

Application Bulletin



Of interest for:
 General laboratories
 Foodstuffs and water analysis laboratories

No. 114/1 e

Polarographic determination of five metal ions (copper, cobalt, nickel, zinc and iron) in a single operation

Summary	Cu^{2+} , Co^{2+} , Ni^{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 threshold of determination is $\rho = 20 \mu\text{g/L}$ for Co and Ni, and $\rho = 50 \mu\text{g/L}$ each for Cu, Zn and Fe.		
Notations	Symbol	Signification	SI-Unit
	<i>c</i>	substance concentration	mol/L
	<i>w</i>	mass fraction	1
	ρ	mass concentration	g/L
Apparatus	<ul style="list-style-type: none"> ▶ 506 Polarecord with 663 Polarography Stand or 646 VA Processor with 647 VA Stand ▶ Working electrode DME ▶ Auxiliary electrode Pt ▶ Reference electrode Ag/AgCl sat. KCl 		
Reagents	<ul style="list-style-type: none"> ▶ Sulfuric acid "Suprapur", $w = 0.96$ (96%) ▶ Nitric acid "Suprapur", $w = 0.65$ (65%) ▶ Ammonium hydroxide "Suprapur", $w = 0.25$ (25%) ▶ Phosphoric acid puriss p.a., $w = 0.85$ (85%) ▶ Electrolyte solution: 5-sulfosalicylic acid $c = 0.4$ mol/L: Take 10.17 g of 5-sulfosalicylic acid, dissolve in distilled water and make up to 100 mL. ▶ $\text{Na}_2\text{-EDTA}$ $c = 0.2$ mol/L: Take 7.445 g of the disodium salt of ethylene diamine tetraacetic acid, dissolve in distilled water and make up to 100 mL. ▶ Dimethylglyoxime: A solution $w = 0.01$ in ethyl alcohol. This solution should be freshly prepared every day. ▶ Standard solutions: ρ (Cu^{2+}, Co^{2+}, Ni^{2+}, Zn^{2+}) = 1 g/L ρ (Fe^{2+}) = 1 g/L The solution contains 1 mL of 5-sulfosalicylic acid per 100 mL. 		
Decomposition	See Application Bulletin No. 113.		

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Method

- ▶ Transfer the cooled decomposition solution with 10 mL of distilled water into the polarography vessel. Add 0.2 mL H_3PO_4 $w = 0.85$ and 2 mL 5-sulfosalicylic acid and adjust the pH to 9.5 with NH_3 $w = 0.25$.

or for higher metal contents:

- ▶ The cooled decomposition is mixed with 0.2 mL H_3PO_4 $w = 0.85$ and 5 mL sulfosalicylic acid and transferred into the polarography vessel with H_2O dist. The pH is adjusted to 9.5 with NH_3 $w = 0.25$.
- ▶ Deaerate with a stream of nitrogen for 10 min and record a DP or AC_1 polarogram with the following settings:

Method	DP	AC_1T
U st	-0.08 V	-0.08 V
Δ U	-1.5 V	-1.5 V
Voltage/drop	0.8 s - 1 mm/drop	0.8 s - 1 mm/drop
Sensitivity	acc. to sample	acc. to sample
U ~	---	5 mV
Amplitude DP	-30 mV	---

$E_{\text{P(DP)}}$ (Ag/AgCl sat. KCl)

Cu^{2+}	-0.17 V	Ni^{2+}	-1.02 V
Pb^{2+}	-0.44 V	Co^{2+}	-1.24 V
Sn^{2+}	-0.57 V	Zn^{2+}	-1.32 V
Cd^{2+}	-0.74 V	$\text{Fe}^{2+}/\text{Fe}^{3+}$	-1.47 V

Calculation

The metals are determined quantitatively by the standard addition method. Any quantities originally present in the reagents used must be subtracted.

Remarks

- ▶ 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 (an nickel) complex thus formed can be recorded far more sensitively.
(Co $E_{\text{P(DP)}}$ -1.20 V, separated from Zn).
- ▶ 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 polarograph again. ($E_{\text{P(DP)}}$ -0.73 V.)
- ▶ The complex of iron salicylate or iron sulfosalicylate respectively forms slowly (appr. 10 min). To do standard addition with the complex directly is recommended.
- ▶ 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 trivalent Cr by adding 1 mL ethanol to the digestion solution while it still contains sulphuric acid and boiling out.
- ▶ Sn^{4+} , aluminium, manganese, and the alkali and alkaline-earth metals are not detected, and do not interfere with the determination of the metals in question.

