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Original Paper

Determination of trace elements in siliceous samples by ICP-MS after precipitation of silicon as sodium fluorosilicate

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Abstract. A matrix removal procedure has been developed for the determination of trace elements, including As, Cd, Co, Cr, Cu, Hg, Ni, Pb, Sb, Se, Sn, Tl, Zn and V, in siliceous materials by inductively coupled plasma mass spectrometry (ICP-MS). Soil and sediment samples were dissolved in a mixture of HNO₃ and HF in sealed vessels by using a microwave oven. Silicon matrix in the solutions was precipitated as sparingly soluble sodium fluorosilicate (Na₂SiF₆) by adding 0.5 mL of 300 mg mL⁻¹ NaCl solution. Simultaneous precipitation of sodium and silicon was achieved in highly acidic solutions containing 30–40% (v/v) HNO₃. A mixture of methanol and nitric acid afforded back-extraction of the trace elements without significant dissolution of the Na₂SiF₆. Samples were analyzed by ICP-MS for trace elements and residual silicon. Calibration was made by aqueous multi-element standard solutions. Up to 95% of the silicon was successfully removed yielding solutions suitable for introduction to ICP-MS. The method was validated by analysis of two NIST certified reference materials; SRM 2711 (Montana Soil) and SRM 2704 (Buffalo River Sediment). Accurate results were obtained for all elements, including those for As, Hg and Se that suffer

from losses due to the presence of their volatile species when silicon was converted to volatile SiF₄ via heat-assisted evaporation to dryness. The recoveries from the SRM samples varied between 80% (Cr) and 109% (Hg). No significant interferences were observed from molecular ions of chloride and residual sodium on ⁷⁵As, ⁶³Cu, ⁶⁰Ni, ⁷⁷Se and ⁵¹V.

Keywords: Soil; trace element; silicon; precipitation; sodium fluorosilicate; ICP-MS

Over the last two decades, inductively coupled plasma mass spectrometry (ICP-MS) has developed into a powerful analytical technique to advance our capabilities in trace element analysis. ICP-MS offers high sensitivity which, when coupled with very low background signals, produces solution detection limits in the sub-parts per trillion levels, wide dynamic range extending over approximately seven orders of magnitude, excellent performance in semi-quantitative mode, multi-element and isotopic measurement capability, and the convenience of solution-based sampling [1–3]. To date, ICP-MS has been successfully used for quantification of trace and rare elements from numerous environmental and biological materials [4–13]. Despite its advantageous features, ICP-MS does suffer from spectral and non-spectral interferences, especially in the analysis of solutions with high salt content [2, 6, 14, 15]. The spectral interferences are due to the

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spectral overlaps of atomic and molecular ion signals with that of the analyte at the same mass-to-charge (m/z) ratio, such as ^{54}Cr on ^{54}Fe , ^{58}Ni on ^{58}Fe , and $^{40}\text{Ar}^{16}\text{O}$ on ^{56}Fe and $^{40}\text{Ar}^{35}\text{Cl}$ on ^{75}As . The non-spectral interferences are usually manifested by attenuation or enhancement of the ion signals due to the nature and the salt content of sample as well as the plasma operating conditions. While atomic interferences can be overcome by utilizing alternative isotopes, molecular ion and non-spectral interferences necessitate the use of alternative sample preparation/introduction methods, such as coprecipitation/preconcentration [11, 16–18] electrothermal vaporization [12, 19, 20] and high-resolution ICP-MS [21–23].

Complete dissolution of sample is critical to achieve accurate determination of elemental concentrations. In ICP-MS determinations, nitric acid along with hydrogen peroxide (H_2O_2) is the preferred reagent for dissolution and oxidation of organic materials by using open- or closed-vessels protocols. The latter is usually of choice to reach higher temperatures and to prevent the losses of volatile species of some elements, such as Se and Hg [8, 24]. Other strong acids, such as HCl, H_3PO_4 and H_2SO_4 are usually avoided to alleviate the spectral interferences from molecular ions of Cl, P and S, respectively [1–13]. Hydrofluoric acid (HF) is an essential ingredient in combination with the strong acids for the dissolution of silicates [3, 4, 8, 25–28]. Hoenig et al. [27] reported that the recoveries of Al, Ca, Fe and Ni were low when plant materials containing silicon were digested with $\text{HNO}_3/\text{H}_2\text{O}_2$. Similarly, Quevauviller et al. [28] found that recoveries for Cd, Cr, Cu and Pb obtained from digestion of a freshwater plankton material in HNO_3 were significantly lower than those of HNO_3/HF since the material was a mixture of organic matter and silicates [28]. Thus, the authors recommended closed-vessel pressurized digestion with HNO_3/HF mixture using microwave heating for the dissolution of such materials.

