
Application Bulletin

Of interest to: General analytical laboratories, Waters,
Environmental protection, Trace analysis

B 1, 2, 9, 16

Voltammetric determination of zinc, cadmium, lead, copper, thallium, nickel, and cobalt in water samples according to DIN 38406 Part 16

Summary

The prepared standard method in DIN 38406 Part 16, describes the determination of Zn, Cd, Pb, Cu, Tl, Ni and Co in drinking, ground, surface and precipitating (e.g. rain) waters. Because the presence of organic substances in the water samples can strongly interfere with the voltammetric determination, a pretreatment with UV digestion using hydrogen peroxide is necessary. This digestion ensures the elimination of all organic substances without introduction of blank values.

These methods can, of course, also be applied for trace analysis in other materials, e.g. trace analysis in the production of semiconductor chips with a silicon basis.

Zn, Cd, Pb, Cu and Tl are determined on the HMDE by means of anodic stripping voltammetry (ASV), Ni and Co by means of adsorptive stripping voltammetry (AdSV).

Apparatus and accessories

- 746 VA Trace Analyzer with 747 VA Stand or
 - 757 VA Computrace
-

Sample preparation

- Immediately upon taking the water sample, filter it through a microfilter (0.45 µm). The filtrates and filters with residues are treated separately. Acidify the filtrates, per litre, with 1 mL conc. HNO₃ or HCl. The pH value of the acidified filtrates should lie between 1.7 and 2.0. If this is not the case, more acid must be added.

Organic matter often interferes with voltammetric determinations and therefore sample solutions usually have to be digested.

- Tap water, surface waters, mineral waters and drinking waters can usually be analysed without pre-treatment.
- Low polluted waste waters can be digested with the 705 UV Digester. Add 50 - 100 µL hydrogen peroxide $w(\text{H}_2\text{O}_2) = 30\%$ to 10 mL acidified samples ($\text{pH} = 2$). The quartz tubes are irradiated for 1h at 90°C . After cooling to room temperature, the digested samples can be transferred directly to the polarographic vessel. The blank value of this digestion is relatively small.
- Filters, filter residues and samples with organic matter (foods, pharmaceuticals etc.) must be digested.
 - High-pressure asher
 - Microwave digestion
 Both techniques oxidise the samples in a closed digestion vessel by means of a mixture of concentrated mineral acids.
 - According to Application Bulletin 113, open wet digestion with H_2SO_4 and H_2O_2
- Preparation of sample for the analysis of semiconductor chips: Place a drop of hydrofluoric acid $w(\text{HF}) = 40\%$ on chip and fume off by heating. A white, powdery residue forms. Dissolve this with a drop of nitric acid $w(\text{HNO}_3) = 65\%$ and rinse into a polarographic vessel. Prepare a blank value with the same reagents

Remarks

- These metals can be determined in the following ranges:

Element	Determination limits	Concentration max.
Zn	1.0 µg/L	50 mg/L
Cd	0.1 µg/L	50 mg/L
Pb	0.1 µg/L	50 mg/L
Cu	1.0 µg/L	50 mg/L
Tl	0.1 µg/L	50 mg/L
Ni	0.1 µg/L	10 µg/L
Co	0.1 µg/L	10 µg/L

- Samples with higher concentrations must be diluted.
- Metals with high concentrations (>50 mg/L) can also be determined on the DME or SMDE without enrichment. For methods 1 and 2 the sweep must be reversed from positive to negative potentials.
- The analysis of the digested filters and that of the filtrates is identical.
- The blank values of the digestions and the chemicals must be taken into consideration.
- If samples contain higher contents of humic acids, these must be digested immediately to avoid formation of precipitation.
- If Fe must also be determined, e.g. for trace analysis for the production of semiconductor chips, please refer to Application Bulletin No. 74.

Literature

- DIN 38406 Teil 16
Verfahren zur Bestimmung von Zink, Cadmium, Blei, Kupfer, Thallium, Nickel, Cobalt mittels Voltammetrie. E16 Deutsche Einheitsverfahren.
- Ostapczuk, M. Goedde, M. Stöppler, H.W. Nürnberg
Kontroll- und Routinebestimmung von Zn, Cd, Pb, Cu, Ni und Co mit differentieller Pulsvoltammetrie in Materialien der deutschen Umweltbank
Fresenius, Z. anal. Chem. 318 (1984) 321-326
- Braun, M. Metzger
Umweltanalytische Nickel-Bestimmung durch Adsorptionsvoltammetrie mit der Quecksilberfilmelektrode
Fresenius, Z. Anal. Chem. 318 (1984) 321-326
- G. Van den Berg
Determining trace concentration of copper in water by cathodic film stripping voltammetry with adsorptive collection
Anal. Lett. 17 A, (1984) 2141-2157 und AB 74
- Axel Meyer, Rolf Neeb
Determination of cobalt and nickel by adsorption voltammetry in supporting electrolytes containing triethanolamine and dimethylglyoxime
Fresenius, Z. Anal. Chem. 315 (1983) 118-120
- Metrohm Application Bulletin No. 113

