Determination of Inorganic Selenium Species in Natural Waters by Preconcentration and Cathodic Stripping Voltammetry

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This paper describes a method, which employs an anion-exchange procedure and differential pulse cathodic stripping voltammetry (DPCSV) with hanging mercury drop electrode in the presence of added copper(II) for the determination of low levels of inorganic selenium species in natural waters. Optimum procedure for preconcentration and separation of Se(IV) and Se(VI) as well as optimum conditions for electrochemical determination itself were investigated. The preconcentration/separation step prior to determination improves the detection limit and removes matrix interference. The detection limit of 10 ng dm$^{-3}$ was obtained on the basis of enrichment factor of 15 and a 120 s deposition. The precision and accuracy of the pretreatment procedure and DPCSV technique were evaluated by analyzing synthetic water spiked with known amounts of Se(IV) and Se(VI). The relative standard deviations ranged from 0.3 to 3.5 % and the recoveries were > 95 % for both Se species. Finally, the developed method was successfully applied to the analysis of Se(IV) and Se(VI) in natural waters.

In recent years, there has been increasing interest in the trace determination of selenium because of its dual role as an essential nutrient at low concentration levels and as a toxic substance at higher concentration levels. As the concentration range within which Se is essential, is very narrow, precise knowledge of the selenium content in the environment has become important.

The concentration of total selenium in natural waters lies in general below 1 µg dm$^{-3}$ and seldom reaches higher values. Selenites and selenates are predominantly soluble forms of the element in most natural waters. In aquatic systems with high contents of dissolved organic carbon, however, different organo-selenium compounds are present [1].

The low content of Se in waters demands a high sensitivity of the analytical method used for its determination. Among the methods which can be applied for the determination of traces of Se electroanalytical technique such as stripping voltammetry is important. The method has high sensitivity and high precision and is simple and inexpensive. Therefore, the method seems to be an attractive alternative to atomic absorption spectrometry for the determination of Se. Various stripping voltammetric techniques have been shown to be useful for Se determination with detection limit down to the sub-parts per billion levels.

Cathodic stripping voltammetry (CSV) with a hanging mercury drop electrode (HMDE) as the working electrode is the most often used electroanalytical method for the determination of traces of Se in waters. Selenium is accumulated at an electrode surface by electroreduction either in the form of HgSe [2—4] or intermetallic compounds: copper—selenium [5—7] and rhodium—selenium [8]. Selenium can also be determined by CSV after adsorptive collection in the form of complexes with 3,3′-diaminobenzidine on HMDE [9]. Recently Ishiyama and Tanaka [10] described the possibility of using a rotating silver disc electrode for the CSV of nanogram quantities of Se(IV). Anodic stripping voltammetry can be applied only in connection with a solid electrode, e.g. Au [11], the poly(3,3′-diaminobenzidine) modified gold electrode [12]. Since the toxicological properties of different Se compounds differ, analytical procedures must be available to determine not only total Se but also the various Se species encountered in the environment. Consequently, the aim of present work was to develop a procedure based on Se(IV) voltammetric determination for speciation of inorganic Se in natural waters.

EXPERIMENTAL

Hydrochloric acid (Lachema) purified by isothermal distillation was used. Strongly basic anion-exchange resin Dowex $1 \times 8$, $\Phi = 0.30–0.15$ mm was obtained from Bio Rad, chelating sorbent Spheron Oxin 1000 from Lachema and reference humic acid ($M$ = 500—1000) from Fluka. All other chemicals used were of anal. grade from Lachema and Fluka and were
not further purified. The water used had been deionized and further purified in Labconco Water Pro PS system to 18 MΩ quality.

The Se(IV) standard stock solution (1 × 10⁻² mol dm⁻³) was prepared by dissolving a measured quantity of selenium dioxide (BDH standard) in 0.1 M HCl. The stock solution of Se(VI) (1 × 10⁻⁴ mol dm⁻³) was prepared by oxidation of Se(IV) stock solution by addition of chlorine solution and by appropriate dilution. Working standard solutions of lower concentrations 2 × 10⁻⁶ to 1 × 10⁻⁵ mol dm⁻³ Se(IV) or Se(VI) were prepared before analysis by dilution of the stock solutions. Synthetic water spiked with known amounts of Se was used as model sample. Its composition was: ρ(CaCl₂ 2H₂O) = 0.294 g dm⁻³, ρ(NaCl) = 0.216 g dm⁻³, ρ(MgSO₄ 7H₂O) = 0.086 g dm⁻³, ρ(KCl) = 9.5 mg dm⁻³, ρ(NH₄)₂HPO₄ = 7.3 mg dm⁻³, and ρ(humic acids) = 0—10 mg dm⁻³.