Silicon is the second most abundant element (27.6% m/m) next to oxygen in the earth's crust. It occurs mainly in the form of dioxide and its hydrates, silicates and alumino-silicates [29]. Silicon compounds are also contained in waters, both fresh and saline, in plant and animal tissues, and even in the most primitive algae and sea animals (diatoms) [29, 30]. Further, the dissolution of silicates with HF leads to significant increase in the content of total dissolved salts which subsequently causes severe suppression of ion sig-

nals in the ICP-MS determinations [3, 4, 8]. Practically, silicon matrix is eliminated by heating the solution in the presence of HF to dryness by which fluorosilicic acid (H_2SiF_6) is converted into volatile silicon tetrafluoride (SiF_4) [27, 29, 31, 32]. However, this procedure is not pertinent to samples that contain considerably high levels of sodium and potassium, because sodium and potassium fluorosilicates are among the most sparingly soluble salts of inorganic fluorosilicates; solubilities in water are 0.625% (m/m) for Na_2SiF_6 and 0.40% (m/m) for K_2SiF_6 [29, 33]. Boer et al. [33] reported by X-ray diffraction (XRD) analysis that the residue from the evaporation of solutions of geological samples that were dissolved in HNO_3/HF was an isometric mineral phase with chemical composition of hieratite (K_2SiF_6) and ralstonite, a complex fluoride with a chemical formula of $\text{Na}_{0.88}\text{Mg}_{0.88}\text{Al}_{1.12}(\text{F},\text{OH}) \cdot \text{H}_2\text{O}$.

The precipitation of silicon as fluorosilicate has been used for the separation of beryllium [29] and boron [34] from silicon, and silica from rocks [35]. On the basis of this chemistry, in this study, we developed a method for trace element determination by ICP-MS from samples containing high levels of silicon and/or sodium. The objective of the method was to achieve simultaneous removal of silicon and sodium to overcome matrix-induced interferences in ICP-MS. Silicon from dissolution of soil and sediments was precipitated as sodium fluorosilicate (Na_2SiF_6) upon addition of NaCl solution in a highly acidic medium. The effects of various parameters, including solution volume, extraction medium, and amount of NaCl as well as molecular ion interferences were discussed. The performance of the method was evaluated by the analysis real samples for a suite of trace elements by ICP-MS.

Experimental methods

Instrumentation

Measurements were performed by using a Perkin-Elmer Sciex Elan[®] 5000 ICP-MS (Perkin Elmer, Shelton, USA) equipped with a standard ICP torch, removable alumina injector, cross flow nebulizer, nickel sampler and skimmer cones and a four-channel mass flow controller. The instrument was optimized daily by aspirating a $10\ \mu\text{g L}^{-1}$ solution of ^{24}Mg , ^{105}Rh and ^{208}Pb in 1% HNO_3 (v/v) solution. No specific corrections were performed for the polyatomic ion interferences, while isotopic overlaps were corrected by ELAN software. The instrumental parameters are listed in Table 1. For dissolution of samples, a CEM (www.cem.com) Model MSD-81D microwave oven providing 630 ± 70 W output power at 100% power setting was used. The digestion vessels (100 mL) and the

Table 1. Elan 5000 ICP-MS operating parameters

Rf power, W	1000
Plasma gas flow, L min ⁻¹	15.0
Nebulizer gas flow, L min ⁻¹	0.90–0.95
Auxiliary gas flow, L min ⁻¹	0.80
Nebulizer	cross flow
Spray chamber	double pass
Scanning mode	peak hop
Replicate time, msec	300
Dwell time, msec	100
Sweeps/reading	3
Readings/replicate	1
Number of replicates	3
Points per spectral peak	1

cover were made up of Teflon[®]-perfluoroalkoxy (PFA). The vessel body was polyetherimide (Ultem).

Reagents and standard solutions

High-purity deionized distilled water (18 M Ω) and sub-boiled HNO₃ (EM Science, www.emscience.com) were used throughout. Silicon stock solution (10 mg mL⁻¹ Si) was prepared by dissolving 5.384 g of H₂SiO₃ (Aldrich, www.sigma-aldrich.com) in 5 mL HF (EM Science, 99.995%) and diluting to 100 mL with water. A 300 mg mL⁻¹ NaCl solution was prepared by dissolving 3 g of NaCl (EM Science) in 10 mL of water. High-purity methanol (MeOH, Fisher Scientific, www.fishersci.com) was used for the back-extractions after the precipitation. A 10 μ g mL⁻¹ multi-element standard stock solution of Al, As, Ba, Ca, Cd, Co, Cr, Cu, Fe, Hg, Mg, Mn, Ni, Pb, Sb, Se, Si, Sn, Sr, Tl, Zn and V in 2% (v/v) HNO₃ was used throughout for preparation of standards and samples.

