## Determination of Major and Trace Elements in Japanese Rock Reference Samples by ICP-MS

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# DETERMINATION OF MAJOR AND TRACE ELEMENTS IN JAPANESE ROCK REFERENCE SAMPLES BY ICP-MS

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Analysis were made, using inductively coupled plasma-mass spectrometry (ICP-MS), to measure 59 major and trace elements in 6 rock reference samples, JB-1, JB-3, JG-1, JR-2, JGb-1 and JA-2, prepared and distributed by the Geological Survey of Japan (GSJ). Sample preparation and analytical conditions were investigated to set up a simple routine procedure for measuring a large range of elements. Detection limits, reproducibility, accuracy, dilution factors, possible interferences, and stability of standard solutions were also studied. For a prompt sample decomposition, a microwave digestion technique was successfully used with an acid mixture of HF, $HClO_4$ and $HNO_3$. Low background counts and the high sensitivity of ICP-MS provided extremely low detection limits for most elements (0.2–2 ng/l). Precisions were typically better than 5% RSD (relative standard deviation). Generally, the ICP-MS data presented here agreed well with the published GSJ consensus values. In about 40 elements, errors of measured values were less than 10% of the certified values, and for 52 elements, errors were less than 30%.

KEY WORDS: ICP-MS, trace elements, rock reference samples.

## INTRODUCTION

Major and trace elements in rock and soil samples have been analyzed for many purposes. Analyses of rare earth elements (REEs) in rock samples are geochemically important, because they are valuable indicators in petrogenetic studies[1]. Heavy metals such as Cr, Cu, Zn, Cd and Pb in soil samples have been analyzed by environmental chemists with regard to soil pollution[2]. Natural radionuclides such as U and Th in rock and soil are also important from a radiation protection viewpoint[3,4]. Analytical methods commonly used in the determination of these elements are neutron activation analysis (NAA), atomic absorption spectrometry (AAS), X-ray fluorescence (XRF), inductively coupled plasma-atomic emission spectrometry (ICP-AES), inductively coupled plasma-optic emission spectrometry (ICP-OES) and low background activity counting.

Recently inductively coupled plasma-mass spectrometry (ICP-MS) has been used for accurate and precise determination of trace elements in a variety of materials including geological and environmental samples[5]. The main advantages of ICP-MS over the classical methods are its lower detection limits, analytical speed and relative lack of chemical interferences. Due to its multi-element capability, Casetta *et al.*[6] measured 30 elements in rock samples, Jenner *et al.*[7] measured 28 elements in 7 different USGS rock standards, Alaimo and Censi[8] measured 47 elements in USGS rock standards, and Schönberg[9] measured 37 trace elements in 28 international rock standards. Soil samples

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were also analysed for more than 30 elements[10]. However, this method was usually applied in the determinations of specific group of elements such as REEs[11,12], Pt group elements[13], U and Th[14] and Zr, Nb, Hf and Ta[15], in rocks and soils.

In the present study, we have tried to develop a reliable method, including a sample dissolution procedure with a microwave oven, for the routine analysis of a large range of elements in geological materials. To validate the method, 6 Japanese rock reference samples were prepared as solutions and analyzed for 59 elements. Detection limits, reproducibility, accuracy, dilution factors, possible interferences, and stability of standard solutions are all discussed in this paper.

## MATERIALS AND METHODS

### Samples

Six rock reference samples, issued by the Geological Survey of Japan (GSJ), were used for the determinations. They were JB-1 (basalt), JB-3 (basalt), JG-1 (granodiorite), JR-2 (rhyolite), JGb-1 (gabbro) and JA-2 (andesite). Elemental composition data for major and trace elements in these samples were compiled by the GSJ as 1988 consensus values[16], and are regarded as certified values.

### Sample preparation

Rock samples (0.1 g) were dried at 110°C for 3 hours in an electric oven and then placed in Teflon™ PFA pressure decomposition vessels (CEM, liner type microwave decomposition vessel). To each sample, 5 mL $HNO_3$ (68%), 7.5 mL HF (38%) and 0.5–4.0 mL $HClO_4$ (70%) were added. All acids used were high purity acids, TAMAPURE-AA-100 (Tama Chemicals Co., Ltd.).

The sealed vessels were placed in a microwave digester (CEM, MDS-2000) and heated for 0.5–1 hour. For 9 vessels, the digester power was about 420 W. Pressure in the vessels usually reached about 70 psi. After cooling, the contents were transferred to Teflon™ beakers (50 mL) and evaporated to dryness on a hot plate (at about 150°C). Then, 1 mL $HNO_3$ was added, and the contents were heated to dryness again. The residues were dissolved in 2 mL (1:10) $HNO_3$ and made up to a 20 mL final volume, yielding the "original solutions". The dilution factor of this solution (ratio of the sample weight (g) included in the solution to the volume of the solution (mL)) was 1/200. Then, rock samples were omitted and the same procedures were followed to yield blank solution samples. Deionized water (> 17.8 MΩcm), produced with TORAYPURE (Toray, LV-308), was used throughout for rinsing and solution preparation. Bottles (polyethylene or polypropylene) were washed with 5% $HNO_3$ before use. Each original solution was diluted to four different factors. Major elements were measured by using 1/100,000 or 1/1,000,000 solutions. Trace elements were measured by 1/1000 and 1/10,000 solutions. Most of the elements which can be determined by ICP-MS were covered, excluded were P, Ca, Ru, Rh, Pd, Os and Ir. Although the concentrations of P and Ca in rock samples are high, their determinations by ICP-MS are difficult due to interference by oxides derived from the plasma gas, $H_2O$ and $HNO_3$. For Ru, Rh, Pd, Os and Ir, there are few published values and their concentrations were expected to be too low without any preconcentration procedures.

Expected concentrations of the elements in the solutions were in the range from 0.1 to 100 μg/l. Rhodium (20 μg/l) and/or In (20 μg/l) were used as internal standards to compensate for any changes in analytical signals and to improve measurement precision. Standard solutions were prepared from SPEX Multi-Element Plasma Standards (SPEX Industries Inc., XSTC-1, 7, 8 and 13) for making calibration curves. Concentrations of $HNO_3$ in the sample and standard solutions were 1%.

