

Determination of selenium by catalytic cathodic stripping voltammetry

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Abstract

A procedure is described for the determination of selenium in natural waters using cathodic stripping voltammetry in the presence of rhodium. Advantage is taken from a catalytic effect on the electrochemical reduction of protons in the presence of a mixed complex of selenide with rhodium and chloride, containing Cl–Rh–SeH species. The catalysis causes a very large peak-current at a negative peak potential for low (picomolar) selenium concentrations, close to the hydrogen wave. In addition to the selenium concentration, the peak height depends on the concentrations of acid (H^+) and chloride, and suffers from strong interference by organic surfactants. Optimised conditions include 0.3 M HCl, 75 ppb Rh(III) and a deposition potential of -0.2 V. UV-digestion was used to eliminate the interference caused by organic material and to convert Se(VI) to Se(IV). A 3σ detection limit of 2.4 pM Se(IV) was calculated from the standard deviation of a low selenium concentration (17 pM) using a deposition time of 50 s. © 2000 Elsevier Science B.V. All rights reserved.

Keywords: Selenium; Cathodic stripping voltammetry; Rhodium

1. Introduction

Selenium is an essential trace element but at elevated levels, it can be toxic to organisms, including man. Selenium occurs naturally in soils, rocks, and waters. Elevated selenium concentrations in water are principally found in drain water, groundwater, ponds and wetlands. Many articles on selenium biogeochemistry and transport have been published in recent years in response to wildlife problems at Kesterson Wildlife refuge in California [1]. Those problems have been attributed to irrigation water contaminated with selenium that leached from cultivated soil. Health problems can arise from excess as well as from a deficiency of selenium and there is only a narrow range

between essential and toxic action [2]. A few places in the western US, Australia, and China do not have enough natural selenium. Keshan disease, a selenium deficiency that affects the heart, is named after the province in China where it was first documented [2].

Selenium can exist in several oxidation states ($-II$, 0 , $+IV$, $+VI$). In natural waters, selenium(VI) is the major species in aerobic and neutral to alkaline environments; in aerobic, more acidic, waters speciation goes towards selenium(IV). Under reducing conditions Se($-II$) can occur [1].

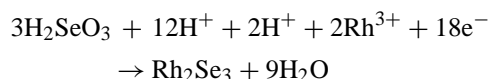
A great variety of methods to determine selenium has been reported over the years [2–4], including spectrofluorimetry, neutron activation analysis, atomic absorption spectrometry, gas chromatography, and voltammetry. Voltammetric methods include anodic stripping voltammetry (ASV) at gold electrodes [5,6] and cathodic stripping voltammetry (CSV) at mercury and solid electrodes [7–9].

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1.1. Cathodic stripping voltammetry of selenium

The voltammetric scan in CSV is preceded by electrolytic deposition of selenium on the electrode to enhance the sensitivity. During the deposition step, a metal selenide M_xSe_y is formed at the electrode surface [10]. Reduction of the metal ion in this compound produces an electrochemical response which increases linearly with the concentration of selenium(IV) in the solution. Table 1 shows a number of different CSV methods for the determination of selenium. Several of the described procedures have been carried out in the presence of copper(II) using the reduction of copper in Cu_2Se to produce the voltammetric response.

The most sensitive voltammetric procedure for the determination of selenium is CSV in the presence of rhodium(III) (Table 1). The reaction mechanism for the deposition step is [11]:



The CSV response at -0.97 V was attributed to the reduction of rhodium(III) and was 10–50-fold larger than the analogous Cu_2Se or $HgSe$ peaks.

The CSV procedure reported in the present paper is adapted from the rhodium method [11]. We found that two peaks were formed during the cathodic scan; the sensitivity of the more negative peak is greatly enhanced by a catalytic hydrogen effect at high rhodium concentrations. The new procedure is applied to the determination of selenium in lake water and sea water.