Optimization studies

To test the influence of sodium on the removal of Si as volatile SiF₄, approximately 100 mg sample of Montana Soil (SRM 2711, www.nist.gov/srm) was spiked with 0.25 g solid NaCl and digested in 3 mL HNO₃ + 1 mL HF in the microwave oven. After the digestion, the contents were diluted to 50 mL in a polypropylene volumetric flask. This solution was then divided into two 25-mL portions. One of the portions was first evaporated to dryness in a teflon beaker to eliminate Si as SiF₄. The residue was then redissolved and diluted to 25 mL in 2% (v/v) HNO₃. Both solutions were analyzed by ICP-MS for Si content in diluted solutions.

Studies for optimization of volumes of sample and NaCl solutions as well as the identification of the extraction medium to achieve quantitative recoveries without significant dissolution of sodium fluorosilicate were carried out with synthetic solutions that imitated the concentrations of major constituents (Al, Ca, Fe, Mg and Si) in soil and sediment samples. To a 15-mL test tube, 3 mL HNO₃, 0.5 mL HF, 2.5 mL of 10 mg mL⁻¹ Si, 0.25 mL of 10 mg mL⁻¹ Al, Ca, Fe and Mg, and 1 mL of the 10 μ g mL⁻¹ multi-element solution were placed. These volumes yielded 6% (v/v) HNO₃, 2% (v/v) HF, 500 μ g mL⁻¹ Si, 50 μ g mL⁻¹ Al, Ca, Fe and Mg, and 0.2 μ g mL⁻¹ for all other elements in 50-mL analysis solution.

The initial volume in the 15-mL test tube was 7.25 mL; therefore, the volume prior to addition of NaCl solution (300 mg mL⁻¹) was varied from 8 to 14 mL to determine the precipitation profile of Si and other sparingly soluble fluorides. The volume of the NaCl solution was varied from 0.25 to 0.75 mL. Extractions after the precipitation were performed with water, HNO₃, MeOH/HNO₃ and MeOH (methanol) to find the best medium that afforded quantitative

recoveries without a significant redissolution of sodium fluorosilicate. The volume of water was kept constant at 1 mL, while those of HNO₃ and MeOH were varied from 0.25 to 1 mL and 1–4 mL, respectively.

Procedure

Soil and sediment samples, SRM 2711 Montana Soil (Moderately Elevated Traces) and SRM 2704 Buffalo River Sediment, were dissolved in a mixture of HNO₃/HF by closed vessel microwave-assisted digestion method which had been developed previously [8, 31]. Approximately 100 mg of sample, 3 mL HNO₃ and 1 mL of HF were placed into the Teflon[®]-PFA vessels of the microwave digestion system. Four vessels were tightly capped and irradiated at 40% power for total 30 min in 10-min intervals. At the end of each program, the vessels were cooled for 3–4 min and the digestion program was repeated. After the third program, the vessels were cooled to room temperature and the contents were transferred to 15-mL centrifuge tubes. The vessels were rinsed twice with 1 mL H₂O into the test tubes and the volumes were adjusted to 8 mL.

Precipitation of Si as Na₂SiF₆ was made by adding 0.5 mL of 300 mg mL⁻¹ NaCl solution to the sample solution. The contents were centrifuged for 2 min at 1000 rpm and then the liquid phase was transferred to 50-mL polyethylene volumetric flask by an Eppendorf pipet without disturbing the precipitate. To the precipitate, 2 mL MeOH and 0.5 mL HNO₃ were added and the precipitate was agitated strongly for about 3 min to extract the fraction of trace elements from the precipitate. This extraction was repeated three times. After each step, the suspension was centrifuged similarly and the MeOH/HNO₃ phase was collected in a separate teflon beaker. Finally, the contents in the teflon beakers were heated slowly at around 70 °C to evaporate MeOH until a small amount of aliquot (~0.25–0.5 mL) remained. At this stage, 10 mL deionized water was added to the beakers and the contents were added to the 50-mL volumetric flasks. The beakers were rinsed twice with 2 mL water into the flasks. Volume was completed to 50 mL with water after adding 100 μ L of 10 μ g mL⁻¹ Ge, In and Rh internal standard solution (20 μ g L⁻¹ of each). To bring the levels of concentrated elements to the range of calibration standards, 10-fold dilution was also performed in separate 25-mL polyethylene volumetric flasks with water. The concentration of the internal standards was adjusted to 20 μ g L⁻¹ by adding appropriate volume from its stock solution. For the preparation of the reagent blank, 1.5 mL HNO₃/6 mL MeOH mixture was first evaporated in a teflon beaker to dryness and then washed with water into 50-mL flask which contained 0.5 mL of the NaCl solution, 3 mL of HNO₃, 1 mL of HF and 100 μ L of the internal standard solution. Volume was adjusted to 50 mL with water.

