

PP053
USING THIOUREA AS A SOURCE OF SULFUR FOR
ELECTROCHEMICAL GENERATION OF METAL
SULFIDES

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Metal sulfide chemistry is a topic of particular interest for geochemistry and environmental chemistry. However, manipulation of the sulfide ion is not a straightforward task due to its volatility at pH < 12, interaction with metal ion impurities, easy oxidation and formation of polysulfides. We describe here a method for electrochemical investigation of metal sulfides that makes use of a stable sulfur derivative (like thiourea, TU) in order to prepare a layer of metal sulfide by the anodic reaction of the electrode metal. Other metal sulfides can be prepared by exchange reaction with the metal ion of interest. This procedure was inspired by analogous investigation using sulfide ion as starting material¹.

Anodic reaction of TU at a mercury electrode results in an HgS surface layer. Mercury reduction in this compound occurs in a good agreement with the model that assumes a reversible electron transfer reaction and a constant activity of the surface compound^{1,2}. If a metal ion is present in the solution phase, Hg²⁺ is released by an exchange reaction and the cathodic peak gets shifted to less cathodic potentials.

It is possible therefore to prepare metal sulfides using a stable sulfur derivative as a starting material. Metal sulfides prepared in this way are amenable to electrochemical investi-

gations. This method can easily be transposed to metal selenides investigation if an organic selenium derivative (like selenourea) is used as starting material. It would also be of interest to perform such investigations using silver as electrode in order to prepare and study silver chalcogenides. On the other hand, the matter here presented is of relevance for research of metal sulfides in natural waters. A proposed method for investigating soluble metal ion complexes with the hydrogen-sulfide anion is based on square-wave cathodic stripping voltammetry of sulfide ion in the presence of the metal of interest⁷. In the frame of this method, the DeFord and Hume approach was employed to infer the composition and stability of the complexes from the shift of the peak potential in the presence of the metal ion. Severe faults of this method were already emphasized^{8,9}. Data in Ref. 1, as well as the results in this paper point out an additional drawback of the method in Ref. 7, namely the omission of the exchange of Hg²⁺ in HgS with the metal ion in the solution. The exchange reaction renders the DeFord and Hume approach not suitable under these circumstances.

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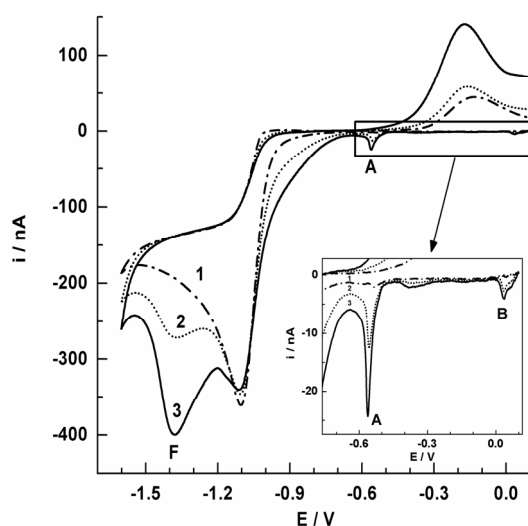


Fig. Electrochemical reactions in the presence of Ni²⁺ after anodic polarization at +0.1 V in the presence of TU. Phosphate buffer, pH 6.5; 2.10⁻⁷ M TU; 4.10⁻⁴ M Ni²⁺; t_d (s): (1) 0; (2) 30; (3) 60