

Total Elemental Analysis of Solis by Inductively Coupled Plasma-Mass Spectrometry (ICP-MS)

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Abstract

Inductively coupled plasma-mass spectrometry (ICP-MS) is a relatively new technique that combines two well established analytical systems (ICP and MS) to produce an instrument with a great potential in the field of multi-element trace analysis. ICP is not used as a source of optical emission measurement (as in the case of ICP-atomic emission spectrometry, ICP-AES) but as a source of ions. The major advantages of ICP-MS over other analytical methods are as follows: 1) increased sensitivity and wide dynamic range, 2) high selectivity, 3) rapid multi-element capability, 4) simplicity in the spectra, 5) low and uniform background, and 6) the ability to measure specific isotopes. Samples should be in a liquid form and are basically introduced into the plasma through pneumatic nebulization. In order to apply ICP-MS for the total elemental analysis of soil samples, suitable techniques of dissolution of the elements in the samples must be developed. In principle, widely used HNO_3 - HClO_4 -HF digestion procedure for silicate materials is satisfactory, though considerable improvement is required to avoid possible contamination and/or complete dissolution of certain acid-tolerant minerals. It was possible to determine 10 major ($>0.1\%$) elements, together with more than 40 trace (1-1,000ppm) and ultra-trace (>1 ppm) elements in soils simultaneously by simply aspirating the above acid digests after a 10 to 10,000-fold dilution. There was a fair agreement between the results obtained by ICP-MS and those by other analytical techniques, such as atomic absorption spectrometry (AAS), X-ray fluorescence (XRF), and ICP-AES, in most of the cases.

Discipline: Soils, fertilizers and plant nutrition

Additional key words: trace elements, ultra-trace elements, acid digestion, simultaneous multi-element determination

Introduction

The first report on ICP-MS appeared in 1980¹⁰⁾. Although the total number of publications on ICP-MS had exceeded 900 by October 1993²³⁾, the applications of ICP-MS for the analysis of soil samples and related materials are still rather limited, and summarized in Table 1^{2,4-6,11,12,15,20-22,24)}. The high cost of the instrument appears to be the major constraint on widespread use among soil scientists. However, the price is dramatically decreasing as the number of instruments annually produced has been increasing in recent years. It can be expected, therefore, that ICP-MS will become one of the most widely used techniques for the determination of trace and ultra-trace elements, as well as for isotope ratio measurements, in soil samples in the near future.

Methods of dissolution

For the total elemental analysis of soil samples, all the elements must be dissolved, though such techniques as laser ablation^{6,15)}, and slurry introduction can be used. As solutions with high salt content are not suitable for ICP-MS, fusion methods can not be used, unless components for analysis are subsequently separated by applying appropriate chemical techniques. A further problem associated with this method is the difficulty in obtaining high purity fusion reagents (fluxes), such as NaCO_3 and $\text{Na}_2\text{B}_4\text{O}_7$. As a consequence, digestion with strong acids is exclusively used in ICP-MS, though the fusion techniques are often required for the substances that cannot be readily dissolved. Acids with ultra-high purity are commercially available now.

Table 1. Applications of ICP-MS to soil analysis

Reference	Samples, techniques, and elements
2	Soil leachates, combined with chromatography, Al, Mn, Fe, Ni, Cu, Zn, Cd, La.
4	Plants and soil, tracer technique, ^{10}B .
5	Soil colloids, chemical and mineralogical properties of soil particles up to $0.5\ \mu\text{m}$.
6	Seven Chinese reference soils, laser ablation, 30 elements.
11	Thirty soil samples, feasibility test of laser ablation, As, Ba, Cr, Pb.
12	Plants and soil, Mn, Co, Ni, Cu, Zn, As, Mo, Sr.
15	Molten borax or pressed polyethylene disk, laser ablation, 41 elements.
20	Various soils, HF-HClO ₄ digestion, comparison with ICP-AES, Na, Mg, Al, Ca, Ti, Mn, Fe, Ni, Cu, Zn, Pb.
21	Various soils and standard reference materials, HF-HClO ₄ digestion, 47 trace and ultra-trace elements.
22	Review in general.
24	Reference soils, HF-HClO ₄ digestion, comparison with photon activation analysis, 42 elements.

