Determination of Selenium in Seafoods Using Electrothermal Atomic Absorption Spectrometry with Slurry Sample Introduction

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An electrothermal atomic absorption spectrometric procedure for the rapid determination of selenium in seafoods without previous dissolution of the samples is discussed. The lyophilized samples are suspended in 5 mL of double-distilled water containing 10% v/v ethanol, 10% v/v concentrated hydrogen peroxide, 1% v/v concentrated nitric acid, and 0.08 g of nickel nitrate. A fast-heating program, with no ashing or cleaning stage, is used. By introducing a delay time of 1 s between the start of atomization and the start of the measurement of the integrated absorbance, reliable results are obtained using a spectrometer equipped with a deuterium-arc background corrector. Simple aqueous standards are used for calibration. The results agree with those obtained by hydride generation atomic absorption spectrometry. The detection limit is 0.2 μg/g of selenium when using the maximum recommended percentage of 1% w/v for the slurry preparation.

Keywords: *Selenium; AAS; ETAAS; seafood; slurry*

INTRODUCTION

Because of its high sensitivity, electrothermal atomic absorption spectrometry (ETAAS) is a suitable technique for determining low amounts of selenium. However, the determination is not free of problems and, as pointed out (Carnrick et al., 1983), there are probably more contradictory or confusing reports on the topic than for any other analyte. The difficulties begin during sample preparation; the procedures used for dissolution must be carefully selected to prevent loss of volatile selenium compounds (Radziuk and Thomassen, 1992). Other analytical problems are related to thermal preatomization losses and to spectral and chemical interference (Aller and García-Olalla, 1992; García-Olalla and Aller, 1992; Johannessen et al., 1993; Kumpulainen and Saarela, 1992; Welz et al., 1992). The literature has proved that most of the spectral interferences are eliminated by Zeeman correction (Aller and García-Olalla, 1992; García-Olalla and Aller, 1992; Johannessen et al., 1993; Kumpulainen and Saarela, 1992; Welz et al., 1988, 1992), although it does not appear to be absolutely necessary for all analytical situations, since some authors have reported accurate results using deuterium devices for correction when dealing with samples as diverse as whole blood, tissues, skimmed milk, or bovine liver (Bauslaugh et al., 1984).

Most of the numerous papers published to date on the ETAAS determination of selenium are based on the previous dissolution of the samples. However, despite the advantages of using suspensions in ETAAS (Bendicho and de Loos-Vollebregt, 1991; Miller-Ihli, 1993), there are few studies which deal with the determination of selenium in slurried samples. To the best of our knowledge, since the work of Ebdon and Parry (1988) on selenium determination in coal samples, the slurry-ETAAS approach has only been used to analyze fly ash (Bradshaw and Slavin, 1989), milk (Wagley et al., 1989), and wheat flour (Bendicho and Sancho, 1993). These studies were based on the use of Zeeman correction except in the case of coal, for which a comparison of the deuterium and Smith−Hieftje correction systems was carried out.

The aim of the work reported here was to develop a slurry-based procedure for the rapid determination of selenium in seafood samples. The procedure uses a commercial instrument equipped with a deuterium device, which is still the most commonly used system for correction in many laboratories involved with routine analyses. Our results indicate that, by using appropriate experimental conditions, rapid and reliable analytical data on selenium content can be obtained using this low-cost correction system.

EXPERIMENTAL PROCEDURES

Apparatus. A Perkin-Elmer Model 1100B atomic absorption spectrometer equipped with deuterium arc background correction and an HGA-400 electrothermal atomizer were used. Measurements were performed at 196.0 nm using an electrodeless discharge lamp operated at 210 mA from an external power supply (Perkin-Elmer System 2). A spectral bandpass of 2.0 nm was selected. Argon was used as the inert gas at 300 mL/min except during the atomization step, when the flow was stopped. Pyrolytic graphite coated graphite tubes with fork pyrolytic graphite platforms (Perkin-Elmer B050-5057) were used for all experiments.

Manual homogenization vessels (potters) of 10 mL equipped with Teflon plungers were also used. A Branson ultrasonic bath of 14-W constant power was ocassionally used.

The Perkin-Elmer MHS-10 hydride generation system was used for comparison purposes. The hydride generator was connected to a 10 cm long T-shaped silica tube, which was heated in an air−acetylene flame using a 10 cm single-slot burner. Argon was used as the carrier gas.

