

VOLTAMMETRY AS A TOOL FOR DETECTION OF METAL SULFIDE PARTICLES AND NANOPARTICLES

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Abstract

In this work we investigated the possibility of reduction of metal sulfide particles (Ag, Cd, Hg, Pb, Zn and Fe) at the Hg electrode in electrolyte solutions containing μM levels of different metals and sulfide. In all investigated solutions metal sulfide particles are formed and subjected to the reduction at the Hg electrode resulting with voltammetric peaks situated between -0.9 and -1.7 V vs. Ag/AgCl, respectively. An electrochemical approach for detection of possible presence of metal sulfide species in anoxic natural samples was proposed.

Keywords : *Electrochemistry, Metals, Anoxia.*

It was shown that natural anoxic waters, containing Fe(II) and S(-II) and analogue model solutions, contain species which are reducible at the mercury electrode at -1.1 V vs. Ag/AgCl [1]. However, Ciglencečki et al. [2] have reported that in the solutions containing μM concentrations of copper and sulfide very similar reduction peaks can be observed (situated at the -0.9 to -1.0 V vs. Ag/AgCl) and can be assigned to the reduction of CuS solid phase particles.

In this study we investigated possibility of reduction at the Hg electrode of other metal sulfide particles as well as possibility of application of voltammetric measurements in detection of metal sulfide particles in natural samples. Proposed method was tested in measurements of samples collected from two meromictic, anoxic environments, seawater lake, Rogoznica Lake in Eastern Adriatic coast and Pavin Lake, crater lake in Central massifs, France [3,4].

Cyclic voltammetric, CV, curves obtained in investigated metal sulfide electrolyte solutions are characterized by two reduction peaks: C2 situated at around -0.6 V and C3 situated between -0.9 and -1.7 V, respectively (Fig. 1A). The C2/A2 peak couple corresponds to the well documented HgS layer dissolution and formation processes [2] while C3 in comparison with our previously published data on CuS particles and nanoparticles [2], can be assigned to the reduction and dissolution process of the attached metal sulfide particles.

already detected in model solutions, was observed (Fig. 1B). We ascribed the peak to the presence of metal sulfide particles.

The most interesting finding here is that in the case of ZnS, FeS and CuS similar voltammetric responses have been already reported for aqueous, soluble species of those metal sulfides in sulfidic environment. Evidence in this paper raises a cautionary flag regarding previous voltammetric studies of trace metal speciation in anoxic, sulfide rich marine environment. This implies that obtained voltammetric signal strongly depends on both solution i.e. solid and electrochemical conditions and therefore it should be interpreted with more caution.

References

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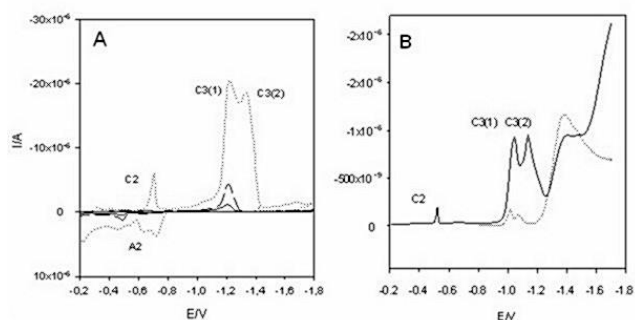


Fig. 1. CV curves for electrolyte solution containing: (A) $10.5 \mu\text{M Pb}^{2+}$ and $10.5 \mu\text{M HS}^-$; Initial potential, $E_D = -0.2$ V, scan rate 100 mV/s ; accumulation period, $t_d = 60$ s (solid lines), 100 s (dashed lines) and 220 s (dotted lines). LSV curves for (B) Pavin lake sample taken at 75 m depth. Initial potential, $E_D = -0.2$ V (solid line) and $E_D = -0.8$ V (dotted line) without accumulation, $t_d = 0$ s.

Our investigations showed that different experimental conditions i.e. ageing of the particles, deposition potential and accumulation time can effect shape and position of the C3 reduction peak. C3 shifts with increased accumulation time and consists of two or more superimposed reduction peaks; which we marked as C3(1) and C3(2) (Fig. 1A). The same effect was observed with ageing of the solutions and aggregation of the particles.

In investigated natural samples, reduction peak similarly situated to C3,