Method 1
Determination of Zn, Cd, Pb and Cu

Reagents

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

- Sodium hydroxide solution, suprapur, $w(\text{NaOH}) = 30\%$
- Acetic acid, suprapur, $w(\text{CH}_3\text{COOH}) = 100\%$
- KCl, suprapur
- Zn stock solution, $\beta(\text{Zn}^{2+}) = 1\text{ g/L}$ (commercially available)
- Cd stock solution, $\beta(\text{Cd}^{2+}) = 1\text{ g/L}$ (commercially available)
- Pb stock solution, $\beta(\text{Pb}^{2+}) = 1\text{ g/L}$ (commercially available)
- Cu stock solution, $\beta(\text{Cu}^{2+}) = 1\text{ g/L}$ (commercially available)

Ready-to-use solutions:

- KCl-sodium acetate solution: $c(\text{KCl}) = 1.5\text{ mol/L}$, $c(\text{CH}_3\text{COONa}) = 0.5\text{ mol/L}$
55.9 g KCl + 25 mL NaOH + 14.2 mL CH_3COOH filled up to 500 mL with high purity water.
- Standard solutions: $\beta(\text{Zn}^{2+}) = 10\text{ mg/L}$
 $\beta(\text{Cd}^{2+}) = 0.1\text{ mg/L}$
 $\beta(\text{Pb}^{2+}) = 0.5\text{ mg/L}$
 $\beta(\text{Cu}^{2+}) = 2.5\text{ mg/L}$

Diluted solutions are prepared using $c(\text{HNO}_3) = 0.014\text{ mol/L}$.

Analysis

Measuring solution:

10 mL (diluted) sample
 + 1 mL KCl-sodium acetate solution

If necessary, adjust the pH of the solution should to 4.6 ± 0.2 .

The voltammogram is recorded with the following parameters:

Working electrode	HMDE
Drop Size	4
Stirrer/RDE	2000 rpm
Measurement mode	DP
Purge time	300 s
Pulse amplitude	0.05 V
Deposition potential	- 1.15 V
Deposition time	90 s
Equilibration time	10 s
Start potential	- 1.15 V
End potential	0.05 V
Voltage step	0.006 V
Voltage step time	0.1 s
Sweep rate	0.06 V/s
Peak potential (Zn)	- 0.98 V
Peak potential (Cd)	- 0.56 V
Peak potential (Pb)	- 0.38 V
Peak potential (Cu)	- 0.10 V

The concentration is determined by standard addition.

