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Assessment of matrix-dependent analyte stability and volatility during open-vessel sample dissolution for arsenic, cadmium, mercury and selenium

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Abstract

Abstract The effects of calcium and magnesium (as nitrates) and phosphorous (as hydrogen phosphate) were investigated on the stability of As, Cd, Hg, and Se during open-vessel dissolution in Teflon vessels. Samples of mainly inorganic and biological matrices were dissolved in screw-capped Teflon tubes in HNO₃ only or in a mixture of HNO₃-HF. The caps were then removed and the solutions were simultaneously evaporated at 120 °C to near dryness without drying the contents (Method I) or to complete dryness with extended heating for 20 min at dryness (Method II). ICP-MS analysis indicated that the stabilities of Se and Hg were highly influenced by Ca, Mg and PO₄ content in the sample. Arsenic (As) and Cd did not show any significant instability or volatility. Selenium was lost in Method II from biological samples containing trace levels of Ca, Mg and PO₄. Mercury was unstable during heating in all samples, except bone ash for which no significant loss was detected in Method I. Losses observed for Hg and Se were consistent with Ca, Mg and PO₄ deficiency in the samples and hence indicated that nitrate and hydrogen phosphate salts of these matrix elements do improve stability of the relatively volatile elements during open-vessel dissolution in teflon vessels. While Se was effectively stabilized with sub-per cent levels of Ca, Mg and PO₄, Hg due its high volatility required significantly higher levels of Ca and PO₄ in the bone ash.

Keywords

Arsenic; Cadmium; Mercury; Selenium; Volatility; Heating; Matrix effect; Open-vessel dissolution; ICP-MS

Introduction

Rapid industrial and technological advancements and urban development have raised significant public awareness to environmental and toxicological issues related with trace

toxic heavy metals [1–3]. Heavy metals, including arsenic (As), cadmium (Cd), and mercury (Hg) are among the potential toxic elements that bioaccumulate in the environment and consequently enter the food chain [2,3]. Effects are significant even at low levels usually found in environmental samples, and therefore, sample preparation is critical for accurate determination of these toxic metals without losing information contained in the sample.

Inductively coupled plasma mass spectrometry (ICPMS) is today the standard technique in elemental analysis owing to its high sensitivity for measurements at parts per billion levels, although the sensitivity degrades in saline solutions [1–4]. Sample preparation by and large contributes the most to the inaccuracy through either incomplete dissolution, contamination or and analyte loss during the dissolution [5–9]. Closed-vessel digestion procedures are advantageous to minimize the analyte loss, but sample size is usually limited to 0.1–0.25 g to avoid damage to the digestion apparatus at high pressures [10–14]. Alternatively, open-vessel digestion procedures offer the ability to dissolve larger samples under relatively mild conditions. They are also advantageous to eliminate residual concentrated acids and volatile matrix constituents by evaporation.

Major concern with the open-vessels procedures is the risk of loss of relatively volatile elements, such as As, Cd, Hg and Se during dissolution. Matrix constituents in a sample could aid in improving stability of the elements during heating or evaporation, yet circumstances, efficiency and merits of such stabilization for quantitative analysis are not completely understood for samples of different nature and matrix composition. In this study, we examined stability/volatility issues for As, Cd, Hg and Se in open-vessel sample dissolution across different samples with special emphasis on the effects of Ca, Mg and PO₄ on analyte stabilization.

Experimental

Instrumentation

A DigiPrep Cube model block digestion unit (SCP Science, www.scpscience.com) was used for temperature controlled dissolution of the samples. The unit consisted of 20 wells accommodating 4-mL size Teflon tubes. Elemental measurements were carried out by using Perkin Elmer ELAN 6000 ICP-MS instrument (Shelton, CT, USA, www.perkinelmer.com). The instrumental conditions are listed in Table 1. Rhodium (¹⁰³Rh) was used as internal standard element to correct for the instrumental sensitivity changes induced by sample matrix and acidity.

