Application Bulletin 117/4 e

Determination of selenium by cathodic stripping voltammetry

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/m^3), 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 β(Se(IV)) = 0.3 µg/L.

Instruments

VA instrument capable of operating a Multi-Mode Electrode and supporting DP mode	
909 UV Digester	2.909.0014

Electrodes

WE	Multi-Mode Electrode pro Mercury drop capillary	6.1246.120 6.1226.030 or 6.1226.050
RE	Ag/AgCl reference electrode Ag/AgCl/KCl (3 mol/L) Electrolyte vessel Filled with c(KCl) = 3 mol/L	6.0728.x20 6.1245.010
AE	Pt rod electrode	6.0343.x00

Reagents

All of the used reagents must be of purest quality possible (for analysis or for trace analysis*).

- Sulfuric acid, w(H_2SO_4) = 96%, for trace analysis*, CAS 7664-93-9
- Nitric acid, w(HNO_3) = 65%, for trace analysis*, CAS 7697-37-2
- Sodium hydroxide solution, w(NaOH) = 30%, for trace analysis*, CAS 1310-73-2
- Ammonium sulfate, for trace analysis*, CAS 7783-20-2
- Ethylenedinitrilotetraacetic acid disodium salt dihydrate, $Na_2EDTA \cdot 2\ H_2O$, for analysis, CAS 6381-92-6
- Copper standard stock solution, β(Cu) = 1.0 g/L (commercially available)
- Selenium standard stock solution, β(Se(IV)) = 1.0 g/L (commercially available)
- Ultrapure water, resistivity >18 MΩ·cm (25 °C), type I grade (ASTM D1193)

* e.g., Merck suprapur®, Honeywell Fluka TraceSelect® or equivalent

Solutions

EDTA solution	c(Na_2EDTA) = 0.1 mol/L 3.72 g $Na_2EDTA \cdot 2\ H_2O$ are dissolved in 100 mL ultrapure water.
Sulfuric acid	c(H_2SO_4) = 0.01 mol/L
Cu solution	β(Cu) = 0.1 g/L The diluted Cu solution is preprared by diluting the concentrated Cu standard stock solution with c(H_2SO_4) = 0.01 mol/L.

Standard solutions

Se standard solution	β(Se(IV)) = 1 mg/L The diluted Se standard solution is preprared by diluting the concentrated Se standard stock solution with c(H2SO4) = 0.01 mol/L.

Sample preparation

- Ground water, surface waters, mineral waters and drinking waters can usually be analyzed without pretreatment.

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

- Low polluted waste waters can be digested with the 909 UV Digester. Add 50 µL hydrogen peroxide solution w(H_2O_2) = 30% and 10 µL hydrochloric acid w(HCl) = 30% to 10 mL acidified sample (pH = 2) and irradiate for 90 minutes at 90°C.
- Samples with organic matter (foods, pharmaceuticals etc.) must be digested in a high-pressure asher or with microwave digestion. Both techniques oxidize 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 is also possible (Investigations have shown that selenium is not lost by this digestion method).

Reduction of Se(VI) to Se(IV) with UV in the 909 UV Digester at pH 7-9

In neutral or slightly alkaline solution it is possible to reduce Se(VI) to Se(IV) using the 909 UV Digester.

Use diluted sulfuric acid or diluted sodium hydroxide solution to adjust pH 7-9 if the pH is not already in this range. Without the addition of further reagents irradiate the sample solution for 60 min at 90 °C.

Analysis

Measuring solution

10 mL (diluted) sample or digestion solution

3.3 g ammonium sulfate

1 mL EDTA solution

1 mL Cu solution

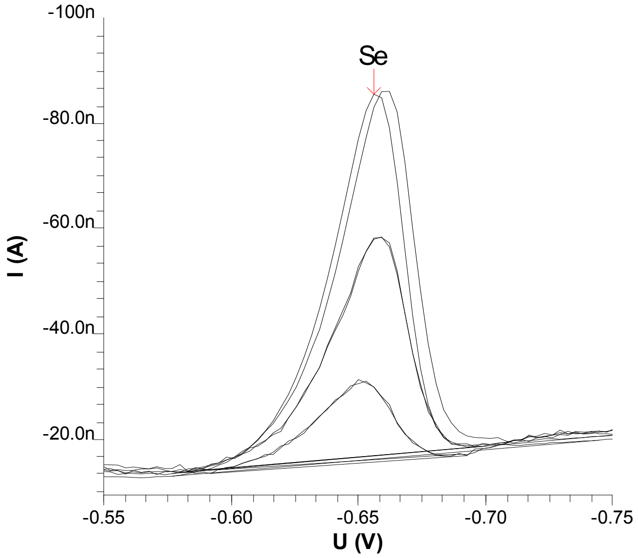
Adjust the pH value of the solution with sulfuric acid to pH 2.2 ± 0.1. If necessary, allow to cool.

The concentration of selenium is determined by standard addition technique.

