Metrohm

Application Bulletin 176/5 e

Determination of lead and tin by anodic stripping voltammetry

Summary

In most electrolytes the peak potentials of lead and tin are so close together, that a voltammetric determination is impossible. Difficulties occur especially if one of the metals is present in excess.

Method 1 describes the determination of Pb and Sn. Anodic stripping voltammetry (ASV) is used under addition of cetyltrimethylammonium bromide. This method is used when:

- one is mainly interested in Pb
- Pb is in excess
- Sn/Pb ratio is not higher than 200:1

According to method 1, Sn and Pb can be determined simultaneously if the difference in the concentrations is not too high and Cd is absent.

Method 2 is applied when traces of Sn and Pb are found or interfering Tl and/or Cd ions are present. This method also uses DPASV in an oxalate buffer with methylene blue addition.

Instruments

VA instrument capable of operating a Mulit-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

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.
  - High-pressure asher
  - 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.

Method 1: Determination of lead and tin with cetyltrimethylammonium bromide

Reagents

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

- Hydrochloric acid, w(HCl) = 30%, for trace analysis*, CAS 7647-01-0
- Trisodium citrate dihydrat, for analysis, CAS 6132-04-3

- Oxalic acid monohydrate, for trace analysis*, CAS 6153-56-6
- Cetyl trimethylammonium bromide, (hexadecyl trimethyl ammonium bromide, CTAB), CAS 57-09-0
- Pb standard stock solution, $\beta(Pb^{2+})$ = 1 g/L, commercially available
- Sn standard stock solution, $\beta(Sn^{4+})$ = 1 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

Electrolyte	c(citrate) = 0.1 mol/L c(oxalic acid) = 0.1 mol/L c(HCl) = 0.2 mol/L pH = 2.5 14.7 g sodium citrate and 6.3 g oxalic acid are dissolved in ultrapure water. 10.5 mL hydrochloric acid are added. The solution is made up to 500 mL with ultrapure water.
CTAB solution	c(CTAB) = 0.005 mol/L 0.46 g cetyl trimethylammonium bromide are dissolved in 250 mL ultrapure water

Standard solutions

Pb standard solution	$\beta(Pb^{2+})$ = 1 mg/L
Sn standard solution	$\beta(Sn^{4+})$ = 1 mg/L
	The solution is diluted with c(HCl) = 0.01 mol/L. It is stable for max. 1 week.

References

- Hernandez Mendez J., Carabis Martinez R., Gonzales Lopez M.E., Simultaneous determination of tin and lead by AC anodic stripping voltammetry at a hanging mercury drop electrode sensitized by cetyltrimethylammonium bromide, Anal. Chim. Acta 138 (1982), 47-54
- Ciszewski A., Lukaszewski Z., The influence on long-chain amine and ammonium salts on the anodic stripping voltammetry of thallium, lead, tin, cadmium, and indium, Anal. Chim. Acta 146(1983), 51-59

Method 1a: Determination of lead in the presence of tin

Theory

In presence of cetyltrimethylammonium bromide it is possible to determine Pb, even when a great excess of Sn is present. The maximum Sn:Pb ratio is approx. 200:1.

The limit of detection in the absence of Sn is 1 µg/L of Pb. With high excess of Sn the limit of detection is 5 µg/L of Pb.

Analysis

Measuring solution

5 mL (diluted) sample (mix while stirring without nitrogen)

