

Voltammetric analysis methods for thallium, antimony, bismuth, iron, copper and vanadium

Of interest to:

General analytical laboratories, Environmental protection, Food, Biology, Trace analysis, Galvanic industry
B 1, 2, 7, 8, 9, 10

Summary

This Bulletin describes the voltammetric trace analysis of the elements Tl, Sb, Bi, Fe, Cu and V. The limits of determination lie by 0.5 ... 1 µg/L for Sb, Bi, Fe, Cu, V and 3 µg/L for Tl.

Apparatus and accessories

- 746 VA Trace Analyzer with 747 VA Stand
- 757 VA Computrace
- Ev. 705 UV Digester (for digestions)

Reagents

These are mentioned under the individual determinations and must have the greatest possible purity. High purity water is used to prepare solutions.

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 $w(\text{H}_2\text{O}_2) = 30\%$ and 10 µL hydrochloric acid $w(\text{HCl}) = 30\%$ to 10 mL acidified sample ($\text{pH} = 2$) and irradiate for 60 minutes at 90°C.
- Samples with organic matter (foods, pharmaceuticals etc.) must be digested.
 - High-pressure asher
 - Microwave digestionBoth techniques oxidise 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 Tl

Principle

Thallium is determined in acetate buffer $\text{pH} = 4.6$ at the HMDE by anodic stripping voltammetry (ASV). Cd and Pb, which interfere, are masked by addition of EDTA. Make sure that the EDTA excess is not too large, otherwise copper will interfere, particularly if present in large amounts.

Reagents

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

- Ammonia solution, suprapur, $w(\text{NH}_3) = 25\%$
- Acetic acid, suprapur, $w(\text{CH}_3\text{COOH}) = 100\%$
- EDTA- Na_2 dihydrate, p.a., CAS 6381-92-6
- Thallium standard stock solution: $\beta(\text{Tl}^+) = 1 \text{ g/L}$ Commercially available.

Ready-to-use solutions:

Acetate buffer pH 4.6	$c(\text{CH}_3\text{COOH}) = 2 \text{ mol/L}$ + $c(\text{NH}_3) = 1 \text{ mol/L}$
	800 mL ultrapure water are mixed with 113.6 mL acetic acid and 74.6 mL ammonia solution. After cooling to room temperature the solution is filled up to 1000 mL.
EDTA solution	$c(\text{EDTA-Na}_2) = 0.1 \text{ mol/L}$
	3.72 g EDTA-Na ₂ werden in 100 mL Reinstwasser gelöst.
Tl standard solution	$\beta(\text{Tl}^+) = 1 \text{ mg/L}$
	The solution is diluted with $c(\text{HNO}_3) = 0.015 \text{ mol/L}$ and stored in plastic bottles. It is stable for max. 1 week.

Analysis

10 mL (diluted) sample solution
 + 0.1 mL EDTA solution
 + 0.1 mL acetate buffer

If necessary, adjust the pH value to 4.6 with ammonia.

The measuring vessel should contain between 30 ng and 500 ng Tl.

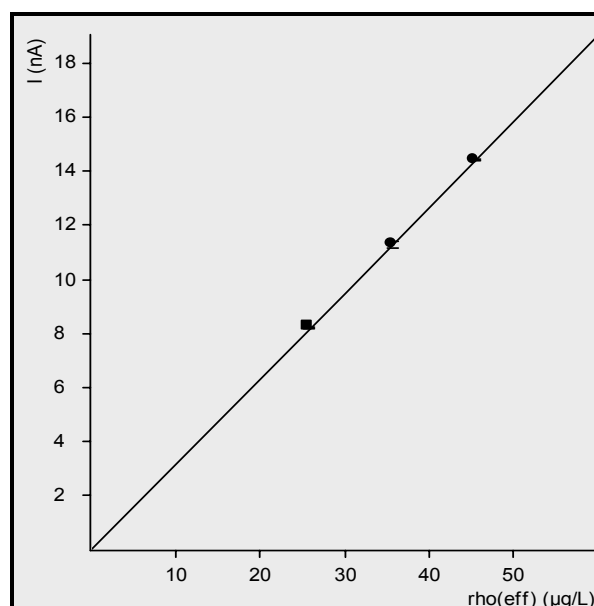
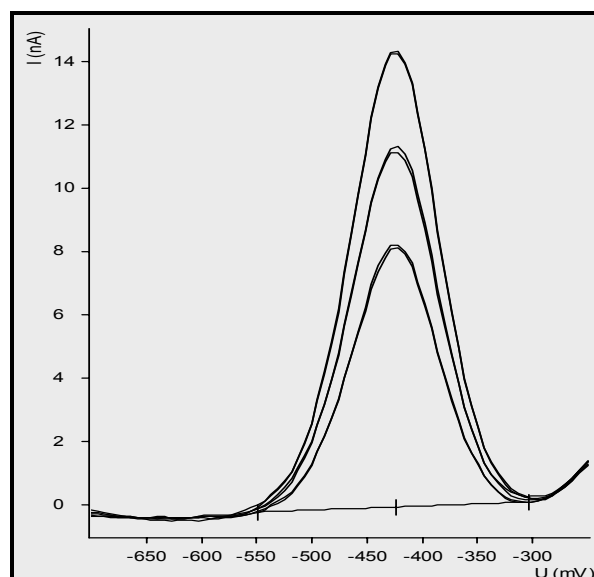
The voltammogramm is recorded using following parameters:

working electrode	HMDE
drop size	7
stirrer speed	2000 rpm
mode	DP
purge time	300 s
deposition potential	-700 mV
deposition time	60 s
equilibration time	5 s
pulse amplitude	50 mV
start potential	-700 mV
end potential	-250 mV
voltage step	6 mV
voltage step time	0.3 s
sweep rate	20 mV/s
peak potential	-430 mV

The concentration is determined by 2 standard additions.

Example:

Determination of thallium in water



Sample volume 10 mL

Result 26.4 µg/L Tl

Remarks

- If a great excess of Pb and Cd is present, it is possibly necessary to add more EDTA (up to 1 mL).
- Large excess of Cu makes the determination of thallium impossible. The Cu-EDTA peak is located close to the thallium signal. With high copper concentrations the Tl peak is vanishing in the slope of the Cu-EDTA peak.

