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ARTICLES

Electrochemical Reduction of Selenium on a Silver Electrode and Its Determination in River Water[1]

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Abstract—A new, simple, and fast method is described for determining selenium based on a silver wire electrode flow-through voltammetric detector. A comparison was done between the sensitivity of disk silver, mercury-modified glassy carbon, and mercury-modified gold electrodes. The response of the flow-through voltammetric detector was evaluated with respect to each electrode's operating potential and pH in direct current mode. The limit of detection (3σ) for Se(IV) was below 0.01 mg/L. The flow-through system does not need deposition times and the organic matter does not need to be removed before determining selenium in river water.

Keywords: flow-through voltammetric sensor, silver electrode, selenium, river water

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Selenium is a component of glutathione peroxidase and iodothyronine-5'-deiodinase. Selenium deficiencies may occur in patients on long-term total parenteral nutrition with inadequate supplements, and where soil selenium levels are low. Selenium can protect against urothelial carcinomas [1]. There is selenium in all biological and environmental systems; it has a very narrow concentration range between essentiality, deficiency, and toxicity. It has been proved that in human beings and many mammals, selenium levels correlate with the risk for cancer [2]: prostate [3], skin [4], esophageal [5], arsenicosis and cancer [6], and lung [7] cancer. However, a high uptake of selenium from the environment, e.g., with food or water, can lead to various diseases that cause embryonic deformities, reduce hatchling survival, and kill aquatic organisms. Selenium pollutants in the aquatic, solid, and atmospheric environments were measured, and their contents and health risks were assessed [8–10].

Atomic absorption spectrometry (**AAS**) is the most common analytical method used to analyze trace selenium [11–16]. Others are instrumental methods such as neutron activation analysis [17, 18] and inductively coupled plasma mass spectrometry (**ICP-MS**) [19, 20] and electrochemical methods such as stripping voltammetry and potentiometry [21–28]. Compared with AAS and ICP-MS, electrochemical methods enable selective determination of particular selenium species because only tetravalent selenium is electrochemically active [29–34].

There are some reports on determining selenium in water samples [24, 25, 33–35]. Solid phase extraction coupled with different detection systems such as graphite furnace atomic absorption, inductively coupled plasma atomic emission spectrometry, and ICP-MS are widely used to determine low concentrations of selenium. However, they are too expensive to use for most researchers. Electrochemical methods are less time consuming and less expensive.

Our literature search suggested that no one has reported using a silver electrode as a voltammetric sensor with high-performance liquid chromatography electrochemical detection when determining selenium content in real samples.

In the present study, we investigated the electrochemical reduction of selenium on a silver electrode, a mercury-modified gold electrode, and a mercury-modified glassy carbon electrode, using impedance, cyclic voltammetry, and differential pulse voltammetry. We also designed electrochemical flow-cell devices to study electrochemical processes during selenium flow through the silver electrode. Optimum experimental conditions for determining selenium in river water are described in this paper.

EXPERIMENTAL

Apparatus and materials. All electrochemical measurements were done using a potentiostat-galvanostat

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[1] The article is published in the original.

(SP-150; Bio-Logic SAS, CLAIX, France) with a conventional three-electrode configuration with silver disk, glassy carbon disk, and gold disk (i.d. 3 mm for all disks) as working electrodes. Potentials were measured versus the Ag/AgCl reference electrode (RE-1; Bioanalytical Systems, West Lafayette, IN, USA), and a platinum wire was used as the auxiliary electrode. HPLC system (LC-10 ADvp; Shimadzu, Kyoto, Japan) containing a Rheodine 7125 injection valve with a 20 μL sample loop was coupled to an amperometric detector (Decade SDC; Antec Leyden B.V., Zoeterwoude, The Netherlands). The flow cell was designed with the following electrodes: an Ag/AgCl/0.1 M KCl reference electrode (Bioanalytical Systems), a stainless steel auxiliary electrode, and a silver wire electrode (length 8 cm; i.d. 0.3 mm) as the working electrode for detecting Se(IV). Selenium dioxide (SeO_2) was purchased from Alfa Aesar (Ward Hill, MA, USA). Stock standard Se(IV) solution was prepared by dissolving 0.01 g of SeO_2 in 10 mL of Milli-Q water (Millipore, Billerica, MA, USA). Dilute solutions were prepared before every use. Water sampling was done in March 2013. The water was from the island over the river downstream and from the ditch for the neighboring crop (vegetable, rice, areca palm, banana) in Taiwan. The water samples were collected in clean polyethylene containers and stored at 4°C. All other reagents were locally purchased and were of analytical grade. Liquid chromatography with electrochemical detection (**LC-ECD**) has the advantage of using a flowing stream which helps to remove redox products, and deals with much lower concentrations of analytes than does voltammetry. Electrodes used in liquid chromatography may last for several months without repolishing in some applications. But silver is easily oxidized under such conditions and should be carefully repolished to remove oxides prior to use. In this experiment, it is easily regenerated by immersing the silver wire in diluted HNO_3 for 30 to 60 s until a white-gray color is observed.