5 mL electrolyte

0.05 mL CTAB solution

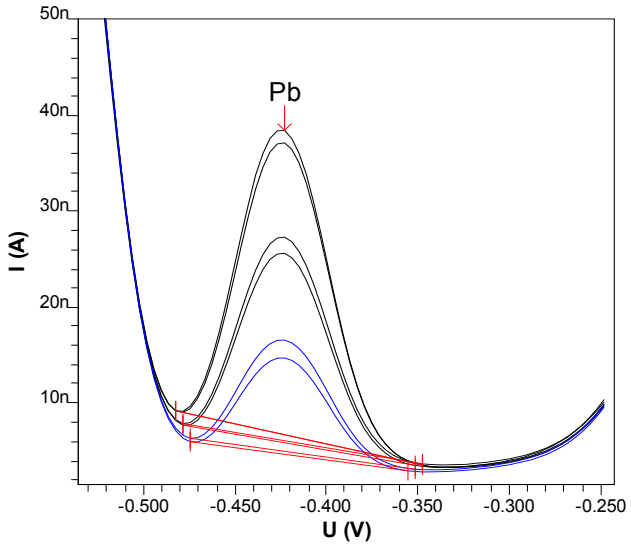
The concentration is determined by standard addition.

Parameters

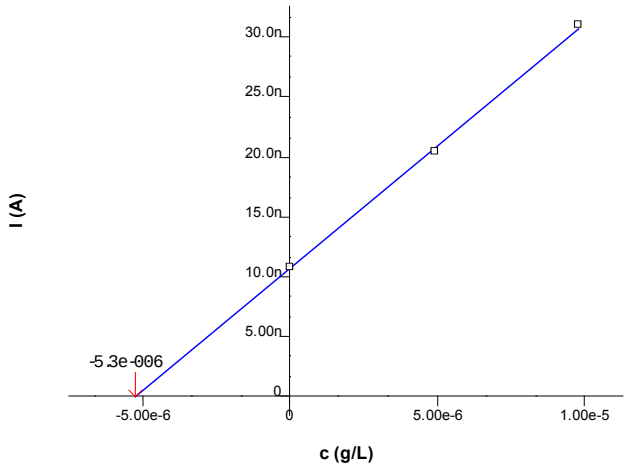
Voltammetric	
Electrode operating mode	HMDE
Measuring mode	DP – Differential pulse
Stirring rate	2000 min^{-1}
Potentiostatic pretreatment	
Potential 1	-0.48 V
Waiting time 1	90 s
Equilibration time	20 s
Sweep	
Start potential	-0.53 V
End potential	-0.25 V
Potential step	0.004 V
Potential step time	0.2 s
Sweep rate	0.02 V/s
Pulse amplitude	0.05 V
Substance	
Name	Pb
Characteristic potential	-0.42 V

Example

Determination of Pb in presence of Sn (200 fold excess)




```
Pb
c =   10.581 ug/l
+/-    1.093 ug/l (10.33%)
```



Results

Sample size	5.0 mL
β(Pb)	10.6 µg/L

Method 1b: Determination of tin and lead simultaneously

Theory

In presence of cetyltrimethylammonium bromide it is possible to determine Pb and Sn simultaneously. The maximum Pb:Sn ratio is appr. 50:1. The simultaneous determination of tin and lead is only possible if Cd is absent.

The limit of detection for Pb is 1 µg/L. The limit of detection for Sn is 10 µg/L.

Analysis

Measuring solution

5 mL (diluted) sample (mix while stirring without nitrogen)