Materials and solutions

Six different certified reference materials (CRM), including Montana Soil (SRM 2710), Marine sediment (PACS-2), Bone Ash (SRM 1400), Freshwater Plankton (CRM 414), Lobster Hepatopancreas (TORT-2) and Dogfish Liver (DOLT-2), were used to test the effects of sample matrix on the analyte stability. Trace metal grade HNO₃ and HF were obtained from Fisher Scientific (www.fishersci.com). Deionized water (18 MΩ cm⁻¹) was produced by Barnstead E-Pure system (www.thermo.com). A multielement stock standard solution (10 µg mL⁻¹) was made from 1000 µg mL⁻¹ single element standards (Fisher Scientific). This stock solution was used throughout for preparation of calibration standards. Mercury (Hg) was added from its 10 µg mL⁻¹ stock solution because of its incompatibility with other elements. Teflon tubes (4 mL) with screw caps were purchased from Savillex, Minnetonka, MN (www.savillex.com).

Dissolution procedures

All plastic ware and Teflon ware were cleaned by soaking in 5% HNO_3 solution overnight. Then they were dried under a laminar flow hood in the laboratory. For dissolution of soil (SRM 2710) and sediment (PACS-2) reference materials, approximately 0.15 g samples were measured into 4-mL Teflon tubes followed by addition of 2 mL concentrated HNO_3 and 1 mL HF. Initially, the tubes were screw-capped and heated in the digestion block at 140°C. Once entire sample was dissolved the cap was removed to evaporate the solution at 120°C. In Method I, the contents were evaporated to near dryness, but not dried. Approximately 0.5 mL solution was left at the bottom of the tube. In Method II, entire solution was first evaporated to dryness followed by continuous heating of dried residue at 120°C for about 20 min. At the end, samples from both procedures were dissolved and diluted with 5% HNO_3 to 10 mL in polypropylene tubes.

For Lobster Hepatopancreas (TORT-2), Dogfish Liver (DOLT-2) and Freshwater Plankton (CRM 414), approximately 0.25 g samples were digested in 3 mL HNO_3 and 0.5 mL HF in the Teflon tubes in the same way as the soil and sediment. Digests were also diluted to 10 mL with 5% HNO_3 after evaporating the solvent. In the case of Bone Ash (SRM 1400), about 0.10 g samples were weighed into the Teflon tubes. Before adding HNO_3 , each sample was spiked with 250 μL of 10 $\mu\text{g mL}^{-1}$ multielement solution and 250 μL of 10 $\mu\text{g mL}^{-1}$ Hg standard solution since this material has not been certified for the elements of interest yet. Then, 3 mL concentrated HNO_3 was added to tubes and the samples were digested at 140°C using the digestion block. Evaporations after dissolution were carried out according to Method I and Method II as described above and then the samples were redissolved and diluted to 10 mL with 5% HNO_3 . For closed-vessel digestion, approximately 0.1 g samples from SRM 2710, PACS-2, DOLT-2 and TORT-2 were digested with volumes of acids described above for particular materials in sealed Teflon vessels in a microwave oven. The contents were then diluted to 20 mL with water. Five replicate samples of each reference material were prepared for Method I and Method II.

Calibration and data analysis

External calibration was used with aqueous standard solutions of 0, 1, 5, 20, 50, 100 and 500 $\mu\text{g L}^{-1}$. Calibration standards for Hg were prepared separately as 0, 1, 5, 20 and 50 $\mu\text{g L}^{-1}$ from 10 $\mu\text{g mL}^{-1}$ Hg. Calibration blanks were prepared for Method I and Method II by treating the appropriate volumes of the acids used. Internal standard correction was made with ^{103}Rh which was added on-line to the sample solution by means of a Y-connection from its 100 $\mu\text{g L}^{-1}$ solution. Statistical analysis of the data was performed by using SYSTAT statistics package (Version 10). Paired t-test used for comparing the means between the methods. One sample t-test was used for comparing the experimental means with the certified values.

