

Determination of Arsenic, Antimony and Selenium after Preconcentration onto the Reticulated Vitreous Carbon with MIP-AES Detection

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A method is described for the determination of As, Sb and Se by hydride generation with hot trapping on reticulated vitreous carbon (RVC) followed by the electrothermal vaporization of the analytes and their detection with microwave-induced plasma atomic emission spectrometry (MIP-AES). A comparison between the results of conventional graphite tubes and those filled with RVC shows, that the use of the latter results in enhanced power of detection to the value comparable with those obtained by the direct injection of the same amount of the analyte into the graphite tube. A surfatron is used for sustain an argon MIP. Absolute detection limits (3σ) of 0.09 ng, 0.10 ng and 0.13 ng were obtained for As, Sb and Se respectively. The accuracy of the method was confirmed by the determination of As and Se in SRM 1643c water standard reference material.

Przedstawiono metodę oznaczania As, Sb i Se wykorzystującą generowanie wodorków, rozkład w podwyższonej temperaturze i osadzanie analitu na powierzchni grafitu. W pracy porównano efektywność osadzania As, Sb i Se na powierzchni elektrografitu i grafitu siatkowego (RVC). Zastosowanie grafitu RVC umożliwiło efektywniejsze osadzanie oznaczanych pierwiastków i uzyskanie wykrywalności takiej, jak przy bezpośrednim wprowadzaniu próbki ciekłej do rurki grafitowej. Po odparowaniu analitu z powierzchni grafitu i wprowadzeniu do plazmy mikrofalowej, oznaczenie prowadzono metodą atomowej spektrometrii emisyjnej. Plazma mikrofalowa wytwarzana była we wnętrzu rezonansowej typu surfatron. Granice wykrywalności metody wykorzystującej osadzanie analitu na graficie RVC wynoszą odpowiednio 0,09 ng dla As, 0,10 ng dla Sb i 0,13 ng dla Se. Opisana procedura została sprawdzona przy oznaczaniu arsenu i selenu w próbce wody SRM 1643c o certyfikowanej zawartości oznaczanych pierwiastków.

The principal advantages of the hydride generation technique for atomic spectrometric analysis are the chemical separation of the analyte of interest from potential matrix interferences and highly efficient sample introduction mode [1]. However, the main limitation is that the hydrides are present together with an excess of evolved hydrogen and carrier gas. Therefore, the power of detection may be further improved by collection and concentration of hydrides prior to their determination. Such preconcentration may be achieved by freezing the hydrides at liquid nitrogen temperature [2] and was used in many AAS [3,4] and AES [5-7] studies.

It has later been demonstrated that hydride forming elements can be also collected by the thermal decomposition of the hydrides on the surface of a graphite furnace atomizer heated to a suitable temperature [8-10]. This may result in efficient fixation of the analyte when the temperature lies between the decomposition temperature of the hydrides and the volatilization temperature of the element. Originally proposed by Drasch *et al.* [8] for As, the technique has been applied in the determination of Bi, Sb, Se, Sn, Te, Ge and Pb [11-16] by AAS using hydride generation.

The successful combination of MIP-AES detection and electrothermal vaporisation has been described by several authors [17-19]. *In situ* trapping of volatile hydrides in a preheated graphite furnace followed by analyte evaporation and MIP-AES detection was demonstrated to be a powerful analytical technique for As [20]. In our previous paper we described this technique in detail for As, Sb and Se [7] while preserving multielement conditions in each single step and using a TM₀₁₀ MIP cavity according to Beenakker. In the present work an attempt has been made to enhance the trapping efficiency for the hydrides by using preheated graphite tubes filled with reticulated vitreous carbon (RVC).

The power of detection was also improved by using a surfatron instead of the Beenakker TM₀₁₀ resonator. Indeed, as demonstrated in several studies, the plasma sustained in the surfatron offers some advantages over the TM₀₁₀ cavity [21,22]. The detection limits mostly are lower, the linear dynamic ranges in the case of the surfatron is larger and matrix interferences are lower.