Using electrochemical techniques to determine Se(IV). Electrochemical techniques, including cyclic voltammetry (**CV**), differential pulse voltammetry (**DPV**), and electrochemical impedance spectroscopy (**EIS**) were used in Britton–Robison buffer solutions (pH 2.53–10.47) as supporting electrolytes. CV potentials ranged from –1.0 to 0.0 V at a scan rate of 25 mV/s. The EIS and CV data were acquired using SP-150, Bio-Logic SAS, and EC-Lab® software. The impedance spectra were recorded over a frequency range of 0.01 to 100 kHz, using a sinusoidal excitation signal superimposed on a DC potential of +0.2 V. Excitation amplitude of 10 mV was used throughout.

The water samples (0.5 mL) were centrifuged, diluted with 0.5 M nitric acid and poured into 10-mL calibrated flasks. An aliquot of the solution was filtered through a 0.45-μm membrane filter before the HPLC analysis. We used a simple dilution process for the DPV experiments and for the standard solution.

Using a flow-through voltammetric detector to determine selenium. A flow-through electrolysis cell was used for DC-mode electrochemical detection. The detection cell was constructed in our laboratory. Reversed-phase HPLC was done on a LiChroCART® (250 × 4.6 mm) column eluted with methanol–water (10 : 90, v/v) containing 1.0 mM of KH_2PO_4 (pH 3.5) as the mobile phase, at a flow rate of 1.0 mL/min. The voltammetric detector was operated at –0.3 to –0.9 V. Chromatograms were obtained using 20 mL of the prepared standard solution under the operating conditions described above.

RESULTS AND DISCUSSION

Choice of analytical method. The reduction of Se(IV) on various electrode materials (mercury, silver, glassy carbon) in acidic medium were compared. CV was used to determine Se(IV) on bare Ag, bare Au, and bare glassy carbon electrodes (**GCEs**) in Britton–Robison buffer (pH 3.5). The peak of Se(IV) was not detected on the GCE, and peak current on the Ag electrode was three times higher than on the Au electrode. A comparison was made between the sensitivity of disk Ag electrodes, mercury-modified GCEs (**Hg/GCEs**), and mercury-modified gold (**Hg/Au**) electrodes. For the wave of selenium, the potential and current were –0.772 V and –13.7 μA on the Ag electrode, –0.676 V and –2.32 μA on the Hg/Au electrode, and –0.704 V and –5.28 μA on the Hg/GCE (Fig. 1). Se(IV) was electrochemically reduced more efficiently on Ag than on Hg/GCE or Hg/Au electrodes. Therefore, we chose the Ag electrode to determine selenium in river water. Typical impedance results of the adsorbed selenium on Ag are given in Fig. 2a, where the effect of the 5th, 10th, and 20th scans with the development of the Ag electrode can be observed. The fifth scan at electrode Ag showed almost straight lines, characteristic of a diffusion rate-limiting step of the electrochemical process, and 20th scan showed a pronounced electrochemical Nyquist plot (Fig. 2). The charge transfer resistance increased because of the adsorption of 10th, and 20th scans due to a blocking effect at the interface. These semicircles are related to the electron transfer resistance (R_{et}) (i.e., the semicircle's diameter is equal to the R_{et}); the R_{et} of the 20th scan (230 ± 42 Ω) is lower than that of the 5th scan (1240 ± 146 Ω) and 10th scan (596 ± 59 Ω). CV experiments confirmed that Se(IV) adsorbed on the Ag. Se(IV) was selectively preconcentrate on Ag surface, and the surface-bound species was measured, which showed a peak current higher for the 20th scan than for the 10th scan. The CV peak currents of Se(IV) at –0.87 V during 5th, 10th, and 20th scans were 158, 207 and 248 μA, respectively (Fig. 2b).