Remarks

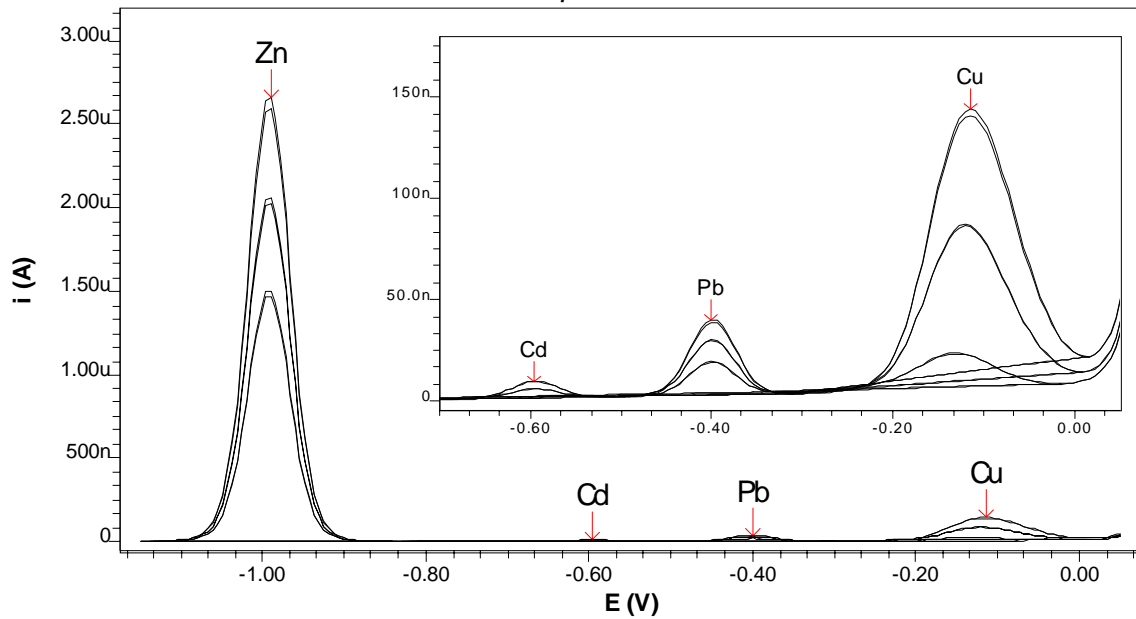
- Ammonium acetate buffer pH 4.6 can be used instead of KCl-sodium acetate solution. If the sample contains no chloride, it is preferable to use this buffer instead of the KCl/Na acetate solution. Cu achieves peaks with more positive potential (Peak potential Cu: +0.05 V), which are easier to evaluate.
 NH₄ acetate buffer pH 4.6: c(CH₃COOH) = 2 mol/L, c(NH₃) = 1 mol/L
 55.5 mL w(CH₃COOH) = 100 % + 37 mL w(NH₃) = 25 % filled up to 500 mL.
- Zn is often present in tap water in higher concentrations as the other metals. In this case, Zn should be determined separately with shorter enrichment time or after being diluted to a greater extent.
- Seeing that the difference of the half wave potentials of Tl and Pb is only approx. 50 mV, Tl and Pb are determined together in acetate solutions. For this reason, following the analysis of Zn, Cd, Pb and Cu, the Tl content is then determined according to method 2. If the concentration of Tl is less than 50% of the concentration of Pb the error for the Pb determination is less than 10%.
- If the Tl concentration is more than 50% of the Pb concentration it is not recommended to use method 1 for determination of Pb.
 An alternative is a post-electrolysis where a large quantity of the Tl deposited on the electrode is removed before the determination of Pb.

- Another possibility is the determination of Pb and Tl at a pH>12 (NH₃Cl buffer according to method 3 + NaOH). With this electrolyte it is possible to separate the peaks of Pb and Tl. But in this case Cd interferes the determination of Pb.

Peak potential Tl	-0.43 V
Peak potential Pb	-0.61 V
Peak potential Cd	-0.68 V

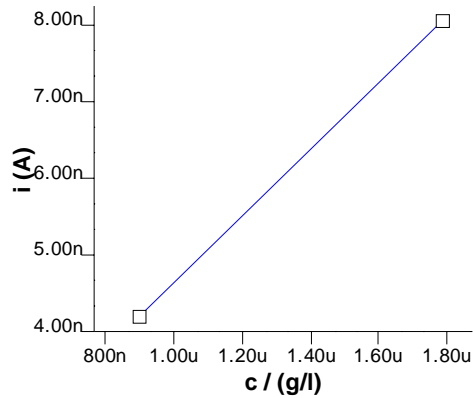
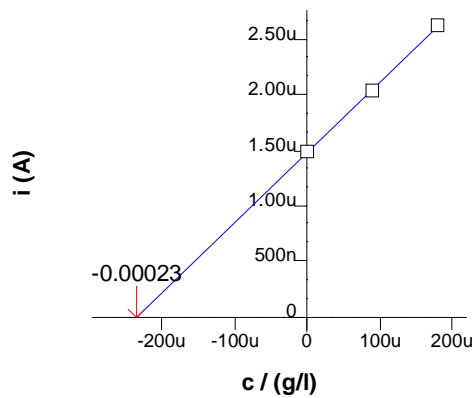
Figures

Determination of Zinc, Cadmium, Lead, and Copper acc. to DIN38406/16 tap water



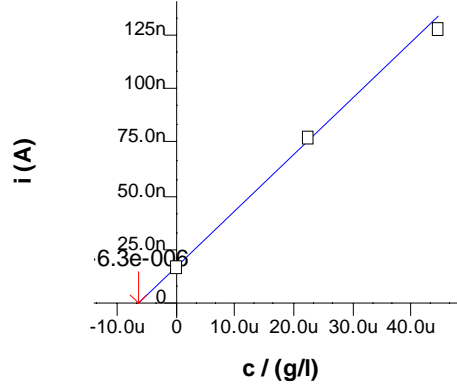
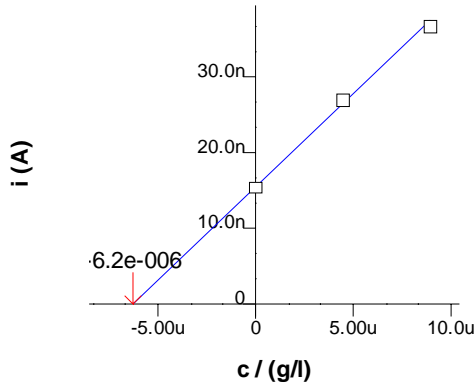
Zn
 c = 0.258 mg/l
 +/- 0.015 mg/l (6.01%)

