Comparative Characterization of Two Techniques for Selenium(IV) Preconcentration on a Film Mercury Electrode with the Use of an Automated Solution Replacement System without Circuit Disconnection

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Abstract—Two versions of selenium(IV) preconcentration and determination on a mercury film electrode (MFE) by cathode stripping voltammetry with an automated solution replacement system without circuit disconnection are compared. In one version, selenium(IV) is preconcentrated together with copper(II); in the other, selenium is preconcentrated on a copper-modified MFE. Under optimum conditions (against the 0.1 M HCl background at selenium electrolysis potentials from −350 to −400 mV and electrolysis times of 180–300 s), calibration curves for both selenium preconcentration versions are linear over the concentration ranges from 2.5 to 20 µg/L and from 50 to 250 mg/L. The selenium peak heights are well reproduced in both cases (in the range of the concentrations studied, S_r lie in the range from 0.02 to 0.05). Sequential copper and selenium preconcentration is more convenient: there is no need to add copper to each analyzed solution, and it is possible to optimize selenium preconcentration parameters (solution composition, electrolysis potential, and electrolysis time) regardless of the copper preconcentration parameters.

Selenium is an essential microelement [1–2]. Excessive selenium levels in an organism, however, can cause great damage to the nervous system [3]. The environmental levels of selenium are very low, which requires high-sensitivity determination methods. Atomic absorption spectrometry with electrothermic atomization, luminescence, gas and liquid chromatography, neutron activation analysis, mass spectrometry, and various voltammetry variants, cathode stripping voltammetry being important, are widely used for these purposes. The strengths of cathode stripping voltammetry are high sensitivity (up to 10^{-12} mol/L), selectivity, rapidity of analysis, small sizes of equipment, and simple automation.

In cathode stripping voltammetry, selenium(IV) is electrochemically concentrated on the electrode surface, as a rule, as copper compounds [4–6].

$$Cu^{2+} + 2e + Hg \longrightarrow Cu^0(Hg),$$

$$SeO_3^{2-} + xCu(Hg) + 6H^+ + 4e$$
$$\longrightarrow Cu_xSe(Hg) + 3H_2O.$$
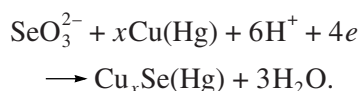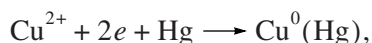
The electrochemical reduction of the resulting Cu_xSe concentrate is usually carried out in the same solution; the height of the relevant voltammetric peak is functionally related to the selenium(IV) concentration in the test solution:

$$Cu_xSe(Hg) + 2H^+ + 2e \longrightarrow H_2Se + xCu(Hg).$$

It was noted [7] that only mercury (dropping or pool) indicator electrodes can provide a high sensitivity of selenium determination via preconcentration into a sparingly soluble copper compound. The transfer from a dropping to film mercury electrode (MFE), as a rule, appreciably deteriorates the precision of the parameters of the selenium peak [4]. The use of an automated solution replacement system without circuit disconnection has overcome this drawback [8]. In this case, the generation and regeneration of a mercury film on the carbon glass electrode was separated from copper and selenium preconcentration on an MFE [9], and the solution compositions for both stages have been optimized. The authors believe that an additional stage (renewal of the mercury film on the working electrode between measurements and selenium(IV) electroconcentration on an MFE premodified with copper considerably improved the precision of the selenium peak parameters and the metrological characteristics of the analysis.