Reagents. Doubly distilled water was used throughout. High-quality ethanol (Riedel-de Haën) and concentrated nitric acid (Merck) were used. Concentrated hydrogen peroxide and the other chemicals used were obtained from Fluka. A stock solution of selenium (1000 μg/mL) was obtained from Panreac (Spain), and appropriate working standards were prepared from this solution.

For the hydride generation procedure a 1% w/v solution of sodium tetrahydroborate containing 1% w/v of sodium hydroxide was used.

Procedures. All of the samples were purchased in a local market. They were thoroughly washed with pure water and freeze-dried before being ground in a domestic mill for 2 min

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Table 1. Furnace Program[a]

step	temp (°C)	ramp time (s)	hold time (s)
dry	400	20	15
atomize	2400	0	4[b]

[a] All temperatures and times quoted are values set on the HGA-400 power supply. [b] Delay time 1 s, integration time 3 s, stop flow −5 s.

Table 2. Results for the Determination of Selenium in Different Samples

sample	selenium content[a] (μg/g)	
	slurry procedure	HGAAS
mussel	2.05 ± 0.08	2.07 ± 0.15
canned mussel	1.92 ± 0.09	1.78 ± 0.11
clam	0.41 ± 0.06	0.43 ± 0.04
canned clam	0.92 ± 0.06	0.90 ± 0.21
swordfish liver	18.2 ± 0.95	17.3 ± 1.22
cat food	0.68 ± 0.03	0.60 ± 0.12
SRM 1566a (oyster tissue)	2.10 ± 0.11	2.21 ± 0.24[b]

[a] Mean ± SD (n = 5). [b] Certified value.

and then in a ball mill for another 15 min, the powdered materials being kept in tightly closed plastic containers. No sieving was carried out. Slurries were prepared by adding 5 mL of a solution containing 10% v/v ethanol, 10% v/v hydrogen peroxide, 1% v/v nitric acid, and 0.08 g of $Ni(NO_3)_2 \cdot 6H_2O$ to the ground sample, which was weighed directly in a potter. The slurries were homogenized by repeated movements of the plunger. It was verified that 20 slow movements of the plunger (about 5 min) sufficed to obtain a good dispersion of the powders. Next, the vessels containing the slurries were placed in a magnetic stirrer and, while they were being continuously stirred, 20 μL aliquots were taken and injected into the furnace. The heating program given in Table 1 was run and the background-corrected peak area due to selenium obtained. Calibration was performed using aqueous standards. The certified reference material was analyzed in the same way, including the grinding stage with the ball mill.

For comparison purposes, the samples were also analyzed by using hydride generation atomic absorption spectrometry. For this, 0.5 g fractions of the powdered samples were dissolved as indicated elsewhere (Hershey et al., 1988), and the solutions were finally made up to 10 mL. Selenium was determined (Welz and Schubert-Jacobs, 1986) by using 1−2 mL aliquots diluted to 10 mL with a 5 M hydrochloric acid solution. Integrated absorbance was used as the analytical signal.

RESULTS AND DISCUSSION

The preliminary experiments revealed problems in the obtention of suitable slurries from the samples quoted in Table 2. This was due to the physicochemical properties of these powdered samples which, once suspended, tended to agglomerate, making reproducible sampling with the micropipet very difficult. The best way to overcome this difficulty would have been to use a high-power ultrasonic probe (Miller-Ihli, 1988), but this accessory was not available in our laboratory. Several other approaches, such as the addition of surfactants or the use of a common ultrasonic bath, proved to be unsatisfactory. The best results were obtained when homogenization was carried out by using hand homogenizers (potters) of the type commonly used for biochemical or medical purposes, as indicated under Experimental Procedures.