Table 1
CSV methods for the determination of selenium in the presence of various metals

M^{z+}	Electrode	Formed compound	Detection limit using adsorption times ≤ 3 min	References
Hg^{2+}	HMDE	$HgSe$	1.4 nM	[31]
			<75 pM	[9]
Hg^{2+}	MFE (GC)	$HgSe$	6.3 nM	[32]
Cu^{2+}	HMDE	Cu_2Se	250 pM	[10]
			60 pM	[8]
			25 pM	[7]
			13 pM	[33]
			9 pM	[34]
Ag^+	Ag	Ag_2Se	6.3 nM	[35]
Rh^{3+}	HMDE	Rh_2Se_3	6 pM	[11]

2. Experimental

2.1. Instrumentation and reagents

All measurements were performed with an Autolab PSTAT 10 (ECO-Chemie, The Netherlands) and a static mercury drop electrode (VA 663, Metrohm, Switzerland), connected to a 486 personal computer. The reference electrode (Metrohm, Switzerland) was a double-junction Ag/AgCl electrode with 3 M KCl in the salt bridge ($E=0.208$ V versus SHE), and the counter electrode (Metrohm, Switzerland) was a glassy carbon rod. All measurements were carried out in solutions which were thoroughly deaerated with high-purity nitrogen for at least 5 min.

Water was purified by a Millipore reverse-osmosis, ion exchange water purification system (Milli-Q water). Acids were purified by sub-boiling distillation in a quartz still. Stock solutions of selenium(IV) (0.1 mM, 0.1 μ M, 10 nM) and rhodium(III) (1 mg l⁻¹) were prepared daily by dilution of Fluka atomic spectroscopy standard solutions (SeO_2 in 0.5 M HNO_3 , 1 g l⁻¹ and $RhCl_3$ in 1 M HCl, 1 g l⁻¹) and stored in Teflon bottles. A standard selenium(VI) solution was made up by dissolving sodium selenate (BDH, AnalaR) in Milli-Q water. Sodium chloride (BDH, AnalaR) and sodium hydrogen carbonate (BDH, AnalaR) were dissolved in Milli-Q water to give stock solutions of 1 M $NaHCO_3$ and 4 M NaCl. Stock solutions of various trace metals tested for interferences were prepared by dilution of BDH standard solutions.

The analytical parameters were evaluated using Milli-Q water or sea water originating from the Atlantic that had been filtered and stored at its natural pH. Samples from the water column of a lake (lake Neadalsvatn, Norway) were collected using a plastic Niskin bottle. These samples were not filtered and stored at 4°C in a refrigerator.

2.2. Determination of total dissolved selenium in natural waters

Natural waters (lake water, sea water) were UV-digested in silica tubes (30 ml) for 150 min at pH 8.3 (the lake water pH was adjusted to 8.3 by addition of 2 mM $NaHCO_3$) to destroy organic material and convert Se(VI) to Se(IV) [8]. All measurements

were performed within 2 h after the digestion to avoid re-oxidation to Se(VI).

Water (10 ml) was pipetted into the voltammetric cell which was carefully cleaned with 0.1 M HNO₃ between measurements. HCl (final concentration of 0.15–0.3 M) and Rh(III) (75 ppb) were added and the solution was deaerated with high-purity nitrogen for 5 min. After the deposition a cathodic scan was carried out between –0.7 and –1.35 V. The linear sweep (LSCSV) wave-form was used for the CSV measurements unless indicated differently: scan rate 50 mV s⁻¹, step size 5 mV. The standard addition method was used to calculate the Se(IV) concentration in the samples.

3. Results and discussion

3.1. Cathodic stripping voltammetry in the presence of rhodium(III)

CSV measurements of Se(IV) in the presence of low rhodium(III) concentrations (<10 ppb) produced a single reduction peak at about –0.7 V (Fig. 1a). This peak attained greatest peak height at 5 ppb rhodium. An increase of the rhodium content of the solution led to a second, much larger reduction peak

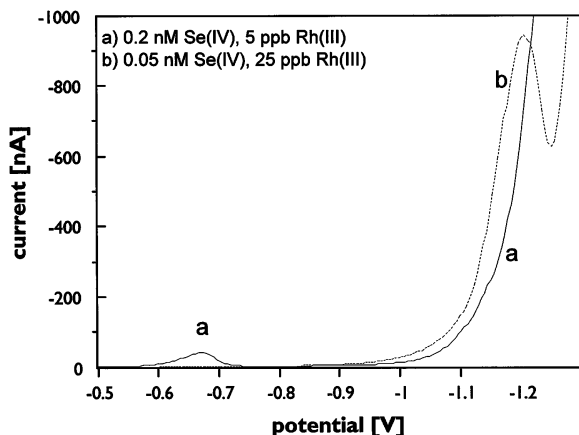


Fig. 1. CSV reduction peaks for selenium(IV) in the presence of different rhodium(III) concentrations. (a) 5 ppb Rh(III), 0.2 nM Se(IV); (b) 25 ppb Rh(III), 0.05 nM Se(IV), 0.3 M HCl, deposition potential –0.2 V, deposition time 50 s.

at about –1.15 V (Fig. 1b), and the first peak disappeared. Neither of the peaks was present without the rhodium.