1) Open digestion systems

For the dissolution of samples for the determination of the total element content of soils, HF, in combination with HClO₄ and HNO₃, is generally used, and has been extensively applied in AAS and ICP-AES^{9,14,17}. Although Si is lost by evaporation of gaseous SiF₄ when an open system is used, no problem will arise, because ICP-MS is mostly applied for the analysis of trace and ultra-trace elements. The real problem is, however, that minerals, such as chromite (FeCr₂O₄), magnetite (Fe₃O₄), zircon (ZrSiO₄), and garnet ($\text{R}''_3\text{R}'''\text{}_2(\text{SiO}_4)_3$, where R'' may consist of Ca, Mg, Fe, and Mn, and R''' of Al, Fe, Cr and Mn) show a high tolerance toward acid attack and remain undissolved even after repeated treatments. As these minerals almost always contain a large variety of elements as 'impurities' (for example, Hf and heavy rare earth elements in zircon), special dissolution techniques should be applied for samples containing considerable amounts of these minerals. Care is also required when the HClO₄-HF mixture is evaporated to dryness, for acid insoluble oxides will again be formed if too much heat is applied. The advantages of the open digestion systems are as follows: 1) silicon and the excess HF are easily removed by heating, 2) the final solutions are stable (silica-bearing solutions tend to hydrolyze and precipitate on standing), 3) the removal of corrosive HF allows the solution to be handled in conventional glassware for periods of at least a couple of days, and 4) the salt content of the resultant solutions is low.

A typical procedure, employed in our laboratory for ICP-MS analysis, is schematically shown in Fig. 1.

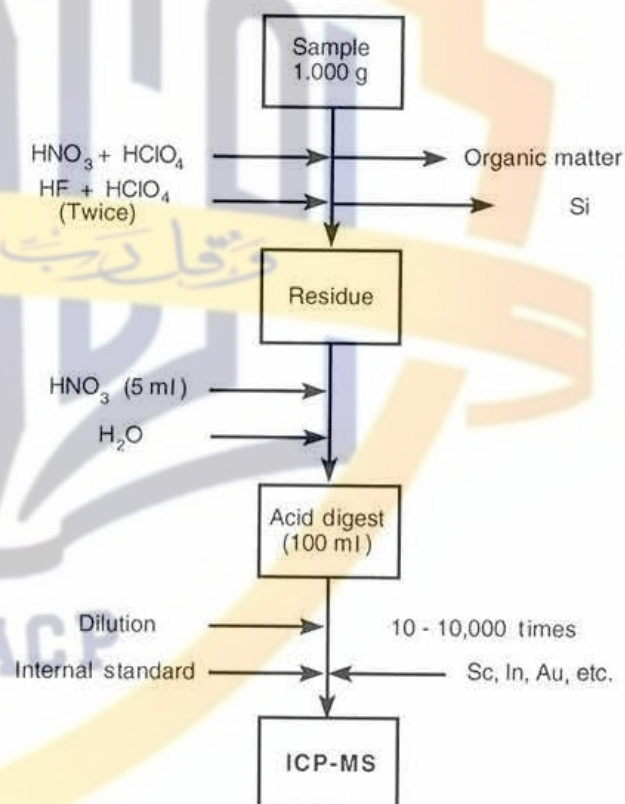


Fig. 1. Scheme for the decomposition of soil samples for ICP-MS determination

One (1.000) g of finely powdered sample is weighed accurately in a Teflon (polytetrafluoroethylene) beaker, and treated with 10 ml of HClO₄-HNO₃ (1:1 mixture) to destroy the organic matter in soils. If the sample lacks organic matter, this step can be omitted. Five ml of HClO₄ and 10 ml of HF are slowly added and the sample is evaporated on a hot

plate until a crystalline paste is formed. This step is repeated once more and the sample is evaporated to initial dryness to completely remove HF. For AAS and ICP-AES, the residue is heated with 5 ml of HCl and dissolved by the addition of 30–50 ml of water with gentle boiling, and finally made up to 100 ml¹⁹⁾. But for ICP-MS, HCl is replaced with HNO₃ to avoid possible interferences due to the existence of large amounts of Cl. The final solutions are stored in plastic bottles.

