Metrohm

Application Bulletin 231/3 e

Determination of zinc, cadmium, lead, copper, thallium, nickel and cobalt in water samples by anodic and adsorptive stripping voltammetry according to DIN 38406-16

Summary

The standard method in DIN 38406-16, 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 on 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).

These metals can be determined in the following ranges:

Element	Determination limit	Max. concentration
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 mg/L
Co	0.1 µg/L	10 mg/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 Mercury drop capillary	6.1246.120 6.1226.030 or 6.1226.050
RE	Ag/AgCl reference electrode Ag/AgCl/KCl (3 mol/L) Electrolyte vessel Filled with c(KCl) = 3 mol/L	6.0728.x20 6.1245.010
AE	Pt rod electrode	6.0343.x00

Sample preparation

Reagents

All of the used reagents must be of purest quality possible (for analysis or for trace analysis*).

- Nitric acid, w(HNO_3) = 65%, for trace analysis*, CAS 7697-37-2

or

- Hydrochloric acid, w(HCl) = 30%, for trace analysis*, CAS 7647-01-0

If UV digestion is required:

- Hydrogen peroxide, w(H_2O_2) = 30%, for trace analysis*, CAS 7722-84-1

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

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 liter, with 1 mL conc. HNO_3 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.

- Tap water, surface waters, mineral waters and drinking waters can usually be analyzed without pretreatment.

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 hydrogen peroxide w(H_2O_2) = 30% to 10 mL acidified samples (pH = 2). The quartz tubes are irradiated for 90 min 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, pharmaceutics etc.) must be digested.
    - High-pressure asher
    - Microwave digestion

  Both techniques oxidize the samples in a closed digestion vessel by means of a mixture of concentrated mineral acids.
    - According to Application Bulletin113, 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(HF) = 40% on chip and fume off by heating. A white, powdery residue forms. Dissolve this with a drop of nitric acid w(HNO_3) = 65% and rinse into a polarographic vessel. Prepare a blank value with the same reagents

Comments

- 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 74.

Method 1: Determination of Zn, Cd, Pb and Cu

Zinc, cadmium, lead and copper are determined in KCl sodium acetate solution at the HMDE by anodic stripping voltammetry (ASV).

Reagents

All of the used reagents must be of purest quality possible (for analysis or for trace analysis*).

- Sodium hydroxide solution, for trace analysis*, w(NaOH) = 30 %, CAS 1310-73-2
- Acetic acid, for trace analysis*, w(CH_3COOH) = 100 %, CAS 64-19-7
- Potassium chloride, KCl, for trace analysis*, CAS 7447-40-7
- Zn standard stock solution, β(Zn^{2+}) = 1 g/L (commercially available)
- Cd standard stock solution, β(Cd^{2+}) = 1 g/L (commercially available)
- Pb standard stock solution, β(Pb^{2+}) = 1 g/L (commercially available)
- Cu standard stock solution, β(Cu^{2+}) = 1 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

Solutions

KCl sodium acetate solution	c(KCl) = 1.5 mol/L c(CH_3COONa) = 0.5 mol/L 55.9 g KCl + 25 mL NaOH + 14.2 mL CH_3COOH are filled up to 500 mL with ultrapure water.

Standard solutions

Zn standard solution	β(Zn^{2+}) = 10 mg/L The solution is prepared using c(HNO_3) = 0.014 mol/L.
Cd standard solution	β(Cd^{2+}) = 0.1 mg/L The solution is prepared using c(HNO_3) = 0.014 mol/L.
Pb standard solution	β(Pb^{2+}) = 0.5 mg/L

	The solution is prepared using $c(HNO_3) = 0.014$ mol/L.
Cu standard solution	$\beta(Cu^{2+}) = 2.5$ mg/L The solution is prepared using $c(HNO_3) = 0.014$ mol/L.

Analysis

Measuring solution

10 mL (diluted) sample

1 mL KCl sodium acetate solution

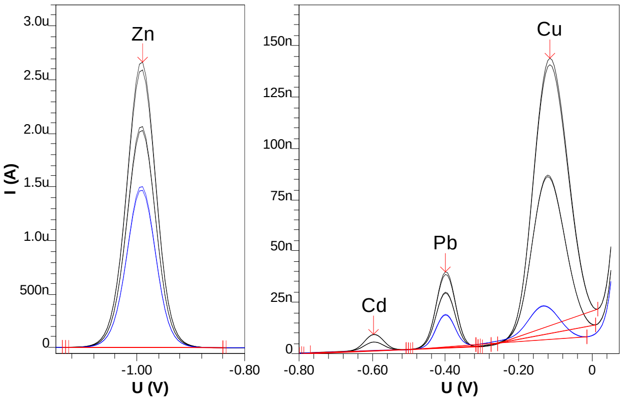
If necessary, adjust the pH of the solution to 4.6 ± 0.2.