The reduction peak at –0.7 V increased linearly with the selenium(IV) concentration but the calibration curve did not go through the origin, instead the calibration graph intersected the X-axis at about 0.15 nM Se. For this reason, this CSV response cannot be used to determine low concentrations of Se(IV).

The second peak at –1.15 V observed at higher rhodium concentrations increased linearly with the concentration of selenium(IV) and at much greater sensitivity. Low selenium concentrations (0.2 nM) produced peak currents in the μ A current range with deposition times <100 s. That is significantly more sensitive than other CSV methods, and this method was further optimised.

3.1.1. Effects of varying the rhodium and acid concentrations

The reduction peak at about –1.15 V first appeared at a rhodium concentration of 5 ppb and increased significantly up to 25 ppb Rh(III) for 0.2 nM Se(IV) (Fig. 2a). The peak is situated just positive of, at the beginning of, the hydrogen wave in acidic solution. The peak height levelled off at this rhodium concentration, and interferences (peak splitting) occurred at rhodium concentrations higher than 80 ppb. Therefore, concentrations between 25 and 75 ppb Rh(III) were applied for further measurements.

Different acids (H₂SO₄, HCl, HClO₄, HNO₃) were compared as supporting electrolyte. No response was obtained for low selenium levels in HClO₄ and HNO₃. Measurements in H₂SO₄ produced good results but best performance was obtained in HCl. Fig. 2b shows the influence of the concentration of HCl on the peak current for a selenium concentration of 0.5 nM Se(IV). The peak height increased almost exponentially with the acid concentration. But the peak became distorted and split at concentrations >0.5 M HCl. The great increase with the acid concentration, and the location of the peak as a shoulder on the hydrogen wave, are an indication that catalytic evolution of hydrogen may play a role in the reaction mechanism of the stripping step.

Further measurements were performed in a supporting electrolyte containing 0.15 M HCl (in sea

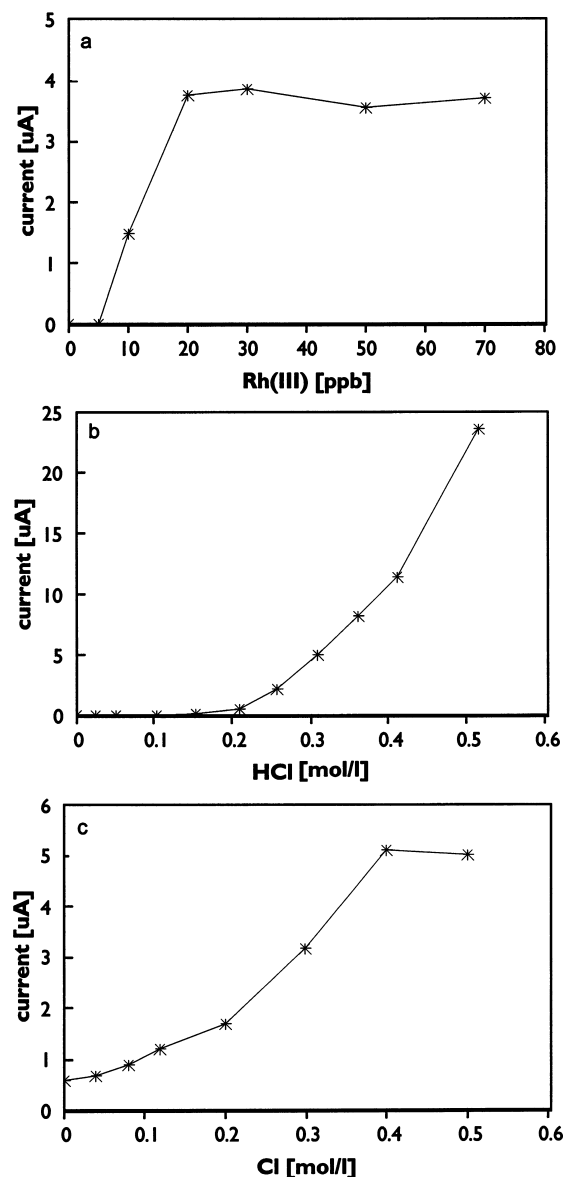


Fig. 2. Dependence of the peak current of selenium(IV) on the electrolyte composition. (a) Dependence on the rhodium(III) concentration, 0.2 nM Se(IV), 0.3 M HCl; (b) dependence on the HCl concentration, 0.5 nM Se(IV), 30 ppb Rh(III); (c) dependence on the Cl^- concentration, 0.5 nM Se(IV), 0.3 M HCl, 30 ppb Rh(III), deposition potential -0.2 V, deposition time 50 s.

