Determination of lead and tin by stripping voltammetry

Of interest to:
General analytical laboratories; Environmental protection; Food analysis, Metals
B 1, 2, 7, 10

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. Differential pulse anodic stripping voltammetry (DPASV) is used under addition of cetyltrimethylammonium bromide. This method is used when:
• one is mainly interested in Pb
• Pb is in excess
• the 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 Ti and/or Cd ions are present. This method also uses DPASV in an oxalate buffer with methylene blue addition.

Method 3 in this bulletin describes the determination of Sn(II) in presence of Sn(IV) by DPASV. Using an electrolyte containing fluoride, Sn(IV) gives no signal, so that a speciation is possible.

Apparatus and accessories
• 746 VA Trace Analyzer with 747 VA Stand or
• 757 VA Computrace
• 705 UV Digester

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(H₂O₂) = 30% and 10 µL hydrochloric acid w(HCl) = 30% to 10 mL acidified sample (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 H₂SO₄ and H₂O₂ 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 (analytical grade or suprapur). Only ultrapure water should be used.
• Hydrochloric acid, suprapur, w(HCl) = 30%
• Trisodium citrate dihydrat puriss.p.a., CAS 6132-04-3
• Oxalic acid monohydrate puriss.p.a. or suprapur, CAS 6153-56-6
• Cetyl trimethylammonium bromide, CTAB, CAS 57-09-0

• Pb standard stock solution β(Pb²⁺) = 1 g/L, commercially available
• Sn standard stock solution β(Sn⁴⁺) = 1 g/L, commercially available
Ready-to-use solutions:

<table>
<thead>
<tr>
<th>Component</th>
<th>Concentration</th>
</tr>
</thead>
<tbody>
<tr>
<td>Base electrolyte</td>
<td>c(citrate) = 0.1 mol/L, c(oxalic acid) = 0.1 mol/L, c(HCl) = 0.2 mol/L, pH = 2.5</td>
</tr>
<tr>
<td></td>
<td>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.</td>
</tr>
<tr>
<td>CTAB solution</td>
<td>c(CTAB) = 0.005 mol/L, 0.46 g CTAB are dissolved in 250 mL ultrapure water</td>
</tr>
<tr>
<td>Pb standard solution</td>
<td>( \beta(Pb^{2+}) = 1 \text{ mg/L} )</td>
</tr>
<tr>
<td>Sn standard solution</td>
<td>( \beta(Sn^{4+}) = 1 \text{ mg/L} )</td>
</tr>
</tbody>
</table>

The solution is diluted with c(HCl) = 0.01 mol/L. It is stable for max. 1 week.

Literature


Method 1a: Determination of lead in presence of tin

Principle

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

The detection limit is 1 µg/L of Pb and with high excess of Sn, 5 µg/L of Pb.

Analyse

5 mL (diluted) sample + 5 mL base electrolyte + 0.05 mL CTAB solution

The voltammogram is recorded with the following parameters:

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Working electrode</td>
<td>HMDE</td>
</tr>
<tr>
<td>Stirrer speed</td>
<td>2000 rpm</td>
</tr>
<tr>
<td>Mode</td>
<td>DP</td>
</tr>
<tr>
<td>drop size</td>
<td>4</td>
</tr>
<tr>
<td>Purge time</td>
<td>300 s</td>
</tr>
<tr>
<td>Deposition potential</td>
<td>-480 mV</td>
</tr>
<tr>
<td>Deposition time</td>
<td>90 s</td>
</tr>
<tr>
<td>Equilibration time</td>
<td>20 s</td>
</tr>
<tr>
<td>Pulse amplitude</td>
<td>50 mV</td>
</tr>
<tr>
<td>Start potential</td>
<td>-530 mV</td>
</tr>
<tr>
<td>End potential</td>
<td>-250 mV</td>
</tr>
<tr>
<td>Voltage step</td>
<td>4 mV</td>
</tr>
<tr>
<td>Voltage step time</td>
<td>0.2 s</td>
</tr>
<tr>
<td>Sweep rate</td>
<td>20 mV/s</td>
</tr>
<tr>
<td>Peak potential Pb</td>
<td>-420 mV</td>
</tr>
</tbody>
</table>

The concentration is determined by standard addition.