The concentration is determined by standard addition.

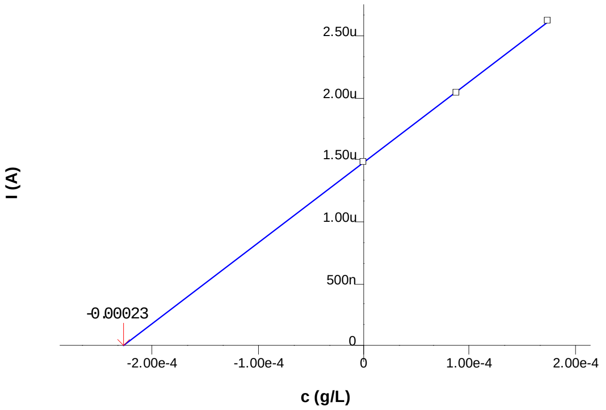
Parameters

Voltammetric	
Electrode operating mode	HMDE
Measuring mode	DP – Differential pulse
Stirring rate	2000 min^{-1}
Potentiostatic pretreatment	
Potential 1	-1.15 V
Waiting time 1	90 s
Equilibration time	10 s
Sweep	
Start potential	-1.15 V
End potential	0.05 V
Potential step	0.006 V
Potential step time	0.1 s
Sweep rate	0.06 V/s
Pulse amplitude	0.05 V
Substance	
Name	Zn
Characteristic potential	-0.98 V
Name	Cd
Characteristic potential	-0.56 V
Name	Pb
Characteristic potential	-0.38 V
Name	Cu
Characteristic potential	-0.1 V

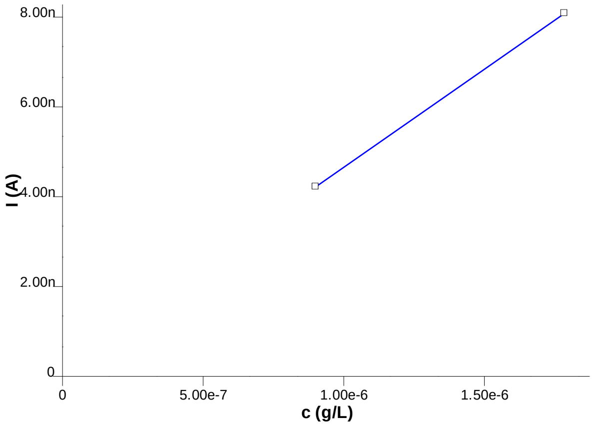
Example



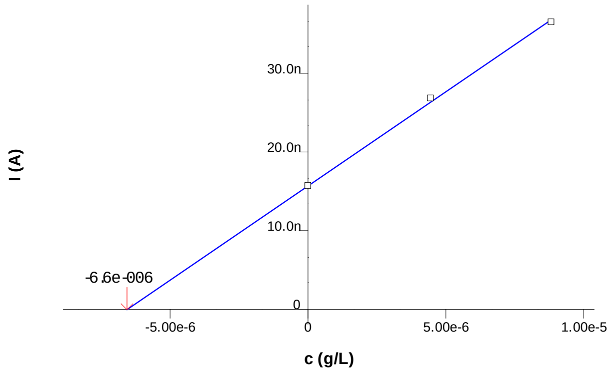
```
Zn
c =  250.125 ug/l
+/-     9.603 ug/l (3.84%)
```



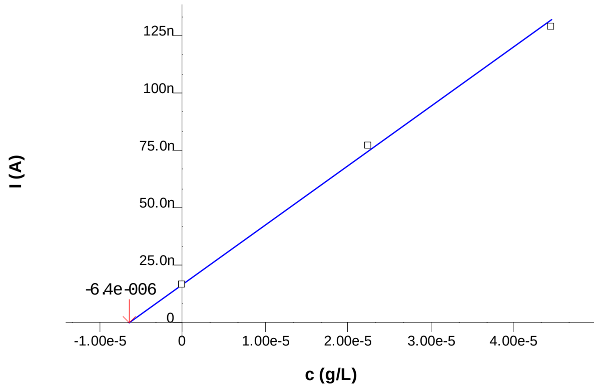
```
Cd
c = ---
```



```
Pb
c =     7.233 ug/l
+/-     0.321 ug/l (4.44%)
```



```
Cu
c =     7.035 ug/l
+/-     0.254 ug/l (3.61%)
```



Results

Sample	Tap water
Sample size	10.0 mL
β(Zn)	250.1 µg/L
β(Cd)	n/a
β(Pb)	7.2 µg/L
β(Cu)	7.0 µg/L