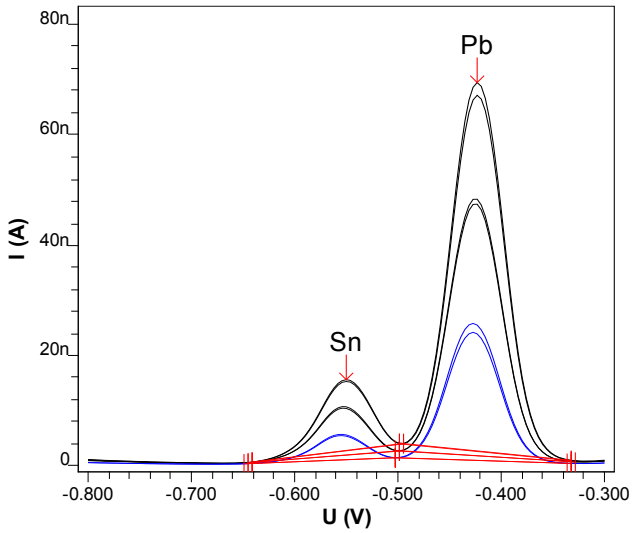
5 mL electrolyte

0.05 mL CTAB solution

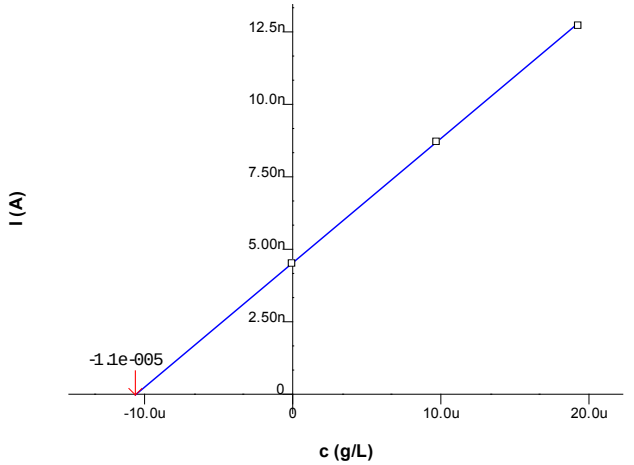
Parameters

Voltammetric	
Electrode operating mode	HMDE
Measuring mode	DP – Differential pulse
Stirring rate	2000 min^{-1}
Potentiostatic pretreatment	
Potential 1	-0.7 V
Waiting time 1	90 s
Equilibration time	20 s
Sweep	
Start potential	-0.8 V
End potential	-0.3 V
Potential step	0.004 V
Potential step time	0.2 s
Sweep rate	0.02 V/s
Pulse amplitude	0.05 V
Substance	
Name	Sn
Characteristic potential	-0.55 V
Name	Pb
Characteristic potential	-0.42 V

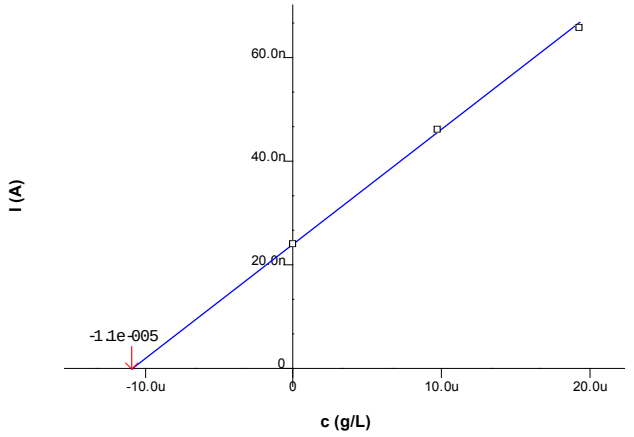
Example




```
Sn
c =   21.278 ug/l
+/-    0.887 ug/l (4.17%)
```




```
Pb
c =   21.882 ug/l
+/-    1.100 ug/l (5.03%)
```



Results

Sample size	5.0 mL
β(Sn)	21.3 µg/L
β(Pb)	22.4 µg/L

Method 2: Determination of lead and tin with methylene blue

Theory

Traces of Sn and Pb can be determined in oxalate buffer in presence of methylene blue. Interferences by Cd or Tl can be eliminated by modifying the pH and an intermediate electrolysis procedure.

The limit of detection of Sn and of Pb is 1 µg/L.