Example: Determination of Pb in presence of Sn (200 fold excess)
**Method 1b: Determination of tin and lead simultaneously**

**Principle**
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 detection limit is 1 µg/L of Pb. The detection limit for Sn is 2 µg/L on the 746 and 10 µg/L on the 757.

**Analyse**
5 mL (diluted) sample
+ 5 mL base electrolyte
+ 0.05 mL CTAB solution

The voltammogram is recorded with the following parameters:

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Working electrode</td>
<td>HMDE</td>
</tr>
<tr>
<td>Stirrer speed</td>
<td>2000 rpm</td>
</tr>
<tr>
<td>Mode</td>
<td>DP</td>
</tr>
<tr>
<td>drop size</td>
<td>4</td>
</tr>
<tr>
<td>Purge time</td>
<td>300 s</td>
</tr>
<tr>
<td>Deposition potential</td>
<td>-700 mV</td>
</tr>
<tr>
<td>Deposition time</td>
<td>90 s</td>
</tr>
<tr>
<td>Equilibration time</td>
<td>20 s</td>
</tr>
<tr>
<td>Pulse amplitude</td>
<td>50 mV</td>
</tr>
<tr>
<td>Start potential</td>
<td>-800 mV</td>
</tr>
<tr>
<td>End potential</td>
<td>-300 mV</td>
</tr>
<tr>
<td>Voltage step</td>
<td>4 mV</td>
</tr>
<tr>
<td>Voltage step time</td>
<td>0.2 s</td>
</tr>
<tr>
<td>Sweep rate</td>
<td>20 mV/s</td>
</tr>
<tr>
<td>Peak potential (Sn)</td>
<td>-550 mV</td>
</tr>
<tr>
<td>Peak potential (Pb)</td>
<td>-420 mV</td>
</tr>
</tbody>
</table>

The concentration is determined by standard addition.

**Example:**

**Determination of Pb and Sn simultaneously**

Sample Volume 5 mL
Results 21.3 µg/L Sn
22.4 µg/L Pb
Appendix

Full Report of a determination of Pb in presence of Sn (200 fold excess) acc. to method 1a with the 757 VA Computrace

<table>
<thead>
<tr>
<th>Substance</th>
<th>Pb</th>
<th>Comments</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mass conc.</td>
<td>5.211 µg/l</td>
<td></td>
</tr>
<tr>
<td>MC.dev.</td>
<td>0.844</td>
<td>(16.19%)</td>
</tr>
<tr>
<td>Mass</td>
<td>52.366 ng</td>
<td></td>
</tr>
<tr>
<td>Add.mass</td>
<td>50,000 ng</td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>VR</th>
<th>V</th>
<th>nA</th>
<th>i.mean</th>
<th>Std.Dev.</th>
<th>i.delta</th>
<th>Comments</th>
</tr>
</thead>
<tbody>
<tr>
<td>1-1</td>
<td>-0.423</td>
<td>11.57</td>
<td>10.80</td>
<td>1.096</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1-2</td>
<td>-0.423</td>
<td>10.02</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2-1</td>
<td>-0.423</td>
<td>21.18</td>
<td>20.44</td>
<td>1.040</td>
<td>9.64</td>
<td></td>
</tr>
<tr>
<td>2-2</td>
<td>-0.423</td>
<td>19.71</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>3-1</td>
<td>-0.423</td>
<td>30.37</td>
<td>31.01</td>
<td>0.907</td>
<td>10.57</td>
<td></td>
</tr>
<tr>
<td>3-2</td>
<td>-0.423</td>
<td>31.66</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Substance Calibr.</th>
<th>Y.reg/offset</th>
<th>Slope</th>
<th>Nonlin.</th>
<th>Mean deviat.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pb std.add.</td>
<td>1.060 e-008</td>
<td>2.058 e-003</td>
<td>9.879 e-010</td>
<td></td>
</tr>
</tbody>
</table>