## ICP-MS instrumentation and data acquisition

The ICP-MS used for this work was the PMS-2000 (YOKOGAWA Analytical Systems, Tokyo, Japan), controlled by a personal computer and associated software. The instrumental parameters are summarized in Table 1. Under these conditions, the oxide formation level of Ce was found to be 0.5–2% ($CeO^+/Ce^+$). Isotope masses used for determination, and dwell time and analysis time for each element are given in Table 2.

## RESULTS AND DISCUSSION

### Stability of standard solutions

The standard solutions (1% $HNO_3$) containing the trace elements at 0.1 to 1 μg/l levels were found to be stable over a period of 9 days, except for Au and Hg which decreased 20–30% within 1 day from preparation. Stability of these elements might be improved if the acidity were maintained more than 1% $HNO_3$. However, high concentration of $HNO_3$ caused a loss of efficiency; counts decreased about 20% by using 5% $HNO_3$. This was due to inefficient sample introduction related to the high viscosity of the solution and drift of the signal during the measurements.Therefore, in the present study, the standard solutions were prepared with 1% $HNO_3$ just before taking measurements. Stability of

**Table 1**  Instrumental parameters for the ICP-MS.

| | |
|---|---|
| Plasma | |
|     Frequency (MHz) | 27.12 |
|     RF power (kW) | 1.2 |
| Argon flow (L/min) | |
|     Plasma | 14 |
|     Auxiliary | 1.2 |
|     Carrier | 0.83 |
| Sampling distance (mm) | 4.8 |
| Sample uptake rate (mL/min) | 0.8 |
| | |
| Data Acquisition | |
|     Mode | Peak jumping mode |
|     No. points per peak | 3 |
|     No. sweeps | 20 |
|     Dwell time per point | see Table 2 |
|     No. replicates | 3 |
|     Analysis time (min) | solution 1:1.5 |
| | solution 2:11 |
| | solution 3:8.0 |

**Table 2**   Isotope and time selected for analysis of each element.

| Elements | m/z | Dwell time (ms) | Time (s) | Elements | m/z | Dwell time (ms) | Time (s) |
|---|---|---|---|---|---|---|---|
| Major elements | | | | Trace elements | | | |
| Na | 23 | 100 | 2 | Sn | 120 | 200 | 4 |
| Mg | 24 | 100 | 2 | Sb | 121 | 500 | 10 |
| Al | 27 | 100 | 2 | Cs | 133 | 200 | 4 |
| K | 39 | 100 | 2 | Ba | 138 | 100 | 2 |
| Ti | 47 | 200 | 4 | La | 139 | 100 | 2 |
| Mn | 55 | 100 | 2 | Ce | 140 | 100 | 2 |
| Fe | 57 | 200 | 4 | Pr | 141 | 100 | 2 |
| Trace elements | | | | Nd | 146 | 100 | 2 |
| Li | 7 | 100 | 2 | Sm | 147 | 200 | 4 |
| Be | 9 | 500 | 10 | Eu | 153 | 200 | 4 |
| Sc | 45 | 100 | 2 | Gd | 157 | 200 | 4 |
| V | 51 | 100 | 2 | Tb | 159 | 200 | 4 |
| Cr | 52 | 100 | 2 | Dy | 164 | 200 | 4 |
| Co | 59 | 100 | 2 | Ho | 165 | 200 | 4 |
| Ni | 60 | 100 | 2 | Er | 166 | 200 | 4 |
| Cu | 63 | 100 | 2 | Tm | 169 | 200 | 4 |
| Zn | 66 | 100 | 2 | Yb | 174 | 200 | 4 |
| Ga | 71 | 100 | 2 | Lu | 175 | 200 | 4 |
| Ge | 74 | 500 | 10 | Hf | 178 | 500 | 10 |
| As | 75 | 500 | 10 | Ta | 181 | 500 | 10 |
| Se | 82 | 500 | 10 | W | 182 | 500 | 10 |
| Rb | 85 | 100 | 2 | Re | 185 | 500 | 10 |
| Sr | 88 | 100 | 2 | Pt | 195 | 500 | 10 |
| Y | 89 | 100 | 2 | Au | 197 | 500 | 10 |
| Zr | 90 | 100 | 2 | Hg | 202 | 500 | 10 |
| Nb | 93 | 100 | 2 | Tl | 205 | 500 | 10 |
| Mo | 95 | 500 | 10 | Pb | 208 | 200 | 4 |
| Ag | 107 | 500 | 10 | Bi | 209 | 500 | 10 |
| Cd | 113 | 500 | 10 | Th | 232 | 200 | 4 |
| In | 115 | 500 | 10 | U | 238 | 500 | 10 |

most elements in the samples was much better than that of the standard ones, because of their high matrix concentrations.

*Calibration curve and detection limits*

The calibration curves were usually made in concentration ranges of 0.01–10 µg/l for trace elements and 1–100 µg/l for major elements, and good linearities were observed with most elements. But for $^{23}$Na, $^{27}$Al, $^{39}$K and $^{57}$Fe, linearity were observed at concentrations above 5 µg/l because of high background counts at these masses as mentioned below.

The calibration curve for $^{202}$Hg was not linear over the concentration range measured. The Hg was easily retained in the sample passages, e.g. the tube of the peristaltic pump, the neblizer and the spray chamber. This memory effect made determination of Hg difficult. A relatively high memory was also observed in the determination of Th, although the calibration curve was linear. After measurements of the 10 µg/l standard solution ($^{232}$Th; ca. 80,000 count/s), the background count increased from 15 to 200

count/s, and this affected the analysis of Th in the rock reference samples. However, this memory could be removed by injecting 5% $HNO_3$ for 2 min. The memory of Th was not observed after measurement of reference samples which contained 0.05–3 µg/l of Th. The matrix elements contained in the sample solutions might be reducing the memory of Th, i.e. Th might not be adsorbed on the inner surface of the path tubes due to high concentrations of coexisting elements.

