

Application Bulletin 74/4 e

Determination of antimony, bismuth, and copper by anodic stripping voltammetry

Summary

This Application Bulletin describes the voltammetric determination of the elements antimony, bismuth, and copper.

The limit of detection for the three elements is 0.5 ... 1 µg/L.

Instruments

| | |
|---|------------|
| VA instrument capable of operating a Multi-Mode Electrode and supporting differential pulse (DP) measuring mode | |
| 909 UV Digester | 2.909.0014 |

Electrodes

| | | |
|----|---|------------|
| WE | Multi-Mode Electrode pro | 6.1246.120 |
| | Mercury drop capillary | 6.1226.030 |
| | or | 6.1226.050 |
| RE | Ag/AgCl reference electrode | 6.0728.x20 |
| | Ag/AgCl/KCl (3 mol/L) | |
| | Electrolyte vessel Filled with c(KCl) = 3 mol/L | 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
- Antimony standard stock solution: $\beta(\text{Sb}^{3+}) = 1 \text{ g/L}$ Commercially available.
- Bismuth standard stock solution: $\beta(\text{Bi}^{3+}) = 1 \text{ g/L}$ Commercially available.
- Copper standard stock solution: $\beta(\text{Cu}^{2+}) = 1 \text{ g/L}$ Commercially available.
- Ultrapure water, resistivity >18 MΩ·cm (25 °C), type I grade (ASTM D1193)

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

Standard solutions

| | |
|----------------------|--|
| Sb standard solution | $\beta(\text{Sb}^{3+}) = 1 \text{ mg/L}$ The solution is diluted with c(HCl) = 0.1 mol/L. It is stable for max. 1 week. |
| Bi standard solution | $\beta(\text{Bi}^{3+}) = 1 \text{ mg/L}$ The solution is diluted with c(HCl) = 0.1 mol/L. It is stable for max. 1 week. |
| Cu standard solution | $\beta(\text{Cu}^{2+}) = 1 \text{ mg/L}$ The solution is diluted with c(HCl) = 0.1 mol/L. It is stable for max. 1 week. |

Sample preparation

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

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 - 100 µL w(H₂O₂) = 30% and 10 µL w(HCl) = 30% to 10 mL acidified sample (pH = 2) and irradiate for 1 h at 90 °C. After cooling to room temperature, the digested sample can be transferred directly to the polarographic vessel.
- Samples with organic matter (foods, pharmaceuticals etc.) must be digested.
 - High-pressure ashers
 - 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 H₂SO₄ and H₂O₂ according to Application Bulletin 113.

Method 1: Determination of Bi and Sb(III) or Cu

Bi and Sb(III) can be determined simultaneously in $c(\text{HCl}) = 0.6 \text{ mol/L}$. In this electrolyte Cu interferes with the Sb determination since their peak potentials are very close together. The interference can be eliminated by selective oxidation of the Cu after the deposition, prior to the sweep.

Analysis

Measuring solution

10 mL (diluted) sample

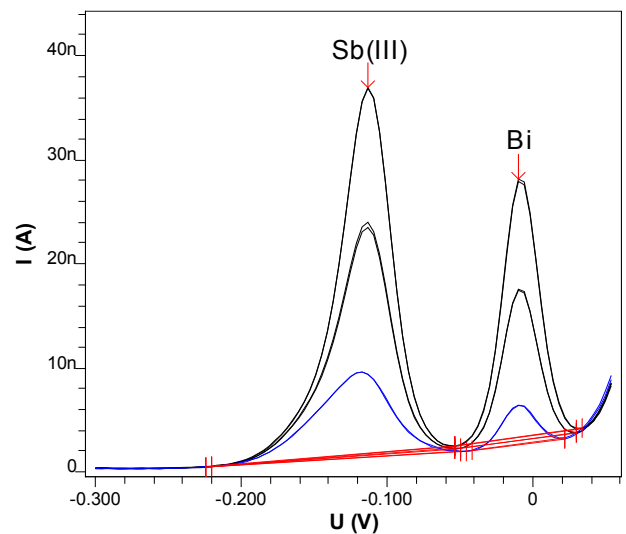
0.6 mL hydrochloric acid

The concentration is determined by standard addition.