Final results

<table>
<thead>
<tr>
<th>Pb =</th>
<th>10.473 µg/l</th>
<th>+/-</th>
<th>Res. dev. %</th>
<th>Comments</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.696</td>
<td>16.190</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Method parameters of a determination of Pb in presence of Sn (200 fold excess) acc. to method 1a with the 746 VA Trace Analyzer

Instructions t/s Main parameters Auxiliary parameters
1 | DOS/M | V.added | 5.050 mL |
2 | REM | 5 mL 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 | 30.0 Rot.speed | 2000 /min |
8 | OPRG | |
9 | REP | |
10 | SEGMENT | Segm.name asv |
11 | REP1 | |
12 | PURGE | |
13 | STIR | Rot.speed | 2000 /min |
14 | ADD>M | Soln.name | Pb-std | V.add | 0.100 mL |
15 | ADD2 | |
16 | END | |

Instructions t/s Main parameters Auxiliary parameters
1 | STIR | 5.0 Rot.speed | 2000 /min |
2 | HMODE | Drop size | 4 |
3 | DPMODE | U.ampl | 50 mV | t.meas | 20.0 ms |
| | | U.meas | -480 mV | t.step | 0.20 s |
| | | | | t.pulse | 40.0 ms |
4 | MEAS | 90.0 U.meas |
5 | OISTR | 20.0 U.start | -530 mV |
6 | SWEEP | 14.8 U.end | -250 mV |
| | | | | Sweep rate | 20 mV/s |
7 | OMEAS | | |
8 | END | | |

Instructions t/s Main parameters Auxiliary parameters
1 | STIR | 5.0 Rot.speed | 2000 /min |
2 | HMODE | Drop size | 4 |
3 | DPMODE | U.ampl | 50 mV | t.meas | 20.0 ms |
| | | U.meas | -480 mV | t.step | 0.20 s |
| | | | | t.pulse | 40.0 ms |
4 | MEAS | 90.0 U.meas |
5 | OISTR | 20.0 U.start | -530 mV |
6 | SWEEP | 14.8 U.end | -250 mV |
| | | | | Sweep rate | 20 mV/s |
7 | OMEAS | | |
8 | END | | |

Method: AB176_1a CALCULATION

<table>
<thead>
<tr>
<th>Quantity</th>
<th>Formula (R##, C##, A##)</th>
<th>Res.unit</th>
<th>Sig.dig.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pb</td>
<td>R1000=MC:Pb</td>
<td>#/L</td>
<td>5</td>
</tr>
</tbody>
</table>
Full Report of a determination of Pb and Sn simultaneously acc. to method 1b with the 757 VA Computrace