Calibration

Aqueous multi-element standard solutions were used for calibration. The concentrations of the elements ranged from 0.5 to 500 μ g L⁻¹ for As, Ba, Cd, Co, Cr, Hg, Pb, Sb, Se, Sr, Sn, Tl and V, and those for Al, Ca, Cu, Fe, Mg, Mn, Ni, Si and Zn were 10-fold higher (e.g., 5–5000 μ g L⁻¹). All standard solutions contained 20 μ g L⁻¹ Ge, In and Rh as internal standard. Of those only the most suitable one was used for a suite of elements. Internal standard element was ⁷²Ge for As, Co, Se, Cu, Fe, Mn, Ni and Si, ¹¹⁵In for Al, Ba, Ca, Sr, Tl, V and Zn, and ¹⁰³Rh for Mg, Cd, Cr, Hg, Pb, Sb and Sn. Three replicate measurements were made for each solution. The blank subtractions and the internal standard correction of ions signals (Std/IntStd ratio) were made by the ELAN software (version 2.2). In constructing the calibration curves, the Std/IntStd ratio of six standards bracketing that of the sample were used.

Results and discussion

Effect of sodium on the removal of silicon as SiF_4

To convert Si from the dissolution of silicates to volatile SiF_4 , the sample solution needs to be heated to dryness [8, 29, 31, 32]. Nevertheless, considerably high levels of Si remained in the matrix of marine phytoplankton samples when HNO_3/HF digests were heated to dryness in open vessels to eliminate Si matrix [8]. This phenomenon was attributed to the presence of sodium ($1.5\text{--}2\text{ mg mL}^{-1}$) as NaCl in the plankton solutions that hindered the conversion of Si to SiF_4 . The results of the experiments performed with Montana Soil (SRM 2711) samples did confirm this hypothesis that elevated levels of sodium did indeed prevent complete removal of Si as SiF_4 despite heating soil digests in HNO_3/HF at dryness. The heating was implemented at around 200°C by means of a sand bath placed on a hot place to achieve higher temperatures. The recoveries for silicon obtained from the evaporated portion of the solutions were about 72–83% of those from their counterparts that had only received the closed-vessel microwave-assisted digestion protocol (Fig. 1). In other words, only a small fraction (17–28%) of Si in solution was converted to volatile SiF_4 . Contrary to silicon, significant losses were observed for As, Cu, Pb, Sb and Sn (e.g., 15–26%) besides completely lost Hg and Se as a result of heating in the sand bath at 200°C .

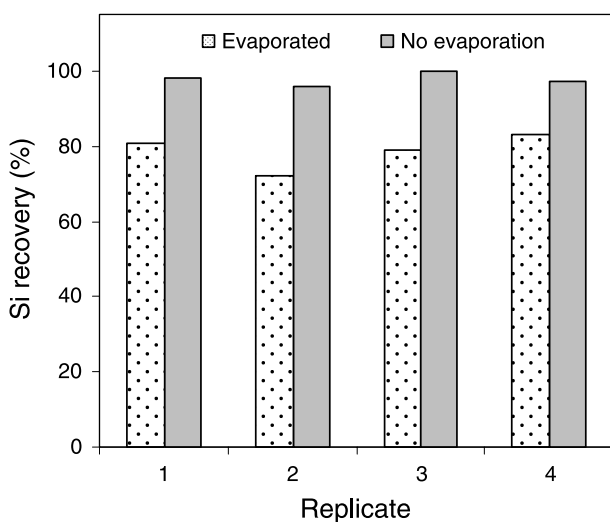
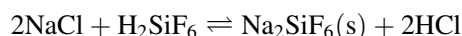


Fig. 1. The effect of sodium on the removal of silicon as SiF_4 by dry-heating. Soil samples were spiked with 0.25 g NaCl and digested in 3 mL HNO_3 + 1 mL HF in sealed vessels in a microwave oven. Evaporation was performed in teflon beakers at around 200°C