Comments

- 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 sodium acetate solution. Cu achieves peaks with more positive potential (Peak potential Cu: +0.05 V), which are easier to evaluate.
  - NH_4 acetate buffer pH 4.6:
    $c(CH_3COOH)$ = 2 mol/L
    $c(NH_3)$ = 1 mol/L
    55.5 mL $w(CH_3COOH)$ = 100 % + 37 mL $w(NH_3)$ = 25 % filled up to 500 mL.
- For samples with higher concentrations the time for deposition (Waiting time 1) can be reduced to 60 s or even 30 s.
- Samples with higher concentrations can also be diluted.
- Metals with concentrations >50 mg/L can also be determined on the DME or SMDE without deposition. In this case start and end potential have to be swapped reversing the sweep from positive to negative potentials.
- Zn is often present in tap water in higher concentrations as the other metals. In this case, Zn should be determined separately with shorter deposition 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 (NH_4Cl 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. The resulting peak potentials are:

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

Method 2: Determination of Tl

Thallium is determined in KCl sodium acetate solution at the HMDE by anodic stripping voltammetry (ASV). Cd and Pb, which interfere, are masked by addition of EDTA.

Reagents

All of the used reagents must be of purest quality possible (for analysis or for trace analysis*).

- Sodium hydroxide solution, for trace analysis*, w(NaOH) = 30 %, CAS 1310-73-2
- Acetic acid, for trace analysis*, $w(CH_3COOH)$ = 100 %, CAS 64-19-7
- Potassium chloride, KCl, for trace analysis*, CAS 7447-40-7
- Ethylenediaminetetraacetic acid disodium salt dihydrate, $Na_2\text{-EDTA}\cdot 2H_2O$, for analysis, CAS 6381-92-6
- Tl standard stock solution, $\beta(Tl^+)$ = 1 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

Solutions

KCl sodium acetate solution	c(KCl) = 1.5 mol/L $c(CH_3COONa)$ = 0.5 mol/L 55.9 g KCl + 25 mL NaOH + 14.2 mL CH_3COOH are filled up to 500 mL with high purity water.
EDTA solution	c(EDTA) = 0.1 mol/L Dissolve 0.93 g $Na_2\text{-EDTA}\cdot 2H_2O$ in ultrapure water and fill up to 25 mL.

Standard solutions

Tl standard solution	$\beta(Tl^+)$ = 0.5 mg/L The solution is prepared using $c(HNO_3)$ = 0.014 mol/L.

Analysis

Measuring solution

10 mL (diluted) sample

1 mL KCl sodium acetate solution

(or measuring solution from method 1)

0.2 mL EDTA solution

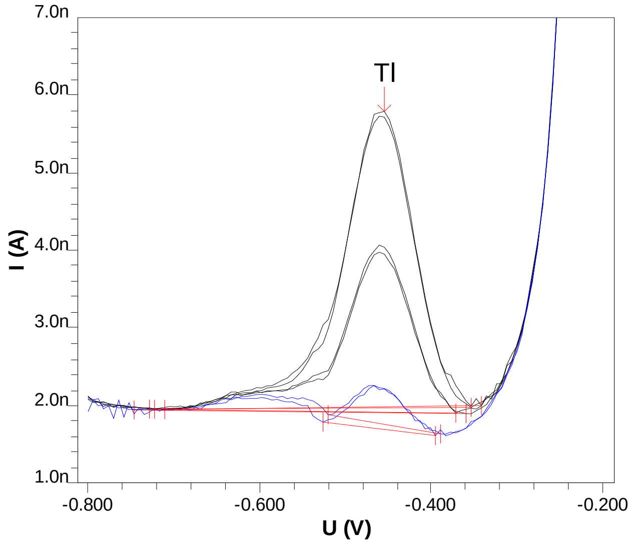
If necessary, adjust the pH of the solution to 4.6 ± 0.2.

The concentration is determined by standard addition.

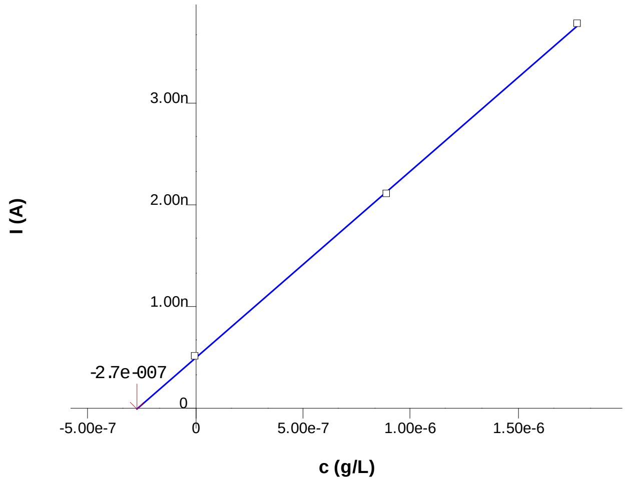
Parameters

Voltammetric	
Electrode operating mode	HMDE
Measuring mode	DP – Differential pulse
Stirring rate	2000 min^{-1}
Potentiostatic pretreatment	
Potential 1	-0.8 V
Waiting time 1	180 s
Equilibration time	10 s
Sweep	
Start potential	-0.8 V
End potential	-0.2 V
Potential step	0.006 V
Potential step time	0.1 s
Sweep rate	0.06 V/s
Pulse amplitude	0.05 V
Substance	
Name	Tl
Characteristic potential	-0.45 V