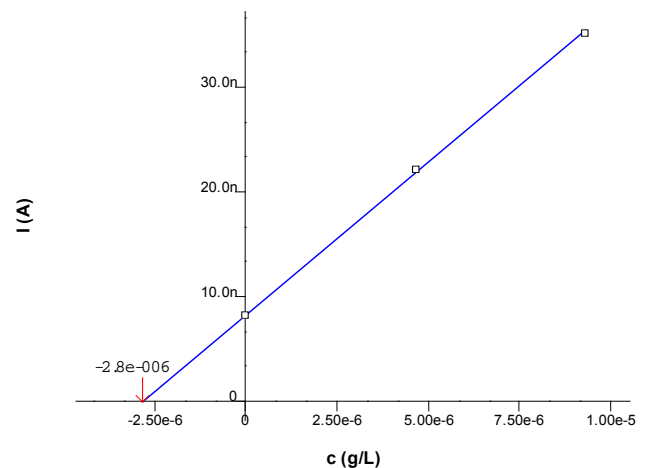
Parameters

| Voltammetric | |
|-----------------------------|-------------------------|
| Electrode operating mode | HMDE |
| Measuring mode | DP – Differential pulse |
| Stirring rate | 2000 min^{-1} |
| Potentiostatic pretreatment | |
| Potential 1 | -0.24 V |
| Waiting time 1 | 180 s |
| Potential 2 | -0.15 V |
| Waiting time 2 | 20 s |
| Equilibration time | 10 s |
| Sweep | |
| Start potential | -0.3 V |
| End potential | 0.05 V |
| Potential step | 0.004 V |
| Potential step time | 0.2 s |
| Sweep rate | 0.02 V/s |
| Pulse amplitude | 0.01 V |
| Substance | |
| Name | Bi |
| Characteristic potential | -0.01 V |
| Name | Sb(III) |
| Characteristic potential | -0.11 V |
| Name | Cu |
| Characteristic potential | -0.15 V |

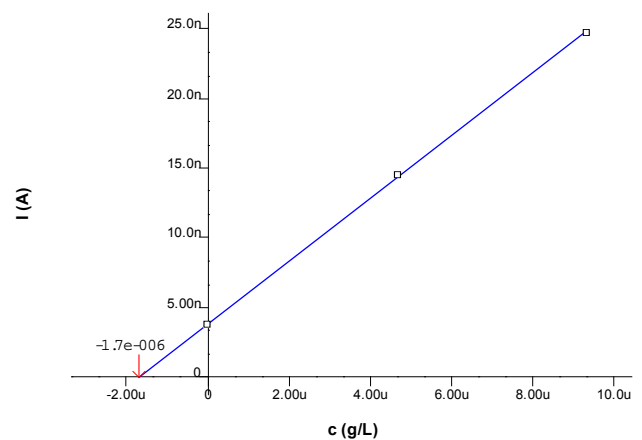
Example



Sb(III)
 $c = 2.998 \text{ ug/l}$
 $\pm 0.077 \text{ ug/l (2.57\%)}$



Bi
 $c = 1.794 \text{ ug/l}$
 $\pm 0.055 \text{ ug/l (3.09\%)}$



Result

| | |
|---------------------------------|---------------------|
| Sample | Tap water |
| Sample size | 10 mL |
| $\beta(\text{Sb}^{\text{III}})$ | 3.0 $\mu\text{g/L}$ |
| $\beta(\text{Bi})$ | 1.8 $\mu\text{g/L}$ |

Comments

- The measuring vessel should contain between 10 ng and 1 μg Sb and Bi each.
- To obtain a better peak shape it is recommended to apply a pulse amplitude of only 10 mV.
- In $c(\text{HCl}) = 0.6 \text{ mol/L}$ only Sb(III) can be determined. Sb(V) must first be reduced to Sb(III) in this solution. (Evaporate to dryness with sufficient hydrazine sulfate to cover the tip of a spatula). In this way it is also possible to speciate between both oxidation states.
- In $w(\text{HCl}) = 10\%$ the sum Sb(III) + Sb(V) is determined (refer to method 2).

Method 2: Determination of Cu besides Sb or Bi

In $w(\text{HCl}) = 10\%$ Cu can be determined simultaneously with Sb(total) or Bi. A separation of Sb and Bi in this electrolyte is not possible since both elements show a peak at the same potential.

Analysis
Measuring solution

10 mL (diluted) sample

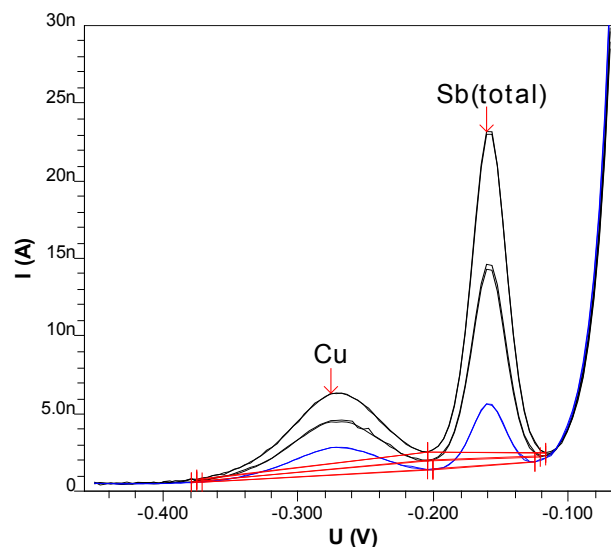
5 mL hydrochloric acid

The concentration is determined by two standard additions.