water)–0.3 M HCl (in Milli-Q water and freshwater). Comparison of the results obtained in different acids suggested that the Cl^- ions of the HCl play a role in the voltammetric response. Variation of the chloride

concentration at a constant acid concentration (0.3 M HCl) showed that the peak height for 0.5 nM Se(IV) increased up to an addition of 0.4 M Cl^- (Fig. 2c), levelling off at higher chloride concentrations.

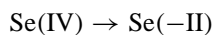
Chloride ions are known to stabilise certain metal complexes at the electrode surface [12,13] and to effect catalytic hydrogen evolution reactions [14]. The strong effect of chloride on the peak height for selenium suggests that chloride is involved in the catalytic reaction, probably via a mixed Cl-Rh-SeH complex species.

Rhodium, like other platinum-group metals, is known to catalyse proton reduction processes [15–18]. A catalytic hydrogen wave is produced by CSV of rhodium at -1.27 V in the presence of formazone [19], at -1.45 V in the presence of KCl/ethylenediamine [20], and in the presence of diethyldithiocarbamate [21].

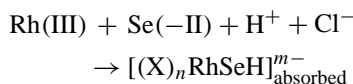
Rhodium forms strong chloride complexes of the type $\text{RhCl}_3 \times 3\text{H}_2\text{O}$ [22]. Compounds like $\text{Rh}_2\text{Se}_3 \times 3\text{H}_2\text{Se}$ are known to be formed under strong acidic conditions in the presence of selenium(IV) [23]. SeH^- is very similar to SH^- which is known to be involved in catalytic hydrogen effects, often as a cobalt complex [24–27]. An analogous catalytic effect for rhodium in the presence of a SeH-containing complex could explain the voltammetric response produced here at low selenium concentrations in acidic conditions. Catalytic hydrogen evolution produced by SeH-groups instead of SH-groups was predicted by Stackelberg and Fassbender [24].

A possible reaction mechanism for the electrode reactions during the voltammetric analysis is shown below:

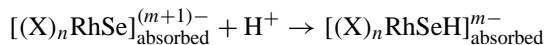
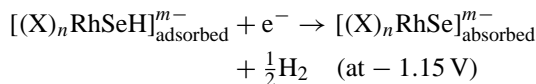
Adsorption at -0.2 V:



followed by



Potential scan:



where $\text{X}=\text{Cl}, \text{Se}, \text{SeH}, \text{SeH}_2$, or Rh.

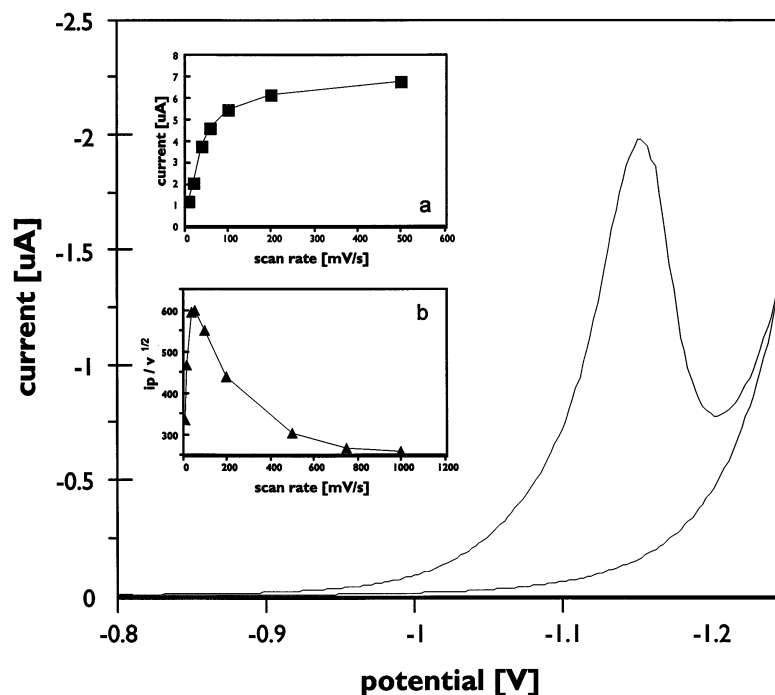


Fig. 3. Cyclic voltammogram of 1 nM Se(IV), 0.3 HCl, 75 ppb Rh(III), 50 s deposition at -0.2 V, scan rate 50 mV s^{-1} . (a) Effect of the scan rate on the peak height; (b) dependence of $(i_p/v^{1/2})$ on the scan rate, same conditions.