Here, we attempt to use an automated solution replacement system without circuit disconnection for comparing two versions of selenium determination by cathode stripping voltammetry: (1) selenium(IV) preconcentration occurs on an MFE premodified with copper and (2) selenium is preconcentrated concurrently with copper from one solution. In the second version,
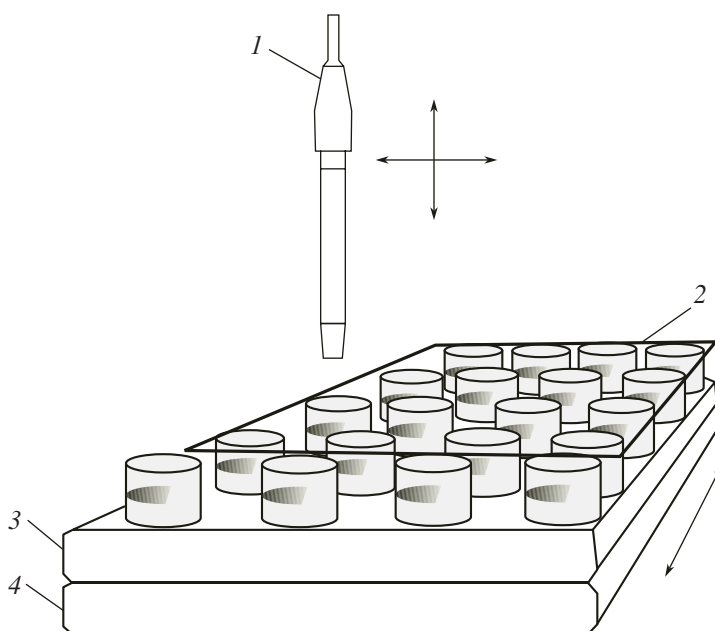
Fig. 1. Exterior of an Expertise-VA-2D automated unit: (*1*) 3-in-1 sensor, (*2*) 20 cells with solutions, (*3*) mobile platform, and (*4*) immobile platform.

an additional stage of mercury-film regeneration is included into the cycle, and the selenium electroconcentration and electrostripping of the concentrate were carried out in solutions of different compositions, optimum for each stage.

EXPERIMENTAL

Voltammograms were recorded on a computer-monitored Ecotest-VA (Econix-Expert) voltammetric analyzer. The electrode system used was a 3-in-1 sensor, which was an electrochemical cell implemented in one case so that the carbon glass indicator electrode and the key leading to the cell with an auxiliary and reference electrodes lay in one plane [8]. The specific feature of this design is that the sensor taken from the solution bears on top a drop of the solution attached due to surface tension, which keeps the circuit from disconnecting when the sensor is transferred from one solution to another.

Solution replacement and renewal of the electrode surface were performed automatically using an Expertise-VA-2D attachment (Fig. 1) to the Ecotest-VA voltammetric analyzer.

The solution compositions and experimental parameters for each voltammetry stage in version A (sequential concentration of copper and selenium on an MFE) and version B (concurrent concentration of selenium and copper on an MFE) are displayed on Fig. 2.

The following chemicals were used in the work: HCl (pure for analysis), HNO_3 (chemically pure), $Hg(NO_3)_2 \cdot 2H_2O$ (pure for analysis), SeO_2 (chemically pure), $CuSO_4$ (chemically pure), and KCl (chemically pure). All solutions were prepared from twice distilled water.
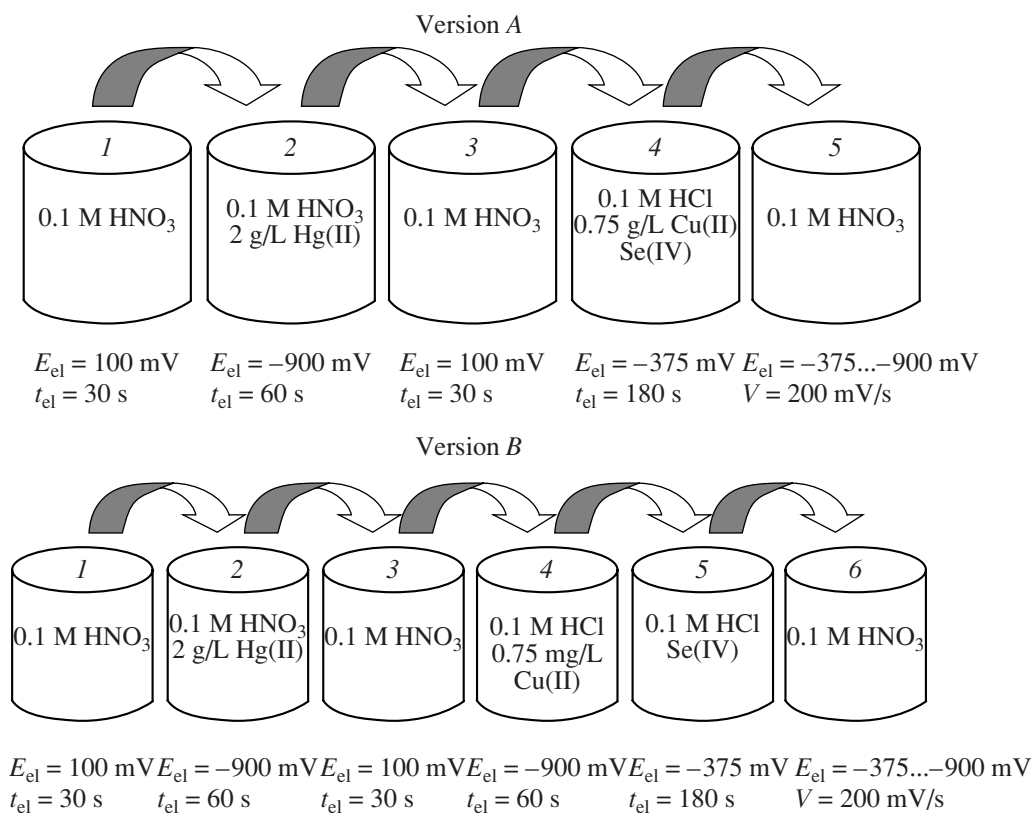
RESULTS AND DISCUSSION