Literature

- DIN 38406, part 16

Appendix

Full Report of a determination of thallium with the 746 VA Trace Analyzer

```

===== METROHM 746 VA TRACE ANALYZER (5.746.0100) =====
Determ.      : 09270753          User:          Date: 99-09-27
Modified     : no                Run : 2          Time: 07:53:09
Sample table: -
    
```

Pos.	Ident.1/S1	Ident.2/S2	Ident.3/S3	Method.call	Sample size/S0
	Tl-detAB74				10 mL

```

-----
Method : AB74_1Tl
Title  : Determination of Thallium according to AB74
Remark1:
Remark2:
    
```

Substance	Techn.	Y.reg/offset	Slope	Nonlin.	Mean deviat.
Thallium	std.add.	8.196e-09	3.168e-04		6.481e-11

```

-----
Substance : Thallium
Mass conc.: 26.39 ug/L
MC.dev.   : 0.443 ug/L (1.68%)
Cal.dev.  : -
Mass      : 263.9 ng
Add.mass  : 100 ng
V0.sample: 10 mL
    
```

VR	U/mV	I/nA	I.mean	Std.dev.	I.delta	Comments
00	-423	8.183	8.205	0.0303		
01	-424	8.226				
10	-423	11.25	11.17	0.1143	2.969	
11	-425	11.09				
20	-424	14.11	14.14	0.0388	2.966	
21	-424	14.17				

```

-----
Final results
-----
Thallium = 26.392 ug/L +/- Res.dev. 0.443 % 1.68
    
```

Method print of a determination of thallium with the 746 VA Trace Analyzer

```

===== METROHM 746 VA TRACE ANALYZER (5.746.0101) =====
Method: AB74_1 .mth          OPERATION SEQUENCE
Title : Determination of Thallium. AB 74 Method 1
    
```

Instructions	t/s	Main parameters	Auxiliary parameters
1 SMPL>M		V.fraction mL	V.total L
2 DOS>M		Soln.name EDTA	V.add 0.100 mL
3 DOS>M		Soln.name NH4acBuf	V.add 0.100 mL
4 PURGE			
5 STIR	300.0	Rot.speed 2000 /min	
6 (ADD			
7 (REP			
8 PURGE			
9 STIR	30.0	Rot.speed 2000 /min	
10 SEGMENT		Segm.name Tl_ASV	
11 REP)1			
12 ADD>M		Soln.name std-Tl	V.add 0.100 mL
13 ADD)2			
14 END			

```

-----
Method: AB74_1          SEGMENT
                        Tl_ASV
    
```

Instructions	t/s	Main parameters	Auxiliary parameters
1 OPURGE	5.0		
2 HMDE		Drop size 7	Meas.cell normal
3 DPMode		U.ampl 50 mV	t.meas 20.0 ms
		t.step 0.30 s	t.pulse 40.0 ms
4 MEAS	60.0	U.meas -700 mV	
5 OSTIR	5.0		
6 SWEEP	23.4	U.start -700 mV	U.step 6 mV
		U.end -250 mV	Sweep rate 20 mV/s
7 OMEAS		U.standby mV	
8 END			

Method 2

Determination of Sb, Bi and Cu

Principle

Antimony and bismuth can be determined in HCl at the HMDE by anodic stripping voltammetry (ASV). Simultaneous determination is possible in HCl 0.6 mol/L, but Cu interferes with the Sb determination. This interference can be eliminated by post-electrolysis.

Copper can be determined in $w(\text{HCl}) = 10\%$. If only antimony or bismuth is present the determination besides copper is possible in $w(\text{HCl}) = 10\%$. If both metals are present the determination is not possible because under these conditions both substances appear at the same half wave potential.

Peak potentials

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

Reagents

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

- Hydrochloric acid, suprapur, $w = 0.3$ (30%)
- 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.

Ready-to-use solutions:

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

Method 2a: Determination of Sb and Bi

Analysis

10 mL (diluted) sample solution
 + 0.6 mL hydrochloric acid

The measuring vessel should contain between 10 ng and 1 μg Sb and Bi each.

The voltammogram is recorded using following parameters:

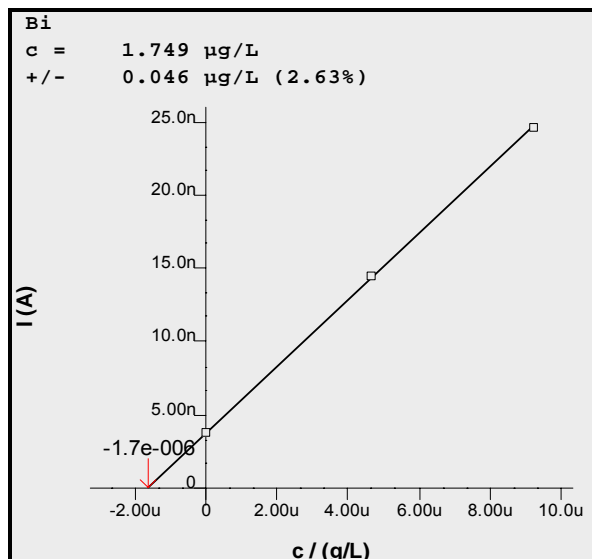
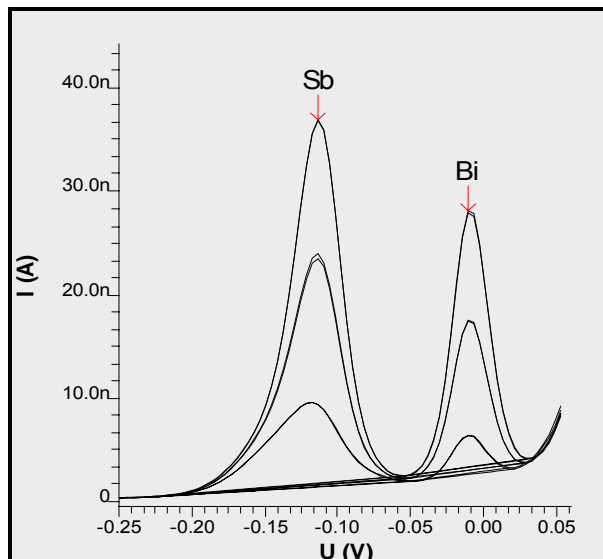
working electrode	HMDE
drop size	4
stirrer speed	2000 rpm
mode	DP
purge time	300 s
deposition potential (cleaning potential)	-240 mV
deposition time (cleaning time)	180 s
post electrolysis potential (deposition potential)	-150 mV

post electrolysis time (deposition time)	20 s
equilibration time	10 s
pulse amplitude	10 mV
start potential	-300 mV
end potential	50 mV
voltage step	4 mV
voltage step time	0.2 s
sweep rate	20 mV/s
peak potential (Sb)	-110 mV
peak potential (Bi)	-10 mV

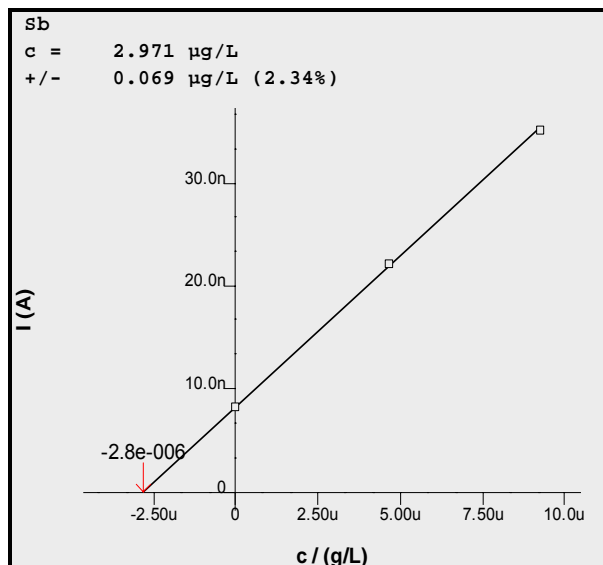
The concentration is determined by 2 standard additions.