Cd
 c = n/a



Pb
 c = 6.844 µg/l
 +/- 0.398 µg/l (5.82%)

Cu
 c = 6.979 µg/l
 +/- 0.223 µg/l (3.19%)



```

===== METROHM 757 VA COMPUTRACE (5.757.0010) =====
Determ.   : 06051547_tap water.dth
Date      : 2001-06-05           Time: 15:47:51
Modified  : 2001-06-05 15:48:55 User:
Cell volume: 11.000 ml
-----
Ident     : tap water           Sample volume
                                           10.000 ml
-----
Method    : AB231_1_Det of Zn Cd Pb Cu with HMDE.mth
Title     : Determination of Zinc, Cadmium, Lead, and Copper acc. to DIN38406/16
Remark1   : 10 ml sample + 1 ml acetate buffer (1.5mol/l KCl + 0.5mol/l NaAc)
Remark2   : pH 4.6
    
```

```

Substance : Zn
Mass conc.: 234.485 ug/l
MC.dev.   : 14.086 ug/l ( 6.01%)
Mass      : 2.579 ug
Add.mass  : 1.000 ug
Comments  : -----
    
```

VR	V	uA	i.mean	Std.Dev.	i.delta	Comments
1-1	-0.989	1.501	1.483	0.024		
1-2	-0.989	1.466				
2-1	-0.989	2.024	2.042	0.026	0.559	Ovl. in scan
2-2	-0.989	2.061				
3-1	-0.989	2.589	2.626	0.052	0.583	Ovl. in scan
3-2	-0.989	2.663				Ovl. in scan

```

Substance : Cd
Mass conc.: n/a
MC.dev.   : n/a
Add.mass  : 10.000 ng
Comments  : -----
    
```

VR	V	nA	i.mean	Std.Dev.	i.delta	Comments
1-1	---	---	---	---		No peak found
1-2	---	---				No peak found
2-1	-0.596	4.168	4.191	0.050		Ovl. in scan
2-2	-0.596	4.215				
3-1	-0.596	7.877	8.044	0.237	3.853	Ovl. in scan
3-2	-0.596	8.211				Ovl. in scan

```

Substance : Pb
Mass conc.: 6.222 ug/l
MC.dev.   : 0.362 ug/l ( 5.82%)
Mass      : 68.441 ng
Add.mass  : 50.000 ng
Comments  : -----
    
```

VR	V	nA	i.mean	Std.Dev.	i.delta	Comments
1-1	-0.400	15.51	15.27	0.339		
1-2	-0.400	15.03				
2-1	-0.400	26.56	26.84	0.403	11.57	Ovl. in scan
2-2	-0.400	27.13				
3-1	-0.400	35.81	36.52	1.008	9.68	Ovl. in scan
3-2	-0.400	37.23				Ovl. in scan

```

Substance : Cu
Mass conc.: 6.345 ug/l
Comments  : -----
    
```

MC.dev. : 0.203 ug/l (3.19%)
 Mass : 69.791 ng
 Add.mass : 250.000 ng

VR	V	nA	i.mean	Std.Dev.	i.delta	Comments
1-1	-0.132	16.8	16.5	0.349		
1-2	-0.132	16.3				
2-1	-0.120	76.4	76.8	0.684	60.3	Ovl. in scan
2-2	-0.120	77.3				
3-1	-0.114	126.5	128.1	2.260	51.2	Ovl. in scan
3-2	-0.114	129.6				Ovl. in scan

Substance	Calibr.	Y.reg/offset	Slope	Nonlin.	Mean deviat.
Zn	std.add.	1.480e-006	6.328e-003		2.309e-008
Cd	std.add.	2.687e-010	4.354e-003		2.612e-010
Pb	std.add.	1.538e-008	2.477e-003		3.278e-010
Cu	std.add.	1.665e-008	2.626e-003		3.462e-010

Final results		+/- Res. dev.	%	Comments
Zn =	0.258 mg/l	0.015	6.007	
Cd =	n/a µg/l			
Pb =	6.844 µg/l	0.398	5.822	
Cu =	6.979 µg/l	0.223	3.193	