The polarographic Analyzer PA 4 with X—Y recorder 4103 and Static Mercury Drop Electrode SMDE 1 (Laboratorní přístroje, Prague) were used for FSDPCSV measurements. The electrochemical cell was equipped with Ag/AgCl reference electrode (saturated KCl), the platinum auxiliary electrode, and the working electrode which was used in the HMDE mode. Voltammetric measurements were made under the following conditions: deposition potential −0.35 V, deposition time 120 s, drop size 160 ms (2.3 mg), pulse amplitude −50 mV, scan rate 10 mV s⁻¹, current sensitivity 2 to 5 nA cm⁻¹, time constant of memory 100 ms.

Deaeration of analyzed solutions was performed with nitrogen which was passed through an acidic vanadium(II) scrubber solution in contact with zinc amalgam.

Voltammetric Determination of Se(IV)

The treated water samples (1—5 cm³) were pipetted into the polarographic cell and diluted to 10 cm³ so that the resulting concentration of HCl in the analyzed solution was in the range 0.1—0.5 mol dm⁻³. Then 20 mm³ of 1 × 10⁻² mol dm⁻³ CuCl₂ was added to measured solution. The solution was deaerated for 5 min by bubbling nitrogen saturated with water vapour. After deaeration of the sample the Se(IV) peak was recorded under the conditions mentioned above in the potential range of −0.35 to −0.75 V by cathodic stripping voltammetry with fast scan differential pulse record of the stripping step. The Se(IV) peak in these conditions was located at the potential of −0.55 to −0.59 V in dependence on the HCl concentration. For determination of Se(IV) the method of standard additions was used. It was realized by three additions (10 to 50 mm³) of 2 × 10⁻⁶ to 1 × 10⁻⁵ mol dm⁻³ Se(IV) standard solutions. The height of the Se(IV) peak was used for its quantification.

The content of Se was estimated after a preconcentration/separation step and a reduction of Se(VI) to Se(IV). The synthetic waters spiked with standard solutions of Se(IV) and Se(VI) and natural waters were analyzed.

Reduction of Se(VI) to Se(IV)

In preliminary tests of the reduction process, the standard 1 × 10⁻⁵ mol dm⁻³ Se(VI) solution (0.05 to 0.2 cm³) was mixed with 7.5 M HCl (2 to 4 cm³) and diluted to volume of 5 cm³ in 20 cm³ flask so that final concentration of HCl in this solution was 3 to 6 mol dm⁻³. The resulting solution was maintained in a boiling water bath for 10 to 50 min. After the reduction, the solution was cooled and quantitatively transferred into 10 cm³ volumetric flask and diluted with deionized water to the mark. For one determination 1 to 5 cm³ of this solution was pipetted into the polarographic cell for the voltammetric measurement.

The reduction of Se(VI) in synthetic water samples and natural waters was realized after preconcentration step by heating of Se(VI) eluate with 5 mol dm⁻³ HCl in a boiling water bath for 30 min.

Preconcentration and Separation of Se(IV) and Se(VI)

For the selective determination of selenite and selenate, water sample (100—1000 cm³) at the natural pH was passed through a column (plastic tube with a diameter of 0.9 cm) that was packed to a height of 1.5 cm with the anion-exchange resin Dowex 1 × 8 in the chloride form. After rinsing the column with water, selenite and selenate were successively eluted with 6 cm³ of 0.05 mol dm⁻³ HCl and 5 cm³ of 5 mol dm⁻³ HCl, respectively. The selenite fraction can be directly determined after transferring an aliquot of the sample to the polarographic cell. The selenate fraction, however, was reduced to selenite as described above. For the determination of total inorganic selenium Se(IV) and Se(VI) were desorbed with 5 cm³ of 5 mol dm⁻³ HCl solution and Se(VI) subsequently reduced by boiling. The flows during preconcentration and elution were approximately 1—2 cm³ min⁻¹.