Results and discussion

Analyte stabilization via chemical modification is well documented in elemental determinations by graphite furnace atomic absorption spectrometry to reduce the volatility of the analyte during drying and high temperature charring [15–17]. In general, stabilization of analyte in the graphite furnace occurs by formation of inter-metallic compounds with the modifier or by the formation of thermally stable metal oxides. Most often solutions of precious metals, such as $\text{Ir}(\text{NO}_3)_3$ and $\text{Pd}(\text{NO}_3)_2$ are employed, yet solutions of $\text{Mg}(\text{NO}_3)_2$, $(\text{NH}_4)_3\text{PO}_4$ or $(\text{NH}_4)\text{H}_2\text{PO}_4$ and $\text{Ca}(\text{NO}_3)_2$ are also used successfully to reduce analyte volatility [15–17]. Although mechanisms of chemical stabilization in graphite furnaces may not be fully extrapolated to heating or drying in Teflon vessels, still high levels of calcium and magnesium nitrates and hydrogen phosphates resulting from nitric dissolution of a

sample are expected to induce measurable differences in chemical stability of the volatile elements during heating for dissolution in open vessels. .

Samples tested in this study were made up of either mostly inorganic (soil and sediment, bone ash) or organic matrix (plankton, lobster hepatopancreas and dogfish liver). Major constituents of soil and sediments are Si (ca. 28%) followed by Ca, Mg and P at percent levels. Bone ash (SRM 1400) is primarily calcium phosphate (39% Ca and 61% PO₄) from calcinations of bone. On the other hand, lobster hepatopancreas (TORT-2) and dogfish liver (DOLT-2) contain mainly proteinaceous material with trace levels of Ca, Mg and P. Freshwater plankton is mainly made up of organic material, but do contain siliceous material (1.3–1.5% Si) with Ca, Mg and P at percent levels [11,25].

Dissolution by digestion block

Successful dissolution was achieved for all samples under temperature-controlled heating at 140°C using the digestion block system. The heating time varied depending on the type of sample and was longer for TORT-2 and DOLT-2 due to prolonged heating needed for the destruction of the organic material. However, no visible loss in solution occurred during this period as the screw-cap of Teflon tube provided sufficient sealing. For evaporation of the solutions, temperature of the digestion block was reduced to 120°C. Evaporation in all solutions was almost uniform. Samples for Method I were removed from the digestion system when approximately 0.5 mL aliquot remained in the tubes. The other set of samples prepared for Method II were first completely dried and then heated for about 20 min at the dryness at 120°C. This extended heating procedure resulted in mild charring as detected from coloration of the residue, which was expected lead to losses through volatility for the elements of interest unless matrix elements did not influence their stability.

Effect of inorganic matrix on stability of elements

Soil and sediments—The results for Montana Soil (SRM 2710) and Marine Sediment (PACS-2) samples are summarized in Table 2 along with those from closed-vessel microwave-assisted digestion procedure. As expected, no analyte loss occurred in closed-vessel dissolution procedure for the elements since the environment was completely sealed. Paired t-test did not detect any significant differences between the mean values obtained by Method I and Method II ($p>0.05$), except those of Hg ($p<0.002$) and Se ($p<0.017$). Mercury was lost substantially even in Method I. Selenium values by Method I and closed-vessel dissolution were significantly higher, up to 45%, than those of Method II for SRM 2710 and PACS-2 ($p<0.05$). However, Method II provided better accuracy for Se with the certified concentration as it is clear from the results for PACS-2 ($p>0.05$), suggesting Se was indeed not affected from heating at dryness (Method II) despite its volatile nature (mp. 221°C). This effect is due to efficient stabilization of Se in solution, most likely by nitrates and hydrogen phosphates of Ca and Mg from acid dissolution of Ca, Mg, and PO₄ in the soil and sediments.

Selenium is not only a relatively insensitive element in ICP-MS, but also suffers from spectral interferences in argon plasma that are manifested by degraded precision and accuracy for determinations at depressingly low concentrations. Yet, accuracy can be achieved when samples are treated according to Method II based on the results from PACS-2, which in due course suggests that Se concentration obtained by Method II in SRM 2710 is closer to its true value. Improved accuracy for Se in Method II also suggests that higher results observed with Method I and closed-vessel dissolution are likely caused by spectral interferences of argon silicates on ⁸²Se isotope rather than degraded sensitivity, which are explained later in this section (see Freshwater plankton).

