ELECTROANALYTICAL METHODS IN DETECTION AND CHARACTERIZATION OF ELEMENTAL SULPHUR NANOPARTICLES IN THE SEAWATER ENVIRONMENT

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Abstract
Electroanalytical methods, voltammetry and chronoamperometry were applied for detection and characterization of reduced sulphur species in euxinic seawater. Colloidal finest fraction, i.e. elemental sulphur nanoparticles (S(0) NPs), were detected. Chronoamperometric signals recorded in acidified euxinic seawater samples were used for evaluation of S(0) concentration and size of formed NPs. The observed results indicate a great potential of chronoamperometic measurements in characterization of similarly sulphur containing NPs (metal sulphides) in aquatic environment.

Keywords: Analytical methods, Central Adriatic Sea, Anoxia, Chemical speciation

Introduction

The dramatic change in physical and chemical characteristics that substances experience at reduced length scales and potential toxicity of such nano-sized material triggered scientific interest for characterization of natural and engineered NPs in aquatic environment. Rogoznica Lake (RL), permanently stratified marine lake with euxinic conditions in the deeper water layer where hydrogen sulphide can be found in milimolar concentrations (Fig. 1), was used as study site for reduced sulphur species (RSS) characterization. Differentiation between volatile and non-volatile RSS (RSSv, RSSnv) was done by voltammetric measurements in original and acidified samples (Fig. 1) [1,2]. In acidification step the S(0) is released by hydrolyses mainly from polysulfide in form of NPs [1,2 3] and measured by chronoamperometry (Fig. 2) [3].

Materials and methods

Natural water samples were collected at marine lake, Rogoznica Lake (Eastern Adriatic Coast). All electrochemical measurements were performed with Autolab PGSTAT 128N (Eco Chemie, Netherlands) in combination with an automatic Hg electrode (VA Stand 663, Metrohm, Switzerland). Voltammetric measurements of RSS_{total} are based on interaction between sulphur and Hg electrode. To differentiate between RSS_v and RSS_{nv} acidification step is used [1,2]. Chronamperometric measurement, where interaction of S(0) NPs and Hg electrode results in spike like signals superimposed on background diffusion limited curve were monitored in acidified RL samples at -0,8V (vs. Ag/AgCl). Spikes are consequence of S(0) NPs reduction during the contact with the Hg electrode when potentials are more negative than -0,6 V (vs. Ag/AgCl) [3]. Frequency and charge of the signals can be related with concentration and size of the colloidal S(0) [3].
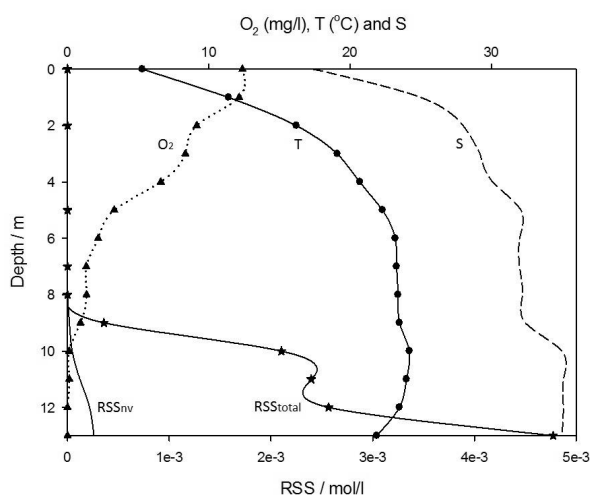
Results and Discussion

Fig. 1. Vertical profile of temperature, salinity, dissolved oxygen and RSS concentration in Rogoznica Lake

During the sampled period the RL was stratified with halocline at 9 m. The upper part was saturated with the dissolved oxygen, while under the halocline dissolved oxygen was absent and consequently free sulphide was accumulated (Fig. 1). High concentration of sulphide in the anoxic part of RL increases solubility of the elemental sulphur and formation of the polysulphides as the most stabile non-volatile RSS fraction [1,2]. Concentration of RSS_{total} and RSS_{nv} reflects the physico-chemical characteristics of the water column (Fig. 1). Chronoampetometric measurements in the acidified RL samples provided information on S(0) content (Fig. 2). Frequency of the recorded spikes, related to reduction of S(0) NPs, can be coupled with the concentration of the S(0) in samples. From charge of the spike signals size of the S(0) NPs was calculated. Similar methodology was tested for characterization of metal sulphide NPs.
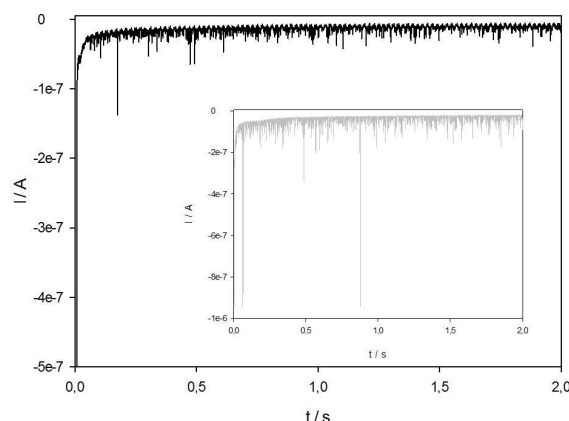

Fig. 2. Chronoamperogram of 10m RL sample and (insert) partly oxidize 10m RL sample

Conclusion

For the first time, the chronoamperometry was used for detection and size determination of colloidal S(0) in natural aquatic samples. Observed results are a base for further development of electroanalytical methodology for polysulfide, as well as natural and engineered NPs determination in natural waters.

References

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