EXPERIMENTAL

Instrumental

Spectrometer: 0.5 m Ebert monochromator (Jarrell-Ash), wavelength range: 200-450 nm, grating constant: 1/2242 mm, width: 54 mm, reciprocal linear dispersion: 0.8 nm/mm, slit width: 30 μ m, potentiometric recorder: Beckman, type 610 000.

Electrodeless discharge lamps for As (8W), Sb (9W) and Se (6W) powered by EDL Power Supply (Perkin-Elmer) were used for wavelength selection.

Cavity: Surfatron as described by Selby and Hieftje [23]. Suprasil quartz capillary (Hereaus, Quarzschmelze, FRG) with a diameter of 6.0 mm o.d./ 4.0 mm i.d. have been used.

Microwave generator: EMS-Microtron Mark III, type EMS 6000, frequency 2.45 GHz, maximal forward power 200 W.

Hydride generation graphite furnace trapping (HG-GFT) unit: The hydride generation system used for *in situ* concentration has been described previously [7]. A schematic diagram of the manifold

used is shown in Fig. 1. For the preconcentration of the hydrides by hot trapping in a graphite furnace a simple gas circulation system (as compared to the one used in ETV coupled to MIP-AES [17]) was used. The gaseous products from the hydride generator are transported into the preheated graphite tube. The graphite tube is coupled directly to the capillary situated in the surfatron and thus the evaporated analytes can be directly delivered into the plasma.

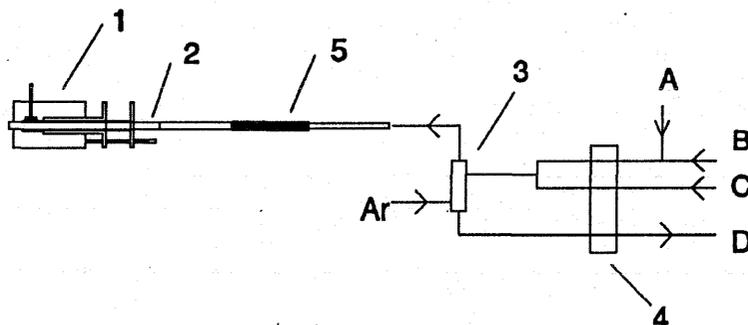


Figure 1. Schematic diagram of the introduction system for As, Sb and Se determination by MIP-AES in surfatron: 1 surfatron; 2 suprasil discharge tube; 3 gas/liquid separator; 4 peristaltic pump; 5 graphite furnace; A – sample; B – carrier solution; C – reductant solution; D – waste

Preconcentration cells: Graphite tube of 5.0 mm o.d., 1.0 mm i.d. and 18 mm in length were machined from a solid graphite rod of high density graphite (quality RWO, Ringsdorff GmbH, Bonn-Bad Godesberg, FRG). The tubes are positioned between 3 supporting rods so as to achieve a high heating efficiency and a rather uniform temperature distribution in the graphite tube. A CRA power supply unit Model 61 (Varian techtron, Pty Ltd Mulgrave, Australia) was used.

Two types of tubes were used during the experiments. The type A was an empty tube with the above pointed diameters. The type B was as type A but was filled with reticulated vitreous carbon. This material has a porosity of 100 pores per linear inch (Electrosynthesis, Co., Inc., East Amherst, NY, USA), with bulk void volume of 97% and bulk density 0.05 g cm^{-3} respectively (Fig. 2).

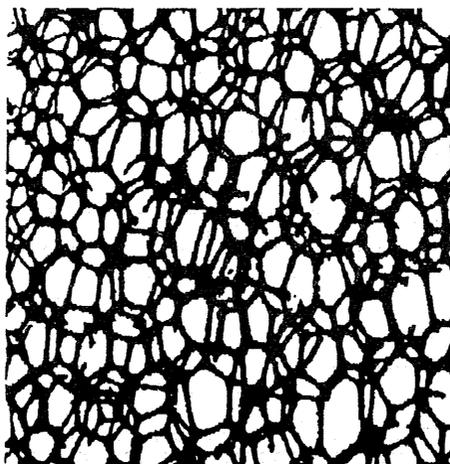


Figure 2. Enlarged view of the structure of Reticulated Vitreous Carbon (RVC)

Measurements: The emission lines are: As 228.8 nm; Sb 217.6 nm; Se 203.9 nm. As analytical signals the peak heights on the recorder chart were selected.