The approximate detection limit for each element was calculated by using the counts obtained from 1% $HNO_3$ solution (blank) and 10 µg/l multi-element standard solutions under the normal operation conditions. Low background and high sensitivity of the ICP-MS yielded the extremely low detection limits in most elements (0.2–2 ng/l). However, in real sample solutions containing high matrix concentrations, the detection limits were poorer than the values. Relatively high detection limits (10–150 ng/l) were observed for Na, Al, K, Fe, Ti, Cr, Cu, Zn and Se. They were due to the high background counts for these masses. The high background counts for $^{39}$K, $^{57}$Fe, $^{52}$Cr and $^{82}$Se were due to interference from plasma gas, i.e. $^{38}$Ar$^1$H$^+$ and $^{23}$Na$^{16}$O$^+$ for $^{39}$K, $^{40}$Ar$^{16}$O$^1$H$^+$ for $^{57}$Fe, $^{40}$Ar$^{12}$C$^+$ for $^{52}$Cr and $^{82}$Kr$^+$ for $^{82}$Se. Some elevation of Na, Al, Ti, Cu and Zn concentrations in the blank solution might result from contamination during sample preparation and measurement and impurities in water. $HNO_3$ and internal standards. However, such potential contamination was negligibly small compared to the concentration in the sample solutions.

*Analysis of reference samples*

Analytical results and their related standard deviations are reported along with the 1988 GSJ consensus values in Table 3. The major elements in the table were mostly determined by using 1/1,000,000 solutions, and trace elements were determined by using 1/10,000 solutions. For K in JB-1, JB-3, JR-2 and JGb-1, and Mg and Fe in JR-2, the results obtained from 1/100,000 solutions were listed because of relatively low concentrations in the reference samples. The results for trace elements determined by using 1/1000 solutions are not listed in the table, because their accuracies were generally poorer, as mentioned below.

Precisions calculated using three (or two for JA-2) independent runs of these samples were typically better than 5% RSD (relative standard deviation) for most trace elements. The RSDs for major elements tended to be high (usually 10–20%). The high background counts as mentioned above might cause the high RSD values. For some trace elements (i.e. Ag, Hg, Tl and Re in JB-1, Sn and W in JB-3, Pt, Cu and U in JG-1, V, Co and Ni in JR-2, Hg, Sn and Se in JGb-1, Cd in JA-2) the RSDs were higher than 20%. Their high RSD values might be attributable to the low concentrations of these elements. For example, the highest RSD for Ni was observed in JR-2 (62.4%), and it had the lowest Ni concentration of all the reference samples analyzed.

Trace elements were measured by using both 1/10,000 and 1/1000 solutions. Accuracies of many elements depended on the dilution factor of the solution used for measurements. For example, analytical results of U obtained from 1/10,000 solutions agreed well with the consensus values, while those obtained from 1/1000 solutions tended to be about 30% larger. Other elements such as lanthanide elements, Tl, Pb, and Th showed the same tendency. In the 1/1000 solutions, high concentrations of major elements (e.g. 70–90 mg/l of Al, 3–90 mg/l of Ca) were presented. High matrix concentrations are known to cause a change in sensitivity[17]. The effects can originate in the aerosol generation and transport processes or in the plasma itself. An accumulation of