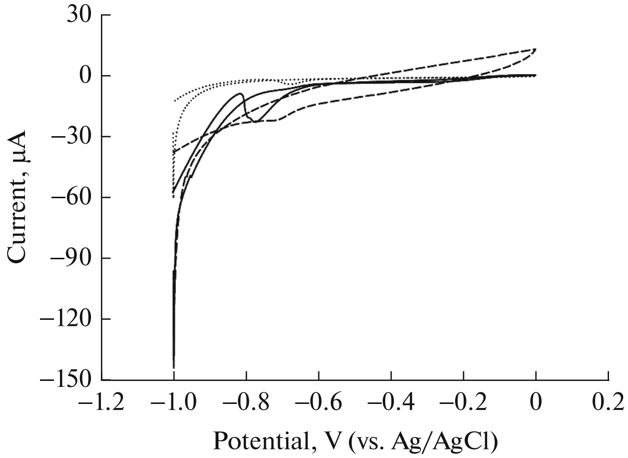

Fig. 1. Cyclic voltammograms of the disk electrodes: silver electrode (—), Hg/GCE (---), and Hg/Au (····) electrodes (i.d. 3 mm for all electrodes) in Britton–Robison buffer (pH 3.5) containing Se(IV) (38 mg/L).

Effect of the solution pH and of the supporting electrolyte pH. Voltammograms of Se(IV) were taken on the Ag electrode in Britton–Robinson buffer solutions (pH 2.5–9.4), acetate buffer (pH 4.3), phosphate buffer (pH 6.6), lithium perchlorate (pH 6.01), tetraethylammonium tetrafluoroborate (Et_4NBF_4), and tetraethylammonium perchlorate (Et_4NClO_4). The influence of the pH and supporting electrolyte pH is reported in Table 1. Both the cathodic potentials of ~0.6 and ~0.2 V data reported that a decrease in peak current is a function of pH, up to 6.5 and above this pH wave peak current had a nearly constant value. The cathodic peak potential of Se(IV) showed a more negative increase with pH. The peak current of Se(IV) in the Britton–Robinson buffer (pH 2.5) was higher than that at the other pH and in other supporting electrolytes. Figure 3 was obtained for Se(IV) solution using differential pulse voltammetry and the Ag electrode as the working electrode in Britton–Robinson buffer (pH 3.86). Figure 3 shows one well-defined reduction peak at ~0.7 V and a round one at ~0.2 V, for an adsorption–desorption peak of AgSe at ~0.7 V and a kinetic peak of Ag_2Se at ~0.2 V. The reduction of Se(IV) on the Ag electrode involves a six-electron reduction. Possibly, the reactions occurring at peaks *a* and *b*, respectively, may be described as follows:

$$H_2SeO_3 + 2Ag + 4H^+ + 4e^- \rightarrow Ag_2Se + 3H_2O \quad (1)$$

and

$$Ag_2Se + 2H^+ + 2e^- \rightarrow H_2Se + 2Ag. \quad (2)$$

Reaction (1) agrees with that suggested by Ishiyama [28], Pezzatini [30], and Zuman [32]. The calibration plot obtained by plotting the peak current against the concentration of Se(IV) shows good linearity over the range of 5–240 mg/L. However, for LC-ECD analysis, the best pH range for determining Se(IV) in the Britton–Robinson buffer is 3.7–4.5; these conditions are more stable, more sensitive and more suitable for LC-ECD than the others in this range.

