

## Application Bulletin 440/1

# Determination of nickel and cobalt in water samples by adsorptive stripping voltammetry with a Bi drop electrode

### Summary

Cobalt is an essential element for humans because it is a component of vitamin B12. While small overdoses of cobalt compounds are only slightly toxic to humans, larger doses from 25–30 mg per day may lead to skin, lung, and stomach diseases, as well as liver, heart, and kidney damage, and even cancerous growths. The same is valid for nickel, which can lead to inflammation at higher concentrations. Drinking a large amount of water containing nickel can cause discomfort and nausea. In the EU the legislation specifies 0.02 mg/L as the limit value for the nickel concentration in drinking water. This concentration can be reliably determined with the method described in this Application Bulletin.

The simultaneous and straightforward determination of nickel and cobalt is based on adsorptive stripping voltammetry (AdSV) using dimethylglyoxime (DMG) as a complexing agent in an alkaline electrolyte (pH 9.6). This method can be successfully applied to tap water, mineral water, and sea water samples using the 884 Professional VA and the non-toxic Bi drop electrode. The limit of detection for 30 s deposition time is approximately 0.2 µg/L for nickel and 0.1 µg/L for cobalt, and can be lowered further by increasing the deposition time. With 30 s deposition time the maximum concentration of the linear range of the method is ca. 15 µg/L for Ni and ca. 20 µg/L for Co, allowing reliable determination in samples containing Ni concentrations between 0.2–8 µg/L and Co between 0.1–12 µg/L.

### Samples

Tap water, mineral water, and sea water

### Instruments and accessories

884 Professional VA manual for MME	2.884.0110
Electrode equipment with Bi drop electrode for 884 Professional VA	6.5339.080
Containing:	
Stirrer for 884	6.1204.500
Measuring vessel 10 mL	6.1415.210
Threaded stopper	6.1446.040
Cap	6.2753.210
viva 2.1	6.6065.21X

### Electrodes

WE	Bi drop electrode	6.0346.000
RE	Ag/AgCl reference electrode	6.0728.120
	Ag/AgCl/c(KCl) = 3 mol/L	
	Electrolyte vessel	6.1245.010
	Filled with c(KCl) = 3 mol/L	
AE	Glassy carbon rod	6.1247.000
	Electrode holder	6.1241.120

### Overview

The Application Bulletin describes the following methods:

#### **Activation/cleaning of Bi drop electrode**

A new sensor needs to be activated first. The activation must be carried out prior to the first use, and whenever the sensor has not been used for more than 1 hour. If the electrode needs to be cleaned either before, in between, or after determinations, the procedure described in the subchapter «Activation/cleaning of Bi drop electrode» should be used.

#### **Determination of nickel and cobalt**

Nickel and cobalt are determined by adsorptive stripping voltammetry (AdSV). In an alkaline electrolyte (pH 9.6), free ions are complexed by dimethylglyoxime (DMG) and accumulated at the surface of the Bi drop electrode. In the subsequent stripping step the Ni/Co-DMG-complex is reduced giving the analytical signal.

#### **Standard operating procedure**

- Activation of the Bi drop electrode
- Determination of nickel and cobalt in a blank or a check standard solution to validate electrode performance
- Determination of samples
- Rinsing of the Bi drop electrode with ultrapure water
- Dry storage in the storage vessel 6.2008.040

For more information about the standard operating procedure, please refer to the comments in the chapters

«Activation/cleaning of the Bi drop electrode» and «Comments» at the end of this document.

## Reagents

- Co(II) standard stock solution,  $\beta(\text{Co(II)}) = 1 \text{ g/L}$ , commercially available
- Ni(II) standard stock solution,  $\beta(\text{Ni(II)}) = 1 \text{ g/L}$ , commercially available
- Ammonium hydroxide solution,  $w(\text{NH}_3) \geq 25\%$ , for trace analysis\*, CAS 1336-21-6
- Nitric acid,  $w(\text{HNO}_3) = 65\%$ , for trace analysis\*, CAS 7697-37-2
- Hydrochloric acid,  $w(\text{HCl}) = 30\%$ , for analysis, CAS 7647-01-0
- Sodium hydroxide solution,  $w(\text{NaOH}) = 30\%$ , for trace analysis\*, CAS 1310-73-2
- Triethanolamine,  $w(\text{triethanolamine}) \geq 99.0\%$ , for analysis, CAS 102-71-6
- Potassium bromate,  $w(\text{KBrO}_3) \geq 99.8\%$ , for analysis, CAS 7758-01-2
- Dimethylglyoxime disodium salt octahydrate ( $\text{Na}_2\text{DMG}$ ), puriss p.a., CAS 75006-64-3
- Hydrogen peroxide solution,  $w(\text{H}_2\text{O}_2) = 30\%$ , for trace analysis\*, CAS 7722-84-1
- Ultrapure water, resistivity  $>18 \text{ M}\Omega \cdot \text{cm}$  ( $25 \text{ }^\circ\text{C}$ ), type I grade (ASTM D1193)