**Table 3**  Analytical results obtained by ICP-MS in comparison with consensus values.

|     | JB-1 | | | | JB-3 | | | |
| --- | --- | --- | --- | --- | --- | --- | --- | --- |
|     | Mean (μg/g) | RSD (%) | Consensus (μg/g) | Mean/ Consensus | Mean (μg/g) | RSD (%) | Consensus (μg/g) | Mean/ Consensus |
| Na | 19400 | 10.0 | 20700 | 0.94 | 18700 | 7.1 | 20900 | 0.89 |
| Mg | 42800 | 9.8 | 46600 | 0.92 | 28000 | 8.0 | 31400 | 0.89 |
| Al | 73800 | 9.3 | 76900 | 0.96 | 85900 | 6.0 | 89300 | 0.96 |
| K | 11307 | 4.2 | 11900 | 0.95 | 5892 | 3.5 | 6470 | 0.91 |
| Ti | 7920 | 13.2 | 8030 | 0.99 | 7270 | 9.6 | 8690 | 0.84 |
| Mn | 1030 | 13.7 | 1240 | 0.83 | 1200 | 11.3 | 1240 | 0.97 |
| Fe | 60900 | 11.2 | 62600 | 0.97 | 85100 | 18.7 | 83100 | 1.02 |
| Li | 10.1 | 1.7 | 11.5 | 0.88 | 7.02 | 0.9 | 7.2 | 0.98 |
| Be | 1.30 | 1.9 | 1.5 | 0.86 | 0.64 | 1.6 | 0.74 | 0.86 |
| Sc | 26.8 | 1.5 | 27.4 | 0.98 | 33.0 | 2.2 | 35 | 0.94 |
| V | 226 | 2.7 | 212 | 1.07 | 414 | 1.9 | 383 | 1.08 |
| Cr | 429 | 1.6 | 469 | 0.91 | 60.2 | 3.1 | 60.4 | 1.00 |
| Co | 38.8 | 2.1 | 38.7 | 1.00 | 38.3 | 0.5 | 36.3 | 1.06 |
| Ni | 138 | 1.6 | 139 | 0.99 | 40.3 | 2.2 | 38.8 | 1.04 |
| Cu | 53.2 | 0.4 | 56.3 | 0.94 | 198 | 1.2 | 198 | 1.00 |
| Zn | 93.3 | 0.8 | 83 | 1.12 | 119 | 0.9 | 106 | 1.12 |
| Ga | 19.4 | 0.6 | 18.1 | 1.07 | 20.7 | 1.6 | 20.7 | 1.00 |
| Ge | 1.64 | 5.2 | 0.8 | 2.05 | 1.57 | 3.0 | 0.72 | 2.18 |
| As | 6.15 | 1.7 | 2.48 | 2.48 | 5.74 | 0.3 | 1.66 | 3.46 |
| Se | < 0.7 | – | 0.026 | 26.92 | < 0.7 | – | 0.08 | 8.75 |
| Rb | 52.5 | 1.5 | 41.2 | 1.27 | 19.5 | 2.4 | 13 | 1.50 |
| Sr | 435 | 1.4 | 435 | 1.00 | 408 | 1.7 | 395 | 1.03 |
| Y | 20.5 | 1.1 | 24 | 0.85 | 23.4 | 2.7 | 28 | 0.84 |
| Zr | 128 | 1.7 | 143 | 0.90 | 90.3 | 2.5 | 99.4 | 0.91 |
| Nb | 34.2 | 3.2 | 34.5 | 0.99 | 2.13 | 5.8 | 2.3 | 0.93 |
| Mo | 23.7 | 7.6 | 34 | 0.70 | 1.23 | 2.9 | 1.1 | 1.12 |
| Ag | 0.034 | 60.4 | 0.041 | 0.83 | < 0.007 | – | – | – |
| Cd | 0.091 | 2.9 | 0.103 | 0.89 | 0.059 | 10.1 | 0.082 | 0.72 |
| In | 0.070 | 1.8 | 0.0523 | 1.33 | 0.076 | 2.3 | 0.0622 | 1.23 |
| Sn | 2.05 | 4.4 | 1.8 | 1.14 | 1.46 | 23.8 | 0.86 | 1.70 |
| Sb | 0.31 | 3.9 | 0.35 | 0.89 | 0.10 | 3.4 | 0.15 | 0.69 |
| Cs | 1.39 | 0.4 | 1.19 | 1.17 | 0.98 | 1.9 | 1.1 | 0.89 |
| Ba | 492 | 0.9 | 490 | 1.00 | 239 | 2.0 | 251 | 0.95 |
| La | 37.1 | 0.9 | 38 | 0.98 | 8.53 | 2.6 | 9.1 | 0.94 |
| Ce | 65.3 | 1.0 | 67 | 0.97 | 21.2 | 1.8 | 20.5 | 1.03 |
| Pr | 7.06 | 1.1 | 7.5 | 0.94 | 3.26 | 2.2 | 3.2 | 1.02 |
| Nd | 25.0 | 1.4 | 27 | 0.93 | 15.1 | 1.7 | 16.6 | 0.91 |
| Sm | 4.84 | 0.9 | 5 | 0.97 | 4.05 | 2.1 | 4.3 | 0.94 |
| Eu | 1.57 | 1.3 | 1.52 | 1.03 | 1.36 | 1.8 | 1.3 | 1.04 |
| Gd | 5.14 | 1.5 | 4.7 | 1.09 | 4.47 | 1.1 | 4.6 | 0.97 |
| Tb | 0.71 | 1.8 | 0.76 | 0.94 | 0.73 | 1.7 | 0.82 | 0.89 |
| Dy | 3.84 | 1.3 | 4 | 0.96 | 4.27 | 1.9 | 4.4 | 0.97 |
| Ho | 0.79 | 1.7 | 0.7 | 1.12 | 0.90 | 2.0 | 0.84 | 1.07 |
| Er | 2.18 | 2.3 | 2.2 | 0.99 | 2.54 | 1.7 | 2.5 | 1.01 |
| Tm | 0.32 | 1.3 | 0.35 | 0.92 | 0.38 | 1.9 | 0.5 | 0.75 |
| Yb | 1.96 | 2.0 | 2.1 | 0.94 | 2.37 | 2.3 | 2.4 | 0.99 |
| Lu | 0.30 | 3.0 | 0.31 | 0.96 | 0.36 | 3.0 | 0.38 | 0.95 |
| Hf | 3.43 | 1.4 | 3.4 | 1.01 | 2.72 | 1.6 | 2.7 | 1.01 |
| Ta | 2.24 | 5.8 | 2.7 | 0.83 | 0.16 | 4.5 | 0.15 | 1.07 |
| W | 17.5 | 6.1 | 20 | 0.88 | 2.07 | 22.8 | 0.9 | 2.30 |
| Re | 0.002 | 26.5 | 0.0049 | 0.45 | < 0.002 | – | – | – |

*Continued*

**Table 3** Continued.

| | JB-1 | | | | JB-3 | | | |
|---|---|---|---|---|---|---|---|---|
| | Mean (µg/g) | RSD (%) | Consensus (µg/g) | Mean/ Consensus | Mean (µg/g) | RSD (%) | Consensus (µg/g) | Mean/ Consensus |
| Pt | 0.012 | 5.1 | – | – | 0.01 | 18.8 | – | – |
| Au | 0.19 | 4.8 | 0.0007 | 269.18 | 0.13 | 1.0 | 0.0021 | 64.19 |
| Hg | 0.23 | 60.0 | 0.028 | 8.08 | < 0.04 | – | – | – |
| Tl | 0.024 | 31.1 | 0.11 | 0.22 | < 0.005 | – | 0.05 | 0.10 |
| Pb | 6.77 | 1.7 | 7.1 | 0.95 | 5.03 | 1.1 | 5.5 | 0.91 |
| Bi | 0.028 | 13.0 | 0.031 | 0.92 | 0.017 | 15.6 | 0.02 | 0.84 |
| Th | 9.09 | 1.3 | 9.2 | 0.99 | 1.33 | 3.5 | 1.3 | 1.03 |
| U | 1.57 | 1.0 | 1.7 | 0.92 | 0.46 | 1.9 | 0.46 | 1.00 |