Analyses of natural water samples were completed within 24 h of collection. The surface waters were filtered through a 0.45 μm membrane filter.

RESULTS AND DISCUSSION

DPCSV is preferred stripping technique in most of the determinations of selenium at mercury electrode [2—7]. The form in which Se is deposited on HMDE is mainly dependent upon the composition of the chosen supporting electrolyte. Selenium(IV) during the deposition step can be accumulated either in the form of HgSe according to the reaction.

H₂SeO₃ + 4H⁺ + Hg + 4e⁻ → HgSe + 3H₂O (A)
or in the presence of Cu(II) ions as intermetallic compounds Cu₂Se

H₂SeO₃ + 4H⁺ + 2xCu²⁺ + (4 + 2x)e⁻ →
→ Cu₂Se + 3H₂O (B)
The selenide deposit is stripped cathodically

HgSe + 2H⁺ + 2e⁻ → H₂Se + Hg (C)

Cu₂Se + 2H⁺ + 2e⁻ → H₂Se + xCu(Hg) (D)

In preliminary experiments the applicability of CSV determination of Se(IV) by deposition of HgSe and Cu₂Se was tested. The change of shape of HgSe stripping peak with increasing Se(IV) concentration results in nonlinear calibration curves. Coelectrodeposition of Se(IV) and added Cu(II) at a mercury electrode, subsequently giving rise to a copper selenide stripping peak appears to be the most convenient and reliable way to perform CSV determination of Se(IV) and it was exploited in this work.

In the presence of Cu(II) the peak of Se(IV) is narrower, appears at more negative potentials than HgSe stripping peak with increasing Se(IV) concentration results in nonlinear calibration curves. Coelectrodeposition of Se(IV) and added Cu(II) at a mercury electrode, subsequently giving rise to a copper selenide stripping peak appears to be the most convenient and reliable way to perform CSV determination of Se(IV) and it was exploited in this work.

The observed peak currents at the scan rate 10 mV s⁻¹ increased linearly with amplitude up to 25 mV. At higher amplitude a departure from linearity occurs. The use of amplitude of 50 mV enabled sufficient sensitivity and was applied in all further measurements.

The dependence of the stripping peak current on deposition time (tₐ) was studied for tₐ from 40 to 480 s using optimized parameters. Examination of the plot revealed that the initial slopes, at shorter deposition times, were steeper and became more gentle at longer deposition times. It was found that increasing the de-

H₂SeO₃ + 4H⁺ + Hg + 4e⁻ → HgSe + 3H₂O (A)
or in the presence of Cu(II) ions as intermetallic compounds Cu₂Se

H₂SeO₃ + 4H⁺ + 2xCu²⁺ + (4 + 2x)e⁻ →
→ Cu₂Se + 3H₂O (B)
The selenide deposit is stripped cathodically

HgSe + 2H⁺ + 2e⁻ → H₂Se + Hg (C)

Cu₂Se + 2H⁺ + 2e⁻ → H₂Se + xCu(Hg) (D)

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SELENIUM IN NATURAL WATERS

Fig. 1. Effect of the deposition potential on the CSV peak height obtained for \( p(\text{Se(IV)}) = 4 \mu g \text{ dm}^{-3} \) in HCl medium of various concentration: 1. 1 mol dm\(^{-3}\), 2. 0.5 mol dm\(^{-3}\), 3. 0.1 mol dm\(^{-3}\).

position time from 120 s to 240 s produced a small rise in the stripping current therefore \( t_d = 120 \) s was recommended for the Se(IV) determination. Simultaneously with increasing \( t_d \) a shift of the peak potential in negative direction was observed from \(-0.56 \) V at 40 s to \(-0.62 \) V at 480 s deposition.