From this work the exact composition of the adsorbed species is not clear; in view of the importance of chloride it is likely that Cl^- is involved in the complex; furthermore, it is possible that more than one Se(–II) ion is involved in the species, which could occur as SeH^- or SeH_2 ; finally, it is not clear whether one or more Rh groups are involved in the complex. The catalytic nature of the reaction explains the large peak currents and high sensitivity, the very negative peak potential and the serious interference of organic surfactants, as described for other catalysed hydrogen wave systems [15,20].

Cyclic voltammetry (CV) was used to confirm the catalytic effect in a solution containing 0.3 HCl, 1 nM Se(IV) and 75 ppb Rh(III) (Fig. 3). The cyclic scan was preceded by 50 s deposition at -0.2 V, and the forward going scan was made towards negative potentials. The absence of an oxidation peak in the reverse scan showed that the reduction is totally irreversible. This is consistent with the reaction mechanism of a catalysed reduction cycle. However, in CV of catalytic

reactions often a reduction peak appears also in the reverse scan caused by the diffusion of fresh oxidant and analyte species to the electrode surface, as was the case for platinum and cobalt [13,19]. We did not find such a reduction peak during the reverse scan because the electroactive complex does not occur in the solution. It is only formed at the electrode surface from Se(–II) and Rh(III) in a narrow potential range between -0.1 and -0.3 V. Therefore, diffusion of the compound to the electrode surface during the reverse scan does not take place.

In the reversible reduction of adsorbed species the peak height should increase linearly with the scan rate, whereas the increase would be non-linear for catalytic reactions where the increase of i_p should be linear to $(\text{scan rate})^{1/2}$. Variation of the scan rate showed (Fig. 3a) a non-linear increase of the peak current with increasing scan rate (v), consistent with the catalytic nature of the hydrogen production [19]. The dependence of $(i_p/v^{1/2})$ on the scan rate is used as a diagnostic test for catalytic reactions [28]. The

ratio of $i_p/v^{1/2}$ is supposed to decrease with increasing scan rate. This ratio was found to decrease at scan rates $\geq 50 \text{ mV s}^{-1}$ (Fig. 3b).

Variation of the scan rate showed that the peak potential shifted in a negative direction by 30 mV when the scan rate was increased from 10 to 50 mV s^{-1} . A negative shift is in line with expectation for electrochemically irreversible reactions.

3.1.2. Effects of varying the deposition potential and deposition time

Variation of the deposition potential showed (Fig. 4a) that the height of the selenium peak increased rapidly using deposition potentials between -0.1 and -0.15 V , had a maximum at -0.2 V and

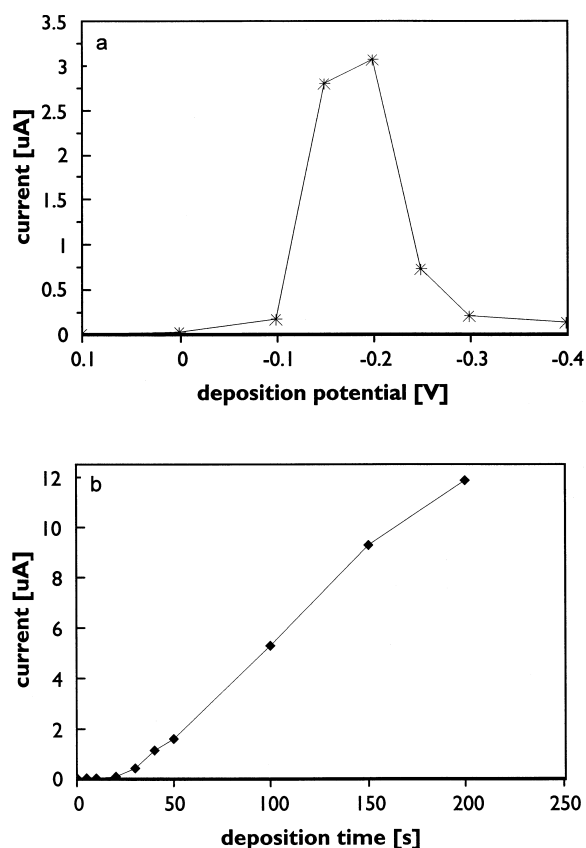


Fig. 4. Dependence of the peak current of 0.2 nM Se(IV) in 0.3 M HCl on the deposition potential (a) and the deposition time (b). The experiment in (a) used 25 ppb Rh(III) and a 50 s deposition time; the experiment in (b) used 50 ppb Rh(III) and a deposition potential of -0.2 V .