<table>
<thead>
<tr>
<th>Substance</th>
<th>Comments</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sn</td>
<td></td>
</tr>
<tr>
<td>Mass conc.: 10.580 µg/l</td>
<td></td>
</tr>
<tr>
<td>MC.dev.: 0.617 µg/l (5.83%)</td>
<td></td>
</tr>
<tr>
<td>Mass: 106.331 ng</td>
<td></td>
</tr>
<tr>
<td>Add.mass: 100.000 ng</td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>VR</th>
<th>V</th>
<th>nA</th>
<th>i.mean</th>
<th>Std.Dev.</th>
<th>i.delta</th>
<th>Comments</th>
</tr>
</thead>
<tbody>
<tr>
<td>1-1</td>
<td>-0.554</td>
<td>4.42</td>
<td>4.52</td>
<td>0.145</td>
<td>4.00</td>
<td></td>
</tr>
<tr>
<td>1-2</td>
<td>-0.554</td>
<td>4.62</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2-1</td>
<td>-0.554</td>
<td>8.59</td>
<td>8.71</td>
<td>0.167</td>
<td>4.19</td>
<td></td>
</tr>
<tr>
<td>2-2</td>
<td>-0.554</td>
<td>8.83</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>3-1</td>
<td>-0.550</td>
<td>12.84</td>
<td>12.71</td>
<td>0.184</td>
<td>4.00</td>
<td></td>
</tr>
<tr>
<td>3-2</td>
<td>-0.550</td>
<td>12.58</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Substance</th>
<th>Comments</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pb</td>
<td></td>
</tr>
<tr>
<td>Mass conc.: 11.138 µg/l</td>
<td></td>
</tr>
<tr>
<td>MC.dev.: 0.938 µg/l (8.42%)</td>
<td></td>
</tr>
<tr>
<td>Mass: 111.936 ng</td>
<td></td>
</tr>
<tr>
<td>Add.mass: 100.000 ng</td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>VR</th>
<th>V</th>
<th>nA</th>
<th>i.mean</th>
<th>Std.Dev.</th>
<th>i.delta</th>
<th>Comments</th>
</tr>
</thead>
<tbody>
<tr>
<td>1-1</td>
<td>-0.427</td>
<td>23.24</td>
<td>24.03</td>
<td>1.126</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1-2</td>
<td>-0.427</td>
<td>24.83</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2-1</td>
<td>-0.423</td>
<td>45.69</td>
<td>46.13</td>
<td>0.615</td>
<td>22.09</td>
<td></td>
</tr>
<tr>
<td>2-2</td>
<td>-0.423</td>
<td>46.56</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>3-1</td>
<td>-0.423</td>
<td>66.87</td>
<td>65.76</td>
<td>1.564</td>
<td>19.64</td>
<td></td>
</tr>
<tr>
<td>3-2</td>
<td>-0.423</td>
<td>64.66</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Substance</th>
<th>Calibr. Y.reg/offset</th>
<th>Slope</th>
<th>Nonlin.</th>
<th>Mean deviat.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sn std.add.</td>
<td>4.523e-009</td>
<td>4.282e-004</td>
<td>1.360e-10</td>
<td></td>
</tr>
<tr>
<td>Pb std.add.</td>
<td>2.442e-008</td>
<td>2.201e-003</td>
<td>9.876e-010</td>
<td></td>
</tr>
</tbody>
</table>

Final results +/- Res. dev. % Comments
Sn = 21.266 µg/l 1.240 5.829  |
Pb = 22.387 µg/l 1.885 8.419  |

Method parameters of a determination of Pb and Sn simultaneously acc. to method 1b with the 746 VA Trace Analyzer

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 mL |
4 PURGE |  |
5 STIR | Rot.speed 2000 /min |
6 ADD |  |
7 PURGE |  |
8 STIR | Rot.speed 2000 /min |
9 OFPURGE |  |
10 SEGMENT | Segm.name asvSn |
11 REP |  |
12 REP1 |  |
13 PURGE |  |
14 STIR | Rot.speed 2000 /min |
15 ADD+M | Soln.name Pb-std V.add 0.100 mL |
16 ADD+M | Soln.name Sn-std V.add 0.100 mL |
17 ADD+2 |  |
18 END |  |

Method: AB176_1bb SEGMENT asvSn

Instructions t/s Main parameters Auxiliary parameters
1 STIR | Rot.speed 2000 /min |
2 HMDE | Drop size 4 |
3 DMODE | U.ampl 50 mV t.meas 20.0 ms t.step 0.20 s t.pulse 40.0 ms |
4 MEAS | U.meas -700 mV |
Method 2: Determination of lead and tin with methylene blue

Principle

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

Reagents

All of the used reagents must be of purest quality possible (analytical grade or suprapur). Only ultrapure water should be used.

