 3.34 | 2.21 | <0.03 | <0.03 |
| K ₂ O | 4.45 | 5.58 | 2.96 | 1.70 | 0.647 | <0.02 | <0.014 |
| MgO | 0.799 | 0.989 | 1.53 | 3.45 | 6.74 | 47.5 | 43.4 |
| CaO | 1.94 | 2.01 | 4.91 | 6.67 | 10.52 | 0.119 | 1.5 |
| Fe ₂ O ₃ | 2.71 | 4.34 | 6.76 | 13.15 | 10.91 | 8.04 | 0.0004 |
| Al ₂ O ₃ | 15.37 | 15.05 | 17.53 | 13.49 | 15.05 | 0.219 | 0.18 |
| TiO ₂ | 0.480 | 0.657 | 1.04 | 2.20 | 1.06 | 0.054 | 0.008 |
| P ₂ O ₅ | 0.135 | 0.277 | 0.488 | 0.351 | 0.133 | 0.0044 | 0.0002 |
| Li | 32.6 | 28.4 | 9.2 | 11.3 | 9.8 | <2 | <2 |
| Be | 2.48 | 1.32 | 2.3 | 1.8 | 0.85 | 0.06 | 0.08 |
| Sr | 468 | 233 | 641 | 328 | 183 | 0.43 | 0.40 |
| Ba | 1860 | 1275 | 1200 | 673 | 154 | 3.0 | 0.48 |
| La | 91 | 187 | 38 | 26.2 | 12 | <3 | <3 |
| Ce | 158 | 425 | 60 | 51 | 25 | <15 | <15 |
| Nd | 52 | 205 | 34 | 37 | <20 | <20 | <20 |
| Sm | 7.3 | 22.2 | 6.1 | 6.3 | <5 | <5 | <5 |
| Eu | 1.55 | 2.9 | 1.8 | 2.1 | 1.2 | <0.6 | <0.6 |
| Gd | 4.4 | 13.2 | 5.2 | 6.9 | 3.9 | <2 | <2 |
| Yb | 0.68 | 1.36 | 1.7 | 3.4 | 2.0 | <0.2 | <0.2 |
| Zr | -- | -- | 240 | 194 | 95 | 6.3 | 2.1 |
| U | <20 | <20 | <25 | <25 | <25 | <20 | <20 |
| Th | <25 | 80 | <25 | <25 | <25 | <25 | <25 |
| V | 34.2 | 50.1 | 118 | 405 | 265 | 10.5 | 36 |
| Cr | 6.5 | 11.8 | 12.7 | 15.0 | 116 | 2630 | 2680 |
| Mn | 264 | 305 | 740 | 1420 | 1305 | 895 | 915 |
| Co | 4.8 | 6.8 | 15.1 | 36.5 | 45.0 | 130 | 116 |
| Ni | 5.8 | 10.0 | 15.7 | 12.4 | 81.2 | 2380 | 2380 |
| Cu | 9.1 | 30.7 | 56.5 | 12.8 | 110 | 4 | 9.4 |
| Zn | 84.5 | 104 | 91.8 | 133 | 87.8 | 43.5 | 47.5 |
| Mo | <3 | <3 | <4 | <5 | <5 | <4 | <4 |
| W | <7 | <7 | <7 | <8 | <7 | <7 | <7 |
| Ag | <2 | <2 | <2 | <3 | <3 | <2 | <2 |
| Au | <3 | <3 | <3 | <3 | <3 | <3 | <3 |
| Cd | <2 | <2 | <2 | <2 | <2 | <3 | <3 |
| Pb | <3 | 5.2 | 5.4 | 5.1 | 3.6 | <3 | <3 |
| Sn | 26 | 25 | 25 | <25 | <11 | 15 | 26 |
| Bi | <25 | <25 | <25 | <25 | <25 | <25 | <25 |
| As | <5 | <5 | <6 | <5 | <5 | <5 | <5 |
| Sb | <18 | <18 | <18 | <18 | <14 | <12 | <12 |
| Se | <30 | <30 | <30 | <30 | <30 | <30 | <30 |

1 F. J. Flanagan, U.S. Geological Survey, MS 972, Reston, VA 22092.
 2 Major elements expressed as weight percent oxide; others expressed in parts per million.

Table 6. ICP data on major, minor and trace elements : GRS from USGS (STM-1, RGM-1, QL0-1, SDC-1, BRVO-1)

| Element ¹ or Oxide | STM-1 | RGM-1 | QL0-1 | SDC-1 | BRVO-1 |
|-------------------------------------|-------|-------|-------|-------|--------|
| Na ₂ O | 8.90 | 4.12 | 0.13 | 2.03 | 2.39 |
| K ₂ O | 3.86 | >4.3 | 0.13 | 3.15 | 0.546 |
| MgO | 0.102 | 0.283 | 0.03 | 1.75 | 7.53 |
| CaO | 1.14 | 1.23 | 0.10 | 1.42 | 11.24 |
| Fe ₂ O ₃ | 5.30 | 1.93 | 0.10 | 6.91 | 12.37 |
| Al ₂ O ₃ | 18.30 | 14.06 | 0.51 | 15.65 | 14.16 |
| TiO ₂ | 0.132 | 0.267 | 0.015 | 0.979 | 2.75 |
| P ₂ O ₅ | 0.160 | 0.048 | 0.007 | 0.148 | 0.280 |
| Li | 35.1 | 62 | 1.24 | 32.6 | 2.0 |
| Be | 9.8 | 2.48 | 0.05 | 3.07 | 1.36 |
| Sr | 701 | 102 | 2.0 | 182 | 413 |
| Ba | 580 | 836 | 17 | 644 | 139 |
| La | 153 | 23 | 0.5 | 41 | 17 |
| Ce | 258 | 32 | 7.7 | 88 | 46 |
| Nd | 78 | 15 | 3.2 | 35 | 26 |
| Sm | 8.0 | <5 | <5 | 6.7 | 13.9 |
| Eu | 4.0 | 0.62 | 0.15 | 1.8 | 2.6 |
| Gd | 9.0 | 3.1 | 0.4 | 7.4 | 7.0 |
| Yb | 4.3 | 2.3 | 0.07 | 3.2 | 2.1 |
| Zr | 1340 | 233 | 7.0 | (59) | 187 |
| U | <20 | <20 | <20 | <25 | <25 |
| Th | <25 | <25 | <25 | <25 | <25 |
| V | 6.0 | 12.0 | 0.6 | 94.8 | 315 |
| Cr | 9.0 | 3.0 | 1.0 | 64.0 | 294 |
| Mn | 1750 | 294 | 8.8 | 904 | 1385 |
| Co | 2.0 | 2.5 | 0.5 | 17.3 | 44.5 |
| Ni | 5.2 | 2.5 | 1.0 | 38.0 | 131 |
| Cu | <1 | 9.7 | 0.5 | 27.3 | 141 |
| Zn | 248 | 33.0 | 1.0 | 105 | 109 |
| Mo | 6 | <3 | <3 | <4 | <5 |
| W | <7 | <7 | <7 | <7 | <8 |
| Ag | <2 | <2 | <2 | <2 | <2 |
| Au | <3 | <3 | <3 | <3 | <3 |
| Cd | <2 | <2 | <2 | <2 | <3 |
| Sb | 5 | 6 | 3.0 | <3 | 3 |
| Pb | 20 | <23 | 19 | 22 | <11 |
| Bi | <25 | <25 | <25 | <25 | <25 |
| As | <6 | <5 | <5 | <5 | <5 |
| Se | <18 | <14 | <18 | <18 | <14 |
| Sn | <30 | <30 | <30 | <30 | <30 |

¹ Major elements expressed in weight percent oxide; others expressed in parts per million.

Table 7. ICP data on major, minor and trace elements : GRS from Geological Survey of Canada¹
(MRG-1, SY-2, SY-3)

| Element ² or Oxide | MRG-1 | | | SY-2 | | | SY-3 | | |
|-------------------------------------|-------|---|-------|-------|---|-------|-------|---|-------|
| Na ₂ O | 0.742 | + | 0.02 | 4.45 | + | 0.14 | 4.14 | + | 0.13 |
| K ₂ O | 0.182 | + | 0.004 | 4.47 | + | 0.11 | 4.17 | + | 0.10 |
| MgO | 13.26 | + | 0.41 | 2.75 | + | 0.09 | 2.66 | + | 0.08 |
| CaO | 13.73 | + | 0.45 | 8.00 | + | 0.26 | 8.19 | + | 0.27 |
| Fe ₂ O ₃ | 17.18 | + | 0.38 | 6.41 | + | 0.14 | 6.44 | + | 0.14 |
| Al ₂ O ₃ | 8.37 | + | 0.30 | 12.40 | + | 0.45 | 11.70 | + | 0.42 |
| TiO ₂ | 3.61 | + | 0.09 | 0.138 | + | 0.004 | 0.154 | + | 0.004 |
| P ₂ O ₅ | 0.057 | + | 0.003 | 0.435 | + | 0.011 | 0.545 | + | 0.014 |
| Li | <2 | | | 96.5 | + | 1.9 | 89.0 | + | 1.8 |
| Be | 1.0 | + | 0.02 | 23.7 | + | 0.47 | 23.1 | + | 0.46 |
| Sr | 270 | + | 5.4 | 279 | + | 5.6 | 307 | + | 6.2 |
| Ba | 48.0 | + | 0.96 | 458 | + | 9.2 | 440 | + | 8.8 |
| La | 11 | + | 1.7 | 74 | + | 2.2 | 1380 | + | 28 |
| Ce | 19 | + | 4.0 | 182 | + | 5.5 | 2260 | + | 45 |
| Nd | <20 | | | 55 | + | 11 | 870 | + | 175 |
| Sm | <5.0 | | | 14.8 | + | 1.5 | 97 | + | 3.0 |
| Eu | 1.7 | + | 0.35 | 2.9 | + | 0.3 | 16.8 | + | 0.35 |
| Gd | 4.5 | + | 0.45 | 15.5 | + | 0.47 | (95) | + | 3.0 |
| Yb | 0.78 | + | 0.12 | 17.5 | + | 0.53 | 61.3 | + | 1.8 |
| Zr | 103 | + | 3.1 | 308 | + | 9.2 | 393 | + | 12 |
| U | <30 | | | 265 | + | 21 | 760 | + | 38 |
| Th | <25 | | | 355 | + | 11 | 940 | + | 28 |
| V | 527 | + | 16 | 56.3 | + | 1.7 | 57.8 | + | 1.7 |
| Cr | 429 | + | 13 | 8.9 | + | 0.5 | 10.5 | + | 1.0 |
| Mn | 1282 | + | 39 | 2510 | + | 75 | 2490 | + | 75 |
| Co | 86.3 | + | 2.6 | 8.7 | + | 0.4 | 9.5 | + | 0.5 |
| Ni | 185 | + | 5.6 | 10.0 | + | 1.0 | 11.5 | + | 1.0 |
| Cu | 127 | + | 3.8 | 2.2 | + | 0.5 | 23.3 | + | 1.2 |
| Zn | 187 | + | 5.6 | 265 | + | 8.0 | 251 | + | 7.5 |
| Mo | <7 | | | <4 | | | <4 | | |
| W | <9 | | | <7 | | | <7 | | |
| Ag | <3 | | | <2 | | | 5 | + | 2 |
| Au | <3 | | | <3 | | | <3 | | |
| Cd | <2 | | | <2 | | | <2 | | |
| Sn | 4 | + | 2 | <3 | | | 6 | + | 2 |
| Pb | 10 | + | 5 | 91 | + | 5 | 181 | + | 5 |
| Bi | <25 | | | <25 | | | <25 | | |
| As | <5 | | | 17 | + | 5 | 14 | + | 5 |
| Sb | <10 | | | <14 | | | <14 | | |
| Se | <30 | | | <30 | | | <30 | | |

