

# Determination of Selenium in Soils by Cathodic Stripping Voltammetry after Separation as Gaseous Selenium Tetrabromide

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A procedure for soils has been developed that uses a nitric/sulfuric acids digestion to solubilize total selenium and a distillation treatment to release selenite and selenate in the form of gaseous  $\text{SeBr}_4$ . The advantage of distillation treatment procedure is that analyte is separated from the interfering matrix and simultaneously converted to electroactive form  $\text{Se(IV)}$ . Optimum procedures for decomposition of the soil samples and for separation of low contents of Se from the interfering components were investigated. This procedure was used for determination of extractable forms of Se as well. The selenium(IV) was determined by differential pulse cathodic stripping voltammetry (DPCSV) with hanging mercury drop electrode in the presence of added copper(II). Concentration of Se was evaluated by the method of standard additions on the basis of the signal arising on reduction of  $\text{Cu(I)}$  in the deposited copper(I) selenide. The developed procedure is simple as to the number of operations preceding the determination itself and reliable for determination of very low contents of Se in various types of soils and soil extracts as evidenced by low values of relative standard deviations (0.8–4.9 %). The detection limit for total selenium is  $w = 5 \times 10^{-9}$  using a sample size of 0.3 g.

Selenium is an important metalloid with industrial, environmental, biological, and toxicological significance. Recent increased awareness of the biological role of Se has produced a revival of interest in methods for the determination of Se and its speciation at trace concentration. Measurement of Se in environmental samples is important as at low concentrations it is an essential trace element whereas at higher concentrations toxic effects occur. The narrow concentration range between deficient and toxic level of selenium requires precise knowledge of the selenium content in environment.

The content of total selenium in soils lies in general below  $w = 1 \times 10^{-6}$  and seldom reaches higher values [1]. The low content of Se in soils demands a high sensitivity of the analytical method used for its determination as well as sample handling procedures. Among the methods which can be applied for the determination of traces of Se molecular fluorescence spectrometry, gas chromatography with electron capture detection, spectrophotometry and atomic spectrometry together with hydride generation are usefully employed for the routine laboratory determination of Se in environmental samples [2–4]. From electroanalytical methods stripping voltammetry is a suitable

alternative to the methods mentioned above for the determination of low contents of Se. The advantage of this method is its simplicity, excellent sensitivity as well as inexpensive instrumentation.

Cathodic stripping voltammetry (CSV) with hanging mercury drop electrode (HMDE) is the most often used electroanalytical method for the determination of traces of Se and it was applied to analysis of soil samples, too [1, 5–7]. There is evaluated the signal arising on cathodic stripping of the deposited Se either in the form of  $\text{Cu}_2\text{Se}$  or  $\text{HgSe}$ . Under interference-free conditions, CSV can easily detect nanogram levels of Se in a sample with good accuracy and precision. However, in real sample, interferences from other elements can greatly limit the sensitivity of Se determination by CSV. Therefore, voltammetric determination requires separation of Se from the soil matrix. Selenium can be separated either directly from matrix by combustion of samples in oxygen [4, 5] or from digests using *e.g.* distillation in the form of  $\text{SeCl}_4$ , or  $\text{SeBr}_4$  [4, 8, 9], coprecipitation with hydroxides and hydrated oxides and extraction of selenium(IV) halides into organic solvents [4, 8]. We have coped with this problem using distillation of Se in the form of gaseous selenium(IV) bromide prior to voltammetric determination. The ad-

vantage of this separation method lies in that reduction of the inactive Se(VI) to active Se(IV) takes place simultaneously with separation of Se from interfering matrix components.

## EXPERIMENTAL

Hydrochloric, nitric, and sulfuric acids were Merck, suprapur. All other chemicals used were of anal. grade from Lachema, Fluka and were not further purified. The water used had been deionized and further purified in Labconco Water Pro PS system to "18 M $\Omega$  quality"

The Se(IV) standard stock solution ( $1 \times 10^{-2}$  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) ( $c = 1 \times 10^{-4}$  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  $2 \times 10^{-6}$  to  $1 \times 10^{-5}$  mol dm $^{-3}$  Se(IV) or Se(VI) were prepared before analysis by dilution of the stock solutions.