Under conditions mentioned above linearity of the dependence of the peak height on concentration was tested by standard additions of Se(IV) to basic electrolyte (0.1—0.5 M-HCl) in the concentration range from 0.4 to 10 \( \mu g \text{ dm}^{-3} \). The linear calibration plots were obtained in the concentration range from 0.4 to 5 \( \mu g \text{ dm}^{-3} \) in the presence of \( 2 \times 10^{-5} \) mol dm\(^{-3}\) Cu(II) at the deposition potential \( E_d \) of \(-0.35 \) V and the deposition time of 120 s. The slope of the calibration line was 2.18 nA dm\(^{-3}\) \( \mu g^{-1} \) with intercept \(-0.036 \) nA and correlation coefficient 0.9994 in 0.1 M-HCl medium. The results presented verify the very high sensitivity of CSV for Se(IV). The detection limit of this method was \( 0.15 \mu g \text{ dm}^{-3} \) for a 120 s deposition.

Major chemical forms of Se in waters are SeO\(_2^2-\) and SeO\(_4^{3-}\). Voltammetric methods are sensitive only for Se(IV), as Se(VI) cannot be reduced electrochemically. In order to determine the concentration of Se(VI) in a sample, the Se(VI) species must be reduced to Se(IV) prior to the determination. Many reducing species are able to reduce Se(VI). Various published reduction methods used in selenium analysis are summarized in paper [14]. Reduction of Se(VI) by standard chemical reducing agents is kinetically slow and complicated by the fact that strong reducing agents will reduce any Se(VI) directly to the elemental form. Cutter [15] discussed several methods for reduction of Se(VI) and recommended the reduction with hydrochloric acid as a suitable method. The efficiency of the reduction depends, however, on many factors, e.g. concentration of HCl, reduction time, temperature of the solution. It is recommended to perform this reduction process at high temperature (90—100°C) as this redox equilibrium is strongly temperature-depending. The kinetic parameters for the reduction of Se(VI) with HCl at 91°C were investigated by Brimmer et al. [16]. The use of hydrochloric acid, as reducing agent, is advantageous also for CSV determination of Se because HCl medium is suitable supporting electrolyte. In the literature very different experimental conditions are used. The complete conversion of selenate to selenite is mostly achieved by heating the sample with 4—7 M-HCl in a boiling water bath for 5 to 30 min. In order to verify optimum conditions for reduction of Se(VI), in our experiments the reduction process of 158 ng of Se(VI) was reexamined in 3—6 M-HCl solutions at 100°C. The yields of Se(IV) are plotted as a function of time in Fig. 2. From the results it follows that complete recovery of Se was obtained at \( c(\text{HCl}) \geq 4 \) mol dm\(^{-3}\), whereas the yield decreased rapidly at \( c(\text{HCl}) < 4 \) mol dm\(^{-3}\). To obtain an efficient reduction of SeO\(_2^2-\) the acidity of the sample should be \( \geq 4 \) mol dm\(^{-3}\) HCl and reaction time of at least 20 min should be allowed. The low yield caused by reduction to elemental Se or the formation of volatile compounds if the reduction time was prolonged up to 90 min as some authors [4, 14—16] mentioned was not observed. The results of Se(VI) standard samples of various concentration summarized in Table 1 confirm that the proposed procedure allows quantification of Se(VI) at the low levels (\( \geq 20 \) ng). The successful recoveries of Se(VI) were obtained (94.6—102.0 %) and the relative standard deviations were between 1.2 % and 6.6 % (\( s_x \) calculated for \( \alpha = 0.05 \)).
Concentrations of Se in natural waters are generally very low (below 0.2 μg dm\(^{-3}\)) and seldom achieve 1 μg dm\(^{-3}\) level. Consequently CSV technique is not sensitive enough for direct determination of Se(IV) in waters. To enhance sensitivity and enable speciation analysis, the analytical techniques are generally combined with selective preconcentration steps. Since tetra- and hexavalent selenium occur in natural waters as negatively charged species, ion-exchange chromatography offers a way to preconcentrate and separate the two valency states \([1, 17, 18]\). Selenite and selenate are collected on a strong anion exchanger and then sequentially eluted using HCl of different concentrations. This procedure simultaneously separates Se(IV) and Se(VI) from possible organic interferents, metal ions and allows quantification of both species at the ng dm\(^{-3}\) level. With ion chromatography—CSV technique it is possible to reach a detection limit of 10 ng dm\(^{-3}\) on the basis of enrichment factor of 15. The results obtained show that sorption of Se(IV) is complete over a wide pH range and it can be preconcentrated effectively at natural pH of waters, i.e. without any pH adjustment. The dissociation constant for the selenic acid is \(pK_2 = 1.9\). Hence at pH > 3 the binegative selenate ions become the dominant species with a high affinity towards the anion-exchange resins. The effective elution of Se(IV) retained on Dowex 1 × 8 was achieved using 6 cm\(^3\) of 0.05 M-HCl. In such conditions Se(IV) remains completely on the column. This fact allows the separation of selenite and selenate. A hydrochloric acid concentration of 5 mol dm\(^{-3}\) was applied for