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Literature

- ▶ S. Rubel, J. Golimowski, M. Wojciechowski
Polarographic methods of galvanic wastes analysis.
I. Determination of Fe, Cu and Cr
Chem. Analyt. (Warsaw) 19, (1974) 41-52 (englisch)
Ref.: Electroanal. Abstr. 12, (1974) 487

- ▶ J. Golimowski and S. Rubel
Polarographic methods in galvanic wastes analysis.
II. Determination of Cu, Zn, Fe, Ni, Pb and Cd
Chem. Analyt. (Warsaw) 19, (1974) 1155-1166 (englisch)
Ref.: Z. Anal. Chem. 277, (1975) 408

- ▶ M.I. Abdullah and L.G. Royle
The determination of Cu, Pb, Cd, Zn and Co in natural waters by pulse polarography
Anal. Chim. Acta 58, (1972) 283-288

Examples of curves

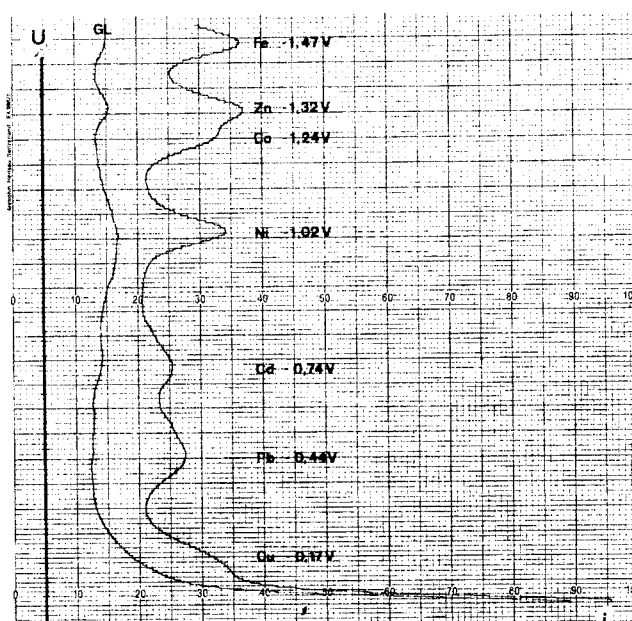


Fig. 1 Cu, Pb, Cd, Ni, Co, Zn and Fe together
 Digestion solution + 0.2 mL phosphoric acid + 5 mL sulfosalicylic acid.
 Adjust to pH 9.5 with NH_3 .
 U_{start} : -0.084 V , ΔU : -1.5 V , DP-amplitude: -30 mV ,
 Voltage drop: 0.8 s resp. 1 mm, sensitivity: $4 \cdot 10^{-10} \text{ A/mm}$,
 Sample containing $10 \mu\text{g}$ of each of the above metals.

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Examples of
curves
(continued)

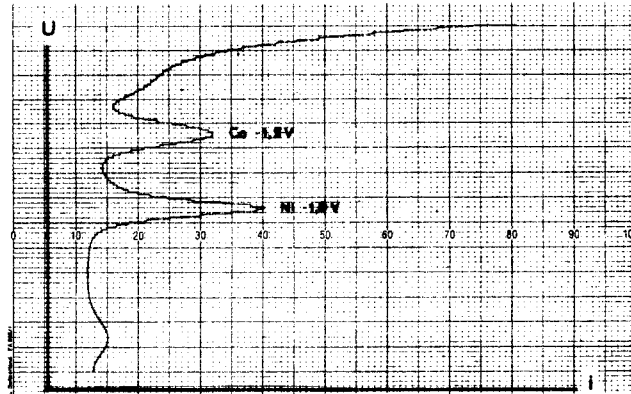


Fig. 2 Nickel and cobalt together after addition of dimethylglyoxime

U_{start} : -0.6 V, ΔU : -1.5 V, DP-amplitude: -30 mV,
Drop/voltage: 0.8 s or 1 mm respectively, sensitivity: $2.5 \cdot 10^{-9}$ A/mm.

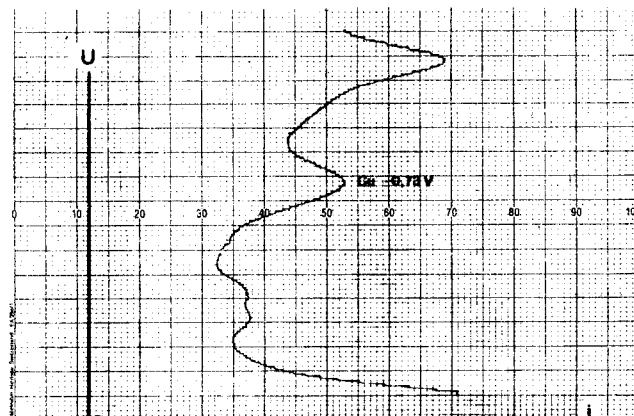


Fig. 3 Copper after addition of $\text{Na}_2\text{-EDTA}$

U_{start} : -0.2 V, ΔU : -1.5 V, DP-amplitude: -30 mV,
Drop/voltage: 0.8 s or 1 mm respectively, sensitivity: $2.5 \cdot 10^{-10}$ A/mm.