Analyzed were soil samples from Slovakia, taken according to usual procedure in the Agricultural Research Institute (Bratislava) (designed by N) and standard materials ECH No.12-1-03 and EOP No. 12-1-02 (light ashes from thermal power stations) (Institute of Radioecology and Utilization of Nuclear Technique, Košice). The soil samples were dried, homogenized and sieved to 0.2 mm.

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 had passed through an acidic vanadium(II) scrubber solution in contact with zinc amalgam.

### Decomposition of Samples

#### Procedure A

To the sample (0.3—0.4 g) in teflon crucible concentrated HNO $_3$  (4 cm $^3$ ) and H $_2$ O $_2$  (0.5 cm $^3$ ) were added. The crucible was closed and the mixture was heated on a sand bath at 110—115 °C for at least 6 h until a feebly yellow solution resulted. If the diges-

tion was incomplete the procedure was repeated. Then the mixture was carefully evaporated until most of the acid was removed (moist residue).

#### Procedure B

Procedure B is identical to procedure A except that decomposition mixture H $_2$ SO $_4$ —HNO $_3$  ( $\varphi_r = 1 : 1$ ) (4 cm $^3$ ) was applied. After decomposition the mixture was carefully evaporated until dense fumes of SO $_3$  appeared.

#### Procedure C

To the sample (0.3—0.4 g) in teflon crucible concentrated H $_2$ SO $_4$  (2 cm $^3$ ) was added, followed by gradual addition of concentrated HF (2 cm $^3$ ) in small portions. The crucible was closed and the mixture was heated on a sand bath at 110—115 °C for 6 h. Then the mixture was cooled down to ambient temperature, concentrated HNO $_3$  (2 cm $^3$ ) was added and the mixture was heated again. After complete decomposition solution was carefully evaporated until dense fumes of SO $_3$  appeared.

### Distillation of Se

The soil digest was quantitatively transferred into distillation flask with 10 cm $^3$  of 10.5 M-H $_2$ SO $_4$  and 200 mg of KBr and 10 mg of KBrO $_3$  were added. Distillation of SeBr $_4$  was performed in slow stream of nitrogen (100—120 cm $^3$  min $^{-1}$ ) at 250—260 °C for 30 min using a simple glass apparatus. Gaseous SeBr $_4$  was collected in 5 cm $^3$  of 0.3 M-HCl and after dilution to 10 cm $^3$  the resulting solution for CSV measurement was obtained.

### Extraction of Se from Soil Samples

Soil sample (2 g) was shaken with 20 cm $^3$  of 2 M-HNO $_3$  (1 M-NaOH) for 6 h in polyethylene flask. Then soil extract was filtered (Filtrak 390), evaporated on a sand bath to near dryness and digested with HNO $_3$  (2 cm $^3$ ) and HClO $_4$  (0.5 cm $^3$ ). If the digestion of organic matter was incomplete and the final solution was not clear yellow, the acid mixture was added and heated again. This digest was elaborated by distillation as it was mentioned above.