As the sensitivity of ICP-MS is far higher than that of AAS and ICP-AES, dissolution using only 0.1 g of the sample or less appears to be possible. However, such an approach is not considered to be appropriate, because the errors associated with sample inhomogeneity and contamination during the decomposition process as well as during the storage of the acid digests become very large when the amount of sample is small. Determination of elements is carried out after a 10–1,000-fold dilution of the above acid digests.

2) Closed digestion systems

An alternative dissolution procedure using HF is to digest the soil samples in a sealed Teflon vessel, or "Teflon bomb" placed in a stainless steel casing^{3,13,18)}. Bombs with different designs are now commercially available. After the addition of sample and acid, the bomb is sealed and heated in an electric oven. The advantages of closed digestion systems over the open vessel techniques are as follows: 1) digestions at higher temperatures are possible because the boiling point of the reagents is raised by the pressure generated in the vessel, which may shorten the time needed for decomposition, and also enable the dissolution of some acid-tolerant minerals, 2) volatile elements, such as B, Cr, As, Se, Sn and Hg, will remain within the vessel, 3) smaller amounts of acids are sufficient for the digestion because evaporation does not occur, which decreases the reagent blank level considerably, and 4) contamination is significantly reduced because the sealed system prevents the introduction of airborne particles during decomposition.

The disadvantages are as follows: 1) the maximum amount of sample that can be processed is rather limited, usually less than 0.5 g, in particular when the content of organic matter in the sample is high, 2) a large amount of H₃BO₃ should be added to complex the excess HF, which results in a high salt content in the solutions analyzed, and 3) subsequent open vessel procedures are needed when

the removal of Si and HF is required.

Heating needed for the acid decomposition of samples is traditionally provided from outside by chemical flames or electricity on hot plates. Recently, however, a new method using microwave energy for heating has been developed¹⁶⁾. This technique is most suitable for close digestion systems because the sample solutions can be heated directly in microwave "transparent" vessels. Although domestic microwave ovens can be used successfully, purpose-built microwave digestion systems are commercially available now. Very rapid heating is possible as compared with the above-mentioned open digestion system and the bomb method, because the heat is generated from inside, rather than supplied from outside.

Detectable elements

In ICP-MS, it is rather common to carry out a rapid scanning of the whole mass range to obtain information on the kind of detectable elements, and also to estimate their rough concentrations prior to the detailed quantitative analyses. Time needed for the rapid scanning is 1–2 min per sample. Typical results of such qualitative analyses obtained by Yamasaki and Tamura²⁰⁾ are described below.

About 100 soil samples were selected to cover a wide range of chemical as well as mineralogical composition. A large number of elements were positively (more than 10 times greater than the blank) identified for most soil samples. These elements are conveniently classified into 4 groups and shown in Fig. 2 using the periodic table.

The elements classified in Group 1 were identified for all of the samples examined. The obvious problem associated with these elements (except for Cu and Zn) is that high and varying dilution (100–1,000-fold) ratios must be employed to adjust the concentration of each element to an appropriate range. This procedure requires time-consuming manipulations and also greatly reduces the multi-element capability of ICP-MS.

The elements belonging to Group 2 were detected in more than 90% of the samples. The unparalleled detection power of ICP-MS is clearly demonstrated by the fact that it was possible to confirm the occurrence of more than 40 elements (Group 1 + Group 2) within several minutes. In addition to these elements, those classified in Group 3 were also detected in about 70% of the samples. The elements in Group 4 were, however, detected only in less than 50% of the samples, indicating that there are still a consider-