Example



```
Tl
c =     0.305 ug/l
+/-     0.028 ug/l (9.04%)
```



Result

Sample	Tap water
Sample size	10.0 mL
β(Tl)	0.3 µg/L

Comments

- Ammonium acetate buffer pH 4.6 can be used instead of KCl sodium acetate solution.
    - NH_4 acetate buffer pH 4.6:
      $c(CH_3COOH)$ = 2 mol/L
      $c(NH_3)$ = 1 mol/L
      55.5 mL $w(CH_3COOH)$ = 100 % + 37 mL $w(NH_3)$ = 25 % filled up to 500 mL.
- For samples with higher concentrations the time for deposition (Waiting time 1) can be reduced to 60 s or even 30 s.
- Samples with higher concentrations can also be diluted.
- Metals with concentrations >50 mg/L can also be determined on the DME or SMDE without deposition. In this case start and end potential have to be swapped reversing the sweep from positive to negative potentials.
- 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.

Method 3: Determination of Ni and Co

Reagents

All of the used reagents must be of purest quality possible (for analysis or for trace analysis*).

- Hydrochloric acid, $w(HCl)$ = 30%, for trace analysis*, CAS 7647-01-0
- Ammonia solution, for trace analysis*, $w(NH_3)$ = 25%, CAS 1336-21-6
- Dimethylglyoxime disodium salt octahydrate, DMG, for analysis, CAS 75006-64-3
- Ni standard stock solution, $\beta(Ni^{2+})$ = 1 g/L (commercially available)
- Co standard stock solution, $\beta(Co^{2+})$ = 1 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

Solutions

NH_4Cl buffer pH 9.5	$c(NH_4Cl)$ = 1 mol/L $c(NH_3)$ = 2 mol/L 112.5 mL NH_3 + 53 mL HCl, filled up to 500 mL with ultrapure water.
DMG solution	$c(Na_2DMG)$ = 0.1 mol/L Dissolve 0.304 g dimethylglyoxime disodium salt in 10 mL ultrapure water.

Standard solutions

Ni standard solution	$\beta(Ni^{2+})$ = 1 mg/L The solution is prepared using $c(HNO_3)$ = 0.014 mol/L.
Co standard solution	$\beta(Co^{2+})$ = 0.1 mg/L The solution is prepared using $c(HNO_3)$ = 0.014 mol/L.

Analysis

Measuring solution

10 mL (diluted) sample

0.5 mL NH_4Cl buffer

0.1 mL DMG solution

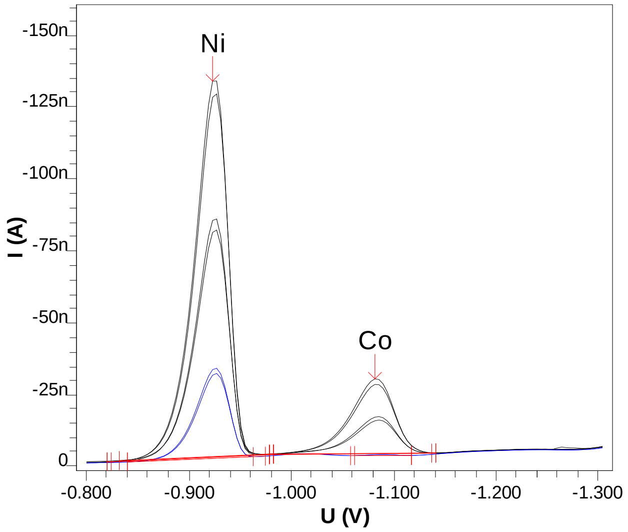
If necessary, adjust the pH of the solution to 9.5 ± 0.2.

The concentration is determined by standard addition.