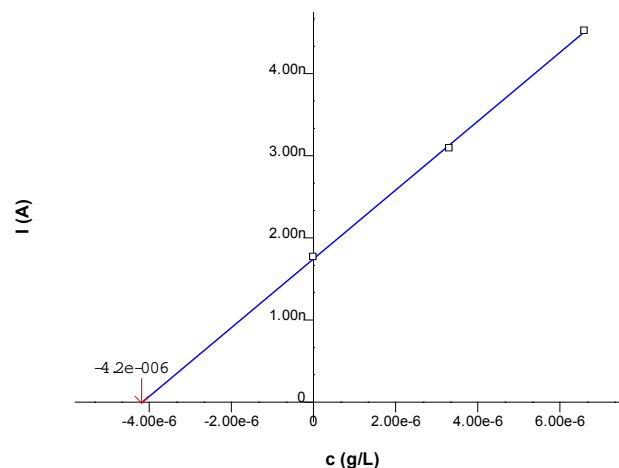
Parameters

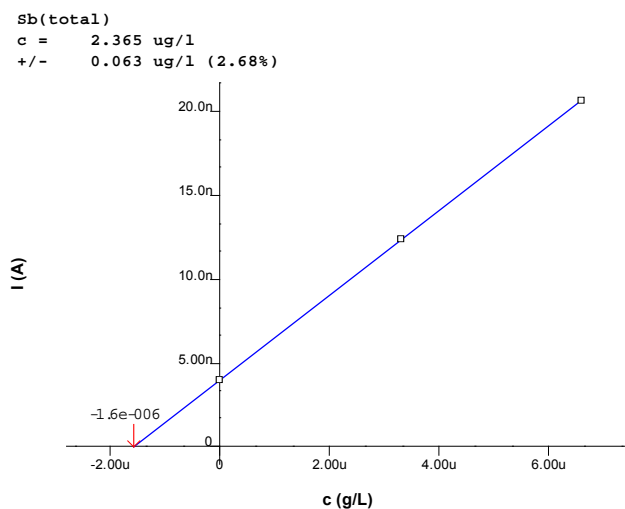
| Voltammetric | |
|-----------------------------|-------------------------|
| Electrode operating mode | HMDE |
| Measuring mode | DP – Differential pulse |
| Stirring rate | 2000 min^{-1} |
| Potentiostatic pretreatment | |
| Potential 1 | -0.4 V |
| Waiting time 1 | 180 s |

| Equilibration time | 10 s |
|--------------------------|-----------|
| Sweep | |
| Start potential | -0.45 V |
| End potential | -0.07 V |
| Potential step | 0.004 V |
| Potential step time | 0.2 s |
| Sweep rate | 0.02 V/s |
| Pulse amplitude | 0.01 V |
| Substance | |
| Name | Cu |
| Characteristic potential | -0.27 V |
| Name | Sb(total) |
| Characteristic potential | -0.16 V |
| Name | Bi |
| Characteristic potential | -0.16 V |

Example


Cu
 $c = 6.270 \text{ } \mu\text{g/l}$
 $+/- 0.209 \text{ } \mu\text{g/l} (3.33\%)$





Result

| | |
|-----------------------------------|-----------|
| Sample | Tap water |
| Sample size | 10 mL |
| $\beta(\text{Cu})$ | 6.3 µg/L |
| $\beta(\text{Sb}^{\text{total}})$ | 2.4 µg/L |

Comments

- In HCl 10% the sum Sb(III) + Sb(V) is determined with the same sensitivity for both species.

Method 3: Determination of Sb, Bi and Cu

The combination of method 1 and 2 allows the determination of all three elements. First antimony and bismuth are determined in $c(\text{HCl}) = 0.6 \text{ mol/L}$. After further addition of hydrochloric acid also the copper is determined.

| | Method 1 $c(\text{HCl}) = 0.6 \text{ mol/L}$ | Method 2 $w(\text{HCl}) = 10 \%$ |
|----|---|-------------------------------------|
| Sb | -110 mV | -160 mV |
| Bi | -10 mV | -160 mV |
| Cu | -150 mV | -270 mV |

Analysis

Measuring solution for the determination of Sb and Bi

10 mL (diluted) sample solution

0.6 mL hydrochloric acid

The Sb and Bi concentrations are determined by 2 standard additions each.

Measuring solution for the determination of Cu

Measuring solution from Sb and Bi determination

+ 5 mL hydrochloric acid

The Cu concentration is determined by 2 standard additions.

Parameters

For the determination of Sb and Bi

| Voltammetric | |
|-----------------------------|-------------------------|
| Electrode operating mode | HMDE |
| Measuring mode | DP – Differential pulse |
| Stirring rate | 2000 min ⁻¹ |
| Potentiostatic pretreatment | |
| Potential 1 | -0.24 V |
| Waiting time 1 | 180 s |
| Potential 2 | -0.15 V |
| Waiting time 2 | 20 s |
| Equilibration time | 10 s |
| Sweep | |
| Start potential | -0.3 V |
| End potential | 0.05 V |
| Potential step | 0.004 V |
| Potential step time | 0.2 s |
| Sweep rate | 0.02 V/s |
| Pulse amplitude | 0.01 V |
| Substance | |
| Name | Bi |
| Characteristic potential | -0.01 V |
| Name | Sb(III) |
| Characteristic potential | -0.11 V |

For the determination of Cu

| Voltammetric | |
|--------------------------|-------------------------|
| Electrode operating mode | HMDE |
| Measuring mode | DP – Differential pulse |
| Stirring rate | 2000 min ⁻¹ |

