Interferences of Selected Transition and Noble Metals and Hydride-Forming Elements in Electrochemical Hydride Generation of H_2Se*

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Interferences of selected transition and noble metals and hydride-forming elements in the electrochemical generation of selenium hydride in continuous flow mode were studied. For comparison the study of these interference effects in the chemical generation of selenium hydride was also performed under the same experimental conditions. The attention was concentrated upon the interferences of 16 selected transition and noble metals and hydride-forming elements: Cu(II), V(V), Cr(III), Mn(II), Fe(II), Co(II), Ni(II), Ag(I), Cd(II), Au(III), Pb(II), Hg(II), Sn(II), As(III), Sb(III), Te(IV). The influence of the interferents on the analyte signal (50.0 μg dm^{-3} Se(IV)) was measured in the concentration interval 0—20.0 μg cm^{-3}. The transition and noble metals were divided into three basic groups according to their behaviour during electrochemical and chemical generation of H_2Se.

The electrochemical generation (EcHG) of volatile selenium hydride is a suitable alternative technique to the original chemical generation (CHG) using $NaBH_4$ as a reducing agent. The significant advantage of the electrochemical H_2Se generation technique is a fact that only pure acid solutions are used as the electrolytes. Therefore the sample contamination is reduced to a minimum and it is possible to attain very low detection limits [1—3].

Interferences occurring during the hydride generation can significantly influence the analytical results and the measurement accuracy. Nonspectral interferences express themselves during the hydride generation in the liquid phase (during the analyte reduction to the volatile hydride form or during the hydride release from the solution), and also in the gaseous phase (during the hydride transport or during the atomization) [1].

Inorganic interferents can be divided into three basic groups: strong oxidants, ions of transition and noble metals, and other species [1].

The major action of the interference took place not in the solution phase, but on the surface of the cathode during the electrochemical hydride generation. The most severe interferences are the interferences caused by the cathode surface modification. The change of the hydrogen overpotential takes place on this modified electrode during this process and thus it leads to the generation efficiency decrease [4—7].

Transition metal ions are reduced to metal on the surface of the cathode, as long as the hydrides are formed, with the possibility that they are also subsequently dispersed as fine metal particles within the cathode chamber and as a result, decompose or capture the hydrides [5].

The aim of the present work is to study selected transition and noble metals interferences in the electrochemical generation of volatile selenium hydride with the thin-layer electrochemical cell and to compare magnitudes of these interferences during the electrochemical generation and the chemical generation of H_2Se.

EXPERIMENTAL

Standard solutions of interfering transition and noble metals – Ag(I), Co(II), Cu(II), Fe(II), Hg(II), Mn(II), Ni(II), Cd(II) in 2.0 % HNO_3; Cr(III) in 2.0 % HCl, Au(III) in 5.0 % HCl, V(V) in 2.0 % H_2SO_4 (Analytika, Prague) and standard solutions of hydride-forming elements – As(III), Se(IV), Pb(II) in 2.0 % HNO_3; Sb(III), Sn(II), Te(IV) in 20.0 % HCl (Analytika, Prague) were used. Working solutions were prepared in 1.0 mol dm^{-3} HCl. Deionized water (Milli

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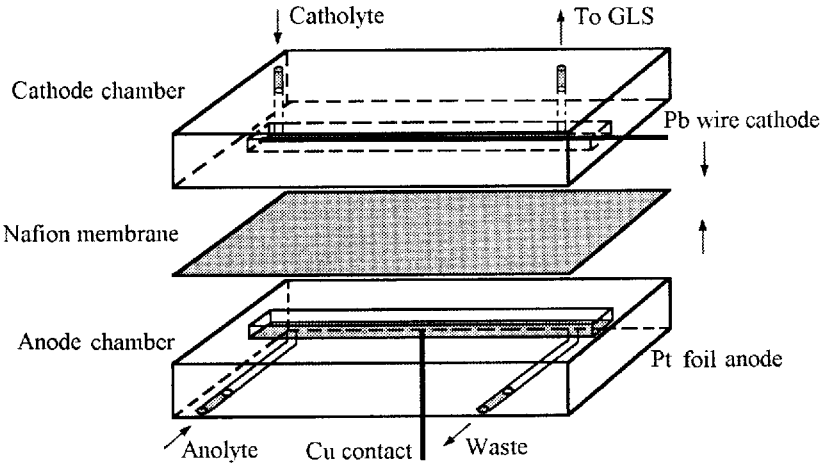

Fig. 1. Scheme of the electrochemical cell.