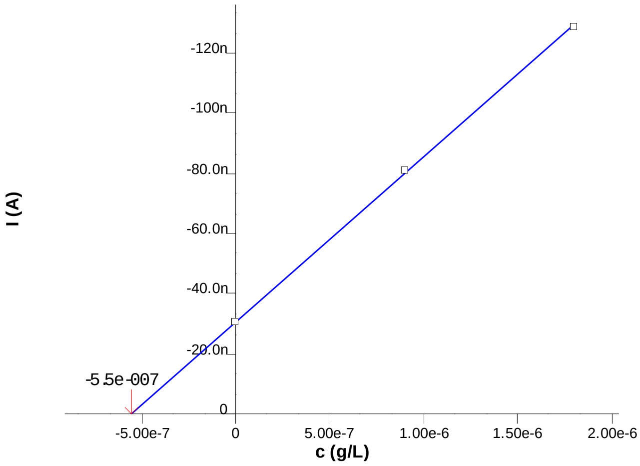
Parameters

Voltammetric	
Electrode operating mode	HMDE
Measuring mode	DP – Differential pulse
Stirring rate	2000 min^{-1}
Potentiostatic pretreatment	
Potential 1	-0.7 V
Waiting time 1	90 s
Equilibration time	10 s
Sweep	
Start potential	-0.8 V
End potential	-1.25 V
Potential step	0.004 V
Potential step time	0.3 s
Sweep rate	0.013 V/s
Pulse amplitude	0.05 V
Substance	
Name	Ni
Characteristic potential	-0.97 V
Name	Co
Characteristic potential	-1.13 V

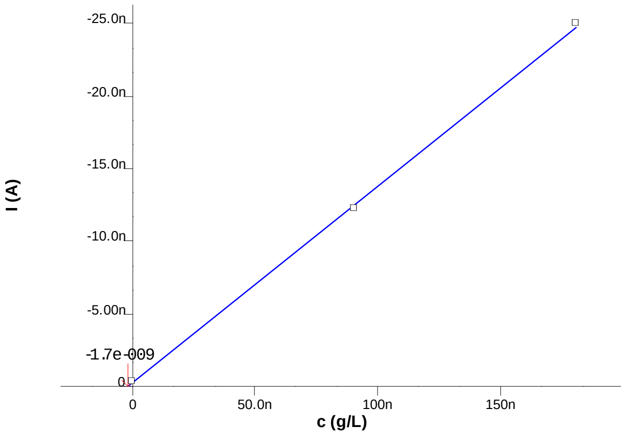
Example



```
Ni
c =     0.611 ug/l
+/-     0.027 ug/l (4.41%)
```



```
Co
c =    1.860 ng/l
+/-    3.947 ng/l (212.22%)
```



Result

Sample	Sea water
Sample size	2.0 mL
β(Ni)	0.61 µg/L
β(Co)	0.002 µg/L

Comments

- For samples with higher concentrations the time for deposition (Waiting time 1) can be reduced to 60 s or even 30 s.
- Samples with higher concentrations can also be diluted.
- If the disodium salt of the dimethylglyoxime should not be used, DMG can be dissolved in ethanol or triethanolamine.
  - DMG in ethanol: c(DMG) = 0.1 mol/L
    Dissolve 0.29 g dimethylglyoxime in ethanol and fill up to 25 mL.

    or
  - DMG in triethanolamine: c(DMG) = saturated
    Dissolve 500 mg dimethylglyoxime in 100 mL TEA:H_2O (1:1). This solution is used when a big excess of Zn disturbs the Co determination.
- Higher Zn concentrations (low mg/L-range) interfere with the determination of Co.
  - In the DIN standard c(Na_2-Iminodiacetate) = 0.2 mol/L is used to mask Zn in the Co determination. Our tests have shown that the determination of Ni besides Co is then not possible anymore because Ni is also complexed.
  - To determine Co in the presence of excess Zn the complexing agent α-furildioxime (CAS 6035-71-8) can be used, see Application Note V-172. With this complexing agent a simultaneous determination of Ni is not possible.

References

- DIN 38406-16
  German standard methods for the examination of water, waste water and sludge; cations; determination of 7 metals (zinc, cadmium, lead, copper, thallium, nickel, cobalt) by voltammetry
- 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 Application Bulletin 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 113