Potentiostatic pretreatment

Potential 1 -0.4 V

Waiting time 1 180 s

Equilibration time 10 s

Sweep

Start potential -0.45 V

End potential -0.07 V

Potential step 0.004 V

Potential step time 0.2 s

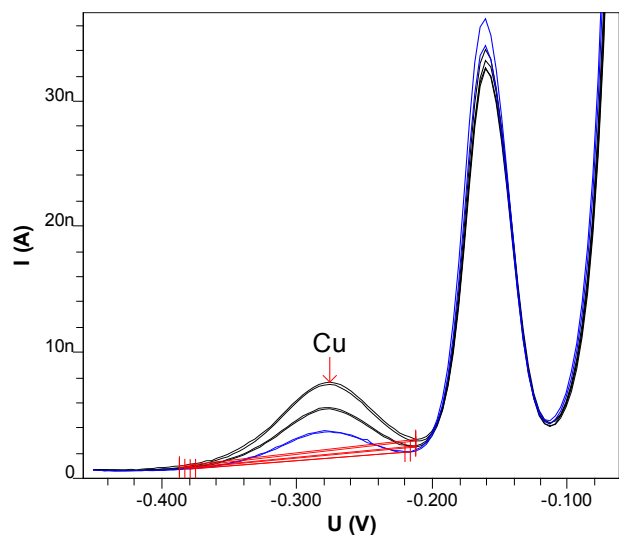
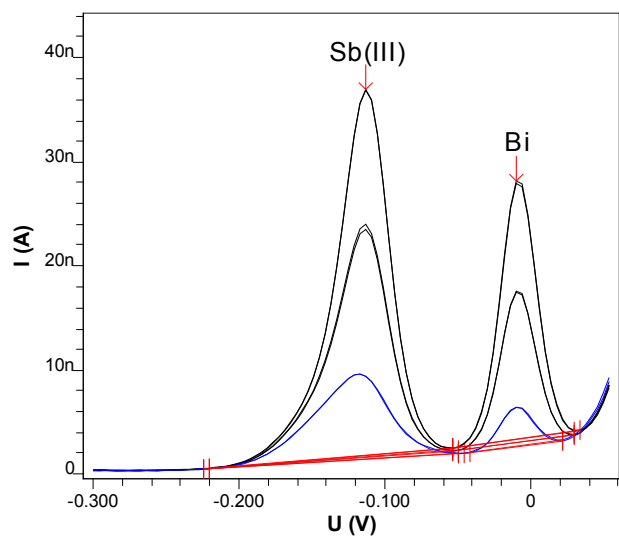
Sweep rate 0.02 V/s

Pulse amplitude 0.01 V

Substance

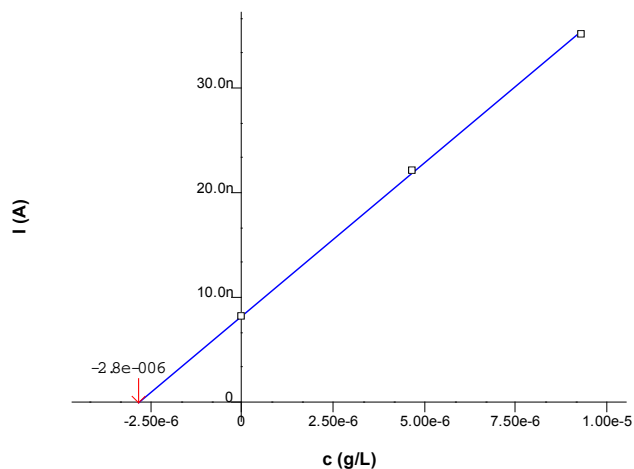
Name Cu

Characteristic potential -0.27 V

Example

Sb(III)

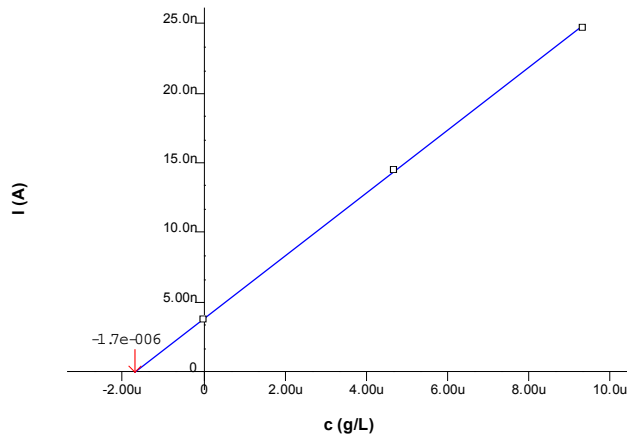
c = 2.998 ug/l

+/- 0.077 ug/l (2.57%)