| | JG-1 | | | | JR-2 | | | |
|---|---|---|---|---|---|---|---|---|
| | Mean (µg/g) | RSD (%) | Consensus (µg/g) | Mean/ Consensus | Mean (µg/g) | RSD (%) | Consensus (µg/g) | Mean/ Consensus |
| Na | 22000 | 9.9 | 25200 | 0.87 | 26500 | 7.6 | 29900 | 0.89 |
| Mg | 3590 | 21.0 | 4460 | 0.80 | 339 | 3.8 | 302 | 1.12 |
| Al | 64700 | 10.4 | 75100 | 0.86 | 57400 | 17.6 | 67800 | 0.85 |
| K | 26200 | 15.0 | 33000 | 0.79 | 34386 | 3.1 | 36900 | 0.93 |
| Ti | 1360 | 12.1 | 1560 | 0.87 | 373 | 24.8 | 539 | 0.69 |
| Mn | 389 | 15.4 | 488 | 0.80 | 690 | 17.3 | 851 | 0.81 |
| Fe | 12200 | 14.8 | 15400 | 0.79 | 5144 | 1.1 | 6000 | 0.86 |
| Li | 75.4 | 0.7 | 85.9 | 0.88 | 76.5 | 2.5 | 83 | 0.92 |
| Be | 2.99 | 2.8 | 3.1 | 0.96 | 3.61 | 2.4 | 3.4 | 1.06 |
| Sc | 6.15 | 0.6 | 6.5 | 0.95 | 4.95 | 9.9 | 5.4 | 0.92 |
| V | 28.3 | 1.6 | 25 | 1.13 | 40.7 | 138.3 | < 8 | – |
| Cr | 50.6 | 3.1 | 64.6 | 0.78 | 1.37 | 18.8 | 2.6 | 0.53 |
| Co | 3.87 | 1.2 | 4 | 0.97 | 0.032 | 96.7 | 0.4 | 0.08 |
| Ni | 6.23 | 1.4 | 6 | 1.04 | 0.49 | 62.4 | 0.84 | 0.59 |
| Cu | 0.40 | 36.3 | 1.5 | 0.26 | 1.21 | 9.4 | 1.4 | 0.87 |
| Zn | 45.2 | 0.8 | 41.5 | 1.09 | 30.2 | 2.2 | 27.2 | 1.11 |
| Ga | 18.1 | 1.2 | 17 | 1.06 | 18.5 | 2.4 | 18.2 | 1.02 |
| Ge | 1.87 | 6.1 | 1.7 | 1.10 | 2.84 | 4.0 | 2.4 | 1.18 |
| As | 1.65 | 8.4 | 0.36 | 4.60 | 19.6 | 1.5 | 19.5 | 1.01 |
| Se | < 0.7 | – | 0.0028 | 250.00 | 1.80 | 14.4 | 0.0026 | 690.67 |
| Rb | 234 | 0.5 | 181 | 1.29 | 392 | 1.8 | 297 | 1.32 |
| Sr | 182 | 1.1 | 184 | 0.99 | 7.40 | 10.3 | 8 | 0.92 |
| Y | 17.6 | 7.3 | 30 | 0.59 | 39.0 | 15.6 | 51 | 0.76 |
| Zr | 40.4 | 8.7 | 108 | 0.37 | 85.9 | 1.8 | 98.5 | 0.87 |
| Nb | 11.1 | 1.2 | 12.6 | 0.88 | 17.6 | 1.9 | 19.2 | 0.92 |
| Mo | 1.08 | 11.1 | 1.46 | 0.74 | 2.88 | 3.0 | 2.9 | 0.99 |
| Ag | < 0.007 | – | 0.026 | 0.27 | 0.18 | 1.5 | – | – |
| Cd | 0.008 | 18.9 | 0.037 | 0.21 | 0.025 | 19.0 | 0.019 | 1.32 |
| In | 0.063 | 2.7 | 0.0398 | 1.58 | 0.060 | 2.5 | – | – |
| Sn | 4.52 | 4.7 | 4.1 | 1.10 | 3.56 | 12.9 | 3.2 | 1.11 |
| Sb | 0.054 | 1.5 | 0.08 | 0.68 | 1.41 | 2.0 | 1.83 | 0.77 |
| Cs | 10.6 | 0.8 | 10.2 | 1.04 | 26.4 | 2.1 | 26 | 1.02 |
| Ba | 467 | 0.6 | 462 | 1.01 | 28.2 | 6.7 | 39 | 0.72 |
| La | 22.8 | 14.4 | 23 | 0.99 | 13.9 | 14.0 | 17.5 | 0.79 |
| Ce | 49.5 | 15.6 | 46.6 | 1.06 | 36.2 | 8.6 | 38 | 0.95 |
| Pr | 5.67 | 15.8 | 4.5 | 1.26 | 4.51 | 11.7 | 5.5 | 0.82 |

*Continued*

**Table 3** Continued.

| | JG-1 | | | | JR-2 | | | |
|---|---|---|---|---|---|---|---|---|
| | Mean (μg/g) | RSD (%) | Consensus (μg/g) | Mean/ Consensus | Mean (μg/g) | RSD (%) | Consensus (μg/g) | Mean/ Consensus |
| Nd | 20.5 | 15.3 | 20 | 1.03 | 17.2 | 11.6 | 24.8 | 0.69 |
| Sm | 4.71 | 14.0 | 5.1 | 0.92 | 4.82 | 12.5 | 6.2 | 0.78 |
| Eu | 0.81 | 0.3 | 0.76 | 1.07 | 0.12 | 9.6 | 0.13 | 0.89 |
| Gd | 4.48 | 10.5 | 3.7 | 1.21 | 5.07 | 13.2 | 7.8 | 0.65 |
| Tb | 0.67 | 8.0 | 0.84 | 0.80 | 0.93 | 12.8 | 1.2 | 0.77 |
| Dy | 3.48 | 7.0 | 4.6 | 0.76 | 5.85 | 13.9 | 7.7 | 0.76 |
| Ho | 0.66 | 6.4 | 0.95 | 0.70 | 1.27 | 13.7 | 1.7 | 0.75 |
| Er | 1.80 | 7.7 | 1.69 | 1.07 | 3.99 | 13.6 | 5.2 | 0.77 |
| Tm | 0.28 | 6.7 | 0.5 | 0.56 | 0.67 | 13.2 | 0.86 | 0.78 |
| Yb | 1.74 | 6.7 | 2.7 | 0.64 | 4.72 | 12.2 | 5.4 | 0.87 |
| Lu | 0.26 | 4.9 | 0.46 | 0.57 | 0.73 | 12.0 | 0.92 | 0.80 |
| Hf | 1.90 | 8.6 | 3.5 | 0.54 | 5.29 | 1.6 | 5.2 | 1.02 |
| Ta | 1.41 | 0.9 | 1.7 | 0.83 | 1.94 | 1.7 | 2.4 | 0.81 |
| W | 1.36 | 5.3 | 1.7 | 0.80 | 3.15 | 7.6 | – | – |
| Re | < 0.002 | – | 0.000098 | 20.41 | < 0.002 | – | – | – |
| Pt | 0.003 | 76.6 | – | – | 0.02 | 5.4 | 5.5 | 0.004 |
| Au | 0.16 | 2.6 | 0.00013 | 1234.27 | 0.17 | 2.3 | – | – |
| Hg | < 0.04 | – | 0.016 | 2.50 | 0.16 | 18.7 | 0.0002 | 780.51 |
| Tl | 0.90 | 0.9 | 1 | 0.90 | 1.85 | 2.4 | 1.8 | 1.03 |
| Pb | 25.9 | 0.3 | 26.2 | 0.99 | 21.9 | 2.7 | 21.9 | 1.00 |
| Bi | 0.45 | 3.4 | 0.52 | 0.87 | 0.68 | 2.8 | 0.65 | 1.05 |
| Th | 15.2 | 17.2 | 13.5 | 1.13 | 27.2 | 16.1 | 32.2 | 0.84 |
| U | 3.53 | 28.0 | 3.3 | 1.07 | 10.9 | 3.5 | 10.5 | 1.04 |