Precipitation and extraction conditions

The precipitation of sodium fluorosilicate was greatly dependent on the initial volume of the sample solution. Intense precipitation occurred in synthetic solutions with volumes around 8 mL upon addition of NaCl solution. For volumes above 10 mL, significant amount of Si did not precipitate such that the concentration of Si in the 50-mL analysis solutions varied between 85 and $115\text{ }\mu\text{g mL}^{-1}$. The precipitation efficiency was also dependent on the volume of NaCl solution (300 mg mL^{-1}). Optimum volume was around 0.5 mL (0.3 mol L^{-1} NaCl) for the precipitation of approximately 0.1 mol L^{-1} SiF_6^{2-} (2.5 mL of 10 mg mL^{-1} Si as H_2SiF_6) in 8 mL synthetic solution. The formation of Na_2SiF_6 occurs via the reaction:



In strongly acidic medium (e.g., 35% v/v HNO_3), precipitation was fast though it demanded higher concentration of NaCl solution than the stoichiometric value due the considerably high solubility of Na_2SiF_6 . At lower volumes (e.g., 250 μL) of the NaCl solution, faint turbidity was observed. Volumes greater than 500 μL were not advantageous due to the interferences from excess NaCl matrix.

Figure 2 shows the effects of the reagents on the dissolution of Na_2SiF_6 precipitate during the back-extractions. The least suitable medium was water for which there was a substantial dissolution of the precipitate. The concentration of Si in the solution (50 mL) increased up to $110\text{ }\mu\text{g mL}^{-1}$. Extractions with concentrated HNO_3 (0.5–1 mL) performed better to reduce the levels of Si in the solution to about $42\text{--}50\text{ }\mu\text{g mL}^{-1}$. The concentration of Si was further

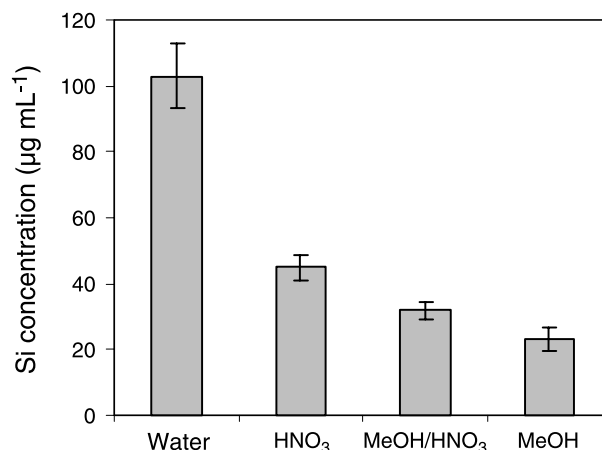


Fig. 2. The effect of extraction medium on dissolution of Na_2SiF_6

Table 2. Elemental recoveries from synthetic solutions following precipitation of Si as Na₂SiF₆. Extractions were performed three times with a mixture of 2 mL MeOH and 0.5 mL HNO₃. Spike concentrations for Al, Ca, Fe and Mg were 50 µg mL⁻¹ and 200 µg L⁻¹ for all other elements. Silicon concentration was 500 µg mL⁻¹

Element	Isotope	Found (µg L ⁻¹)	Recovery (%)
Al*	27	50.8 ± 1.1	102
As	75	195 ± 3	98
Ba	138	183 ± 7	92
Ca*	44	48.7 ± 2.4	97
Cd	114	183 ± 6	92
Co	59	204 ± 6	102
Cr	53	214 ± 12	107
Cu	63	211 ± 5	105
Cu	65	205 ± 9	103
Fe*	57	50.2 ± 0.5	100
Hg	202	196 ± 6	98
Mg*	24	50.7 ± 1.3	101
Mn	55	221 ± 6	111
Ni	60	194 ± 8	97
Pb	208	188 ± 4	94
Sb	121	188 ± 9	94
Se	77	178 ± 10	89
Se	82	188 ± 8	94
Sn	120	181 ± 3	91
Sr	88	198 ± 8	99
Tl	205	182 ± 8	91
V	51	217 ± 10	109
Zn	66	218 ± 7	109

Results are given as mean ± standard deviation for 3 separate analyses.