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² Major and minor elements in %; trace elements in ppm.

Table 8. ICP data on major, minor and trace elements : GRS from ANRT-CRPG¹ (BE-N, DR-N, GS-N, MA-N)

| Element ² or Oxide | BE-N | | | DR-N | | | GS-N | | | MA-N | | |
|-------------------------------------|-------|---|------|-------|---|-------|-------|---|-------|-------|---|-------|
| Na ₂ O | 3.21 | + | 0.10 | 2.96 | + | 0.09 | 3.70 | + | 0.12 | 5.82 | + | 0.19 |
| K ₂ O | 1.42 | + | 0.04 | 1.73 | + | 0.04 | 3.96 | + | 0.10 | 3.07 | + | 0.08 |
| MgO | 12.94 | + | 0.40 | 4.38 | + | 0.14 | 2.30 | + | 0.07 | 0.044 | + | 0.002 |
| CaO | 13.04 | + | 0.43 | 6.85 | + | 0.22 | 2.45 | + | 0.08 | 0.600 | + | 0.02 |
| Fe ₂ O ₃ | 12.28 | + | 0.27 | 9.52 | + | 0.21 | 3.68 | + | 0.08 | 0.474 | + | 0.01 |
| Al ₂ O ₃ | 9.87 | + | 0.36 | 17.67 | + | 0.64 | 14.58 | + | 0.53 | 17.20 | + | 0.62 |
| TiO ₂ | 2.50 | + | 0.06 | 1.04 | + | 0.03 | 0.645 | + | 0.016 | 0.126 | + | 0.003 |
| P ₂ O ₅ | 1.00 | + | 0.03 | 0.222 | + | 0.006 | 0.275 | + | 0.007 | 1.41 | + | 0.04 |
| Li | -- | | | 35.1 | + | 0.70 | 50 | + | 1.0 | -- | | |
| Be | -- | | | 1.78 | + | 0.04 | 5.33 | + | 0.11 | -- | | |
| Sr | -- | | | 389 | + | 7.8 | 565 | + | 11 | -- | | |
| Ba | 1015 | + | 20 | 374 | + | 7.5 | 1370 | + | 28 | 42 | + | 1.0 |
| La | 88 | + | 2.6 | 24 | + | 1.0 | 75 | + | 1.5 | 6.5 | + | 1.0 |
| Ce | 142 | + | 7.1 | 59 | + | 1.5 | 155 | + | 4.0 | 20 | + | 4.0 |
| Nd | -- | | | 27 | + | 8 | 50 | + | 10 | -- | | |
| Sm | -- | | | 6 | + | 2 | 7.2 | + | 1.8 | -- | | |
| Eu | -- | | | 1.6 | + | 0.25 | 1.8 | + | 0.1 | -- | | |
| Gd | -- | | | 4.7 | + | 0.5 | 5.4 | + | 0.5 | -- | | |
| Yb | -- | | | 2.79 | + | 0.08 | 1.32 | + | 0.04 | -- | | |
| Zr | 277 | + | 8.3 | (32) | | | (99) | | | (24) | | |
| U | <25 | | | <20 | | | <20 | | | <20 | | |
| Th | <25 | | | <25 | | | <32 | + | 6.0 | <25 | | |
| V | 235 | + | 7.1 | 217 | + | 6.5 | 62.9 | + | 1.9 | <2 | | |
| Cr | 340 | + | 10.2 | 6.5 | + | 1.1 | 53.8 | + | 1.6 | <5 | | |
| Mn | 1500 | + | 45 | 1665 | + | 50 | 408 | + | 12 | 310 | + | 9.3 |
| Co | 62.5 | + | 1.9 | 39.4 | + | 2.0 | 66.4 | + | 2.0 | 1.5 | + | 1.0 |
| Ni | 270 | + | 8.1 | 23.0 | + | 2.3 | 37.0 | + | 1.9 | 8.5 | + | 1.0 |
| Cu | 67.0 | + | 2.0 | 45.2 | + | 2.3 | 21.3 | + | 1.1 | 154 | + | 4.6 |
| Zn | 120 | + | 3.6 | 147 | + | 7.4 | 48.5 | + | 2.5 | 229 | + | 6.9 |
| Mo | <5 | | | <4 | | | <3 | | | 3 | | |
| W | -- | | | -- | | | -- | | | -- | | |
| Ag | -- | | | <3 | | | <2 | | | -- | | |
| Au | -- | | | <3 | | | <3 | | | -- | | |
| Cd | <2 | | | <2 | | | <2 | | | <2 | | |
| Sn | <5 | | | 7 | + | 3 | 6 | + | 3.0 | 86 | + | 5 |
| Pb | 23 | + | 7 | 47 | + | 12 | 54 | + | 11 | 57 | + | 12 |
| Bi | <25 | | | <25 | | | <25 | | | <25 | | |
| As | <5 | | | <6 | | | <5 | | | 12 | + | 5 |
| Sb | <10 | | | <18 | | | <14 | | | <18 | | |
| Se | -- | | | <30 | | | <30 | | | -- | | |

¹ K. Govindaraju, Centre de Recherches Pétrographiques et Géochimiques, C.O. N°1, 54500 Vandoeuvre-lès-Nancy, France.² Major and minor elements in %; trace elements in ppm.

Table 9. ICP data on major, minor and trace elements : GRS from ANRT-CRPG¹ (AN-G, BR, GA, GH)

| Element ² or Oxide | AN-G | | | BR | | | GA | | | GH | | |
|-------------------------------------|-------|---|-------|-------|---|------|-------|---|-------|-------|---|-------|
| Na ₂ O | 1.68 | + | 0.05 | 3.11 | + | 0.10 | 3.49 | + | 0.11 | 3.82 | + | 0.12 |
| K ₂ O | 0.15 | + | 0.01 | 1.43 | + | 0.04 | >3.84 | | | >4.26 | | |
| MgO | 1.75 | + | 0.05 | 13.28 | + | 0.41 | 0.957 | + | 0.03 | 0.029 | + | 0.001 |
| CaO | 15.32 | + | 0.50 | 12.95 | + | 0.43 | 2.46 | + | 0.08 | 0.739 | + | 0.02 |
| Fe ₂ O ₃ | 3.21 | + | 0.07 | 12.45 | + | 0.27 | 2.80 | + | 0.06 | 1.39 | + | 0.03 |
| Al ₂ O ₃ | 28.63 | + | 1.03 | 10.06 | + | 0.36 | 14.83 | + | 0.53 | 12.78 | + | 0.46 |
| TiO ₂ | 0.217 | + | 0.005 | 2.59 | + | 0.06 | 0.365 | + | 0.009 | 0.076 | + | 0.002 |
| P ₂ O ₅ | 0.014 | + | 0.001 | 1.02 | + | 0.03 | 0.126 | + | 0.004 | 0.008 | + | 0.002 |
| Li | -- | | | 9.0 | + | 0.2 | 89 | + | 1.8 | 45 | + | 1.0 |
| Be | -- | | | 2.09 | + | 0.04 | 3.56 | + | 0.07 | 5.67 | + | 0.11 |
| Sr | -- | | | 1330 | + | 27 | 301 | + | 6 | 9.36 | + | 0.19 |
| Ba | 33 | + | 1.0 | 1053 | + | 21 | 821 | + | 16 | 17.5 | + | 0.35 |
| La | 5 | + | 1.3 | 83 | + | 2.5 | 42 | + | 1.0 | 27 | + | 1.0 |
| Ce | 20 | + | 3.0 | 168 | + | 5.0 | 85 | + | 2.5 | 66 | + | 2.0 |
| Nd | -- | | | 70 | + | 14 | 35 | + | 9 | -- | | |
| Sm | -- | | | 17 | + | 1.2 | 5 | + | 2.0 | 10.8 | + | 1.0 |
| Eu | -- | | | 4.0 | + | 1.2 | 1.3 | + | 0.2 | <0.6 | | |
| Gd | -- | | | 8.5 | + | 0.4 | 3.7 | + | 0.4 | 11.2 | + | 0.5 |
| Yb | -- | | | 1.7 | + | 0.09 | 2.0 | + | 0.06 | 8.0 | + | 0.24 |
| Zr | 12 | + | 1.0 | 281 | + | 8.4 | (90) | | | 162 | + | 5.0 |
| U | <20 | | | <25 | | | <20 | | | <20 | | |
| Th | <25 | | | <25 | | | <25 | | | 87 | + | 5.0 |
| V | 74 | + | 2.2 | 239 | + | 7.2 | 39.2 | + | 1.2 | 3.0 | + | 1.0 |
| Cr | 39.7 | + | 2.0 | 339 | + | 10 | 10.5 | + | 1.0 | 4.0 | + | 1.0 |
| Mn | 340 | + | 10 | 1502 | + | 45 | 660 | + | 20 | 370 | + | 11 |
| Co | 26.2 | + | 1.3 | 51.5 | + | 2.7 | 6.4 | + | 1.0 | 1.3 | + | 1.0 |
| Ni | 41.5 | + | 2.1 | 264 | + | 7.9 | 8.2 | + | 1.0 | 3.0 | + | 1.0 |
| Cu | 20.0 | + | 1.0 | 82.4 | + | 2.5 | 23.9 | + | 1.2 | 15.7 | + | 1.0 |
| Zn | 17.7 | + | 1.0 | 160 | + | 4.8 | 79.5 | + | 2.4 | 72.7 | + | 2.2 |
| Mo | <4 | | | <5 | | | <3 | | | 4 | + | 2 |
| W | -- | | | <8 | | | -- | | | -- | | |
| Ag | -- | | | <3 | | | <2 | | | <2 | | |
| Au | -- | | | <3 | | | <3 | | | <3 | | |
| Cd | <2 | | | <2 | | | <2 | | | <2 | | |
| Sn | <4 | | | 8 | + | 4 | 5 | + | 2 | 9 | + | 2 |
| Pb | <17 | | | 25 | + | 8 | 31 | + | 10 | 56 | + | 8 |
| Bi | <25 | | | <25 | | | <25 | | | <25 | | |
| As | <9 | | | <5 | | | <5 | | | <5 | | |
| Sb | <26 | | | <10 | | | <14 | | | <14 | | |
| Se | -- | | | <30 | | | <30 | | | <30 | | |