Example:

Determination of antimony and bismuth in tap water



Sample volume 10 mL
 Results 3.0 µg/L Sb
 1.8 µg/L Bi



Remarks

- To obtain a better peak shape it is recommended to apply a pulse amplitude of only 10 mV.
- 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 sulphate to cover the tip of a spatula). In this way it is also possible to speciate between both oxidation states.
- In w(HCl) = 10% the sum Sb(III) + Sb(V) is determined (refer to method 2b).

Appendix

Full Report of a determination of Sb and Bi with the 757 VA Computrace

```

===== METROHM 757 VA COMPUTRACE (5.757.0020) =====
Determ.      : 08161516_SbBi tap water.dth
Sample ID    : SbBi tap water
Creator      : ---
Modified by  :
User         :
Date        : 2000-08-16
Date        : 2001-06-21
Date        : 2001-06-21
Time        : 15:16:45
Time        : 14:41:24
Time        : 14:41:24
-----
Cell volume: 10.600 mL
Sample amount: 10.000 mL
-----
Method      : AB74_2_Det of Sb Bi.mth
Title       : Determination of Antimony and Bismuth. AB 74 Method 2a
Remark1     : 10 ml water + 0.6 ml HCl (30%)
Remark2     :
-----
Substance   : Sb
Mass conc.  : 2.803 ug/L
MC.dev.     : 0.066 ug/L ( 2.34%)
Mass        : 29.712 ng
Comments    :
    
```

Add.mass : 50.000 ng						
VR	V	nA	I.mean	Std.Dev.	I.delta	Comments
1-1	-0.117	8.22	8.20	0.050		
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						
Mass conc.: 1.650 ug/L						
MC.dev. : 0.043 ug/L (2.63%)						
Mass : 17.491 ng						
Add.mass : 50.000 ng						
VR	V	nA	I.mean	Std.Dev.	I.delta	Comments
1-1	-0.010	3.76	3.72	0.061		
1-2	-0.010	3.67				
2-1	-0.010	14.49	14.45	0.060	10.74	
2-2	-0.010	14.41				
3-1	-0.010	24.57	24.66	0.131	10.21	
3-2	-0.010	24.75				
Substance	Calibr.	Y.reg/offset	Slope	Std.Dev.		
Sb	std.add.	8.241e-009	2.940e-003	5.000e-011		
Bi	std.add.	3.758e-009	2.278e-003	6.041e-011		
Final results			+/- Res. dev.	%	Comments	
Sb:						
Antimony	=	2.971 ug/L	0.069	2.337		
Bi:						
Bismuth	=	1.749 ug/L	0.046	2.628		

Method print of a determination of Sb and Bi with the 746 VA Trace Analyzer

```

===== METROHM 746 VA TRACE ANALYZER (5.746.0101) =====
Method: AB74_2a .mth OPERATION SEQUENCE
Title : Determination of Sb and Bi. AB 74 Method 2a
=====

```

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 END				

```

Method: AB74_2a 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 2b: Determination of Cu besides Sb or Bi

Analysis

10 mL (diluted) sample solution
 + 5 mL hydrochloric acid

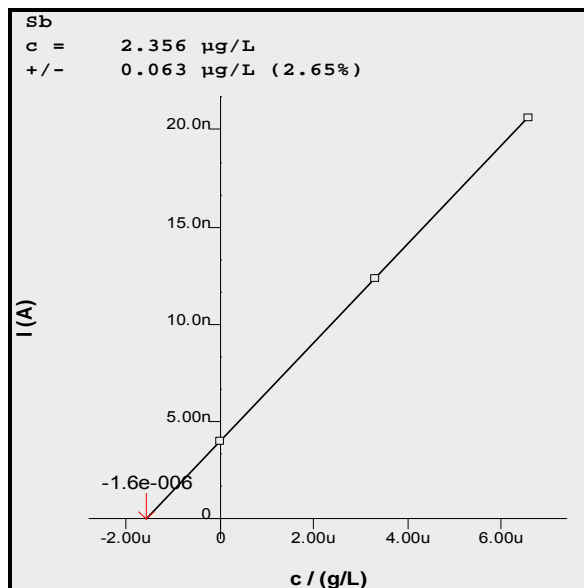
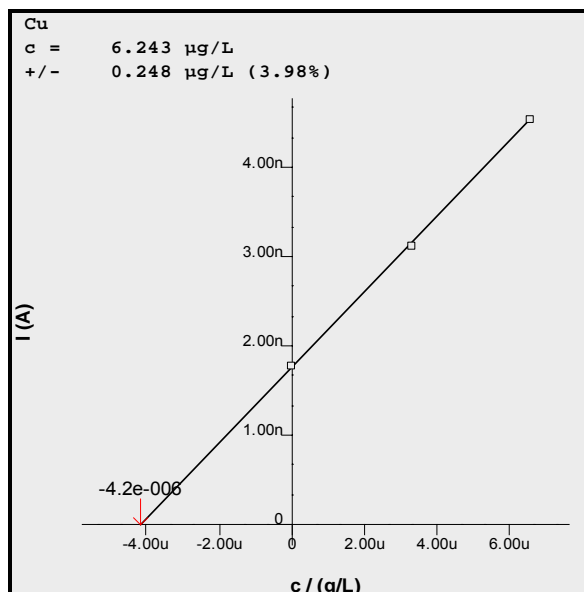
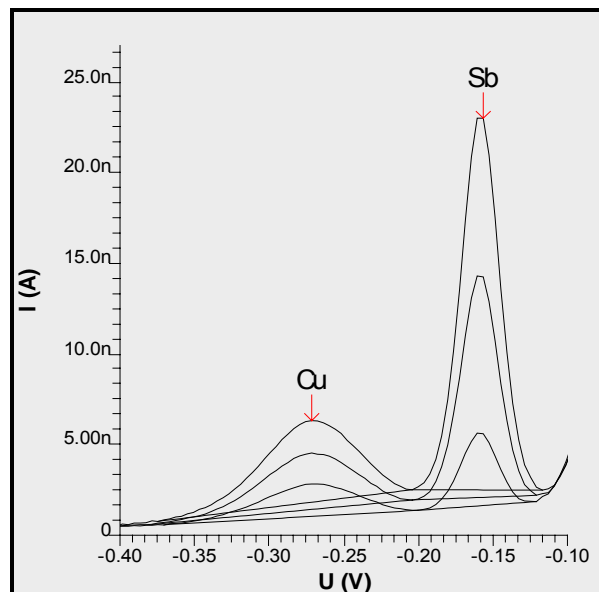
The voltammogram is recorded using following parameters:

working electrode	HMDE
drop size	4
stirrer speed	2000 rpm
mode	DP
purge time	300 s
deposition potential	-400 mV
deposition time	180 s
equilibration time	10 s
pulse amplitude	10 mV
start potential	-450 mV
end potential	-70 mV
voltage step	4 mV
voltage step time	0.2 s
sweep rate	20 mV/s
peak potential (Cu)	-270 mV
peak potential (Sb/Bi)	-160 mV

The concentration is determined by 2 standard additions.

Example:

Determination of copper and antimony In water



Sample volume 10 mL

Results 6.2 µg/L Cu

2.4 µg/L Sb

Remarks

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

Appendix

Full Report of a determination of Sb and Cu with the 757 VA Computrace