then decreased sharply. The peak currents obtained at adsorption potentials more positive than -0.1 V could be low due to incomplete reduction of Se(IV) to Se(-II) during the deposition step. It is likely that the lower peak heights obtained after deposition at potentials more negative than -0.2 V are due to the reduction of free Rh which would lower the amount of Rh(III) available for the formation of possibly mixed Cl-Rh-SeH-complex species with Se(-II) during the deposition step. All subsequent work used an adsorption potential of -0.2 V .

Variation of the deposition time showed that the increase of peak current for 0.2 nM Se(IV) was non-linear (S-shaped) (Fig. 4b). The slope increased with increasing deposition time at deposition times $< 30 \text{ s}$, was constant between 30 and 150 s and decreased at deposition times $> 150 \text{ s}$ due to distortion of the peak. The increasing slope at short deposition times is unusual, but has been observed before in CSV for the determination of selenium [8].

3.1.3. Linear range and limit of detection

Using the optimised electrochemical parameters very sensitive measurements of selenium can be performed. Voltammograms for standard additions of 50 pM – 0.5 nM Se(IV) using a deposition time of 50 s are shown in Fig. 5. The sensitivity under optimised

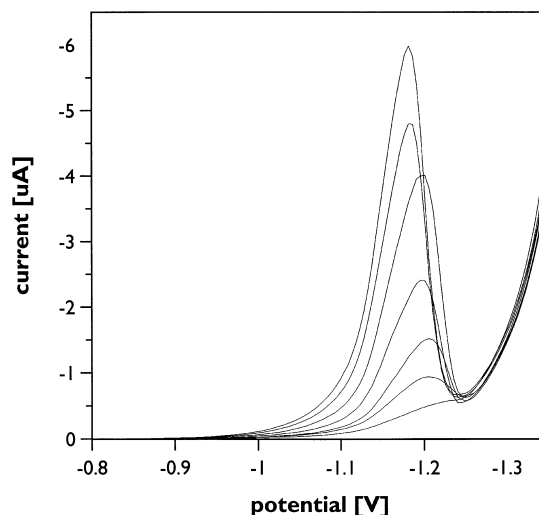


Fig. 5. Voltammograms of standard additions of Se(IV) to 0.3 M HCl ; additions were: $50, 100, 200, 300, 400$ and 500 pM to a background concentration of $\sim 17 \text{ pM}$. Conditions were: 25 ppb Rh(III) , deposition potential -0.2 V , and a 50 s deposition time.

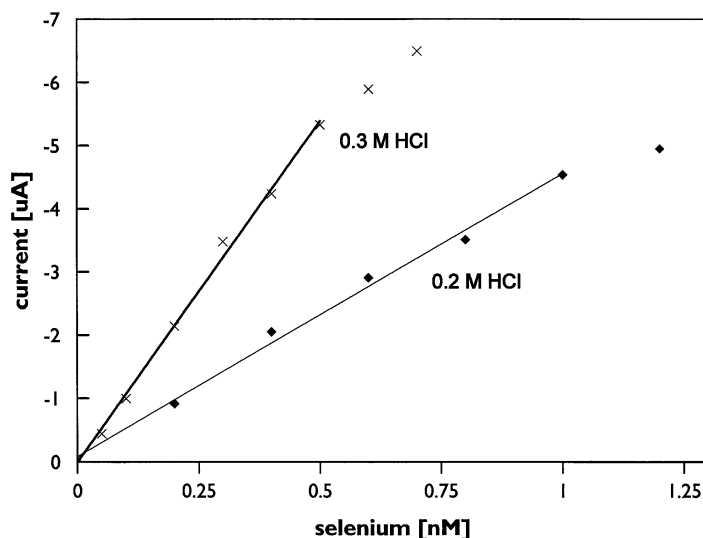


Fig. 6. Calibration curves of selenium(IV) for different HCl concentrations: 25 ppb Rh(III), deposition time 50 s, deposition potential -0.2 V.

conditions was about $10 \mu\text{A/nM Se(IV)}$ using the 50 s adsorption time. The linear concentration range was restricted to 0.5 nM Se(IV) in 0.3 M HCl , but this can be extended to approximately 1.5 nM Se(IV) by lowering the acid concentration to 0.2 M , and further by using a shorter adsorption time. Two calibration curves for different acid concentrations are shown in Fig. 6. With increasing acid concentration, the sensitivity of the method was found to increase but the linear concentration range decreased.