\*e.g. Honeywell Fluka TraceSELECT® or Merck Suprapur®

## Solutions

Supporting electrolyte	Ammonium buffer pH 9.6 $c(\text{NH}_3) = 2 \text{ mol/L}$ $c(\text{NH}_4\text{Cl}) = 1 \text{ mol/L}$ 10.6 mL $w(\text{HCl}) = 30\%$ and 22.5 mL $w(\text{NH}_4\text{OH}) = 25\%$ are diluted in 50 mL ultrapure water and made up to the mark in a 100 mL volumetric flask.
Dimethylglyoxime ( $\text{Na}_2\text{DMG}$ ) solution	$c(\text{Na}_2\text{DMG}) = 10 \text{ mmol/L}$ In a 100 mL volumetric flask 304 mg of dimethylglyoxime disodium salt octahydrate are dissolved in 80 mL ultrapure water and filled up to the mark. The solution must be freshly prepared every day.
Cleaning electrolyte	$c(\text{NaOH}) = 1 \text{ mol/L}$

$c(\text{triethanolamine}) = 0.1 \text{ mol/L}$   
 $c(\text{KBrO}_3) = 0.4 \text{ mol/L}$   
 10 mL sodium hydroxide solution, 1.32 mL triethanolamine, and 6.7 g potassium bromate are dissolved and filled up to 100 mL with ultrapure water in a volumetric flask.

## Standard solutions

Standard addition solution 1	$\beta(\text{Co(II)}) = 1 \text{ mg/L}$ $\beta(\text{Ni(II)}) = 1 \text{ mg/L}$ 0.1 mL Co(II) standard stock solution, 0.1 mL Ni(II) standard stock solution, and 0.1 mL nitric acid are added and made up to 100 mL with ultrapure water in a 100 mL volumetric flask.
Standard addition solution 2	$\beta(\text{Co(II)}) = 0.1 \text{ mg/L}$ $\beta(\text{Ni(II)}) = 0.1 \text{ mg/L}$ 10 mL standard addition solution 1 and 0.1 mL nitric acid are added and made up to 100 mL with ultrapure water in a 100 mL volumetric flask.

## Sample preparation

- Ground water, drinking water, sea water, and mineral water can usually be analyzed directly.
- Water that contains interfering organic substances is digested using the 909 UV Digester: 10 mL acidified water sample ( $\text{pH} = 2$ ) with  $10 \mu\text{L } w(\text{HNO}_3) = 65\%$  and  $100 \mu\text{L } w(\text{H}_2\text{O}_2) = 30\%$  are irradiated for 90 min at  $90 \text{ }^\circ\text{C}$ .

## Activation/cleaning of the Bi drop electrode

### Analysis

10 mL ultrapure water and 1 mL cleaning electrolyte are pipetted into the measuring vessel. The activation/cleaning is carried out using the parameters given under «Parameters for activation/cleaning». The measuring solution is purged for 5 minutes before the activation/cleaning.