Table 1. Determination of Se(VI) in Standard Samples after Reduction with 4 mol dm\(^{-3}\) HCl

<table>
<thead>
<tr>
<th>(m(\text{Se(VI)}, \text{given})/\text{ng})</th>
<th>(m(\text{Se(VI)}, \text{found})/\text{ng})</th>
<th>(s_b/%)</th>
<th>Recovery/%</th>
<th>Number of measurements</th>
</tr>
</thead>
<tbody>
<tr>
<td>197.4</td>
<td>201.3 ± 20.2</td>
<td>3.8</td>
<td>102.0</td>
<td>5</td>
</tr>
<tr>
<td>157.9</td>
<td>158.7 ± 7.2</td>
<td>1.2</td>
<td>100.5</td>
<td>3</td>
</tr>
<tr>
<td>78.9</td>
<td>79.2 ± 8.1</td>
<td>2.7</td>
<td>100.4</td>
<td>3</td>
</tr>
<tr>
<td>39.5</td>
<td>39.2 ± 2.7</td>
<td>2.6</td>
<td>99.2</td>
<td>5</td>
</tr>
<tr>
<td>19.7</td>
<td>18.7 ± 3.7</td>
<td>6.6</td>
<td>94.6</td>
<td>4</td>
</tr>
</tbody>
</table>

Numerous tests have been carried out to optimize the preconcentration and separation of SeO\(_3^{2-}\) and SeO\(_4^{2-}\) for subsequent combination with CSV. In this work two resins (Dowex 1 × 8, Ostion AT) were tested for retention of Se(IV) and Se(VI) in dynamic condition. The better results were obtained with Dowex 1 × 8. Consequently this anion exchanger was applied in all further work for the pretreatment of water samples.

In acidic solution (pH < 3) the retention of SeO\(_3^{2-}\) is mainly limited by protonation of mononegative hydrogen selenite to neutral species (\(pK_1 = 2.62; pK_2 = 8.3\) for \(H_2SeO_3\)). At higher pH values (pH > 4) HSeO\(_3^-\) and SeO\(_3^{2-}\) are present, the collection efficiency of Se(IV) is close to 100 %. The results obtained show that sorption of Se(IV) is complete over a wide pH range and it can be preconcentrated effectively at natural pH of waters, i.e. without any pH adjustment. The dissociation constant for the selenic acid is \(pK_2 = 1.9\). Hence at pH > 3 the binegative selenate ions become the dominant species with a high affinity towards the anion-exchange resins. The effective elution of Se(IV) retained on Dowex 1 × 8 was achieved using 6 cm\(^3\) of 0.05 M-HCl. In such conditions Se(IV) remains completely on the column. This fact allows the separation of selenite and selenate. A hydrochloric acid concentration of 5 mol dm\(^{-3}\) was applied for
the elution of Se(VI). This concentration elutes Se(VI) quantitatively in 5 cm$^3$ and is, at the same time, the proper medium for reduction of Se(VI) to Se(IV). Content of Se(IV) is determined directly in eluate whereas CSV determination of Se(VI) is possible after reduction. Recovery experiments of spiked synthetic water samples are summarized in Table 2. Se(IV) was recovered from those solutions within 96.2—102.5 % and relative standard deviation $s_\%$ was 0.3—2.6 %. The recovery of Se(VI) was 93.8—100.8 % with $s_\% = 0.9—3.5 \%$. These results demonstrate the utility of the method for determination of Se at nanogram level in waters.