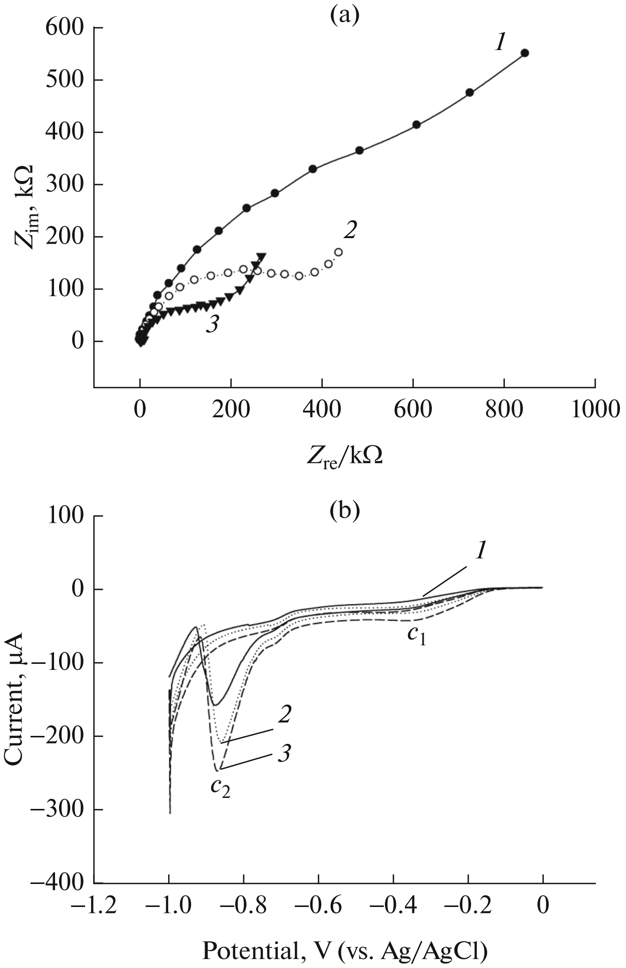

Fig. 2. Electrochemical impedance spectrum (a) and cyclic voltammograms (b) of 120 mg/L Se(IV) recorded from −1.0 to 0.0 V on the silver electrode during the 5th (*1*), 10th (*2*), and 20th (*3*) scans at the scan rate of 25 mV/s.

Interference study. Because the proposed method has analytical importance for determining selenium in real samples, we did an interference study. Copper ions are important for determining selenium because of the formation of an insoluble layer of Cu_2Se. Thin films of Se, Cu, and Cu_2Se were deposited on the Ag electrode (Figs. 4a–4c). Cu_2Se particles (co-deposited) are distributed more uniformly and in larger, denser aggregates on Ag than are the other two. The effect of copper concentration in the supporting electrolytes on the Se(IV) signal alone was also studied. With the increasing copper concentration from 2 to 80 mg/L, the peak current of Se(IV) at the –0.2 V peak slightly increased, but there was little effect on the current of Se(IV) at the –0.7 V peak. There was no

Table 1. Effect of pH and supporting electrolyte on the differential pulse voltammetric peak potential and peak current of selenium(IV) at the silver electrode

Supporting electrolyte	pH	Potential, V	Current, μA	Potential, V	Current, μA
Britton–Robison buffer	2.53	–0.66	70.50	–0.11	71.60
	3.66	–0.70	48.80	–0.20	26.40
	4.51	–0.74	38.40	–0.27	13.40
	5.68	–0.76	19.70	–0.30	3.00
	6.50	–0.78	13.70	–*	–
	7.45	–0.80	7.33	–	–
	8.44	–0.82	7.05	–	–
	9.40	–0.87	4.60	–	–
	4.26	–0.67	14.30	–0.25	3.47
Phosphate buffer	6.58	–0.77	15.30	–	–
$LiClO_4$	6.01	–0.81	3.70	–	–
Et_4NBF_4	–	–0.60	12.80	–0.13	9.40
Et_4NClO_4	–	–0.68	8.68	–0.20	3.49

* Not determined.

interference due to 74–138 mg/L of Ni(II), Zn(II), Cd(II), and Co(II) when determining 5.0 mg/L of Se(IV). These results for the interferences with the determination of Se(IV) with the Ag agreed with those reported [28, 34].

Quantification and sensitivity of voltammetric sensors. To determine the optimum applied potential for electrochemical detection, after the LC analysis, hydrodynamic voltammograms were constructed for Se(IV) (Fig. 5). The maximum current, measured at chromatographic peak, occurred at a range from –0.7 to 0.9 V. The peak height (current) of the chromatogram had a good linear relationship with Se(IV) concentration in the range of 0.2–1.6 mg/L (Fig. 6). If it exceeds 1.6 mg/L, the chromatogram will overfill the scale, because the sensitivity of LC-ECD is too high. The limit of detection calculated as 3σ (standard deviation) of the blank measurement was 0.01 mg/L.