Cadmium (Cd) did not show any significant differences between the procedural treatments ($p=0.276$) in SRM 2710. However, Method I provided better agreement with the certified value ($p=0.065$) while those from Method II were marginally lower ($p=0.036$). Similar pattern was also observed in PACS-2 and the results from Method I overlapped with the certified value ($p=0.264$), but those from Method II were marginally lower ($p=0.035$). Cadmium (mp. 321°C) is the third most volatile element among those studied. These results indicate that Cd is relatively stabilized in soil and sediment matrices under mild heating at dryness at 120°C ; however, significant analyte loss may occur at higher temperatures.

No significant differences were found between the procedural results for As ($p>0.05$) in SRM 2710, nor did the results differ significantly from the certified value. In PACS-2, the results obtained by Method I were significantly higher for As ($p=0.029$) than those of Method II. However, the range of experimental results (mean $\pm$ std. dev.) from both methods overlapped the certified concentration. It is clear from this information that As was not affected from heating at dryness in soil and sediment samples.

Bone ash—Bone ash (SRM 1400) is primarily made up of calcium phosphate since all organics in bone are completely destroyed by high temperature calcination. Certificate values are not available for As, Cd, Hg and Se, therefore, the samples were spiked with Hg and multielement solutions to yield $25\text{ }\mu\text{g g}^{-1}$ levels for each element. Dissolution by HNO_3 yielded trace elements in a matrix of calcium nitrate and highly soluble calcium dihydrogen phosphate, $\text{Ca}(\text{H}_2\text{PO}_4)_2$, so that the dried residue readily dissolved in 5% HNO_3 . The results are shown in Table 2. Unlike its instability in soil and sediments, Hg was stable during heating at 120°C in Method I that consequently provided accurate results without any significant loss ($p=0.084$). Nevertheless, substantial loss occurred in samples treated by Method II ($p<0.001$). Additional experiments performed with another set of samples further confirmed this behavior that Hg was stable in bone ash solutions unless the samples were exposed to heat at dryness.

Mercury forms inter-metallic compounds with noble metals, such as Pb and Ir that are commonly used for stabilization of Hg during determination by graphite furnace atomic absorption spectrometry [15–20]. In most attempts, Pd proved to be the most effective chemical stabilization alone [18–20] or as a mixed-modifier with magnesium nitrate [18,19], potassium permanganate [21] and DDC [22], though silver nitrate (AgNO_3) and potassium permanganate (KMnO_4) also afforded accurate determinations in fast-furnace programs without Pd [23]. Calcium nitrate was reported to be suitable for stabilization of As [15,16,20] and boron (B) [25] during atomization from graphite platforms. In view of the results from SRM 1400 for Hg in Table 2, it can be suggested $\text{Ca}(\text{NO}_3)_2$ and $\text{Ca}(\text{H}_2\text{PO}_4)_2$ improves stability of Hg in solution, and hence loss through volatility is minimal during open-vessel dissolution of calcium—and phosphate-rich samples. Based on this, the instability observed for Hg in soil and sediments treated by Method I can be explained by the insufficient concentrations of the Ca, Mg and PO_4 (as nitrates and hydrogen phosphates) in soil and sediment solutions when compared to that of bone ash (39% Ca and 61% PO_4).

The results for As, Cd and Se did not show any significant loss due to heating at dryness (Method II) and the values agreed with those from Method I. This behavior can also be explained with effective stabilization by predominant $\text{Ca}(\text{NO}_3)_2$ and $\text{Ca}(\text{H}_2\text{PO}_4)_2$ matrix on these elements since solutions of calcium nitrate and dihydrogen phosphate have been found to reduce the volatility of a suite of trace elements at similar temperatures applied to dry aliquots in platform atomization [15–20,24].

