Metrohm

Application Bulletin 432/1 e

Determination of tin(II) by anodic stripping voltammetry

Summary

This Application Bulletin describes the determination of Sn(II) in presence of Sn(IV) by anodic stripping voltammetry (ASV). Using an electrolyte containing fluoride, Sn(IV) gives no signal, so that a speciation is possible. The limit of detection is 2.5 µg/L.

Instruments

VA instrument capable of operating a Multi-Mode Electrode and supporting differential pulse (DP) measuring mode	
Measuring vessel of PFA	6.1450.210

Electrodes

WE	Multi-Mode Electrode pro Mercury drop capillary	6.1246.120 6.1226.030
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*).

- Hydrochloric acid, for trace analysis*, w(HCl) = 30%, CAS 7647-01-0
- PIPES, Piperazine-1,4-bis(2-ethane sulfonic acid), CAS 5625-37-6
- Sodium hydroxide solution, w(NaOH) = 30%, for trace analysis*, CAS 1310-73-2
- Ammonia solution, w(NH_3) = 25%, for trace analysis*, CAS 1336-21-6
- Sodium nitrate, $NaNO_3$, for trace analysis*, CAS 7631-99-4
- Sodium floride, NaF, for trace analysis*, CAS 7681-49-4
- Tin(II) chloride dihydrate, $SnCl_2 \cdot 2H_2O$, for analysis, CAS 10025-69-1
- Ultrapure water, resistivity >18 MΩ·cm (25 °C), type I grade (ASTM D1193)

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

Solutions

PIPES buffer	c(PIPES) = 1 mol/L, pH 8 7.6 g PIPES are mixed with 1 mL sodium hydroxide solution and 5 mL high purity water. The pH is adjusted to 8 ± 0.1 with ammonia solution. The solution is filled up to 25 mL.
$NaNO_3$ solution	c($NaNO_3$) = 1 mol/L 4.25 g $NaNO_3$ are dissolved in 50 mL ultrapure water.
NaF solution	c(NaF) = 1 mol/L 2.1 g NaF are dissolved in 50 mL ultrapure water.
Ammonia solution diluted	w(NH_3) = 10%

Standard solutions

Sn(II) standard stock solution	β(Sn^{2+}) = 1 g/L 0.190 g $SnCl_2 \cdot 2H_2O$ are dissolved in 50 mL oxygen free water. 10 mL hydrochloric acid are added. The solution is made up to 100 mL using oxygen free water. The solution is sensitive against oxidation and should prepared fresh daily.
Sn(II) standard solution	β(Sn^{2+}) = 1 mg/L The diluted working solutions are prepared from standard stock solutions by dilution in c(HCl) = 0.01 mol/L. Oxygen free water has to be used.

Analysis

Measuring solution

5 mL (diluted) sample

0.5 mL $NaNO_3$ solution

3.5 mL NaF solution

0.5 mL PIPES buffer

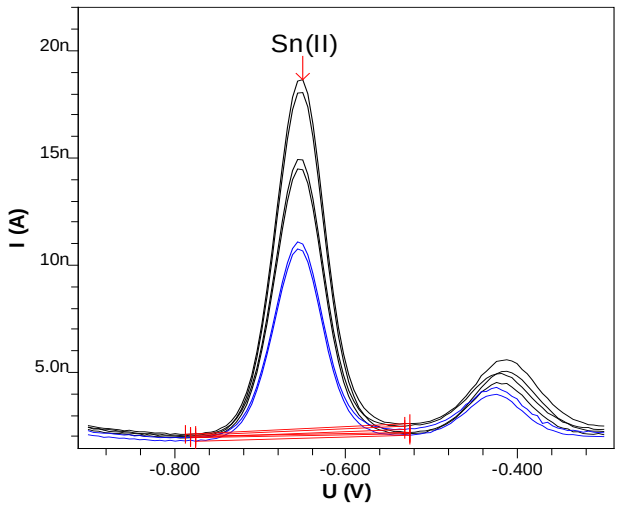
The pH is adjusted to 8.0 with diluted ammonia solution.

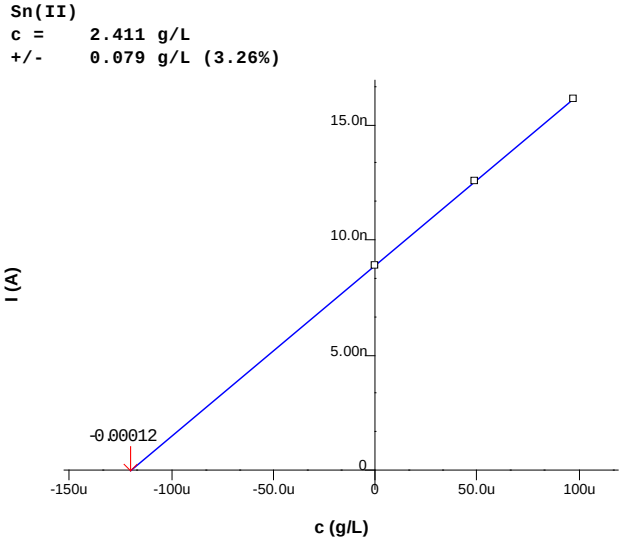
The concentration is determined by standard addition.

