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Optimization of electrochemical hydride generation in a miniaturized electrolytic flow cell coupled to microwave-induced plasma atomic emission spectrometry for the determination of selenium

Received: 25 April 2001 / Revised: 2 July 2001 / Accepted: 10 July 2001 / Published online: 12 October 2001

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Abstract The optimization of a continuous flow system for electrochemical hydride generation coupled to microwave-induced plasma atomic emission spectrometry (MIP–AES) for the determination of Se is presented. A small electrolytic cell with a porous glassy carbon working electrode was used for hydride generation. When using an Ar MIP operated in a TE₁₀₁ cavity a detection limit of 0.6 ng mL⁻¹ (3σ) could be achieved. The calibration curve was linear up to 1 μg mL⁻¹. A standard deviation of less than 2% (10 replicate analyses) could be achieved. It was shown that interferences of transition metals are of the same order of magnitude as with a larger electrolysis cell described earlier, and light elements hardly caused any signal depression as tested. It was possible to distinguish between Se(IV) and Se(VI) species and seleno-DL-methionine, because under optimized conditions of an electrolysis current of 10 mA, a microwave power of 210 W, an Ar flow rate of 15 L h⁻¹ and a sample flow rate of 2.5 mL min⁻¹ only Se(IV) was transformed to H₂Se and transferred into the plasma. Finally, the possibility of an electrochemical pre-enrichment was shown to enable it to further decrease the detection limit.

Introduction

Selenium in low concentrations is known to act as an essential element in the biosphere. On the other hand at

higher concentration levels it is toxic. Therefore, the accurate determination of selenium in the different compartments of the environment at trace levels and the mobilization of its compounds have become increasingly important. The generation of selenium hydride coupled to atomic spectrometric methods is well known for this purpose.

Instead of the commonly used hydride generation (HG) with sodium borohydride (NaBH₄) as reductant, electrolysis cells for the electrochemical generation of hydrides have been developed [1, 2, 3, 4, 5, 6, 7]. In this way no sodium borohydride solutions are needed, which are not stable and must be freshly prepared every day. Additionally, the risk for contamination by reagent blanks can be decreased.

In this work, a system with a miniature electrochemical flow cell coupled to microwave induced plasma atomic emission spectrometry (MIP–AES) using an Ar plasma in a rectangular TE₁₀₁ cavity [8] is developed for selenium determination. In contrast to the often used atomic absorption spectrometry (AAS) [6] the MIP–AES offers a multi-element capacity. The optimization of this system done included studies of the influence of the microwave power, the working gas flow rate, the electrolysis current, the acid concentration and the sample flow rate. The figures of merit are presented and the influence of different matrix elements was investigated. It could be shown that a distinction between Se(IV) and Se(VI) compounds as well as seleno-DL-methionine is possible. Finally, the possibility of an electrochemical pre-enrichment of Se in a second electrochemical cell was investigated.

Dedicated to Professor Dr. Bernd Neidhart on the occasion of his 60th birthday

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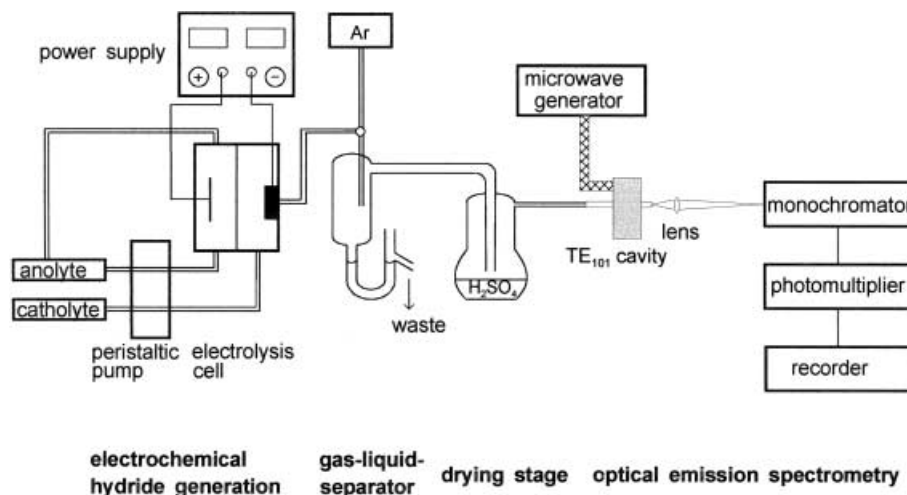
Experimental