```

===== METROHM 757 VA COMPUTRACE (5.757.0020) =====
Determ.      : 08141708_CuSb 10mV.dth
Sample ID    : CuSb 10mV
Creator      : ---
Modified by  : ---
User         : ---
Date        : 2000-08-14
Date        : 2001-06-21
Date        : 2001-06-21
Time        : 17:08:32
Time        : 15:44:38
Time        : 15:44:38
-----
Cell volume: 15.000 mL
Sample amount: 10.000 mL
-----
Method      : AB74_2b_Det of Cu Sb.mth
Title       : Determination of Copper and Antimon. AB 74 Method 2b
Remark1    : 10 ml sample + 5 ml HCl (30%)
Remark2    :
-----
Substance   : Cu
Mass conc.  : 4.162 ug/L
MC.dev.     : 0.166 ug/L ( 3.98%)
Mass        : 62.429 ng
Add.mass    : 50.000 ng
-----
          VR      V      nA      I.mean  Std.Dev.  I.delta  Comments
          ---      ---      ---      ---      ---      ---      ---
          1-1    -0.271  1.763  1.773   0.050
          1-2    -0.275  1.783
          2-1    -0.275  3.109  3.114   0.050   1.340
          2-2    -0.271  3.118
          3-1    -0.271  4.506  4.529   0.050   1.415
          3-2    -0.275  4.551
-----
Substance   : Sb
Mass conc.  : 1.571 ug/L
MC.dev.     : 0.042 ug/L ( 2.65%)
Mass        : 23.561 ng
Add.mass    : 50.000 ng
-----
          VR      V      nA      I.mean  Std.Dev.  I.delta  Comments
          ---      ---      ---      ---      ---      ---      ---
          1-1    -0.160  3.95   3.98   0.050
          1-2    -0.160  4.01
          2-1    -0.160  12.47  12.35   0.178   8.37
          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      Std.Dev.
-----
Cu          std.add.      1.758e-009      4.223e-004  4.780e-011
Sb          std.add.      3.980e-009      2.534e-003  4.998e-011
-----
Final results      +/- Res. dev.  %      Comments
-----
Cu:
Copper            =      6.243  µg/L      0.248      3.979
Sb:
Antimony          =      2.356  µg/L      0.063      2.655
    
```

Method print of a determination of Sb and Cu with the 746 VA Trace Analyzer

```

===== METROHM 746 VA TRACE ANALYZER (5.746.0101) =====
Method: AB74_2b .mth OPERATION SEQUENCE
Title : Determination of Cu and Sb or Bi. AB74 Method 2b
-----
Instructions      t/s      Main parameters      Auxiliary parameters
-----
1  SMPL>M          V.fraction      mL      V.total      L
2  DOS>M          Soln.name      HCl      V.add      5.000 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      CuSb_ASV
    
```

```

11      REP)1
12      PURGE
13      ADD>M          Soln.name   Cu_Std          V.add           0.050 mL
14      ADD>M          Soln.name   Sb_Std          V.add           0.050 mL
15      ADD)2
16      END

Method: AB74_2b          SEGMENT
                        CuSb_ASV
-----
Instructions   t/s   Main parameters           Auxiliary parameters
-----
1  STIR         5.0   Rot.speed                2000 /min
2  HMDE         5.0   Drop size                 4
3  DP MODE      5.0   U.ampl                   10 mV
                        t.step                 0.20 s
                        U.meas                 -400 mV
4  MEAS        180.0
5  OSTIR       10.0
6  SWEEP       19.6   U.start                  -450 mV
                        U.end                  -70 mV
                        U.step                 4 mV
                        Sweep rate            20 mV/s
7  OMEAS
8  END
    
```

Method 2c: Determination of Sb, Bi and Cu

Analysis

Determination of Sb, Bi:

10 mL (diluted) sample solution
 + 0.6 mL hydrochloric acid

The voltammogram is recorded using following parameters:

working electrode	HMDE
drop size	4
stirrer speed	2000 rpm
mode	DP
purge time	300 s
deposition potential (cleaning potential)	-240 mV
deposition time (cleaning time)	180 s
post electrolysis potential (deposition potential)	-150 mV
post electrolysis time (deposition time)	20 s
equilibration time	10 s
pulse amplitude	10 mV
start potential	-300 mV
end potential	50 mV
voltage step	4 mV
voltage step time	0.2 s
sweep rate	20 mV/s
peak potential (Sb)	-110 mV
peak potential (Bi)	-10 mV

The concentration is determined by 2 standard additions.

Following, Determination of Cu:

Measuring solution of the determination Sb, Bi
 + 5 mL hydrochloric acid

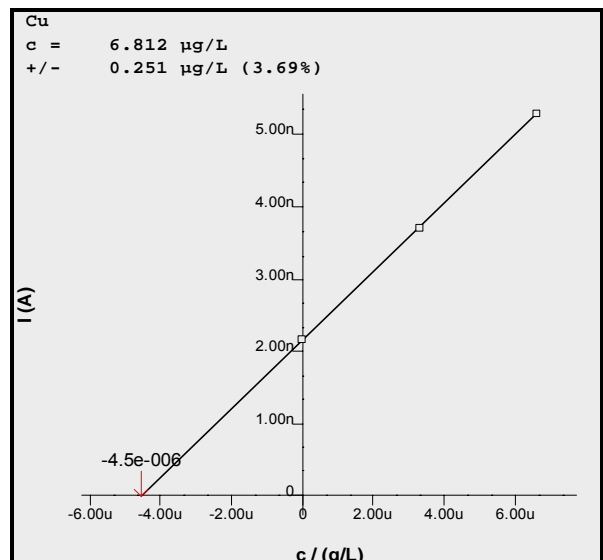
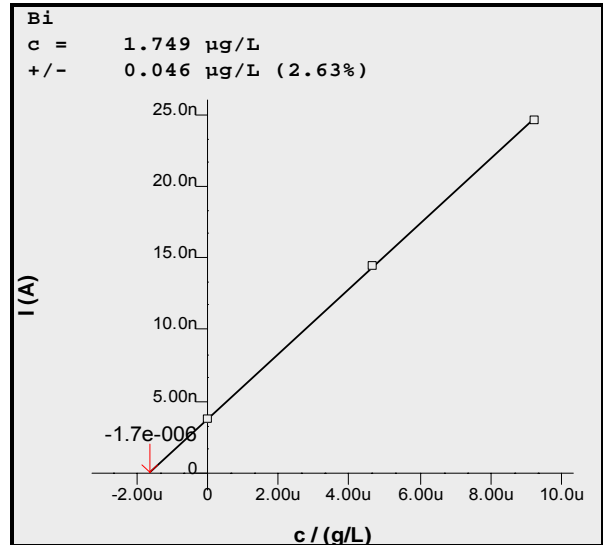
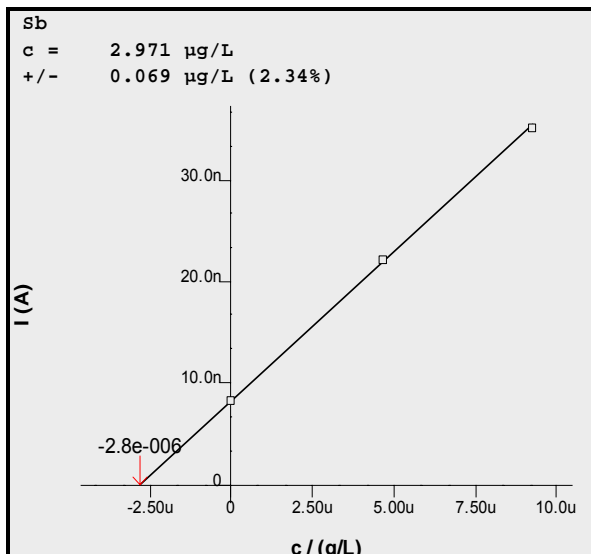
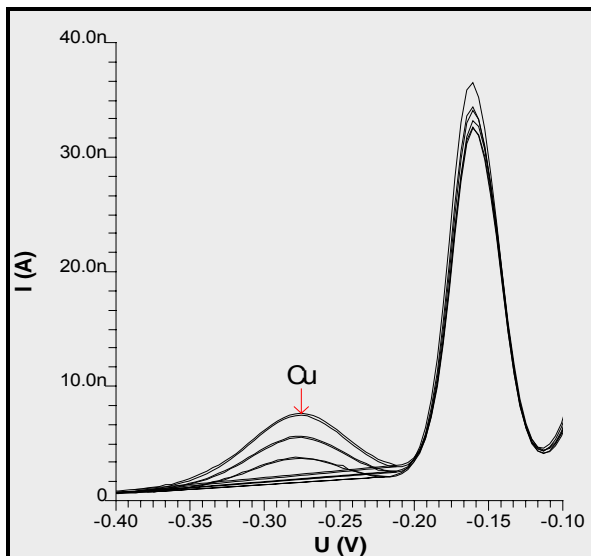
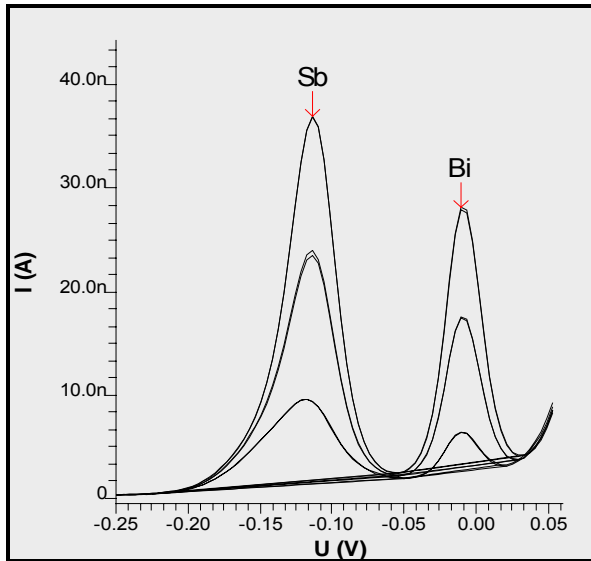
The voltammogram is recorded using following parameters:

working electrode	HMDE
drop size	4
stirrer speed	2000 rpm
mode	DP
purge time	300 s
deposition potential	-400 mV
deposition time	180 s
equilibration time	10 s
pulse amplitude	10 mV
start potential	-450 mV
end potential	-70 mV
voltage step	4 mV
voltage step time	0.2 s
sweep rate	20 mV/s
peak potential (Cu)	-270 mV

The concentration is determined by 2 standard additions.

Example:

Determination of Sb, Bi and Cu in tap water



Sample volume 10 mL

Results 3.0 $\mu\text{g/L}$ Sb

1.8 $\mu\text{g/L}$ Bi

6.8 $\mu\text{g/L}$ Cu

Remarks

- 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 sulphate to cover the tip of a spatula). In this way it is also possible to speciate between both oxidation states.
- By combination of method 2a and 2b 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

Full Report of a determination of Sb, Bi and Cu in tap water with the 757 VA Computrace

Determination of Sb and Bi