Appendix

Report for the example determination of Zn, Cd, Pb and Cu in tap water according to method 1

```
========== METROHM 797 VA COMPUTRACE (Version 1.0.0.1) (Serial No. 0) ==========
 Determination  : 06051547_tap water_ZnCdPbCu.dth
 Sample ID      :
 Creator method :                   Date :                     Time:
 Creator determ.:                   Date : 2001-06-05          Time:  15:47:51
 Modified by    :                   Date : 2017-07-11          Time:  14:36:09
--------------------------------------------------------------------------------
 Method         : AB231_1_Det of Zn Cd Pb Cu with HMDE.mth
 Title          :
 Remark1        : 10 ml sample + 1 ml acetate buffer (1.5mol/l KCl + 0.5mol/l NaAc)
 Remark2        :
--------------------------------------------------------------------------------
 Sample amount  :  10.000 mL
 Cell volume    :  11.000 mL
--------------------------------------------------------------------------------
 Substance      : Zn
 Conc.          : 227.386 ug/L
 Conc.dev.      :   8.730 ug/L     ( 3.84%)
 Amount         :   2.501 ug
 Add.amount     :   1.000 ug

 VR     V       uA      I.mean  Std.Dev.  I.delta   Comments
 -----  ------  ------  ------  --------  --------  ----------------------
 1 - 1  -0.989   1.501   1.483     0.024     0.000
 1 - 2  -0.989   1.466
 2 - 1  -0.989   2.024   2.042     0.026     0.559  Ovl. in sweep
 2 - 2  -0.989   2.061
 3 - 1  -0.989   2.589   2.626     0.052     0.583  Ovl. in sweep
 3 - 2  -0.989   2.663                              Ovl. in sweep

 Substance      : Cd
 Conc.          : ---
 Conc.dev.      : ---
 Add.amount     :  10.000 ng

 VR     V       nA      I.mean  Std.Dev.  I.delta   Comments
 -----  ------  ------  ------  --------  --------  ----------------------
 1 - 1     ---     ---     ---       ---            No peak found
 1 - 2     ---     ---                              No peak found
 2 - 1  -0.596   4.175   4.218     0.061            Ovl. in sweep
 2 - 2  -0.596   4.261
 3 - 1  -0.596   7.922   8.077     0.219     3.859  Ovl. in sweep
 3 - 2  -0.596   8.232                              Ovl. in sweep

 Substance      : Pb
 Conc.          :   6.575 ug/L
 Conc.dev.      :   0.292 ug/L     ( 4.44%)
 Amount         :  72.328 ng
 Add.amount     :  50.000 ng

 VR     V       nA      I.mean  Std.Dev.  I.delta   Comments
 -----  ------  ------  ------  --------  --------  ----------------------
 1 - 1  -0.400   15.96   15.71     0.348      0.00
 1 - 2  -0.400   15.46
 2 - 1  -0.400   26.55   26.85     0.427     11.14  Ovl. in sweep
 2 - 2  -0.400   27.16
 3 - 1  -0.400   35.85   36.54     0.978      9.69  Ovl. in sweep
 3 - 2  -0.400   37.23                              Ovl. in sweep

 Substance      : Cu
 Conc.          :   6.396 ug/L
 Conc.dev.      :   0.231 ug/L     ( 3.61%)
 Amount         :  70.355 ng
 Add.amount     : 250.000 ng

 VR     V       nA      I.mean  Std.Dev.  I.delta   Comments
 -----  ------  ------  ------  --------  --------  ----------------------
 1 - 1  -0.132    16.8    16.5     0.336       0.0
 1 - 2  -0.132    16.3
 2 - 1  -0.120    76.6    77.0     0.662      60.5  Ovl. in sweep
 2 - 2  -0.120    77.5
 3 - 1  -0.114   127.2   128.8     2.307      51.8  Ovl. in sweep
 3 - 2  -0.114   130.4                              Ovl. in sweep


 Substance    Calibr.      Y.reg/offset        Slope Mean deviat. Corr.Coeff.
 ------------ ------------ ------------ ------------ ------------ ------------
 Zn           std.add.       1.480e-006   6.511e-003   4.062e-008      0.99842
 Cd           std.add.       2.884e-010   4.362e-003   2.276e-010      0.99827
```

```
 Pb           std.add.       1.578e-008   2.400e-003   7.292e-010      0.99801
 Cu           std.add.       1.658e-008   2.592e-003   1.201e-009      0.99900


 Final results                         +/- Res. dev.   %     Comments
-----------------------------------    ------------------    -------------------

 Zn:
 default           =  250.125  ug/l    9.603        3.839

 Cd:
 default           =      ---  ug/l                          No result found

 Pb:
 default           =    7.233  ug/l    0.321        4.439

 Cu:
 default           =    7.035  ug/l    0.254        3.612
```

Method print for the determination of Zn, Cd, Pb, Cu according to method 1

```
--------------------------------------------------------------------------------
 Method parameters
--------------------------------------------------------------------------------
Method          : AB231_1_Det of Zn Cd Pb Cu.mth
Title           : Determination of Zinc, Cadmium, Lead, and Copper acc. to DIN38
406/16
Remark1         : 10 mL sample + 1 mL acetate buffer (1.5mol/L KCl + 0.5mol/L Na
Ac)
Remark2         :

Calibration     : Standard addition
Technique       : Batch
Addition        : Manual

Sample ID       : tap water
Sample amount (mL): 10.000
Cell volume (mL): 11.000

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)            : 10

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)           :   -1.150
Deposition time (s)                :   90.000

Sweep
Equilibration time (s)             :   10.000
Start potential (V)                :   -1.150
End potential (V)                  :    0.050
Voltage step (V)                   :    0.006
Voltage step time (s)              :    0.100
Sweep rate (V/s)                   :    0.060
Pulse amplitude (V)                :    0.050
Pulse time (s)                     :    0.040

Cell off after measurement         :      Yes
```

