



Towards a zero-blank, preconcentration-free voltammetric method for iron analysis at picomolar concentrations in unbuffered seawater



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ABSTRACT

A method with negligible blank values for the determination of total iron at the ultratrace level in seawater has been optimized and validated exploring for the first time the performance and limitations of Adsorptive Cathodic Stripping Voltammetry (AdCSV) in non-buffered solutions. The method is based on the CSV determination of the Fe-dihydroxynaphthalene (DHN) complex using atmospheric oxygen to catalytically enhance the signal via hydrogen peroxide formation at the electrode/solution interface. The accumulation of hydroxyl ions, the by-product of the hydrogen peroxide formation, increased the pH in the diffusion layer in the absence of buffer bringing it to 9, the optimum for the analytical performance of the method. Voltammograms in UV digested seawater showed no stability or reproducibility drawbacks. The negligible, lower than 5 pM, blank level, is due to the simplicity of the procedure requiring no sample manipulation and a maximum of three reagents only, necessarily the ligand DHN and a base only for those samples previously acidified to raise the pH to circumneutral values (here HCl and NH₃ according to common trace metals protocols). These reagents do not require cleaning before use, further simplifying the overall procedure. Analysis of seawater previously acidified at pH ~1.5 with HCl and neutralized with ammonia showed interferences due to the buffering properties of the NH₃/NH₄Cl couple and the transient formation of a volatile electroactive interference that can be easily removed by simply allowing a set time before analysis. In general, the proposed method features several advantages, including high sample throughput, an excellent limit of detection at 12 pM, minimum sample handling (no preconcentration or change of matrix is required), cost effectiveness and mainly a negligible blank. The method was successfully validated using open ocean consensus samples (SAFE D2 and S).

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1. Introduction

Iron is a key micronutrient for the understanding of primary productivity and the cycles of other elements in the ocean [1]. Its low solubility and strong particle reactivity are behind the low natural concentrations found in ocean waters (<0.1 to few nanomols l⁻¹) despite being one of the more abundant elements of the Earth crust [2]. Sample collection and clean analysis of dissolved iron in seawater are one of the most challenging tasks in oceanography. In the last few decades new protocols have been developed for the analysis of iron at the subnanomolar level by a battery of different analytical techniques: ICP-MS [3,4], spectrophotometry [5], chemiluminescence [6] and voltammetry [7,8]. Voltammetry is scarcely used for the determination of total iron in oceanography despite its low cost, the excellent sensitivity

allowing analysis without a preconcentration step and the portability that permits its use in oceanographic cruises. This is caused by environmental concerns about the use of mercury electrodes, the necessity in many cases of an UV digestion step [9] and the lack of commercial flow cells that could allow its automation for flow analysis. However, despite all the effort invested in the last few decades on the development of electrodes based on new materials and surface functionalization, little to none progress has been done on providing a substitute to mercury for the analysis of iron at subnanomolar concentrations [10]. As a consequence, voltammetry on the mercury electrode is still the only electroanalytical technique for the study of the organic speciation of trace metals in seawater [11].

Iron analysis by adsorptive cathodic stripping voltammetry (AdCSV) at the picomolar level requires of a catalytic step to enhance the current resulting from the cathodic reduction of the complex formed by Fe(III) and an electroactive ligand. So far, the ligand that gives the best analytical performance is 2,3 dihydroxynaphthalene (DHN) [7] that allows to reach a limit of detection (LOD) of 5 pM if combined with bromate [8] or naturally present

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dissolved oxygen [12] to ensure catalytic enhancement. The recent substitution of bromate by oxygen was a major improvement in terms of reduction of reagent requirements and throughput as the purging time was cancelled.

Allowing air saturation in solution transforms the conventional interpretation of electrode processes during AdCSV. During the measurement, dissolved oxygen generates two reduction waves at the mercury electrode, the first one at potentials around -0.1 V corresponding to a reduction to hydrogen peroxide and hydroxyl ions and a second wave (~ -1.0 V) due to the reduction of hydrogen peroxide with hydroxyl ions or water as final products [13,14]. Electrogenerated hydrogen peroxide at the electrode/surface interface is responsible of the catalytic effect found for iron determination according to a Haber–Weiss mechanism which detailed description can be found elsewhere [15]. Even after purge with an inert gas for several minutes, traces of oxygen are efficiently converted at the electrode surface. During the deposition time, that is usually performed at potentials close to -0.1 V or even more negative [16], the stirrer is activated to facilitate adsorption of complexes to the electrode and electrogenerated hydrogen peroxide and hydroxyl ions are partially dispersed by convection. During the potential sweep those same ions are still generated in the solution closest to the electrode surface (diffusion layer) refuelling the catalytic process. Hydroxyl generation as by product has a major impact on the pH in the diffusion layer, effect that cannot be evaluated with conventional pH electrodes. Modelling work supported by differential pulsed polarography estimated that pH values as high as 10.3 could be found at the surface of a screen printed electrode working in non-purged solutions [17]. One common misunderstanding in the use of voltammetry by environmentalist is the belief that the addition of the buffering reagent to the sample is exclusively to prevent pH changes after the addition of acidified reagents or the removal of the natural hydrogen carbonate/carbonate buffer in those methods requiring of a purge step caused by CO_2 removal by nitrogen purging. The key role of the buffer and the reason behind its use at concentrations of 0.01 N, is to counter the local rise of pH in the diffusion layer of the electrode with respect to the bulk of the solution caused by the referred reduction of dissolved dioxygen molecules at trace concentrations [16].