```

===== METROHM 757 VA COMPUTRACE (5.757.0020) =====
Determ.      : 08161516_SbBi tap water.dth
Sample ID    : SbBi tap water
Creator      : ---                      Date : 2000-08-16      Time: 15:16:45
Modified by  : ---                      Date : 2001-06-21      Time: 14:41:24
User        : ---                      Date : 2001-06-21      Time: 14:41:24
-----
Cell volume: 10.600 mL
Sample amount: 10.000 mL
-----
Method      : AB74_2_Det of Sb Bi.mth
Title       : Determination of Antimony and Bismuth. AB 74 Method 2a
Remark1     : 10 ml water + 0.6 ml HCl (30%)
Remark2     :
-----
Substance   : Sb                               Comments
Mass conc.  : 2.803 ug/L
MC.dev.     : 0.066 ug/L      ( 2.34%)
Mass        : 29.712 ng
Add.mass    : 50.000 ng
-----
          VR      V      nA      I.mean  Std.Dev.  I.delta  Comments
          ---      ---      ---      ---      ---      ---      ---
          1-1     -0.117  8.22   8.20    0.050
          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                               Comments
Mass conc.  : 1.650 ug/L
MC.dev.     : 0.043 ug/L      ( 2.63%)
Mass        : 17.491 ng
Add.mass    : 50.000 ng
-----
          VR      V      nA      I.mean  Std.Dev.  I.delta  Comments
          ---      ---      ---      ---      ---      ---      ---
          1-1     -0.010  3.76   3.72    0.061
          1-2     -0.010  3.67
          2-1     -0.010  14.49  14.45   0.060   10.74
          2-2     -0.010  14.41
          3-1     -0.010  24.57  24.66   0.131   10.21
          3-2     -0.010  24.75
-----
Substance   Calibr.      Y.reg/offset      Slope      Std.Dev.
-----
          Sb      std.add.      8.241e-009      2.940e-003  5.000e-011
          Bi      std.add.      3.758e-009      2.278e-003  6.041e-011
-----
Final results
-----
          +/- Res. dev.  %      Comments
-----
Sb:
Antimony    =      2.971 ug/L      0.069      2.337
Bi:
Bismuth     =      1.749 ug/L      0.046      2.628
    
```

Determination of Cu

```

===== METROHM 757 VA COMPUTRACE (5.757.0020) =====
Determ.      : 08161556_Cu tap water.dth
Sample ID    : Cu tap water
Creator      : ---                      Date : 2000-08-16      Time: 15:56:29
Modified by  : ---                      Date : 2001-06-21      Time: 16:09:54
User        : ---                      Date : 2001-06-21      Time: 16:09:54
-----
Cell volume: 15.000 mL
Sample amount: 10.000 mL
-----
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     :
-----
Substance   : Cu                               Comments
Mass conc.  : 4.541 ug/L
MC.dev.     : 0.167 ug/L      ( 3.69%)
Mass        : 68.118 ng
Add.mass    : 50.000 ng
    
```

	VR	V	nA	I.mean	Std.Dev.	I.delta	Comments
	1-1	-0.279	2.219	2.163	0.080		
	1-2	-0.279	2.106				
	2-1	-0.279	3.727	3.705	0.050	1.542	
	2-2	-0.279	3.683				
	3-1	-0.275	5.322	5.290	0.050	1.585	
	3-2	-0.275	5.257				
Substance	Calibr.	Y.reg/offset	Slope	Std.Dev.			
Cu	std.add.	2.154e-009	4.743e-004	6.493e-011			
Final results				+/- Res. dev.	%	Comments	
Cu: Copper	=	6.812 µg/L	0.251	3.688			

Method print of a determination of Sb, Bi and Cu with the 746 VA Trace Analyzer

