Talanta 116 (2013) 195–198

Contents lists available at ScienceDirect

Talanta

journal homepage: www.elsevier.com/locate/talanta

Determination of ultra trace concentrations of selenium using the GFAAS technique following on-line electrochemical pre-concentration on a gold-coated porous carbon electrode

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ARTICLE INFO

Article history:
Received 5 February 2013
Received in revised form
6 May 2013
Accepted 10 May 2013
Available online 18 May 2013

Keywords:
Selenium
Elektrochemical pre- concentration
GFAAS

ABSTRACT

In this work the possibility of determination of selenium in water samples was studied by on-line coupling of electrochemical pre-concentration flow through unit and GFAAS. The pre-concentration unit was created from a commercial electrochemical flow through analyser EcaFlow (Istran Ltd.) and a special two-electrode electrochemical flow through cell. The pre-concentration cell consisted of a working electrode made of gold-coated porous carbon and auxiliary electrode made of a Pt-wire. The pre-concentration unit was connected with electrothermal atomisers through 6-way valve with sampling loop. Using the proposed on-line coupling the limit of detection reached 0.01 μg L^{-1} for a 10 mL sample. The total linear range was between 0.03 and 10 μg L^{-1}. From the number of ions tested only PO$_4^{3-}$ ions reduced the signal by about 10% for 50-fold excess. Using this method it was possible to determine Se (IV) or the total inorganic selenium following reduction of Se (VI) by boiling the sample in HCl. The procedure was validated by analysing reference materials and a variety of water samples. A good agreement with the results of ICP-MS was achieved for all samples.

1. Introduction

Selenium is a relatively rare element. It is present in the environment except organically bound selenium as inorganic selenium (IV) and selenium (VI) [1]. Selenium works at low concentrations as a bio-essential element, and therefore it is very important for living organisms [2]. However, at higher concentrations, selenium is a toxic element and its toxicity increases in the series: selenite < selenate < hydrogen selenide [3,4]. The techniques commonly used for determination of selenium include HGAAS, HGAFS, GFAAS, ICP-MS, NAA and electroanalytical methods [5–10].

The most commonly used analytical methods for the determination of trace concentrations of metals and metalloids include GFAAS. This is exceptional especially for its speed and accuracy. However, if it is necessary to establish lower concentrations of analyte in samples using this technique, it is necessary to use an appropriate pre-concentration method.

Electrochemical pre-concentration is one of the techniques used. In this method, the analyte is accumulated on the electrode from the sample solution and after stripping it is transported to the atomiser. This makes it possible to determine trace concentrations of various analytes. The electrochemical accumulation is a highly efficient process and a simple method for separating interferents from the sample.

According to the method of transport and the type of the working electrode used it is possible to divide electrochemical pre-concentration techniques into several groups:

- in situ accumulation in graphite cuvette, when it is the working electrode [11].

- pre-concentration on probe (coil, rod, etc.). The analyte is accumulated on the probe in an external vessel and the probe is placed in a probe tube atomizer [12].

- use of the flow- through system. The analyte from the flowing solution is eliminated on the working electrode, dissolved in on-line or off-line configuration and transported to the atomiser's cuvette [13].

The flow- through systems are easily automated by and have been used in pre-concentration systems of different designs. In the papers published, the most commonly used were planar metal (Au, Pt, Pb, etc.) or carbon electrodes [14–16]. They have good electrochemical properties but a small active surface. To enhance the effectiveness of pre-concentration it is necessary to use the electrochemical cell with minimum internal volume, and a

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http://dx.doi.org/10.1016/j.talanta.2013.05.018

working electrode with large active surface. In this work, gold-coated crushed porous carbon was used as the electrode material. This electrode has got good electrochemical properties, a large surface, and it is suitable for electrochemical pre-concentration [17].

The goal of this work was to create an electrochemical pre-concentration flow- through system for on-line coupling with GFAAS, to be used in determining selenium in water samples.

2. Experimental

2.1. Reagents and solutions

All solutions were prepared in high-purity water (18.5 M Ω cm^{-1}). The primary electrolyte was a 0.1 mol L^{-1} solution of HCl, the secondary electrolyte was a 2 mol L^{-1} solution HNO_3. The standard solutions of selenium (IV) and selenium (VI) were prepared by dissolving the Na_2SeO_3. $5H_2O$, or Na_2SeO_4. $10H_2O$ (p.a., content ≥99.999%, Sigma-Aldrich) in 0.1 mol L^{-1} HCl (Slavus, Bratislava, Slovakia).