Matrix stabilization of trace elements in biological samples

Freshwater plankton—Freshwater plankton contain high levels of Ca (6.5%), Mg (0.24%), P (1.23%) and Si (1.3%) [26]. Treatment with HNO_3 was insufficient for complete dissolution as there was undissolved material in the tubes. Adding with 0.5 mL concentrated HF and further heating enabled successful dissolution of the particulate matter. The results from the ICP-MS analysis of the CRM 414 are given in Table 3. Differences between Method I and Method II were marginal for As ($p=0.035$) and Cd ($p=0.085$). The results were lower in Method II than in Method I; however, the range of the experimental values was within that of the certified concentrations for As and Cd indicating that matrix stabilization was sufficient during dry heating. Hg was unstable both in Method I and Method II, and was lost substantially as in the soil and sediments. This result was attributed to the fact levels of calcium and magnesium nitrate and phosphates were not sufficiently high to achieve desired stabilization for Hg as in bone ash.

Selenium results were significantly lower in Method II than were in Method I ($p=0.001$). However, Method II yielded better agreement with the certified value as was observed for SRM 2710 and PACS-2, suggesting that high levels of nitrates and hydrogen phosphates of calcium and magnesium do afford efficient stabilization for Se in plankton which is largely made up of organics. Similarly, Se values measured by Method I were higher than those of Method II as in the soil and sediments. Because silicon is a major constituent of plankton, this discrepancy is indicative of spectral overlaps of various molecular ions, such as $^{34}\text{S}^{16}\text{O}_3$, $^{40}\text{Ar}^{28}\text{Si}^{14}\text{N}$ and $^{40}\text{Ar}^{30}\text{Si}^{12}\text{C}$ on ^{82}Se as mentioned earlier on soil and sediments. Hydrofluoric acid is a versatile reagent in eliminating Si as volatile SiH_4 from dissolution of silicates. However, this elimination takes place mostly when sample is heated at dryness as in Method II, which also aids in effective oxidation (e.g., charring) of organic components [11]. On the basis of this information, it can be clearly stated that higher values for Se from soil, sediment and plankton samples dissolved by Method I and closed-vessel procedure are caused by spectral overlaps on ^{82}Se from molecular ions containing Si, such as $^{40}\text{Ar}^{28}\text{Si}^{14}\text{N}$ and $^{40}\text{Ar}^{30}\text{Si}^{12}\text{C}$. Because samples treated by Method I and closed vessel dissolution procedures still contain substantially high concentrations of Si, such interferences are expected to induce incorrectly high results on Se present at low levels in the samples (see Tables 2 and 3).

Dogfish liver and lobster hepatopancreas

Unlike other samples, Dogfish liver (DOLT-2) and Lobster hepatopancreas (TORT-2) are mainly proteinaceous material (e.g., 23% lipids for DOLT-2) with trace levels ($\mu\text{g g}^{-1}$) of matrix elements (Ca, Mg, Fe, PO_4 etc.). Because of small size of the teflon tubes (4-mL), foaming occurred when samples were heated rapidly to 140°C . To avoid possible loss of solution due to over-boiling, samples were first heated slowly without closing the screw-caps until foaming ceased. Then the cap was tightened and the contents were digested as described above. The results are summarized in Table 3 with those obtained by closed-vessel digestion procedure.

Differences in the elemental results for Cd, Hg and Se were significant. Because Hg required substantially high amount of calcium nitrate and dihydrogen phosphate (see bone ash), the extent of loss in Hg was similar to that occurred in soil, sediment and plankton. Selenium results showed consistency between Method I and closed-vessel digestion, for which mean Se values were within the range of certified values for DOLT-2 and TORT-2 ($p>0.05$). However, the results from Method II were significantly lower ($p<0.008$). This information pinpoints to the loss of Se through volatility during heating at dryness (Method II). Unlike other samples (e.g. soil and plankton), both DOLT-2 and TORT-2 contain only trace levels of Ca, Mg and PO_4 . Thus, the loss of Se is thought to occur as a result of

insufficient stabilization by the matrix elements and hence clearly prove that Ca and Mg and PO₄ matrices assist in improving stability of Se during dissolution in Teflon vessels. This statement is also supported by the results from Method II for Se in other samples (e.g., soil and plankton) that contain Ca, Mg and PO₄ at percent levels.