Fig. 1 Determination of Zn, Cd, Pb and Cu according to method 1 with the 757 VA Computrace

===== METROHM 746 VA TRACE ANALYZER (5.746.0101) =====
 Method: AB231_1.mth OPERATION SEQUENCE
 Title : Det. of Zn, Cd, Pb, Cu acc. to DIN 38406/16

	Instructions	t/s	Main parameters	Auxiliary parameters
1	SMPL>M		V.fraction mL	V.total L
2	DOS>M		Soln.name buffer	V.add 1.000 mL
3	PURGE			
4	STIR	300.0	Rot.speed 2000 /min	
5	(ADD			
6	PURGE			
7	STIR	10.0	Rot.speed 2000 /min	
8	OPURGE			
9	(REP			
10	SEGMENT		Segm.name ZnCdPbCu	
11	REP)1			
12	PURGE			
13	ADD>M		Soln.name ZnCdPbCu	V.add 0.100 mL
14	ADD)2			
15	END			

Method: AB231_1 SEGMENT
 ZnCdPbCu

	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 50 mV	t.meas 20.0 ms
			t.step 0.10 s	t.pulse 40.0 ms
4	MEAS	90.0	U.meas -1150 mV	
5	OSTIR	10.0		
6	SWEEP	20.3	U.start -1150 mV	U.step 6 mV
			U.end 50 mV	Sweep rate 60 mV/s
7	OMEAS		U.standby mV	
8	END			

Fig. 2 Parameters for the determination of Zn, Cd, Pb, Cu according to method 1 with the 746 VA Trace Analyzer

Method 2

Determination of Tl

Reagents

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

- Sodium hydroxide solution, suprapur, $w(\text{NaOH}) = 30\%$
- Acetic acid, suprapur, $w(\text{CH}_3\text{COOH}) = 100\%$
- KCl, suprapur
- Ethylenediaminetetraacetic acid disodium salt dihydrate, puriss.p.a., CAS 6381-92-6
- Tl stock solution, $\beta(\text{Tl}^+) = 1\text{ g/L}$ (commercially available)

Ready-to-use solutions:

- KCl-sodium acetate solution: $c(\text{KCl}) = 1.5\text{ mol/L}$, $c(\text{CH}_3\text{COONa}) = 0.5\text{ mol/L}$
55.9 g KCl + 25 mL NaOH + 14.2 mL CH_3COOH filled up to 500 mL with high purity water.
- EDTA solution: $c(\text{EDTA}) = 0.1\text{ mol/L}$:
Dissolve 0.93 g $\text{Na}_2\text{-EDTA}\cdot 2\text{H}_2\text{O}$ in H_2O and fill up to 25 mL.
- Standard solution: $\beta(\text{Tl}^+) = 0.5\text{ mg/L}$
Diluted solutions are prepared using $c(\text{HNO}_3) = 0.014\text{ mol/L}$.

Analysis

Measuring solution:

10 mL (diluted) sample
 + 1 mL KCl-sodium acetate solution
 (or measuring solution from method 1)
 + 200 μL EDTA solution

If necessary, adjust the pH of the solution should to 4.6 ± 0.2 .

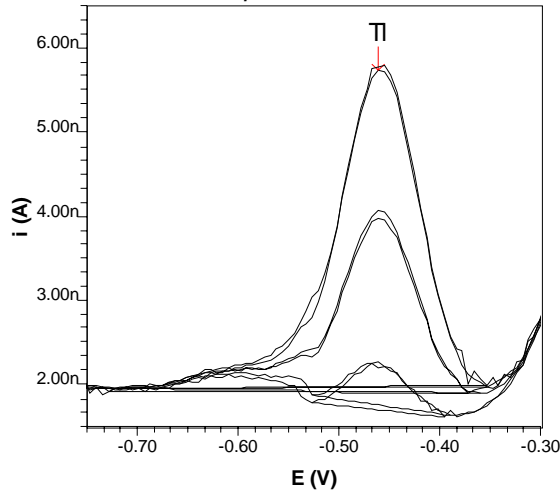
The voltammogram is recorded with the following parameters:

Working electrode	HMDE
Stirrer/RDE	2000 rpm
Drop size	4
Measurement mode	DP
Purge time	300 s
Pulse amplitude	0.05 V
Deposition potential	- 0.8 V
Deposition time	180 s
Equilibration time	10 s
Start potential	- 0.8 V
End potential	- 0.2 V
Voltage step	0.006 V
Voltage step time	0.1 s
Sweep rate	0.06 V/s
Peak potential (Tl)	- 0.45 V