Bi

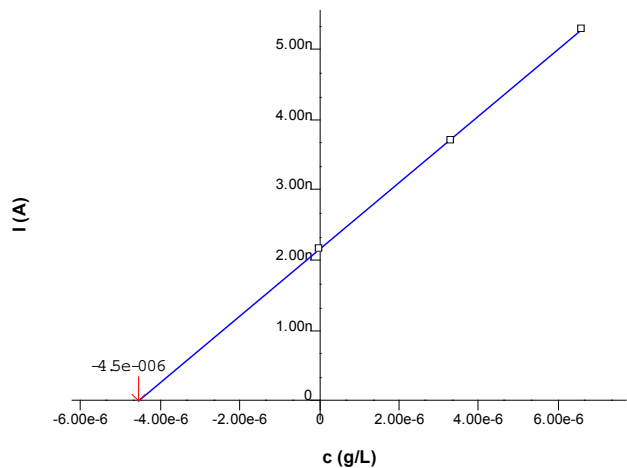
c = 1.794 ug/l

+/- 0.055 ug/l (3.09%)


Cu

c = 6.812 ug/l

+/- 0.231 ug/l (3.39%)



Result

| | |
|---------------------------------|---------------------|
| Sample | Tap water |
| Sample size | 10 mL |
| $\beta(\text{Sb}^{\text{III}})$ | 3.0 $\mu\text{g/L}$ |
| $\beta(\text{Bi})$ | 1.8 $\mu\text{g/L}$ |
| $\beta(\text{Cu})$ | 6.8 $\mu\text{g/L}$ |

Comments

- In 0.6 mol/L HCl only Sb(III) can be determined. Sb(V) must first be reduced to Sb(III) in this solution. (Evaporate to dryness with sufficient hydrazine sulfate to cover the tip of a spatula). In this way it is also possible to speciate between both oxidation states.
- By combination of method 1 and 2 it is also possible to speciate between both oxidation states of Sb. In $c(\text{HCl}) = 0.6 \text{ mol/L}$ only Sb(III) is determined. In $w(\text{HCl}) = 10 \%$ total antimony (Sb(III) + Sb(V)) is determined. That is only possible if Bi is absent.

Appendix

Report of the example determination of Sb and Bi according to method 1

```

===== METROHM 797 VA COMPUTRACE (Version 1.0.0.1) (Serial No. 0) =====
Determination : 08161516_SbBi tap water.dth
Sample ID      : SbBi tap water
Creator method :                               Date :                               Time:
Creator determ.:                               Date : 2000-08-16           Time: 15:16:45
Modified by    :                               Date : 2017-07-13           Time: 13:36:30
  
```

```

-----
Method      : AB74_2_Det of Sb Bi.mth
Title       : Determination of Antimony and Bismuth. AB 74 part 2
Remark1     : 10 ml water + 0.6 ml HCl (30%)
Remark2     :
  
```

```

-----
Sample amount : 10.000 mL
Cell volume   : 10.600 mL
  
```

```

-----
Substance    : Sb(III)
Conc.        : 2.828 ug/L
Conc.dev.    : 0.073 ug/L      ( 2.57%)
Amount       : 29.981 ng
Add.amount   : 50.000 ng
  
```

| VR | V | nA | I.mean | Std.Dev. | I.delta | Comments |
|-------|--------|-------|--------|----------|---------|----------|
| 1 - 1 | -0.117 | 8.22 | 8.20 | 0.031 | 0.00 | |
| 1 - 2 | -0.117 | 8.18 | | | | |
| 2 - 1 | -0.114 | 22.31 | 22.09 | 0.311 | 13.89 | |
| 2 - 2 | -0.114 | 21.87 | | | | |
| 3 - 1 | -0.114 | 35.13 | 35.07 | 0.080 | 12.98 | |
| 3 - 2 | -0.114 | 35.02 | | | | |

```

-----
Substance    : Bi
Conc.        : 1.692 ug/L
Conc.dev.    : 0.052 ug/L      ( 3.09%)
Amount       : 17.935 ng
Add.amount   : 50.000 ng
  
```

| VR | V | nA | I.mean | Std.Dev. | I.delta | Comments |
|-------|--------|-------|--------|----------|---------|----------|
| 1 - 1 | -0.010 | 3.78 | 3.76 | 0.031 | 0.00 | |
| 1 - 2 | -0.010 | 3.74 | | | | |
| 2 - 1 | -0.010 | 14.53 | 14.47 | 0.083 | 10.71 | |
| 2 - 2 | -0.010 | 14.41 | | | | |
| 3 - 1 | -0.010 | 24.57 | 24.66 | 0.131 | 10.19 | |
| 3 - 2 | -0.010 | 24.75 | | | | |

| Substance | Calibr. | Y.reg/offset | Slope | Mean deviat. | Corr.Coeff. |
|-----------|----------|--------------|------------|--------------|-------------|
| Sb(III) | std.add. | 8.249e-009 | 2.917e-003 | 3.422e-010 | 0.99979 |
| Bi | std.add. | 3.814e-009 | 2.254e-003 | 1.960e-010 | 0.99991 |

| Final results | | +/- Res. dev. | % | Comments |
|---------------------|---|---------------|-------|----------|
| Sb(III): default | = | 2.998 ug/l | 0.077 | 2.572 |
| Bi: default | = | 1.794 ug/l | 0.055 | 3.093 |

Method print for the determination of Sb and Bi according to method 1

```

-----
Method parameters
-----
Method      : AB074_2a_Det of Sb Bi.mth
Title       : Determination of Antimony and Bismuth. AB 74 Method 1
Remark1     : 10 ml water + 0.6 ml HCl (30%)
Remark2     :

Calibration : Standard addition
Technique   : Batch
Addition    : Manual

Sample ID    : Sample
Sample amount (mL): 10.000
Cell volume (mL): 10.600
  