It can be seen that As was not affected from heating at dryness in either sample since the procedural results were not statistically different, nor did they differ from the certified concentrations. Similarly, Cd did not show any sign of loss due to heating in DOLT-2 (Table 3). In TORT-2, the recoveries for Cd were 85% by Method I, 85% by Method II and 91% by closed vessel dissolution. Though the experimental values did not fall into the range of the certified concentration, the procedural variations between Method I and Method II were insignificant ($p=0.2$), nor were they statistically different from those by closed vessel dissolution ($p>0.05$). These results suggest that heating at dryness did not lead to any instability to induce measurable loss for Cd. Low recoveries were likely to arise from sampling of relatively small masses that may not represent the true sample. Such hurdles could be eliminated by digesting larger samples.

Conclusion

In this study, the effects of common matrix elements (Ca, Mg and PO₄) in a sample were investigated to understand the extent of possible chemical stabilization of relatively volatile elements in open vessel dissolution procedures in Teflon vessels. Figures 1 and 2 illustrate the recoveries for Hg and Se, respectively, to summarize the variations in their stabilities with sample type and heating scheme. Mercury as the most volatile element showed substantial loss during the heating of sample solutions in both methods. However, the same element was successfully stabilized in Method I in the presence of high calcium nitrate and dihydrogen phosphate matrix (e.g. bone ash solution, Fig. 1). Selenium is not affected from heating in Method I, but accuracy degrades in highly siliceous materials due to the significant spectral interferences from argon silicates (Fig. 2). Method II alleviates this problem and hence appears to be suitable for determination of Se in silicon-containing samples. On the other hand, Se did show instability in Method II for proteinaceous materials (DOLT-2 and TORT-2 in Fig. 2) resulting in losses via volatility. Such loss was not observed in Method II for soil, sediment and bone ash, nor did occur in mainly organic plankton sample. It is therefore concluded that Se is susceptible to loss through volatility in Method II if samples are deficient in or contain trace levels of Ca, Mg and PO₄.

Both Method I and Method II are equally suitable for determination of As and Cd since both elements remained relatively stable regardless of sample matrix. Though heating at dryness (Method II) yielded slightly lower results for Cd, the differences between recoveries from Method I and Method II were not significant among inorganic and biological samples. Thus, it can be concluded that Ca, Mg and PO₄ levels found in natural samples afford adequate stabilization for Cd if drying or evaporation in Teflon vessels is carried out at low temperatures. The same conclusion can be extended for As that was stable against evaporative heating at low temperatures even in largely biological samples.

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Fig. 1. Recoveries for Hg obtained by Method I and Method II from Montana Soil (SRM 2710), Marine sediment (PACS-2), Dogfish Liver (DOLT-2), Lobster Hepatopancreas (TORT-2), Freshwater Plankton (CRM 414) and Bone Ash (SRM 1400)

Fig. 2.
Recoveries for Se obtained by Method I and Method II from Montana Soil (SRM 2710), Marine sediment (PACS-2), Dogfish Liver (DOLT-2), Lobster Hepatopancreas (TORT-2), Freshwater Plankton (CRM 414) and Bone Ash (SRM 1400)

Table 1

Operating conditions of ELAN 6000 ICP-MS instrument

RF power, W	1200
Plasma gas flow, L/min	16
Nebulizer gas flow, L/min	0.85
Auxiliary gas flow, L/min	0.6
Nebulizer	Cross flow
Spray chamber	Double pass
Scanning mode	Peak Hop
Dwell time, ms	50
Sweeps/Reading	10
Readings/Replicate	1
Number of replicates	3
Resolution	Normal
Points per spectral pea	3