Suspension Medium. The atomization of slurries prepared from seafoods for selenium determination resulted in very high backgrounds, which usually exceeded the correction performance of the deuterium device. To reduce this problem, hydrogen peroxide was incorporated in the suspension medium. This is a simple way of obtaining an oxidizing environment for the heating cycle, which was already tried (Ebdon and Parry, 1988) and which has recently proved (Viñas et al., 1994, 1995) to be a useful alternative to an air-ashing stage. The decomposition of the chemical when the furnace program is run destroys a part of the organic matter. The considerable reduction in background level is illustrated in Figure 1, which shows atomization profiles of selenium obtained from slurries prepared in the absence and presence of the oxidant. An additional benefit obtained from using hydrogen peroxide is the decrease in the accumulation of carbonaceous residues inside the atomizer, a problem commonly found when slurries prepared from samples with a high organic content are atomized, especially if the fast-heating approach is used. Thus, when using 10% v/v of concentrated hydrogen peroxide in the suspension medium, it was possible to make 50 injections of a 1% w/v mussel slurry before it was necessary to mechanically clean the residues inside the atomizer. In the absence of the oxidant, cleaning was necessary after only four or five injections of the same slurry.

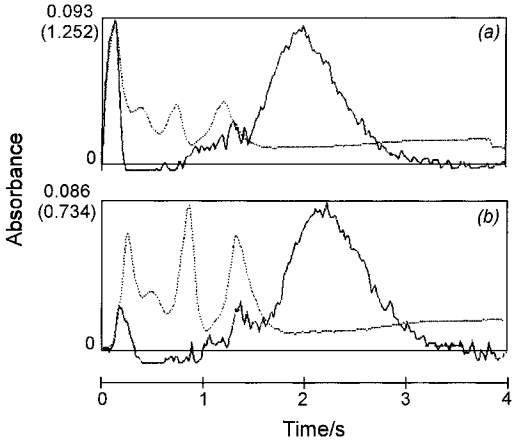

Figure 1. Atomization profiles obtained from a 20 μL aliquot of a 1% mussel suspension; dotted lines are background absorbances. The numbers on the ordinate axis indicate the maximum value reached by the corrected absorbance and the background (value in parentheses) (a) in the absence of hydrogen peroxide and (b) in the presence of 10% concentrated hydrogen peroxide.

Figure 1 shows that most of the background appeared at the beginning of the atomization stage, and it was mainly during these first tenths of a second that the deuterium device was unable to carry out a reliable correction, leading to evident overcompensation effects. At the same time, the instrument provided an apparently atomic signal, associated with the very high background. We think this was a false analyte peak for the following reasons. First, since the experiments were performed in the presence of nickel (or palladium), atomic signals would not be expected as early as 0.2−0.4 s after the beginning of the atomization stage, when the furnace is still relatively cool. Second, when aqueous selenium was added to the slurries, the apparent atomic signal did not increase, although the signal appearing at 2 s did so. However, these observations are not absolute proof that the signals below 1 s are not due to selenium, because the analyte might have been present in the sample as two compounds with different volatilities. To clarify this, the heating program was modified by introducing a 1 s delay between the start of the atomization stage and the beginning of absorbance integration. When this modification was

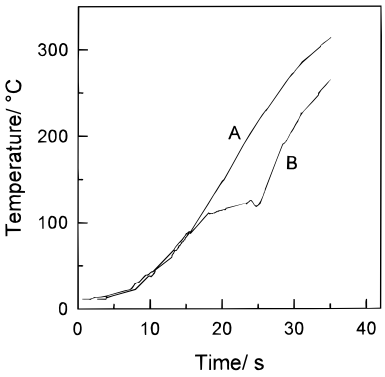

Figure 2. Temperature response of a thermocouple in the drying stage: (A) no sample injected; (B) 20 μL of the suspension medium.

used, the results referring to the selenium content obtained by standard addition calibration graphs and by direct calibration against aqueous standards agreed with those found by hydride generation atomic absorption spectrometry (HGAAS). This was considered to be more solid proof that the signal was a false peak and, so, the remaining experiments were performed with the delay time incorporated. This also prevented the high backgrounds appearing during the first second of atomization when the deuterium device was unable to provide an adequate correction.