### Measuring solution

10 mL ultrapure water

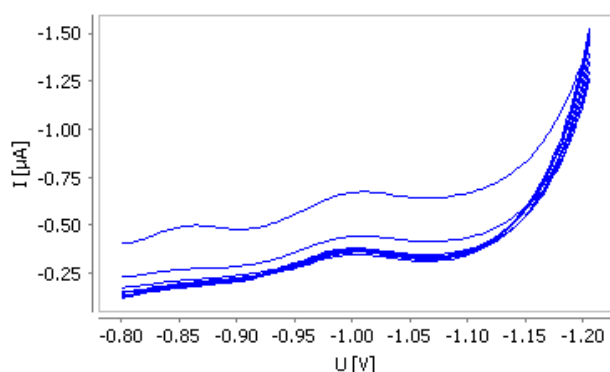
1 mL cleaning electrolyte

### Parameters for activation/cleaning

Voltammetric	
Measuring mode	DP – Differential pulse
Cyclovoltammetric pretreatment	
Start potential	0.2 V
Vertex potential	-1 V
No. of cycles	10
Potentiostatic pretreatment	
Potential	-2 V
Waiting time	15 s
Sweep	
Start potential	-0.8 V
End potential	-1.2 V
Potential step	0.006 V
Potential step time	0.1 s
Pulse amplitude	0.05 V
Potentiostat	
Highest current range	2 mA
Lowest current range	200 $\mu$ A

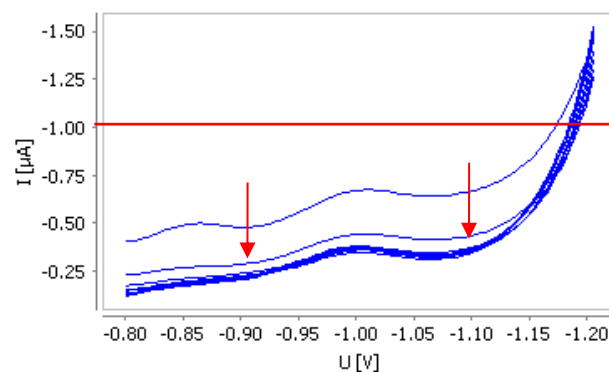
More detailed method parameters can be found in the method printout, which is available as a separate document.

### Example



### Comments

The current at -0.9 V and -1.1 V should not be more negative than -1  $\mu$ A. If the current is more negative than -1  $\mu$ A, further cleaning is required.



## Determination of Ni and Co

### Analysis

10 mL sample, 1 mL supporting electrolyte, and 0.1 mL dimethylglyoxime solution are pipetted into the measuring vessel. The Ni, Co determination is carried out using the parameters given under «Parameters for Ni and Co determination». The measuring solution is purged for 5 min before the determination.

### Measuring solution

10 mL sample

1 mL supporting electrolyte

0.1 mL dimethylglyoxime solution

Quantification is carried out by two standard additions of the standard addition solution.

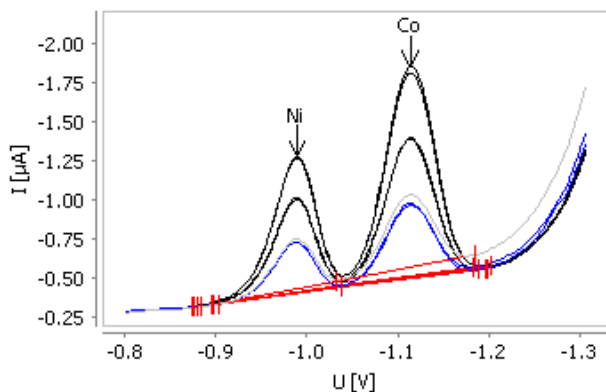
### Parameters for Ni and Co determination

Voltammetric	
Measuring mode	SQW – square wave
Cyclovoltammetric pretreatment	
Start potential	0.1 V
Vertex potential	-0.2 V
No. of cycles	2
Potentiostatic pretreatment	
Potential 1	-1.3 V
Waiting time 1	10 s
Potential 2	-0.8 V
Waiting time 2	30 s
Sweep	
Start potential	-0.8 V

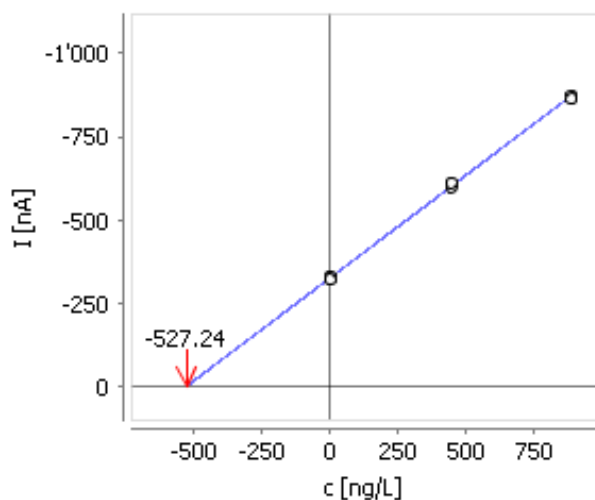
End potential	-1.3 V
Potential step	0.006 V
Frequency	25 Hz
Pulse amplitude	0.02 V
<b>Potentiostat</b>	
Highest current range	2 mA
Lowest current range	200 $\mu$ A
<b>Substance</b>	
Name	Ni
Characteristic potential	-1.0 V
Name	Co
Characteristic potential	-1.12 V

More detailed method parameters can be found in the method printout which is available as a separate document.