Table 2

Results from the elemental analysis of Montana Soil (SRM 2710), Marine Sediment (PACS-2) and Bone Ash (SRM 1400). Values are given as $\mu\text{g g}^{-1}$ (mean $\pm$ std. deviation) for five replicate analyses. Bone Ash samples contained $25 \mu\text{g g}^{-1}$ spike of each element. Values in parenthesis are “information only”

Sample	Method	^{75}As	^{114}Cd	^{202}Hg	^{82}Se
Montana Soil (SRM 2710)	Closed vessel	635 ± 24	20.3 ± 1.1	32.7 ± 2.7	1.35 ± 0.17
	Method I	658 ± 35	19.8 ± 1.3	11.9 ± 1.8	1.35 ± 0.12
	Method II	629 ± 15	19.1 ± 1.8	6.12 ± 0.18	1.10 ± 0.11
	Certified	626 ± 38	21.8 ± 0.2	32.6 ± 1.8	nr
Marine Sediment (PACS-2)	Closed vessel	25.7 ± 1.4	2.10 ± 0.18	3.19 ± 0.20	1.36 ± 0.14
	Method I	26.8 ± 0.51	2.05 ± 0.12	0.38 ± 0.07	1.32 ± 0.05
	Method II	25.4 ± 1.5	1.88 ± 0.13	0.15 ± 0.01	1.05 ± 0.20
	Certified	26.2 ± 1.5	2.11 ± 0.1	3.04 ± 0.2	0.92 ± 0.2
Bone Ash (SRM 1400)	Method I	25.9 ± 1.4	23.7 ± 1.4	26.3 ± 2.6	22.7 ± 1.8
	Method II	26.6 ± 1.3	24.3 ± 1.8	10.1 ± 6.3	23.8 ± 1.6
	Certified	(0.4)	(0.03)	nr	(0.08)

Table 3

Results from the elemental analysis of Freshwater Plankton (CRM 414), Dogfish Liver (DOLT-2) and Lobster Hepatopancreas (TORT-2). Values are given as $\mu\text{g g}^{-1}$ (mean $\pm$ std. deviation) for five replicate analyses

Sample	Method	^{75}As	^{114}Cd	^{203}Hg	^{82}Se
Freshwater Plankton (CRM 414)	Method I	7.08 $\pm$ 0.30	0.380 $\pm$ 0.021	0.14 $\pm$ 0.01	2.17 $\pm$ 0.18
	Method II	6.82 $\pm$ 0.38	0.365 $\pm$ 0.032	0.09 $\pm$ 0.01	1.81 $\pm$ 0.11
	Certified	6.82 $\pm$ 0.28	0.383 $\pm$ 0.014	0.276 $\pm$ 0.018	1.75 $\pm$ 0.10
Dogfish liver (DOLT-2)	Closed vessel	17.3 $\pm$ 2.2	20.7 $\pm$ 2.0	2.19 $\pm$ 0.25	6.36 $\pm$ 0.61
	Method I	17.2 $\pm$ 1.0	19.3 $\pm$ 0.7	0.54 $\pm$ 0.02	6.42 $\pm$ 0.25
	Method II	17.0 $\pm$ 1.1	19.1 $\pm$ 0.8	0.38 $\pm$ 0.07	5.36 $\pm$ 0.20
Lobster Hepatopancreas (TORT-2)	Certified	16.6 $\pm$ 1.1	20.8 $\pm$ 0.5	2.14 $\pm$ 0.28	6.06 $\pm$ 0.49
	Closed vessel	21.9 $\pm$ 1.3	24.3 $\pm$ 0.5	0.254 $\pm$ 0.015	5.86 $\pm$ 0.46
	Method I	22.7 $\pm$ 0.8	22.8 $\pm$ 1.3	0.09 $\pm$ 0.001	5.96 $\pm$ 0.63
	Method II	22.3 $\pm$ 1.5	22.2 $\pm$ 1.1	0.06 $\pm$ 0.001	2.87 $\pm$ 0.14
	Certified	21.6 $\pm$ 1.8	26.7 $\pm$ 0.6	0.27 $\pm$ 0.06	5.63 $\pm$ 0.17