Table 2. Optimized conditions for using liquid chromatography with electrochemical detection to determine selenium

LC	ECD
Column: LiChroCART® (250 mm × 4.6 mm)	Flow cell: silver wire (length 8 cm, i.d. 0.3 mm)
Eluent: methanol–water (10 : 90, v/v) containing 1 mM phosphate buffer (pH 3.5)	Potential –0.7 V
Flow rate 1.0 mL/min	Current range 100 nA

Analysis at river-water samples. The proposed LC-ECD method (Table 2) was used to determine SeO_2 in rivers. To test the applicability of the developed Ag electrode, water was analyzed using the standard addition method. The interference caused by the water sample matrix was examined using standard recovery studies. Known amount of Se(IV) standards were spiked into the water samples (n = 3) and subjected to the entire procedure. The recovery of the added standard averaged 99–101%, which showed excellent analytical accuracy in a complex matrix (Table 3). The representative LC-ECD chromatograms for Se(IV) in water after being spiked with SeO_2 and compared with a chromatogram of pure standard are shown in Fig. 7. Sample constituents and their retention characteristics identical to that of Se(IV) were identified and measured. The concentrations of Se(IV) in the river and the ditch ranged from 0.60 to 1.69 mg/L, analyzed using LC-ECD (Table 4). Some vegetables, e.g., garlic, onions, and canola, contain high levels of selenium. There are organoselenium compounds in such crops as wheat, corn, rice, and selenium-enriched plants [36–38]. Rivers and ditches