| | JGb-1 | | | | JA-2 | | | |
|---|---|---|---|---|---|---|---|---|
| | Mean (μg/g) | RSD (%) | Consensus (μg/g) | Mean/ Consensus | Mean (μg/g) | RSD (%) | Consensus (μg/g) | Mean/ Consensus |
| Na | 8320 | 8.3 | 9130 | 0.91 | 22000 | 2.9 | 22900 | 0.96 |
| Mg | 43700 | 3.8 | 47200 | 0.93 | 43300 | 2.7 | 46300 | 0.94 |
| Al | 89400 | 5.2 | 93400 | 0.96 | 80400 | 2.6 | 81000 | 0.99 |
| K | 1614 | 5.3 | 1990 | 0.81 | 11500 | 1.2 | 14900 | 0.77 |
| Ti | 8910 | 8.9 | 9700 | 0.92 | 3820 | 2.8 | 4010 | 0.95 |
| Mn | 1330 | 6.4 | 1320 | 1.01 | 723 | 3.3 | 851 | 0.85 |
| Fe | 111000 | 8.8 | 106000 | 1.05 | 43800 | 2.2 | 42900 | 1.02 |
| Li | 4.36 | 0.8 | 4.3 | 1.01 | 27.0 | 1.2 | 28.7 | 0.94 |
| Be | 0.32 | 0.6 | 0.36 | 0.89 | 2.05 | 0.7 | 2.2 | 0.93 |
| Sc | 24.9 | 62.4 | 35 | 0.71 | 19.4 | 2.3 | 19 | 1.02 |
| V | 883 | 0.2 | 640 | 1.38 | 170 | 1.4 | 130 | 1.31 |
| Cr | 61.7 | 1.9 | 59.3 | 1.04 | 457 | 0.1 | 465 | 0.98 |
| Co | 65.9 | 0.9 | 61.6 | 1.07 | 31.7 | 1.6 | 30 | 1.06 |
| Ni | 29.1 | 1.1 | 25.4 | 1.15 | 154 | 1.0 | 142 | 1.08 |
| Cu | 90.3 | 1.2 | 86.8 | 1.04 | 30.2 | 1.5 | 28.6 | 1.06 |
| Zn | 125 | 0.4 | 111 | 1.13 | 72.3 | 1.5 | 62.7 | 1.15 |
| Ga | 19.2 | 0.5 | 18.9 | 1.02 | 17.5 | 2.0 | 16.4 | 1.07 |
| Ge | 1.32 | 2.6 | 0.84 | 1.57 | 1.37 | 3.6 | – | – |
| As | 5.89 | 4.0 | 1.11 | 5.30 | 3.30 | 0.2 | 0.77 | 4.29 |
| Se | 0.78 | 19.7 | 0.17 | 4.62 | 0.86 | 9.2 | – | – |
| Rb | 8.50 | 3.6 | 4 | 2.13 | 92.6 | 1.7 | 68 | 1.36 |

*Continued*

**Table 3** Continued.

| | JGb-1 | | | | JA-2 | | | |
|---|---|---|---|---|---|---|---|---|
| | Mean (μg/g) | RSD (%) | Consensus (μg/g) | Mean/ Consensus | Mean (μg/g) | RSD (%) | Consensus (μg/g) | Mean/ Consensus |
| Sr | 369 | 1.0 | 321 | 1.15 | 271 | 1.8 | 252 | 1.08 |
| Y | 9.01 | 1.3 | 11 | 0.82 | 15.5 | 1.9 | 18 | 0.86 |
| Zr | 27.5 | 0.7 | 33 | 0.83 | 106 | 1.8 | 119 | 0.89 |
| Nb | 2.34 | 1.9 | 2.8 | 0.84 | 8.67 | 1.5 | 9.8 | 0.88 |
| Mo | 0.37 | 16.9 | 0.45 | 0.82 | 0.61 | 1.8 | 0.54 | 1.13 |
| Ag | 0.14 | 2.7 | – | – | 0.31 | 1.3 | – | – |
| Cd | 0.076 | 5.6 | 0.085 | 0.89 | 0.070 | 27.8 | 0.07 | 1.00 |
| In | 0.062 | 3.8 | – | – | 0.050 | 1.5 | – | – |
| Sn | 1.14 | 39.0 | 0.36 | 3.16 | 1.70 | 4.5 | 1.5 | 1.13 |
| Sb | 0.059 | 10.1 | 0.11 | 0.53 | 0.14 | 5.8 | 0.13 | 1.05 |
| Cs | 0.25 | 2.2 | 0.27 | 0.91 | 4.95 | 2.0 | 4.2 | 1.18 |
| Ba | 65.7 | 0.7 | 63 | 1.04 | 321 | 2.0 | 317 | 1.01 |
| La | 3.69 | 1.0 | 3.95 | 0.93 | 15.9 | 2.0 | 16 | 0.99 |
| Ce | 8.60 | 0.7 | 8 | 1.07 | 33.4 | 1.7 | 33 | 1.01 |
| Pr | 1.21 | 0.3 | 1.1 | 1.10 | 3.73 | 2.7 | 5.9 | 0.63 |
| Nd | 5.25 | 1.7 | 5.7 | 0.92 | 13.8 | 2.0 | 14 | 0.99 |
| Sm | 1.48 | 1.8 | 1.5 | 0.98 | 3.01 | 2.2 | 3.1 | 0.97 |
| Eu | 0.66 | 0.3 | 0.61 | 1.09 | 0.97 | 1.7 | 0.91 | 1.06 |
| Gd | 1.64 | 1.4 | 1.5 | 1.09 | 3.19 | 1.2 | 3.9 | 0.82 |
| Tb | 0.30 | 1.4 | 0.3 | 1.00 | 0.49 | 2.5 | 0.48 | 1.02 |
| Dy | 1.68 | 0.9 | 1.4 | 1.20 | 2.72 | 1.8 | < 1 | – |
| Ho | 0.37 | 0.8 | 0.32 | 1.16 | 0.59 | 2.0 | – | – |
| Er | 0.99 | 0.7 | 0.91 | 1.08 | 1.64 | 1.9 | – | – |
| Tm | 0.16 | 0.8 | 0.17 | 0.95 | 0.26 | 2.5 | – | – |
| Yb | 0.94 | 0.8 | 1 | 0.94 | 1.57 | 1.7 | 1.6 | 0.98 |
| Lu | 0.16 | 1.7 | 0.16 | 1.00 | 0.26 | 1.3 | 0.27 | 0.95 |
| Hf | 0.89 | 1.3 | 0.84 | 1.06 | 2.85 | 2.1 | 2.8 | 1.02 |
| Ta | 0.18 | 6.2 | 0.17 | 1.06 | 0.61 | 1.9 | 0.61 | 1.01 |
| W | 4.00 | 8.0 | 0.81 | 4.94 | 1.64 | 1.1 | – | – |
| Re | < 0.002 | – | – | – | < 0.002 | – | – | – |
| Pt | < 0.004 | – | – | – | 0.008 | 14.1 | – | – |
| Au | 0.13 | 0.9 | 0.001 | 128.23 | 0.14 | 1.0 | – | – |
| Hg | 0.18 | 36.0 | 0.0021 | 84.04 | 0.073 | 6.4 | – | – |
| Tl | 0.043 | 3.5 | 0.06 | 0.71 | 0.33 | 2.4 | 0.35 | 0.95 |
| Pb | 1.59 | 1.7 | 1.9 | 0.84 | 19.0 | 1.4 | 19.3 | 0.98 |
| Bi | 0.021 | 6.1 | 0.014 | 1.52 | 0.10 | 1.7 | – | – |
| Th | 0.50 | 7.6 | 0.53 | 0.94 | 4.51 | 1.7 | 4.7 | 0.96 |
| U | 0.11 | 6.1 | 0.15 | 0.72 | 2.16 | 1.0 | 2.4 | 0.90 |