Instrumentation

A scheme of the HG and MIP–AES experimental set-up used is given in Fig. 1 and details of the instrumentation are given in Table 1.

Electrochemical cell

In contrast with the formerly used electrolysis cell [4] which was similar to the one proposed by Lin et al. [1] for electrochemical hy-

Fig. 1 The experimental equipment**Table 1** Details of instrumentation

Electrolytic flow cell	ECA ^{cell} type 353 (Istran, Bratislava, Slovakia); cathode, porous glassy carbon; anode, Pt wire
Power supply	Digi 40 (Votcraft)
Peristaltic pump	Perimax 12 (Spetec, Erding, Germany)
MIP equipment	TE ₁₀₁ resonator, according to Matusiewicz [8], GMW 24–302 DR microwave generator, 2.45 GHz, 300 W (AHF Analysentechnik)
Plasma tube	Suprasil, i.d. 4 mm
Lens	f=100 mm
Monochromator	1 m Czerny–Turner mounting, grating constant: $a=1/1200$, entrance and exit slit width: 20 μm (ARL, Ecublens, Switzerland)
Photomultiplier	IP28, 900 V (Hamamatsu)
Amplifier/integrator	LEP, Scarsdale, NY, USA
Recorder	056–1002 (Hitachi)
Electrochemical pre-enrichment	ECA ^{flow} Model 110 with a three electrode cell (Istran, Bratislava, Slovakia); working electrode, porous glassy carbon; auxiliary electrode, Pt wire; reference electrode, Ag/AgCl

drude generation a miniaturized electrochemical flow cell of 38 mm length and 32 mm breadth was used (Fig. 2). It is already known that glassy carbon is a suitable electrode material for the generation of H₂Se and Pt can be well used as anode material in the electrolyte solution used. Accordingly, the anode of the miniaturized cell is a Pt coil, the cathode consists of porous glassy carbon. In this way the active surface of the working electrode is much larger than the one of a massive electrode of the same size. The working electrode has a flow-through diameter of about 5 mm. The electrolysis cell is divided into two chambers. The cathodic and anodic chamber of the electrolytic flow cell are separated by an ion exchange membrane.

Procedure

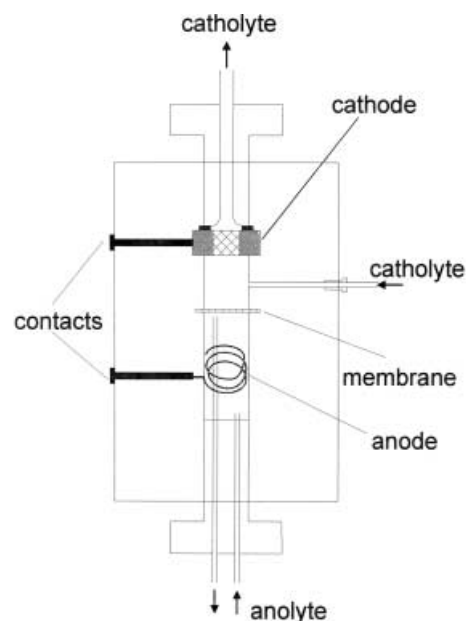
The analyte solution (H₂SO₄ or Na₂SO₄ at concentrations in the ranges of 0.15 mol L⁻¹ and 1 mol L⁻¹, respectively) is pumped through the anodic chamber with the aid of a peristaltic pump (Fig. 1). At the anode O₂ is generated. The analyte circulates and can be used for several weeks. The acidified sample solution is

pumped through the porous cathode where H₂ and H₂Se are generated. The gaseous products leaving the cathodic compartment are mixed with an Ar working gas flow, separated from the liquid and dried by conducting the gases over concentrated H₂SO₄. Afterwards the gas mixture is transferred into the plasma cavity. The Ar MIP is sustained in a rectangular TE₁₀₁ cavity and viewed axially. A plasma geometry with usually one or two filaments was observed. The emitted radiation was focused by a lens on to the entrance slit of the monochromator. The Se I 203.985 nm line was used for all analytical measurements.