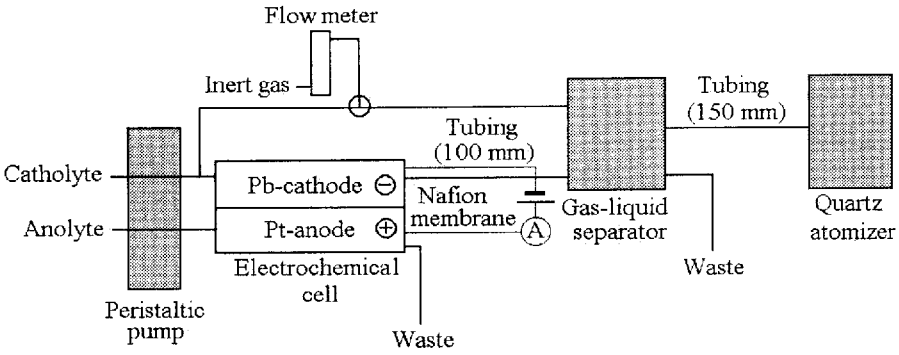

Fig. 2. Scheme of the electrochemical generation system.

Q^+, Millipore, U.S.A.) was used for preparation of solutions.

Typically, 1.0 mol dm^{-3} HCl (37.0 % HCl, reagent grade, Penta, Prague) and 2.0 mol dm^{-3} H_2SO_4 (96.0 % H_2SO_4, reagent grade, Lachema, Brno) were used as the catholyte and anolyte solutions, respectively.

The reducing agent, 1.5 mass % solution of $NaBH_4$ (Merck, Darmstadt) was prepared in 0.5 mass % NaOH solution (Lachema, Brno).

The concentration of Se(IV) sample was 50.0 μg dm^{-3}.

A Unicam 939 (Unicam, U.K.) atomic absorption spectrometer equipped with an externally heated quartz tube atomizer EHA 10 (RMI, Czech Republic) was used. Hollow cathode lamp (λ_{Se} = 196.0 nm) served as the source of the radiation. Deuterium background correction was used for all measurements. A hydrostatic gas-liquid separator served for the separation of generated hydrides. Linear power supply LPS 303 (American Reliance, I_{max} = 3 A, U_{max} = 30 V) provided constant generation current for the electrochemical cell. Computer-controlled eight-channel eight-roller peristaltic pump (Cole—Parmer) was used for the pumping of all solutions. The carrier gas flow was checked using a flow meter model 3216-45, tube 102-05 (Cole—Parmer).

The surface of the Pb cathode was imaged using a Tesla BS 300 scanning electron microscope (SEM) (Tesla, Czech Republic), capable of 5000-fold magnification.

Electrochemical Cell

A sandwich thin-layer electrolytic flow-through cell consisted of the anode chamber (inner volume of 0.9 cm^3) and the cathode chamber (inner volume of 0.9 cm^3) separated by a Nafion 117 ion-exchange membrane. The upper and the lower blocks (made of Perspex) and the membrane were held together with screws. A Pb-wire (99.999 %, Aldrich) (diameter of 2 mm, surface of 600 mm^2) was selected as a cathode material. As an anode material the Pt-plate (surface of 300 mm^2, cleaned by the cathodic polarization) was used. The scheme of the cell is shown in Fig. 1.

Instrumental Conditions and Procedures

Interferences were studied using the manifolds shown in Fig. 2 (electrochemical generation) and Fig. 3 (chemical generation).

