Metrohm

Application Bulletin 114/2 e

Determination of copper, nickel, cobalt, zinc, and iron in a single operation by polarography

Summary

Cu^{2+}, Ni^{2+}, Co^{2+}, Zn^{2+} and Fe^{2+}/Fe^{3+} are determined simultaneously. Interference due to the presence of other metals is mentioned, and methods given to eliminate it. The limit of determination is 20 µg/L for Co and Ni, and 50 µg/L each for Cu, Zn and Fe.

Instruments

VA instrument capable of operating a Multi-Mode Electrode and supporting differential pulse (DP) measuring mode

Reagents

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

- Sulfuric acid, w(H_2SO_4) = 96 %, for trace analysis*, CAS 7664-93-9
- Nitric acid, w(HNO_3) = 65 %, for trace analysis*, CAS 7697-37-2
- Ammonium hydroxide, w(NH_3) = 25 %, for trace analysis*, CAS 1336-21-6
- Phosphoric acid, w(H_3PO_4) = 85 %, for trace analysis*, CAS 7664-38-2
- Ethylenediaminetetraacetic acid disodium salt dihydrate, Na_2-EDTA·$2H_2O$, for analysis, CAS 6381-92-6
- Dimethylglyoxime, DMG, for analysis, CAS 95-45-4
- Ethanol, for analysis, CAS 64-17-5
- Ultrapure water, resistivity >18 MΩ·cm (25 °C), type I grade (ASTM D1193)

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

Solutions

Electrolyte	c(5-sulfosalicylic acid) = 0.4 mol/L Dissolve 10.17 g of 5-sulfosalicylic acid in ultrapure water and fill up to 100 mL.
Na_2-EDTA solution	c(Na_2-EDTA) = 0.1 mol/L Dissolve 0.93 g Na_2-EDTA·$2H_2O$ in ultrapure water and fill up to 25 mL.
Dimethylglyoxime	c(Dimethylglyoxime) = 0.1 mol/L Dissolve 0.29 g dimethylglyoxime in ethanol and fill up to 25 mL. This solution should be freshly prepared every day.

Standard Solutions

Cu, Co, Ni and Zn standard solution	c(Cu^{2+}, Co^{2+}, Ni^{2+}, Zn^{2+}) = 1 g/L Diluted solutions are prepared using c(HNO_3) = 0.014 mol/L.
Fe standard solution	c(Fe^{3+}) = 1 g/L The solution contains 1 mL of 5-sulfosalicylic acid per 100 mL.

Sample preparation

See Application Bulletin 113

Determination of Cu, Pb, Cd, Ni, Co, Zn and Fe

Analysis

Measuring solution

Digestion solution

10 mL water

0.2 mL phosphoric acid

2 mL electrolyte

Adjust the pH of the solution to 9.5 with ammonium hydroxide solution.

Measuring solution for higher metal concentrations

Digestion solution

10 mL water

0.2 mL phosphoric acid

5 mL electrolyte

Adjust the pH of the solution to 9.5 with ammonium hydroxide solution.

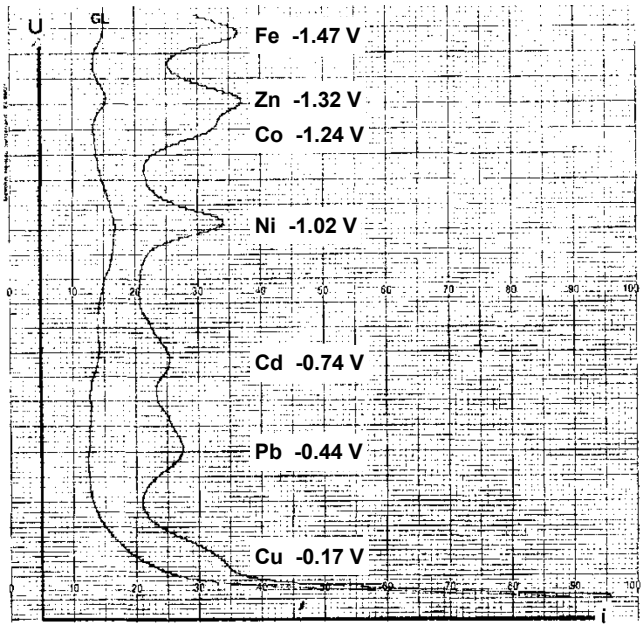
The concentration is determined by standard addition.

