CAPSULES
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Determination of Trace Levels of Bismuth by Adsorptive Stripping Voltammetry

Purpose

Bismuth is widely used in the nuclear, metallurgical and pharmaceutical industries: hence, a sensitive technique for the determination of trace concentrations in industrial effluents and natural waters is required.

Method

The basis of electrochemical trace analysis is the accumulation (or pre-concentration) of the analyte at the working electrode before the potential scan. The classical voltammetric method for the detection of bismuth is Anodic Stripping Voltammetry (ASV); in this technique, the Bi^{3+} ions in solution are reduced to the zero oxidation state, which then amalgamate with the mercury electrode. Although this method has a low detection limit for bismuth (sub-nanomolar), it is subject to interference by other metal ions with similar redox potentials, particularly antimony.

In Adsorptive Stripping Voltammetry (AdSV), the accumulation occurs via non-electrolytic adsorption of the analyte on the surface of the working electrode (the mercury drop electrode is most commonly used). AdSV can be used for the detection of metal ions via the adsorption of metal ion complexes.

Results

In this study, the complex of bismuth with cupferron was studied. The adsorption of the bismuth-cupferron complex is shown the difference in the cyclic voltammograms recorded after a 120 s accumulation time (F1a) and after zero accumulation (F1b). The 120 s accumulation leads to a 20-fold increase in the peak current. Differential pulse voltammetry was used for the AdSV experiment, and the optimum experimental conditions were found to be as follows: 5×10^{-4} M H_2SO_4, 2.5×10^{-5} M cupferron, accumulation potential = -0.1 V (vs. Ag/AgCl).

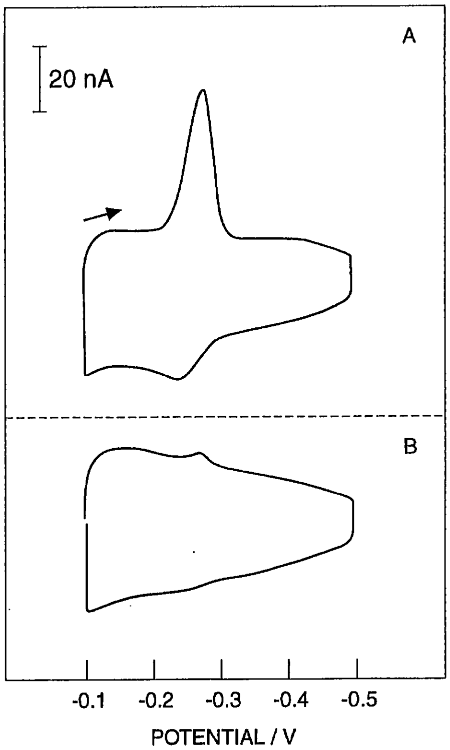

Figure 1. Cyclic voltammograms of a solution of Bi(III) (20 ppb) and cupferron (5×10^{-5} M) in H_2SO_4 (0.5 mM) following 120 s accumulation time (a) and zero accumulation time (b) at -0.1 V vs. Ag/AgCl. Scan rate = 50 mV s^{-1}. Figure adapted from primary reference.

The current response for a 45 s accumulation time was linear over the range 1 - 25 ppb bismuth, whereas for a 90 s accumulation time it was only linear up to 20 ppb (this behavior is typical for surface adsorption). The detection limit (for a 10 minute accumulation time) was 6 ppt. The standard deviation for 4 ppb with an accumulation time of 60s was 1.6% (12 successive measurements).

The increased sensitivity of this AdSV method compared to the ASV method is illustrated in F2, which shows the AdSV (F2a) and ASV (F2b) responses for 2 ppb bismuth with a 120 s accumulation time. Another advantage of the AdSV method is the absence of interference by antimony. However, it has been suggested that the relative merits of the two methods may depend on the application; that is, both methods should be tried. Other ligands that have been used for the analysis of bismuth by AdSV include 5-Br-PADAP (1).

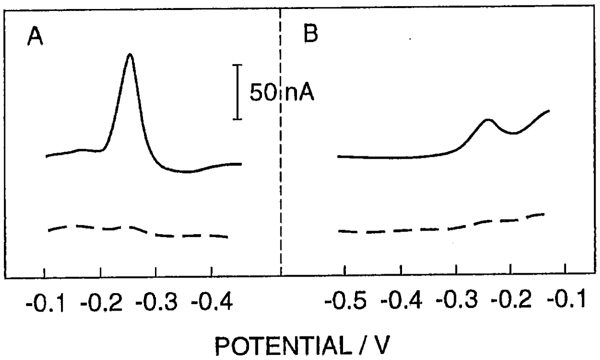

Figure 2. Comparison of AdSV (a) and ASV (b) for the determination of 2 ppb Bi(III) (dashed lined - zero accumulation time, full line - 120 s accumulation time). Figure adapted from primary reference.

Reference

Adsorptive Stripping Measurements of Bismuth, J. Wang, J. Lu and R. Setiadji, Electroanalysis, 5 (1993) 319-324.

Additional Reference

1) *J. Zhao and W. Jin, J. Electroanal. Chem. 256 (1989) 181.*