

COPPER SPECIATION IN THE KRKA RIVER ESTUARY (CROATIA)

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Abstract

Determination of trace-metal organic interactions in natural water is still very challenging task. Currently, the most used methodology is the competitive ligand equilibrium adsorptive cathodic stripping voltammetry (CLE-AdCSV). The technique relies on the competitive effect of added ligand (AL) which forms know complex with target metal. Methodology is mostly used at one concentration of AL, despite multi-detection window approach was recommended because it is time and sample volume consuming. In this study we are proposing a revised approach, called "segmented multi-detection window" (SMDW). The proposed method was first verified on model titrations, and thereafter experimentally tested on copper speciation analysis in the vertical salinity gradient and surface microlayer, in the Krka River estuary (Croatia).

Keywords: Estuaries, Vertical profile, Trace elements, Electrochemistry, Adriatic Sea

Characterization and discrimination of trace metal-organic ligand complexes in natural waters commonly rely on determination of their conditional stability constants (K'_{ML_i}) and concentrations of corresponding discrete ligand classes ($[L_i]_T$). Electrochemical techniques are the main tool in these studies. Among them competitive ligand equilibrium adsorptive cathodic stripping voltammetry (CLE-AdCSV) is most widely used. It is based on the re-distribution of metal between the natural organic ligands present in the sample and added competitive ligand (AL) which forms the electroactive complex with known stability constant. The newly formed complex is accumulated by adsorption onto the electrode surface (Hg drop) and then stripped by reduction scan. Previous studies have shown that complexation parameters are partially dependent on AL concentration and in order to attain more reliable results it was recommended to conduct multiple individual titrations at different concentrations of AL (MultiDetection Window – MDW) and their modeling (fitting) as a single set of data.[1] Disadvantages of this approach are the longer time needed to perform multiple titrations and requirement for larger sample volume. In order to overcome these shortcomings, we have proposed and tested a revised method called "Segmented MultiDetection Window" (SMDW) which consists in multiple change of AL concentrations (2-4) along only one titration experiment. Support for modeling and processing of these titration curves is incorporated within the already existing ProMCC program.[2] The proposed method was first verified on model titrations encompassing one and two ligand systems (example shown in Figure 1), and thereafter experimentally tested on copper (Cu) speciation analysis in the vertical salinity gradient and surface microlayer, in the pristine Krka River estuary (Croatia).

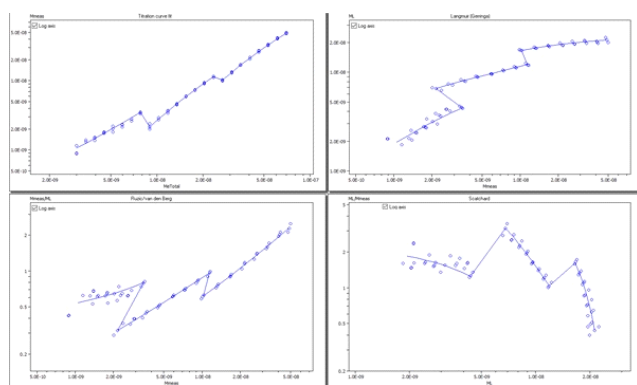


Fig. 1. SMDW titration set for 2-L model at decreasing AL concentration. Circles- titration points, Line - fitted curve.

SMDW approach gave complexation parameters comparable to the "classical" approach (Figure 2), indicating that the proposed methodology is very robust and can be used successfully for this type of studies, with less sample consumption and a shorter total time analysis.

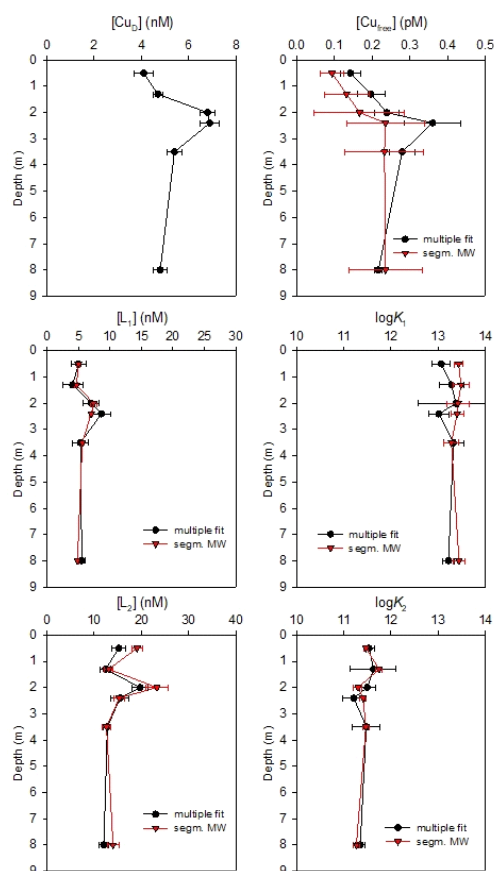


Fig. 2. Comparison of the new "Segmented" MultiDetection window (SMDW) method and the classic "multiple-fit" method in two sample detection windows.

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References

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