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

Substances
--------------------------------------------------------------------------------
Zn                       : -0.980 V   +/- 0.050 V

Standard solution        : 1   10.000 mg/L
Addition volume (mL)     : 0.100

default                  : Final result (Zn) =
                           Conc * (11 / 10) * (1e+006 / 1) + 0 - 0

Cd                       : -0.560 V   +/- 0.050 V

Standard solution        : 1   0.100 mg/L
Addition volume (mL)     : 0.100

default                  : Final result (Cd) =
                           Conc * (11 / 10) * (1e+006 / 1) + 0 - 0

Pb                       : -0.380 V   +/- 0.050 V

Standard solution        : 1   0.500 mg/L
Addition volume (mL)     : 0.100

default                  : Final result (Pb) =
                           Conc * (11 / 10) * (1e+006 / 1) + 0 - 0

Cu                       : -0.100 V   +/- 0.050 V

Standard solution        : 1   2.500 mg/L
Addition volume (mL)     : 0.100

default                  : Final result (Cu) =
                           Conc * (11 / 10) * (1e+006 / 1) + 0 - 0

Baseline
--------------------------------------------------------------------------------
Substance Addition    automatic start (V) end (V) type        scope
--------------------------------------------------------------------------------
Zn        Sample      yes        ---       ---     linear      wholePeak
          Addition 1  yes        ---       ---     linear      wholePeak
          Addition 2  yes        ---       ---     linear      wholePeak
--------------------------------------------------------------------------------
Cd        Sample      yes        ---       ---     linear      wholePeak
          Addition 1  yes        ---       ---     linear      wholePeak
          Addition 2  yes        ---       ---     linear      wholePeak
--------------------------------------------------------------------------------
Pb        Sample      yes        ---       ---     linear      wholePeak
          Addition 1  yes        ---       ---     linear      wholePeak
          Addition 2  yes        ---       ---     linear      wholePeak
--------------------------------------------------------------------------------
Cu        Sample      yes        ---       ---     linear      wholePeak
          Addition 1  yes        ---       ---     linear      wholePeak
          Addition 2  yes        ---       ---     linear      wholePeak
--------------------------------------------------------------------------------
```

Report for the example determination of Tl according to method 2

```
========== METROHM 797 VA COMPUTRACE (Version 1.0.0.1) (Serial No. 0) ==========
 Determination  : 06051653_tap water_Tl.dth
 Sample ID      : tap water_Tl
 Creator method :                   Date :                     Time:
 Creator determ.:                   Date : 2001-06-05          Time:  16:53:19
 Modified by    : ---               Date :                     Time:
--------------------------------------------------------------------------------
 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/l KCl + 0.5mol/l Na
Ac)
 Remark2        : + 200µl EDTA-Na2 (0.1 mol/l)
--------------------------------------------------------------------------------
 Sample amount  :  10.000 mL
 Cell volume    :  11.200 mL
--------------------------------------------------------------------------------
```

```
 Substance      : Tl
 Conc.          : 272.059 ng/L
 Conc.dev.      :  24.589 ng/L     ( 9.04%)
 Amount         :   3.047 ng
 Add.amount     :  10.000 ng

 VR     V       nA      I.mean  Std.Dev.  I.delta   Comments
 -----  ------  ------  ------  --------  --------  ----------------------
 1 - 1  -0.467   0.549   0.514     0.049     0.000
 1 - 2  -0.467   0.480
 2 - 1  -0.461   2.063   2.112     0.069     1.598
 2 - 2  -0.461   2.161
 3 - 1  -0.455   3.809   3.786     0.033     1.674
 3 - 2  -0.461   3.763


 Final results                         +/- Res. dev.   %     Comments
-----------------------------------    ------------------    -------------------

 Tl:
 default            =    0.305  ug/l    0.028        9.038
```

Method print for the determination of Tl according to method 2

```
--------------------------------------------------------------------------------
 Method parameters
--------------------------------------------------------------------------------
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/L KCl + 0.5mol/L Na
Ac)
Remark2         : + 200µl EDTA-Na2 (0.1 mol/L)

Calibration     : Standard addition
Technique       : Batch
Addition        : Manual

Sample ID       : sample
Sample amount (mL): 10.000
Cell volume (mL): 11.200

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

Highest current range              : 10  mA
Lowest current range               : 100 nA