¹ K. Govindaraju, Centre de Recherches Pétrographiques et Géochimiques, C.O. N°1, 54500 Vandoeuvre-les-Nancy, France.² Major and minor elements in %; trace elements in ppm.

Table 10. ICP data on major, minor and trace elements : GRS from NIM¹ (NIM-G, NIM-S, NIM-L, NIM-N, NIM-D, NIM-P)

| Element ² or oxide | NIM-G | NIM-S | NIM-L | NIM-N | NIM-D | NIM-P | | | | | | |
|-------------------------------------|-------|-------|-------|-------|-------|-------|-------|-------|---|-------|-------|-------|
| Na ₂ O | 3.25 | 0.11 | 0.433 | + | 0.02 | 0.08 | 0.001 | 0.02 | + | 0.001 | 0.37 | 0.01 |
| K ₂ O | 5.04 | 0.13 | >10.0 | + | 0.14 | 0.258 | + | 0.007 | + | 0.001 | 0.107 | 0.003 |
| MgO | 0.035 | 0.002 | 0.470 | + | 0.008 | 7.53 | + | 0.23 | + | 1.32 | 25.69 | 0.80 |
| CaO | 0.785 | 0.03 | 0.694 | + | 0.10 | 10.94 | + | 0.36 | + | 0.01 | 2.55 | 0.08 |
| Fe ₂ O ₃ | 2.06 | 0.05 | 1.49 | + | 0.23 | 8.71 | + | 0.19 | + | 0.36 | 11.67 | 0.26 |
| Al ₂ O ₃ | 12.06 | 0.43 | 17.42 | + | 0.63 | 16.39 | + | 0.59 | + | 0.008 | 3.78 | 0.14 |
| TiO ₂ | 0.092 | 0.002 | 0.041 | + | 0.001 | 0.185 | + | 0.005 | + | 0.004 | 0.162 | 0.004 |
| P ₂ O ₅ | 0.006 | 0.002 | 0.012 | + | 0.001 | 0.018 | + | 0.002 | + | 0.002 | 0.025 | 0.002 |
| Li | 10.9 | 0.55 | <2 | + | 0.78 | <2 | + | 0.02 | + | | <2 | 0.02 |
| Be | 7.77 | 0.16 | 1.61 | + | 0.60 | 0.43 | + | 5.1 | + | | 33.3 | 0.67 |
| Sr | 11.1 | 0.22 | 65.4 | + | 94 | 253 | + | 1.6 | + | 0.18 | 33.9 | 0.68 |
| Ba | 115 | 2.3 | 2615 | + | 8.4 | 80.3 | + | | + | | | |
| La | 114 | 2.3 | 6 | + | 1.0 | <5 | + | | + | | <5 | |
| Ce | 216 | 4.3 | 20 | + | 4.0 | <15 | + | | + | | <15 | |
| Nd | 110 | 22 | <20 | + | 10 | <20 | + | | + | | <20 | |
| Sm | 13 | 1.3 | <5 | + | 1.5 | <5 | + | | + | | <5 | |
| Eu | <0.6 | | <0.6 | + | 0.2 | <0.6 | + | | + | | <0.6 | 1 |
| Gd | 13.8 | 0.7 | <2 | + | 0.3 | <2 | + | | + | | <2 | |
| Yb | 12.9 | 0.39 | <2 | + | 0.1 | 0.97 | + | 0.05 | + | | 0.6 | 0.1 |
| Zr | 306 | 9.2 | 17 | + | 350 | 17 | + | 1.0 | + | 1.0 | 12 | 1.0 |
| U | <20 | | <20 | + | | <20 | + | | + | | <25 | |
| Th | 48 | 5.0 | <25 | + | 8.3 | <25 | + | | + | | <25 | |
| V | 2.0 | 1.0 | 10.0 | + | 2.5 | 225 | + | 6.8 | + | 2.2 | 261 | 13 |
| Cr | 11.5 | 1.0 | 12.7 | + | 1.2 | 31.1 | + | 1.6 | + | 140 | 21350 | 1070 |
| Mn | 140 | 4.2 | 69.7 | + | 178 | 1380 | + | 41 | + | 49 | 1680 | 50 |
| Co | <1 | | 2.5 | + | 1.0 | 56.4 | + | 1.7 | + | 10 | 113 | 5.7 |
| Ni | 3.0 | 1.0 | 6.0 | + | 1.0 | 117 | + | 3.5 | + | 60 | 550 | 17 |
| Cu | 11.0 | 1.0 | 18.4 | + | 1.3 | 8 | + | 1.0 | + | 1.0 | 20.0 | 1.0 |
| Zn | 54.4 | 1.7 | 10.3 | + | 13 | 61.9 | + | 3.1 | + | 5.0 | 106 | 5.3 |
| Mo | <3 | | <3 | + | | <4 | + | | + | | <5 | |
| W | <7 | | <8 | + | | <7 | + | | + | | -- | |
| Ag | <2 | | <2 | + | | <3 | + | | + | | -- | |
| Au | <3 | | <4 | + | | <3 | + | | + | | -- | |
| Cd | <2 | | <2 | + | | <2 | + | | + | | <3 | |
| Sn | 6 | 2 | <13 | + | 2 | <13 | + | | + | 1.7 | <5 | 1.4 |
| Pb | 44 | 7 | 68 | + | 7 | <25 | + | | + | | <25 | |
| Bi | <25 | | <6 | + | | <6 | + | | + | | <5 | |
| As | 14 | 4 | <18 | + | | <14 | + | | + | | <50 | |
| Sb | <14 | | <30 | + | | <30 | + | | + | | <30 | |
| Se | <30 | | | + | | | + | | + | | -- | |

¹ National Institute for Metallurgy, Private Bag X3015, Randburg, 2125, South Africa.

² Major and minor elements in %; trace elements in ppm.

SY-2, SY-3, and NIM-G. Comparisons with the data compiled by Abbey (29) for As in SY-2 show excellent agreement (17:18), but the value determined for As in SY-3 is low (14:21). A value of 14 ppm As in NIM-G falls within the range of reported values (9-17 ppm) given by Steele et al. (37). Both Sn and Pb have been determined in most samples, and agreement with recommended values (27, 29, 35, 37) is generally within the quoted range of error, although values less than 20 ppm have a significant uncertainty due to the correction caused by Al interference (Table 2).

Igneous Minerals

Analyses of the six igneous mineral samples undertaken during the study are given in Table 11. Sample DT-N was not successfully digested, so it could not be analyzed. Unfortunately, the NBS feldspar samples were not available for analysis. A discussion of the data from the feldspar samples is given, followed by a discussion of the more mafic minerals.

Analytical results for the major elements in the three feldspar reference materials (BCS-375, BCS-376, and FK-N) agree very well with the values certified by the Bureau of Analysed Samples, Ltd. (55) and with the data of La Roche and Govindaraju (34), with the exception of the value for TiO₂ in sample FK-N for which the value of 0.0052 weight percent (31 ppm) is below the range of values (291-404 ppm) given by de la Roche and Govindaraju (34) and the value recommended by Abbey (29). The values determined for K₂O in BCS-376 and FK-N are low because of the solubility limit of KClO₄ (19).

Values measured for Li in FK-N are low (4.5:9-10) with respect to that given by La Roche and Govindaraju (34). No data are available for Be. Good agreement is obtained for Sr (35 ppm, 34; 34 ppm, 57) and Ba (215 ppm, 57; 198 ppm, 48; 200 ppm, 56; 190 ppm, 51). The concentration of Ba determined in BCS-376 agrees well with the published value (268:280, 56), but the value determined for Ba in BCS-375 (43.7:140) is in marked contrast with the data of Flanagan et al. (56).