Reagents

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

- Hydrochloric acid, w(HCl) = 30%, for trace analysis*, CAS 7647-01-0
- Di-ammonium oxalate monohydrate, for analysis, CAS 6009-70-7
- Ammonium chloride, NH_4Cl, for trace analysis*, CAS 12125-02-9
- Methylene blue, C.I. 52015, CAS 61-73-4
- Sn standard stock solution, $\beta(Sn^{4+})$ = 1 g/L, commercially available
- Pb standard stock solution, $\beta(Pb^{2+})$ = 1 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

Electrolyte	c(oxalate) = 0.14 mol/L $c(NH_4Cl)$ = 0.17 mol/L c(HCl) = 0.15 mol/L pH = 1.6 19.2 g ammonium oxalate and 9.2 g ammonium chloride are

	dissolved in ultrapure water. 15.8 mL hydrochloric acid are added. The solution is made up to 1000 mL with ultrapure water
Methylene blue solution	β(methylene blue) = 1g/L 0.1 g methylene blue are dissolved in 100 mL ultrapure water. The solution is stable for one week.
Pb standard solution	$\beta(Pb^{2+})$ = 1 mg/L
Sn standard solution	$\beta(Sn^{4+})$ = 1 mg/L
	The solution is diluted with c(HCl) = 0.01 mol/L. It is stable for max. 1 week.

Analysis

Measuring solution

5 mL (diluted) sample

5 mL electrolyte

0.05 mL methylene blue solution

The pH of the solution should be 1.8.

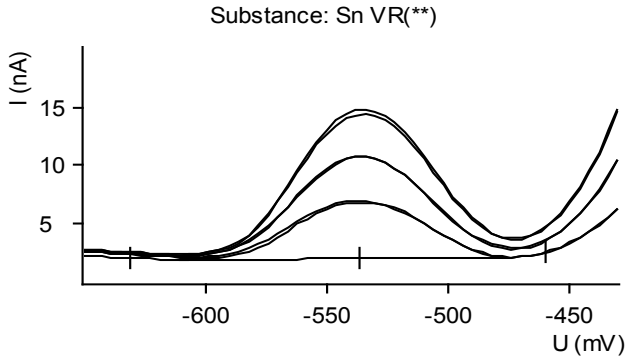
The concentration is determined by standard addition.

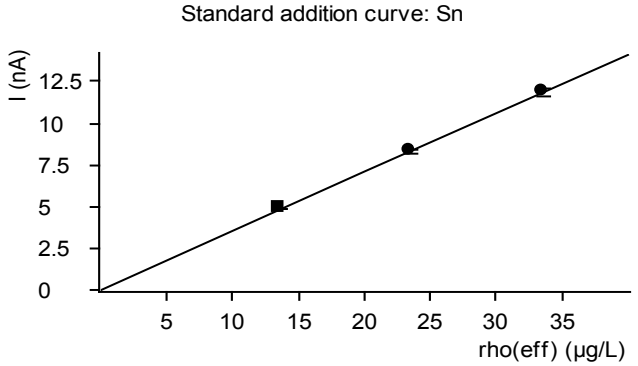
Parameters

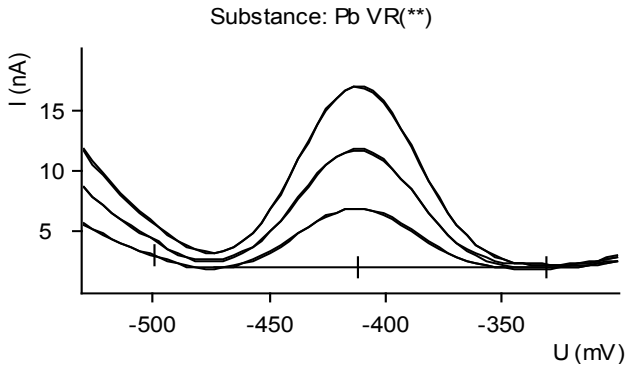
Voltammetric	
Electrode operating mode	HMDE
Measuring mode	DP – Differential pulse
Stirring rate	2000 min^{-1}
Potentiostatic pretreatment	
Potential 1	-0.8 V
Waiting time 1	90 s
Potential 2	-0.58 V
Waiting time 2	20 s
Equilibration time	10 s
Sweep	
Start potential	-0.8 V
End potential	-0.25 V
Potential step	0.004 V
Potential step time	0.2 s
Sweep rate	0.02 V/s
Pulse amplitude	0.05 V
Substance	