salts around the hole of the sampling cone and skimmer might cause a signal intensity drift during the measurements. The salt accumulation by the 1/1000 solution was higher than that of the 1/10,000 solution. For these reasons, the 1/10,000 solution is better for the determination of many elements by the present analytical procedures.

Accuracies of analytical results were verified by comparing them with the consensus values as reported in Table 3 and Figure 1. Good agreements between the consensus and the measured values were observed in the reference samples analyzed in this study. For about 40 elements, errors of measured values were less than 10% of the consensus values. And errors were less than 30% for 52 of elements, i.e. Li, Be, Na, Mg, Al, K, Sc, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, Ga, Ge, Rb, Sr, Y, Zr, Nb, Mo, Cd, In, Sn, Sb, Cs, Ba,

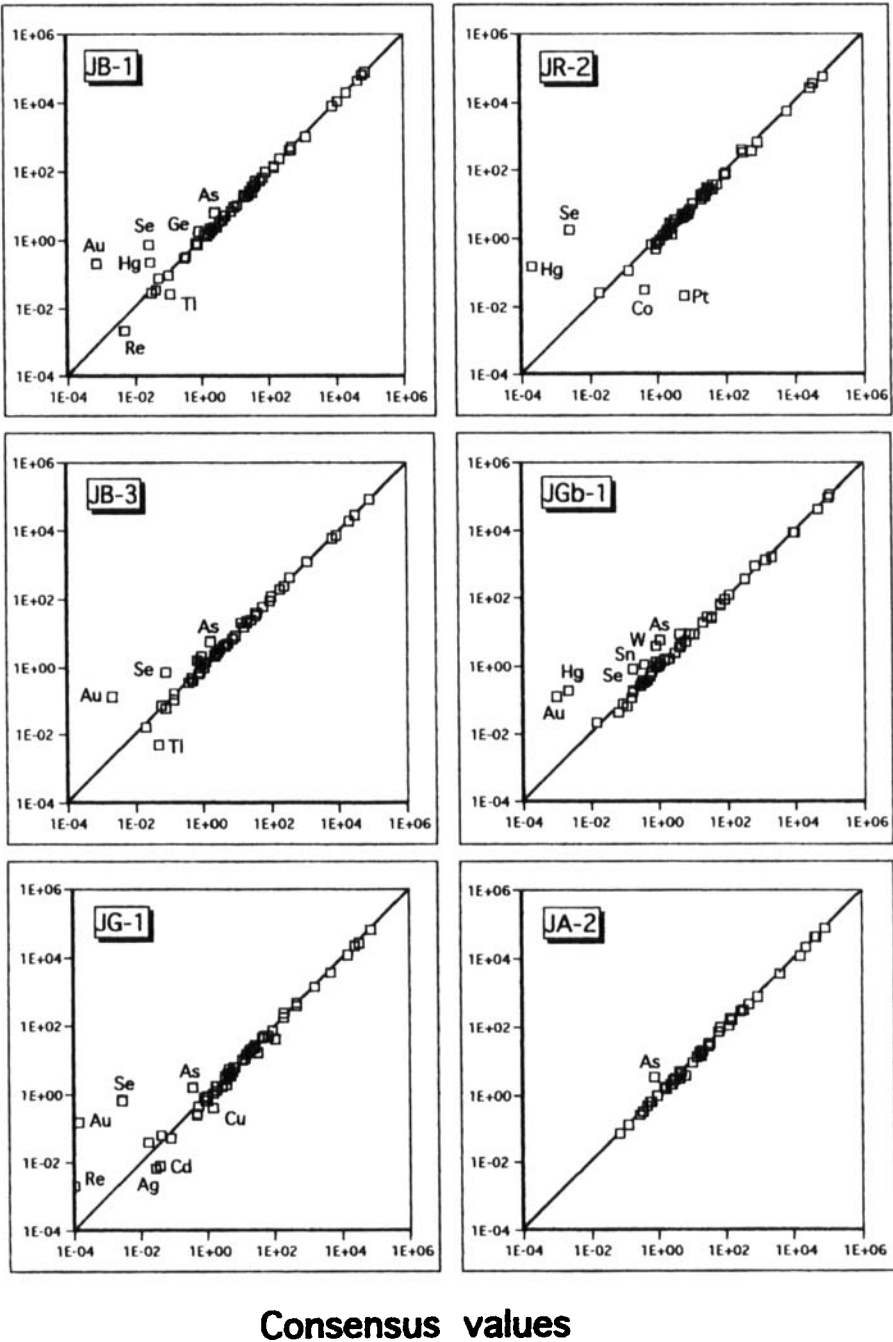**Figure 1** Binary plots of analytical results versus consensus values (in µg/g) for six rock reference samples. Solid line: slope unity.

