NOTE

TRACE ANALYSIS OF NICKEL MICROSAMPLES FOR LEAD AND COPPER
BY ANODIC STRIPPING VOLTAMMETRY

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Nanogram quantities of lead and copper are electrodeposited together with mercury on a silver-plated glassy carbon electrode from 100 μ l of 0.6 M hydrochloric acid, and then anodically stripped by the linear scan technique. This method is applied to the simultaneous determination of lead and copper at the low ppm level in 0.5 to 1 mg of sponge nickel.

The presence of traces of lead in high-purity nickel is harmful on hot workability and also deteriorates capabilities of the products. To determine the lead content, anodic stripping voltammetry appears to be one of the most useful methods. Previously¹⁾, we reported anodic stripping voltammetry of lead using the silver-plated glassy carbon electrode [Ag(GC)E] and 100 μ l of dilute hydrochloric acid electrolytes. The method, however, can not be applied to the determination of lead in the presence of copper in excess because of an imperfect separation of the peaks. The present paper describes an improved method for the simultaneous determination of lead and copper, in which both peaks are separated with excellent reproducibility by addition of traces of mercury(II) to the electrolyte.

EXPERIMENTAL

Reagent

Water was purified successively by: (1) ion exchange, (2) distillation with permanganate, and (3) a Millipore Milli-Q adsorption - ion exchange - filtration system. Reagent-grade hydrochloric and nitric acids were further purified in a vitreous-silica sub-boiling distillation unit. Standard metal solutions, 1 g l⁻¹ in 0.1 M HCl or HNO₃, were prepared from high-purity metals (99.99 %) or reagent-grade salts, and diluted with water immediately before use. A mercury(II) stock solution, 1 g l⁻¹ in 0.1 M HNO₃, was prepared from triply-distilled mercury. Nitrogen was filtered through a 0.1- μ m membrane filter.

Apparatus

A Yanaco P8-D polarograph (Yanagimoto Mfg. Co., Ltd., Kyoto, Japan) was employed for pre-electrolysis and recording of stripping (current-voltage) curves. The microelectrolysis cell is shown in Fig. 1. Glassy carbon electrodes [GCE] and silver-plated glassy carbon electrodes [Ag(GC)E] were prepared as described previously¹⁾. Mercury was plated in situ on these electrodes. A clean bench was used to avoid airborne contamination during the preparation of all solutions.

Fig. 1 Microelectrolysis cell

Recommended procedure

A 0.5- to 1-mg metal sample is dissolved in 50 μl of 7 M nitric acid in a 2-ml Teflon vessel with a lid. After complete dissolution, 50 μl of 6 M hydrochloric acid is added, and the solution is evaporated to dryness. The residue is dissolved in 50 μl of 6 M hydrochloric acid, the solution evaporated to dryness, and the residue dissolved in 50 μl of 0.6 M hydrochloric acid. The solution and 50 μl of mercury(II) solution (30 $\text{ng } \mu\text{l}^{-1}$) are transferred to the microelectrolysis cell. The lower 4.5-mm part of the Ag(GC)E (effective surface area: 13 mm^2) is immersed in the electrolyte and pre-electrolysis is carried out at -0.7 V vs. Ag/AgCl for 3 min while stirring by nitrogen bubbling at a flow-rate of ca. 10 ml min^{-1} . The tip of the Teflon tubing for nitrogen is then removed from the solution so that the nitrogen stream is used only for purging the cell space. After 30 s, the electrode potential is scanned to 0.0 V vs. Ag/AgCl at a scan rate of 2 V min^{-1} , a stripping curve being recorded.