Reagents

0.5 g of NaBH₄ (Merck, Darmstadt, FRG) was dissolved in 100 ml of bi-distilled water and stabilised with NaOH (0.5%). The solution was filtered before use and stored in a refrigerator. High-purity subboiling distilled HCl was used for the sample dilution. As reported elsewhere [14] the purity of NaBH₄ and HCl is the major limitation of the method when used for ultra-trace analysis. NaBH₄ was purified as described by Piwonka *et al.* [4]. HCl was purified prior to use by pre-mixing with NaBH₄ [24]. A reagent blank signal has not been detected under the above conditions.

Certified material: Water SRM 1643c, NIST, USA; with certified content of As: 82.1±5.1 ng ml⁻¹ and Se: 12.7±0.7 ng ml⁻¹ respectively.

As(III), Sb(III) and Se(IV) stock standard solutions were prepared from Titrisol^R solutions (Merck, Darmstadt, FRG), containing 2 g l⁻¹ of the element. Aliquots were diluted with 3 mol l⁻¹ HCl so as to obtain working reference solutions in the concentration range: 0.1 ng ml⁻¹ to 1 g ml⁻¹.

As gases 99.99% pure Ar (plasma gas) and N₂ (shielding gas for the graphite furnace) were used.

Procedure

Details of the procedure for hydride generation, *in situ* trapping and evaporation of the analyte have been described earlier [7] and a brief summary is given in Table 1. The sequence of operation of a hydride generation cycle consists of different steps. First, the furnace is preheated to the absorption temperature, then peristaltic pump is started and the sample and reductant solutions are pumped into the reaction coil. The generated hydrides are swept with Ar into the furnace, where they are trapped onto the graphite surface. In the next step the plasma is ignited and the analytes are vaporised by heating the furnace up to about 2000°C. The released analytes are finally transported into the plasma for excitation. A gas flow-rate of 30 l h⁻¹ is used during the whole procedure except during the deposition step, when it is reduced to 0.5 l h⁻¹. The time required for sweeping the hydrides into the graphite tube depends on the sample volume injected and varied from 10 s for 0.1 ml to about 3 min for 5 ml.

Table 1. Experimental conditions for the hydride generation followed by GF preconcentration

Step	Temperature, °C	Time, s	Ar flow, l h ⁻¹
1. Preheating	400	10	0.5
2. Trapping	400	#	0.5
3. Plasma ignition	ambient	5	30
4. Evaporation	2000	3	30

Depending on the sample volume.

In the case of water samples a 3 mol l⁻¹ HCl solution containing 2% KI and 1% ascorbic acid was added to the samples so as to ensure a complete reduction of As, Sb and Se to the trivalent or divalent state respectively prior to hydride generation.

RESULTS AND DISCUSSION

This study reports on an improvement of the sensitivity of the method by increasing the trapping efficiency and by an increase of power in the plasma. Each step of the procedure was carefully optimized.

Hydride generation

Hydride generation was performed in a flow system and involves acidifying of the analyte solution followed by its mixing with the reductant solution in order to form volatile hydrides. The concentration of acid and reductant were optimized separately for each single element and then compromise conditions were chosen so as to provide conditions for multielement determination. At a concentration of 0.5% (m/V) NaBH_4 , the optimum concentration of HCl is 2.5–4 mol l^{-1} . Thus a concentration of 3 mol l^{-1} HCl was selected for further experiments.

In situ trapping

The collection efficiency of the hydrides strongly depends on the graphite surface [25]. It has been reported, that by the use of a Pd treated graphite tube, an improvement in sensitivity and precision can be achieved [14,24,26,27]. The graphite tubes treated with Zr exhibit also considerable enhancements in sensitivity over non-treated tubes [27].