For preparing the gold-coated electrodes a solution containing 0.0002 mol L^{-1} $HAuCl_4$, 0.002 mol L^{-1} KSCN and 0.02 mol L^{-1} HCl was used.

For validation purposes certified reference materials of “Trace Elements in Water” (SRM 1643 e, NIST, Gaithersburg, USA) and “Primary Drinking Water Metals” (CRM DWPS, High- Purity Standards, Charleston, USA) were employed. Samples of surface water were obtained from Moldavia.

2.2. Instruments

The measurements were performed on the Shimadzu AA-6300 atomic absorption spectrometer with the GFA-EX7i electrothermal atomiser. Pyrolytically coated graphite tubes were used. A HCL lamp for selenium (current 15 mA, wavelenght 196.0 nm, slit 0.5 nm) was used as the primary source of radiation. A D_2 lamp was used for background correction.

The computer-controlled electrochemical flow- through analyser EcaFlow (Istran Ltd., Bratislava, Slovakia) with peristaltic pump and switch valves was used for electrochemical pre-concentration of selenium. The flow rate for all the solutions was 3 mL min^{-1}.

The two-electrode pre-concentration cell with minimal internal volume (Fig. 1) was made of a commercial three-electrode flow- through measuring cell (Istran Ltd., Bratislava). The pre-concentrated solution was discharged from the vicinity of the electrode. The space above the electrode's surface had the shape of a cone (height of about 0.5 mm, volume of about 3 μL).

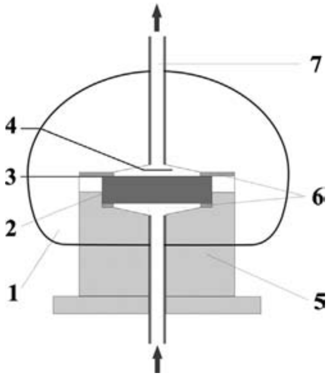

Fig. 1. Scheme of the pre-concentration cell. 1—Cell body, 2—working electrode, 3—platinum contact to the working electrode, 4—platinum auxiliary electrode (0.5 mm diameter), 5—screw holding the working electrode, 6—silicone O-rings and 7—PTFE Tube (internal diameter 1 mm). The flow direction is indicated by arrows.

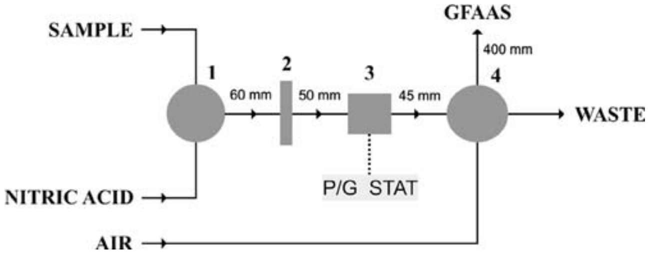

Fig. 2. The flow- through scheme of on-line coupling 1—two-way solenoid inert valve, 2—peristaltic pump, 3—pre-concentration cell controlled by universal potentiostat/galvanostat, 4–6—way valve with sampling loop (PTFE tubing of 1 mm inner diameter). Lengths indicated in the figure were used.

The working electrode was made of a carbon cylinder (height 4 mm, inner diameter 5 mm). The cylinder was filled with crushed gold-plated porous carbon and closed using porous frits. The effective volume of the electrode was 20 μL and the active surface area was 25 cm^2.

The pre-concentration unit was connected with the atomiser via a manually controlled six-way valve (LATEK, Germany). The sampling loop (Volume of 67 μL—internal diameter of 1 mm, length of 85 mm—same connexion as used in HPLC injection valves.), the supply of pre-concentrated solution from the cell, the supply of compressed air and the tube leading into the atomizer were attached to the valve. PTFE tubes were used. The flow- through scheme of on-line coupling is shown in Fig. 2

2.3. Analysis procedure

Using a constant current of −1.5 mA (result of optimisation), selenium (0) was accumulated in the working electrode from the flowing selenium (IV) solution in 0.1 mol L^{-1} hydrochloric acid. The electrode was washed with 2 mol L^{-1} nitric acid to remove chlorides. Selenium was stripping with constant current of 120 μA (a result of optimisation) and discharged into the sampling loop with 2 mol L^{-1} nitric acid. The pre-concentrated solution was transported from the loop after switching the valve by air stream through the 40 cm-long PTFE tube into the electrothermal atomiser.