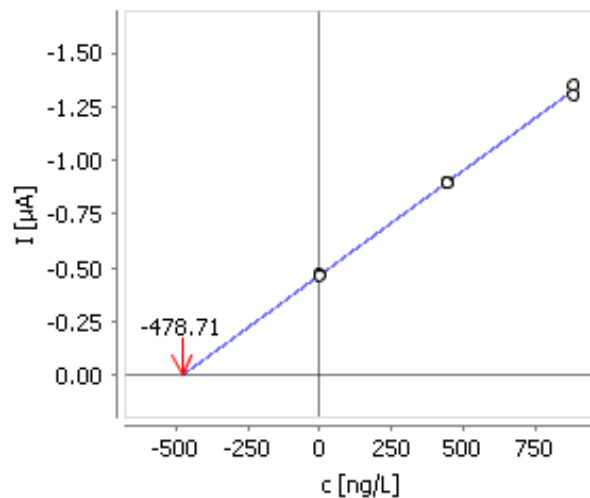
#### Example determination in tap water sample spiked with $\beta(\text{Ni}) = 0.5 \mu\text{g/L}$ and $\beta(\text{Co}) = 0.5 \mu\text{g/L}$



#### Standard addition curve for Ni



#### Standard addition curve for Co



### Results

#### Nickel

Sample	$\beta(\text{Ni})^*$ $\mu\text{g/L}$	RSD	Recovery
Check standard 0.5 $\mu\text{g/L}$ Ni	0.49	4%	98%
Tap water	< LOD		
Tap water spiked 0.5 $\mu\text{g/L}$ Ni	0.45	3%	92%
Mineral water	< LOD		
Mineral water spiked 0.5 $\mu\text{g/L}$ Ni	0.47	3%	94%
Sea water	< LOD		
Sea water spiked 0.5 $\mu\text{g/L}$ Ni	0.42	3%	86%

\* - mean value of 3 determinations (5 determinations for check standard 0.5  $\mu\text{g/L}$ )

RSD - relative standard deviation

Recovery – Recovery of the spiked amount

#### Cobalt

Sample	$\beta(\text{Co})^*$ $\mu\text{g/L}$	RSD	Recovery
Check standard 0.5 $\mu\text{g/L}$ Co	0.57	1%	114%
Tap water	< LOD		
Tap water spiked 0.5 $\mu\text{g/L}$ Co	0.52	1%	105%
Mineral water	< LOD		

Mineral water spiked 0.5 µg/L Co	0.54	2%	108%
Sea water	< LOD		
Sea water spiked 0.5 µg/L Co	0.49	11%	98%

\* - mean value of 3 determinations (5 determinations for check standard 0.5 µg/L)

RSD - relative standard deviation

Recovery – Recovery of the spiked amount

## Comments

### Electrode activation, electrode cleaning

Prior to the first use, the Bi drop electrode has to be activated by using the procedure described under «Activation/cleaning of the Bi drop electrode». This procedure can be used for both the activation and cleaning of the Bi drop electrode, and is repeated until the background current is more positive than  $-1 \mu\text{A}$ . It is recommended to run the activation/cleaning procedure if the electrode has not been used for more than one hour.

### Electrode storage

When the electrode is not used for <12 h (e.g., overnight), it can be stored in diluted cleaning electrolyte (10 mL ultrapure water + 1 mL cleaning electrolyte). Keeping the electrode in ultrapure water or a different solution will cause the bismuth drop to turn black, which will require the aggressive regeneration of the surface (see «Regeneration of the Bi drop electrode»).

When the electrode is not used for a longer period of time, it must be stored dry. Before storage, thoroughly rinse the Bi drop with ultrapure water and leave it to dry. When the electrode is completely dry, store it in the storage vessel 6.2008.040 for mechanical protection.