* Values are µg mL⁻¹.

reduced to 32–37 µg mL⁻¹ when extractions were made by a mixture of 2 mL MeOH and 0.5 mL HNO₃ for which elemental recoveries varied between 89 and 111% (Table 2). Because Na₂SiF₆ is insoluble in alcohols [29], all elements, except Ca (~40% recovery) were quantitatively recovered from synthetic solutions by MeOH extraction with minimum levels of Si (18–25 µg mL⁻¹). Unfortunately, MeOH was not suitable for extractions from real samples. In soil sample (SRM 2711), accuracy for Cr, Cu, V and Zn was less than 80%, while that for Al, Ba, Ca, Fe, Mg, Mn and Sr was within 40–55%. The MeOH/HNO₃ (2/0.5 mL) mixture improved the recoveries for Cr, Cu, V and Zn by 8–14%, and thus, proved to be advantageous over MeOH to extract as many trace elements as possible despite slightly higher levels of Si in the solution.

Application to real samples

The procedure was applied to NIST soil and sediment reference materials (SRM 2711-Montana Soil and SRM 2704-Buffalo River Sediment) to evaluate the

applicability to the determination of the trace elements by ICP-MS. Soil and sediment samples, after microwave digestion in HNO₃/HF, were processed as described above (see Procedures) for removal of Si and extraction of trace elements. All elements were determined both in concentrated and diluted solutions. The results are summarized in Table 3. The recoveries for Al, Ba, Ca, Fe, Mg, Mn and Sr were low (~50–60%), most likely due to the formation of insoluble soluble fluorides or complex fluorosilicates. Attempts were made by adding boric acid (H₃BO₃) to another set of samples to prevent the precipitation of fluorides by complexing excess fluoride as BF₄⁻. However, the recoveries were not significantly different, suggesting that these elements were mainly co-precipitated within the sodium fluorosilicate.

The certified values of Si are 30.44 and 29.08% (m/m) for SRM 2711 and SRM 2704, respectively. The Si concentration from analysis solutions varied from 1.4 to 1.9% (m/m), which indicates that Si as the major constituent of the matrix was eliminated with 93–95% efficiency. In the presence of 550–600 µg mL⁻¹ Si, the suppression in the analyte ion signals was approximately 40–45% [8]. By the precipitation of Si as Na₂SiF₆, the magnitude of suppression in the concentrated sample solutions was decreased to 8–10%, which was attributed to the excess of the sodium chloride. By 10-fold dilution, this suppression was completely eliminated and accurate results were obtained for Cr, Cu, Ni, V and Zn.

Two isotopes, ⁶³Cu and ⁶⁵Cu, were used for the determination of Cu. The former suffers from the spectral overlap of ⁴⁰Ar²³Na if solutions contain high levels of sodium. The results in Table 3 indicate that there was not any significant contribution from ⁴⁰Ar²³Na to ⁶³Cu for which values were not significantly different from those obtained for ⁶⁵Cu. Molecular ion interferences of chloride include ⁴⁰Ar³⁵Cl on ⁷⁵As, ⁴⁰Ar³⁷Cl on ⁷⁷Se, ²³Na³⁷Cl on ⁶⁰Ni, and ¹⁶O³⁵Cl on ⁵¹V [15].²³ Despite the high concentration of chloride (e.g., 1200 µg mL⁻¹) in solutions, no significant interferences were observed on ⁷⁵As, ⁶⁰Ni and ⁵¹V, and the results agreed with the certified values. To elucidate the spectral interference of ⁴⁰Ar³⁷Cl on ⁷⁷Se, measurement was also performed using ⁸²Se which is virtually free from interferences of argon chlorides. There was not any evidence of the interference of ⁴⁰Ar³⁷Cl on ⁷⁷Se. Despite the fact the results for ⁷⁷Se and ⁸²Se were accurate in synthetic solutions, inter-isotopic results for Se in soil and sediments were

Table 3. Results for NIST soil and sediment samples obtained by ICP-MS after precipitation of Si ($\mu\text{g g}^{-1}$)

Element	Isotope	SRM 2711 Montana Soil		SRM 2704 Buffalo River sediment	
		Found	Certified	Found	Certified
As	75	102 ± 3	105 ± 8	19.7 ± 0.9	23.4 ± 0.8
Cd	114	41.3 ± 3.1	41.7 ± 0.25	3.54 ± 0.11	3.45 ± 0.22
Co	59	8.63 ± 0.68	10*	12.2 ± 0.3	14.0 ± 0.6
Cr	53	37.6 ± 4.7	47*	114 ± 8	135 ± 5
Cu	63	97.5 ± 15	114 ± 2	82.8 ± 4.5	98.6 ± 5
Cu	65	101 ± 12	114 ± 2	86.1 ± 2.5	98.6 ± 5
Hg	202	5.96 ± 0.97	6.25 ± 0.19	1.57 ± 0.06	1.44 ± 0.07
Ni	60	16.6 ± 1.6	20.6 ± 1.1	37.5 ± 2.7	44.1 ± 3
Pb	208	1178 ± 84	1162 ± 31	161 ± 8	161 ± 17
Sb	121	19.1 ± 1.1	19.4 ± 1.8	3.97 ± 0.21	3.79 ± 0.15
Se	77	1.28 ± 0.41	1.52 ± 0.14	0.763 ± 0.124	1.1*
Se	82	0.937 ± 0.433	1.52 ± 0.14	1.01 ± 0.50	1.1*
Sn	120	3.77 ± 0.72	nr	9.87 ± 0.71	9.5*
Tl	205	2.37 ± 0.14	2.47 ± 0.15	1.13 ± 0.12	1.2 ± 0.2
V	51	75 ± 3.2	81.6 ± 2.9	87 ± 6	95 ± 4
Zn	66	316 ± 15	350.4 ± 4.8	381 ± 21	438 ± 12

