Hydride Generation Atomic Absorption Spectrometry with insitu Graphite Tube Trapping for the Determination of Se (IV) and Se (VI) in Baltic Sea Water Samples

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Abstract: This paper reports the results of an optimisation study for a procedure to determine the total selenium and its inorganic species, Se(IV) and Se(VI) using atomic absorption spectrometry combined with hydride generation and in-situ trapping of the analyte on the inner walls of the graphite tube. With the use of the proposed modification, a detection limit (3σ) of 0.018 ng/ml is achieved. This paper presents exemplary results, according to the proposed procedure, for selenium determination in samples of marine water. The concentrations of selenium in the samples ranged from < 0.02 ng/ml to 0.16 ng/ml of Se(IV) and from < 0.02 ng/ml to 0.10 ng/ml of Se(VI).

Keywords: selenium, atomic absorption spectrometry, hydride generation, in-situ trapping

1 Introduction

Selenium can be easily separated from a matrix by its conversion into a volatile hydride, which can be trapped on the inner walls of a graphite tube in the presence of an previously introduced modifier. This procedure, known as in-situ pre-concentration, ensures a lower

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detection limit, simplicity of operation, high accuracy and precision, control the reaction and its automation, and a limit of determination lower than via flame graphite tube atomisation. The procedure also allows for the elimination of interferences appearing as a result of different hydride generation rates and ensures almost complete separation of selenium from other potentially interfering compounds in the matrix [1].

The in-situ pre-concentration of the analyte in a graphite tube was reported for the first time by Drasch in 1980 [2]. In this method, the generated hydride is introduced by a carrier gas (Ar or He) into a graphite tube heated to the proper temperature. There, as a result of thermal decomposition, the element under determination is adsorbed on the inner walls of the graphite tube. The concentrated analyte is then atomised at about 2000 °C. In order to enhance the effectiveness of the pre-concentration, the walls of the graphite tube are covered with a modifier, which is either introduced at the appropriate stage of the thermal cycle or electrothermally deposited [3]. The modifiers can be the compounds of palladium [4-8], magnesium [6,9,10], zirconium [11], iridium [8,11-14], or permanent modifiers like Zr, Ir, W, Nb [5,15,16]. Palladium and other metals are able to bind selenium as intermetallic compounds, which evaporate at temperatures higher than selenium itself [17,18], although this mechanism has been criticised by other authors [19].

The use of the hydride generation technique for the separation of an element under determination from its matrix, followed by in situ trapping, permits the determination of not only the total concentration of selenium in the sample but also differentiates selenium by species. This paper presents results of determination of both Se(IV) and Se(VI). The effectiveness of pre-concentration in the graphite tube is evaluated relative to the type and mass of the modifier and the temperature. The determination of the selenium species is performed by taking advantage of the differences in the kinetics of hydride generation from the compounds of Se(IV) and Se(VI). The determination was performed on samples of marine water, using thiourea as a reducing agent and palladium as a modifier.

2 Experimental

2.1 Reagents

The chemical reagents were of analytical grade; water was redistilled and subjected to ion-exchange in a MilliQ (Milipore) unit. Standard solutions of Se (IV) and Se(VI) of the concentration of 1 mg/ml were made from weighed portions of sodium selenite (IV) and sodium selenate (VI) (Sigma Aldrich). Solutions of lower concentrations were prepared by dilution on the day of the analysis; the solutions were stored in polyethylene flasks. A solution of sodium borohydride was made on the day of the analysis by dissolving NaBH₄ in 1% (w/v) sodium hydroxide (Sigma Aldrich). Modifier solutions of Pd, Ir, Ni, Os, Ru, and Rh (0.5 mg/ml) were made by dilution of appropriate commercial solutions (chloride or nitrate). The thiourea solution (1 mol/l), used for the preliminary reduction of Se(VI) to Se(IV), was prepared from a weighed portion. The solutions of the hydrochloric acid (Merck) (3% and 30%), were prepared by the appropriate dilutions.
2.2 Instruments

The main instrument was an atomic absorption spectrometer SpectrAA 20 Plus made by Varian with a HCL lamp (Varian): wavelength, 196.0 nm; gap, 1 nm; lamp current, 5 mA. A GTA96 atomiser was used for analyses with atomisation in a graphite tube (GFAAS) and in-situ trapping. An autosampler was used for introduction of the modifier doses. The process of hydride generation was carried out in a VGA-77 unit connected to the graphite tube by an elastomer cable ending with a capillary tube, and removed from the atomiser for the process of atomisation. The capillary tube was inserted manually with a special Teflon insert ensuring that the capillary tube end was set inside the graphite tube. The graphite tubes used for the analyses with in-situ trapping were covered with pyrolitic graphite and without platforms. The carrier gas was argon. The analytical conditions for HGAAS and HG-GFAAS (atomic absorption spectrometry with generation of hydrides and in-situ pre-concentration on the graphite tube) determinations are shown in Table 1.

| Parameter                        | Value       |
|----------------------------------|-------------|
| Sample flow rate                 | 5 ml/min    |
| Reducing agent (NaBH₄) flow rate | 1 ml/min    |
| NaBH₄ concentration              | 0.3 %       |
| Acid flow rate                   | 1 ml/min    |
| HCl concentration                | 1 mol/l     |

Table 1 Parameters of the analytical system used for hydride generation.