- Hydrochloric acid, suprapur, w(HCl) = 30%
- Di-ammonium oxalate monohydrate, puriss. p. a., CAS 6009-70-7
- Ammonium chloride, suprapur, CAS 12125-02-9
- Methylene blue, C.I. 52015, CAS 61-73-4
- Sn standard stock solution, β(Sn⁴⁺) = 1 g/L, commercially available
- Pb standard stock solution, β(Pb²⁺) = 1 g/L, commercially available

Ready-to-use solutions:

<table>
<thead>
<tr>
<th>Base electrolyte</th>
<th>Formula</th>
<th>Concentration</th>
<th>Stability</th>
</tr>
</thead>
<tbody>
<tr>
<td>c(oxalate) = 0.14 mol/L</td>
<td>(Ammoniumchlorid) = 0.17mol/L</td>
<td>c(HCl) = 0.15 mol/L</td>
<td>pH = 1.6</td>
</tr>
<tr>
<td>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 500 mL with ultrapure water.</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

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

β(Pb²⁺) = 1 mg/L

Analysis

5 mL (diluted) sample
+ 5 mL base electrolyte
+ 0.05 mL methylene blue solution

The pH of the solution should be 1.8.

The voltammogram is recorded with the following parameters:

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Working electrode</td>
<td>HMDE</td>
</tr>
<tr>
<td>Stirrer speed</td>
<td>2000 rpm</td>
</tr>
<tr>
<td>Mode</td>
<td>DP</td>
</tr>
<tr>
<td>drop size</td>
<td>4</td>
</tr>
<tr>
<td>Purge time</td>
<td>300 s</td>
</tr>
<tr>
<td>Cleaning potential (deposition)</td>
<td>-800 mV</td>
</tr>
<tr>
<td>Cleaning time</td>
<td>90 s</td>
</tr>
<tr>
<td>Deposition potential (intermediate electrolysis)</td>
<td>-580 mV</td>
</tr>
<tr>
<td>Deposition time</td>
<td>20 s</td>
</tr>
<tr>
<td>Equilibration time</td>
<td>10 s</td>
</tr>
<tr>
<td>Pulse amplitude</td>
<td>50 mV</td>
</tr>
<tr>
<td>Start potential</td>
<td>-800 mV</td>
</tr>
<tr>
<td>End potential</td>
<td>-250 mV</td>
</tr>
<tr>
<td>Voltage step</td>
<td>4 mV</td>
</tr>
<tr>
<td>Voltage step time</td>
<td>0.2 s</td>
</tr>
<tr>
<td>Sweep rate</td>
<td>20 mV/s</td>
</tr>
<tr>
<td>Peak potential (Sn)</td>
<td>-540 mV</td>
</tr>
<tr>
<td>Peak potential (Pb)</td>
<td>-400 mV</td>
</tr>
</tbody>
</table>

The concentration is determined by standard addition.
Example

Determination of Pb and Sn

**Remarks**

- 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(NH₃) = 25%). One must work fast because at this pH value tin already hydrolysies.

  peak potentials:
  - Pb: -370 mV
  - Tl: -410 mV
  - Sn: -540 mV

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 hydrochlorid 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.

  peak potentials:
  - Pb: -400 mV
  - Sn: -500 mV
  - Cd: -600 mV

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.