Result are given as mean ± 95% confidence interval of 4 separate analyses.

* NIST indicative value.

nr Not reported.

not only sporadic, but also were somewhat lower than the reported values. Selenium is relatively less sensitive in ICP-MS due to high first ionization potential (9.75 eV) as well as lower natural abundance of ^{77}Se (7.63%) and ^{82}Se (8.73%), therefore, the sporadic results for Se are attributed to the low levels of Se in these samples.

Conclusion

This study demonstrates an alternative analytical procedure to eliminate silicon matrix for analysis of high-silicon content materials by ICP-MS. The method is suitable for the determination of 14 trace elements, including As, Hg and Se for which determinations suffer from losses due to their volatile species for conventional heat-assisted elimination of silicon matrix. Precipitation of Si as Na_2SiF_6 is highly efficient and offers the capability for simultaneous removal of sodium and silicon that are usually present at considerably high levels in environmental samples. In addition, alkaline earth elements (Ca and Mg) do coprecipitate substantially within Na_2SiF_6 . Within this context, the method has the potential for matrix elimination in saline solutions, such as seawater and wastewater to alleviate the effects of matrix salts in ICP-MS determinations.

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References

- Hieftje G M, Myers D P, Li G, Mhoney P P, Burgoyne T W, Ray S J, Guzowski J P (1997) Toward the next generation of atomic mass spectrometers. *J Anal At Spectrom* 12: 287
- Beauchemin D (2004) Inductively coupled plasma mass spectrometry. *Anal Chem* 76: 3395
- Butler O T, Cook J M, Harrington C F, Hill S J, Rieuwerts J, Miles D L (2006) Atomic spectrometry update. *Environmental analysis*. *J Anal At Spectrom* 21: 217
- Wu S, Zhao Y, Feng X, Wittmeier A J (1996) Application of inductively coupled plasma mass spectrometry for total metal determination in silicon-containing solid samples using the microwave-assisted nitric acid-hydrofluoric acid-hydrogen peroxide-boric acid digestion system. *J Anal At Spectrom* 11: 287
- Moens L (1997) Applications of mass spectrometry in the trace element analysis of biological materials. *Fresen J Anal Chem* 359: 309
- Falk H, Geerling R, Hattendorf B, Kregel-Rothensee K, Schmidt K P (1997) Capabilities and limits of ICP-MS for direct determination of element traces in saline solutions. *Fresen J Anal Chem* 359: 352
- Inagaki K, Haraguchi H (2000) Determination of rare earth elements in human blood serum by inductively coupled plasma mass spectrometry after chelating resin preconcentration. *Analyst* 125: 191
- Arslan Z, Ertas N, Tyson J F, Uden P C, Denoyer E R (2000) Determination of trace elements in marine plankton by inductively coupled plasma mass spectrometry (ICP-MS). *Fresen J Anal Chem* 366: 273
- Palacios M A, Gomez M, Moldovan M, Gomez B (2000) Assessment of environmental contamination risk by Pt, Rh and Pd from automobile catalyst. *Microchem J* 67: 105

