

Application Bulletin

Of interest to: General Analytical analysis, Foodstuffs, Water, Biology

B 1, 2, 7, 8, 11

Voltammetric determination of selenium

Summary

In the past, selenium determinations have always been either unreliable or only possible by complicated methods. However, as it is on the one hand a biologically essential element (vegetable and animal tissues contains about 10 µg/kg), while on the other hand it is very toxic (threshold limit value 0.1 mg/m³), it is very important to be able to determine it in the micro range.

Cathodic Stripping voltammetry (CSV) enables selenium to be determined in mass concentrations down to $\beta(\text{Se(IV)}) = 0.3 \mu\text{g/L}$.

Apparatus and accessories

- 746 VA Trace Analyzer with 747 VA Stand or
- 757 VA Computrace

Reagents

All of the used reagents must be of purest quality possible (p.a. or suprapur). Only high purity water should be used.

- Sulphuric acid, suprapur, $w(\text{H}_2\text{SO}_4) = 96\%$
- Nitric acid, suprapur, $w(\text{HNO}_3) = 65\%$
- Sodium hydroxide solution, suprapur, $w(\text{NaOH}) = 30\%$
- Ammonium sulphate, suprapur, CAS 7783-20-2
- Na₂EDTA dihydrate, puriss. p.a., CAS 6381-92-6
- Cu standard stock solution: $\beta(\text{Cu}) = 1.0 \text{ g/L}$
commercially available
- Se standard stock solution: $\beta(\text{Se(IV)}) = 1.0 \text{ g/L}$
commercially available

Ready to use solutions

- EDTA-solution: $c(\text{Na}_2\text{EDTA}) = 0.1 \text{ mol/L}$
3.72 g Na₂EDTA · 2 H₂O are dissolved in 100 mL ultrapure water.
- Sulphuric acid: $c(\text{H}_2\text{SO}_4) = 0.01 \text{ mol/L}$
- Cu solution: $\beta(\text{Cu}) = 0.1 \text{ g/L}$
The diluted Cu standard solution is made by diluting the concentrated Cu standard stock solution with $c(\text{H}_2\text{SO}_4) = 0.01 \text{ mol/L}$.
- Se standard solution: $\beta(\text{Se(IV)}) = 1 \text{ mg/L}$
The diluted Se standard solution is made by diluting the concentrated Se standard stock solution with $c(\text{H}_2\text{SO}_4) = 0.01 \text{ mol/L}$.

Sample preparation

Organic matter often interferes with voltammetric determinations and therefore sample solutions usually have to be digested.

- Ground water, surface waters, mineral waters and drinking waters can usually be analysed without pretreatment.
- Low polluted waste waters can be digested with the 705 UV-Digester.
Add 50 µL hydrogen peroxide solution $w(\text{H}_2\text{O}_2) = 30\%$ and 10 µL hydrochloric acid $w(\text{HCl}) = 30\%$ to 10 mL acidified sample ($\text{pH} = 2$) and irradiate for 60 minutes at 90°C.
- Samples with organic matter (foods, pharmaceuticals etc.) must be digested.
 - High-pressure asher
 - Microwave digestion
 Both techniques oxidise the sample in a closed digestion vessel by means of a mixture of concentrated mineral acids.
 - Open wet digestion with H_2SO_4 and H_2O_2 According to Application Bulletin 113. (Investigations have shown that selenium is not lost by this method).

Analysis

Measuring solution:

10 mL (diluted) sample or digestion solution
 + 3.3 g ammonium sulphate
 + 1 mL EDTA solution
 + 1 mL Cu solution

Adjust the pH value of the solution with sulphuric acid to $\text{pH } 2.2 \pm 0.1$. If necessary, allow to cool.

The voltammogram is recorded with the following parameters:

working electrode	HMDE
stirrer speed	2000 rpm
drop size	4
mode	DP
purge time	300 s
deposition potential	-0.4 V
deposition time	90 s
equilibration time	10 s
pulse amplitude	0.08 V
start potential	-0.45 V
end potential	-0.85 V
voltage step	0.004 V
voltage step time	0.1 s
sweep rate	0.04 V/s
peak potential Se	-0.65 V

The concentration is determined by standard addition.