```

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) : 20

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) : -0.240
Cleaning time (s) : 180.000
Deposition potential (V) : -0.150
Deposition time (s) : 20.000

Sweep
Equilibration time (s) : 10.000
Start potential (V) : -0.300
End potential (V) : 0.050
Voltage step (V) : 0.004
Voltage step time (s) : 0.200
Sweep rate (V/s) : 0.020
Pulse amplitude (V) : 0.010
Pulse time (s) : 0.040

Cell off after measurement : Yes
  
```

Peak evaluation

```

-----
Regression technique : Linear Regression
Peak evaluation : Height
Minimum peak width (V.steps) : 10
Minimum peak height (A) : 1.000e-010
Reverse peaks : No
Smooth factor : 4
Eliminate spikes : Yes
  
```

Substances

```

-----
Sb : -0.110 V +/- 0.050 V

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

Antimony : Final result (Sb) =
          Conc * (10.6 / 10) * (1e+006 / 1) + 0 - 0

Bi : -0.010 V +/- 0.050 V

Standard solution : 2 1.000 mg/L
Addition volume (mL) : 0.050

Bismuth : Final result (Bi) =
          Conc * (10.6 / 10) * (1e+006 / 1) + 0 - 0
  
```

Baseline

```

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


Report of the example determination of Sb and Cu in tap water according to method 2

===== METROHM 797 VA COMPUTRACE (Version 1.0.0.1) (Serial No. 0) =====

Determination : 08141708_CuSb 10mV.dth
 Sample ID : CuSb 10mV
 Creator method : Date : Time:
 Creator determ.: Date : 2000-08-14 Time: 17:08:32
 Modified by : Date : 2017-07-13 Time: 13:43:34

Method : AB74_2b_Det of Cu Sb.mth
 Title : Determination of Copper and Antimon. AB 74 part 2
 Remark1 : 10 ml sample + 5 ml HCl (30%)
 Remark2 :

Sample amount : 10.000 mL
 Cell volume : 15.000 mL

Substance : Cu
 Conc. : 4.180 ug/L
 Conc.dev. : 0.139 ug/L (3.33%)
 Amount : 62.696 ng
 Add.amount : 50.000 ng

| VR | V | nA | I.mean | Std.Dev. | I.delta | Comments |
|-------|--------|-------|--------|----------|---------|----------|
| 1 - 1 | -0.271 | 1.763 | 1.773 | 0.014 | 0.000 | |
| 1 - 2 | -0.275 | 1.783 | | | | |
| 2 - 1 | -0.275 | 3.125 | 3.097 | 0.039 | 1.324 | |
| 2 - 2 | -0.275 | 3.070 | | | | |
| 3 - 1 | -0.271 | 4.506 | 4.529 | 0.032 | 1.431 | |
| 3 - 2 | -0.275 | 4.551 | | | | |

Substance : Sb(total)
 Conc. : 1.577 ug/L
 Conc.dev. : 0.042 ug/L (2.68%)
 Amount : 23.648 ng
 Add.amount : 50.000 ng

| VR | V | nA | I.mean | Std.Dev. | I.delta | Comments |
|-------|--------|-------|--------|----------|---------|----------|
| 1 - 1 | -0.160 | 3.94 | 3.96 | 0.038 | 0.00 | |
| 1 - 2 | -0.160 | 3.99 | | | | |
| 2 - 1 | -0.160 | 12.47 | 12.35 | 0.178 | 8.38 | |
| 2 - 2 | -0.160 | 12.22 | | | | |
| 3 - 1 | -0.156 | 20.50 | 20.59 | 0.135 | 8.25 | |
| 3 - 2 | -0.160 | 20.69 | | | | |

| Substance | Calibr. | Y.reg/offset | Slope | Mean deviat. | Corr.Coeff. |
|-----------|----------|--------------|------------|--------------|-------------|
| Cu | std.add. | 1.754e-009 | 4.196e-004 | 6.064e-011 | 0.99954 |
| Sb(total) | std.add. | 3.974e-009 | 2.521e-003 | 1.641e-010 | 0.99990 |

| Final results | | +/- | Res. dev. | % | Comments |
|---------------|---|-------|-----------|-------|----------|
| Cu: | | | | | |
| default | = | 6.270 | ug/l | 0.209 | 3.334 |
| Sb(total): | | | | | |
| default | = | 2.365 | ug/l | 0.063 | 2.682 |

Method print for the determination of Sb and Cu according to method 2

Method parameters

Method : AB074_2b_Det of Cu and Sb or Bi.mth
 Title : Determination of Copper and Antimon or Bismuth. AB 74 Method 2
 Remark1 : 10 ml sample + 5 ml HCl (30%)
 Remark2 :

Calibration : Standard addition
 Technique : Batch
 Addition : Manual

Sample ID : Sample
 Sample amount (mL): 10.000
 Cell volume (mL): 15.000

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) : 20

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) : 0.000
Cleaning time (s) : 0.000
Deposition potential (V) : -0.400
Deposition time (s) : 180.000