Where present at concentrations above the limit of determination, rare-earth elements in BCS-375 and BCS-376 agree well with values reported by Flanagan et al. (56); an exception is the values measured for Yb, which are lower than the reference values (BCS-375, 1.4:1.7; BCS-376, 0.43:0.7). No rare-earth elements were determined in the feldspar sample FK-N.

The value for Zr is high for BCS-375 (210:180, 57) as noted for the igneous reference rocks, and there is a large discrepancy between the values measured for BCS-376 (7:67, 57) and for FK-N (24:70, 27). No measurable values of U or Th were detected.

The determinations of other trace elements present above the limit of determination agree well with published results (34, 50, 51, 56, 57), except for the values of Cr in FK-N (6.4:1-4), Co in BCS-375 (1.5:0.2), and Zn in FK-N (9:24, 34; 9:9, 57; 9:15, 51). Good agreement was also found with published results for both Sn (FK-N, 250:240, 34) and Pb (BCS-376, 75:75, 57).

Major-element data for samples UB-N, biotite Mica-Fe, and phlogopite Mica-Mg are in good general agreement with published reference values (35, 58), except for the very low value for Ca measured in Mica-Mg. Values of 75-90 ppm were obtained on all four instruments using different matrix calibrations and different analytical lines; no instrumental explanation exists for this wide disparity (0.012:0.08, 58), although some low values (0.01-0.03) were reported by three other workers (see Table 2, reference 58). The concentration of TiO₂ and P₂O₅ measured in the serpentine sample UB-N are also somewhat low (0.098:0.12, 35; 0.017:0.03, 35).

Values reported for Li in all samples are low (UB-N, 19.6:30; Mica-Fe, 1095:1400, 58; Mica-Mg, 99:120, 58) when compared with the average of all values determined using both flame and emission spectrometry (35, 58). However, when the data for Li as determined by flame atomic absorption methods following acid dissolution are examined, the ICP-AES values reported fall within the range of values given for the two mica samples (Mica-Fe, 1095:833-1400, 58 and Mica-Mg, 99:53-114, 58).

Results obtained for the alkaline-earth trace elements Be, Sr, and Ba, in general, show good agreement with those published (35, 48, 50, 51, 58). However, the value of 4.6 ppm for Be in the biotite is not in good agreement with the average of 8 ppm, but it lies within the range of values (2.4-4.7 ppm) determined by flame-atomic-absorption methods following acid digestion. The value of 7.7 ppm for Sr is high with respect to the recommended value of 5 ppm for the biotite (58).

Rare-earth elements were determined in the biotite reference standard. The ICP-AES data agree better with recently published neutron-activation results (48, 50, 51) than with the average values reported (58). The value for Eu (1.6 ppm) is high with respect to reported values (0.65-0.80), and the value measured for Gd (28 ppm) is in error because of the presence of an unidentified spectral interference.

Results obtained for the rest of the trace elements present above the limit of determination agree favorably ($\pm 10\%$) with previously reported values (50-58). However, the accurate determination of Cd in the biotite GRS is critically dependent on the correction for the spectral interference from iron on Cd 236.50 nm (19).

Synthetic Glass and Slags

The synthetic glass standard VS-N, prepared by the CRPG, was analyzed during the study for two purposes: the first objective was to examine the accuracy of the ICP-AES method at high concentrations in a silicate matrix, and the second was to verify that elements that are volatile are, or are not, lost during sample digestion. Only 0.5 g of sample was used because of the small amount of the sample available.

Major-element data, except for K₂O, agree well with published values within the analytical errors reported in Table 12.

Not all of the elements analyzed were added to the synthetic glass sample when it was made (59). Of those that were, the following agree within $\pm 5\%$ with the values reported by de la Roche and Govindaraju (59): Li, Sr, Ba, La, Ce, Zr, Cr, Co, Mo, Cd, and Sb. Values determined for V, Mn, Ni, Cu, and Zn are in error by less than 10% when compared with the reference values (59). The value for Pb is high by about 15% (1075:930, 59). Recoveries for both Sn (720:788, 59) and Bi (800:900, 59) are low. The reported value of Th in VS-N (180 ppm, 51) was not found using the ICP, and the value determined for As was <10 ppm.

The generalizations that can be made from this study are that accurate trace element determinations can be made at the ± 5 -10% level using the ICP-AES method, even in trace-element-rich rock matrices. Elemental loss due to the formation of volatile species during the sample-digestion procedure used in this study does not occur for any of the elements present at detectable levels in the synthetic glass sample. Separate experiments were run to check for losses of As, Sb, Sn, Cr, Cd, and Pb, using an artificial sample prepared from reagents, and recoveries for all elements were in the 90-110% range. No experiments have been run to check for volatile loss of Se. Data on As in the GX1-6 samples also indicate that As was retained in the solutions following digestion (60).

Results obtained on the three slags (Table 12) show a definite negative bias for a number of elements. This phenomenon is related to the amount of sample digested. The process is described in detail in a later section. Low recoveries of Ca, Mg, and Mn were observed in BCS-367; low recoveries were observed for all elements for which comparisons could be made with data from samples BCS-381 and BCS-382. Recoveries were generally in the 90-95% range, but for Cr and V, recoveries were in the 75-90% range (55).

Sedimentary Rocks

Analytical results for a number of sedimentary reference rocks are presented in Table 13. The samples include the two NBS limestone standards, the dolomite BCS-368, the magnesite BCS-319, the NBS phosphate rock, two laterites, the two U.S. Geological Survey (USGS-GRS-III) sediments, and the NBS coal and flyash samples. Little if any data, other than the values certified by the issuing agencies (55, 61), are available on the carbonate and phosphate rocks or the two laterites (55,

Table 12. ICP data on major, minor and trace elements in the glass VS-N and three slags from BAS¹ (BCS-367, BCS-381, BCS-382)

| Element ² or Oxide | VS-N ³ | | | BCS-367 | | | BCS-381 | | | BCS-382 | | |
|-------------------------------------|-------------------|---|-------|---------|---|-------|---------|---|-------|---------|---|-------|
| Na ₂ O | 6.11 | + | 0.20 | 0.469 | + | 0.02 | 0.281 | + | 0.01 | 0.122 | + | 0.004 |
| K ₂ O | >7.5 | + | | 1.18 | + | 0.03 | 0.075 | + | 0.004 | 0.071 | + | 0.004 |
| MgO | 4.52 | + | 0.14 | 6.71 | + | 0.21 | 0.907 | + | 0.03 | 10.12 | + | 0.31 |
| CaO | 4.38 | + | 0.14 | 30.53 | + | 1.05 | 43.35 | + | 1.60 | 30.42 | + | 1.06 |
| Fe ₂ O ₃ | 4.13 | + | 0.09 | 1.06 | + | 0.02 | 17.86 | + | 0.40 | 15.62 | + | 0.34 |
| Al ₂ O ₃ | 13.07 | + | 0.47 | 19.81 | + | 0.71 | 0.636 | + | 0.02 | 6.54 | + | 0.24 |
| TiO ₂ | 1.06 | + | 0.03 | 0.754 | + | 0.02 | 0.302 | + | 0.008 | 0.445 | + | 0.01 |
| P ₂ O ₅ | 0.02 | + | 0.005 | 0.138 | + | 0.004 | 14.37 | + | 0.36 | 1.09 | + | 0.03 |
| Li | 464 | + | 9.3 | -- | | | -- | | | -- | | |
| Be | 0.70 | + | 0.014 | -- | | | -- | | | -- | | |
| Sr | 753 | + | 15 | -- | | | -- | | | -- | | |
| Ba | 920 | + | 18 | 675 | + | 13 | 365 | + | 7.3 | 2510 | + | 50 |
| La | 830 | + | 17 | 200 | + | 6 | <10 | | | 13 | + | 4.0 |
| Ce | 825 | + | 17 | 530 | + | 11 | 30 | + | 1.5 | 70 | + | 2.0 |
| Nd | -- | | | -- | | | -- | | | -- | | |
| Sm | 8 | + | 2.0 | -- | | | -- | | | -- | | |
| Eu | <1.2 | | | -- | | | -- | | | -- | | |
| Gd | 18 | + | 0.5 | -- | | | -- | | | -- | | |
| Yb | 800 | + | 24 | -- | | | -- | | | -- | | |
| Zr | 765 | + | 23 | 455 | + | 14 | 9.0 | + | 1.0 | 134 | + | 4.0 |
| U | <40 | | | -- | | | -- | | | -- | | |
| Th | <50 | | | -- | | | -- | | | -- | | |
| V | 657 | + | 20 | 297 | + | 8.9 | 5185 | + | 160 | 650 | + | 20 |
| Cr | 654 | + | 20 | 126 | + | 3.8 | 1975 | + | 60 | 665 | + | 20 |
| Mn | 790 | + | 24 | 8400 | + | 250 | 22500 | + | 1200 | 66200 | + | 3300 |
| Co | 757 | + | 23 | 5.0 | + | 1.0 | 2.0 | + | 1.0 | 3.0 | + | 1.0 |
| Ni | 842 | + | 25 | 11 | + | 1.0 | 25 | + | 1.3 | 33 | + | 1.7 |
| Cu | 875 | + | 26 | 17 | + | 1.0 | <5 | | | 55 | + | 1.8 |
| Zn | 849 | + | 25 | 43 | + | 2.2 | 8.0 | + | 1.0 | 28 | + | 1.4 |
| Mo | 680 | + | 20 | <3 | | | <7 | | | <6 | | |
| W | -- | | | -- | | | -- | | | -- | | |
| Ag | <4 | | | -- | | | -- | | | -- | | |
| Au | <6 | | | -- | | | -- | | | -- | | |
| Cd | 850 | + | 25 | <2 | | | <2 | | | <2 | | |
| Sn | 720 | + | 22 | <3 | | | <3 | | | <3 | | |
| Pb | 1075 | + | 32 | <13 | | | 35 | + | 2 | 315 | + | 9.5 |
| Bi | 800 | + | 24 | <25 | | | <25 | | | <25 | | |
| As | <10 | | | <6 | | | <5 | | | <5 | | |
| Sb | 840 | + | 25 | <14 | | | <10 | | | <10 | | |
| Se | <50 | | | -- | | | -- | | | -- | | |

¹ Bureau of Analysed Samples, Ltd., Newham Hall, Newby, Middlebrough, Cleveland, England, TS8 9EA.