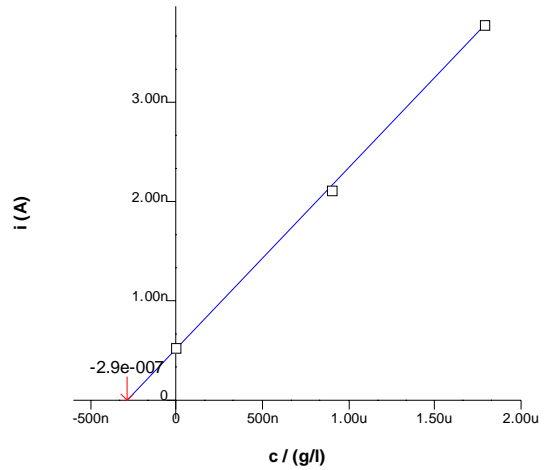
The concentration is determined by standard addition.

Figures

Determination of Thallium acc. to DIN38406/16
tap water_Tl



Tl
c = 0.319 µg/l
+/- 0.036 µg/l (11.28%)



```
===== METROHM 757 VA COMPUTRACE (5.757.0010) =====
Determ.   : 06051653_tap water_Tl.dth
Date      : 2001-06-05           Time: 16:53:19
Modified  : 2001-06-05 17:01:16 User:
Cell volume: 11.100 ml
```

```
Ident      tap water_Tl
Sample volume 10.000 ml
```

```
Method : AB231_2_Det of Tl.mth
Title  : Determination of Thallium acc. to DIN38406/16
Remark1 : 10 ml sample + 1 ml acetate buffer (1.5mol/ol KCl + 0.5mol/l NaAc)
Remark2 : + 200µl EDTA-Na2 (0.1 mol/l)
```

```
Substance : Tl
Mass conc. : 287.597 ng/l
MC.dev.    : 32.444 ng/l ( 11.28%)
Mass       : 3.192 ng
Add.mass   : 10.000 ng
Comments
```

VR	V	nA	i.mean	Std.Dev.	i.delta	Comments
1-1	-0.467	0.549	0.530	0.050		
1-2	-0.461	0.511				
2-1	-0.461	2.063	2.114	0.073	1.584	
2-2	-0.461	2.165				
3-1	-0.455	3.812	3.788	0.050	1.674	
3-2	-0.461	3.764				

Substance	Calibr.	Y.reg/offset	Slope	Nonlin.	Mean deviat.
Tl	std.add.	5.207e-010	1.815e-003		4.755e-011

Final results	+/- Res. dev.	%	Comments
Tl = 0.319 µg/l	0.036	11.281	

Fig. 3 Determination of Tl according to method 2 with the 757 VA Computrace

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===== METROHM 746 VA TRACE ANALYZER (5.746.0101) =====
Method: AB231_2 .mth OPERATION SEQUENCE
Title : Det. of Tl acc. to DIN 38406/16
    