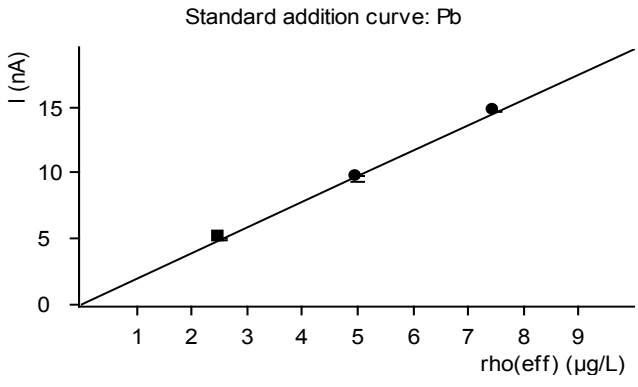
Name	Sn
Characteristic potential	-0.54 V
Name	Pb
Characteristic potential	-0.4 V

Example









Results

Sample size	5.0 mL
β(Sn)	27.4 µg/L
β(Pb)	5.1 µg/L

Comments

- If the tin excess is great, one must work with two segments, intermediate electrolysis (intermediate electrolysis potential approx. -540 mV) and perhaps two standard addition loops.
- If the sample contains Tl, the Pb peak can be adjusted to more positive values by raising the pH value to 2.4 (addition of ammonia solution w(NH_3) = 25%). One must work fast because at this pH value tin already hydrolyses. The peak potentials are:

Pb	-0.37 V
Tl	-0.41 V
Sn	-0.54 V

  A good separation under these conditions can still be performed when the ratio Sn:Tl lies at 1:2. Lead cannot be determined.
- If the sample contains Cd, the pH value can be lowered to 1.6 with hydrochloric acid (w(HCl) = 30%). The Sn peak adjusts then to more positive values improving the separation between Cd and Sn. The Pb and the Tl concentration should, however, not be too high. The peak potentials are:

Pb	-0.40 V
Tl	-0.50 V
Sn	-0.60 V

  For separation, it is better to perform an intermediate electrolysis (intermediate electrolysis potential approx. -580 mV). An excess Cd:Pb of 50:1 does not show any interference.

Appendix

Report for the example determination of Pb in the presence of excess Sn according to method 1a

```
========== METROHM 797 VA COMPUTRACE (Version 1.0.0.1) (Serial No. 0) ==========
 Determination  : 06161543_Pb(excessSn200).dth
 Sample ID      : Pb(excessSn200)
 Creator method :                  Date :                    Time:
 Creator determ.:                  Date : 1999-06-16         Time:  15:43:09
 Modified by    : ---              Date :                    Time:
--------------------------------------------------------------------------------
 Method         : AB176_1a.mth
 Title          : Determination of Lead, AB176 method 1a
 Remark1        : 5ml sample + 5ml electrolyte + 50µl cetyltrimethylammoniumbromide
 Remark2        : el.: 0.1mol/l trisodiumcitrate + 0.1mol/l oxalic acid + 0.2mol/l HCl
--------------------------------------------------------------------------------
 Sample amount  :   5.000 mL
 Cell volume    :  10.050 mL
--------------------------------------------------------------------------------
 Substance      : Pb
 Conc.          :   5.264 ug/L
 Conc.dev.      :   0.544 ug/L     (10.33%)
 Amount         :  52.904 ng
 Add.amount     :  50.000 ng

 VR     V       nA      I.mean  Std.Dev.  I.delta   Comments
 -----  ------  ------  ------  --------  --------  ----------------------
 1 - 1  -0.423   11.57   10.80     1.096      0.00
 1 - 2  -0.423   10.02
 2 - 1  -0.423   21.18   20.44     1.040      9.64
 2 - 2  -0.423   19.71
 3 - 1  -0.423   30.37   31.01     0.907     10.57
 3 - 2  -0.423   31.66


 Substance    Calibr.      Y.reg/offset        Slope Mean deviat. Corr.Coeff.
 ------------ ------------ ------------ ------------ ------------ ------------
 Pb           std.add.       1.072e-008   2.036e-003   1.350e-009      0.99589


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

 Pb:
 default           =   10.581  ug/l    1.093       10.329
```