For the electrochemical preconcentration the outlet of a pre-enrichment cell, in which Se was deposited on to a Au-coated porous glassy carbon electrode (Istran, Bratislava, Slovakia), is coupled to the cathodic chamber of the HG cell.

Reagents and standard solutions

Standard solutions of Se(IV) were prepared by diluting a Titrisol (Merck, Darmstadt, Germany) stock solution with de-ionized water (MilliQ Water System, Millipore, Eschborn, Germany). Solu-

**Fig. 2** The electrochemical flow cell with porous working electrode

tions of Se(VI) were prepared from solid Na_2SeO_4 (Sigma-Aldrich, Taufkirchen, Germany) and solutions of seleno-DL-methionine were also prepared from solid seleno-DL-methionine (Sigma-Aldrich). Solutions of potential interfering elements were prepared from the corresponding Titrisol (Merck) and Fixanal (Riedel de Haen Laboratory Chemicals, Seelze, Germany) stock solutions by appropriate dilution. The acids used for the preparation of the electrolyte and sample solutions were of analytical-reagent grade. As working gas Ar with a purity of 99.998% (Messer-Griesheim, Frankfurt, Germany) was used.

Results and discussion

Optimization of electrochemical HG coupled to MIP–AES

A univariant optimization of the microwave power, Ar flow rate, electrolysis current, acid (H_2SO_4) concentration in the sample and sample flow rate as working conditions with respect to the signal to background ratio (SBR) was performed (Fig. 3) to achieve a high power of detection. A catholyte containing 100 ng mL^{-1} of Se(IV) was used for these studies.

The detection limit was calculated by use of the equation:

$$c_L = \frac{3\sqrt{2}\sigma_B}{S}$$

where σ_B is the standard deviation of the blank and S is the sensitivity.

The optimum conditions are listed in Table 2. At these conditions resulting from the optimization for Se(IV) a detection limit (3σ) of 0.6 ng mL^{-1} was obtained and the calibration curve (9 standard solutions, blank, 10, 50, 100, 200, 400, 600, 800 and 1000 ng mL^{-1}) was linear up to a concentration of $1 \mu\text{g mL}^{-1}$.

Influence of some light metals and transition metals

The influence of the light metals Na, K, Mg, and Al and the transition metals Cu, Ni, Fe, and Co on the Se signal was investigated (Fig. 4) and therefore they were added to a 100 ng mL^{-1} Se(IV) solution at concentrations in the range of $0.1\text{--}100 \mu\text{g mL}^{-1}$. Light metals were found hardly to interfere, but for the transition metals the well-known interferences could be observed.

The elements Cu, Ni, Fe, and Co were found to change the intensity of the Se(IV) signal in different ways: Cu, Ni, and Fe reduce the signal intensities, but high concentrations of Co were found to increase them.

Fig. 3 Effect of the microwave power (a), the Ar flow rate (b), the electrolysis current (c), the catholytic concentration of H_2SO_4 (d), and the sample flow rate (e) on the signal to background ratio (SBR) for the Se I 203.985 nm line in electrochemical hydride generation coupled to AES with an Ar MIP operated in a TE₁₀₁ cavity