La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu, Hf, Ta, W, Tl, Pb, Bi, Th and U.

Analytical results for As, Se, Ag, Hg, Re, Pt and Au did not agree with the consensus values in most reference samples. High RSD values were also observed for these elements as noted above. The errors of measured values were usually higher than 30% of the consensus values. The $^{75}As^+$ was interfered with $^{40}Ar^{35}Cl^+$ and $^{40}Ca^{35}Cl^+$. Most of the Cl in the sample solutions would be derived from $HClO_4$ added during the decomposition procedure. The $^{82}Se^+$ and $^{107}Ag^+$ were interfered with $^{82}Kr^+$ and $^{91}Zr^{16}O^+$, respectively. The concentrations of Re and Au in the sample solutions were low and close to their detection limits. More concentrated solutions and longer dwell times should be used for the precise determination of these elements. A certified value for Pt is known only for JR-2. The measured values were considerably lower than the consensus values. For the measurement of Pt, the stability of the element in the sample solution should be checked. The determination of Hg was difficult because of the memory effect already mentioned above, in addition to possible material loss during the sample digestion.

The accuracy of some elements such as Co, Cu, Ge, Rb, Cd, Sn, Sb, W and Tl depended on their concentrations in the reference samples. The minimum concentrations in the reference samples required for measurements with < 30% error were 0.05 μg/g for Cd, 0.3 μg/g for Sb, 0.5 μg/g for Tl, 1 μg/g for Co, Ge, Sn and W, 2 μg/g for Cu, and 40 μg/g for Rb, at the dilution factors mentioned above.

Analytical results for Zr in JG-1 were clearly underestimated. Elements which usually accompany Zr in the rock crystal lattice such as Hf and heavy REEs (i.e. Tb, Dy, Ho, Tm, Yb and Lu) were also systematically underestimated in the sample. This might be due to incomplete decomposition of zircon in which the above-mentioned elements are concentrated. It is known that zircon in granodiorite is not easily decomposed by acid. Therefore, attention should be paid to the digestion of samples having zircon contents such as granites. In such cases, further examinations of digesting acid combinations are necessary. Alternatively, another decomposition procedure such as lithium borate fusion attack[9] might be used. However, the borate fusion method can cause matrix effects and contamination problems.


CONCLUSIONS

A reliable, routine analytical method by ICP-MS for a large range of elements in geological materials was proposed by using 6 Japanese rock reference samples. Samples could be decomposed successfully with an acid mixture of $HNO_3$, HF and $HClO_4$ by using a microwave digestion technique. Superior detection limits (0.2–2 ng/l) were obtained for many elements. A sample dilution factor of 1/10,000 with an internal standard of Rh or In (20 μg/l) provided accurate and precise analyses of standard reference samples for trace elements. Major elements were measured by using 1/1,000,000 or 1/100,000 solutions. Fifty-two elements, Li, Be, Na, Mg, Al, K, Sc, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, Ga, Ge, Rb, Sr, Y, Zr, Nb, Mo, Cd, In, Sn, Sb, Cs, Ba, La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu, Hf, Ta, W, Tl, Pb, Bi, Th and U, could be measured quantitatively within 20 minutes in geological materials by the method. However, accuracy and precision for certain elements (Co, Cu, Ge, Rb, Cd, Sn, Sb, W and Tl) were poor at extremely low concentrations. The elements As, Se, Ag, Hg, Re, Pt and Au could not be determined due to interferences by molecular peaks or low concentration of the elements.

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## References

1. P. Henderson, *Rare Earth Element Geochemistry* (Elsevier, Amsterdam, Holland, 1984) pp. 467–495.
2. M. K. Hughes, N. W. Lepp and D. A. Phipps, *Adv. Ecol. Res.*, **11**, 217–327 (1980).
3. N. Yamagata and K. Iwashima, *Health Phys.*, **13**, 1145–1148 (1967).
4. M. M. Makweba and E. Holm, *Sci. Total Environ.*, **133**, 99–110 (1993).
5. J. W. Mclaren, *At. Spectrosc.*, **13**, 81–88 (1992).
6. B. Casetta, A. Giaretta and G. Mezzacasa, *At. Spectrosc.*, **11**, 222–227 (1990).
7. G. A. Jenner, H. P. Longerich, S. E. Jackson and B. J. Fryer, *Chem. Geol.*, **83**, 133–148 (1990).
8. R. Alaimo and P. Censi, *At. Spectrosc.*, **13**, 113–117 (1992).
9. G. Schönberg, *Geostandards Newsletter*, **17**, 81–97 (1993).
10. S. Yamasaki and Y. Tamura. *Commun. in Soil Sci. Plant Anal.*, **21**, 2017–2028 (1990).
11. W. Doherty and A.V. Voet, *Can. J. Spectrosc.*, **30**, 135–141 (1985) .
12. V. Balaram, C. Manikyamba, S. L. Ramesh and V. K. Saxena, *At. Spectrosc.*, **11**, 19–23 (1990).
13. D. C. Gregoire, J. Anal. At. Spectrom., **3**, 309–314 (1988).
14. E. H. Bailey, A. J. Kemp and K. V. Ragnarsdottir, *J. Anal. At. Spectrom.*, **8**, 551–556 (1993).
15. G. E. M. Hall, J. C. Pelchat and J. Loop, *J. Anal. At. Spectrom.*, **5**, 339–349 (1990).
16. A. Ando, H. Kamioka, S. Terashima and S. Itoh, *Geochem. J.*, **23**, 143–148 (1989).
17. J. W. Olesik, *Anal. Chem.*, **63**, 12A–21A (1991).