### Voltammetric Determination of Se(IV)

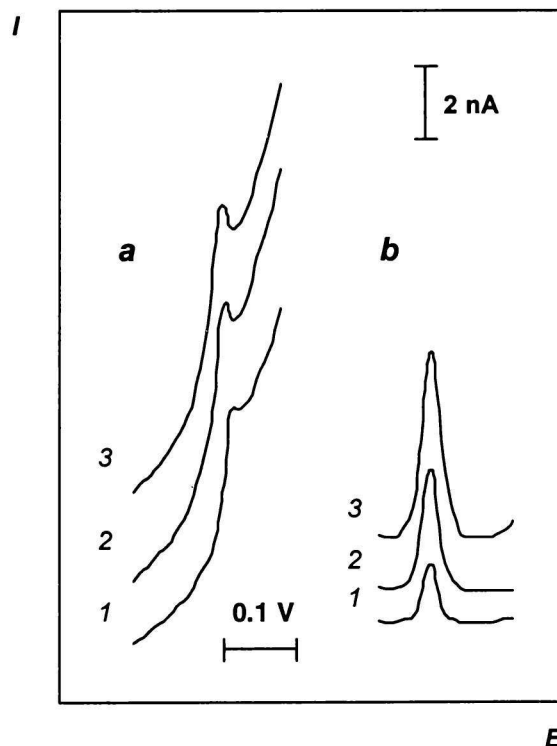
Distillate (0.5—2 cm $^3$ ) was transferred into the polarographic cell and diluted to 10 cm $^3$  with the solution of 0.1 mol dm $^{-3}$  HCl. Then 20 mm $^3$  of CuCl $_2$  ( $c = 1 \times 10^{-2}$  mol dm $^{-3}$ ) was added to measured solution. The solution was deaerated for 5 min by bubbling nitrogen 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 (FSDPCS). For determination of Se(IV) the method of standard additions was used. It was realized by three additions ( $10$  to  $50$  mm<sup>3</sup>) of Se(IV) standard solutions ( $c = 2 \times 10^{-6}$  to  $1 \times 10^{-5}$  mol dm<sup>-3</sup>). The concentration of Se(IV) was evaluated using the peak height.

## RESULTS AND DISCUSSION

The optimization of chemical and instrumental parameters for CSV determination of Se(IV) was realized in the previous work [10]. Deposition of Se on HMDE in the form of intermetallic compound Cu<sub>2</sub>Se at a large excess of Cu(II) over Se(IV) has shown to be more suitable for analytical applications than deposition of HgSe and it was exploited in all measurements. In the presence of Cu(II) detection limit was lower, linear range of calibration curve was prolonged and the influence of interfering metal ions and splitting of peaks was suppressed. Concentration of Se(IV) was evaluated on the basis of the signal arising on reduction of Cu(I) in the deposited copper(I) selenide during the cathodic polarization of the HMDE. The results presented made it possible to specify the optimum conditions for the CSV determination of trace amounts of Se(IV), *i.e.* supporting electrolyte  $0.01$  to  $0.5$  M-HCl,  $c(\text{Cu(II)}) = 1-2 \times 10^{-5}$  mol dm<sup>-3</sup>, deposition potential  $-0.3$  to  $-0.35$  V, deposition time  $120$  s, scan rate  $10-20$  mV s<sup>-1</sup>. The instrumental response under these experimental conditions was linear up to concentration of  $5$  μg dm<sup>-3</sup> (correlation coefficient =  $0.999$ ). The detection limit for direct DPCS under adopted conditions is  $0.15$  μg dm<sup>-3</sup>.

In the environment Se is present in inorganic and organic forms. Inorganic selenium can exist in several oxidation states: selenide, elemental selenium, selenite, and selenate. Organic selenium is generally present in the form of selenoamino acids and their derivatives or more or less volatile methylated species. First the procedure has been optimized for the determination of total selenium in soils. Most procedures for the determination of total selenium employ wet oxidation with acid mixtures to solubilize selenium. Comparative tests of digestion method employing various acid mixtures such as HClO<sub>4</sub> and HNO<sub>3</sub>, HNO<sub>3</sub> and H<sub>2</sub>SO<sub>4</sub>, HNO<sub>3</sub>, HF, and H<sub>2</sub>SO<sub>4</sub>, HNO<sub>3</sub> and H<sub>2</sub>O<sub>2</sub> were conducted to ensure the total recovery of Se from the soil. Data obtained showed that digestion procedures proposed gave comparable concentrations for selenium in soil samples. Repeated digestion of soil samples with additional acids did not change the results of analyses. Despite of volatility of SeF<sub>4</sub> and SeF<sub>6</sub> no less of Se was found out if digestions, which included hydrofluoric acid were applied. The possible volatilization of Se from the system HF-HClO<sub>4</sub> under con-