² Major elements expressed as weight percent oxide, total iron as Fe₂O₃; other elements expressed in parts per million.

³ Synthetic glass from K. Govindaraju, Centre de Recherches Pétrographiques et Géochimiques, C.O. N°1, 54500 Vandoeuvre-les-Nancy, France.

61), with the exception of the data on NBS-88a by Van der Sloot and Zonderhuis (51). In general, excellent agreement for the major, minor, and trace elements was achieved over very wide dynamic ranges (55, 61, 62). Values for Cr (11.7 ppm) and Co (3 ppm) in NBS-88a are high when compared with the data for these elements by Van der Sloot and Zonderhuis (51) (2 ppm and 0.4 ppm). As Cr 283.56 nm has a spectral interference from Mg (19), the high value reported here for the concentration of Cr may be due to the uncertainty from the Mg correction on this analytical channel. Certainly the high Cr values obtained for BCS-319, BCS-368, and NBS-1B would appear to support such a bias; however, the analysis of these samples using Cr 205.55 nm on a second instrument (19), where no Mg interference was found (Table 2), should have isolated this bias. Values measured on a second instrument were all in good agreement with values reported. An explanation for this discrepancy must await further study. The value measured for Co in NBS-88a also does not agree with that previously published (3:0.4, 51). Most of these samples have no reported trace-element determinations, and no further evaluation of the data reported in Table 13 can be made.

A detailed evaluation of U.S. Geological Survey samples MAG-1 and SCo-1 is not made here, but good agreement was obtained with the data of Thomas et al. (44) and Abbey (29)

for the values of Na₂O, K₂O, and MgO and with the data of Fabbri and Espos (28) for the remaining major elements. The value of 81 ppm for Li in MAG-1 is high with respect to reported values. Values for Ba for SCo-1 is low and for MAG-1 is high. Good comparisons can be made with published data for all the trace elements (28, 39-46).

Coal and Flyash

When larger amounts of material were digested, lower sample dilutions were needed; higher concentrations of elements in the final solution resulted in better sensitivity for the determination of trace elements in the NBS coal and NBS flyash samples.

Values obtained for the major elements present in these two samples are in good general agreement with data of Ondov et al. (63) and with the preliminary certificates of analysis (61). However, several discrepancies do exist. The values measured for MgO in both samples are low and are in better agreement with the HF bomb-digestion data of Ward and Marciello (64). The value of 1375 ppm Mg measured in this study is low with respect to the data of Ondov et al. (63) of 2000 ppm, and with respect to the values of 1500-1800 reported by Ward and Marciello (64). Likewise, the value of

Table 13. ICP data on major, minor and trace elements in some sedimentary rock reference samples (BCS-319, NBS-1B, NBS-368, BCS-88a, NBS-1208)

| Element ¹ or Oxide | Magnesite BCS-319 | | Argillaceous Ls. ² NBS-1B | | Dolomitic Ls. NBS-88a | | Dolomite BCS-368 | | Phosphate Rock NBS-1208 | |
|-------------------------------------|----------------------|---------|---|---------|--------------------------|----------|---------------------|----------|----------------------------|---------|
| | | | | | | | | | | |
| Na ₂ O | <0.013 | | 0.035 | + 0.002 | 0.014 | + 0.001 | 0.022 | + 0.002 | 0.355 | + 0.01 |
| K ₂ O | 0.027 | + 0.002 | 0.24 | + 0.006 | 0.12 | + 0.003 | <0.01 | + 0.002 | 0.141 | + 0.003 |
| MgO | 88.87 | + 2.75 | 0.339 | + 0.01 | 21.65 | + 0.67 | 21.35 | + 0.66 | 0.310 | + 0.01 |
| CaO | 2.34 | + 0.08 | 50.25 | + 1.66 | 29.32 | + 0.97 | 29.85 | + 0.99 | 49.03 | + 1.62 |
| Fe ₂ O ₃ | 4.55 | + 0.10 | 0.781 | + 0.02 | 0.293 | + 0.006 | 0.223 | + 0.005 | 1.13 | + 0.03 |
| Al ₂ O ₃ | 0.976 | + 0.03 | 1.07 | + 0.04 | 0.170 | + 0.006 | 0.170 | + 0.006 | 1.11 | + 0.04 |
| TiO ₂ | 0.031 | + 0.001 | 0.0487 | + 0.001 | 0.011 | + 0.0003 | 0.006 | + 0.0002 | 0.124 | + 0.003 |
| P ₂ O ₅ | 0.023 | + 0.001 | 0.086 | + 0.002 | 0.016 | + 0.001 | 0.008 | + 0.001 | 34.88 | + 0.87 |
| Li | <2 | | <2 | | <2 | | <2 | | <2 | |
| Be | 0.55 | + 0.05 | 0.42 | + 0.05 | 0.18 | + 0.02 | 0.11 | + 0.02 | 2.9 | + 0.06 |
| Sr | 31 | + 0.6 | 1208 | + 24 | 41 | + 0.8 | 76 | + 1.52 | 705 | + 14 |
| Ba | 26.3 | + 0.53 | 86 | + 1.7 | 13 | + 0.26 | 24.4 | + 0.49 | 61 | + 1.2 |
| La | 12 | + 1.0 | <5 | | <5 | | 8 | + 1.0 | 89 | + 4.0 |
| Ce | <15 | | <15 | | <15 | | 24 | + 1.0 | 182 | + 3.6 |
| Nd | <20 | | <20 | | <20 | | <20 | | 127 | + 25 |
| Sm | <5 | | <5 | | <5 | | <5 | | 38 | + 1.9 |
| Eu | 0.85 | + 0.05 | 1.7 | + 1.2 | 1.2 | + 0.6 | 1.14 | + 0.6 | 4.8 | + 1.0 |
| Gd | <2 | | <5 | | 3.4 | + 0.35 | 4.0 | + 0.4 | 21 | + 0.6 |
| Yb | 0.36 | + 0.04 | 2.1 | + 0.1 | 1.2 | + 0.04 | 1.15 | + 0.04 | 12.7 | + 0.4 |
| Zr | 10 | + 1.0 | 16 | + 1.0 | <1 | | 2.7 | + 0.5 | 12 | + 1.2 |
| U | <20 | | <30 | | <25 | | <25 | | <30 | |
| Th | <25 | | <25 | | <25 | | <25 | | <25 | |
| V | 28.4 | + 1.4 | 30.1 | + 1.4 | 9.0 | + 1.0 | 8.5 | + 1.0 | 103 | + 3.1 |
| Cr | 42.6 | + 1.3 | 15.7 | + 1.0 | 11.7 | + 1.0 | 37.0 | + 1.9 | 63.1 | + 1.9 |
| Mn | 1070 | + 32 | 1510 | + 45 | 210 | + 6.3 | 481 | + 15 | 260 | + 7.8 |
| Co | 32.1 | + 1.0 | 4.1 | + 1.0 | 3.0 | + 1.0 | 4.0 | + 1.0 | 3.0 | + 1.0 |
| Ni | 31.0 | + 1.6 | 11.0 | + 1.0 | <3 | | 5.0 | + 2.0 | 15.4 | + 1.0 |
| Cu | 8.9 | + 1.0 | 5.5 | + 1.0 | 2.5 | + 1.0 | 7.8 | + 1.0 | 8.6 | + 1.0 |
| Zn | 252 | + 7.6 | 40.7 | + 2.0 | 4.1 | + 1.0 | 78.0 | + 2.5 | 127 | + 3.9 |
| Mo | <3 | | <3 | | <3 | | <3 | | <5 | |
| W | -- | | -- | | -- | | -- | | -- | |
| Ag | <2 | | <5 | | <3 | | <3 | | 5 | |
| Au | <3 | | <3 | | <3 | | <3 | | <3 | |
| Cd | <5 | | <2 | | <2 | | <2 | | 22 | |
| Sn | <3 | | <3 | | <3 | | <3 | | <3 | |
| Pb | 23 | + 2 | 17 | + 2 | 27 | + 3.0 | 61 | + 3.0 | 25 | + 10.0 |
| Bi | <25 | | <25 | | <25 | | <25 | | <25 | |
| As | <5 | | <5 | | <5 | | <5 | | <5 | |
| Sb | <10 | | <10 | | <10 | | <10 | | 10 | |
| Se | <30 | | <30 | | <30 | | <30 | | <30 | |