Parameters

Voltammetric	
Electrode operating mode	DME
Measuring mode	DP – Differential pulse
Stirring rate	2000 min^{-1}
Sweep	
Start potential	-0.08 V
End potential	-1.5 V
Potential step	0.005 V
Potential step time	0.8 s
Sweep rate	0.006 V/s
Pulse amplitude	0.03 V
Substance	
Name	Cu
Characteristic potential	-0.17 V
Name	Pb
Characteristic potential	-0.44 V
Name	Sn
Characteristic potential	-0.57 V
Name	Cd
Characteristic potential	-0.74 V
Name	Ni
Characteristic potential	-1.02 V
Name	Co
Characteristic potential	-1.24 V
Name	Zn
Characteristic potential	-1.32 V
Name	Fe
Characteristic potential	-1.47 V

Example

Sample containing 10 µg of each of the above metals.



Comments

- The complex of iron salicylate or iron sulfosalicylate respectively forms slowly (approx. 10 min). It is recommended to do standard addition with the complex directly.
- Fe^{2+} and Fe^{3+} give the same reduction wave, and are thus determined together.
- Cr^{6+} interferes with iron determination. If present, it must be reduced to the less active Cr^{3+} by adding 1 mL ethanol to the digestion solution while it still contains sulfuric acid and boiling out.
- Sn^{4+}, aluminum, manganese, and the alkali and alkaline-earth metals are not detected and do not interfere with the determination of the metals in question.

Determination of Co beside Zn after addition of DMG

If a small quantity of cobalt is present together with a large quantity of zinc (as is usually the case), the cobalt will be detected qualitatively, but cannot be directly determined quantitatively. In such a case, add 0.2 mL of the dimethylglyoxime solution to the contents of the polarography vessel, mix by passing nitrogen for 2 min and record another

polarogram. The cobalt (and nickel) complex thus formed can be recorded far more sensitively (peak potential Co: -1.20 V, separated from Zn).

Measuring solution

Digestion solution

10 mL water

0.2 mL phosphoric acid

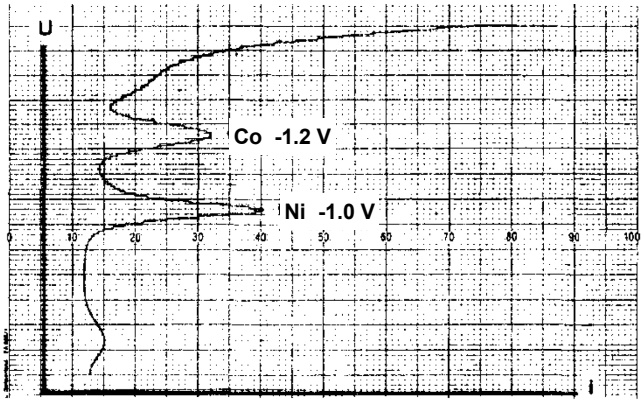
5 mL electrolyte

0.2 mL DMG solution

Adjust the pH of the solution to 9.5 with ammonium hydroxide solution.

The determination is carried out with the parameters specified for the determination of Cu, Pb, Cd, Ni, Co, Zn and Fe. The concentration is determined by standard addition.

Example (Nickel and cobalt together after addition of dimethylglyoxime)



Determination of Cu after addition of EDTA

Small quantities of copper also cannot be determined very accurately. In this case, add 5 mL of the Na_2-EDTA solution to the contents of the polarography vessel, mix by passing nitrogen for 1 min and record another polarogram (peak potential Cu: -0.73 V.)

Measuring solution

Digestion solution

10 mL water

0.2 mL phosphoric acid

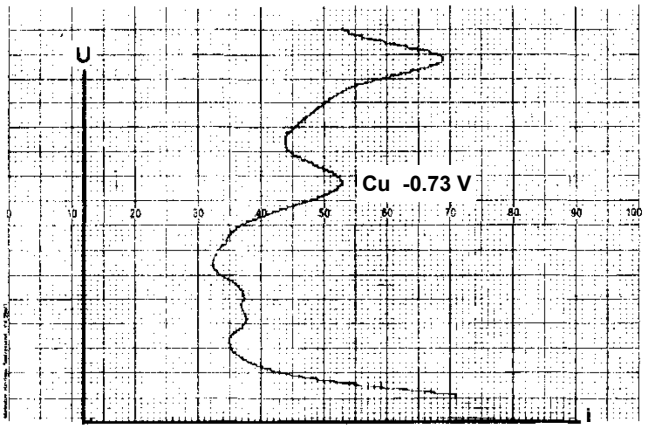
5 mL electrolyte

5 mL EDTA solution

Adjust the pH of the solution to 9.5 with ammonium hydroxide solution.

The determination is carried out with the parameters specified for the determination of Cu, Pb, Cd, Ni, Co, Zn and Fe. The concentration is determined by standard addition.

Example (Copper after addition of Na_2EDTA)



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