**Fig. 1.** Voltammogram for Se(IV) recorded by FSDPCS directly in soil digest (a) and after distillation pretreatment (b). 1. Signal of Se(IV) in sample ECH; 2, 3. after standard additions of  $20$  mm<sup>3</sup>,  $40$  mm<sup>3</sup> of solution ( $c(\text{Se(IV)}) = 1 \times 10^{-5}$  mol dm<sup>-3</sup>).

ditions that are representative for the dissolution of silicates was investigated by *Bajo* [11]. No losses of Se by volatilization during the decomposition step were observed, which is in accord with our results.

After oxidative digestion all selenium is present in inorganic form as Se(IV) and Se(VI). Voltammetric methods are sensitive only for Se(IV) as Se(VI) cannot be reduced electrochemically. Therefore the reduction pretreatment prior to the voltammetric determination of total Se is desirable. The reduction of Se(VI) to Se(IV) with hydrochloric acid [1, 5, 7, 10] is suitable method and it was used in this work. The digestion solution was acidified to  $4$  M-HCl and heated in boiling water bath for at least  $20$  min. As follows from Fig. 1a the high concentration of acids and relatively large amounts of interfering metal ions interfere with Se(IV) measurements by DPCS and make the determination of very low content of Se in soil digest difficult. Only a very small, scarcely discernible stripping peak situated on a high and sloping background current was obtained directly from sample digest. This means that the analyte has to be separated from decomposition solution prior to its voltammetric determination by use of a suitable separation method. Several separation procedures for selenium have been described in the literature, including distillation of volatile com-

pounds of Se [4, 8, 9], coprecipitation [4, 8], derivatization followed by extraction into a small volume of an organic solvent [12, 13], and solid phase extraction [14]. This separation step prior to determination improves the detection limit and increases the precision and accuracy of the results.

The high concentration of ions in soil digest limits the application of anion-exchange resins but the volatility of some Se compounds can be successfully used for separation of Se from the complex matrix by distillation. In this work the reaction of Se(IV) and Se(VI) with HBr has been utilized for separation of selenium from the soil matrix. These forms of Se by heating the samples with HBr—Br<sub>2</sub>—H<sub>2</sub>SO<sub>4</sub> [8] and NH<sub>4</sub>Br—condensed phosphoric acid reagent [9] evolve gaseous selenium tetrabromide. The choice of suitable reagent for distillation method was the problem because NH<sub>4</sub>Br and HBr were not available for us. Therefore the effect of various amounts of KBr (NaBr) on distillation recovery of selenium(IV) standard samples both in concentrated H<sub>3</sub>PO<sub>4</sub> medium and 7.5—10 M-H<sub>2</sub>SO<sub>4</sub> was investigated. Initial experiments demonstrated that full recoveries of Se were not achieved. The yields of Se varied from 30 to 70 % for 300 ng of selenium. Various kinds of absorption solutions for trapping of the distilled selenium tetrabromide were examined, too. Higher recovery was not obtained even in the absorbing solution of 0.3 M-HCl and 0.6 M-HClO<sub>4</sub> ( $\varphi_r = 1$ ), which was recommended by *Terada et al.* [9] as the most suitable. Quantitative recoveries were found when small amount of KBrO<sub>3</sub> was added. The bromine—bromide redox buffer solution prevented the reduction of Se(IV) to the elemental form. From the results it follows that 100—200 mg of KBr (NaBr) and 10 mg of KBrO<sub>3</sub> seem appropriate. Under these conditions both Se(IV) and Se(VI) are converted into gaseous selenium tetrabro-

mid. The distillation serves as the simultaneous reduction and separation step. Selenium has been completely distilled during 15—20 min when the temperature has reached about 250°C. The recoveries of 79—315.8 ng of Se(IV) and Se(VI) heated with 10 mg of KBrO<sub>3</sub> and 200 mg of KBr both in 10.5 M-H<sub>2</sub>SO<sub>4</sub> and concentrated H<sub>3</sub>PO<sub>4</sub> are shown in Table 1. Selenium was recovered from these solutions within 94.1—101.4 % with relative standard deviations less than 5 % in each case. These results demonstrate the utility of the method for separation of Se at the nanogram level.