### Blackening of the Bi drop electrode

When the electrode has been stored under unsuitable conditions, the bismuth drop surface tends to turn completely black as soon as the first potential in the method is applied. To the best of our knowledge, this behavior does not depend on the measuring solution or the first applied potential. When the bismuth drop has turned black, the electrode has to be regenerated as described under «Regeneration of the Bi drop electrode».

### Regeneration of the Bi drop electrode

If the bismuth drop is covered with a black film (not dark gray), proceed as follows:

Dip the black-colored bismuth drop for a short period of time (3–5 s) in concentrated nitric acid ( $w(\text{HNO}_3) = 65\%$ ), rinse thoroughly with ultrapure water and perform the electrochemical cleaning procedure as described under «Activation/cleaning of Bi drop electrode». The electrochemical cleaning procedure may have to be repeated several times, always in a new cleaning solution, until the baseline current is more positive than  $-1 \mu\text{A}$ .

No other procedures, such as e.g. prolonged cleaning without treatment with nitric acid, results in a satisfactory baseline. It is necessary to remove a portion of the bismuth surface to restore the performance.

The regeneration procedure is aggressive to the electrode and should be carried out only when the surface of the bismuth drop has turned completely black, but not when it is only dark gray. The treatment with nitric acid can only be repeated 2–3 times in the lifetime of the electrode. Then the Bi drop electrode cannot be recovered anymore.

### Automation

When the Bi drop electrode is used in an automated system, it is recommended to run one activation/cleaning method at the end of the determination series, and to keep the measuring vessel filled with the measuring solution (diluted cleaning electrolyte). It is important that the Bi drop electrode is stored in the cleaning electrolyte to prevent the Bi from turning black. However, the electrode should not be in solution for more than 12 hours (see «Electrode storage»). If the electrode is kept in the cleaning electrolyte for more than 12 hours, repeated cleaning/activation is required.

### Interference of heavy metals

The influence of different anions ( $\text{Cl}^-$ ) and cations (Cd, Fe, Mn, Pb) on the determination of a check standard solution of  $\beta(\text{Ni}) = 2 \mu\text{g/L}$  and  $\beta(\text{Co}) = 2 \mu\text{g/L}$  was tested with a deposition time of 30 s. The shape of the background current, height and shape of Ni and Co peaks were evaluated.

Cd	Cd does not interfere directly with the determination. No effect was observed up to a concentration of 35 µg/L Cd.
Fe	Fe does not interfere with the Co and Ni determination up to a concentration of 0.4 mg/L Fe in the measuring vessel. 1 mg/L Fe results in an increase of the

background current behind Ni peak and the sensitivity of Co drops by 50%. The Ni peak itself is unaffected by presence of Fe.

**Mn** Mn does not interfere directly with the determination. No effect was observed up to a concentration of 200 µg/L.

**Pb** Pb does not interfere directly with the determination. No effect was observed up to a concentration of 200 µg/L.

**Cl<sup>-</sup>** A slight decrease of ca. 25% for Co peak height was observed for chloride concentrations higher than 0.3 mol/L in the measuring cell.

### Limit of detection

The limit of detection was set to the smallest possible concentration which can be determined with the recovery rate of 50% in a check standard solution.

Deposition	Ni	Co
30 s	0.2 µg/L	0.1 µg/L

### Maximum concentration of the linear range

The maximum concentration of the linear range was read out from a calibration curve.

Deposition	Ni	Co
30 s	15 µg/L	20 µg/L

### Working range of the method

With a deposition time of 30 s and two standard additions ( $\beta(\text{Ni}) = 4 \mu\text{g/L}$  and  $\beta(\text{Co}) = 4 \mu\text{g/L}$ ), the method is suitable for samples with Ni concentrations between 0.2–8 µg/L and Co concentrations between 0.1–12 µg/L. This allows monitoring of the regulatory limits for Ni in drinking water.

### DMG

Alternatively to the dimethylglyoxime disodium salt octahydrate ( $\text{Na}_2\text{DMG}$ ), pure dimethylglyoxime can be used. However, this compound is insoluble in water and has to be dissolved in ethanol.

### Reproducibility and recovery rate

The overview for reproducibility and recovery rate is shown in the following illustration.