RESULTS AND DISCUSSION

When the concentration of copper exceeds that of lead in anodic stripping voltammetry with the Ag(GC)E in 0.6 M hydrochloric acid¹⁾, the peaks of the two elements are not fully separated from each other (Fig. 2, a). Therefore, mercury(II) ions were added to the electrolyte²⁾. Thus the resolution was improved by peak potential shifts of ca. -70 mV for lead and -10 mV for copper, and by sharpening of the peaks (Fig. 2, b). The peak heights of lead and copper increased with increasing mercury concentration in the electrolyte. Above 1 $\mu\text{g Hg}$ in 100 μl , the Hg·Ag(GC)E [in situ mercury-plated Ag(GC)E] gave nearly the same peak potentials, peak heights and peak widths as those with the Hg(GC)E (in situ mercury-plated GCE) for lead and copper. The optimum mercury concentration ranged from 1 to 1.5 $\mu\text{g Hg}$ in 100 μl . At higher mercury concentrations, surface amalgam films often flaked off in some spots on the electrodes during the pre-electrolysis.

The reproducibility, i.e. relative standard deviation, of the peak height of lead of the Hg·Ag(GC)E was 4 % at 5 ng Pb in 100 μl , compared with 8 % for the

Ag(GC)E and 12 % for the Hg(GC)E ($n = 10 - 16$). An Hg-Ag(GC)E, stored in oxygen-free water, was used repeatedly at least 20 times without appreciable change in the stripping curves.

The concentration of hydrochloric acid in the electrolyte has little effect on peak heights of lead and copper over the range of 0.3 to 1 M, but the background current increased with increasing hydrochloric acid concentration. The calibration (peak height vs. concentration) graphs were linear up to at least 20 ng of lead and copper, but only the former passed through the origin. The relative standard deviations at 5 ng of lead and copper were about 4 and 7 % ($n = 16$), respectively. The lower limits of determination were ca. 0.2 ng for lead and ca. 0.5 ng of copper.

No interference resulted from the presence of 1 mg of nickel, 100 ng each of copper and cadmium, 10 ng each of tin(IV), bismuth and antimony(III) in the determination of 10 ng of lead; and 1 mg of nickel, 100 ng each of lead and cadmium, 10 ng of tin(IV) and 5 ng of bismuth in the determination of 10 ng of copper. Antimony(III) interfered with the copper determination severely as shown in Fig. 3.

A sample of sponge nickel (purity: min. 99.99 % through 300 mesh: min. 90 %) was analyzed by the recommended procedure, with the results shown in Table 1. Scattered analytical values show inhomogeneous distribution of impurities in the sample. In the analyses of five aliquots of a sample solution,

Fig. 2 Stripping curves of lead and copper

Electrolyte: 100 μ l of 0.6 M HCl.
Pb, Cu: 5 ng each. Pre-electrolysis
at -0.7 V vs. Ag/AgCl for 3 min.
Scan rate: 2 V min⁻¹.

satisfactory precisions were obtained; i.e. ranges of 0.1 ppm for lead and 0.8 ppm for copper. An analysis required ca. 1.5 h.

Fig. 3 Effect of antimony(III) on stripping curves of lead and copper

— : 10 ng Pb, 10 ng Cu and 1 ng Sb(III),
 --- : 10 ng Pb, 10 ng Cu and 5 ng Sb(III),
 Electrolyte: 100 μ l of 0.6 M HCl.
 Pre-electrolysis at -0.7 V vs. Ag/AgCl for 3 min. Scan rate: 2 V min⁻¹.

Table 1 Determination of lead and copper in sponge nickel

Sample taken mg	Found*, ng		ppm in sample	
	Pb	Cu	Pb	Cu
0.52	0.2	1.2	0.4	2.3
0.52	0.2	2.7	0.4	5.2
0.98	1.1	4.8	1.1	4.9
1.00	0.2	6.0	0.2	6.0
1.00	0.3	4.9	0.3	4.9
1.05	0.2	2.9	0.2	2.8

* Blank values (Pb: 0.2, 0.2, < 0.2 ng, Cu: < 0.5, < 0.5, < 0.5 ng) were subtracted.

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Keyword phrases

anodic stripping voltammetry; determination of lead and copper; trace analysis of nickel microsamples; silver-plated glassy carbon electrode mercury-plated in situ.

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