Sweep
Equilibration time (s) : 10.000
Start potential (V) : -0.450
End potential (V) : -0.070
Voltage step (V) : 0.004
Voltage step time (s) : 0.200
Sweep rate (V/s) : 0.020
Pulse amplitude (V) : 0.010
Pulse time (s) : 0.040

Cell off after measurement : Yes
  
```

Peak evaluation

```

-----
Regression technique : Linear Regression
Peak evaluation : Height
Minimum peak width (V.steps) : 10
Minimum peak height (A) : 1.000e-010
Reverse peaks : No
Smooth factor : 4
Eliminate spikes : Yes
  
```

Substances

```

-----
Cu : -0.270 V +/- 0.050 V

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

Copper : Final result (Cu) =
        Conc * (15 / 10) * (1e+006 / 1) + 0 - 0

Sb/Bi : -0.160 V +/- 0.050 V

Standard solution : 2 1.000 mg/L
Addition volume (mL) : 0.050

Antimony/Bismuth : Final result (Sb/Bi) =
                  Conc * (15 / 10) * (1e+006 / 1) + 0 - 0
  
```

Baseline

```

-----
Substance Addition automatic start (V) end (V) type scope
-----
Cu Sample yes --- --- linear wholePeak
  Addition 1 yes --- --- linear wholePeak
  Addition 2 yes --- --- linear wholePeak
-----
Sb/Bi Sample yes --- --- linear wholePeak
  Addition 1 yes --- --- linear wholePeak
  Addition 2 yes --- --- linear wholePeak
-----
  
```

Report for the example determination of Sb, Bi and Cu in tap water according to method 3

```

===== METROHM 797 VA COMPUTRACE (Version 1.0.0.1) (Serial No. 0) =====
Determination : 08161516_SbBi tap water.dth
Sample ID      : SbBi tap water
Creator method :                               Date :                               Time:
Creator determ.:                               Date : 2000-08-16           Time: 15:16:45
Modified by    :                               Date : 2017-07-13           Time: 13:36:30
  
```

```

-----
Method      : AB74_3_Det of Sb Bi.mth
Title       : Determination of Antimony and Bismuth. AB 74 part 2
Remark1     : 10 ml water + 0.6 ml HCl (30%)
Remark2     :
  
```

```

-----
Sample amount : 10.000 mL
Cell volume   : 10.600 mL
  
```

```

-----
Substance    : Sb(III)
Conc.        : 2.828 ug/L
Conc.dev.    : 0.073 ug/L      ( 2.57%)
Amount       : 29.981 ng
Add.amount   : 50.000 ng
  
```

| VR | V | nA | I.mean | Std.Dev. | I.delta | Comments |
|-------|--------|-------|--------|----------|---------|----------|
| 1 - 1 | -0.117 | 8.22 | 8.20 | 0.031 | 0.00 | |
| 1 - 2 | -0.117 | 8.18 | | | | |
| 2 - 1 | -0.114 | 22.31 | 22.09 | 0.311 | 13.89 | |
| 2 - 2 | -0.114 | 21.87 | | | | |
| 3 - 1 | -0.114 | 35.13 | 35.07 | 0.080 | 12.98 | |
| 3 - 2 | -0.114 | 35.02 | | | | |

```

Substance    : Bi
Conc.        : 1.692 ug/L
Conc.dev.    : 0.052 ug/L      ( 3.09%)
Amount       : 17.935 ng
Add.amount   : 50.000 ng
  
```

| VR | V | nA | I.mean | Std.Dev. | I.delta | Comments |
|-------|--------|-------|--------|----------|---------|----------|
| 1 - 1 | -0.010 | 3.78 | 3.76 | 0.031 | 0.00 | |
| 1 - 2 | -0.010 | 3.74 | | | | |
| 2 - 1 | -0.010 | 14.53 | 14.47 | 0.083 | 10.71 | |
| 2 - 2 | -0.010 | 14.41 | | | | |
| 3 - 1 | -0.010 | 24.57 | 24.66 | 0.131 | 10.19 | |
| 3 - 2 | -0.010 | 24.75 | | | | |

| Substance | Calibr. | Y.reg/offset | Slope | Mean deviat. | Corr.Coeff. |
|-----------|----------|--------------|------------|--------------|-------------|
| Sb(III) | std.add. | 8.249e-009 | 2.917e-003 | 3.422e-010 | 0.99979 |
| Bi | std.add. | 3.814e-009 | 2.254e-003 | 1.960e-010 | 0.99991 |

| Final results | | +/- Res. dev. | % | Comments |
|---------------|---|---------------|-------|----------|
| Sb(III): | | | | |
| default | = | 2.998 ug/l | 0.077 | 2.572 |
| Bi: | | | | |
| default | = | 1.794 ug/l | 0.055 | 3.093 |

```

===== METROHM 797 VA COMPUTRACE (Version 1.0.0.1) (Serial No. 0) =====
Determination : 08161556_Cu tap water.dth
Sample ID      : Cu tap water
Creator method :                               Date :                               Time:
Creator determ.:                               Date : 2000-08-16           Time: 15:56:29
Modified by    : ---                           Date :                               Time:
  
```