```

===== 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
2	DOS>M		Soln.name	HCl
3	PURGE			V.total
4	STIR	300.0	Rot.speed	2000 /min
5	(ADD			V.add
6	PURGE			0.600 mL
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
14	ADD>M		Soln.name	Bi_Std
15	ADD)2			V.add
16	DOS>M		Soln.name	HCl
17	PURGE			V.add
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
28	ADD)2			V.add
29	END			0.050 mL

```

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
3	DPMODE		U.ampl	10 mV
			t.step	0.20 s
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.end	50 mV
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
3	DPMODE		U.ampl	10 mV
			t.step	0.20 s
4	MEAS	180.0	U.meas	-400 mV
5	OSTIR	10.0		
6	SWEEP	19.6	U.start	-450 mV
			U.end	-70 mV
7	OMEAS		U.standby	mV
8	END			

Method 3

Determination of Fe, Cu and V

Principle

Iron can be determined with extreme sensitivity as catechol complex at the HMDE by adsorptive stripping voltammetry (AdSV). For amounts above 100 ng in the polarographic vessel, standard additions are not longer linear. Then, either the amount of the sample must be reduced or a DP-polarographic analysis performed on the SMDE. Fe(II) and Fe(III) are determined collectively. Using this method, purity of the applied reagents is of utmost importance. Small concentrations of surface-active substances (detergents, organic complexing agents such as humic acids etc.) are also very interfering. These must be destroyed before beginning the analysis (see "Sample Preparation").

Reagents

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

- Sodium hydroxide solution, suprapur, $w(\text{NaOH}) = 30\%$
- Ammonia solution, suprapur, $w(\text{NH}_3) = 25\%$
- Catechol (pyrocatechol, 1,2-dihydroxybenzene), CAS 120-80-9
Purest catechol is achieved by means of sublimation. Pyrocatechol Fluka Nr. 15890 can be applied directly.
- PIPES, Piperazine-1,4-bis-2-ethane sulfonic acid, CAS 5625-37-6
- Iron standard stock solution: $\beta(\text{Fe}^{3+}) = 1 \text{ g/L}$
Commercially available.
- Copper standard stock solution: $\beta(\text{Cu}^{2+}) = 1 \text{ g/L}$
Commercially available.
- Vanadium standard stock solution: $\beta(\text{V}^{5+}) = 1 \text{ g/L}$
Commercially available.

Ready-to-use solutions:

PIPES buffer	$c(\text{PIPES}) = 1 \text{ mol/L}$ Mix 6.05 g PIPES with 1 mL sodium hydroxide solution and a little high purity water. Adjust the pH value to 8.0 with ammonia solution and fill up to 20 mL with high purity water. This buffer does not contain any Fe.
Catechol solution	$c(\text{Catechol}) = 1 \text{ mol/L}$ Dissolve 2.75 g catechol in 25 mL oxygen-free high purity water, which had been degassed by purging with nitrogen. Store the solution in a tightly closed dark bottle. Stability of the solution depends on the purity of the used brencatechine and can vary from 1 day to 1 month. The solution must rest for a few hours before use.
Ammonia solution diluted	$w(\text{NH}_3) = 10\%$
Iron standard solution	$\beta(\text{Fe}^{3+}) = 1 \text{ mg/L}$
Copper standard solution	$\beta(\text{Cu}^{2+}) = 1 \text{ mg/L}$
Vanadium standard solution	$\beta(\text{V}^{5+}) = 1 \text{ mg/L}$
	The solutions are diluted with $c(\text{HNO}_3) = 0.015 \text{ mol/L}$. They are stable for max. 1 week.

Method 3a: Determination of Fe

Analysis

10 mL acidified (diluted) sample
+ 0.05 mL catechol solution
+ 0.250 mL PIPES buffer

If necessary, adjust the pH value to 7.0 ± 0.1 with $w(\text{NH}_3) = 10\%$.

The measuring vessel should contain at least 10 but not more than 100 ng Fe.

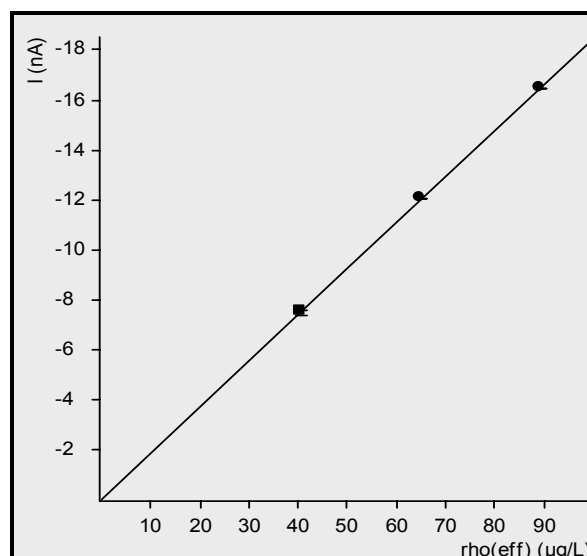
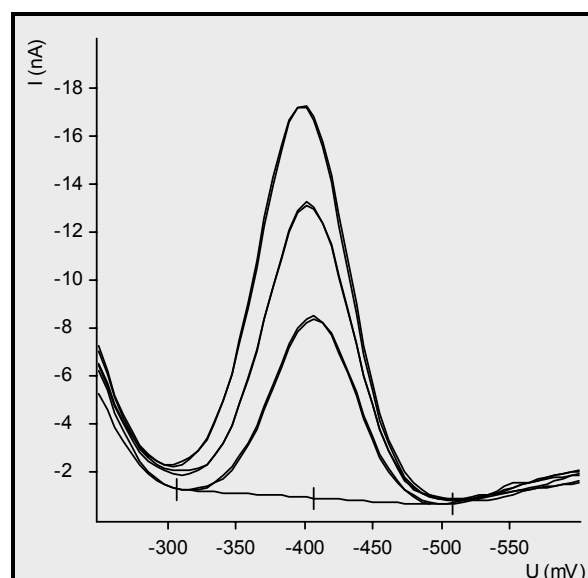
The voltammogram is recorded using following parameters

working electrode	HMDE
drop size	7
stirrer speed	2000 rpm
mode	DP
purge time	300 s
deposition potential	-250 mV
deposition time	60 s
equilibration time	5 s
pulse amplitude	50 mV
start potential	-250 mV
end potential	-600 mV
voltage step	6 mV
voltage step time	0.1 s
sweep rate	60 mV/s
peak potential Fe	-400 mV

The concentration is determined by 2 standard additions.

Example:

Determination of iron in water



Sample volume 10 mL

Results 41.9 µg/L Fe

Remarks

- If the total ion concentration is very high (e.g. sea water), the iron determination is much less sensitive and only relatively small peaks are achieved. Linear standard addition curves are achieved, however, with proportionally large standard additions and a reduction of the enrichment time.
- Catechol should be added to the acidic sample solution before the buffer is added. Otherwise iron may form hydroxo complexes, which cannot be determined any more. This results in low recovery rates.
- The peak potential of Fe is strongly dependent on the exact pH value and the sample matrix and may have to be adjusted.

Literature

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- Huang Z.Q., Van den Berg C.M.G.
Determination of iron in seawater using cathodic stripping voltammetry preceded by adsorptive collection with the hanging mercury drop electrode.
J. Electroanal. Chem. 177, (1984) 269-280
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- Weidenauer M., Lieser K.H.
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Fresenius, Z. Anal. Chem. 320, (1985) 550-555
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 Chelate adsorption of trace voltammetric measurements of iron(III).
Fresenius, Z. Anal., Chem. 327, (1987) 789-793

Appendix

Full Report of the determination of Fe with the 746 VA Trace Analyzer