Sample Volume: 5 mL
Results: 27.4 µg/L Sn
           5.1 µg/L Pb
Appendix

Full Report of a determination of Pb and Sn acc. to method 2 with the 746 VA Trace Analyzer

```
<table>
<thead>
<tr>
<th>Substance</th>
<th>Comments</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sn</td>
<td></td>
</tr>
<tr>
<td>Mass conc.: 27.414 ug/L</td>
<td>Mass : 137.1 ng</td>
</tr>
<tr>
<td>MC.dev.: 0.904 ug/L (3.3%)</td>
<td>Add.mass: 100 ng</td>
</tr>
<tr>
<td>Cal.dev.:</td>
<td>V0.sample: 5 mL</td>
</tr>
<tr>
<td>VR</td>
<td>U/mV</td>
</tr>
<tr>
<td>00</td>
<td>-537</td>
</tr>
<tr>
<td>01</td>
<td>-537</td>
</tr>
<tr>
<td>10</td>
<td>-536</td>
</tr>
<tr>
<td>11</td>
<td>-536</td>
</tr>
<tr>
<td>20</td>
<td>-536</td>
</tr>
<tr>
<td>21</td>
<td>-536</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Substance</th>
<th>Comments</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pb</td>
<td></td>
</tr>
<tr>
<td>Mass conc.: 5.0681 ug/L</td>
<td>Mass : 25.34 ng</td>
</tr>
<tr>
<td>MC.dev.: 0.228 ug/L (4.51%)</td>
<td>Add.mass: 25 ng</td>
</tr>
<tr>
<td>Cal.dev.:</td>
<td>V0.sample: 5 mL</td>
</tr>
<tr>
<td>VR</td>
<td>U/mV</td>
</tr>
<tr>
<td>00</td>
<td>-412</td>
</tr>
<tr>
<td>01</td>
<td>-413</td>
</tr>
<tr>
<td>10</td>
<td>-412</td>
</tr>
<tr>
<td>11</td>
<td>-412</td>
</tr>
<tr>
<td>20</td>
<td>-412</td>
</tr>
<tr>
<td>21</td>
<td>-412</td>
</tr>
</tbody>
</table>
```

Final results +/- Res.dev. % Comments

<table>
<thead>
<tr>
<th>Substance</th>
<th>+/- Res.dev. %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sn</td>
<td>0.904 3.30</td>
</tr>
<tr>
<td>Pb</td>
<td>0.228 4.51</td>
</tr>
</tbody>
</table>

Method parameters of a determination of Pb and Sn acc. to method 2 with the 746 VA Trace Analyzer

```
<table>
<thead>
<tr>
<th>Instructions</th>
<th>t/s</th>
<th>Main parameters</th>
<th>Auxiliary parameters</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 DOS/M</td>
<td></td>
<td>V.added 5.050 mL</td>
<td>5 mL electrolyte 50 µL meth. blue</td>
</tr>
<tr>
<td>2 REM</td>
<td></td>
<td>V.fraction mL</td>
<td>V.total mL</td>
</tr>
<tr>
<td>3 SMPL/M</td>
<td></td>
<td>300.0 Rot.speed 2000 /min</td>
<td></td>
</tr>
<tr>
<td>4 PURGE</td>
<td></td>
<td>30.0 Rot.speed 2000 /min</td>
<td></td>
</tr>
<tr>
<td>5 STIR</td>
<td></td>
<td>30.00 asvSn</td>
<td></td>
</tr>
<tr>
<td>6 ADD</td>
<td></td>
<td>18 END</td>
<td></td>
</tr>
</tbody>
</table>
```

Method 3: Determination of Sn(II) besides Sn(IV) in an electrolyte containing NaF

Principle

In weak alkaline solutions, containing sodium fluoride it is possible to determine Sn(II) besides Sn(IV) by DPASV. The Sn(IV) ions do not give any voltammetric signal under these conditions. The detection limit is 2.5 µg/L.

Accessories

- 6.1450.210 Measuring vessel of PFA

Reagents

All of the used reagents must be of purest quality possible (analytical grade or suprapur). Only ultrapure water should be used.

- Piperazine-1,4-bis(2-ethane sulfonic acid), PIPES, CAS 5625-37-6
- Sodium hydroxide solution, suprapur, w(NaOH) = 30%
- Ammonia solution, suprapur, w(NH₃) = 25%
- Hydrochloric acid, suprapur, w(HCl) = 30%
- NaNO₃, suprapur, CAS 7631-99-4
- NaF suprapur, CAS 7681-49-4
- SnCl₂ dihydrate, p.a., CAS 10025-69-1

Ready-to-use solutions:

<table>
<thead>
<tr>
<th>PIPES buffer</th>
<th>c(PIPES) = 1 mol/L, pH 8</th>
</tr>
</thead>
<tbody>
<tr>
<td>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.</td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>NaNO₃ solution</th>
<th>c(NaNO₃) = 1 mol/L</th>
</tr>
</thead>
<tbody>
<tr>
<td>4.25 g NaNO₃ are dissolved in 50 mL ultrapure water.</td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>NaF solution</th>
<th>c(NaF) = 1 mol/L</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.1 g NaF are dissolved in 50 mL ultrapure water.</td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Sn standard stock solution</th>
<th>c(Sn²⁺) = 1 g/L</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.190 g SnCl₂ are dissolved in 50 mL oxygen free water. 10 mL hydrochloric acid are added and the solution is made up to 100 mL using oxygen free water. The solution is sensitive against oxidation and should be prepared freshly in regular intervals.</td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Sn(II) standard solution</th>
<th>c(Sn²⁺) = 1 mg/L</th>
</tr>
</thead>
<tbody>
<tr>
<td>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.</td>
<td></td>
</tr>
</tbody>
</table>

Analysis

5 mL sample
+ 0.5 mL NaNO₃ solution
+ 3.5 mL NaF solution
+ 0.5 mL PIPES buffer

The pH is adjusted to 8.0 with ammonia solution.
The voltammogram is recorded with the following parameters:

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Working electrode</td>
<td>HMDE</td>
</tr>
<tr>
<td>Stirrer speed</td>
<td>2000 rpm</td>
</tr>
<tr>
<td>Mode</td>
<td>DP</td>
</tr>
<tr>
<td>Drop size</td>
<td>4</td>
</tr>
<tr>
<td>Purge time</td>
<td>300 s</td>
</tr>
<tr>
<td>Deposition potential</td>
<td>-800 mV</td>
</tr>
<tr>
<td>Deposition time</td>
<td>90 s</td>
</tr>
<tr>
<td>Equilibration time</td>
<td>10 s</td>
</tr>
<tr>
<td>Pulse amplitude</td>
<td>50 mV</td>
</tr>
<tr>
<td>Start potential</td>
<td>-800 mV</td>
</tr>
<tr>
<td>End potential</td>
<td>-500 mV</td>
</tr>
<tr>
<td>Voltage step</td>
<td>4 mV</td>
</tr>
<tr>
<td>Voltage step time</td>
<td>0.1 s</td>
</tr>
<tr>
<td>Sweep rate</td>
<td>40 mV/s</td>
</tr>
<tr>
<td>Peak potential (Sn)</td>
<td>-640 mV</td>
</tr>
</tbody>
</table>

The concentration is determined by standard addition.

**Example**

**Determination of Sn(II)**

<table>
<thead>
<tr>
<th>Substance: SnII VR(***)</th>
</tr>
</thead>
<tbody>
<tr>
<td>VR (mV)</td>
</tr>
<tr>
<td>---</td>
</tr>
<tr>
<td>-800</td>
</tr>
<tr>
<td>-750</td>
</tr>
<tr>
<td>-700</td>
</tr>
</tbody>
</table>

**Standard addition curve: SnII**

Sample Volume: 5 mL

Results: 15.6 µg/L Sn(II)

**Literature**

- Lejeune, R., Thunus, J., Thunus, L.
  Polarographic determination of Sn(II) in samples containing Sn(IV) such as in 99m-technitium radio-pharmaceutical kits

**Appendix**

**Full Report of a determination of Sn(II) acc. to method 3 with the 746 VA Trace Analyzer**

<table>
<thead>
<tr>
<th>Substance : SnII</th>
<th>Comments</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mass conc. : 15.64 µg/L</td>
<td>Mass : 78.21 ng</td>
</tr>
<tr>
<td>MC.dev. : 0.632 µg/L (4.04%)</td>
<td>Add.mass : 25 ng</td>
</tr>
<tr>
<td>Cal.dev. : -</td>
<td>V0.sample: 5 mL</td>
</tr>
<tr>
<td></td>
<td>VR U/mV</td>
</tr>
<tr>
<td>VR U/mV</td>
<td>I/nA</td>
</tr>
<tr>
<td>---</td>
<td>---</td>
</tr>
<tr>
<td>00</td>
<td>-630</td>
</tr>
<tr>
<td>01</td>
<td>-629</td>
</tr>
<tr>
<td>02</td>
<td>-629</td>
</tr>
</tbody>
</table>
Method parameters of a determination of Sn(II) acc. to method 3 with the 746 VA Trace Analyzer