In the present study, a graphite tube containing the reticulated vitreous carbon was used in order to increase the surface area and hopefully also the deposition yield. Therefore, a piece of reticulated vitreous carbon of about 9.8 mg was situated inside the graphite tube which has a mass 353.6 mg. As the total mass of the filled tube (B) is only 3% larger than an empty-one (A) a significant difference in the heating efficiency of the used system had not to be expected. The trapping conditions in the empty tube (A) and that with RVC (B) were compared: the trapping temperature of 400°C used for tube A [7] has also been found sufficient for the tube B; the optimal gas flow for tube A and B were 0.5 l h^{-1} and 0.8 l h^{-1} respectively. Vaporisation temperature of 2000°C could be used for all measurements. No significant fluctuation of the baseline were observed during the rapid heating of the furnace. The emission signals for each element were narrow and exhibited no tailing for both trapping cells used.

The collection recovery onto the reticulated vitreous carbon surface depends on the age and history of the cell. In order to maximize the trapping efficiency, a pretreatment with mineral acids as well as with Pd solutions was tested. Pretreatment with 3 mol l^{-1} HNO_3 followed by a (5-8 times) heating of the tube up to the maximum temperature provides best trapping properties and long-term precision better than 6%. Single tube could be used for more than 50 measurement cycles.

MIP-AES

With the argon flow-rate within the range of 30–60 l h^{-1} the MIP could be ignited easily and operated in a stable way. Due to the wide range of the forward power applicable different forms of the argon plasma could be obtained. However, as it was demonstrated previously [22], the 3-filament (3F-Ar-MIP) plasma offers the best analytical performance for investigated elements and therefore only this type was used in this study. The optimal working parameters for 3F-Ar-MIP are presented in Table 2.

Table 2. Optimized working parameters for the 3F-Ar-MIP in surfatron

Parameter	Range	Optimum
Forward power, W	50–150	100
Gas flow, l h ⁻¹	15–60	30
Position observed [#] , mm	0–2	1.5

[#] Distance from the centre of the capillary (0 mm = centre).

Analytical results

Figures of merit. Analytical figures of merit obtained for aqueous solutions of As, Sb and Se are summarized in Table 3. The comparison between the empty tube (A) and the one filled with vitreous carbon (B) shows, that the latter has enhanced sensitivity for As and Sb as well as a better precision for all of the investigated analytes. Indeed, the absolute detection limits were improved by the factor of 2.0, 1.7 and 1.1 for As, Sb and Se, respectively when using the tube B. The investigation thus shows that the trapping efficiency in conventional tubes in the case of As and Sb is below 100% and can be significantly increased by increasing the trapping surface area. The values of the absolute detection limits (Table 3) are close to those obtained with direct evaporation of the analyte solution from the graphite tube. In direct injection procedure (GF) the maximal volume which could be injected is restricted to few μl (5 μl in used system), as in hydride generation with hot trapping onto the graphite surface the 5 ml of the sample could be used, giving in consequence a 1000-fold enhancement of the detection limits for investigated elements. Moreover, separation of the analyte from the sample matrix are also an advantage of described procedure.

Table 3. Comparison of absolute detection limits (3σ) [ng] for As, Sb and Se with MIP-AES detection after evaporation of the analyte from the graphite furnace [based on six determination]. Sample introduction as follow: injection of 5 μl of the solution (GF); *in situ* trapping of the hydrides with the tube A (GFT-A) and tube B (GFT-B); data in brackets are RSD in %

Procedure	As	Sb	Se
GF	0.10 (1.8)	0.08 (2.1)	0.14 (1.6)
GFT-A	0.18 (4.5)	0.17 (4.8)	0.15 (4.6)
GFT-B	0.09 (2.5)	0.10 (2.7)	0.13 (2.0)

The linear dynamic range for the elements investigated extends on 2 orders of magnitude. However, as shown by the results in Table 4 the linear dynamic range for As and Sb for the tube B is lower than with a direct vaporization of the liquid sample from the graphite tube. This can be explained by decreasing a trapping efficiency at increasing amounts of the analyte. Such effect was not observed for Se, which is understandable from its easy trapping at the graphite surface which has been reported in the literature [13].

