

CAPSULES

preliminary notes and applications from Bioanalytical Systems, Inc.

Determination of Trace Levels of Antimony and Bismuth in Snow and Water by Anodic Stripping Voltammetry: Speciation of Antimony

Purpose

The toxicity of trace metals can depend on their physicochemical form (e.g., labile or non-labile complexes, dissolved or particulate). The elucidation of the various states in which a metal is present (i.e., the speciation of the metal) can be highly complex, but some simple distinctions can be made. For example, Sb(III) is electroactive, whereas Sb(V) is not; therefore, the concentration of Sb(III) and the total concentration of Sb (after reduction of Sb(V) to Sb(III)) can be measured in separate experiments.

Reference

Trace Determination of Antimony and Bismuth in Snow and Water Samples by Stripping Voltammetry, A. Postupolski and J. Golimowski, *Electroanalysis* 3 (1991) 793-797.

Method

The basis of electrochemical trace analysis is the accumulation (or preconcentration) of the analyte at the working electrode before the potential scan. The classical method for the trace analysis of many metal ions is Anodic Stripping Voltammetry (ASV). In this technique, the metal ions in solution are reduced to the zero oxidation state, which then amalgamates with the mercury electrode. This method can be used for the simultaneous detection of more than one metal ion, but problems can arise if the metal ions have similar potentials; for example, bismuth, antimony and copper can give rise to overlapping peaks. In this study, the peaks due to these three metals are separated by judicious choice of the supporting electrolyte and the deposition potential.

The preparation of the snow samples was simple, and involved melting followed by acidification to pH 1. The speciation of Sb was studied by reducing the Sb(V) to Sb(III) using boiling hydrazine dihydrochloride. The preparation of the water samples was more complicated in that UV irradiation was required to re-

move organic material which could interfere with the analysis. However, the UV irradiation also oxidized Sb(III) to Sb(V), which prevented Sb speciation studies (since only the total Sb concentration could be measured).

Results

Hydrochloric acid (HCl) at different concentrations has been the favored supporting electrolyte for the analysis of antimony and bismuth.

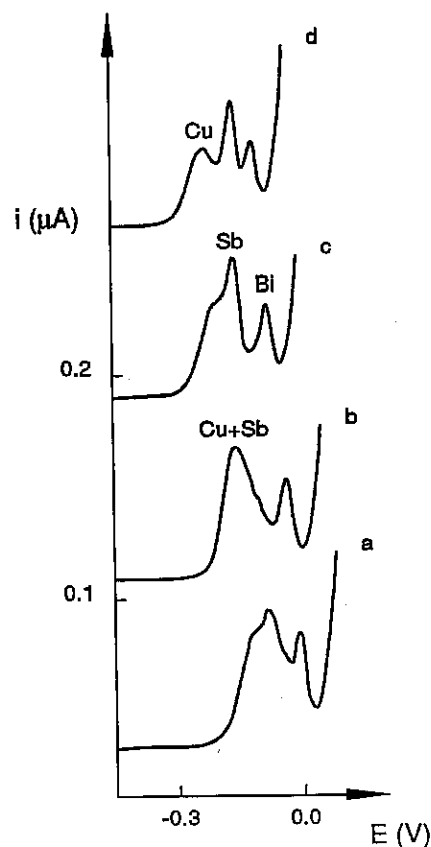


Figure 1. Differential pulse voltammograms of bismuth (5 ppb), antimony (5 ppb) and copper (10 ppb) in 0.1 M hydrazine hydrochloride and hydrochloric acid; hydrochloric acid concentration = 0.01 M (a), 0.1 M (b), 0.5 M (c), 1.0 M (d). Deposition time = 240 s, deposition potential = -0.45 V, pulse amplitude = 10 mV, scan rate = 5 mV/s. Figure adapted from Reference.

The differential pulse stripping voltammograms for a mixture of antimony, bismuth and copper at different HCl concentrations are shown in F1. Increasing the concentration increases the resolution of the copper and antimony peaks, but decreases the resolution of the antimony and bismuth peaks. An HCl concentration of 0.5 M was selected as optimum. The peak resolution was also enhanced by optimizing the parameters for the differential pulse wave form (scan rate = 2 mV/s and pulse amplitude = 10 mV).

The experiments shown in F1 were run using a deposition potential of -0.45 V (vs. Ag/AgCl). Since the copper peak was the most negative of the three peaks, it could be eliminated by using a deposition potential of -0.26 V. A determination limit of 0.02 ppb for both antimony and bismuth was achieved.

This method was used to analyze snow and water samples. The concentrations of antimony and bismuth were quantitated using the method of standard additions. Some typical results are shown in F2 (the concentrations of antimony and bismuth in this snow sample were 3 ppb and 0.4 ppb respectively).

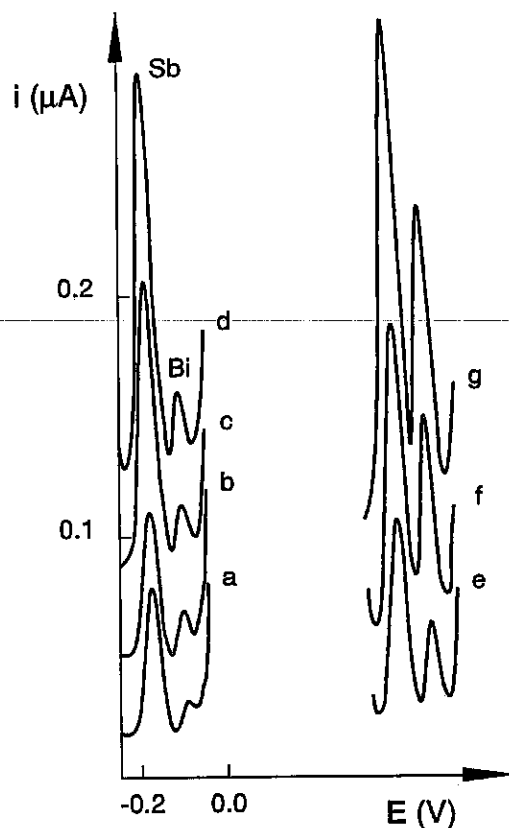


Figure 2. Differential pulse voltammograms of snow samples containing bismuth and antimony. Curves a-d are the sample and standard addition analyses of a solution containing both Sb(III) and Sb(V), and curves e-g are the sample and standard analyses of a solution after reduction with hydrazine dihydrochloride (i.e., only Sb(III) present). Figure adapted from Reference.