The electrochemical reduction was carried out under constant electric generation current of 1.2 A, carrier (inert) gas flow rate of 30 cm^3 min^{-1}, and

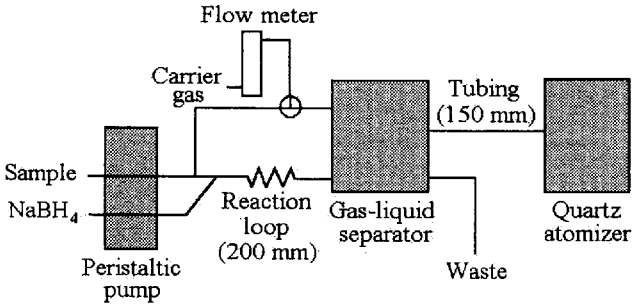

Fig. 3. Scheme of the chemical generation system.

catholyte and anolyte flow rates of 2.0 cm^3 min^{-1}.

The chemical generation was performed with carrier gas flow rate of 30 cm^3 min^{-1}, the sample flow rate of 2.0 cm^3 min^{-1}, and the $NaBH_4$ reducing agent flow rate of 0.5 cm^3 min^{-1}.

Before measurement with a new interferent, the lead cathode was cleaned with 1.0 mol dm^{-3} HNO_3 (Merck, Darmstadt) for the regeneration of an active electrode surface. First the selenium (without the interferent) signal response was measured (50.0 μg dm^{-3}). After that the influence of interferent in concentration ρ/(mg dm^{-3}) 0.1; 0.5; 1.0; 5.0; 10.0; 15.0 and 20.0 was measured. Finally the pure analyte signal response was checked. Performing the chemical hydride generation the procedures were analogous. Interference effect of a selected element was measured performing EcHG and CHG consecutively.

In all cases the relative absorbance value (%) is used for a mutual comparison. The value of 100 % always corresponds with a signal of the analyte without the interferent.

Tolerance limit is an interferent concentration that represents the analyte signal depression or increase of 10 %.

RESULTS AND DISCUSSION

For the monitoring of the interferences during the electrochemical generation of H_2Se the most common inorganic interferents were selected: transi-

