CAPSULES
preliminary notes and applications from Bioanalytical Systems, Inc.

Determination of the Mercaptoundecahydro-closo-dodecarborate Dianion

Purpose

The mercaptoundecahydro-closo-dodecarborate dianion I (F1) accumulates in cancerous tissues, and is used for neutron capture therapy of malignant brain tumors (enriched with boron-10). Therefore, assays for I in pharmaceutical formulations and in body fluid and tissues are required.

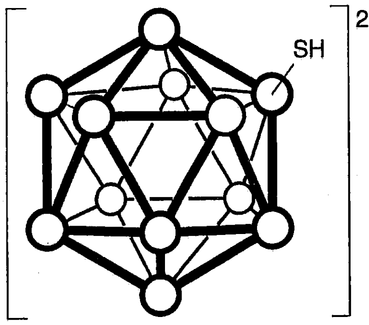

Figure 1. Structure of the mercaptoundecahydro-closo-dodecarborate dianion.

Reference

Polarographic and Voltammetric Determination of Sodium and Tetramethylammonium Mercaptoundecahydro-closo-dodecarborates, F. Jelen, E. Palacek and O. Strouf, Electroanalysis 3 (1991) 97-102.

Method

The determination of molecules containing a thiol or thiolate functional group is based on the interaction of these groups with mercury to form mercurous or mercuric thiolate salts, which are then adsorbed onto the surface of the working electrode. Very low detection limits can be achieved by allowing accumulation of the Hg-thiolate salts before the potential scan - this latter process is generally referred to as Cathodic Stripping Voltammetry (CSV).

Results

The differential pulse polarogram of I in 0.05 M borax buffer (pH 9.2) is shown in F2. There is a linear relationship between the concentration and the peak current over the range 5 x 10^{-7} M - 1.5 x 10^{-5} M, but the peak current tends to a limiting value at higher concentrations. This behavior is typical for a species (in this case an Hg-I salt) adsorbed to the electrode surface, since higher concentrations lead to surface saturation.

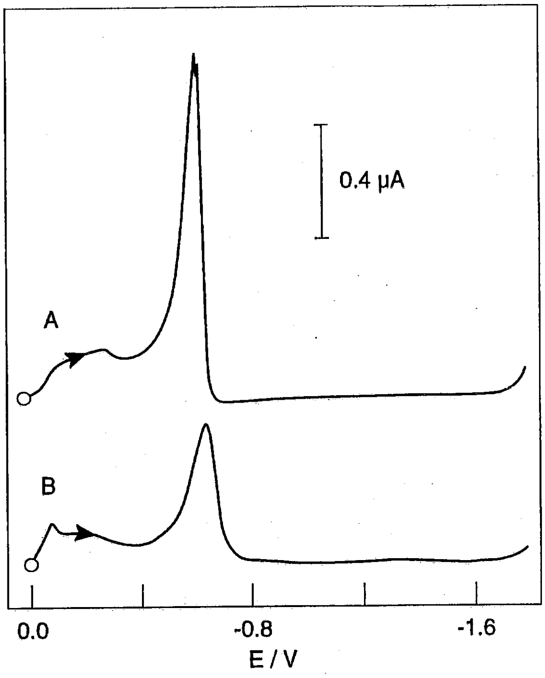

Figure 2. Differential pulse polarogram of mercaptoundecahydro-closo-dodecarborate (50 M) in borax buffer (pH 9.2). Figure adapted from Reference.

The adsorption of I is further shown by the difference between the differential pulse cathodic stripping voltammograms recorded after a 120 s accumulation time at a potential of -0.1 V (F3a) and -0.9 V (F3b). The formation of the Hg-I salt requires oxidation of the surface of the mercury drop electrode, which occurs at -0.1 V but not at -0.9 V.

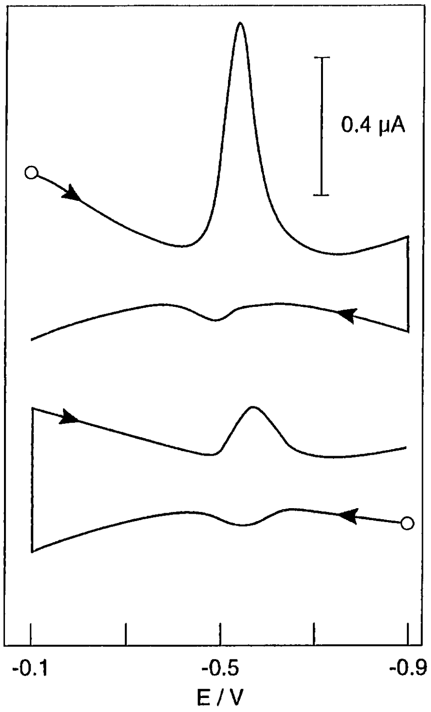

Figure 3. Differential pulse cathodic stripping voltammogram following accumulation at a) -0.1 V and b) -0.9 V. Figure adapted from Reference.

The peak current tended towards a limiting value as either the accumulation time or the concentration of I in solution was increased - again, this is characteristic behavior for an adsorbed analyte. The lower detection limit was 5 x 10^{-9} M, and the upper detection limit (defined by surface saturation) was 9 x 10^{-7} M (for an accumulation time of 120 s). The current response was linear over the range 5 x 10^{-9} M to 1.4 x 10^{-7} M, and the standard deviation at 5 x 10^{-8} M was 3.1%.

Although a number of other techniques have been used for the determination of I, the only one that can equal the sensitivity of CSV is the track etch/thin layer chromatography, which detects B-10. However, CSV is simpler, less expensive and more selective than this technique.