A 3σ detection limit of 2.4 pM Se(IV) was calculated from the standard deviation of a low selenium concentration ($17 \pm 0.8 \text{ pM}$) using a deposition time of 50 s. That is the lowest electroanalytical detection limit reported for selenium for deposition times under 5 min.

3.1.4. Interferences

Possible interferences in the CSV of selenium include adsorption of surface active organic compounds and adsorption of interfering electroactive or selenide forming metals. Since we suppose that a catalytic effect is involved other catalytically active metals could also interfere.

Preliminary experiments using natural water samples showed that the determination of selenium(IV) is not possible in the presence of natural organic surfactants, which is a common problem in CSV of Se

[8,9,29], and of catalytic waves generally [20]. The interfering effect of the organic matter is very strong in the catalytic method. The peaks became distorted and split, or disappeared, when untreated lake water or sea water was analysed. We observed memory effects in subsequent measurements which might be caused by adsorption of organic material on the voltammetric cell or on the tip of the mercury capillary. Therefore, great care must be used in rinsing the voltammetric cell and the electrode between measurements to avoid contamination with surfactants.

Intensive UV-digestion of the samples prior to the voltammetric determination was successfully used to destroy the interfering organic compounds and to remove the interference. The same method causes all Se(VI) to be reduced to Se(IV) , so combined Se(VI) and Se(IV) is measured in natural waters.

The possible interferences of various trace metals and anions were investigated by addition of these ions to a solution containing the electrolyte and 0.5 nM Se(IV) and measurement of the selenium peak. The following ions were added: Cu(II) , Cd(II) , Pb(II) , Zn(II) , Mn(II) , Pt(II) , Fe(III) , Mo(VI) , As(III) , S(-II) , $\text{I/O}_3(-\text{I})$, and Te(IV) . None of these ions produced a peak without selenium(IV) in the solution. Cd(II) , Pb(II) , Zn(II) , Mn(II) and Mo(VI) did not affect the peak current of 0.5 nM Se(IV) in the concentration range from 1 to 100 nM of the added ion. Cu(II) ,

Pt(II) and Fe(III) raised the peak height from a concentration of 5 nM of each metal. Arsenic(III) diminished the peak current at concentrations higher than 3 nM As(III) in the solution. Sulfide, very similar to selenide in its chemical behaviour, did not interfere between 1 and 100 nM but increased the selenium response at higher concentrations. Iodide and iodate showed no influence between 50 and 200 nM, slightly raising the peak height at higher concentrations and led to a distortion at concentrations higher than 2 μ M. Tellurium had no effect between 0.5 and 5 nM.

Most of the tested ions normally occur in unpolluted natural waters in lower concentrations than those used here and do not interfere with the determination of selenium(IV). At higher concentrations, they only change the sensitivity of the method. Since we apply the standard addition method for the determination of selenium(IV) there should be no problem in using this method.

3.2. Application to natural waters

Separate measurements showed that this method responds only to Se(IV) whereas no response was obtained for Se(VI). UV-digestion was therefore used to convert Se(VI) to Se(IV) in natural water samples. This digestion should be carried out at pH > 8 to ensure a full transformation [8,9,30]. We explored briefly the possibility of determining Se(IV) specifically by removing interfering organic matter by passing sea water through a Sep-Pak C-18 column and thus avoiding UV-digestion; however, peak distortion occurred indicating that this procedure was not as good as UV-digestion. UV-digestion was therefore selected as the optimal method for removal of organic interferences. The necessary UV-digestion and the conversion of Se(VI) to Se(IV) means that determination of the speciation of the redox couple Se(IV)/Se(VI) is difficult unless a better procedure is found to remove