The overall pretreatment procedure proposed (digestion with HNO<sub>3</sub> and H<sub>2</sub>O<sub>2</sub> (A), HNO<sub>3</sub> and H<sub>2</sub>SO<sub>4</sub> (B), HNO<sub>3</sub>, H<sub>2</sub>SO<sub>4</sub>, and HF (C) and Se distillation in the form of SeBr<sub>4</sub>) was applied to the choice samples. Concentrated phosphoric acid etches glass walls of distillation flask at temperature about 250°C. On the basis of this fact distillation only from H<sub>2</sub>SO<sub>4</sub> medium was recommended for next analyses. Data summarized in Table 2 show that all digestion procedures give comparable values for selenium, which is in accord with previous experiences.

The adequacy of pretreatment by distillation follows from Fig. 1b. Distillation eliminates the interferences in the DPCSV method that are observed if soil digest is directly analyzed. The Se(IV) peaks are well-defined and adequate for quantification of selenium.

Reference materials ECH, EOP have not certified value of Se. Our results obtained by DPCSV show reasonable agreement with those of hydride generation/AAS (EOP  $w = 0.39 \times 10^{-6}$ , ECH  $w = 2.07 \times 10^{-6}$ ).

The overall pretreatment procedure and the CSV technique for the determination of Se were evaluated by analyzing soil samples spiked with known amounts of Se(IV) and Se(VI) because reference materials with

**Table 1.** Determination of Se in Standard Samples after Distillation in the Form of SeBr<sub>4</sub> from Various Media

$m(\text{Se, given})/\text{ng}$		$m(\text{Se, found})/\text{ng}$		$s_{\bar{x}}/\%$		Recovery/%		Number of measurements
Se(IV)	Se(VI)	Se(IV)	Se(VI)	Se(IV)	Se(VI)	Se(IV)	Se(VI)	
10.5 M-H <sub>2</sub> SO <sub>4</sub>								
315.8		305.3 ± 12.6		1.7		96.7		6
79.8		75.8 ± 6.5		3.7		96.1		7
	315.8		310.2 ± 18.2		2.5		98.2	7
	157.9		156.1 ± 15.6		4.3		98.9	7
	79.0		77.3 ± 5.2		2.9		97.9	7
Concentrated H <sub>3</sub> PO <sub>4</sub>								
315.8		320.2 ± 14.4		1.9		101.4		9
157.9		149.8 ± 12.3		3.1		94.9		5
79.0		77.7 ± 1.6		0.8		98.3		6
	315.8		297.1 ± 22.9		3.3		94.1	8
	197.4		191.1 ± 8.1		1.6		96.8	5

Intervals of reliability and relative standard deviations were computed from the dispersion variance for the significance level 0.05.

**Table 2.** Comparison of Results Obtained by Different Digestion Procedures

Sample	$w \cdot 10^6$	$s_{\bar{x}}/\%$	Digestion method	Number of measurements
N-2-PD	$0.27 \pm 0.01$	0.9	A	5
	$0.29 \pm 0.01$	1.3	B	5
	$0.34 \pm 0.03$	3.4	C	5
N-1-PD	$0.38 \pm 0.01$	1.1	A	6
	$0.35 \pm 0.04$	4.3	B	5
	$0.40 \pm 0.05$	4.9	C	6
N-5-ZV	$0.24 \pm 0.01$	2.1	A	5
	$0.22 \pm 0.01$	1.6	B	5
	$0.26 \pm 0.01$	2.6	C	10
ECH	$2.42 \pm 0.12$	2.2	B	10
	$2.38 \pm 0.09$	1.6	C	5
EOP	$0.52 \pm 0.03$	2.2	A	5
	$0.58 \pm 0.01$	0.8	B	5