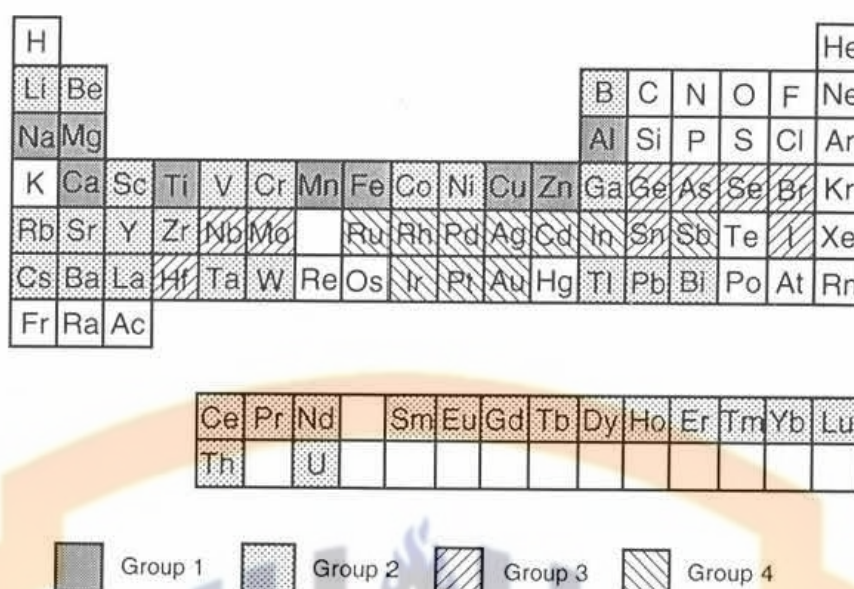


Fig. 2. Periodic table showing the detectable elements in soil samples. The percentage for groups 1, 2, 3 and 4 is 100%, more than 90%, more than 70%, and less than 50%, respectively.

able number of elements for which we need some adequate preconcentration and/or separation techniques even with extremely sensitive ICP-MS.

Quantitative results

Yamasaki et al.²¹⁾ examined the applicability of ICP-MS for systematic studies of elements in soils by analyzing a large number of samples and standard reference materials. Fig. 3 shows the results for Cu and Zn as typical examples. These two elements were selected simply because the concentration levels of the other elements are mostly beyond the reach of AAS. Linear regression analysis revealed that

the values of the correlation coefficients exceeded 0.99 for these two elements. Moreover, the slopes of the regression lines (X coefficient) were very close to unity (1.0), and the intercepts were negligibly small.

As mentioned above, it is rather difficult to examine the reliability of ICP-MS for the other elements in the soil samples due to the lack of other appropriate techniques. Consequently, the results obtained by analyzing various geochemical and environmental standard reference materials of a related nature were compared with the recommended or reported values. The elements examined were (from light to heavy element) Li, Be, B, Sc, V, Cr, Co, Ni, Cu, Zn, Ga, Ge, Rb, Sr, Y, Zr, Nb, Mo, Cd,

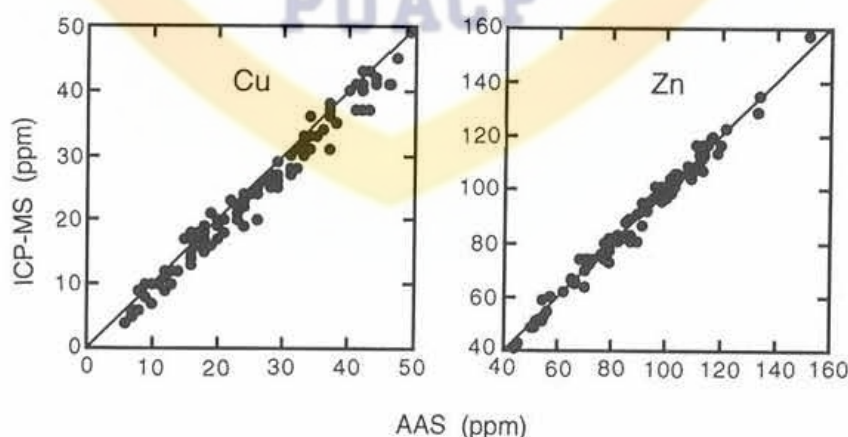


Fig. 3. ICP-MS concentrations for Cu and Zn plotted against the values obtained by AAS