Optimization of the Heating Program. Instrumental Parameters. The heating program was optimized by using fast-program methodology (Halls, 1984). When using this approach, the conventional drying and ashing steps are replaced by a modified drying stage at a temperature higher than that of the boiling point of the solvent. The power supply of the atomizer is programmed to hold this temperature over a sufficiently long period of time for the sample to be dried completely and for smoke to be removed before atomization. However, the presence of ethanol and, especially, of a high percentage of hydrogen peroxide in the suspension medium made it necessary to alter the recommended way in which this modified drying stage is performed. The common practice is to use a 1 s ramp, but this produced sputtering, particularly when aqueous standards were being dried. To avoid this, it was necessary to program the power supply of the HGA-400 to attain a theoretical temperature of 400 °C with a slower heating ramp (20 s). It is interesting to note that, as reported elsewhere (Halls, 1984, 1989; López García et al., 1993), the actual temperature inside the atomizer lags behind the programmed temperature for a noticeable interval of time, especially when low heating rates are programmed on the power supply. This effect is illustrated in Figure 2, which shows the temperature response of a thermocouple placed inside the atomizer while the first step of the program given in Table 1 was run. Although the response of the thermocouple must be considered as approximate rather than absolute due to the operation mode (López García et al., 1993), it is clear that the temperature had barely reached 300 °C at the conclusion of the modified drying stage. Figure 2 also indicates that a 20 μL aliquot needed 25 s from the start of the ramp for it to be completely dried. Taking into account that the electrothermal atomizer used automatically switches off the inner purge gas 5 s before the start of the atomization stage, the holding time of the drying step was fixed at 15 s. In this way, both the complete drying of the aliquot and the removal of smoke at the beginning of the atomization stage were ensured.

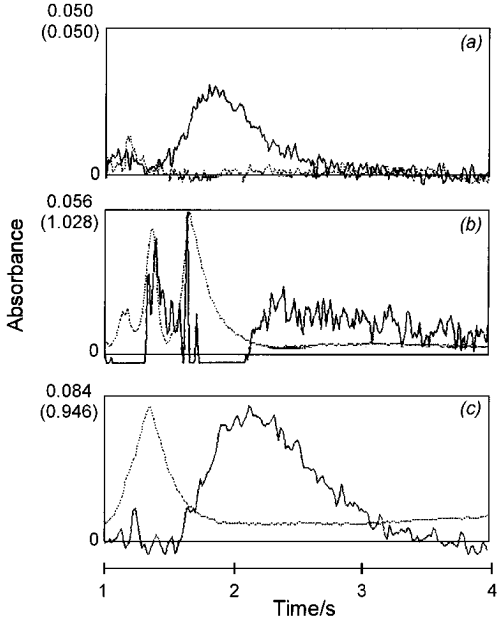

Figure 3. Atomization profiles for (a) 0.28 ng of aqueous selenium, (b) a 20 μL aliquot of a 1% mussel suspension with no modifier, and (c) as (b) but in the presence of nickel.

At first glance and taking into account the relatively low temperature of the atomizer at the end of the drying stage, the use of a modifier in fast-program methodology appears to be unnecessary, since the risk of analyte loss is low. However, as can be seen in Figure 3, a chemical modifier is imperative, because in its absence the analytical signal overlaps the high background. The modifier is necessary, then, to obtain an atomization profile for the analyte which is delayed with respect to that of the background, thus increasing the reliability of the spectral correction.

Special attention was paid to the choice of chemical modifier, a topic of controversy in the literature (Johannessen et al., 1993). Some authors (Laborda et al., 1993; Radziuk and Thomassen, 1992; Saeed and Thomassen, 1981, 1982) recommend nickel, while others (Dočekalová et al., 1991; Johannessen et al., 1993) suggest palladium or mixtures of palladium and magnesium. In addition, it has been pointed out (Dočekalová et al., 1991; Radziuk and Thomassen, 1992) that both the nature and the amount of modifier to be used depend on a number of factors, the type of sample being important for the correct choice. Both palladium and nickel were assayed as modifiers using a 1% w/v slurry prepared from lyophilized mussel. The values of integrated absorbance due to selenium are plotted in Figure 4 against the amount of modifier contained in a 20 μL aliquot of the slurry. Twenty-five micrograms of palladium or 60 μg of nickel sufficed to delay the atomization profile of selenium, giving maximum and reproducible analytical signals. These values agree with those reported in the literature for urine samples (Laborda et al., 1993; Radziuk and Thomassen, 1992; Saeed and Thomassen, 1981).