```

-----
Method      : AB74_3_Det of Cu.mth
Title       : Determination of Copper and Antimon. AB 74 part 2
Remark1     : 10.8 ml solution Sb Bi determination + 5 ml HCl (30%)
Remark2     : contains 10 ml sample
  
```

```

-----
Sample amount : 10.000 mL
Cell volume   : 15.800 mL
  
```

```

-----
Substance    : Cu
Conc.        : 4.541 ug/L
Conc.dev.    : 0.154 ug/L      ( 3.39%)
Amount       : 68.118 ng
Add.amount   : 50.000 ng
  
```

| VR | V | nA | I.mean | Std.Dev. | I.delta | Comments |
|-------|--------|-------|--------|----------|---------|----------|
| 1 - 1 | -0.279 | 2.219 | 2.163 | 0.080 | 0.000 | |
| 1 - 2 | -0.279 | 2.106 | | | | |
| 2 - 1 | -0.279 | 3.727 | 3.705 | 0.031 | 1.542 | |
| 2 - 2 | -0.279 | 3.683 | | | | |
| 3 - 1 | -0.275 | 5.322 | 5.290 | 0.046 | 1.585 | |
| 3 - 2 | -0.275 | 5.257 | | | | |

| Substance | Calibr. | Y.reg/offset | Slope | Mean deviat. | Corr.Coeff. |
|-----------|----------|--------------|------------|--------------|-------------|
| Cu | std.add. | 2.154e-009 | 4.743e-004 | 7.231e-011 | 0.99948 |

| Final results | +/- | Res. dev. | % | Comments |
|----------------|-----|------------|-------|----------|
| Cu: default | = | 6.812 ug/l | 0.231 | 3.387 |

Method print for a determination of Sb, Bi and Cu according to method 3

===== METROHM 746 VA TRACE ANALYZER (5.746.0101) =====
 Method: AB74_2c .mth OPERATION SEQUENCE
 Title : Determination of Sb, Bi and Cu. AB 74 Method 2c

| | Instructions | t/s | Main parameters | | Auxiliary parameters | |
|----|--------------|-------|-----------------|-----------|----------------------|----------|
| 1 | SMPL>M | | V.fraction | mL | V.total | L |
| 2 | DOS>M | | Soln.name | HCl | V.add | 0.600 mL |
| 3 | PURGE | | | | | |
| 4 | STIR | 300.0 | Rot.speed | 2000 /min | | |
| 5 | (ADD | | | | | |
| 6 | PURGE | | | | | |
| 7 | STIR | 20.0 | Rot.speed | 2000 /min | | |
| 8 | OPURGE | | | | | |
| 9 | (REP | | | | | |
| 10 | SEGMENT | | Segm.name | SbBi_ASV | | |
| 11 | REP)1 | | | | | |
| 12 | PURGE | | | | | |
| 13 | ADD>M | | Soln.name | Sb_Std | V.add | 0.050 mL |
| 14 | ADD>M | | Soln.name | Bi_Std | V.add | 0.050 mL |
| 15 | ADD)2 | | | | | |
| 16 | DOS>M | | Soln.name | HCl | V.add | 5.000 mL |
| 17 | PURGE | | | | | |
| 18 | STIR | 300.0 | Rot.speed | 2000 /min | | |
| 19 | (ADD | | | | | |
| 20 | PURGE | | | | | |
| 21 | STIR | 20.0 | Rot.speed | 2000 /min | | |
| 22 | OPURGE | | | | | |
| 23 | (REP | | | | | |
| 24 | SEGMENT | | Segm.name | Cu_ASV | | |
| 25 | REP)1 | | | | | |
| 26 | PURGE | | | | | |
| 27 | ADD>M | | Soln.name | Cu_Std | V.add | 0.050 mL |
| 28 | ADD)2 | | | | | |
| 29 | END | | | | | |

Method: AB74_2c SEGMENT
 SbBi_ASV

| | 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 | 10 mV | t.meas | 20.0 ms |
| | | | t.step | 0.20 s | t.pulse | 40.0 ms |
| 4 | MEAS | 180.0 | U.meas | -240 mV | | |
| 5 | MEAS | 20.0 | U.meas | -150 mV | | |
| 6 | OSTIR | 10.0 | | | | |
| 7 | SWEEP | 18.2 | U.start | -300 mV | U.step | 4 mV |
| | | | U.end | 50 mV | Sweep rate | 20 mV/s |
| 8 | OMEAS | | U.standby | mV | | |
| 9 | END | | | | | |

Method: AB74_2c SEGMENT
 Cu_ASV

| | 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 | 10 mV | t.meas | 20.0 ms |
| | | | t.step | 0.20 s | t.pulse | 40.0 ms |
| 4 | MEAS | 180.0 | U.meas | -400 mV | | |
| 5 | OSTIR | 10.0 | | | | |
| 6 | SWEEP | 19.6 | U.start | -450 mV | U.step | 4 mV |
| | | | U.end | -70 mV | Sweep rate | 20 mV/s |
| 7 | OMEAS | | U.standby | mV | | |
| 8 | END | | | | | |