```

===== METROHM 746 VA TRACE ANALYZER (5.746.0100) =====
Determ.      : 09291112          User:          Date: 99-09-29
Modified     : no                Run : 1          Time: 11:12:16
Sample table: -
-----
  Pos.  Ident.1/S1  Ident.2/S2  Ident.3/S3  Method.call  Sample size/S0
-----
      AB74FeSeawat  Sea Water
-----
Method      : Ab74_3
Title       : Determination of Iron
Remark1     : 10 ml sample + 50 µl catechol + 250 µl buffer --> pH 7.0
Remark2     :
-----
Substance   : Fe
Mass conc.  : 41.94 ug/L          Mass          : 419.4 ng
MC.dev.     : 0.573 ug/L (1.37%) Add.mass      : 250 ng
Cal.dev.    : -                  V0.sample    : 10 mL
-----
          VR    U/mV    I/nA    I.mean  Std.dev.  I.delta  Comments
          ---    ---    ---    ---    ---    ---    -----
          00   -406   -7.561  -7.489   0.1006
          01   -407   -7.418
          10   -403  -11.76  -11.75   0.0127  -4.258
          11   -403  -11.74
          20   -398  -15.67  -15.68   0.0139  -3.934
          21   -400  -15.69
-----
Substance   Techn.      Y.reg/offset  Slope          Nonlin.      Mean deviat.
-----
Fe          std.add.    -7.511e-09   -1.845e-04    -----      6.494e-11
-----
Final results          +/- Res.dev.  %          Comments
-----
Fe = 41.935 ug/L      0.573     1.37
  
```

Method print of a determination of Fe with the 746 VA Trace Analyzer

```

===== METROHM 746 VA TRACE ANALYZER (5.746.0101) =====
Method: AB74_3a.mth          OPERATION SEQUENCE
Title : Determination of Fe. AB 74 Method 3a
-----
Instructions  t/s  Main parameters          Auxiliary parameters
-----
1  SMPL>M          V.fraction          mL  V.total          L
2  DOS>M          Soln.name          Catechol          V.add          0.050 mL
3  DOS>M          Soln.name          Buffer              V.add          0.250 mL
4  PURGE
5  STIR           300.0  Rot.speed          2000 /min
6  (ADD
7  PURGE
8  STIR           60.0   Rot.speed          2000 /min
9  OPURGE
10 (REP
11 SEGMENT        Segm.name          Fe_AdSV
12 REP)1
13 PURGE
14 ADD>M          Soln.name          Fe_Std            V.add          0.250 mL
15 ADD)2
16 END
-----
Method: AB74_3a          SEGMENT
                          Fe_AdSV
-----
Instructions  t/s  Main parameters          Auxiliary parameters
-----
1  STIR           5.0   Rot.speed          2000 /min
2  HMDE           Drop size          7          Meas.cell        normal
  
```

3	DPMODE		U.ampl	-50 mV	t.meas	20.0 ms
4	MEAS	60.0	t.step	0.10 s	t.pulse	40.0 ms
5	OSTIR	5.0	U.meas	-250 mV		
6	FSWEEP	6.2	U.start	-250 mV	U.step	6 mV
7	OMEAS		U.end	-600 mV	Sweep rate	60 mV/s
8	END		U.standby	mV		

Method 3b: Determination of Fe, Cu and V

Analysis

10 mL acidified (diluted) sample
 + 0.05 mL catechol solution
 + 0.250 mL PIPES buffer

If necessary, adjust the pH value to 7.0 ± 0.1 with
 $w(\text{NH}_3) = 10\%$.

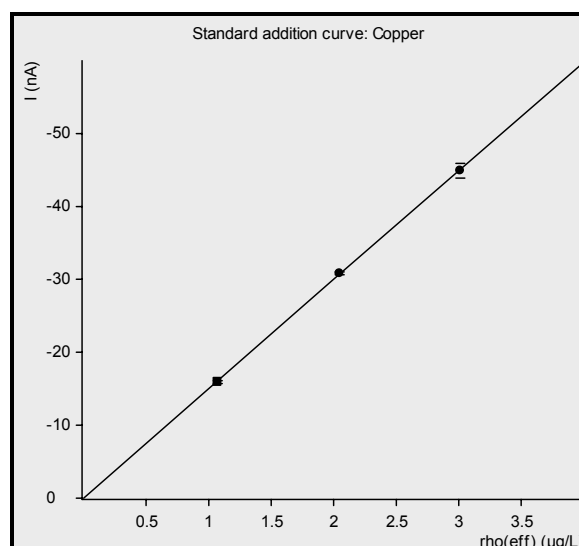
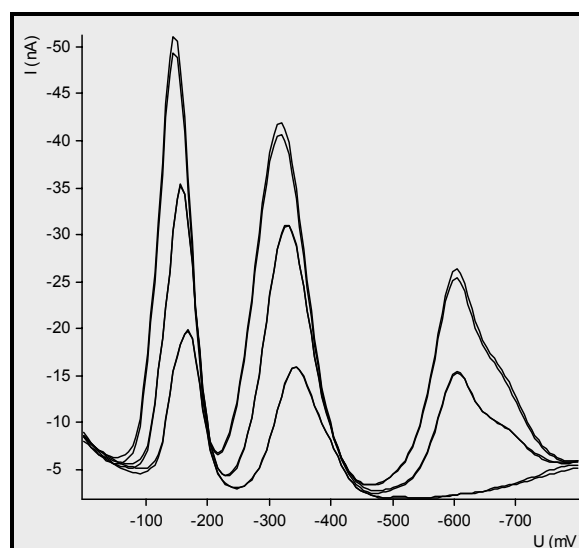
The voltammogram is recorded using following parameters

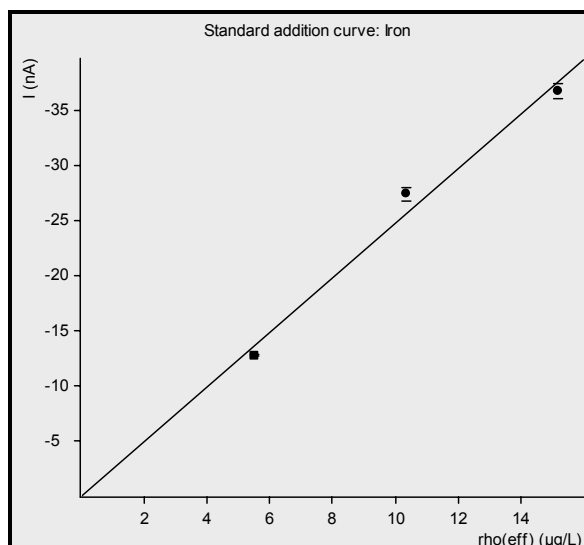
working electrode	HMDE
drop size	7
stirrer speed	2000 rpm
mode	DP
purge time	300 s
deposition potential	0 mV
deposition time	60 s
equilibration time	5 s
pulse amplitude	50 mV
start potential	0 mV
end potential	-800 mV
voltage step	6 mV
voltage step time	0.1 s
sweep rate	60 mV/s
peak potential Cu	-160 mV
peak potential Fe	-340 mV
peak potential V	-600 mV

The concentration is determined by 2 standard additions.

Example:

Determination of Cu, Fe and V in salt solution

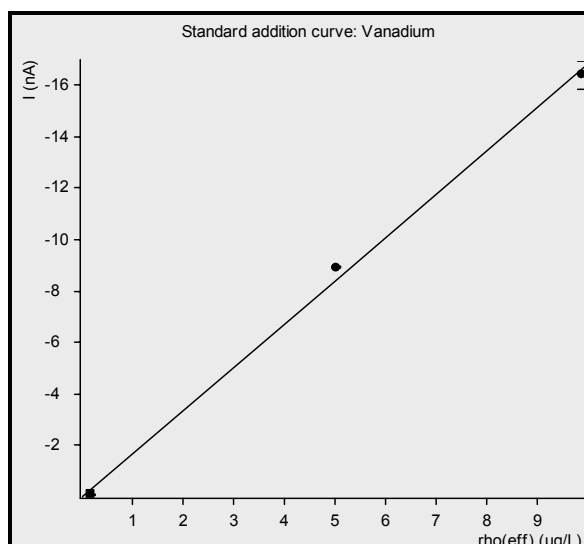




Sample volume 10 mL
 Results 1.1 µg/L Cu
 5.7 µg/L Fe
 < 1 µg/L V

Remarks

- Catechol should be added to the acidic sample solution before the buffer is added. Otherwise iron may form hydroxo complexes, which cannot be determined any more. This results in low recovery rates.
- Vanadium(IV) cannot be determined by voltammetry.
- If a large excess of Cu is present, it is recommended not to preconcentrate this, otherwise the Hg drop is overloaded and neither Fe, nor V can be determined accurately.
- The peak potentials are strongly dependent on the exact pH value and the sample matrix and may have to be adjusted.



Appendix

Full Report of a determination of Cu, Fe and V with the 746 VA Trace Analyzer

