

Summary

Besides nickel as main component, an electroless nickel bath contains further major constituents such as electrolyte, buffer as well as reducing and complexing agents. A minor component is the so-called stabilizer. The concentration of this additive ranges from the millimolar to the micromolar level and determines the stability and performance of the bath, for which reason it has to be accurately monitored. This poster describes simple and fast, but sensitive and robust methods for the determination of the stabilizers antimony, bismuth, and iodate in electroless nickel baths.

Antimony(III) and bismuth are determined in parallel by anodic stripping voltammetry (ASV) in 0.6 mol/L KCl electrolyte at pH < 2, whereas the determination of iodate is carried out by polarography in 0.1 mol/L sodium citrate electrolyte at a pH value between 2.8 and 3.5. Under the tested conditions, the linear working range in the electroless nickel bath is for antimony $\beta(\text{Sb}^{\text{III}}) = 0.02 \dots 7 \text{ mg/L}$, for bismuth $\beta(\text{Bi}) = 0.02 \dots 10 \text{ mg/L}$, and for iodate $\beta(\text{IO}_3^-) = 0.3 \dots 110 \text{ mg/L}$.

Introduction

Electroless nickel plating is an important and well-established process in the surface finishing industry. One of the major users of this plating process is the electronics industry in the manufacture of printed circuit boards. In the past, the addition of small amounts of lead has widely been used to stabilize the plating bath. The lead concentration in the bath was mostly controlled by voltammetry. Not only because voltammetry provides a simple and robust way of determining the additive, but rather because voltammetry only detects the electrochemical active part of the additive. This is a much better measure for the performance of the additive than the total metal concentration.

In recent years, a number of countries have imposed restrictions on the sale of electronics containing environmentally hazardous substances, namely lead. In this context, alternative stabilizers were developed and introduced. Important stabilizers of this new generation are antimony, bismuth, and iodate. They can be used as a single additive or in combination with one or both of the others. Voltammetric analysis, with its capacity to quantify the electrochemical active species, is an excellent tool for controlling the concentrations of these additives.

System setup

Voltammetric system for the semi-automated determination of antimony, bismuth or iodate in electroless nickel baths.



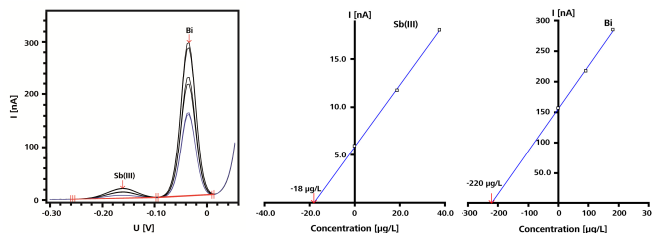
Antimony(III) and bismuth

Principle

Antimony and bismuth are determined by anodic stripping voltammetry in 0.6 mol/L KCl electrolyte at pH < 2. For preconcentration, antimony(III) and bismuth are reduced at a potential of -0.4 V at the hanging mercury drop electrode (HMDE). The two metals dissolve and deposit in the mercury. In the subsequent determination step, the dissolved metals are anodically stripped off the electrode, which results in two distinguished signals, at -0.16 V for antimony(III) and -0.04 V for bismuth.

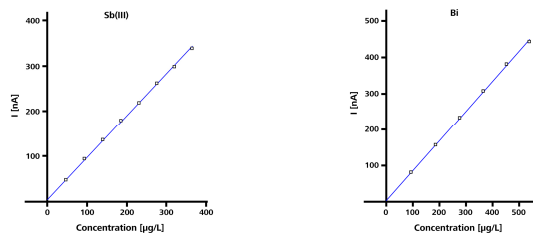
Sample volume	0.5 mL electroless nickel bath
Electrolyte	10 mL supporting electrolyte c (KCl) = 0.6 mol/L c (HNO ₃) = 0.07 mol/L
pH value in the measuring solution	1.3...2
Working electrode	Hanging Mercury Drop Electrode
Reference electrode	Ag/AgCl/KCl (3 mol/L)
Auxiliary electrode	Platinum