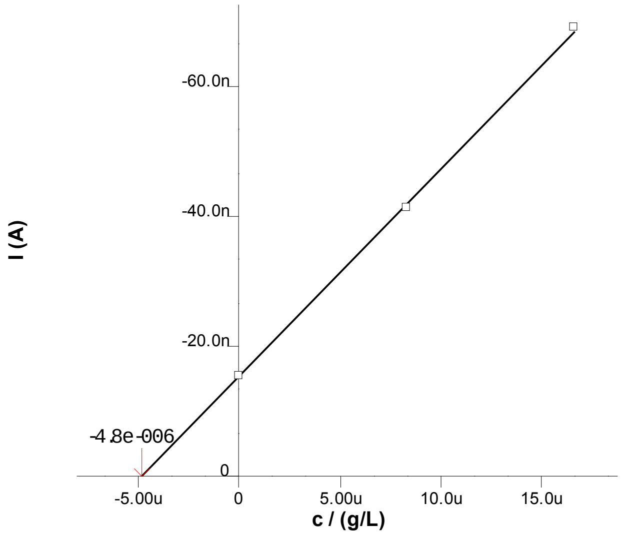
Parameters

Voltammetric	
Electrode operating mode	HMDE
Measuring mode	DP – Differential pulse
Stirring rate	2000 min^{-1}
Potentiostatic pretreatment	
Potential 1	-0.4 V
Waiting time 1	90 s
Equilibration time	10 s
Sweep	
Start potential	-0.45 V
End potential	-0.85 V
Potential step	0.004 V
Potential step time	0.1 s
Sweep rate	0.04 V/s
Pulse amplitude	0.08 V
Substance	
Name	Se
Characteristic potential	-0.65 V

Example



```
Se
c =   29.004 µg/L
+/-    0.952 µg/L (3.28%)
```



Result

Sample size	2.0 mL
β(Se)	29.0 µg/L

Comments

- Se(IV) is the only electrochemically active species. It is also possible, however, to determine Se(-II) and Se(VI) provided that the sample is appropriately prepared beforehand (see references).
- The linearity range strongly depends on the Cu concentration. For higher selenium concentrations (>100 ppb) the copper concentration 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.

References

- 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
  Fres. Z. Anal. Chem 195(1979), 1-6
- 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
- Leandro M. de Carvalho, Georg Schwedt, Günter Henze, Sylvia Sander
  Redoxspeciation of Selenium in water samples by cathodic stripping voltammetry using an automated flow system
  Analyst (1999), 124, 1803 – 1809

Appendix

Report for the example determination of selenium in a digestion solution

```
==================== 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
```

Method print for the determination of selenium

```
--------------------------------------------------------------------------------
 Method parameters
--------------------------------------------------------------------------------
Method          : AB117_Det of Se.mth
Title           : Determination of Selenium. AB 117
Remark1         : 10 mL sample solution + 3.3 g (NH4)2SO4
Remark2         : + 1 mL EDTA solution + 1 mL Cu solution

Calibration     : Standard addition
Technique       : Batch
Addition        : Manual

Sample ID       : sample
Sample amount (mL): 10.000
Cell volume (mL): 12.000

Voltammetric parameters
--------------------------------------------------------------------------------
Mode                               : DP - Differential Pulse

Highest current range              : 10  uA
Lowest current range               : 100 nA

Electrode                          : HMDE
Drop size (1..9)                   : 4
Stirrer speed (rpm)                : 2000

Initial electr. conditioning       : No

No. of additions                   : 2
No. of replications                : 2

Measure blank                      : No
```

```
Addition purge time (s)            : 10

Initial purge time (s)             :      300

Conditioning cycles
Start potential (V)                :   -0.400
End potential (V)                  :   -0.100
No. of cycles                      :        0

Hydrodynamic (measurement)         :      No
Cleaning potential (V)             :   -0.100
Cleaning time (s)                  :    0.000
Deposition potential (V)           :   -0.400
Deposition time (s)                :   90.000

Sweep
Equilibration time (s)             :   10.000
Start potential (V)                :   -0.450
End potential (V)                  :   -0.850
Voltage step (V)                   :    0.004
Voltage step time (s)              :    0.100
Sweep rate (V/s)                   :    0.040
Pulse amplitude (V)                :    0.080
Pulse time (s)                     :    0.040

Cell off after measurement         :      Yes

Peak evaluation
--------------------------------------------------------------------------------
Regression technique               : Linear Regression
Peak evaluation                    : Height
Minimum peak width (V.steps)       : 5
Minimum peak height (A)            : 5.000e-011
Reverse peaks                      : No
Smooth factor                      : 5
Eliminate spikes                   : Yes

Substances
--------------------------------------------------------------------------------
Se                       : -0.650 V   +/- 0.040 V

Standard solution        : 1   1.000 mg/L
Addition volume (mL)     : 0.100

Selenium                 : Final result (Se) =
                           Conc * (12 / 10) * (1e+006 / 1) + 0 - 0

Baseline
--------------------------------------------------------------------------------
Substance Addition    automatic start (V) end (V) type        scope
--------------------------------------------------------------------------------
Se        Sample      yes       ---       ---     linear      wholePeak
          Addition 1  yes       ---       ---     linear      wholePeak
          Addition 2  yes       ---       ---     linear      wholePeak
--------------------------------------------------------------------------------
```