The choice between palladium and nickel was based on the following observations: (*i*) The background in the presence of palladium was slightly lower than that obtained in the presence of nickel, although the solutions of the former gave an atomic signal of selenium

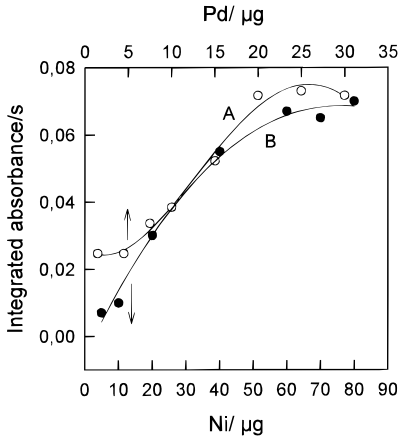

Figure 4. Effect of the modifier on the integrated absorbance from a 20 μL aliquot of a 1% mussel suspension: (A) nickel; (B) palladium.

for the blank assay, while nickel solutions did not. (*ii*) When aqueous standards of selenium were added to the suspension medium containing hydrogen peroxide and palladium, a black precipitate gradually appeared and the absorbances obtained in the atomization stage decreased as the time elapsed from the preparation of the standard increased. A similar effect has already been reported for palladium as modifier when samples such as body fluids were analyzed (Radziuk and Thomassen, 1992). It was proved that the kinetics of this process was mainly dependent on the hydrogen peroxide concentration and on the degree of illumination in the laboratory and, to a lesser extent, on the acidity and aging of the modifier solution. This effect did not occur when using nickel. (*iii*) The price of palladium salts is much higher than that of nickel, an important point if a high number of routine analyses have to be carried out. Consequently, nickel was selected as the more adequate modifier. No advantages were found when magnesium nitrate was used together with nickel or palladium (Laborda et al., 1993).

The atomization temperature was studied in the 2000−2600 °C range. Irrespective of whether nickel or palladium was used as the chemical modifier, the signals reached a maximum and were constant at or above 2400 °C, which was the atomization temperature selected. This was maintained for 4 s, although the absorbance was only integrated during the last 3 s by introducing a delay time of 1 s, as indicated above.

The possible benefits of including a cooling stage in the heating program before atomization were also considered. It has been reported that the inclusion of this step delays the vaporization of the analyte until more isothermal conditions exist, reducing possible gas-phase interferences (Dočekalová et al., 1991; Frech et al., 1992). The cooling stage was discarded because no advantages with regard to sensitivity (Dedina, 1991), accuracy, or reduced background were noted. This is not surprising since a conventional ashing step was not used and, in fact, the furnace was relatively cool when the atomization stage began. The use of a reduced flow of the purging gas during atomization to prevent physical interferences was not considered due to the reduction in sensitivity that would have occurred.

Although preliminary experiments were performed including a cleaning stage (2650 °C, ramp 1 s, hold 3 s) in the program, this proved to be unnecessary. No cross-contamination was observed in the absence of this stage, and the accumulation of residues inside the

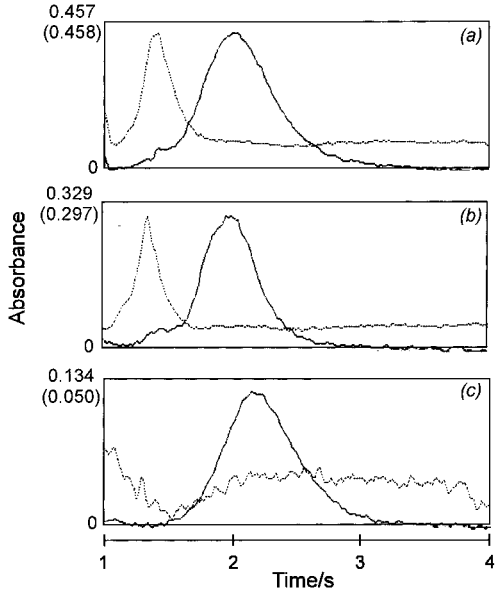

Figure 5. Atomization profiles obtained from a 0.6% swordfish liver slurry by injecting, (a) the suspension, (b) the supernatant, and (c) the solid remainders once resuspended.

atomizer was the same as when it was used. The final heating program consisted of only two stages with a total duration of 39 s (Table 1). It must be noted that the temperatures quoted in the table are values programmed on the HGA-400 power supply. Since there is a lag (Halls, 1984, 1989; López García et al., 1993) between the programmed temperature and the actual temperature reached inside the atomizer, the values given should be checked when other electrothermal atomizers are used. A number of experiments were also made by using the 204 nm line and varying the electrodeless lamp intensity (150−210 mA) and slit width (0.7 and 2.0 nm). However, the best results were obtained when using the values recommended under Experimental Procedures.