Measuring mode	DP (differential pulse)
	Pulse amplitude: 0.02 V
Deposition	potential time
	-0.4 mV 30 s
Potential scan	start end
	-0.3 V 0.05 V
Peak potential	Sb(III) Bi
	-0.16 ± 0.05 V -0.04 ± 0.05 V
Calibration technique	Standard addition



Special care has to be taken for the pH value if both elements have to be determined simultaneously. At pH > 2, the antimony determination does not work anymore and at pH < 1.3, the antimony signal shifts towards the bismuth signal which hinders the separation of the analytical currents for the two elements.

Working range



With a deposition time of 30 s, the calibration curve is linear up to a concentration of $\beta(\text{Sb}^{\text{III}}) \approx 350 \text{ µg/L}$ and $\beta(\text{Bi}) \approx 500 \text{ µg/L}$. The limit of quantification is approximately $\beta(\text{Sb}^{\text{III}}) \approx 4 \text{ µg/L}$ and $\beta(\text{Bi}) \approx 2 \text{ µg/L}$ referring to the total volume of the measuring solution. Using a sample size of 0.5 mL for the analysis, the linear working range for antimony(III) is $\beta(\text{Sb}^{\text{III}}) = 0.08 \dots 7 \text{ mg/L}$ and $\beta(\text{Bi}) = 0.04 \dots 10 \text{ mg/L}$ in the sample. By adjusting sample size and deposition time, the sensitivity of the determination can be adapted to other sample requirements.

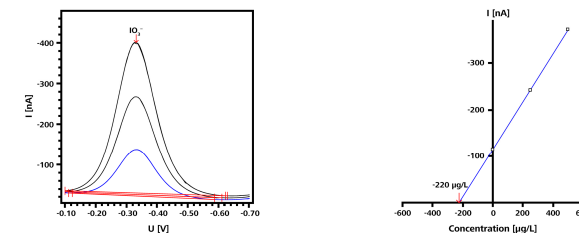
Iodate

Principle

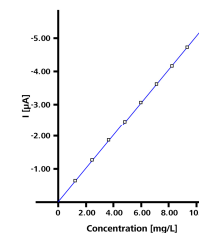
Iodate is determined by polarography in citrate buffer at a pH value around 3. The analytical signal at -0.34 V results from a direct reduction of iodate to iodide on the dropping mercury electrode. This reaction is irreversible. Therefore, it is not possible to increase the sensitivity of the determination by deposition.

Sample volume	1.0 mL electroless nickel bath
Electrolyte	10 mL citrate buffer, pH 2.4 c(trisodium citrate) = 0.1 mol/L c(HCl) = 0.3 mol/L
pH value in the measuring solution	2.8...3.5
Working electrode	Dropping Mercury Electrode (DME)
Reference electrode	Ag/AgCl/KCl (3 mol/L)
Auxiliary electrode	Platinum

Measuring mode	DP (differential pulse)
	Pulse amplitude: 0.05 V
Deposition	potential time
	- -
Potential scan	start end
	-0.1 V -0.7 V
Peak potential	IO ₃ ⁻
	-0.34 ± 0.05 V
Calibration technique	Standard addition



Working range



The calibration curve is at least linear up to a concentration of $\beta(\text{IO}_3^-) \approx 11 \text{ mg/L}$. Higher concentrations have not been tested. The limit of quantification is approximately $\beta(\text{IO}_3^-) \approx 30 \text{ µg/L}$ referring to the total volume of the measuring solution. Using a sample size of 1 mL for the analysis, the linear working range for iodate is $\beta(\text{IO}_3^-) = 0.3 \dots 110 \text{ mg/L}$ in the sample.

References

- Metrohm Application Bulletin AB-074, Polarographic and stripping voltammetric analysis methods for thallium, antimony, bismuth, and iron (copper, vanadium), (downloadable under <http://www.metrohm.com/com/Applications>).
- I.M. Kolthoff and J.J. Lingane, Polarography, 2nd ed., Interscience Publishers, New York (1952).