```

	Instructions	t/s	Main parameters	Auxiliary parameters
1	SMPL>M		V.fraction mL	V.total L
2	DOS>M		Soln.name buffer	V.add 1.000 mL
3	DOS>M		Soln.name EDTA_sol	V.add 0.200 mL
4	PURGE			
5	STIR	300.0	Rot.speed 2000 /min	
6	(ADD			
7	PURGE			
8	STIR	10.0	Rot.speed 2000 /min	
9	OPURGE			
10	(REP			
11	SEGMENT		Segm.name Tl_Seg	
12	REP)1			
13	PURGE			
14	ADD>M		Soln.name Tl_Std	V.add 0.020 mL
15	ADD)2			
16	END			

Method: AB231_2 SEGMENT Tl_Seg

	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 50 mV	t.meas 20.0 ms
			t.step 0.10 s	t.pulse 40.0 ms
4	MEAS	180.0	U.meas -800 mV	
5	OSTIR	10.0		
6	SWEEP	10.3	U.start -800 mV	U.step 6 mV
			U.end -200 mV	Sweep rate 60 mV/s
7	OMEAS		U.standby mV	
8	END			

Fig. 4 Parameters for the determination of Tl according to method 2 with the 746 VA Trace Analyzer

Method 3 Determination of Ni and Co

Reagents

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

- Ammonia solution, suprapur, $w(\text{NH}_3) = 25\%$
- Hydrochloric acid, suprapur, $w(\text{HCl}) = 30\%$
- Dimethylglyoxim disodium salt octahydrate, puriss.p.a., CAS 75006-64-3
- Ni stock solution, $\beta(\text{Ni}^{2+}) = 1 \text{ g/L}$ (commercially available)
- Co stock solution, $\beta(\text{Co}^{2+}) = 1 \text{ g/L}$ (commercially available)

Ready-to-use solutions:

- NH_4Cl buffer pH 9.5: $c(\text{NH}_4\text{Cl}) = 1 \text{ mol/L}$, $c(\text{NH}_3) = 2 \text{ mol/L}$
112.5 mL NH_3 + 53 mL HCl, filled up to 500 mL with high purity water.
- DMG solution: $c(\text{Na}_2\text{DMG}) = 0.1 \text{ mol/L}$
Dissolve 0.304 g Dimethylglyoxim disodium salt in 10 mL ultrapure water.
- Standard solutions: $\beta(\text{Ni}^{2+}) = 1 \text{ mg/L}$
 $\beta(\text{Co}^{2+}) = 0.1 \text{ mg/L}$
Diluted solutions are prepared using $c(\text{HNO}_3) = 0.014 \text{ mol/L}$.

Analysis

Measuring solution:

10 mL (diluted) sample
 + 0.5 mL NH₄Cl buffer
 + 0.1 mL DMG solution

If necessary, adjust the pH of the solution should to 9.5 ± 0.2 .

The voltammogram is recorded with the following parameters:

Working electrode	HMDE
Drop size	4
Stirrer/RDE	2000 rpm
Measurement mode	DP
Purge time	300 s
Pulse amplitude	0.05 V
Deposition potential	- 0.7 V
Deposition time	90 s
Equilibration time	10 s
Start potential	- 0.8 V
End potential	- 1.25 V
Voltage step	0.004 V
Voltage step time	0.3 s
Sweep rate	0.013 V/s
Peak potential (Ni)	- 0.97 V
Peak potential (Co)	- 1.13 V

The concentration is determined by standard addition.

Remarks

- If the disodium salt of the dimethylglyoxime should not be used, DMG can be dissolved in ethanol or triethanolamine.

DMG in ethanol: $c(\text{DMG}) = 0.1 \text{ mol/L}$

Dissolve 0.29 g DMG in ethanol and fill up to 25 mL.

or

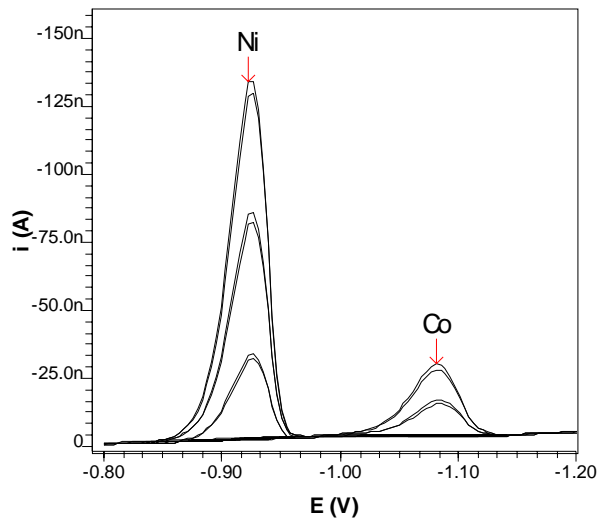
DMG in triethanolamine: $c(\text{DMG}) = \text{saturated}$

Dissolve 500 mg dimethylglyoxime in 100 mL TEA:H₂O (1:1). This solution is used when a big excess of Zn disturbs the Co determination.

- Na₂-Iminodiacetate 0.2 mol/L:
 This solution is used in the DIN norm to mask Zn by the Co determination. Our tests have shown that the determination of Ni besides Co is then not possible any more because Ni is also complexed.

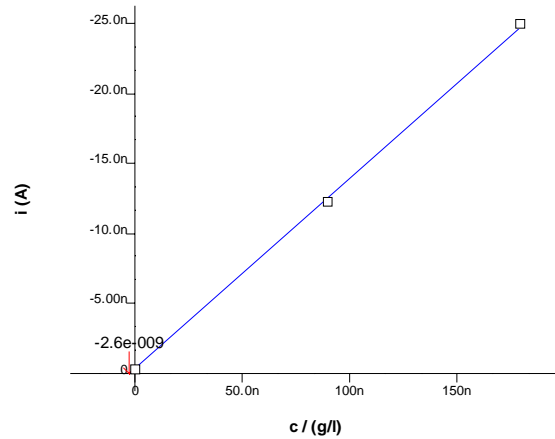
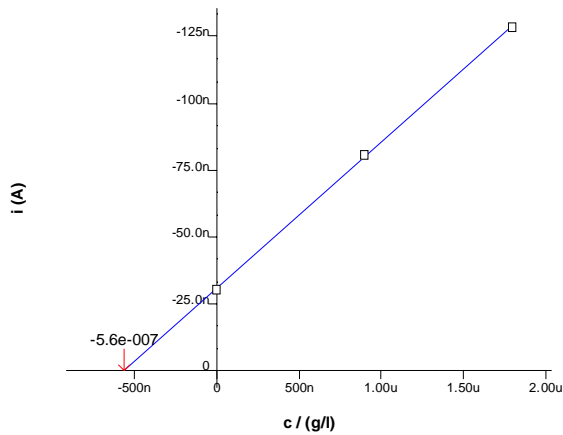
Figures

Ni + Co in Meerwasser
Meerwasser



Ni
c = 0.616 ug/l
+/- 0.046 ug/l (7.39%)

Co
c = 2.820 ng/l
+/- 0.529 ng/l (18.77%)



===== METROHM 757 VA COMPUTRACE (5.757.0010) =====

Determ. : 09151108_MeerwasserNiCo.dth
Date : 1999-09-15 Time: 11:08:54
Modified : --- User: Cell volume: 11.050 ml

Ident : Meerwasser Sample volume : 10.000 ml

Method : Ni-Co Meerwasser.mth
Title : Ni + Co in Meerwasser
Remark1 :

Substance : Ni	Comments
Mass conc.: 557.656 ng/l	
MC.dev. : 41.220 ng/l (7.39%)	
Mass : 6.162 ng	
Add.mass : 10.000 ng	

VR	V	nA	i.mean	Std.Dev.	i.delta	Comments
1-1	-0.927	-29.5	-30.4	1.276		
1-2	-0.927	-31.3				
2-1	-0.927	-78.7	-80.8	2.967	-50.4	
2-2	-0.927	-82.9				
3-1	-0.927	-126.3	-128.6	3.258	-47.8	
3-2	-0.923	-130.9				

Substance : Co Comments

VR	V	nA	i.mean	Std.Dev.	i.delta	Comments
			1-1	-1.089	-0.32	-0.34 0.050
			1-2	-1.086	-0.37	
			2-1	-1.086	-11.62	-12.26 0.900 -11.91
			2-2	-1.086	-12.89	
			3-1	-1.082	-24.10	-25.02 1.290 -12.76
			3-2	-1.082	-25.93	

Substance	Calibr.	Y.reg/offset	Slope	Nonlin.	Mean deviat.
Ni	std.add.	-3.049e-008	-5.482e-002		1.254e-009
Co	std.add.	-3.429e-010	-1.354e-001		4.999e-011

Final results	+/-	Res. dev.	%	Comments
Ni =	0.616	ug/l	0.046	7.392
Co =	2.820	ng/l	0.529	18.770

Fig. 5 Determination of Ni and Co according to method 3 with the 757 VA Computrace