Method print for the determination of Pb according to method 1a

```
--------------------------------------------------------------------------------
 Method parameters
--------------------------------------------------------------------------------
Method          : AB176_1a_Det of Pb.mth
Title           : Determination of Lead. AB176 method 1a
Remark1         : 5ml sample + 5ml electrolyte + 50µl cetyltrimethylammoniumbrom
ide
Remark2         : el.: 0.1mol/l trisodiumcitrate + 0.1mol/l oxalic acid + 0.2mol
/l HCl

Calibration     : Standard addition
Technique       : Batch
Addition        : Manual

Sample ID       : sample
Sample amount (mL): 5.000
Cell volume (mL): 10.050

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

Highest current range             : 1   mA
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)             : 30

Initial purge time (s)              :      300

Conditioning cycles
Start potential (V)                 :    0.000
End potential (V)                   :    0.000
No. of cycles                       :        0

Hydrodynamic (measurement)          :       No
Cleaning potential (V)              :   -0.200
Cleaning time (s)                   :    0.000
Deposition potential (V)            :   -0.480
Deposition time (s)                 :   90.000

Sweep
Equilibration time (s)              :   20.000
Start potential (V)                 :   -0.530
End potential (V)                   :   -0.250
Voltage step (V)                    :    0.004
Voltage step time (s)               :    0.200
Sweep rate (V/s)                    :    0.020
Pulse amplitude (V)                 :    0.050
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-010
Reverse peaks                       : No
Smooth factor                       : 4
Eliminate spikes                    : Yes

Substances
-------------------------------------------------------------------------------
Pb                        : -0.420 V   +/- 0.050 V

Standard solution         : 1   1.000 mg/L
Addition volume (mL)      : 0.050

Lead                      : Final result (Pb) =
                            Conc * (10.05 / 5) * (1e+006 / 1) + 0 - 0

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

Report for the example determination of Pb and Sn according to method 1b

```
========== METROHM 797 VA COMPUTRACE (Version 1.0.0.1) (Serial No. 0) ==========
 Determination  : 06151514_Sn_Pb.dth
 Sample ID      : sample
 Creator method :                  Date :                      Time:
 Creator determ.:                  Date : 1999-06-15           Time:  15:14:57
 Modified by    : ---              Date :                      Time:
-------------------------------------------------------------------------------
 Method         : AB176_1b.mth
 Title          : Determination of Sn and Pb. AB176 method 1b
 Remark1        : 5ml sample + 5ml electrolyte + 50µl cetyltrimethylammoniumbromide
 Remark2        : el.: 0.1mol/l trisodiumcitrate + 0.1mol/l oxalic acid + 0.2mol/l HCl
-------------------------------------------------------------------------------
 Sample amount  :   5.000 mL
 Cell volume    :  10.050 mL
-------------------------------------------------------------------------------
 Substance      : Sn
 Conc.          :  10.586 ug/L
 Conc.dev.      :   0.441 ug/L     ( 4.17%)
 Amount         : 106.390 ng
 Add.amount     : 100.000 ng

 VR     V       nA      I.mean  Std.Dev.  I.delta   Comments
 -----  ------  ------  ------  --------  --------  ----------------------
```

```
1 - 1  -0.554    4.42    4.52     0.145      0.00
1 - 2  -0.554    4.62
2 - 1  -0.554    8.59    8.71     0.167      4.19
2 - 2  -0.554    8.83
3 - 1  -0.550   12.84   12.71     0.184      4.00
3 - 2  -0.550   12.58

Substance      : Pb
Conc.          :  10.887 ug/L
Conc.dev.      :   0.547 ug/L     ( 5.03%)
Amount         : 109.410 ng
Add.amount     : 100.000 ng