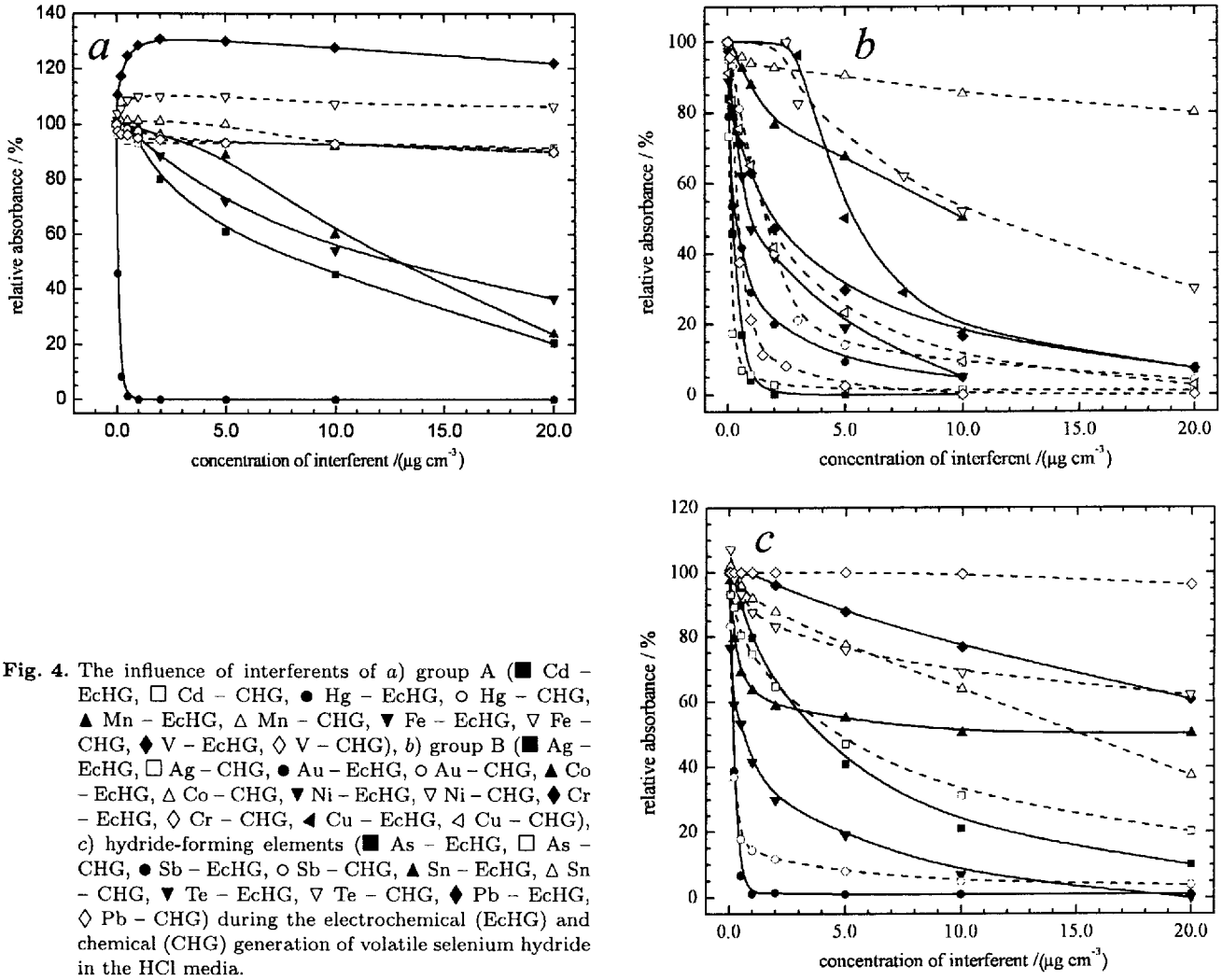

Fig. 4. The influence of interferents of *a*) group A (■ Cd – EcHG, □ Cd – CHG, ● Hg – EcHG, ○ Hg – CHG, ▲ Mn – EcHG, △ Mn – CHG, ▼ Fe – EcHG, ▽ Fe – CHG, ◆ V – EcHG, ◇ V – CHG), *b*) group B (■ Ag – EcHG, □ Ag – CHG, ● Au – EcHG, ○ Au – CHG, ▲ Co – EcHG, △ Co – CHG, ▼ Ni – EcHG, ▽ Ni – CHG, ◆ Cr – EcHG, ◇ Cr – CHG, ◀ Cu – EcHG, ◁ Cu – CHG), *c*) hydride-forming elements (■ As – EcHG, □ As – CHG, ● Sb – EcHG, ○ Sb – CHG, ▲ Sn – EcHG, △ Sn – CHG, ▼ Te – EcHG, ▽ Te – CHG, ◆ Pb – EcHG, ◇ Pb – CHG) during the electrochemical (EcHG) and chemical (CHG) generation of volatile selenium hydride in the HCl media.

Table 1. Tolerance Limits of Individual Interfering Elements

Interferent group	Element	Tolerance limit/(mg dm^{-3})	
		EcHG	CHG
A	Cd	1.30	> 20.0
	Fe	1.80	> 20.0
	Hg	0.01	> 20.0
	Mn	4.20	> 20.0
	V	0.10	> 20.0
B	Ag	0.01	0.01
	Au	0.001	0.30
	Co	0.60	5.10
	Cr	0.04	0.04
	Cu	3.10	0.10
	Ni	0.50	2.80
Hydride-forming elements	As	0.50	0.10
	Pb	4.20	> 20.0
	Sb	0.01	0.01
	Sn	0.10	1.40
	Te	0.05	0.70

tion and noble metals: Cu(II), Ni(II), Co(II), Fe(II), Hg(II), Mn(II), Cd(II), Cr(III), V(V), Au(III), Ag(I) and other hydride-forming elements: As(III), Sb(III), Sn(II), Te(IV), and Pb(II). The interferences were measured under the instrumental conditions described above. The results attained are graphically summarized in Fig. 4.