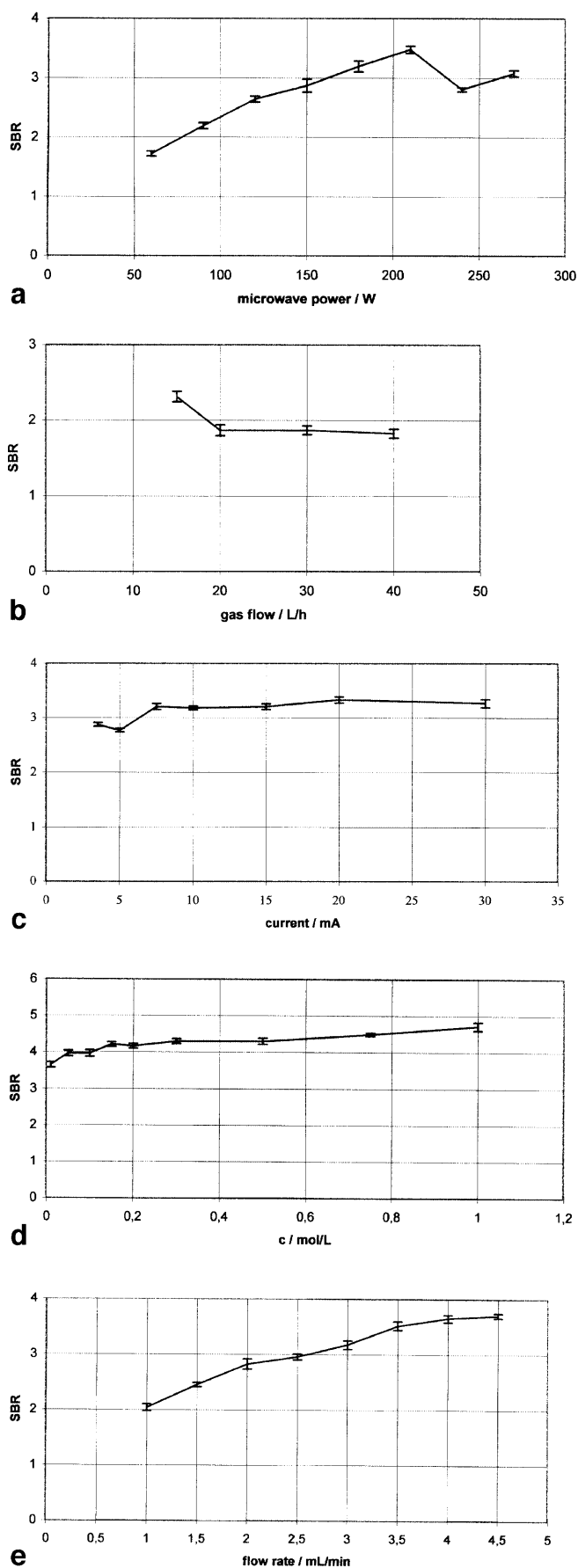
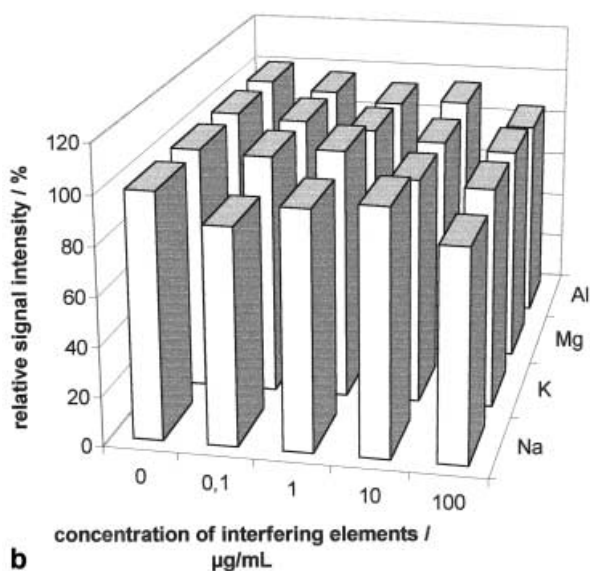
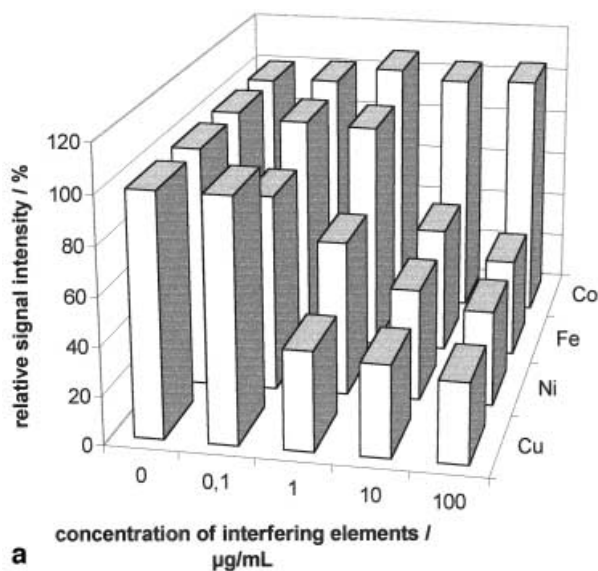


