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Determination of the contribution of humic substances to iron complexation in seawater by catalytic cathodic stripping voltammetry

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Abstract

Improving our understanding of iron cycling in ocean waters is one of the most challenging tasks in oceanographic studies and requires new analytical strategies. The low solubility of inorganic iron in oxygen saturated waters is increased by organic complexation with a variety of natural ligands, the nature of which is a topic of debate. Electrochemical methods are important for speciation studies since they allow direct measurement of iron complexes at limits of detection below iron concentrations in ocean waters. Most of the natural iron ligands do not form electrolabile iron complexes with working electrodes currently in use. Humic substances are the exception as their iron complexes can be detected by cathodic voltammetry if a strong oxidant such as bromate is added for a catalytic reoxidation of iron. Here we propose a rearrangement and extension of the original analytical protocol [1]. Firstly, the humic standard prepared in ultrapure water is carefully saturated with iron before use, preventing underestimation of the iron-humic complexes during calibration. Secondly, before starting the common voltammetric analysis under iron saturation, extra voltammograms are collected at the natural iron concentration. We demonstrate that this rearrangement permits the determination of the percentage of iron-binding groups of humic substances in the sample that were originally bound to iron. After calibration, the concentration of iron present in the sample as humic complexes can be quantified. This is

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