Percentage of the Suspension. The effect of the percentage of solid matter contained in the suspension was studied by using 10 slurries covering the 0.2−3% w/v range prepared from a sample containing 2.05 μg/g of selenium. Nickel was added as the modifier in such a way that 60 μg was contained in a 20 μL aliquot. Ten measurements were obtained from each slurry, and a linear relationship (r = 0.9987) between the mean values of the integrated absorbances and the slurry percentages was found in the 0.2−1.2% w/v range. When using 100 and 200 μg of nickel, the linear range could be extended up to 1.4 and 1.6% w/v, respectively. For slurry percentages above these values, even in the presence of higher amounts of nickel, the background levels were so high that the analytical signals decreased when the slurry percentage increased. This effect was a consequence of the inability of the deuterium device to correct high backgrounds, which led to overcompensation and correspondingly low analytical signals. To ensure reliable correction by the deuterium device, the maximum slurry percentage recommended is 1% w/v.

On the other hand, it is well-known (Bradshaw and Slavin, 1989) that, in dealing with slurries, a fraction of the analyte is extracted into the liquid phase, which improves reproducibility. It was found that 25% of the total selenium in samples was extracted into the liquid phase when using 0.1% v/v of concentrated nitric acid in the suspension medium. The percentage extracted increased to 75% (mean value for three different samples)

when the nitric acid concentration was increased to 1%. The percentage did not significantly increase at higher acid concentrations. These data were obtained by filtering the suspensions through chromatographic membrane filters and determining selenium in the supernatants. It is interesting to note that the background levels obtained when the supernatant solutions were atomized were similar to those obtained in the atomization of slurries. This can be seen in Figure 5, which shows the atomization profiles obtained for the analysis of a 0.6% w/v slurry prepared from swordfish liver (a), the supernatant obtained after filtering through a 0.2 μm filter (b), and the solid residues once they were resuspended (c). This means that slurry filtration cannot be considered as a way of avoiding high backgrounds.

Calibration, Reproducibility, and Results. Standard addition calibration graphs were obtained from five slurries prepared from mussel (selenium content 2.05 μg/g) in the 0.2−1.0% w/v range. Each graph consisted of four points, and five measurements were obtained after each addition of selenium. The slopes of these graphs were in the 0.1462−0.1605 s/ng range, showing no significant differences with the slope of a calibration graph obtained using aqueous standards (slope 0.1576 ± 0.0056 s/ng), meaning that direct calibration using aqueous standards is valid. The characteristic mass was 28 pg, which agreed with previous papers (Laborda et al., 1993), leading to a detection limit (3σ criterium) of 0.18 μg/g for slurries prepared at concentrations of 1% w/v. The sensitivity of the proposed method was not as high as might be wished due to the organic content of the seafood matrix, which makes the preparation of more concentrated suspensions difficult, but it appears to be sufficient for the routine control of the levels normally found in these samples. The repeatability of the measurements was checked by using suspensions also prepared in the 0.2−1% w/v range. Ten successive measurements were obtained at each concentration level. The relative standard deviations (RSD) were in the ±2.5−6.3% range. In addition, to check the repeatability of the whole procedure, 10 suspensions from the same sample were prepared (1% w/v) and each suspension was measured 10 times. The RSD values were in the ±2.5−4.7% range.

Since background correction was carried out by a deuterium device, which certainly performs less well than a device based on Zeeman effect, it was considered to be imperative to check the reliability of the procedure, i.e., its accuracy, by analyzing the samples using another approach not based on ETAAS. Only in this way could the presence of significant errors due to structured background and overcompensation effects be detected. For this reason, once the samples were acid-dissolved, they were analyzed using HGAAS, as indicated elsewhere (Welz and Schubert-Jacobs, 1986). As Table 2 shows, the results obtained in this way agreed with those found by using the slurry approach. The result for the clam sample was the only one that showed a high RSD, as a consequence of the very low content, which was close to the detection limit. The reliability of the procedure was further checked by analyzing a standard reference material (NIST oyster tissue). As is also shown in Table 2, the result agreed with that certified.

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