**Table 3.** Results of Determination of Total Se in Selected Soil Samples

Sample	Horizon	Depth/cm	$w \cdot 10^6$	$s_{\bar{x}}/\%$	Number of measurements
N-1-TT	1	5—15	$0.52 \pm 0.03$	2.4	10
	2	30—40	$0.24 \pm 0.03$	4.9	10
	3	70—80	$0.09 \pm 0.004$	1.6	5
N-2-LM	1	10—20	$0.26 \pm 0.01$	2.3	9
N-3-GA	1	5—15	$0.28 \pm 0.02$	3.3	10
N-1-NR	1	10—20	$0.31 \pm 0.03$	3.7	10
N-17-DS	1	10—20	$0.76 \pm 0.04$	2.2	10
N-5-ZV	1	10—20	$0.22 \pm 0.01$	1.6	5

certified value of Se were not available. The recoveries of the known additions of Se substantiate the accuracy of the procedure and these results demonstrate the utility of the method for determination of Se at the nanogram level in soils.

Data obtained showed that for the determination of selenium total decomposition of soil samples is not necessary. Therefore, only digestion procedure utilizing the  $\text{H}_2\text{SO}_4\text{—HNO}_3$  mixture was applied to next analyses of soils of varying origin. The results of determination of total selenium are presented in Table 3. The Se content is within the range reported for soils and mostly less than the average ( $w = 0.4 \times 10^{-6}$ ) [15]. The Se concentrations were evaluated by the method of standard additions. Peak height measurement was used for the quantification of Se. 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 Se obtained from five to ten determinations of each sample are in the range 0.8—4.9 %.

The present study evaluates the suitability of treat-

ment procedures for the CSV determination of Se in soil samples. The main advantage of this treatment procedure is that analyte is separated from interfering matrix and simultaneously converted to electroactive form with HBr arising from KBr in the presence of  $\text{H}_2\text{SO}_4$ . From the presented data it follows that the proposed digestions are adequate and distillation step prior to determination increases the precision and accuracy of the results. On the basis of these facts we propose distillation using the volatility of  $\text{SeBr}_4$  as the suitable pretreatment procedure prior to the CSV determination of very low contents of Se in complex samples, such as soils.

The measurement of the total concentration of a trace element provides little information about the bioavailability and potential risk since the toxicity of elements and their environmental mobility are dependent on their chemical forms. To obtain information about the bioavailable fraction of elements a simple step extraction procedure is usually used. In the present work only acidic (2 M- $\text{HNO}_3$ ) and alkaline (1 M- $\text{NaOH}$ ) extractions were applied to soil samples. Results of Se for soil extracts are presented in Table 4. Application of the alkaline extraction of the soil

**Table 4.** The NaOH and HNO<sub>3</sub> Extractable Se Contents of Some Selected Soils

Sample	NaOH Extraction			HNO <sub>3</sub> Extraction		
	$w(\text{Se, extracted}) \cdot 10^6$	$s_{\bar{x}}/\%$	Recovery/ $\%^a$	$w(\text{Se, extracted}) \cdot 10^6$	$s_{\bar{x}}/\%$	Recovery/ $\%^a$
N-1-PD	0.25 ± 0.01	2.5	66.3	0.05 ± 0.004	3.9	12.7
N-1-TT/1	0.29 ± 0.02	4.0	55.8	0.03 ± 0.002	3.7	6.0
N-2-PD				0.04 ± 0.002	2.4	12.3
N-17-DS	0.47 ± 0.03	2.9	61.4			

a) Results in Tables 2 and 3 were taken as 100 % recovery.

samples results in (61 ± 5) % reported for total Se. Selenium species solubilized by sodium hydroxide treatment are: selenite, selenate, and Se bound to organic matter (notably humic substances). The content of selenite and selenate in alkaline soil extracts can be estimated after the removal of organic matter from soil extracts using XAD resins. As follows from Table 4 HNO<sub>3</sub> extraction released from soils less than 13 % of selenium.

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