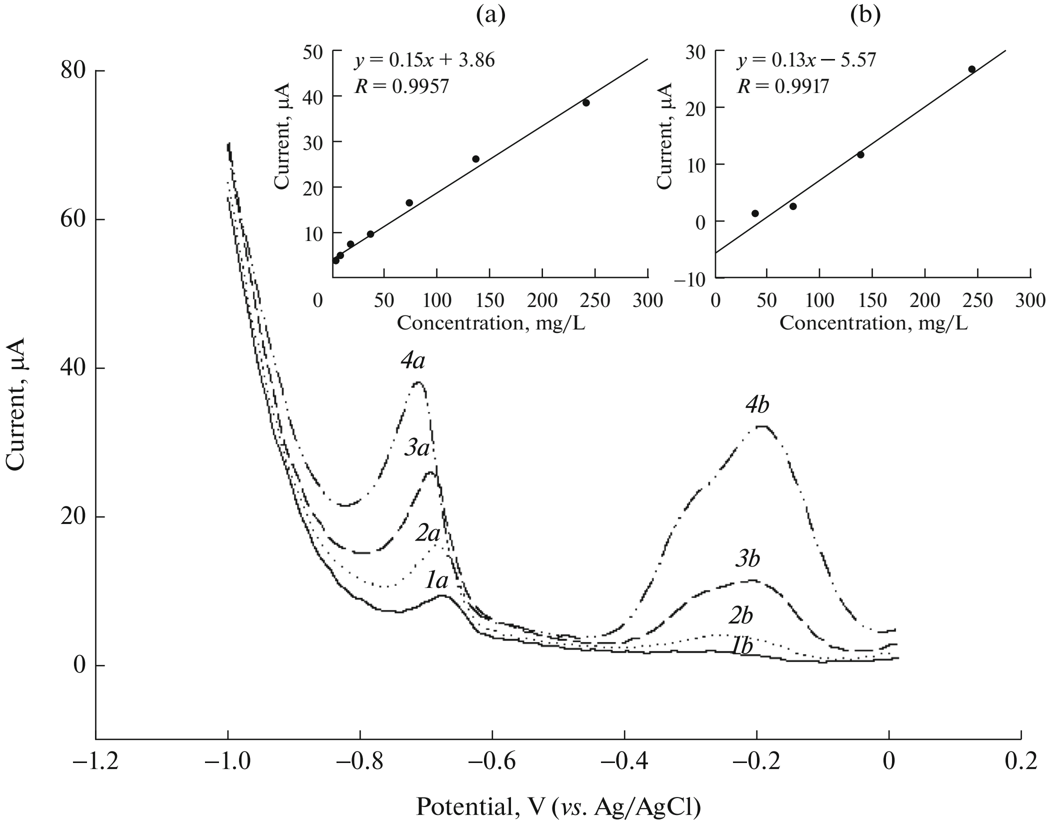

Fig. 3. Calibration curves for Se(IV) using DPV at a silver electrode in Britton–Robison buffer (pH 3.9). Peaks: (*1a*) –0.67 V, 9.63 μA, (*1b*) –0.23 V, 1.43 μA, 30 mg/L Se(IV); (*2a*) –0.68 V, 16.2 μA, (*2b*) –0.23 V, 4.35 μA, 60 mg/L Se(IV); (*3a*) –0.69 V, 25.7 μA, (*3b*) –0.21 V, 11.4 μA, 120 mg/L Se(IV); (*4a*) –0.71 V, 38.7 μA, (*4b*) –0.19 V, 28.5 μA, 240 mg/L Se(IV). Scan rate 10 mV/s, pulse height 0.05 V.

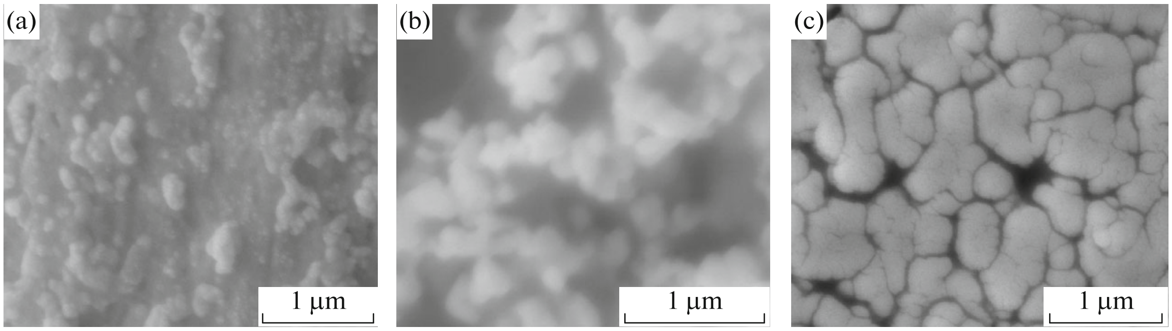

Fig. 4. Scanning electron micrographs of the distribution of Se and Cu particles on the silver surface: (a) Se/Ag, (b) Cu/Ag, (c) Cu/Se/Ag.

on and next to Se-contaminated farmland tend to have high levels of selenium than do natural rivers because the Se-enriched farm plants tend to disperse their selenium into those nearby water. However, with present LC-ECD conditions, the organic forms of selenium in natural water can not be measured.

The literature presents several methods for the determination of selenium in water [24, 25, 33, 34, 39–44]. Hoverer, there were a few using silver as working electrode [34, 41]. Several types of working electrode materials have been reported as useful for selenium determination, and shown in Table 5. Metal film (Hg, Au, and Cu), organo-modified and ceramic composite electrodes exhibit a higher sensitivity and selectivity in comparison with unmodified Ag electrode. Selenium adsorbs to silver, making it suitable for

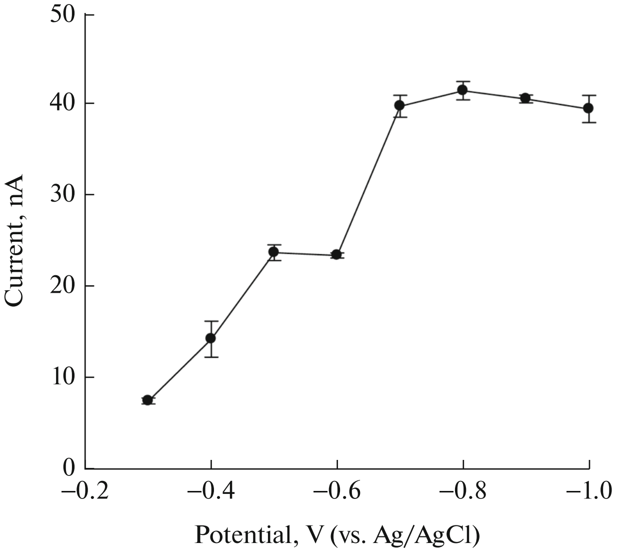

Fig. 5. Hydrodynamic voltammograms obtained for Se(IV) (0.8 mg/L) flow through a flow cell system on silver electrode and methanol–water (10 : 90, v/v) containing 1 mM phosphate buffer (pH 3.5) as an eluent; flow rate 1.0 mL/min.