<table>
<thead>
<tr>
<th>Instructions</th>
<th>t/s</th>
<th>Main parameters</th>
<th>Auxiliary parameters</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>DOS&gt;M</td>
<td>Soln.name NaNO3</td>
<td>V.add 0.500 mL</td>
</tr>
<tr>
<td>2</td>
<td>DOS&gt;M</td>
<td>Soln.name NaF</td>
<td>V.add 3.500 mL</td>
</tr>
<tr>
<td>3</td>
<td>DOS&gt;M</td>
<td>Soln.name PIPES</td>
<td>V.add 0.500 mL</td>
</tr>
<tr>
<td>4</td>
<td>SMPL/M</td>
<td>V.fraction mL</td>
<td>V.total L</td>
</tr>
<tr>
<td>5</td>
<td>PURGE</td>
<td></td>
<td></td>
</tr>
<tr>
<td>6</td>
<td>STIR</td>
<td>300.0 Rot.speed</td>
<td>2000 /min</td>
</tr>
<tr>
<td>7</td>
<td>ADD</td>
<td></td>
<td></td>
</tr>
<tr>
<td>8</td>
<td>PURGE</td>
<td></td>
<td></td>
</tr>
<tr>
<td>9</td>
<td>STIR</td>
<td>30.0 Rot.speed</td>
<td>2000 /min</td>
</tr>
<tr>
<td>10</td>
<td>OPURGE</td>
<td></td>
<td></td>
</tr>
<tr>
<td>11</td>
<td>&lt;/REP&gt;</td>
<td></td>
<td></td>
</tr>
<tr>
<td>12</td>
<td>SEGMENT</td>
<td>Segm.name Tin</td>
<td>Tin</td>
</tr>
<tr>
<td>13</td>
<td>REP12</td>
<td></td>
<td></td>
</tr>
<tr>
<td>14</td>
<td>ADD&gt;M</td>
<td>Soln.name SnIIstd</td>
<td>V.add 0.025 mL</td>
</tr>
<tr>
<td>15</td>
<td>ADD12</td>
<td></td>
<td></td>
</tr>
<tr>
<td>16</td>
<td>END</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Method: AB176_3  

<table>
<thead>
<tr>
<th>Instructions</th>
<th>t/s</th>
<th>Main parameters</th>
<th>Auxiliary parameters</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>STIR</td>
<td>5.0 Rot.speed</td>
<td>2000 /min</td>
</tr>
<tr>
<td>2</td>
<td>HMDE</td>
<td></td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>DPMODE</td>
<td>U.ampl</td>
<td>50 mV</td>
</tr>
<tr>
<td>4</td>
<td>MEAS</td>
<td>90.0 U.meas</td>
<td>-800 mV</td>
</tr>
<tr>
<td>5</td>
<td>OSTIR</td>
<td>10.0</td>
<td>t.meas 20.0 ms</td>
</tr>
<tr>
<td>6</td>
<td>SWEEP</td>
<td>7.8</td>
<td>U.start -800 mV</td>
</tr>
<tr>
<td>7</td>
<td>OMEAS</td>
<td>U.meas</td>
<td>500 mV</td>
</tr>
<tr>
<td>8</td>
<td>END</td>
<td>U.standby mV</td>
<td></td>
</tr>
</tbody>
</table>

Method: AB176_3  

<table>
<thead>
<tr>
<th>Quantity</th>
<th>Formula (R##, C##, A##)</th>
<th>Res.unit</th>
<th>Sig.dig.</th>
</tr>
</thead>
</table>
SnII      | R1000=MC:SnII           | #g/L     | 5        |