Voltammograms were recorded on a preformed MFE. For this purpose, the sensor was first exposed to 0.1 M HNO_3 at the potential $E = 100$ mV for 100 s to electrochemically purify the electrode and then to a solution of mercury(II) ($c = 2$ g/L) in 0.1 HNO_3 at $E = -900$ mV for 300 s to generate the mercury film (Fig. 2, beakers 1–3).

Figure 3 shows cathode stripping voltammograms recorded in the background solution plus selenium(IV), copper(II), or selenium(IV) + copper(II) and the background solution plus selenium(IV) on a copper-modified MFE.

The voltammogram of the background solution under the specified conditions does not show any peak (Fig. 3, curve *1*). When 0.75 mg/L copper is added, a small peak appears at –660 mV (curve *2*). In the presence of 100 μg selenium(IV) without copper(II), a small peak at –610 mV is observed in cathode stripping (curve *3*). When 0.75 mg/L copper(II) is added to this solution, the peak shifts to –655 mV; the peak height increases by several times (curve *4*). We can conclude that, in the last case, the peak is due to the reduction of the copper compound with selenium. The peak observed in the absence of copper can appear due to selenium accumulation in the form of mercury selenide and its subsequent reduction; selenium(IV) concentration in the presence of copper(II) is more efficient. When selenium and copper are sequentially concen-

Version *A*

$E_{el} = 100$ mV
$t_{el} = 30$ s

$E_{el} = -900$ mV
$t_{el} = 60$ s

$E_{el} = 100$ mV
$t_{el} = 30$ s

$E_{el} = -375$ mV
$t_{el} = 180$ s

$E_{el} = -375...-900$ mV
$V = 200$ mV/s

Version *B*

$E_{el} = 100$ mV
$t_{el} = 30$ s

$E_{el} = -900$ mV
$t_{el} = 60$ s

$E_{el} = 100$ mV
$t_{el} = 30$ s

$E_{el} = -900$ mV
$t_{el} = 60$ s

$E_{el} = -375$ mV
$t_{el} = 180$ s

$E_{el} = -375...-900$ mV
$V = 200$ mV/s

Fig. 2. Scheme of an experiment and record of cathode stripping voltammograms for selenium(IV) solutions. Version A: sequential preconcentration of copper and selenium. Version B: simultaneous preconcentration of copper and selenium.

trated on the electrode, the peak potential shifts to −635 mV; the peak acquires a more regular shape, and its height slightly increases.

Apparently, both versions of selenium determination by cathode stripping voltammetry (selenium preconcentration together with copper or sequential preconcentration of copper and selenium) have approximately equal sensitivities. It is of interest to compare the characteristics of the two versions, such as the precision of the selenium peak parameters and the linear range of the analytical signal, as a function of selenium concentration.