2.4. Procedures

Treatment of samples. Reduction selenium (VI) to selenium (IV) was performed in the reference materials and water samples. 25 mL of the sample solution was mixed with 25 mL of concentrated HCl. The solution was boiled for 40 min under reflux cooler, and 10 minutes in an open system (almost to dry). After cooling, the solution was diluted with 0.1 mol L^{-1} HCl to a constant volume and analysed for total selenium content. In all samples, the total selenium was determined with ICP-MS using standardised procedures.

Coating of the electrodes. The porous working electrodes were coated at −2000 mV with the coating solution at a flow rate of 3 mL min^{-1} for 40 min. The coating was done from both sides of the electrode to ensure a homogeneous coating in the whole bulk of the electrode.

3. Results and discussion

3.1. Optimisation of parameters

In the first step the temperature programme was optimised for determination of selenium with GFAAS without using a modifier. An aqueous solution of 2 mol L^{-1} nitric acid was used for optimisation with a selenium concentration of 100 μg L^{-1}. The optimised

Table 1
The temperature programme used for the determination of selenium in the pre-concentrated solution.

Step	Temperature/°C	Ramp/°C s^{-1}	Hold/s	Ar/mL min^{-1}
Drying	120	10	30.0	200
Pyrolysis	600	30	20	200
Atomisation	2200	0[a]	3	0
Cleaning	2800	50	3	300

[a] Full power.

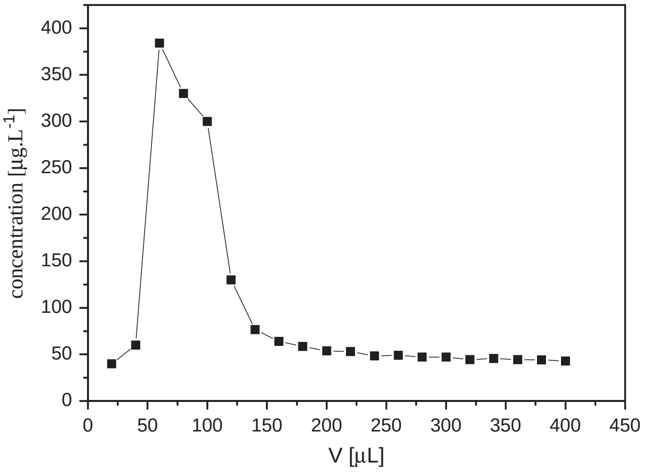

Fig. 3. Determination of the area with maximum concentration of selenium appropriate for sampling into the atomiser. The graph shows the dependency of selenium concentration in the solution flowing out of the pre-concentration cell on the volume flowing out. The volume of 67 µL was injected into the cuvette of the electrothermal atomiser. The selenium concentration in the original solution was 10 µg L^{-1}.

Table 2
The analytical parameters.

Parameter	Sample volume		
	1 mL	5 mL	10 mL
Limit of detection/µg L^{-1}	0.09	0.02	0.01
Limit of quantitation/µg L^{-1}	0.31	0.06	0.03
Linear range/µg L^{-1}	0.31–10	0.06–2.0	0.03–0.8
Repeatability (RSD)/%	1.9	2.6	3.8
Linearity/Coef. of determination R^2	0.999	0.998	0.996
Analysis time/min	3	5	7

Table 3
Analyses of CRMs and water samples.

Sample	Found/µg L^{-1}	Certified/µg L^{-1}	ICP-MS/µg L^{-1}
SRM 1643e	11.7 ± 0.1	11.7 ± 0.1	11.7 ± 0.1
CRM DWPS[a]	50.0 ± 0.2	50.0 ± 0.3	50.0 ± 0.2
Sample 1	1.35 ± 0.05	–	1.34 ± 0.07
Sample 2	3.8 ± 0.1	–	3.8 ± 0.1
Sample 3	0.50 ± 0.03	–	0.51 ± 0.03
Sample 4	0.69 ± 0.02	–	0.71 ± 0.04
Sample 5	6.6 ± 0.1	–	6.5 ± 0.3
Sample 6	1.81 ± 0.05	–	1.83 ± 0.08
Sample 7	1.04 ± 0.02	–	1.02 ± 0.05

[a] Concentration units: mg L^{-1}.

temperature programme is shown in Table 1. Selenium did not volatilise in pyrolysis step at a temperature of 600 °C and so it was possible to carry out measurements without the modifier.