Table 2 Optimum working conditions

Condition	Optimum value
Microwave power	210 W
Ar flow rate	15 L h ⁻¹
Electrolysis current	10 mA
H ₂ SO ₄	0.15 mol L ⁻¹ in sample
Sample flow rate	2.5 mL min ⁻¹
Analyte	1 mol L ⁻¹ Na ₂ SO ₄ or 0.15 mol L ⁻¹ H ₂ SO ₄

**Fig. 4** Influence of transition metals (a) and light metals (b) on the intensity of the Se I 203.985 nm line

A change of the intensity by more than 10% can be observed when Ni in a concentration of 0.1 µg mL⁻¹ is added. At a concentration of 100 µg mL⁻¹ the intensity of the Se signal decreases by about 60% and therewith Ni is

proved to be the strongest interferent. Cu causes a signal depression by more than 10% when it is added in concentrations of 1 µg mL⁻¹, whereas Fe is found to have the same effect when added at a concentration of 10 µg mL⁻¹. The increase of the Se signal caused by the addition of 100 µg mL⁻¹ Co is even smaller than 10%. Therewith Co hardly influences the determination of Se in the case of electrochemical HG, but in the presence of higher amounts of Fe, Cu and especially of Ni large interferences must be expected. For this reason it was decided to investigate the possibilities of a preconcentration method for Se, so that it can be separated from transition metals present in the sample after matrix exchange.

As it can be seen in Fig. 4 the presence of the light elements Na, K, Mg, and Al hardly influences the intensity of the Se I 203.985 nm line. Even at concentrations of the matrix elements of 100 µg mL⁻¹ the signal intensity decreases only a little. The interferences caused by Mg were found to be even less in the case of the miniaturized electrolysis cell than with the larger cell formerly used. For Al the strongest signal depression in this group of elements was observed and it amounted to 15%. Therefore, in the analysis of real samples no or only small interferences from varying concentrations of light elements will occur.

Differentiation between different species of Se

For the investigation of the possibilities of electrochemical hydride generation for a speciation of Se, stock solutions containing 100 µg mL⁻¹ of Se(VI) were prepared by diluting solid Na₂SeO₄ in 0.2 mol L⁻¹ H₂SO₄. For the case of organic Se a solution of seleno-DL-methionine in 0.2 mol L⁻¹ HCl was prepared. For comparison solutions of the same concentration of Se(IV) in H₂SO₄ and HCl were used. In Fig. 5 the results of measurements performed at a concentration of Se of 500 ng mL⁻¹ are presented.

It could be observed that Se(VI) and seleno-DL-methionine were not transformed to H₂Se and transferred into the plasma because no signal of the Se I 203.985 nm line could be observed. As only Se(IV) reacts to H₂Se it can be determined directly and the total concentration of Se can be determined after a pre-reduction of Se(VI) with HCl. The concentration of Se(VI) can then be calculated. For the determination of organic Se compounds such as seleno-DL-methionine a prior oxidation step would be necessary.