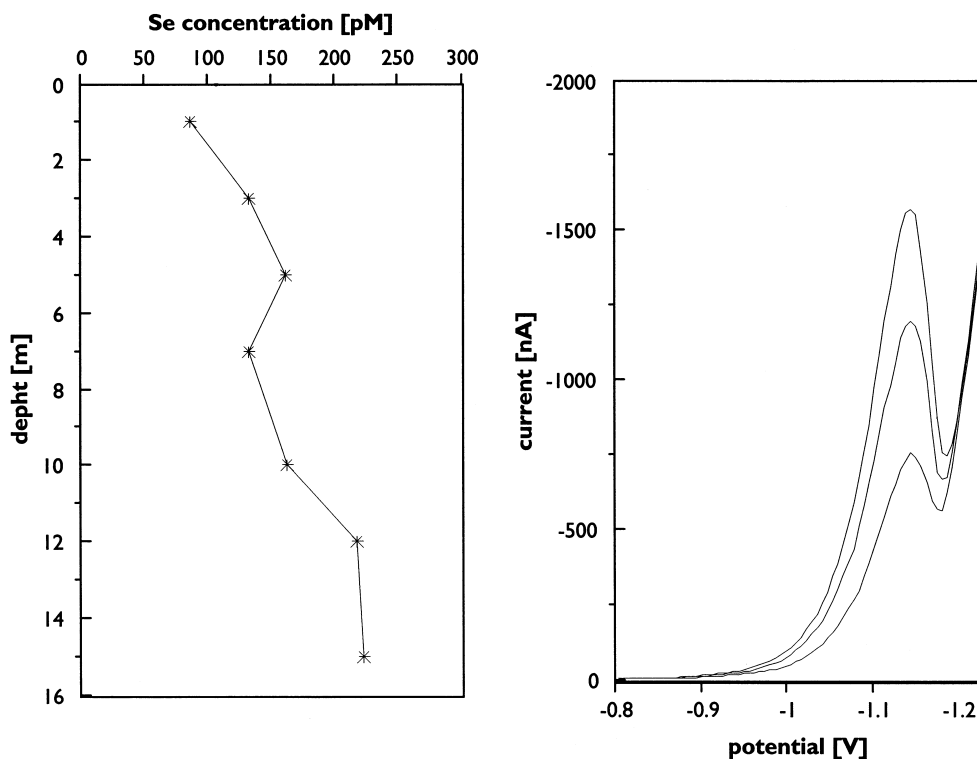


Fig. 7. Voltammograms of lake water (lake Neadalsvatn, depth 7 m, 23/7/98) with two standard additions of 0.2 nM, and a depth profile for the lake. The water was UV-digested (2.5 h) after adjusting the pH to 8.3 using 2 mM NaHCO_3 ; analysis was using 0.3 M HCl, and 75 ppb Rh(III); deposition time 50 s, deposition potential -0.2 V.

organic surfactants without changing the redox specification.

The optimised CSV method was slightly adapted for the greatly differing composition of sea and lake water as described in the figure captions. Fig. 7 shows the voltammograms of selenium, and standard additions, in water from a Norwegian lake, and a depth profile for the lake. Selenium was found to occur at levels between 87 pM near the surface and 224 pM at 15 m depth. The concentrations may appear low for lake water but similar data have been reported for other Scandinavian lakes [2] and probably depend on the source rock, and distance from the sea, of the water.

To show the general applicability of the method for sea water, we measured filtered sea water from a tank that had been stored for 1 year. Concentrations of about 250 pM were found after UV-digestion (261 ± 22 pM Se, $n=5$). The recovery was tested by analysis of sea water to which 500 pM Se(IV) had been added, a concentration of 754 ± 26 pM Se ($n=5$) was found in this sea water, indicating full recovery of the added selenium.

3.3. Conclusions

The sensitivity of CSV of selenium is much enhanced by the development of a catalytic effect in the presence of rhodium, acid and chloride ions. The optimised method can be used to determine very low concentrations of selenium in natural waters with very short preconcentration times. The detection limit was 2.4 pM Se(IV) using a deposition time of only 50 s. The method is reactive to Se(IV) as Se(VI) is electrochemically non-reactive. A drawback of the method is its sensitivity to interference by surface active organic matter. The organic matter is removed by UV-digestion at neutral to alkaline pH (pH 8.3), which causes the simultaneous conversion of selenium(VI) to electroactive selenium(IV).

A reaction mechanism of catalytic hydrogen evolution is consistent with the very large peak currents, the location of the peak potential, an unusual dependence on the acid and chloride concentrations, a strong influence of organic surfactants, and supported by cyclic voltammetry. The catalytic hydrogen effect is initiated by the reduction of an adsorbed rhodium complex of the type $[(X)_nRhSeH]^{m-}$ containing Cl⁻, Se⁻, SeH⁻ and/or SeH₂-species.

Acknowledgements

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