Studied interferents were divided into three basic groups following their nature (transition and noble metals, other hydride-forming elements) and following the differences of their influences during the electrochemical and chemical selenium hydride generation techniques.

Transition and noble metals, almost not interfering in the chemical selenium hydride generation technique but interfering in the electrochemical generation of H_2Se, were included in the "A" group.

Transition and noble metals interfering in the electrochemical and also in the chemical generation of volatile selenium hydride belonged to the "B" group. These interferents can also be grouped according to the stronger effect in EcHG than in CHG and *vice versa*.

The "C" group included other hydride-forming elements as the interferents.

Attained tolerance limits for individual interferents are summarized in Table 1. The tolerance limits attained for the electrochemical generation of selenium hydride are compared in this table with tolerance limits attained during the ordinary chemical generation of H_2Se using $NaBH_4$ as the reducing agent. It is evident from the data that the interference effects of elements (except Cu and As) are more pronounced in the electrochemical generation than in the ordinary chemical generation.

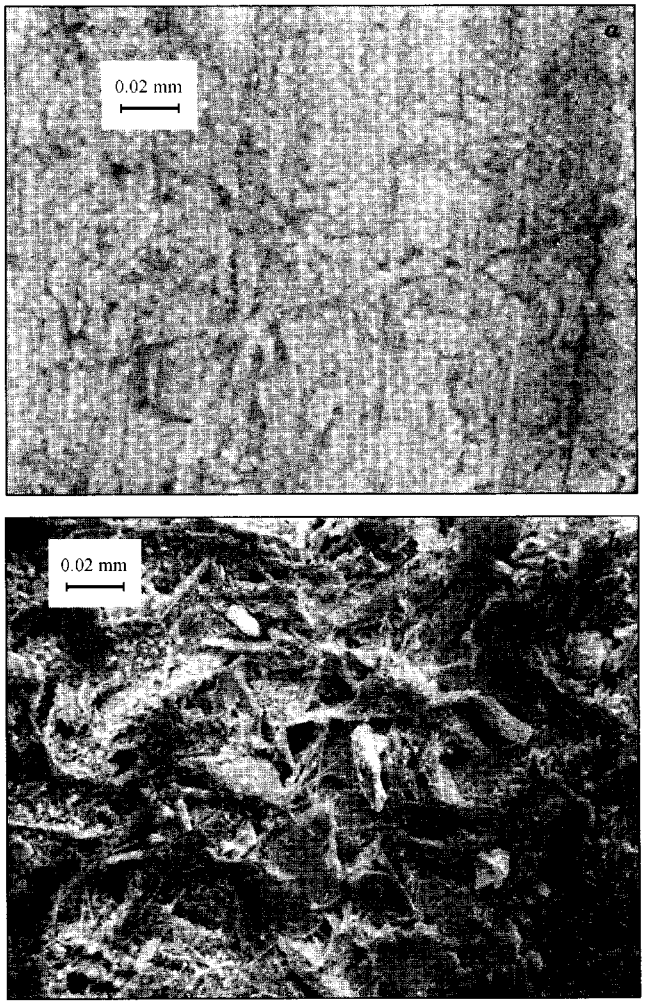

Fig. 5. The SEM photograph of the surface of a new lead wire cathode (*a*) and used cathode after the performing of the set of the interference effects measurements (*b*) (enlargement 600 ×).

The interference effects in the electrochemical generation can be interpreted following the next possible mechanisms. If the solid species (transition and noble metals) are the products of the electrochemical reduction process, they can modify the surface of the cathode and change the hydrogen overpotential on this surface [8]. It can subsequently result in the decrease of selenium hydride generation efficiency. Moreover, these products can pass to the catholyte solution and act as the typical liquid phase interferents [1].

An example of the cathode surface modification after the performing of the set of the interference effects measurements is shown in Fig. 5.

The observed memory effect, and the fact that the presence of a small amount of other element had a substantial effect on the response, pointed to the interference being related to changes occurring mostly on the cathode surface and not in the solution phase.

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