10. Clement R E, Paul W, Yang P W (2001) Environmental analysis. *Anal Chem* 73: 2761
11. Arslan Z, Paulson A J (2002) Analysis of biogenic carbonates by inductively coupled plasma-mass spectrometry (ICP-MS). Flow injection on-line solid-phase preconcentration for trace element determination in fish otoliths. *Anal Bioanal Chem* 372: 776
12. Arslan Z, Paulson A J (2003) Solid phase extraction for analysis of biogenic carbonates by electrothermal vaporization inductively coupled plasma mass spectrometry (ETV-ICP-MS): an investigation of rare earth element signatures in otolith microchemistry. *Anal Chim Acta* 476: 1
13. Webb E, Amarasinghwardena D, Tauch S, Green E F, Jones J, Goodman A H (2005) Inductively coupled plasma-mass (ICP-MS) and atomic emission spectrometry (ICP-AES): versatile analytical techniques to identify the archived elemental information in human teeth. *Microchem J* 81: 201
14. Evans E H, Giglio J J (1993) Interferences in inductively coupled plasma mass spectrometry. A review. *J Anal At Spectrom* 8: 1
15. May T W, Wiedmeyer R H (1998) A table of polyatomic interferences in ICP-MS. *Atomic Spectrosc* 19: 150
16. Nicolai M, Rosin C, Tousset N, Nicolai Y (1999) Trace metals analysis in estuarine and seawater by ICP-MS using on line preconcentration and matrix elimination with chelating resin. *Talanta* 50: 433
17. Chou C L, Moffatt J D (2000) A simple co-precipitation inductively coupled plasma mass spectrometric method for the determination of uranium in seawater. *Fresen J Anal Chem* 368: 59
18. Arslan Z (2005) Analysis of fish otoliths by electrothermal vaporization inductively coupled plasma mass spectrometry: aspects of precipitating otolith calcium with hydrofluoric acid for trace element determination. *Talanta* 65: 1326
19. Li Y C, Jiang S J (1998) Determination of Cu, Zn, Cd and Pb in fish samples by slurry sampling electrothermal vaporization inductively coupled plasma mass spectrometry. *Anal Chim Acta* 359: 205
20. Lee K H, Jiang S J, Liu H W (1998) Determination of mercury in urine by electrothermal vaporization isotope dilution inductively coupled plasma mass spectrometry. *J Anal At Spectrom* 13: 1227
21. Klaue B, Blum J D (1999) Trace analyses of arsenic in drinking water by inductively coupled plasma mass spectrometry: high resolution versus hydride generation. *Anal Chem* 71: 1408
22. Ingle C, Langford N, Harvey L, Dainty J R, Armah C, Fairweather-Tait S, Sharp B, Crews H, Roseb M, Lewis J (2002) Development of a high-resolution ICP-MS method, suitable for the measurement of iron and iron isotope ratios in acid digests of faecal samples from a human nutrition study. *J Anal At Spectrom* 17: 1498
23. Chen Z, Griffin I J, Plumlee L M, Abrams S A (2005) High resolution inductively coupled plasma mass spectrometry allows rapid assessment of iron absorption in infants and children. *J Nutr* 135: 1790
24. Haswell S J, Razagui I B A (1997) The determination of mercury and selenium in maternal and neonatal scalp hair by inductively coupled plasma-mass spectrometry. *J Anal Toxicol* 21: 149
25. Diaz-Somoano M, Martinez-Tarazona M R (1999) Application of ICP-MS to arsenic determination in solid samples containing silica. *J Anal At Spectrom* 14: 1439
26. Sandroni V, Smith C M M (2002) Microwave digestion of sludge, soil and sediment samples for metal analysis by inductively coupled plasma-atomic emission spectrometry. *Anal Chim Acta* 468: 335
27. Hoeing M, Baeten H, Vanhenterijk S, Vassileva E, Quevauviller P (1998) Critical discussion on the need for an efficient mineralization procedure for the analysis of plant material by atomic spectrometric methods. *Anal Chim Acta* 358: 85
28. Quevauviller P, Vercoetere K, Muntau H, Griepink B (1993) Certified reference material (CRM 414) for the quality control of trace element analysis in plankton. *Fresen J Anal Chem* 345: 12
29. Myshlyaeva L V, Krasnoshchekov V V (1974) Analytical chemistry of silicon. Wiley, New York
30. Paasche E (1980) Silicon content of five marine plankton diatom species measured with a rapid filter method. *Limnol Oceanogr* 25: 474
31. Arslan Z, Tyson J F (1999) Determination of calcium, magnesium and strontium in soils by flow injection flame atomic absorption spectrometry. *Talanta* 50: 929
32. Marczenko Z (1986) Separation and spectrophotometric determination of elements. Ellis Horwood, Chichester
33. Boer R H, Beukes G J, Meyer F M, Smith C B (1993) Fluoride precipitation in silicate wet-chemistry: implications on REE fractionation. *Chem Geol* 104: 93
34. Luke C L (1955) Determination of traces of boron in silicon, germanium, and germanium dioxide. *Anal Chem* 27: 1150
35. McLaughlin R J W, Biskupski V S (1965) The rapid determination of silica in rocks and minerals. *Anal Chim Acta* 32: 165