VR     V       nA      I.mean  Std.Dev.  I.delta   Comments
-----  ------  ------  ------  --------  --------  ----------------------
1 - 1  -0.427   23.24   24.03     1.126      0.00
1 - 2  -0.427   24.83
2 - 1  -0.423   45.69   46.13     0.615     22.09
2 - 2  -0.423   46.56
3 - 1  -0.423   66.87   65.76     1.564     19.64
3 - 2  -0.423   64.66


Substance    Calibr.      Y.reg/offset        Slope Mean deviat. Corr.Coeff.
-----------  -----------  ------------ ------------ ------------ ------------
Sn           std.add.       4.538e-009   4.287e-004   2.133e-010      0.99940
Pb           std.add.       2.412e-008   2.216e-003   1.494e-009      0.99854


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

Sn:
default           =   21.278  ug/l    0.887        4.170

Pb:
default           =   21.882  ug/l    1.100        5.026
```

Method print for the determination of Pb and Sn according to method 1b

```
-------------------------------------------------------------------------------
 Method parameters
-------------------------------------------------------------------------------
Method          : AB176_1b_Det of Sn and Pb.mth
Title           : Determination of Sn and Pb. AB176 method 1b
Remark1         : 5ml sample + 5ml electrolyte + 50µl cetyltrimethylammoniumbrom
ide
Remark2         : el.: 0.1mol/l trisodiumcitrate + 0.1mol/l oxalic acid + 0.2mol
/l HCl

Calibration     : Standard addition
Technique       : Batch
Addition        : Manual

Sample ID       : sample
Sample amount (mL): 5.000
Cell volume (mL): 10.050

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

Highest current range             : 1   mA
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)           : 30

Initial purge time (s)            :      300

Conditioning cycles
Start potential (V)               :    0.000
End potential (V)                 :    0.000
No. of cycles                     :        0
```

```
Hydrodynamic (measurement)         :      No
Cleaning potential (V)             :   -0.250
Cleaning time (s)                  :    0.000
Deposition potential (V)           :   -0.700
Deposition time (s)                :   90.000

Sweep
Equilibration time (s)             :   20.000
Start potential (V)                :   -0.800
End potential (V)                  :   -0.300
Voltage step (V)                   :    0.004
Voltage step time (s)              :    0.200
Sweep rate (V/s)                   :    0.020
Pulse amplitude (V)                :    0.050
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-010
Reverse peaks                      : No
Smooth factor                      : 4
Eliminate spikes                   : Yes

Substances
-------------------------------------------------------------------------------
Sn                        : -0.550 V   +/- 0.050 V

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

Tin                       : Final result (Sn) =
                            Conc * (10.05 / 5) * (1e+006 / 1) + 0 - 0

Pb                        : -0.420 V   +/- 0.050 V

Standard solution         : 2   1.000 mg/L
Addition volume (mL)      : 0.100

Lead                      : Final result (Pb) =
                            Conc * (10.05 / 5) * (1e+006 / 1) + 0 - 0