1. Major elements expressed in %; trace elements in ppm.

2. National Bureau of Standards, Office of Standard Reference Materials, Room 8311, Chemistry Bldg., Washington, D.C.

Table 13 (Contd.). ICP data on major, minor and trace elements in some sedimentary rock reference samples (BCS-395, VL-1, MAG-1, SCO-1, NBS-1632, NBS-1633)

| Element or Oxide | Laterites | | Marine Mud | | Shale | | Coal | | Flyash | |
|--------------------------------|-----------|-------------------|--------------------|--------------------|----------|----------|-------|-------|--------|-------|
| | BCS-395 | VL-1 ³ | MAG-1 ⁴ | SCO-1 ⁴ | NBS-1632 | NBS-1633 | | | | |
| Na ₂ O | 0.114 | 0.060 | 3.83 | 0.12 | 0.054 | 0.001 | 0.054 | 0.001 | 0.404 | 0.01 |
| K ₂ O | 0.033 | 0.030 | 3.39 | 0.09 | 0.362 | 0.009 | 0.362 | 0.009 | 1.93 | 0.05 |
| MgO | 0.036 | 0.028 | 3.13 | 0.10 | 0.228 | 0.007 | 0.228 | 0.007 | 2.19 | 0.07 |
| CaO | 0.049 | 0.0091 | 1.37 | 0.05 | 0.579 | 0.019 | 0.579 | 0.019 | 6.50 | 0.21 |
| Fe ₂ O ₃ | 16.75 | 36.05 | 6.96 | 0.15 | 1.26 | 0.03 | 1.26 | 0.03 | 9.24 | 0.20 |
| Al ₂ O ₃ | 52.73 | 37.51 | 16.15 | 0.58 | 3.44 | 0.12 | 3.44 | 0.12 | 24.56 | 0.88 |
| TiO ₂ | 1.89 | 3.05 | 0.704 | 0.018 | 0.158 | 0.004 | 0.158 | 0.004 | 1.18 | 0.03 |
| P ₂ O ₅ | 0.152 | 0.142 | 0.166 | 0.005 | 0.034 | 0.002 | 0.034 | 0.002 | 0.250 | 0.006 |
| Li | -- | -- | 81 | 1.6 | 44 | 0.88 | 28.7 | 0.6 | 1.7 | 0.3 |
| Be | -- | -- | 3.27 | 0.07 | 1.94 | 0.04 | 1.7 | 0.03 | 12.6 | 0.25 |
| Sr | -- | -- | 142 | 2.8 | 167 | 3.3 | 140 | 2.8 | 1375 | 28 |
| Ba | 24 | 12 | 485 | 10 | 571 | 11 | -- | -- | -- | -- |
| La | 75 | -- | 43 | 1.0 | 28 | 1.0 | 9.3 | 0.3 | 79 | 1.6 |
| Ce | 200 | 103 | 80 | 2.5 | 65 | 2.0 | 22.8 | 0.5 | 157 | 3.2 |
| Nd | -- | -- | 34 | 7.0 | <20 | -- | 9.5 | 1.9 | 94 | 19 |
| Sm | -- | -- | 7.8 | 1.5 | <5 | -- | 1.3 | 0.2 | 15.8 | 0.3 |
| Eu | -- | -- | 1.7 | 0.1 | 1.1 | 0.1 | 0.42 | 0.02 | 3.0 | 0.15 |
| Gd | -- | -- | 6.1 | 0.6 | 4.0 | 0.4 | 1.2 | 0.06 | 12.1 | 0.36 |
| Yb | -- | -- | 2.3 | 0.07 | 2.2 | 0.07 | 0.67 | 0.02 | 6.1 | 0.18 |
| Zr | 447 | 427 | 112 | 3.5 | 115 | 3.5 | 25 | 0.75 | 223 | 6.7 |
| U | <30 | <50 | <20 | -- | <20 | -- | -- | -- | -- | -- |
| Th | <25 | <25 | <25 | -- | <25 | -- | -- | -- | -- | -- |
| V | 280 | 795 | 142 | 4.3 | 136 | 4.1 | 38.0 | 1.2 | 224 | 6.7 |
| Cr | 440 | 107 | 103 | 3.1 | 71.3 | 2.1 | 20.8 | 0.6 | 129 | 3.9 |
| Mn | 56.2 | 542 | 765 | 23 | 398 | 12 | 45.0 | 1.4 | 516 | 16 |
| Co | 6.3 | 3.8 | 21.8 | 1.0 | 10.9 | 1.0 | 3.9 | 0.2 | 41.0 | 1.2 |
| Ni | 50 | 30 | 57.5 | 1.7 | 30.0 | 1.5 | 15.2 | 0.5 | 100 | 3.0 |
| Cu | 22 | 92 | 24.6 | 0.8 | 27.5 | 1.4 | 17.2 | 0.5 | 128 | 3.9 |
| Zn | 38 | 47 | 137 | 4.1 | 106 | 3.2 | 40.0 | 1.2 | 228 | 6.9 |
| Mo | <7 | <10 | <5 | -- | <4 | -- | -- | -- | -- | -- |
| W | -- | -- | <7 | -- | <7 | -- | -- | -- | -- | -- |
| Ag | -- | -- | <2 | -- | <2 | -- | <0.2 | -- | <0.3 | -- |
| Au | -- | -- | <3 | -- | <3 | -- | <0.3 | -- | <0.3 | -- |
| Cd | <3 | <3 | <2 | -- | <2 | -- | <0.2 | -- | 1.5 | 0.5 |
| Sn | <6 | 20 | <3 | -- | <3 | -- | -- | -- | -- | -- |
| Pb | 40 | <20 | 22 | 9.0 | 28 | 9.0 | 28.5 | 1.5 | 64 | 13 |
| Bi | <25 | <25 | <25 | -- | <25 | -- | -- | -- | -- | -- |
| As | 70 | <10 | <6 | 5 | 15 | 5 | <10 | -- | 55 | 10 |
| Sb | <40 | <32 | <18 | -- | <14 | -- | <10 | -- | <10 | -- |
| Se | -- | -- | <30 | -- | <30 | -- | <10 | -- | <10 | -- |

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4 F. J. Flanagan, U.S. Geological Survey, MS 972, Reston, Va 22092.

1.3 weight percent Mg measured in the flyash sample (NBS-1633) is in good agreement with that measured by Ward and Marciello (1.3-1.4 weight percent, 64), but it is low with respect to the data of Floyd et al. and Ondov et al. (1.8 weight percent, 18, 63). I cannot rule out the possibility that the low recoveries of MgO may be due to the formation of the BaSO₄ precipitate during sample preparation. The sample preparation difficulties discussed for Ti (64) were not experienced in this study.

Values measured for Sr in the NBS flyash sample are in good agreement with the data of Ward and Marciello (1375:1360, 64) and the data of Giauque et al. (1375:1342, 65), but contrast with the value of 1700±400 ppm reported by Ondov et al. (63) and Floyd et al. (1620 ppm, 18). The rare-earth elements measured in both samples generally agree well with the data of Ondov et al. (63) and Giauque et al. (65), but the values of Eu in the flyash sample agrees with the values reported by Floyd et al. (2.1:3; 18). Abundances determined for the first-series transition metals agree well with published data (18, 63-65) and certificate of analysis values (61), except for the low recovery of Co (3.9:5.7, 63) in the NBS coal (1632).

Several of the toxic elements were also determined. Values obtained for Cd, As, and Pb are in good agreement with published values (18, 63-65) and with NBS certified values (61). The abundance of Se was at or below the limit of determination, and there was not sufficient sample for later analysis of Mo, W, Sn, Bi, and Sb on other instruments (19).

Soils

Results obtained on the four CCRMP reference soils, SO-1 to SO-4, are given in Table 14. The original intent of the author was that the data would be included in the initial compilation of data; however, the analytical work was not completed in time to meet the publication deadline (66). For the most part, the analytical results determined by the ICP-AES method agree very well with published mean values given by Bowman et al. (66). Some values determined for elements whose concentrations are not certified, however, do show real differences.

Major-element analytical results agree with the mean values within the ICP-AES error envelop except for the abundance of Na₂O in SO-1 (2.67:2.56, 66) and SO-2 (2.49:2.35, 66). The values determined in these two samples, however, lie within the reported spread of the round-robin data used for certification (18% and 16% respectively, reference 66, Table 3). A major disagreement was found in the value of TiO₂ for sample SO-1. The value using the ICP-AES method is 0.816 weight percent. The average value reported by Bowman et al. (66) is 0.884±0.036 weight percent; the ICP-AES results are low, and are outside the range of error permitted by the data sets. TiO₂ values for the remaining three soils agree well with published data. Measured values of TiO₂ in reference rocks at high concentrations showed a slight negative bias and may reflect incomplete dissolution and retention of the Ti metal in the standard solution (some TiCl₄ precipitate was observed). Recoveries for TiO₂ are low

Table 14. ICP data on major, minor and trace elements in four soil samples from the Geological Survey of Canada¹ (SO-1, SO-2, SO-3, SO-4)