The proper exploitation and understanding of unpurged voltammetry lead us to the removal of the oxidizer (bromate or added hydrogen peroxide), thus contributing to keep the blank level low. Independently of the analytical technique, blank contamination from reagents is a major issue and is found in the range 15–230 pM, i.e.: concentrations comparable or higher to the lowest concentrations reported in open ocean waters at 20–100 pM [18] (a resume of the performance of the most representative voltammetric and non voltammetric techniques can be found in Table S1). Analytical developments reducing this contribution to a negligible level would be a major improvement. Although the oxidizer contributes to the blank concentration, the most of this contamination comes from the high concentrations of buffer reagents required by all current methods in use (0.01–0.1 M). Buffer solutions can be cleaned by cation exchange with resins or colloids but this is a time consuming step of limited effectiveness: contamination by pH buffer after cleaning should be always checked and the cleaning procedure repeated until satisfactory blank levels are obtained.

In this work we explored for the first time the possibility to remove the buffer reagent in AdCSV. Eliminating the buffer brought the iron blank level below the limit of detection. Moreover, the forecasted rise of pH was associated to a desirable increase of the sensitivity to approximately the optimum value close to 9 found in a previous work [12]. However, drawbacks may also result as the generated hydroxyl ions could interfere with many

processes (Fe-DHN electrolability, DHN stability, solubility of iron species and so on). An extensive investigation on the behaviour of the analytical signal as a function of pH and buffer nature was accordingly performed.

2. Experimental

2.1. Equipment and reagents

The voltammetric apparatus included a 663 VA stand (Metrohm AG) with a hanging mercury drop electrode (HMDE), a glassy carbon counter electrode, and an Ag/AgCl reference electrode, controlled by a μ Autolab voltammeter (Eco Chemie B.V.). Reagents were of the maximum available purity: HCl (Merck, Ultrapur), HNO_3 (Merck, Ultrapur), ammonia (Panreac, Hiperplus-plus) and DHN (Fluka). Iron standards were prepared by dilution (pH=2.0) of an AAS standard solution (BDH, 1 mg L^{-1}). Three different 1 N buffer solutions were prepared by dissolving adequate amounts of piperazine-N,N'-bis-(2-hydroxypropanesulfonic) acid (POPSO, Sigma-Aldrich), boric acid (Sigma-Aldrich) and 4-(2-hydroxyethyl)-1-piperazineethanesulfonic acid (HEPES, Sigma Aldrich) in ultrapure water and adding the ammonia required to bring the pH to 8.2.

Filtered seawater ($0.2 \mu\text{m}$) was collected using trace clean techniques during the ANT-XXVIII/3 cruise in the Southern Ocean [8]. SAFE consensus samples [19] were provided by the Bruland laboratory (University of California Santa Cruz) and used without any intermediate treatment. UV-digested seawater was prepared by irradiating for 2 hours non-acidified filtered seawater using a 150 W home-built system in 30-mL quartz tubes.

2.2. pH Dependence experiments

In cell pH monitoring was carried out inserting a narrow pH electrode (Slimtrode, Hamilton) in the voltammetric cell. The electrode was calibrated with NBS standards. The effect of pH with and without the mentioned pH buffers (boric, POPSO and HEPES) was studied as follows: the pH of four 10 mL seawater aliquots containing $30 \mu\text{M}$ DHN, 10 nM Fe and 3 of them 0.01 N of the three buffers referred above, was lowered to a value close to 7 with a spike of diluted HCl. CSV scans were registered every ~ 0.1 pH units up to pH 9 after successive additions of diluted ammonia.

2.3. Air supply

Preliminary experiments showed that the Fe-DHN signal decreases during consecutive analyses, independently of the presence of a pH buffer. This decrease was reversed by opening the cell allowing its equilibration with atmospheric oxygen. This is caused by the nitrogen flow allowed through the gap where the small knocker that hits the capillary producing the release of the hanging mercury drop (HMD) is inserted. This is a typical feature of the stands produced by Metrohm AG. Cancellation of this flow stops the ability of the equipment to replace the HMD in between analyses.

Experiments were initially carried out by pumping air from the clean environment of the laminar flow hood to the headspace of the voltammetric cell about 0.5 cm on top of the solution in the cell (air was preliminary saturated with water by bubbling in ultrapure water). The original purge tube was in this case replaced by a shorter tube.

After realization that gas flowing over the sample surface was not suitable in the presence of the $\text{NH}_3/\text{NH}_4\text{Cl}$ buffer, we modified the voltammetric stand according to Fig. S1 in order to extract the flux of nitrogen. Actually, preliminary experiments showed that

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