For the application of the analytical method to natural waters it is necessary to consider the effects of any inorganic and organic interferents that may be found in the sample.

The effect of heavy metals on the determination of Se(IV) was studied by applying the method to standard Se(IV) samples containing various amounts of Cd(II), Pb(II), Zn(II), Co(II), Ni(II), Mn(II), As(III), Fe(II), and Fe(III). The considerable interference was found from Cd(II) and especially Pb(II). The presence of metal ion such as Pb(II) in solution leads to the precipitation of selenide on reduction of Se(IV) to hydrogen selenide. Consequently the peak height of Se(IV) at $-0.49$ V diminishes when interfering metal ion is present and simultaneously a second peak arises at more negative potential which increases and shifts to more negative potentials with the increasing concentration of Pb(II). The second peak is attributed to the reduction of Pb(II) in the PbSe surface layer. The magnitude of peak suppression of Se(IV) produced by Pb(II) is shown in Fig. 3.

The addition of Cu(II) can decrease the influence of interfering metal ions (Fig. 3). This was verified by series of measurements in the presence of varied amounts of interfering metal ions. The peak height of Se(IV) was practically unaffected up to the $n$(Pb)/$n$(Se) = 80 and then slowly decreased. The decrease of Se(IV) signal and its deformation caused by Cd(II) was observed at $\rho$(Cd) $>$ 30 $\rho$(Se). At higher concentration of Cd(II) was observed the Cd(II) diffusion peak which is situated very close to the dissolution peak of Cu$_2$Se.

Some experiments were carried out to eliminate the interference of these metals ions. There are several ways of overcoming this. In acidic media the influence of complex-forming reagent is limited. Metal interference can be removed by batch extraction with immobilized 8-hydroxyquinoline (Spheron Oxin) when pre-concentration is not required. This method was successfully applied to analysis of synthetic water samples.

### Table 2. Determination of Se in Synthetic Water Samples after Ion-Exchange Pretreatment

<table>
<thead>
<tr>
<th>$\rho$(Se, given)/($\mu$g dm$^{-3}$)</th>
<th>$\rho$(Se, found)/($\mu$g dm$^{-3}$)</th>
<th>$s_%$/</th>
<th>Recovery/</th>
<th>Number of measurements</th>
</tr>
</thead>
<tbody>
<tr>
<td>Se(IV)</td>
<td>Se(VI)</td>
<td></td>
<td>Se(IV)</td>
<td>Se(VI)</td>
</tr>
<tr>
<td>0.04</td>
<td>0.04 ± 0.002</td>
<td>1.6</td>
<td>100.0</td>
<td>4</td>
</tr>
<tr>
<td>0.40</td>
<td>0.39 ± 0.03</td>
<td>2.6</td>
<td>97.5</td>
<td>4</td>
</tr>
<tr>
<td>0.79</td>
<td>0.76 ± 0.05</td>
<td>1.7</td>
<td>96.2</td>
<td>3</td>
</tr>
<tr>
<td>3.16</td>
<td>3.16</td>
<td>3.21 ± 0.21</td>
<td>3.05 ± 0.41</td>
<td>1.7</td>
</tr>
<tr>
<td>0.79</td>
<td>0.79</td>
<td>0.81 ± 0.07</td>
<td>0.77 ± 0.10</td>
<td>2.3</td>
</tr>
<tr>
<td>3.95</td>
<td>0.40</td>
<td>3.93 ± 0.05</td>
<td>0.40 ± 0.02</td>
<td>0.3</td>
</tr>
<tr>
<td>0.40</td>
<td>3.95</td>
<td>0.39 ± 0.03</td>
<td>3.98 ± 0.13</td>
<td>2.0</td>
</tr>
</tbody>
</table>

**Fig. 3.** Effect of Pb(II) on the dissolution peaks of HgSe and Cu$_2$Se for $\rho$(Se(IV)) = 1.6 $\mu$g dm$^{-3}$. 1. HgSe dissolution peak. 2. HgSe dissolution peak in the presence of $\rho$(Pb(II)) = 40 $\mu$g dm$^{-3}$. 3. Cu$_2$Se dissolution peak. 4. Cu$_2$Se dissolution peak in the presence of $\rho$(Pb(II)) = 40 $\mu$g dm$^{-3}$.
The interfering ions can be effectively removed by using chromatography with an anion-exchange resin which allows both preconcentration and separation of Se(IV) and Se(VI) from interferents. Since contents of Se in water samples are generally extremely low the latter way is more widely accepted.