| Element ² or Oxide | SO-1 | | SO-2 | | SO-3 | | SO-4 | |
|-------------------------------------|-------|----------|-------|---------|-------|---------|-------|---------|
| Na ₂ O | 2.67 | + 0.09 | 2.49 | + 0.08 | 1.01 | + 0.03 | 1.34 | + 0.04 |
| K ₂ O | 3.11 | + 0.07 | 2.89 | + 0.07 | 1.42 | + 0.04 | 2.05 | + 0.05 |
| MgO | 3.94 | + 0.12 | 0.908 | + 0.03 | 8.48 | + 0.26 | 0.974 | + 0.03 |
| CaO | 2.36 | + 0.08 | 2.68 | + 0.09 | 20.21 | + 0.67 | 1.58 | + 0.05 |
| Fe ₂ O ₃ | 8.40 | + 0.18 | 7.97 | + 0.18 | 2.18 | + 0.05 | 3.51 | + 0.08 |
| Al ₂ O ₃ | 17.42 | + 0.63 | 15.13 | + 0.55 | 5.76 | + 0.21 | 10.45 | + 0.38 |
| TiO ₂ | 0.816 | + 0.020 | 1.37 | + 0.03 | 0.323 | + 0.008 | 0.555 | + 0.014 |
| P ₂ O ₅ | 0.151 | + 0.0004 | 0.710 | + 0.018 | 0.103 | + 0.003 | 0.218 | + 0.005 |
| Li | 46 | + 2.0 | 8 | + 1.0 | 5.5 | + 2 | 17.8 | + 1.0 |
| Be | 2.04 | + 0.05 | 2.16 | + 0.05 | 0.82 | + 0.05 | 1.36 | + 0.05 |
| Sr | 327 | + 6.5 | 337 | + 6.7 | 222 | + 4.4 | 168 | + 3.4 |
| Ba | 873 | + 18 | 1015 | + 20 | 281 | + 5.6 | 762 | + 15 |
| La | 52 | + 1.0 | 45 | + 1.0 | 18 | + 1.7 | 29 | + 2.0 |
| Ce | 93 | + 2.0 | 112 | + 2.5 | <20 | | <70 | + 5.0 |
| Nd | 39 | + 8 | 59 | + 12 | <20 | | 23 | + 7 |
| Sm | 6 | + 2 | 10 | + 1.5 | <5 | | 6 | + 2 |
| Eu | 1.8 | + 0.1 | 3.6 | + 0.2 | 0.9 | + 0.3 | 1.1 | + 0.1 |
| Gd | 6 | + 0.3 | 12.4 | + 0.4 | 4.0 | + 0.4 | 5.3 | + 0.5 |
| Yb | 2.1 | + 0.06 | 3.15 | + 0.10 | 2.0 | + 0.06 | 1.75 | + 0.05 |
| Zr | 68 | + 2.0 | 143 | + 4.3 | 87 | + 2.6 | 139 | + 4.2 |
| U | <20 | | <20 | | <20 | | <20 | |
| Th | <25 | | <25 | | <25 | | <25 | |
| V | 131 | + 3.9 | 52.0 | + 1.5 | 35.0 | + 1.1 | 86.5 | + 2.6 |
| Cr | 169 | + 5.1 | 11.1 | + 1.1 | 28.1 | + 1.4 | 59.4 | + 1.8 |
| Mn | 906 | + 27 | 725 | + 22 | 530 | + 16 | 631 | + 19 |
| Co | 27.4 | + 1.4 | 7.0 | + 1.0 | 4.2 | + 1.0 | 9.5 | + 1.0 |
| Ni | 94.8 | + 2.8 | 8.4 | + 1.0 | 13.0 | + 1.3 | 25.5 | + 1.3 |
| Cu | 55.5 | + 1.7 | 2.4 | + 1.0 | 12.0 | + 1.2 | 18.1 | + 1.0 |
| Zn | 145 | + 4.4 | 122 | + 3.7 | 46.0 | + 1.4 | 95.7 | + 2.9 |
| Mo | <4 | | <4 | | <3 | | <3 | |
| W | <7 | | <7 | | <7 | | <7 | |
| Ag | <2 | | <2 | | <2 | | <2 | |
| Au | <3 | | <3 | | <3 | | <3 | |
| Cd | <2 | | <2 | | <3 | | <2 | |
| Sn | <3 | | <3 | | <3 | | 4 | + 1 |
| Pb | <13 | | 17 | + 10 | 11 | + 4 | 12 | + 6 |
| Bi | <25 | | <25 | | <25 | | <25 | |
| As | <6 | | <5 | | <5 | | 5 | + 2 |
| Sb | <18 | | <14 | | <10 | | <10 | |
| Se | <30 | | <30 | | <30 | | <30 | |

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² Major elements expressed as weight percent oxide, total iron as Fe₂O₃; other elements expressed in parts per million.

in a number of the reference igneous rocks by 3-5%, but not as much as 10%, as for sample SO-1. Data for the concentrations of the remaining major and minor elements agree well with mean values reported using a variety of analytical techniques (66).

Values for Li agree very well with the provisional values (reference 66, Table 4) for samples SO-1 (46:40), SO-2 (7.6:9), and SO-4 (17.8:18) but not as well ($5.5 \pm 2.9 \pm 3$) for SO-3. Values reported for Be do not agree with preliminary values in any of the samples, and they do not vary in any systematic way. The data available for comparison (66), however, are sparse. Rare-earth elements determined in all four samples agree remarkably well with provisional results, except for the values of Ce in SO-3 ($<20:34$) and SO-4 (70:54), and the ICP-AES results for Yb in all samples are systematically low. Considering that the ICP-AES results for Yb were generally high with respect to recently determined values for Yb at low concentrations, as discussed above, suggest that the provisional Yb abundances (66) are also somewhat high.

Zirconium values determined for all four samples are low in comparison with the data of Bowman et al. (66). Because these soils all come from granitic source terrains and because zircon appears on the liquidous of granitic melts, the low values for Zr in these soils might well have been anticipated on the basis of the discussion of the limitations of the sample-dissolution methods used. No measurable values of U or Th were detected.

Results on the first-series transition metals are in good agreement with provisional data, except for the abundance of Co which is systematically low in all samples, and for Cu in SO-2 (2.5:7, 66). Values determined for Pb in all samples are less than the provisional mean values reported (66), and the values for Sn and As in SO-4 are also below those reported by Bowman et al. (66).

EVALUATION OF THE INSTRUMENTAL METHOD

During the course of the analyses, samples G-2, GSP-1, AGV-1, and BCR-1 were run as control samples to monitor instrumental changes. The average change in the values determined in the control samples was less than 1% per hour (see Fig. 3; data span a four-hour period). Whereas these corrections have been applied to the data set reported here, the periodic analysis of check samples is adequate to monitor the accuracy of the results in routine analysis. Accuracy of the analytical results can be held within the precision stated so long as the total cation content of the unknowns is held within the 2100-2900 ppm total dissolved salts (TDS) in solution and the matrix calibration approach, discussed earlier, is followed. The accuracy achieved using the matrix calibration approach has been found to be superior to the serial dilution of standards used by earlier workers (e.g., 5, 67, 68). Figure 4 is a summary of the major element data showing percent recovery versus the total cation concentration in solution. Note that the major elements considered fall into two groups: Group 1--Na, K, and Al--show virtually no effect as a function of TDS, whereas Group 2--Mg, Ca, and Fe--show a decrease (or low recoveries) as a function of increasing TDS. These two groups are the elements determined using atom (Group 1) and ion (Group 2) emission lines. In spite of the fact that this relationship exists, accurate analytical results can be obtained for all of these elements so long as the range of concentration of TDS falls within the 2100-2900 ppm range for which the matrix

MATRIX CALIBRATION RANGE

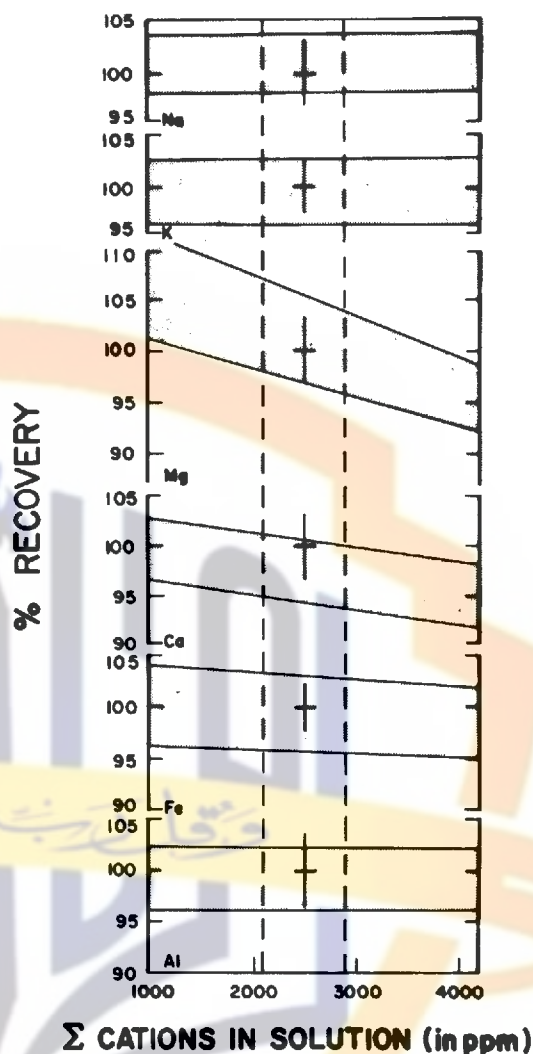


Figure 4. Diagram showing the percent recovery for the major elements whose concentrations were greater than 0.5 weight percent plotted against the sum of the cations present in the solutions prepared for analysis. Data obtained from atom-emission lines (Na, K, and Al) show no change in recovery as a function of total dissolved solids (TDS) or as a function of iron content. However, data obtained from ion-emission lines (Mg, Ca, and Fe) and V, Cr, and Mn (for the basic slags, not shown) indicate low recoveries for samples that contained TDS contents above the range of the matrix calibration method (2100-2900 ppm), and values measured for Mg in samples whose TDS was less than 2100 ppm systematically showed high recoveries relative to accepted values. A few outliers do occur in each data set, but the data clearly indicate the nature of the accuracy of the analysis relative to the TDS of the sample. Results obtained from the two basic slags (BCS-381, BCS-382, Table 12) are indicated by a plus (+) and generally fall below the trend

indicated by the rest of the data set. The error bar for each element is plotted at the center of the matrix calibration range (2500 ± 400 ppm) at 100% recovery to indicate the central region of highest accuracy for the matrix calibration method of ICP-AES analysis described here. Better results could have been obtained if the value of C for Ca of 99% and the value of C for Mg of 98% had been used (see Figure 3).

calibration scheme was designed. Shown in Figure 5 is the relationship between TDS of the rocks prepared according to the sliding weight scale, and the percent SiO_2 in the sample. (For carbonate rocks, the sum of SiO_2 and CO_2 were plotted). Note that a regular, linear relationship exists for the igneous rocks. The use of 0.8 g of the basic slags and the ultrabasic rocks and 1.2 g of granite was insufficient to keep the total TDS within the matrix calibration range. Shown in Figure 6 is the recommended weight of sample which should be used and the distribution of TDS in solution which would result. Note that most of the samples would fall in the range of 2100–2500 ppm. However, dissolution of 1.5–2.0 grams of granitic rock would have resulted in saturation of all of the acidic rock solutions with KClO_4 , rendering K indeterminate in the analysis. Only

0.5 g of sedimentary carbonate (C) and phosphate (P) rocks was dissolved in order to keep the Mg and Ca contents within the matrix calibration range (Table 4). For the soils, 1 g of sample was prepared, but for the laterites, only 0.6–0.7 g was digested. Adjustments of the amount of sample to be digested can be determined from Figure 6 if the rock type is known prior to analysis. Furthermore, the accuracy of the analysis of the unknown can be assured to fall within the analytical accuracy of the method as defined by the measurement precision of the instrument and the accuracy of the curve-fit routine (17), if careful attention is paid to the amount of sample prepared.