Precision and recovery. The RSD values calculated from 10 replicate measurements of emission signal were 2.5%, 2.7% and 2.0% for 3 ng of As, Sb and Se, respectively. The over-all precision reflects the precision of both the hydride generation and the trapping process. The trapping onto the vitreous carbon offers better precision as compared with trapping in a conventional tube (Table 4).

The recovery was checked for various sample volumes (Fig. 3). The recovery was about 100% for a sample volume of 0.1 ml, 96–98% for 1 ml and 86–95% for 5 ml. Generally, the recoveries decreased slightly with increasing sample volumes. Nevertheless, the preconcentration yield was still satisfactorily for sample volumes of up to 5 ml.

Table 4. The linear dynamic range [ng] for the determination of As, Sb and Se by MIP-AES after evaporation of the analyte from the graphite furnace. GF and GFT-B as in Table 3

Element	GF	GFT-B
As	1.0–110	1.0–85
Sb	0.8–105	1.0–60
Se	1.5–125	1.5–120

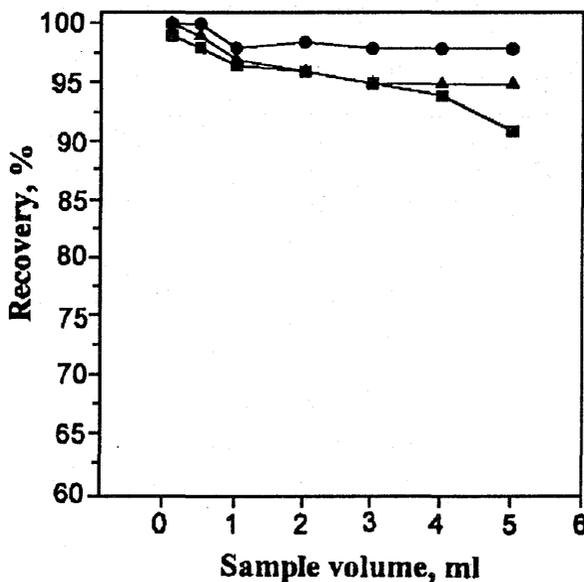


Figure 3. Effect of the sample volume on the analyte response: (---●---) 3 ng of Se, (--▲--) 3 ng of Sb, (---■---) 3 ng of As

Accuracy of the method. Aqueous standards were useful in order to determine sensitivity, precision and detection limit. The real performance of a system, however, can be evaluated only in the analysis of reference materials. A reference water sample SRM 1643c were analyzed for Se and As. The results are presented in Table 5 and

compared with the certified values. The results were well within the tolerance limit given for the reference material indicating that the results are accurate.

Table 5. Comparison of results using hydride generation followed by preconcentration onto the RVC and MIP-AES detection with certified values for SRM 1643c water reference material

Element	Concentration, ng ml ⁻¹	
	found*	certified
As	79.6±1.2	82.1±5.1
Se	11.9±0.4	12.7±0.7

* Mean from six independent determinations ±SD.

Conclusions

It could be shown that the analytical performance of hydride generation in a flow system with *in situ* trapping for the determination of As, Sb and Se by MIP-AES could be well improved by providing vitreous carbon in the hot-trapping system in such a way that it could be comparable with those obtained by the direct injection of the same amount of the analyte to the tube. Indeed the presence of the vitreous carbon pretreated with HNO₃ promotes the deposition of the analytes in a form which can be effectively evaporated into the plasma.

Absolute detection limits of 0.09 ng for As, 0.10 ng for Sb and 0.13 ng for Se were obtained. The detection limit related to the analyte concentration with the procedure GFT-B, is about three orders of magnitude better in comparison to the direct injection of the sample to graphite furnace (procedure GF). In the hydride generation with hot trapping onto the graphite surface the few ml of the sample could be used, which gave a few hundred-fold enhancement in detection limit as compared to direct injection of the sample which is restricted to small sample volume of few µl. The analytical performance of the proposed method was illustrated by the results from reference water sample measurements.

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