Neither Cd(II) nor Pb(II) mostly interfere with the determination of Se in unpolluted natural waters, as their concentrations are normally much lower than those used here to illustrate their potential interfering effect.

In the presence of dissolved organic matter severe interferences can be expected in stripping voltammetry. Humic substances are the main components of organic matter in water (50 % of the DOC) [19]. Many natural waters contain significant amounts of humic substances. The study of interferences generated by humic substances on Se(IV) dissolution peak of the DPCSV method was reduced to the humic acid fraction. Increasing amounts of humic acids (HA) were added to the analysis cell with a fixed concentration of Se(IV) (2 × 10⁻⁸ mol dm⁻³). Low concentrations of humic acids (< 0.8 mg dm⁻³) do not interfere much. But higher concentrations negatively influence Se(IV) measurements by DPCSV. The plot \( I_p = f(c(A)) \) shows a progressive decrease of height of the dissolution peak up to 2.5 mg dm⁻³ HA concentration, then the plot reaches a plateau. For concentration exceeding 6 mg dm⁻³ HA the height of the peaks is difficult to measure. Moreover, the form of the voltammogram changes in the presence of HA as shown in Fig. 4. Without HA the polarization curve presents a horizontal baseline. The presence of HA leads to a growing distortion of the baseline with increasing HA concentration, which deteriorates the quantitative evaluation on the basis of the peak height. The sensitivities decrease as the HA concentration increases confirming the hypothesis of competition between HA adsorption and Cu₂Se film formation at the surface of the working electrode. Fulvic acids (FA), which are generally the main fraction of humic substances in natural waters, cause also a decrease in the peak height and significant shift of the baseline. The influences of FA on the dissolution peak of Se(IV) were evaluated by Potin-Gautier et al. [2]. From these results it follows that fulvic and humic acids interfere with Se(IV) measurements by DPCSV. Therefore, before CSV determination of Se these organics should be removed either by destruction (ultraviolet irradiation, heating with mineral acids) or by separation of humic substances from Se species using chromatographic methods.

Oxidative digestion and UV-photolysis of the samples usually remove organic interferences and permit the determination of total Se. However, this treatment also destroys the natural distribution of Se between its common oxidation states (Se(IV) and Se(VI)). Therefore, both treatment steps cannot be used to obtain information about the speciation of inorganic Se with respect to its oxidized forms in the original sample.

The application of anion-exchange resin Dowex 1 × 8 permits preconcentration and separation of inorganic Se species and simultaneously removing possible inorganic and organic interferents. This pretreatment procedure was applied to the determination of selenite and selenate in synthetic water samples with various contents of HA. These model samples were equilibrated for 24 h in the presence of 2.5 to 10 mg dm⁻³ of humic acids. The height and shape of Se(IV) peaks and results of Table 3 show that the developed procedure effectively separates Se(IV) and Se(VI) from humic acids and allows their quantification at the µg dm⁻³ level. The anion exchanger Dowex 1 × 8 adsorbs part of dissolved organic material (humic substances) from natural waters. To avoid any inconsistency that may arise through a change in the resin condition, a new column should be prepared for each enrichment of selenium species.

The proposed procedure based on preconcentration and separation of the selenium species on anion-exchange resin followed by transformation of Se(VI)
Table 3. Determination of Se in Synthetic Water Samples with Various Concentration of Humic Acids