Investigation of an electrochemical preconcentration step

To separate interfering elements from Se and to achieve a further preconcentration an electrochemical isolation of Se(IV) in a separate three electrode electrochemical flow cell was investigated. This cell contained a porous glassy carbon working electrode, a Pt auxiliary electrode and a Ag/AgCl reference electrode. First the electrochemical working parameters were optimized by a flow-through

Fig. 5 Influence of the oxidation state of Se and of electrolyte composition on the intensities of the Se I 203.985 nm line

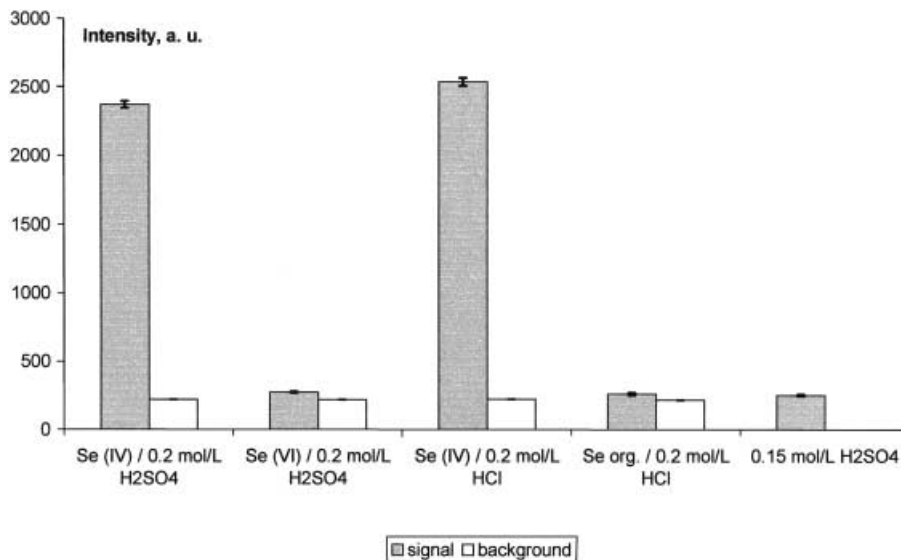
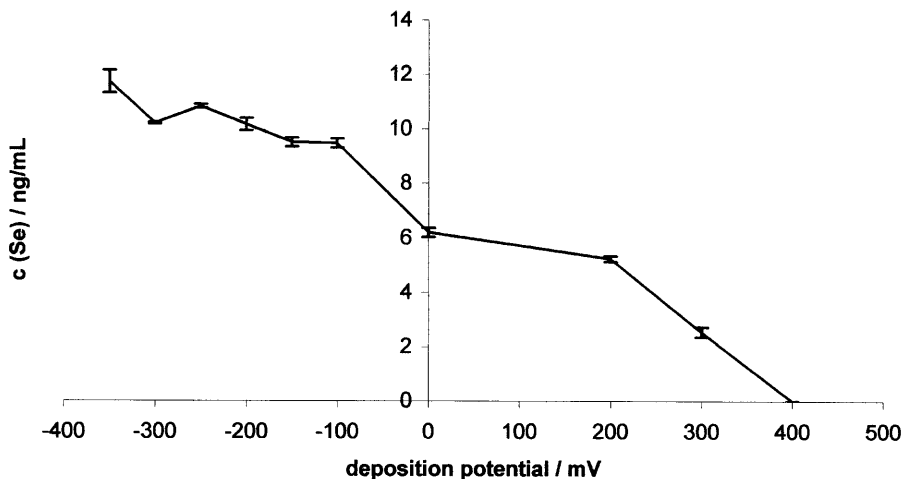


Fig. 6 Influence of the deposition potential on the recovery of Se in flow-through stripping analysis ($c(\text{Se}) = 10 \text{ ng mL}^{-1}$)



stripping analysis of Se using this three electrode cell. For this purpose a definite volume of sample solution is pumped through the porous working electrode coated with Au. Se(IV) is reduced and deposited on to the electrode at a constant deposition potential. Afterwards Se is oxidized at a constant current and a chronopotentiogram is recorded in the potential range from 0 V to 1 V. The oxidized Se is transported by the flowing electrolyte solution to the HG cell. The stripping peak for Se occurs at a potential of about 800 mV. With the help of Faraday's laws the concentration of Se can be automatically calculated after integrating the stripping peak.