```

===== METROHM 746 VA TRACE ANALYZER (5.746.0101) =====
Method: AB231_3 .mth          OPERATION SEQUENCE
Title : Det. of Ni, Co acc. to DIN 38406/16
    
```

	Instructions	t/s	Main parameters	Auxiliary parameters
1	SMPL>M		V.fraction mL	V.total L
2	DOS>M		Soln.name buffer	V.add 0.500 mL
3	DOS>M		Soln.name DMG_sol	V.add 0.100 mL
4	PURGE			
5	STIR	300.0	Rot.speed 2000 /min	
6	(ADD			
7	PURGE			
8	STIR	10.0	Rot.speed 2000 /min	
9	OPURGE			
10	(REP			
11	SEGMENT		Segm.name NiCo_Seg	
12	REP)1			
13	PURGE			
14	ADD>M		Soln.name NiCo_Std	V.add 0.010 mL
15	ADD)2			
16	END			


```

Method: AB231_3          SEGMENT
                        NiCo_Seg
    
```

	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 -50 mV	t.meas 20.0 ms
			t.step 0.30 s	t.pulse 40.0 ms
4	MEAS	90.0	U.meas -700 mV	
5	OSTIR	10.0		
6	FSWEEP	45.9	U.start -700 mV	U.step 4 mV
			U.end -1300 mV	Sweep rate 13.33 mV/s
7	OMEAS		U.standby mV	
8	END			

Fig. 6 Parameters for the determination of Ni and Co according to method 3 with the 746 VA Trace Analyzer