Electrode                          : HMDE
Drop size (1..9)                   : 4
Stirrer speed (rpm)                : 2000

Initial electr. conditioning       : No

No. of additions                   : 2
No. of replications                : 2

Measure blank                      : No
Addition purge time (s)            : 10

Initial purge time (s)             :      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)           :   -0.800
Deposition time (s)                :  180.000

Sweep
Equilibration time (s)             :   10.000
Start potential (V)                :   -0.800
End potential (V)                  :   -0.200
Voltage step (V)                   :    0.006
Voltage step time (s)              :    0.100
Sweep rate (V/s)                   :    0.060
Pulse amplitude (V)                :    0.050
Pulse time (s)                     :    0.040
```

```
Cell off after measurement         :      Yes

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

Substances
--------------------------------------------------------------------------------
Tl                       : -0.450 V   +/- 0.050 V

Standard solution        : 1   0.500 mg/L
Addition volume (mL)     : 0.020

default                  : Final result (Tl) =
                           Conc * (11.2 / 10) * (1e+006 / 1) + 0 - 0

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

Report for the example determination of Ni and Co according to method 3

```
========== METROHM 797 VA COMPUTRACE (Version 1.0.0.1) (Serial No. 0) ==========
 Determination  : 09151108_NiCoMeerwasser.dth
 Sample ID      : Meerwasser
 Creator method :                   Date :                     Time:
 Creator determ.:                   Date : 1999-09-15          Time:  11:08:54
 Modified by    : ---               Date :                     Time:
--------------------------------------------------------------------------------
 Method         : Ni-Co Meerwasser.mth
 Title          : Determination of Nickel and Cobalt acc. to DIN38406/16
 Remark1        : 10 ml sample + 0.5 mL ammonia buffer
 Remark2        : + 0.1 mL DMG solution
--------------------------------------------------------------------------------
 Sample amount  :  10.000 mL
 Cell volume    :  11.050 mL
--------------------------------------------------------------------------------
 Substance      : Ni
 Conc.          : 553.296 ng/L
 Conc.dev.      :  24.389 ng/L     ( 4.41%)
 Amount         :   6.114 ng
 Add.amount     :  10.000 ng

 VR     V       nA      I.mean  Std.Dev.  I.delta   Comments
 -----  ------  ------  ------  --------  --------  ----------------------
 1 - 1  -0.927   -29.5   -30.4     1.276       0.0
 1 - 2  -0.927   -31.3
 2 - 1  -0.927   -78.8   -80.8     2.915     -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
 Conc.          :   1.683 ng/L
 Conc.dev.      :   3.572 ng/L     (212.22%)
 Amount         :  18.597 pg
 Add.amount     :   1.000 ng

 VR     V       nA      I.mean  Std.Dev.  I.delta   Comments
 -----  ------  ------  ------  --------  --------  ----------------------
 1 - 1  -1.089   -0.31    -0.34     0.046      0.00
 1 - 2  -1.086   -0.37
 2 - 1  -1.086  -11.62  -12.26     0.900    -11.92
 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 Mean deviat. Corr.Coeff.
 ------------ ------------ ------------ ------------ ------------ ------------
 Ni            std.add.       -3.047e-008  -5.507e-002   2.146e-009      0.99883
 Co            std.add.       -2.280e-010  -1.355e-001   1.012e-009      0.99778
```

```
 Final results                             +/- Res. dev.   %     Comments
-----------------------------------        ------------------    -------------------

 Ni:
 default            =    0.611  ug/l    0.027        4.408

 Co:
 default            =    1.860  ng/l    3.947      212.215
```

Method print for the determination of Ni and Co according to method 3

```
--------------------------------------------------------------------------------
 Method parameters
--------------------------------------------------------------------------------
Method          : AB231_3_Det of Ni Co.mth
Title           : Determination of Nickel and Cobalt acc. to DIN38406/16
Remark1         : 10 ml sample + 0.5 mL ammonia buffer
Remark2         : + 0.1 mL DMG solution

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)            : 10

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)           :   -0.700
Deposition time (s)                :   90.000

Sweep
Equilibration time (s)             :   10.000
Start potential (V)                :   -0.800
End potential (V)                  :   -1.250
Voltage step (V)                   :    0.004
Voltage step time (s)              :    0.300
Sweep rate (V/s)                   :    0.013
Pulse amplitude (V)                :    0.050
Pulse time (s)                     :    0.040

Cell off after measurement         :      Yes

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

```
Substances
--------------------------------------------------------------------------------
Ni                        : -0.970 V   +/- 0.050 V

Standard solution         : 1   1.000 mg/L
Addition volume (mL)      : 0.010

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

Co                        : -1.130 V   +/- 0.050 V

Standard solution         : 1   0.100 mg/L
Addition volume (mL)      : 0.010

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

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