Optimum Parameters of Selenium Cathode Stripping Voltammograms

Important factors for the parameters of stripping voltammetry peaks are the electrolysis potential E_{el} and electrolysis time t_{el}. It was stated in [9] that −900 mV is the best copper electrolysis potential for a copper-modified MFE.

The parameters of the selenium stripping peak were studied as a function of the selenium electrolysis potential for the sequential preconcentration of copper and selenium in the range from –200 to –500 mV. The peak height increased as $E_{el}(Se)$ changed from –200 mV to −400 mV (Fig. 4); this increase can be due to the ther-

modynamic ease of reduction of both copper(II) and selenium(IV) from the. The dramatic decrease in the peak upon a further cathodic shift of the electrolysis potential is likely due to the loss of accumulated selenium because of its progressive reduction to H_2Se.

For the same preconcentration version, the peak parameters were studied as a function of selenium electrolysis time $t_{el}(Se)$ for three copper electrolysis times: $t_{el}(Cu) = 60, 120,$ and 180 s. The selenium peak height increased in proportion to increasing selenium electrolysis time and increased only slightly with increasing copper electrolysis time (Fig. 5).

Then, the selenium peak parameters were studied as a function of electrolysis time in the range from 30 to 600 s for concurrent selenium and copper preconcentration. The selenium peak height increased in proportion to increasing electrolysis time.

All subsequent experiments were carried out as follows. For version A, $E_{el}(Cu) = -900$ mV, $t_{el}(Cu) = 60$ s, $E_{el}(Se) = -375$ mV, and $t_{el}(Se) = 180$ s. For version B, $E_{el}(Se, Cu) = -375$ mV and $t_{el}(Se, Cu) = 180$ s (Fig. 2).

Comparative Characterization of the Two Selenium Electroconcentration Versions

The linear peak height versus peak area range was found for both selenium preconcentration versions. For
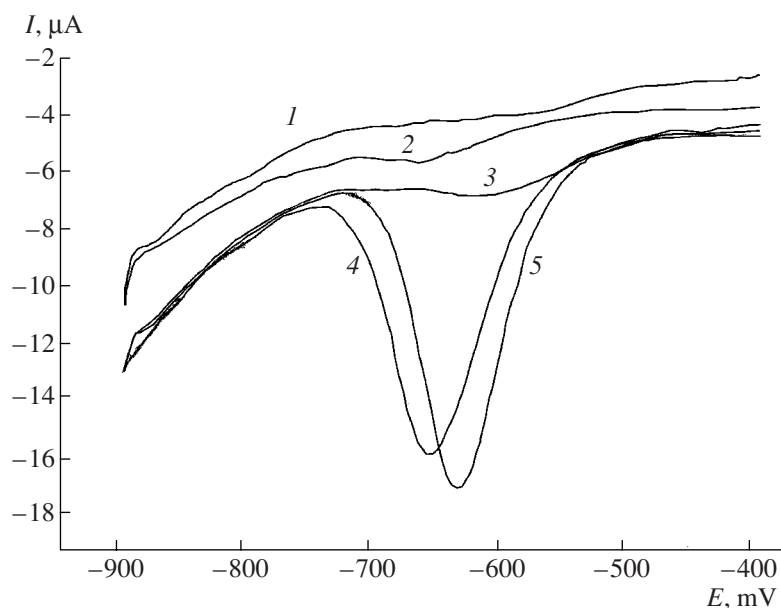
Fig. 3. Cathode stripping voltammograms on an MFE against 0.1 M HCl background: (*1*) without additives, (*2*) 0.75 mg/L copper(II), (*3*) 100 µg/L selenium(IV), (*4*) 100 µg/L selenium(IV) + 0.75 mg/L copper(II), and (*5*) 100 µg/L selenium(IV) with copper-modified electrode.
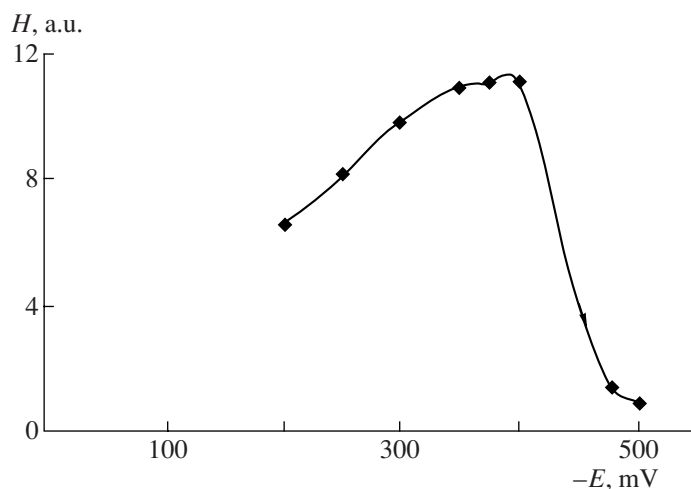
Fig. 4. Selenium peak height vs. electrolysis potential (version A). Parameters: background, 0.1 M HCl; $c(Cu) = 0.75$ mg/L; $E_{el}(Cu) = -900$ mV; $t_{el}(Cu) = 60$ s; $c(Se) = 100$ µg/L; $E_{el}(Se) = -X$ mV; $t_{el}(Se) = 180$ s.