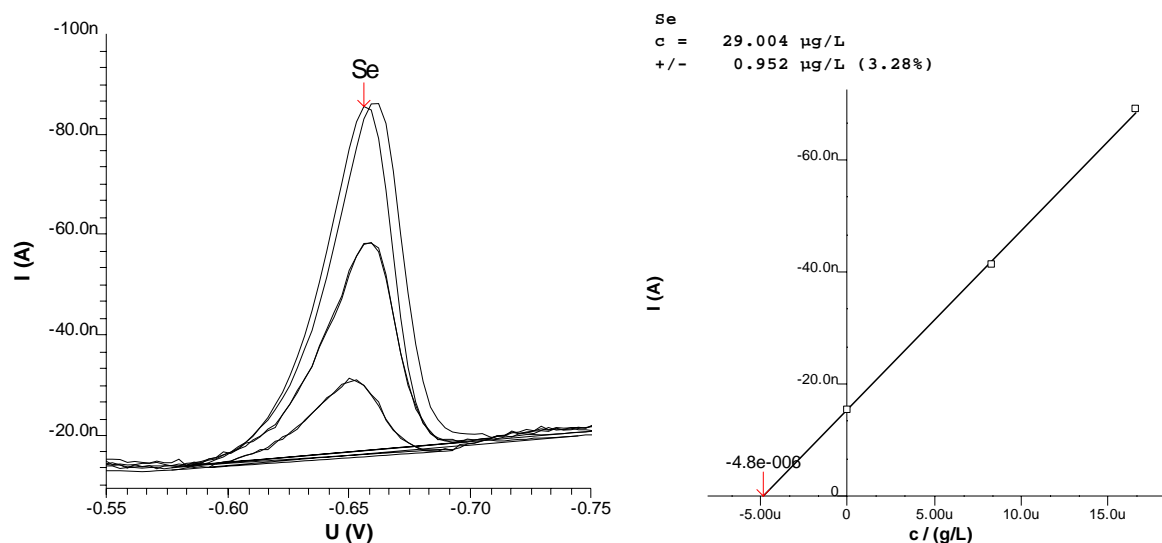
Remarks

- Se(IV) is the only electrochemically active substance. It is also possible, however, to determine Se(-II) and Se(VI) provided that the sample is appropriately prepared beforehand (see literature).
- The linearity range strongly depends on the Cu concentration. By a high selenium concentration (>100 ppb) the copper has to be increased.
- The determination of selenium can also be carried out in square wave mode.
- The standard addition should not exceed 50 % of the peak height.

Literature

- Arlt C., Naumann R.
Vorschlag zur Bestimmung des Selens in Trinkwasser
Z.Anal.Chem 282(1976), 463
- Henze G., Monks P., Tölg G.
Über die simultane Bestimmung von Selen und Tellur im unteren ppb-Bereich durch Cathodic-Stripping-Voltammetrie
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- Ebhardt K.-B., Umland F.
Untersuchung zur Verbesserung der simultanen voltammetrischen Bestimmung von Selen und Tellur durch Cathodic Stripping
Fres.Z.Anal.Chem 310 (1982) 406-409
- van den Berg C.M.G., Khan S.H.
Determination of selenium in sea water by adsorptive cathodic stripping voltammetry
Anal.Chim.Acta 231 (1990), 21-229
- Prasad Pamidi V.A., Arunachalam J., Gangadharan S.
Square Wave Cathodic Stripping Voltammetric Determination of Selenium in Small Quantities of Biological Tissues
Electroanalysis 6 (1994) 589-592
- Rojas C.L., de Maroto S.B., Valenta P.
Determination of selenium in soils with square-wave cathodic stripping voltammetry
Fresenius J Anal Chem 348 (1994) 775-776
- Papoff P., Bocci F., Lanza F.
Speciation of selenium in natural waters and snow by DPCSV at the hanging mercury drop electrode
Microchem. J. 59 (1998) 50-76

Figures



===== METROHM 757 VA COMPUTRACE (5.757.0020) =====

Determ. : 4102p3.dth
 Sample ID : Se in Mn-Aufschl
 Creator : --- Date : 1998-07-15 Time: 10:16:39
 Modified by : Date : 2001-06-27 Time: 14:43:11
 User : Date : 2001-06-27 Time: 14:43:11

Cell volume: 12.000 mL
 Sample amount: 2.000 mL

Method : semnpr3.mth
 Title : Determination of Selenium
 Remark1 : 2 mL digestion solution + 8 mL H2O + 3.3 g (NH4)2SO4
 Remark2 : + 1 mL EDTA solution + 1 mL Cu solution

Substance : Se	Comments
Mass conc.: 4.834 ug/L	-----
MC.dev. : 0.159 ug/L (3.28%)	
Mass : 58.008 ng	
Add.mass : 100.000 ng	

VR	V	nA	I.mean	Std.Dev.	I.delta	Comments
1-1	-0.653	-15.00	-15.44	0.616		
1-2	-0.650	-15.87				
2-1	-0.659	-41.37	-41.35	0.050	-25.91	
2-2	-0.656	-41.32				
3-1	-0.656	-69.28	-69.15	0.176	-27.81	
3-2	-0.659	-69.03				

Substance	Calibr.	Y.reg/offset	Slope	Std.Dev.
Se	std.add.	-1.540e-008	-3.185e-003	1.771e-010

Final results ----- +/- Res. dev. % ----- Comments -----

Se:
 Selenium = 29.004 µg/L 0.952 3.282

Fig. 1 Example of a determination of selenium in a digestion solution with the 757 VA Computrace

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===== METROHM 746 VA TRACE ANALYZER (5.746.0101) =====
Method: AB117 .mth OPERATION SEQUENCE
Title : Determination of Se. AB117
    
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	Instructions	t/s	Main parameters	Auxiliary parameters
1	SMPL>M		V.fraction mL	V.total L
2	DOS>M		Soln.name EDTA_sol	V.add 1.000 mL
3	DOS>M		Soln.name Cu_sol	V.add 1.000 mL
4	PURGE			
5	STIR	300.0	Rot.speed 2000 /min	
6	(ADD			
7	PURGE			
8	STIR	10.0	Rot.speed 2000 /min	
9	OPURGE			
10	(REP			
11	SEGMENT		Segm.name Se_CSV	
12	REP)1			
13	PURGE			
14	ADD>M		Soln.name Se_Std	V.add 0.100 mL
15	ADD)2			
16	END			

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Method: AB117 SEGMENT
Se_CSV
    
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	Instructions	t/s	Main parameters	Auxiliary parameters
1	STIR	5.0	Rot.speed 2000 /min	
2	HMDE		Drop size 4	Meas.cell normal
3	DPMODE		U.ampl -50 mV	t.meas 20.0 ms
			t.step 0.10 s	t.pulse 40.0 ms
4	MEAS	90.0	U.meas -400 mV	
5	OSTIR	10.0		
6	SWEEP	10.3	U.start -450 mV	U.step 4 mV
			U.end -850 mV	Sweep rate 40 mV/s
7	OMEAS		U.standby mV	
8	END			

Fig. 2 Method for the determination of selenium with the 746 VA Trace Analyzer