<table>
<thead>
<tr>
<th>Sample</th>
<th>$\rho$(Se, given)/(µg dm$^{-3}$)</th>
<th>$\rho$(Se, found)/(µg dm$^{-3}$)</th>
<th>$s_%$</th>
<th>Recovery/%</th>
<th>$\rho$(HA)/(mg dm$^{-3}$)</th>
<th>Number of measurements</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Se(IV)</td>
<td>Se(VI)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1.97</td>
<td>1.95 ± 0.21</td>
<td>1.52 ± 0.28</td>
<td>2.8</td>
<td>99.0</td>
<td>2.5</td>
<td>3</td>
</tr>
<tr>
<td>1.58</td>
<td>1.53 ± 0.21</td>
<td>1.56 ± 0.11</td>
<td>3.6</td>
<td>96.8</td>
<td>5.0</td>
<td>3</td>
</tr>
<tr>
<td>1.58</td>
<td>1.58 ± 0.41</td>
<td>1.55 ± 0.10</td>
<td>6.8</td>
<td>100.0</td>
<td>10.0</td>
<td>3</td>
</tr>
<tr>
<td></td>
<td>Se(VI)</td>
<td>Se(VI)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1.97</td>
<td>1.53 ± 0.21</td>
<td>1.56 ± 0.28</td>
<td>6.2</td>
<td>96.2</td>
<td>2.5</td>
<td>4</td>
</tr>
<tr>
<td>1.58</td>
<td>1.56 ± 0.11</td>
<td>1.55 ± 0.10</td>
<td>2.4</td>
<td>98.7</td>
<td>5.0</td>
<td>4</td>
</tr>
<tr>
<td>1.58</td>
<td>1.58 ± 0.41</td>
<td>1.55 ± 0.10</td>
<td>6.8</td>
<td>100.0</td>
<td>10.0</td>
<td>3</td>
</tr>
</tbody>
</table>

Table 4. Determination of Inorganic Se Species in Various Water Samples

<table>
<thead>
<tr>
<th>Sample</th>
<th>$\rho$(Se)/(µg dm$^{-3}$)</th>
<th>$s_%$</th>
<th>$\rho$(Se(IV) + Se(VI))/(µg dm$^{-3}$)</th>
<th>$s_%$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tap water 1</td>
<td>ND</td>
<td>0.23 ± 0.03</td>
<td>-</td>
<td>5.9</td>
</tr>
<tr>
<td>Tap water 2</td>
<td>ND</td>
<td>0.12 ± 0.02</td>
<td>-</td>
<td>7.5</td>
</tr>
<tr>
<td>River water 1</td>
<td>ND</td>
<td>0.23 ± 0.02</td>
<td>-</td>
<td>2.9</td>
</tr>
<tr>
<td>River water 2</td>
<td>ND</td>
<td>0.17 ± 0.01</td>
<td>-</td>
<td>1.6</td>
</tr>
<tr>
<td>Well water 1</td>
<td>ND</td>
<td>0.29 ± 0.01</td>
<td>-</td>
<td>0.9</td>
</tr>
<tr>
<td>Well water 2</td>
<td>0.18 ± 0.03</td>
<td>0.94 ± 0.08</td>
<td>4.5</td>
<td>3.6</td>
</tr>
<tr>
<td>Spring water</td>
<td>0.01 ± 0.003</td>
<td>0.06 ± 0.006</td>
<td>6.7</td>
<td>4.3</td>
</tr>
</tbody>
</table>

ND – not detectable.

to Se(IV) and CSV determination of Se(IV) has been applied to tap, surface, and ground waters. Seven waters of varying origin were analyzed for Se(IV) and Se(VI) or total inorganic Se, which was determined after simultaneous elution of Se(IV) and Se(VI) with 5 M-HCl and reduction of Se(VI) to Se(IV) in boiling water bath. The results of determination of Se in various types of natural waters obtained by the proposed procedures are presented in Table 4.

The Se concentrations were evaluated by the method of standard additions. The plots of peak height vs. added Se(IV) concentration showed good linearity with correlation coefficients $r > 0.999$ ($n = 4$). From the presented data it follows that the precision of determination at this low concentration level is good. The relative standard deviations of inorganic Se obtained from three to ten determinations of each sample are in the range 0.9—7.5%. Blank determination was carried out parallel to analysis, but the blank was always below the detection limit.

The results of Table 4 indicate that Se in these water samples is predominantly as Se(VI), with negligible levels of Se(IV). The absence of Se(IV) in tap waters is due to chlorination in the preparation of potable water.

The analytical procedure obtaining ion-exchange pretreatment and CSV determination is reliable for measuring very low levels of inorganic selenium species in natural water systems.

REFERENCES