

CAPSULES

preliminary notes and applications from Bioanalytical Systems, Inc.

Determination of Trace Concentrations of Iron in Seawater by Adsorptive Stripping Voltammetry

Purpose

Although iron is an essential mineral, it has toxic effects when present above a certain threshold concentration. Therefore, a sensitive technique for the determination of trace concentrations of iron is required.

Reference

The Determination of Trace Levels of Iron in Seawater Using Adsorptive Cathodic Stripping Voltammetry, C.M.G. van den Berg, M. Nimmo, O. Abollino and E. Mentasti, *Electroanalysis* 3 (1991) 477-481.

Method

The basis of electrochemical trace analysis is the accumulation (or preconcentration) of the analyte at the working electrode before the potential scan. In Adsorptive Stripping Voltammetry (AdSV), this accumulation occurs via non-electrolytic adsorption of the analyte on the surface of the working electrode (the mercury drop electrode is most commonly used). AdSV can be used for the detection of metal ions via the adsorption of metal ion complexes.

Voltammetric methods are particularly suited for the analysis of seawater, since a high salt concentration is required for voltammetry experiments (in contrast, the high salt concentration found in seawater can cause problems for other analytical techniques such as atomic adsorption spectroscopy). The sample preparation required acidification of the samples before storage (to prevent adsorption of iron to the walls of the container). The acidified samples were neutralized and buffered before the analysis. As in all trace determination analyses, both the glassware and reagents had to be scrupulously cleaned to remove trace iron contamination. An iron-specific ligand was added to the reagent solutions and these solutions were then passed through a Sep-Pak column to remove both the complexed iron and the excess ligand.

Results

In this study, the complex of iron(III) with 1-nitroso-2-naphthol (1-N-2-N) was used for the detection of iron. The cyclic voltammogram of a solution of seawater containing 0.01 M PIPES buffer, 1.8×10^{-8} M iron(III) and 1×10^{-5} M 1-N-2-N is shown in F1 (a 60 s accumulation time was used). The reduction of the Fe(III) complex occurs at -0.58 V. The peak current increased linearly with the square root of the scan rate (over the range 10 - 100 mV/s), which suggests that the electron transfer kinetics are slow (the peak current for the reversible reduction of an adsorbed species varies linearly with the scan rate). The shift of the reduction potential to more negative potentials with increasing scan rate (and the virtual absence of the reoxidation peak) is further evidence for irreversibility. It was found that using differential pulse voltammetry increased the peak currents of interfering peaks without improving the sensitivity for iron, so linear sweep voltammetry (at a scan rate of 50 mV/s) was used in this analysis.

The various experimental variables were optimized as follows: 0.01 M PIPES buffer (pH = 6.9), 2×10^{-5} M 1-N-2-N, accumulation potential = -0.25 V (vs. Ag/AgCl).

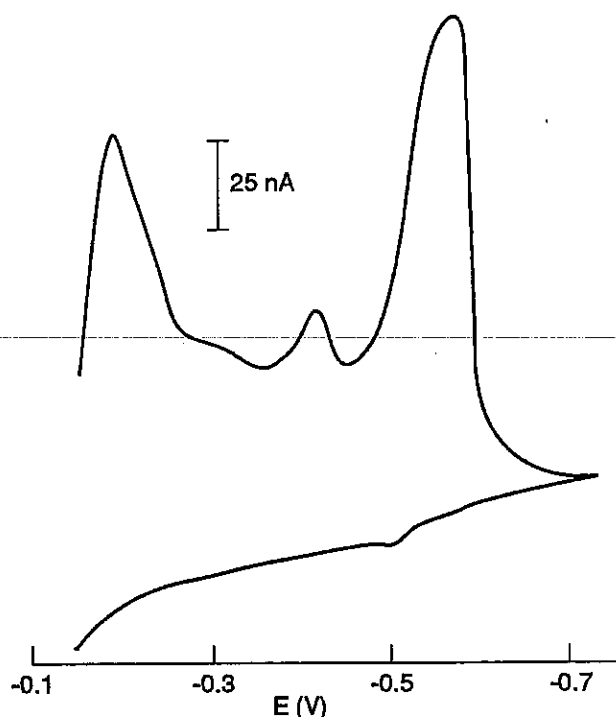


Figure 1. Cyclic voltammogram of the complex of Fe(III) with 1-N-2-N in seawater (containing 0.01 M PIPES buffer), 60 s accumulation time. Figure adapted from primary reference.

The peak current increased with the length of the accumulation time up to 15 minutes, but it slowly decreased for longer times than this. The initial studies showed variations in the peak currents. If the seawater samples had been stored at pH 8 before analysis, the peak current increased in sequential experiments, whereas if the samples had been acidified before storage, there was a gradual decrease in the peak current. The behavior of the non-acidified samples was attributed to the slow dissolution of iron(III) hydroxide, which is known to have limited solubility in seawater. The behavior of the acidified samples was attributed to adsorption of the iron(III) on used mercury drops at the bottom of the voltammetric cell. This effect was eliminated by the addition of 1×10^{-4} M hydroxylammonium hydrochloride, which reduced the iron(III) to iron(II), which did not adsorb as readily to the used mercury. The iron(II) was oxidized to iron(III) at the surface of the mercury drop electrode during the accumulation time.

The detection limit for a 3 minute accumulation time was 6×10^{-10} M, and the standard deviation was

about 7%. The analysis of a standard seawater sample with a certified iron(III) concentration of $4.0 (\pm 0.6) \times 10^{-9}$ M gave a concentration of $4.1 (\pm 0.3) \times 10^{-9}$ M iron(III).

Catechol [1] and Solochrome Violet RS [2] have also been used for the determination of iron(III) by AdSV. The detection limit for the catechol complex was higher than that for the 1-N-2-N complex; this was due in part to competitive adsorption of catechol complexes of uranium, vanadium and copper (these metals did not cause similar interference with 1-N-2-N). In addition, the catechol complex was more sensitive to competitive adsorption by surface-active molecules such as Triton-X 100.

Additional References

1. C.M.G. van den Berg and Z.Q. Huang, *J. Electroanal. Chem.* 177 (1984) 269.
2. J. Wang and J.S. Mahmoud, *J. Electroanal. Chem.* 208 (1986) 383.