Table 2 presents a thermal programme and analytical procedures used for selenium determination by the GFAAS and in-situ trapping method. The thermal treatment programme used included a drying stage, thermal reduction of the modifier, hydride trapping, atomisation and graphite tube cleaning. For each stage the optimum temperature, duration, and gas flow rate were adjusted. The programme started with the autosampler introducing a predetermined volume of modifier solution into the graphite tube. After the drying and reduction stages and when the furnace temperature had decreased to the optimum for hydride trapping, the quartz capillary was inserted into the graphite tube. At that point the process of hydride pre-concentration began, followed by atomisation (preceded by removal of the capillary), and measurement of the analytical signal. The cycle ended with the cleaning of the graphite tube.

2.3 Samples

Samples of marine water were collected at the Gdańsk Depth research station P1 (φ = 54°52’ N, λ = 19°10’ E) at the Polish Navy ship ORP “Kopernik”, from different depths, twice on the same day (at 8 and 16 o’clock). The samples were stored for no longer than a few days, frozen at about −30 °C. For each pair of parallel samples, the determinations were repeated 3 or 4 times using the standard addition method. The final results are
Table 2 The temperature programme followed for determination of selenium by atomic absorption spectrometry with atomisation in a graphite tube (GFAAS) followed for determination of selenium by the method of atomic absorption spectrometry with generation of hydrides and in-situ preconcentration in a graphite tube (in-situ trapping).

| Step of analysis | Temperature, °C | Time, s | Gas flow | Procedure | Reading |
|------------------|----------------|---------|----------|-----------|---------|
| GFAAS            |                |         |          |           |         |
| Drying           | 85–120         | 50.0    | +        | -         |         |
| Ashing           | 1100           | 3.0     | +        | -         |         |
| Atomisation      | 2600           | 2.0     | -        | +         |         |
| Cleaning         | 2600           | 2.0     | +        | -         |         |
| **in-situ**      | **trapping**   |         |          |           |         |
| Drying           | 85–120         | 20.0    | +        | -         |         |
| Reduction        | 1200           | 2.0     | +        | -         |         |
| Concentration    | 200            | 60.0    | -        | -         |         |
| Atomisation      | 2000           | 2.0     | -        | +         |         |
| Cleaning         | 2500           | 2.0     | +        | -         |         |

recorded as an average of these determinations.

3 Results and discussion

3.1 Optimisation of the selenium pre-concentration temperature

The temperature of the volatile hydride pre-concentration step was optimised based upon absorbance measurements of the standard solution (10 ng/ml) with temperatures ranging from 50 to 400 °C and in the presence of the following modifiers: Pd, Ir, Ni, Os, Ru, and Rh at concentrations of 0.5 mg/ml each.

The highest analytical signals are obtained using palladium and ruthenium at 200 °C; diminished signals are obtained with iridium, rhodium, osmium and nickel. In the presence of iridium and rhodium, the signal continues to increase up to 300 °C and then decreases, however, in the presence of osmium and nickel, the signal is the highest at 200 °C.
3.2 Optimisation of the modifier amount

The analytical signal depends not only on the type of the modifier used but also upon the amount added. To optimise both these factors, the absorbance was measured in the presence of palladium, iridium, rhodium, ruthenium, osmium and nickel using as a sample of the standard solution of 10 ng/ml. The determinations were performed for each of the different modifiers using different amounts.

Highest analytical signals are recorded using rhodium, ruthenium and palladium. For palladium the signal increases as the modifier dose increases up to 2 μg, then stabilises, while for ruthenium and rhodium the signal increases as the modifier amount increases up to 3 μg and 4 μg, respectively, before decreasing at higher amounts. A much lower signal is obtained using the iridium, osmium, and nickel modifiers; these modifiers do not meet the demands for selenium determination. The optimum modifier for determination of selenium is palladium. Another argument for this choice is the common use of palladium as a modifier in HG-GFAAS determinations, and there is no threat of contamination (coloured deposits on the metal part of the furnace) with this element, as has been observed when other modifiers are used. This contamination can affect other determinations made on the same GFAAS spectrometer. The optimum amount of the palladium modifier is 2 μg.
3.3 Determination of the selenium species

In selenium determinations, the analytical signal comes mainly from compounds containing Se(IV). The signal assigned to Se(VI) in an HCl environment is about 1% of that obtained for Se(IV). Therefore, the use of HCl permits a selective determination of Se(IV). The total content of selenium in inorganic compounds is determined after the preliminary reduction of Se(VI) to Se(IV) by thiourea with the addition of HCl. The content of Se(VI) is determined as a difference between the total content and that of Se(IV) [20].

3.4 Characterisation of the analytical method

The basic parameters characterising AAS-based analytical methods used for the selenium determinations, such as the detection limit (3σ for 6 independent measurements of blank), sensitivity, and reproducibility were determined for 6 independent measurements of the standard and are presented in Table 3. Moreover, the recovery of selenium was determined based upon the standard addition method (Table 4).