A two-step procedure was found to be optimum for equal coating of the working electrode surface: The working electrode consisting of porous glassy carbon was coated using a solution containing $2 \times 10^{-4} \text{ mol L}^{-1}$ Au in 0.02 mol L^{-1} HCl. This solution was prepared from HAuCl_4 . For the first step 25 mL of this solution were pumped through the electrode at potentials from -1500 mV up to 500 mV . For the second step a potential scan from 500 mV to -1000 mV was applied.

A deposition potential of -200 mV was found to be optimum for the determination of Se, because the recovery for a 10 ng mL^{-1} solution was the best varying the deposition potential between -400 mV and 400 mV (Fig. 6). A mixture of 0.1 mol L^{-1} H_2SO_4 and 0.001 mol L^{-1} HCl was used as an optimum electrolyte solution. When repeating the measurement 9 times at optimum conditions a recovery of 95% with a relative standard deviation of less than 1% could be achieved for 10 ng mL^{-1} solution. The recovery could be reduced to about 85% when using 0.1 mol L^{-1} H_2SO_4 without HCl as electrolyte.

For testing the possibility of a preconcentration of Se the outlet of the preconcentration cell was coupled to the inlet of the cathodic chamber of the HG flow cell. As a result of this experiment transient Se signals for the Se I 203.985 nm line intensity were obtained (Fig. 7). It was shown that an electrochemical pre-enrichment of Se is possible and this offers the possibility of separating the analyte from interfering elements like transition metals in the sample matrix. From an estimation of the SBR for a 20 ng mL^{-1} solution, the detection limit when admitting a

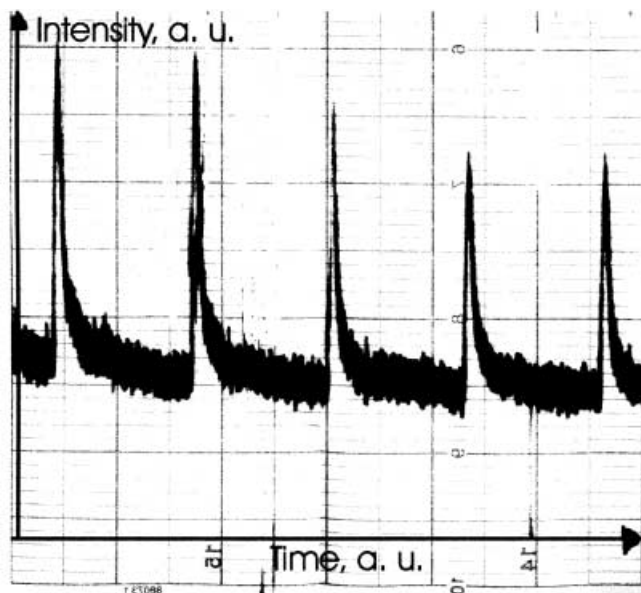


Fig.7 Transient Se signals corresponding to electrochemical preconcentration by deposition on to a Au-coated electrode at -200 mV, re-dissolution at a constant current of 0.5 mA, and electrochemical hydride generation coupled to MIP-AES ($c(\text{Se})=20$ ng mL $^{-1}$, sample volume 5 mL)

relative standard deviation for signals of analyte line and background of 1.4% can be of the order of clearly less than 1 ng mL $^{-1}$ for the preconcentration conditions used.

Conclusions

The experiments reported show that electrochemical hydride generation for the case of Se can be successfully miniaturized without lowering the analytical performance of the approach significantly. This motivates for its use in all types of atomic spectrometry for the determination of elements forming volatile hydrides at trace levels.

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