selenium detection without accumulation and preconcentration. The LODs of Se(IV) differential pulse cathodic stripping voltammetry and differential pulse anodic stripping voltammetry were lower than that of LC-ECD. However, the stripping method the accumulation or deposition time (or both) are higher and these techniques can not eliminate the interference of organic matter determining Se(IV). The total LC-ECD run time at a flow rate of 1 mL/min was approximately 4–5 min.

* * *

We have developed a novel flow-through voltammetric sensor for determining Se(IV) based on its reduction on an Ag electrode. We established the ana-

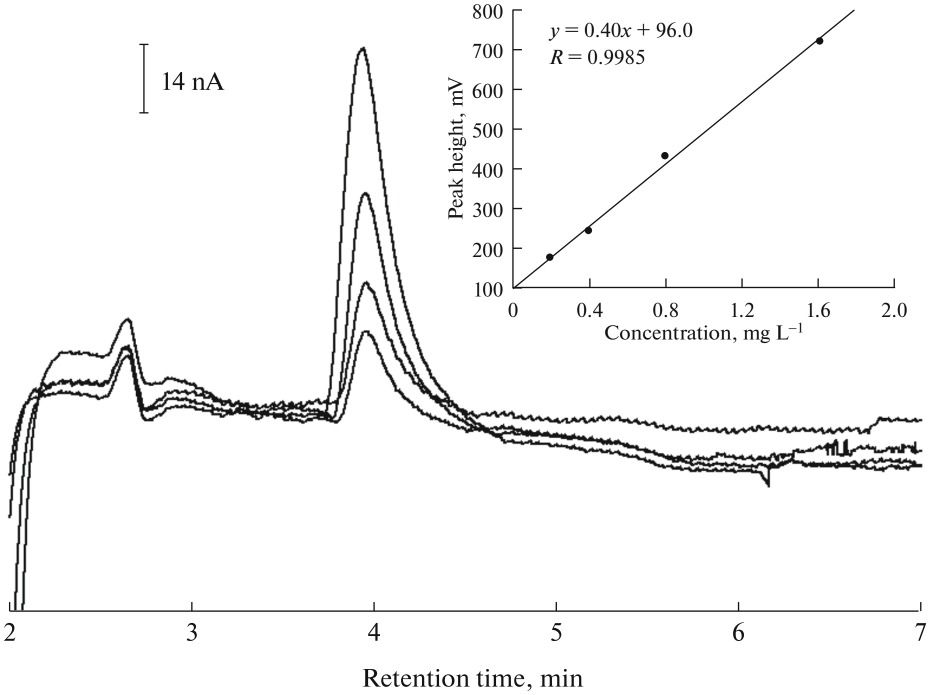

Fig. 6. Calibration graph for Se(IV) using LC-ECD: electrode potential was –0.7 V vs. the Ag/AgCl reference electrode, conditions are as in Fig. 5.

Table 3. Recoveries of selenium in river water by liquid chromatography with electrochemical detection ($n = 3$)

Water sample	Added, mg/L	Found, mg/L	Recovery, %	RSD, %
Taichung Harbor River	0.8	0.79	99.3	2.3
Kaohsiung Love River	0.8	0.81	101.0	1.0
Nantou Nankang Creek	0.4	0.38	95.5	1.6

Table 4. Results of determination of selenium in river water by LC-ECD ($n = 3$)

Water sample	Concentration, mg/L	RSD, %
Taipei river	0.85	3.9
Taichung river next to farmland	1.44	4.9
Taichung ditch next to crop	0.60	2.6
Nantou Nankang Creek next to farmland	1.69	0.1
Nantou Guoshing Township ditch	0.60	5.5