The reproducibility of the results obtained using the method of hydride generation and in-situ pre-concentration of the analyte in the graphite tube are worse than those obtained for determinations by the HGAAS (Table 3 for standards and Table 4 for the standard addition of real samples). The most probable reason for this is due to the manual...
Table 3 Fundamental parameters of the analytical method for the determination of selenium by different variations of the atomic absorption spectrometry method.

| Detection limit (3σ) ng/ml | GFAAS (n=10) | HGAAS (n=10) | HG-GFAAS (n=6) |
|----------------------------|--------------|--------------|----------------|
| Sensitivity ng/ml          | 2.10         | 0.15         | 0.018          |
| Repeatability %            | 2.9*         | 1.5**        | 4.2 **(12.8***)|

Table 4 Recovery of selenium using the standard addition method and by hydride generation and in-situ pre-concentration in graphite tube (HG-GFAAS).

| Sample      | Spiked, ng/ml | Found, ng/ml | Recovery, % |
|-------------|---------------|--------------|-------------|
| Sea water 1 | non spiked    | 0.17 ± 0.02  | -           |
|             | 0.1           | 0.11 ± 0.01  | 110 ± 10    |
|             | 0.5           | 0.55 ± 0.03  | 110 ± 6     |
| Sea water 2 | non spiked    | 0.09 ± 0.01  | -           |
|             | 0.1           | 0.09 ± 0.02  | 90 ± 20     |
|             | 0.5           | 0.49 ± 0.02  | 98 ± 4      |

3.5 Determination of selenium in marine water samples

The results of the determination of inorganic species of selenium in marine water samples are presented in Table 5. A similar level of selenium content in marine water samples with different speciation (0.20 ng/ml Se(VI) and 0.10 ng/ml Se(IV)) was reported Cabon [12] and by Kubota (0.19 ng/ml of total selenium concentration) [23]. Higher concentrations of selenium – up to a few ng/ml – were obtained by Larraya [24], who reported a higher
concentration of Se(IV) (1.8 ng/ml), while the concentration of Se(VI) compounds was 0.98 ng/ml.

| Depth, metres | Se(IV) measured, ng/ml | Se_{total} measured, ng/ml | Se(VI) calculated, ng/ml |
|---------------|------------------------|---------------------------|--------------------------|
| first sampling|                        |                           |                          |
| 0             | 0.15 ± 0.02            | 0.17 ± 0.02               | 0.02                     |
| 5             | 0.15 ± 0.02            | 0.17 ± 0.02               | 0.02                     |
| 10            | 0.06 ± 0.01            | 0.13 ± 0.02               | 0.07                     |
| 20            | < 0.02                 | 0.05 ± 0.01               | 0.05                     |
| 30            | 0.12 ± 0.02            | 0.12 ± 0.01               | < 0.02                   |
| 50            | 0.04 ± 0.01            | 0.11 ± 0.01               | 0.07                     |
| 70            | 0.05 ± 0.01            | 0.15 ± 0.02               | 0.10                     |
| 90            | 0.13 ± 0.01            | 0.17 ± 0.02               | 0.04                     |
| 104           | 0.09 ± 0.01            | 0.11 ± 0.01               | 0.02                     |
| second sampling|                       |                           |                          |
| 0             | 0.05 ± 0.01            | 0.09 ± 0.01               | 0.04                     |
| 1             | 0.11 ± 0.01            | 0.14 ± 0.02               | 0.03                     |
| 5             | 0.12 ± 0.01            | 0.18 ± 0.02               | 0.06                     |
| 10            | 0.06 ± 0.01            | 0.15 ± 0.02               | 0.09                     |
| 20            | 0.08 ± 0.01            | 0.10 ± 0.01               | 0.02                     |
| 30            | 0.09 ± 0.01            | 0.09 ± 0.01               | < 0.02                   |
| 50            | 0.11 ± 0.01            | 0.11 ± 0.01               | < 0.02                   |
| 70            | 0.15 ± 0.02            | 0.17 ± 0.02               | 0.02                     |
| 90            | 0.15 ± 0.02            | 0.17 ± 0.02               | 0.02                     |
| 104           | 0.07 ± 0.01            | 0.07 ± 0.01               | < 0.02                   |

Table 5 Results of the determination of selenium in marine water samples (all measured values are reproducible with relative standard deviations (RSD) below 20%).

### 4 Summary

The advantage of the AAS method using analyte trapping \textit{in situ} in the graphite tube and its further atomisation (HG-GFAAS) over atomisation in quartz tubes, when applied to
selenium determinations in the presence of interfering matrix, is unquestionable. Due to the ability to apply higher temperatures of atomisation and to trap of the analyte on the graphite tube walls, the efficiency of the process increases and the level of interference in the gas phase is decreased. Moreover, this variation in method permits a ten fold decrease of the detection limit with respect to that of methods without analyte pre-concentration. The method can be successfully applied for the determination of selenium in a majority of water samples at an accepted level of reproducibility. It also permits determination of both Se(IV) and Se(VI) concentrations when thiourea is used as a reducing agent.

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