Analytical accuracy for trace elements determined in these samples is very dependent on the accuracy of the corrections for spectral interferences. A detailed discussion of the nature of these corrections (19) and their application to geologic samples has been given. The uncertainty of these spectral interference corrections adds to the uncertainty of the determination, although large errors do not occur until the correction for spectral interferences exceeds 70–80% of the total signal. An evaluation of particular analytical lines for geochemical analysis is given in Church (19).

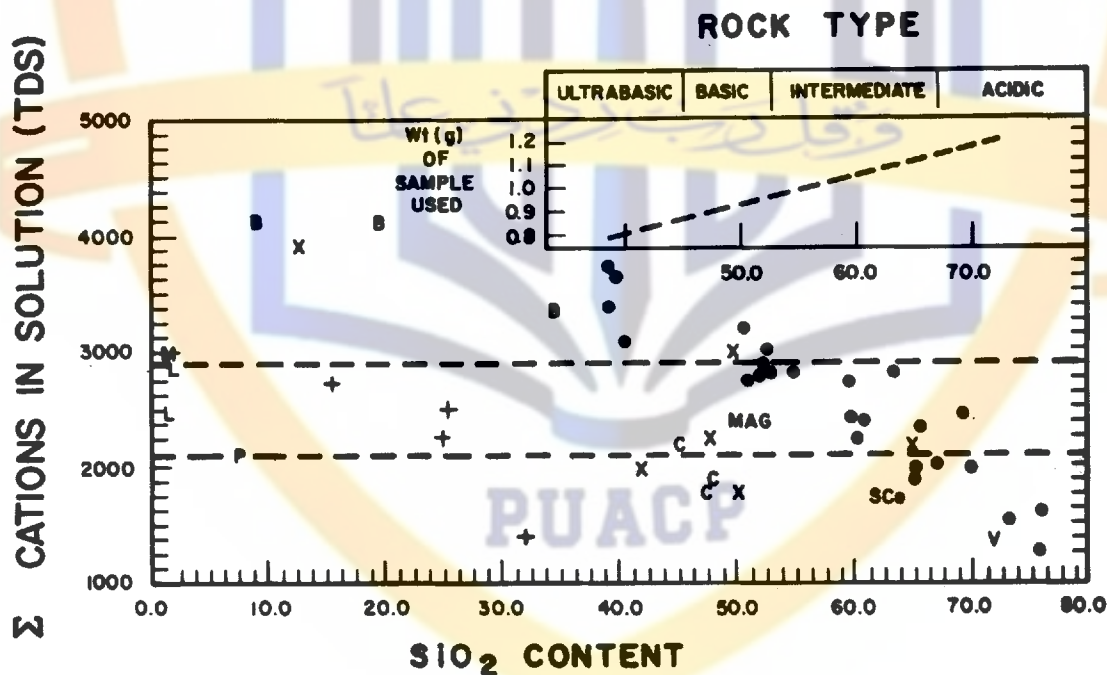


Figure 5. Diagram showing the relationship between TDS as the samples were prepared and percent SiO_2 , assigned by the issuing agency. The solid dots are the igneous rocks data, V represents the synthetic glass VS-N, and sedimentary rocks are coded by sample type: C = carbonate rock samples, P = phosphate rock, M = magnesite, L = laterite, and + or x = soil. The three slags are indicated by B. The matrix calibration range is shown by the dashed lines (2100–2900 ppm). Sample weights used for the silicate rocks are indicated in the inset in the upper right of the diagram. Note that the range of values (TDS) for the igneous rocks as analyzed falls outside the matrix calibration range at both the basic and acidic end-member compositions.

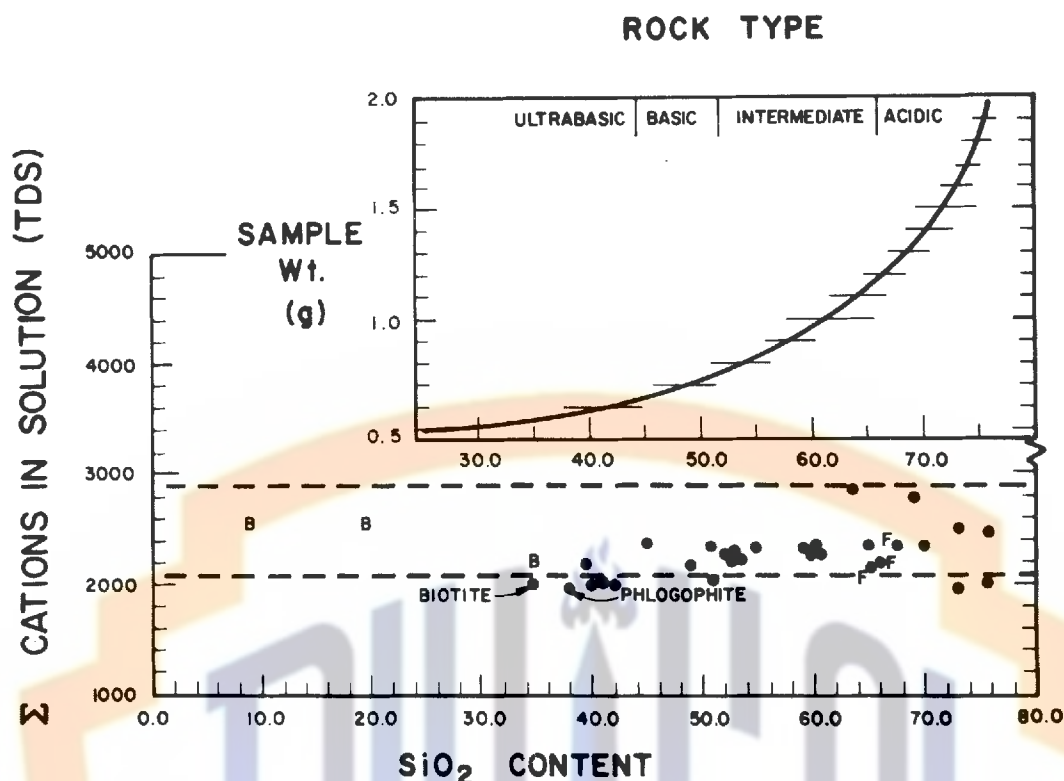


Figure 6. Diagram showing the proposed relationship that should be used to maintain a consistent TDS in unknowns for best results. The curve in the inset in the upper right indicates the weight versus SiO_2 content percent relationship necessary to maintain the TDS of igneous rocks within the matrix calibration band. The distribution of data points within the matrix calibration range shows the calculated TDS content of the solution as a function of SiO_2 for the reference igneous rocks and minerals using this function. The slags are represented by B and the feldspars by F. The biotite and phlogophite mica samples are also shown.

CONCLUSIONS

Accurate elemental-abundance determinations can be made in a wide variety of geological materials for 28 of the 40 elements studied using commercially available ICP-AES instrumentation. Such an instrument should contain the following features if rapid sample analysis is a primary objective:

1. The instrument should be a polychromator.
2. It must have adequate core memory to handle multiple regression curve-fit routines, to store and use a minimum of 200 spectral interference coefficients, and to complete data reduction during the analysis cycle.

However, based on the data obtained from these experiments, before accurate results can be routinely expected, the analyst must:

1. Use a matrix calibration scheme that maintains a constant TDS load in the plasma.

2. Prepare samples at concentrations that fall within the TDS range for which the matrix calibration method was designed.

3. Make accurate, empirical determinations of the spectral interference coefficients necessary for the correction of the data obtained from the particular secondary array.

The matrix-calibration scheme used in this study provides accurate results for samples analyzed so long as these basic approaches are followed. Major-element determinations made using the ICP-AES method are accurate to within $\pm 3.6\%$ or better, depending on the element. As far as the minor and trace elements are concerned, the estimated accuracy is of the order of 5 to 10% in most of the samples for the alkali (Li), the alkaline earth (Be, Sr, Ba), the rare-earth elements (La, Ce, Nd, Sm, Eu, Gd, Yb), and the first-series transition metals (V, Cr, Mn, Co, Ni, Cu, Zn). The concentration of Zr, providing it is not tied up in the mineral zircon, can also be determined to this level of accuracy using the

sample digestion procedures described. The concentration of Pb and Sn can be routinely determined in many rocks, but the accuracy of the determination is strongly dependent on the concentration of Al in the sample. The concentration of several other trace elements of economic interest (Mo, W, Ag, Au, Cd, As, Sb, Se, U, Th) can be determined if the concentration of the element in the sample is several times the crustal abundance of the element. Although the level of accuracy is not as high as can be obtained by X-ray fluorescence for the major elements, the ability of the ICP-AES method to determine the major and minor elements and many trace elements simultaneously with an accuracy of ± 2 -10% offers the analyst a distinct analytical advantage over other analytical schemes currently in use in geochemistry.

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RESUME

En utilisant la spectrométrie d'émission avec une source d'excitation à plasma à couplage inductif, 54 échantillons géochimiques de référence (roches, minéraux, sédiments, cendres) ont été analysés pour 40 éléments majeurs (sauf la silice) et en traces. L'analyse multi-élémentaire simultanée s'effectue après une seule préparation mais avec une simulation unique de la matrice. Le temps d'analyse est court, de l'ordre de 3 minutes, non compris le temps de dissolution. Les données obtenues sur les échantillons de référence indiquent une comparaison favorable avec les données publiées. Dix sept éléments en traces sur les 28 étudiés sont dosables couramment dans les roches communes mais la teneur d'autres éléments sont accessibles seulement si leur niveau de concentration est assez élevé par rapport à leur abondance dans la croûte terrestre.

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