Sulfur (S), an ubiquitous element in the environment, occurs in different oxidation states from -2 (sulfide, S\(_{-2}\)) to +6 (sulfate, SO\(_{4}^{2-}\)). Between the thermodynamically stable end members (S\(_{2}^{2-}\), SO\(_{4}^{2-}\)), a variety of intermediate S species exist, examples of which are sulfites, polythionates, thiosulfate, elemental sulfur (S\(_{2}\)), and polysulfides (S\(_{X}^{2-}\)). S species with intermediate oxidation states are produced during a variety of biotic and abiotic processes including the oxidation of hydrogen sulfide (HS\(_{2}\)) and sulfide minerals, SO\(_{4}^{2-}\) reduction, and the transformation of organic S compounds. Reduced sulfur species (RSS, S\(_{2},\) HS\(_{2},\) S\(_{X}^{2-}\), RSH) are important forms of S in anoxic conditions, and could be relevant in environmental quality monitoring [1, 5]. In natural waters, S\(_{2}^{2-}\) mainly occur as intermediate species due to oxidation-reduction processes, but they can also occur as a result of pollution. Methodology for direct determination of S\(_{2}^{2-}\) in the presence of other RSS is missing.

In this work, for the first time differential pulse voltammetry (DPV) at the Hg electrode [1], was used for determination of S\(_{2}^{2-}\) in natural, sulfidic seawater environment (Rogoznica Lake, Croatia; Figs. 1a, b). Their presence was also confirmed by UV/VIS measurements. Additionally, sampled DC polargraphy (SDC) at the Hg electrode revealed a ratio between anodic and cathodic currents, i.e. the ratio between sulfide and S(0) presence within the S\(_{2}^{2-}\), in the studied samples (Fig. 5) [1,2].

**Materials and methods**

- **Polysulfide model solution K\(_{2}S\(_{2}\)X (Sigma – Aldrich; ≥42 % K,S basis)** was prepared in NaCl/NaHCO\(_{3}\) carbonate buffer (pH=9.5) in the concentration range between 10 mg/L and 500 mg/L (Fig. 3).
- **Natural samples from RL water column taken by diving and SL Niskin bottles from the chemoline and anoxic water layer (10 m) in July 2019**

**Electroanalytical methods**

- **Electrochemical measurements** were performed with a µ-Autolab Electrochemical Instrument (Eco-Chemie) and 663 VA Stand Metrohm Electrode (Metrohm, Switzerland) (Fig.2)
- **Reference electrode**
- **Ag/AgCl (NaCl saturated)**
- **Working electrode**
- **DAPE (static mercury drop electrode)**
- **Counter electrode**
- **Glassy carbon rod**

**Fig. 2: Electrochemical three electrode system**

**Fig. 1: a) Location and photo of RL; b) Vertical profile of RL; and photos taken by diver in the chemoline (8 m) and anoxic water layer (10 m) in July 2019**

**Rogoznica Lake** (RL) is a small seawater lake situated on the eastern Adriatic coast in Croatia (43°32’N, 15°58’E). (Fig. 1). Due to stable seasonal physico-chemical stratification, and almost permanent anoxic conditions below 8 m depths, RL is an ideal study site for RSS speciation, and S\(_{2}^{2-}\) characterization, since there S\(_{2}^{2-}\) are assumed to be present in relatively high concentrations [2, 5].

**Introduction**

**Results & Conclusion**

**Fig. 3: Polysulfide model solution K\(_{2}S\(_{2}\)X: a) DPV voltammograms; b) calibration curve; c) SDC polarogram of K\(_{2}S\(_{2}\)X (v = 30 mg/L)**

**Fig. 4: DPV voltammograms of RL samples**

**Fig. 5: RL sample from July 2019 at 8.30 m depth: a) CV voltammograms; b) SDC polarograms**

**UV/Vis spectroscopy measurements**

**Fig. 6: UV/Vis spectrum of polysulfides in a) model K\(_{2}S\(_{2}\)X solution, and b) RL samples from 9.5 m depth (purple line in Fig. 4)**

- **DPV peaks in polysulfide model solution K\(_{2}S\(_{2}\)X (polysulfidic S\(_{2}^{2-}\)=88%) were recorded in the concentration range between 10 and 500 mg/L** (Fig. 3a).
- **DPV and obtained calibration for model K\(_{2}S\(_{2}\)X (Fig. 3b), demonstrated presence of S\(_{2}^{2-}\) in the RL samples**, in the concentration range between 18 mg/L to 75 mg/L (Fig. 4).
- **Distribution of S\(_{2}^{2-}\) in the euxinic water column of RL varies seasonally (Fig. 4)**, depending on the physo - chemical parameters and biological processes (bacterial activity).
- **SDC measurements in model K\(_{2}S\(_{2}\)X solution gave a ratio S\(_{2}^{2-}\) : S\(_{0}\) = 1 : 2.5** (Fig. 3c), implying that the model polysulfide is K\(_{2}S\(_{2}\)X.
- **SDC measurements of RL July 17th 2019 sample gave a ratio S\(_{2}^{2-}\) : S\(_{0}\) = 1 : 1** (Fig. 5), implying on S\(_{2}^{2-}\) presence.
- **UV/Vis measurements confirmed the presence of polysulfide in RL (Fig. 6)**

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