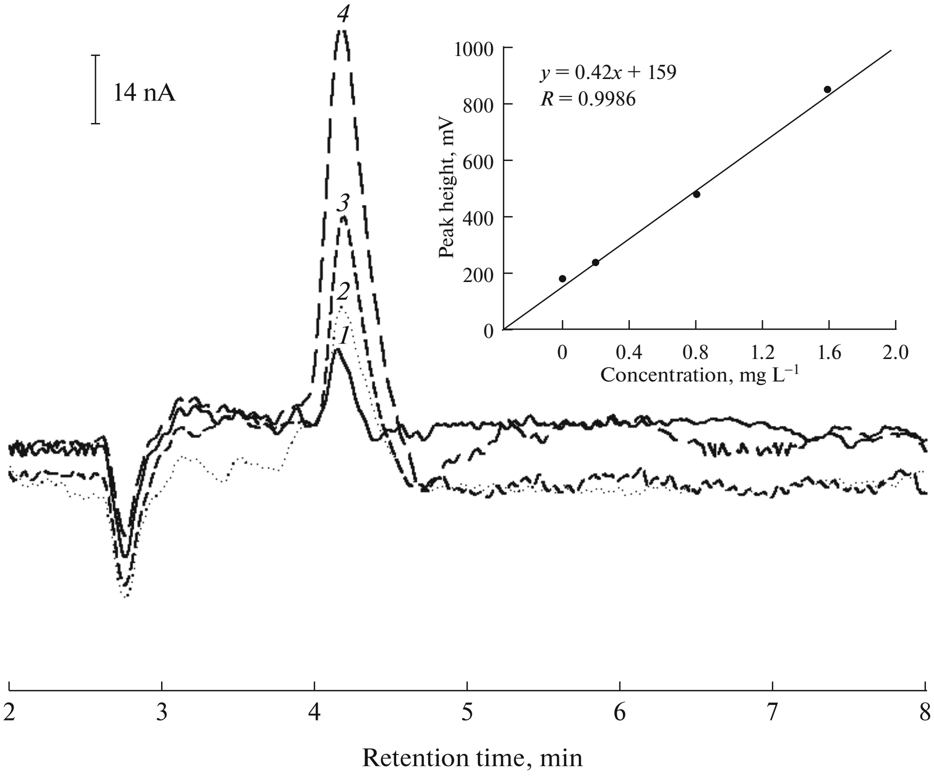

Fig. 7. Chromatograms of selenium in spiked river samples at the Ag electrode. Se(IV) concentration, mg/L: *1*—0, *2*—0.2, *3*—0.8, *4*—1.6. Conditions are as in Fig. 5.

Table 5. Comparison with voltammetric-relevant procedures for selenium in water and hair samples described in the literature

Procedure		LOD, μg/L	Time, min/benefits	Sample	Reference
electrode	method				
Ag	Flow cell	10 (for 20 μL)	5	River and irrigation ditch water	Proposed method
HMDE	DPCSV	0.16	12	Natural lake and river water	[24]
HMDE	DPCSV	0.03	12	Seawater	[25]
Screen-printed graphite	DPASV	19	14	Drinking water	[33]
Ag	DPCSV	0.15	12	Natural water	[34]
Au/C	On-line	0.01 (for 10 mL)	40	Water	[39]
Au wire	Coulometric s tripping	16	No need in calibration	Bottled water	[40]
Organo-modified/Ag	Stripping	3.0	Without oxygen removal	Drinking water	[41]
Ceramic composite	Stripping	0.02	Accumulation time 90 s	Mineral water	[42]
Cu/Hg film	Stripping	0.04	10	Sea water	[43]
TFGE	Stripping	0.10	High reproducibility	Drinking, natural, and waste water	[44]
Hg/GCE	Flow cell with CSV	0.1	Lower solution consumption	Hair	[45]

Notations: LOD—limit of detection, HMDE—hanging mercury drop electrode, DPCSV—differential pulse cathodic stripping voltammetry, DPASV—differential pulse anodic stripping voltammetry, Au/C—gold coated porous carbon, EPC—electrochemical pre-concentration, Cu/Hg film—copper modified mercury film electrode, TFGE—thick-film graphite electrode.

lytical method for Se in river water using a flow-through voltammetric sensor. The advantages of the developed sensors are that: 1—the proposed procedure for determining Se(IV) is fast (retention time 4.07 min) and the organic matter does not need to be removed in an additional step; 2—the working electrode needs no deposition time for the pre-concentration of Se(IV) before the voltammetric measurements; 3—the silver electrode also reduces cost and is less toxic than Hg.

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