In the second step, the conditions of electrochemical pre-concentration were optimised. The measurements were made in off-line coupling. The accumulation voltage, accumulation current and stripping current were optimised. The accumulation voltage was changed gradually from 0 mV to −5000 mV in 500 mV steps. No accumulation of selenium in the electrode occurred at no voltage value. The optimisation of accumulation current was carried out in the same way. The value was changed from 0 mA to −4 mA in 0.2 mA steps. From the value of −1.5 mA, selenium was reduced in the working electrode with approximately constant efficiency. After accumulation, the dissolution current was optimised as well. The current was changed gradually from 0 µA to 300 µA in 20 µA steps. From the values of 200 µA the working electrode was damaged by dissolving the layer of gold. The optimal value of the dissolution current was 120 µA.

In the last step, the concentrations of hydrochloric acid (primary electrolyte) and nitric acid (secondary electrolyte) were optimised. The optimum concentration of hydrochloric acid was 0.1 mol L^{-1}. The use of higher concentrations of HCl did not alter the effectiveness of accumulation. Concentrations of HNO_3 ranging from 0.1 to 2 mol L^{-1} were tested for the secondary electrolyte. Higher concentrations were not used because of their strong corrosive effects. The rate of stripping of the accumulated selenium increased with the growing concentration of nitric acid. Therefore, the optimum concentration of the secondary electrolyte was 2 mol L^{-1} HNO_3. Fig. 3 shows the dependence of the selenium concentration in the solution flowing out of the pre-concentration cell on the volume. The curve shows which area of the solution flowing out contains most selenium. The detection of the curve was used to determine the correct timing for switching the 6-way valve with sampling loop. In case of the on-line coupling, 67 µL of the solution from the beginning of this area were added to the electrothermal atomiser. In this optimisation, a 10 µg L^{-1} solution of selenium was used in 0.1 mol L^{-1} HCl. The volume of the pre-concentrated solution was 5 mL.

3.2. *Validation of the method*

The limit of detection is one of the fundamental characteristics for evaluation of effectiveness of pre-concentration systems. Using the flow- through system allowed easy change of the sample's volume. The values of detection limits and linear ranges changed with the change in volume of the sample used. Increase of the volume by 10-times caused a drop of the detection by about 10-times. The maximum volume of the sample used for validation of the determination was 10 mL. A larger the volume would extend excessively the time of the analysis. The detection limit (defined as 3σ criterion) was 10 ng L^{-1} for 10 mL samples. Limit of quantification was defined as 10σ criterion. The total linear range for volumes of the sample 1–10 mL was 0.03–10 µg L^{-1}. The repeatability of the determination for 10 mL sample ($n=11$) was RSD=3.8%. All qualitative parameters are summarised in Table 2.

The impact of the selected ions which may be present in the samples of water was tested. Up to 100-fold excess of As(III), Bi(III), Mn(II), Pb(II), Cd(II), Cu(II), Fe(II), Sb(III), Ni(II), Zn(II), PO_4^{3-}, SiO_4^{4-} ions was added to 50 ng L^{-1} of Se(IV). Only 50- to 100-fold excess of PO_4^{3-} reduced the selenium signal by 10–30%. Humic acids did not interfere in the concentration of 50 mg L^{-1}.

The addition of 5 µg L^{-1} of Se (VI) to the standard with a concentration of Se (IV) of 50 ng L^{-1} did not change the signal. The system was selective to Se (IV), and therefore it was possible to make speciation study with it.

3.3. *Real samples*

Two types of certified reference materials (appropriately diluted) and surface water samples were analysed by the elaborated method. The water samples were also analysed by the inductively coupled plasma mass spectrometry method (Water

Research Institute in Bratislava, Slovakia). The results are listed in Table 3. A good agreement with the reference values was observed in all cases.

4. Conclusion

The designed pre-concentration flow- through system allowed determination of ultra trace concentrations of inorganic selenium in water samples in on-line coupling with GFAAS. The main advantages were that the effect of potential interferents was suppresses, the detection limit was reduced significantly, and it was possible to set different oxidation forms. The system can also be used to determine other elements (As, Sb, Hg, etc.) and successfully compete with the AAS method by generating hydrides and cold vapour techniques. The pre-concentration system was created for coupling with the method for the analysis of discrete volumes—GFAAS. After a simple modification, however, it is also possible to combine it with atomic spectrometry flow techniques: FAAS, ICP-OES, MIP-OES and others.

Acknowledgement

This work was supported by the Slovak Research and Development Agency under the Contract no. APVV-0797-11 and by the Grant Agency of the Slovak Republic under the Contract no. (1/0419/12).

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