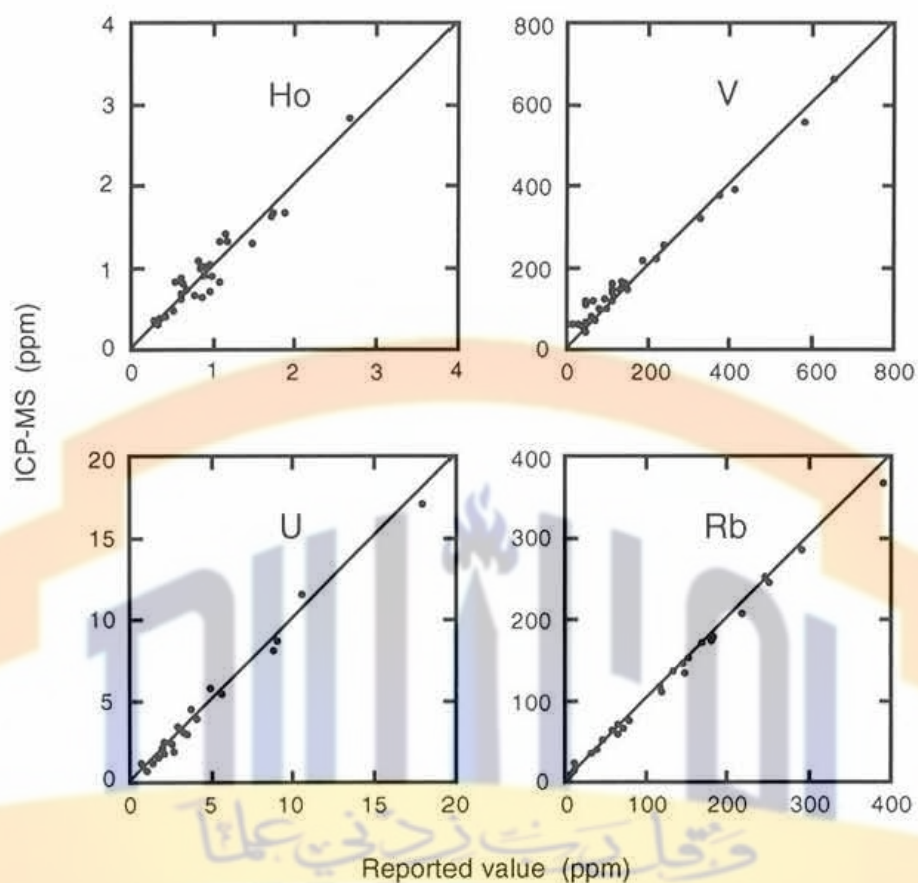


Fig. 4. ICP-MS concentration data for standard reference materials plotted against the recommended or previously reported values
The superimposed line of slope = 1 does not represent a line of 'best fit'.

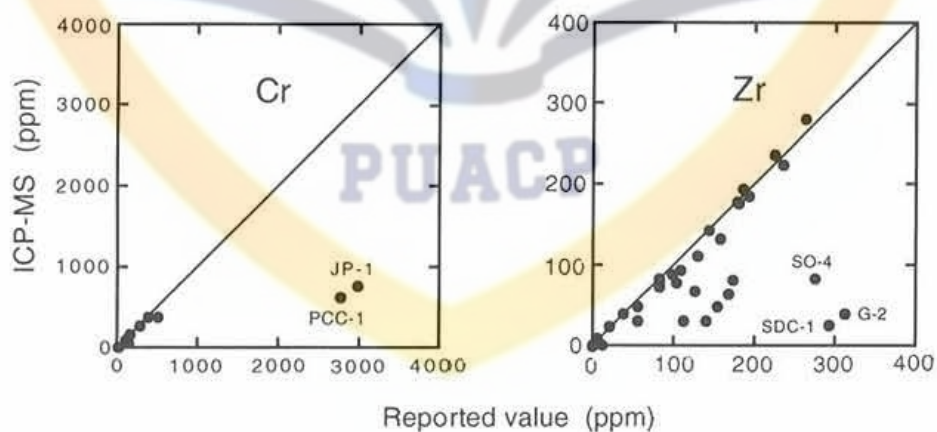


Fig. 5. ICP-MS concentration data for standard reference materials plotted against the recommended or previously reported values
The superimposed line of slope = 1 does not represent a line of 'best fit'.
Name of samples with larger discrepancies is also shown in the figure.

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

The results for four elements (Ho, V, U, and Rb) are graphically presented in Fig. 4, as typical examples. The value of the correlation coefficient for Ho (0.92) was the lowest among the four elements shown here. However, when taking the very low contents (less than 3 ppm) of Ho in samples into consideration, it may be concluded that the agreement of both values is satisfactory. For V, the value of the correlation coefficient was more than 0.99 and the value of the X coefficient was very close to 1.0. It can be seen that each data point was practically superimposed on the 1:1 line. In the case of U, the value of the X coefficient was somewhat higher (nearly 1.3) than that of other elements. However, since the value of the correlation coefficient was almost 1.0, no problem should arise for the results obtained by ICP-MS. The best results were obtained for Rb among the 47 elements examined.