this purpose, voltammograms were recorded in solutions containing various selenium amounts in the range from 2.5 to 250 µg/L.

Calibration curves were plotted as the peak height and peak area versus selenium concentration for both versions. In the range of the selenium concentrations studied, two linear segments were observed on the calibration curves: from 2.5 to 20 µg/L and from 50 to 250 µg/L selenium.

To study the precision of the selenium peak parameters, five cathode stripping voltammograms were recorded one by one under identical conditions for two

selenium concentrations and the peak heights and peak areas were measured. The results were as follows:
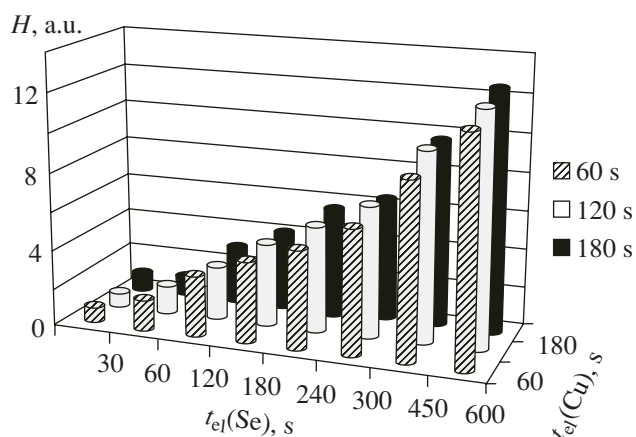
for version A,

$$S_r = 0.036–0.040;$$

for version B,

$$S_r = 0.028–0.051.$$

From these data, it was deduced that the selenium peak potentials are well reproduced in both selenium preconcentration versions and the peak heights rise with increasing selenium concentration.

Fig. 5. Selenium peak height vs. selenium and copper electrolysis time (version A). Parameters: background, 0.1 M HCl; $c(Cu) = 0.75$ mg/L; $E_{el}(Cu) = -900$ mV; $t_{el}(Cu) = 1-3$ min; $c(Se) = 100$ μg/L; $E_{el}(Se) = -375$ mV; $t_{el}(Se) = X$ s.

Both versions have identical linear ranges of the analytical signal versus selenium concentration and have similar precisions: in the range of the concentrations studied, S_r lies in the range from 0.02 to 0.05. Addition of the mercury film regeneration stage to the stripping cycle and the use of different solution compositions for the electroconcentration of selenium and the electrodissolution of the concentrate improve the precision of the selenium signal if selenium is preconcentrated together with copper. For sequential copper and selenium preconcentration on an MFE, a slightly higher sensitivity coefficient ($S = 0.18$ a. u./μg/L) and, accordingly, a lower selenium detection limit ($c_{min} = 1.7$ μg/L are achieved than during concurrent copper and selenium preconcentration ($S = 0.15$ a. u./μg/L, $c_{min} = 2.0$ μg/L). There are no considerable differences in the characteristics. The sequential copper and selenium preconcentration is more convenient from the practical standpoint: there is no need to add copper to each analyzed solution, and there is a possibility of optimizing the selenium preconcentration parameters (solution composition, electrolysis potential and time) regardless of the copper preconcentration parameters.

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