```

===== METROHM 746 VA TRACE ANALYZER (5.746.0101) =====
Determ.      : 02021647          User:                Date: 1998-02-02
Modified    : 1998-02-03 07:48:39 Run : 0                  Time: 16:47:28
Sample table: -
    
```

Pos.	Ident.1/S1	Ident.2/S2	Ident.3/S3	Method.call	Sample size/S0
	FeCuVrecal				10 mL

```

Method      : AB74Aust
Title       : Determination of Iron and Vanadium AB74 Part 3
Remark1     : 1% salt solution
Remark2     :
    
```

Substance	Mass conc.:	MC.dev.:	Cal.dev.:	Mass	Add.mass	V0.sample:	Comments
Fe	5.669 ug/L	0.847 ug/L (14.9%)	-	56.69 ng	50 ng	10 mL	

VR	U/mV	I/nA	I.mean	Std.dev.	I.delta	Comments
00	-341	-12.79	-12.79	0.0041		
01	-341	-12.78				
10	-329	-26.73	-27.11	0.5436	-14.33	front overlapping
11	-328	-27.50				front overlapping
20	-318	-35.53	-36.04	0.7203	-8.924	front overlapping
21	-318	-36.55				front overlapping

Substance : Vanadium
 Comments

Mass conc.: 192.9 ng/L	MC.dev.: 216 ng/L (112%)	Cal.dev.: -	Mass: 1.929 ng	Add.mass: 50 ng	V0.sample: 10 mL	
VR	U/mV	I/nA	I.mean	Std.dev.	I.delta	Comments
00	-607	-0.0845	-0.0966	0.0170		
01	-609	-0.1086				
10	-602	-8.838	-8.819	0.0270	-8.722	
11	-601	-8.800				
20	-599	-15.67	-16.05	0.5327	-7.232	
21	-600	-16.43				
Substance: Copper	Mass conc.: 1.103 ug/L	MC.dev.: 0.047 ug/L (4.23%)	Cal.dev.: -	Mass: 11.03 ng	Add.mass: 10 ng	V0.sample: 10 mL
VR	U/mV	I/nA	I.mean	Std.dev.	I.delta	Comments
00	-167	-16.00	-15.89	0.1642		
01	-168	-15.77				
10	-159	-30.57	-30.45	0.1661	-14.57	rear overlapping
11	-159	-30.34				rear overlapping
20	-148	-43.32	-43.97	0.9232	-13.51	rear overlapping
21	-148	-44.62				rear overlapping
Substance	Techn.	Y.reg/offset	Slope	Nonlin.	Mean deviat.	
Fe	std.add.	-1.364e-08	-0.002478		1.572e-09	
Vanadium	std.add.	-3.145e-10	-0.001680		4.705e-10	
Copper	std.add.	-1.601e-08	-0.01495		5.295e-10	
Final results			+/- Res.dev.	%	Comments	
Fe =	5.6686 ug/L		0.847	14.9		
Vanadium =	192.87 ng/L		216.	112.		
Copper =	1.1031 ug/L		0.047	4.23		

Method print of a determination of Cu, Fe and V with the 746 VA Trace Analyzer

```

===== METROHM 746 VA TRACE ANALYZER (5.746.0101) =====
Method: AB74_3b.mth OPERATION SEQUENCE
Title : Determination of Cu, Fe and V. AB 74 Method 3b
    
```

Instructions	t/s	Main parameters	Auxiliary parameters
1 SMPL>M		V.fraction mL	V.total L
2 DOS>M		Soln.name Catechol	V.add 0.050 mL
3 DOS>M		Soln.name Buffer	V.add 0.250 mL
4 PURGE			
5 STIR	300.0	Rot.speed 2000 /min	
6 (ADD			
7 PURGE			
8 STIR	60.0	Rot.speed 2000 /min	
9 OPURGE			
10 (REP			
11 SEGMENT		Segm.name AdSV	
12 REP)1			
13 PURGE			
14 ADD>M		Soln.name Cu_Std	V.add 0.010 mL
15 ADD>M		Soln.name Fe_Std	V.add 0.050 mL
16 ADD>M		Soln.name V_Std	V.add 0.050 mL
17 ADD)2			
18 END			

```

Method: AB74_3b SEGMENT AdSV
    
```

Instructions	t/s	Main parameters	Auxiliary parameters
1 STIR	5.0	Rot.speed 2000 /min	
2 HMDE		Drop size 7	Meas.cell normal
3 DPMODE		U.ampl -50 mV	t.meas 20.0 ms
		t.step 0.10 s	t.pulse 40.0 ms
4 MEAS	60.0	U.meas 0 mV	
5 OSTIR	5.0		
6 FSWEEEP	13.6	U.start 0 mV	U.step 6 mV
		U.end -800 mV	Sweep rate 60 mV/s
7 OMEAS		U.standby mV	
8 END			