Parameters

Voltammetric	
Electrode operating mode	HMDE
Measuring mode	DP – Differential pulse
Stirring rate	2000 min^{-1}
Potentiostatic pretreatment	
Potential 1	-0.9 V
Waiting time 1	30 s
Equilibration time	10 s
Sweep	
Start potential	-0.9 V
End potential	-0.3 V
Potential step	0.006 V
Potential step time	0.1 s
Sweep rate	0.06 V/s
Pulse amplitude	0.05 V
Substance	
Name	Sn(II)
Characteristic potential	-0.65 V

Example





Results

Sample	Mouthwash
Sample size	0.05 mL (1:100 diluted)
β(Sn(II))	2.4 g/L

Comment

- With a deposition time (Waiting time 1) of 90 s the limit of detection is 2.5 µg/L.
- Any contact of the sample or Sn(II) standards with air should be avoided because Sn(II) is easily oxidized. Therefore it is recommended to purge the electrolyte before the addition of the sample.
- The bridge electrolyte in the reference electrode has to be renewed every day. Otherwise Ag^+ diffusing out of the reference system will be reduced to Ag^0 at the diaphragm of the outer electrolyte vessel by Sn^{2+} ions from the sample solution. That will block the diaphragm of the reference electrode after a certain time.

References

Lejeune, R. Thunus, J. Thunus, L., Polarographic determination of Sn(II) in samples containing Sn(IV) such as in 99m-technitium radiopharmaceutical kits, Anal. Chim. Acta 332, (1996) 67-71

Appendix

Report for the example determination of Sn(II) in mouthwash

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========== METROHM 797 VA COMPUTRACE (Version 1.0.0.1) (Serial No. 0) ==========
 Determination  : 04051019_Lsg04051001.dth
 Sample ID      : Lsg04051001
 Creator method :                  Date :                    Time:
 Creator determ.: zu               Date : 2002-04-05         Time:  10:19:29
 Modified by    : ---              Date :                    Time:
--------------------------------------------------------------------------------
 Method         : SnII in toothpaste.mth
 Title          : Determination of Sn(II) in toothpaste
 Remark1        : 5.5 mL H2O + 3.5 mL NaF + 0.5 mL NaNO3 + 0.5 mL PIPES -> pH 7.8
 Remark2        : 0.05 mL Mundspül-Lösung (1:100 verdünnt, mit 0.1M HCl)
--------------------------------------------------------------------------------
 Sample amount  :   0.0005 mL
 Cell volume    :  10.050 mL
--------------------------------------------------------------------------------
 Substance      : Sn(II)
 Conc.          : 119.927 ug/L
 Conc.dev.      :   3.915 ug/L     ( 3.26%)
 Amount         :   1.205 ug
 Add.amount     : 500.000 ng

 VR     V       nA      I.mean  Std.Dev.  I.delta   Comments
 -----  ------  ------  ------  --------  --------  ----------------------
 1 - 1  -0.656    8.84    8.89     0.072      0.00
 1 - 2  -0.656    8.94
 2 - 1  -0.656   12.45   12.55     0.150      3.66
 2 - 2  -0.656   12.66
 3 - 1  -0.650   15.94   16.11     0.242      3.56
 3 - 2  -0.650   16.28


 Substance    Calibr.      Y.reg/offset        Slope Mean deviat. Corr.Coeff.
 ------------ ------------ ------------ ------------ ------------ ------------
 Sn(II)       std.add.       8.900e-009   7.421e-005   2.053e-010      0.99918


 Final results                         +/- Res. dev.   %     Comments
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 Sn(II):
 Tin(II)           = 2410.539  mg/L    78.691       3.264
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Method print for the determination of Sn(II) in mouthwash

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--------------------------------------------------------------------------------
 Method parameters
--------------------------------------------------------------------------------
Method          : SnII in toothpaste.mth
Title           : Determination of Sn(II) in toothpaste and mouthwash
Remark1         : 5.5 mL H2O + 3.5 mL NaF + 0.5 mL NaNO3 + 0.5 mL PIPES -> pH 7.8
Remark2         : 0.05 mL Mouthwash (1:100 diluted, with 0.1M HCl)

Calibration     : Standard addition
Technique       : Batch
Addition        : Manual

Sample ID       :
Sample amount (mL): 0.001
Cell volume (mL): 10.050

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

Highest current range           : 10  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)            : 10

Initial purge time (s)             :       10

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

Hydrodynamic (measurement)         :       No
Cleaning potential (V)             :    0.000
Cleaning time (s)                  :    0.000
Deposition potential (V)           :   -0.900
Deposition time (s)                :   30.000

Sweep
Equilibration time (s)             :   10.000
Start potential (V)                :   -0.900
End potential (V)                  :   -0.300
Voltage step (V)                   :    0.006
Voltage step time (s)              :    0.100
Sweep rate (V/s)                   :    0.060
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)            : 1.000e-010
Reverse peaks                      : No
Smooth factor                      : 4
Eliminate spikes                   : Yes

Substances
-------------------------------------------------------------------------------
Sn(II)                   : -0.650 V   +/- 0.050 V

Standard solution        : 1   10.000 mg/L
Addition volume (mL)     : 0.050

Tin(II)                  : Final result (Sn(II)) =
                           Conc * (10.05 / 0.0005) * (1 / 1) + 0 - 0

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