As can be seen in Fig. 5, the values obtained by ICP-MS were significantly lower as compared with the recommended values for Cr and Zr in some standard reference materials indicated in Fig. 5. The JP-1¹⁾ and PCC-1⁷⁾ are ultrabasic samples supplied by Geological Survey of Japan (GSJ) and United States Geological Survey (USGS), respectively, and are known to contain considerable amounts of chromite.

G-2⁷⁾ and SDC-1⁸⁾ supplied by USGS are granite and muscovite-quartz schist, respectively and, hence, the occurrence of zircon is rather common. It seems reasonable, therefore, to assume that these discrepancies are a consequence of the incomplete dissolution of these minerals, rather than associated with the ICP-MS analysis itself. In fact, the ICP-AES measurement of Cr and Zr has given practically identical values with those obtained by ICP-MS when the same digested solutions were used.

The results for 28 elements, including those mentioned above, are collectively shown in Fig. 6. The best-fit lines were calculated in such a way as to force the equation to cross the Y-axis at zero when X values are zero. For the calculation of Cr and Zr, the samples likely to be associated with the problems shown in Fig. 5 were excluded. The graph indicates that the values of the correlation coefficients exceeded 0.98 and the slopes of the regression lines all fell between 0.8 and 1.3 for the 28 elements depicted in Fig. 6-B (Be, Sc, V, Cr, Co, Ni, Cu, Zn, Rb, Sr, Y, Zr, Nb, Mo, Cs, Ba, La, Ce, Pr,

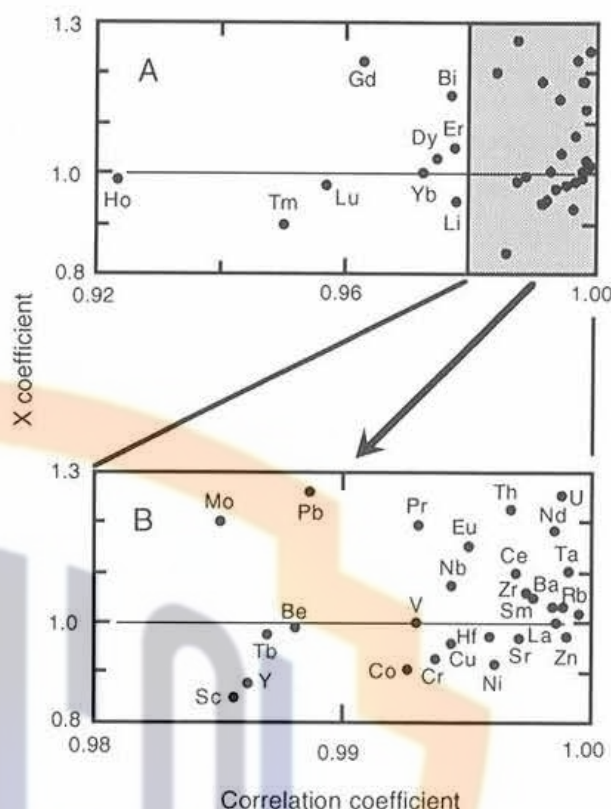


Fig. 6. Comparison of the reported values and those obtained by ICP-MS

Fig. B is an enlarged graph of the shaded part of Fig. A.

Nd, Sm, Eu, Tb, Hf, Ta, Pb, Th, and U). Deviation from the recommended values was less than 20% in most cases, when the contents in the samples exceeded 1 ppm. However, for the 10 elements shown in Fig. 6-A, (Li, Gd, Dy, Ho, Er, Tm, Yb, Lu, Tl, and Bi), considerable scattering around the regression lines was observed, as evidenced by the lower values of the correlation coefficients. However, since the values of the X coefficients still ranged between 0.8 and 1.3, it can be concluded that the technique is also suitable for the analysis of these elements. It was not possible to specify the causes of the scattering in this study. It seems reasonable, however, to assume that the reliability of the recommended values may be somewhat lower than that of the other elements due to their very low contents.

In contrast to these elements mentioned above, only a limited agreement was observed for B, Ga, Ge, and W. Whereas the poor results for B and W may be associated with a strong memory effect, those for ⁶⁹Ga and ⁷⁴Ge can be attributed to the interferences of polyatomic ions, presumably due to ³⁷Cl¹⁶O₂ and ³⁷Cl₂, respectively.

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