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

Report for the example determination of Pb and Sn according to method 2

```
================== METROHM 746 VA TRACE ANALYZER (5.746.0101) ==================
 Determ.     : 03111419             User:                      Date: 1999-03-11
 Modified    : 2000-12-05 19:30:39  Run :  0                   Time: 14:19:11
 Sample table: -
-------------------------------------------------------------------------------
  Pos.  Ident.1/S1    Ident.2/S2    Ident.3/S3    Method.call   Sample size/S0
        sample                                                        5 mL
-------------------------------------------------------------------------------
 Method  :  AB176_2
 Title   :  Det.of Sn and Pb with methylene blue. AB176 part 2
 Remark1 :  5 ml sample + 5 ml electrolyte + 50 µl methylene blue (1g/l)
 Remark2 :  el.: 0.14mol/l oxalate + 0.17mol/l NH4Cl + 0.15mol/l HCl
-------------------------------------------------------------------------------

  Substance : Sn                                          Comments
  Mass conc.:    27.41 ug/L           Mass     : 137.1 ng   ------------------
  MC.dev.   :    0.904 ug/L (3.3%)    Add.mass :   100 ng
  Cal.dev.  :    -                    V0.sample:     5 mL

              VR   U/mV    I/nA   I.mean  Std.dev. I.delta   Comments
              ---  -----  ------  ------  -------  -------   ------------------
```

```
              00   -537    4.808   4.824   0.0222
              01   -537    4.839
              10   -536    8.227   8.166   0.0871    3.342
              11   -536    8.104
              20   -536    11.41   11.55   0.1883    3.381
              21   -536    11.68

  Substance : Pb                                          Comments
  Mass conc.:    5.068 ug/L            Mass     : 25.34 ng   ------------------
  MC.dev.   :    0.228 ug/L (4.51%)    Add.mass :    25 ng
  Cal.dev.  :    -                     V0.sample:     5 mL

              VR   U/mV    I/nA   I.mean  Std.dev. I.delta   Comments
              ---  -----  ------  ------  -------  -------   ------------------
              00   -412    4.895   4.965   0.0987
              01   -413    5.034
              10   -412    9.579   9.435   0.2038    4.470
              11   -412    9.291
              20   -412    14.24   14.26   0.0323    4.823
              21   -412    14.28

 Substance    Techn.     Y.reg/offset   Slope        Nonlin.      Mean deviat.
 ---------    --------   ------------   ----------   ----------   ------------
 Sn           std.add.     4.804e-09     3.522e-04                 1.114e-10
 Pb           std.add.     4.888e-09      0.001938                 1.789e-10


Final results                         +/- Res.dev.   %      Comments
 --------------------------------     -----------------     ------------------
        Sn =   27.414 ug/L               0.904    3.30
        Pb =   5.0681 ug/L               0.228    4.51
```

Method print for the determination of Pb and Sn according to method 2

```
================== METROHM 746 VA TRACE ANALYZER (5.746.0101) ==================
 Method: AB176_2 .mth         OPERATION SEQUENCE
 Title : Det.of Sn and Pb with methylene blue. AB176 part 2
--------------------------------------------------------------------------------

      Instructions   t/s   Main parameters            Auxiliary parameters
      ------------ -----  ------------------------  -------------------------
 1    DOS/M                V.added       5.050 mL
 2    REM                  5mL sample + 5 mL electrolyte + 50 µL meth. blue
 3    SMPL/M               V.fraction          mL     V.total              L
 4    PURGE
 5    STIR          300.0  Rot.speed      2000 /min
 6    (ADD
 7      PURGE
 8      STIR         30.0   Rot.speed      2000 /min
 9      0PURGE
10      (REP
11        SEGMENT          Segm.name   asvSn
12      REP)1
13      PURGE
14      STIR               Rot.speed      2000 /min
15      ADD>M              Soln.name   Pb-std         V.add         0.025 mL
16      ADD>M              Soln.name   Sn-std         V.add         0.100 mL
17    ADD)2
18    END


Method: AB176_2              SEGMENT
                                 asvSn
--------------------------------------------------------------------------------

      Instructions   t/s   Main parameters            Auxiliary parameters
      ------------ -----  ------------------------  -------------------------
 1    STIR           2.0   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         0.20 s      t.pulse        40.0 ms
 4    MEAS          90.0   U.meas         -800 mV
 5    MEAS          20.0   U.meas         -580 mV
 6    0STIR         10.0
 7    SWEEP         28.2   U.start        -800 mV     U.step            4 mV
                           U.end          -250 mV     Sweep rate       20 mV/s
 8    0MEAS                U.standby           mV
 9    END

Method: AB176_2              CALCULATION
                             max. 15 lines
--------------------------------------------------------------------------------
```

Quantity	Formula (R##, C##, A##)	Res.unit	Sig.dig.
Sn	R1000=MC:Sn	#g/L	5
Pb	R1001=MC:Pb	#g/L	5