Determination of Iron and Its Redox Speciation in Seawater Using Catalytic Cathodic Stripping Voltammetry

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Abstract
Existing electrochemical methods for the determination of iron require long deposition times to determine low iron levels. Here a new method, based on catalytic cathodic stripping voltammetry, is described to determine subnanomolar levels of iron in seawater. The new method has a better baseline and is generally simplified, leading to a lower reagent blank and minimized sample handling compared to a previous catalytic method [1]. Optimized conditions include the addition of 20 μM 1-nitroso-2-naphthol (NN), 40 mM bromate, and 0.01 M HEPPS pH buffer, giving measurements in pH 8 seawater. The detection limit is 0.08 nM Fe after an adsorption time of 30 s; the detection limit is lowered by increasing the adsorption time. The method can also be used to determine the redox speciation of iron: Fe^{III} is determined specifically by masking Fe^{II} with 2,2-bipyridyl (Bp). The concentration of Fe^{II} can then be calculated by difference from the total iron concentration.

Keywords: Iron, Speciation, Striping voltammetry

1. Introduction

The hypothesis that iron may be the limiting factor for primary productivity in some parts of the equatorial Pacific, subarctic Pacific and the Southern Ocean (high nutrient low chlorophyll areas) has stimulated research in the chemistry of iron over the past ten years [2, 3]. It was realized shortly how little is known about the marine chemistry of iron and its uptake by microorganisms. Several species of iron are known to exist in seawater. Fe^{II} is the more soluble form, but is readily oxidized to the insoluble Fe^{III} [4, 5]. Nevertheless, Fe^{II} has been found in seawater [6–9].

The solubility of Fe^{III} has been widely debated and concentrations from 0.1 nM [10] to nearly 10 nM [11, 12] have been suggested. These differences may be explained by the existence of natural organic Fe^{III} chelators in seawater [13] or by the difficulties in separating dissolved, monomeric iron from colloidal iron [14]. At levels above its solubility Fe^{III} forms insoluble colloidal Fe^{III} oxides and hydroxides [7], which are not directly taken up by phytoplankton [15].

In order to better understand the bioavailability of iron to microorganisms it is necessary to improve our knowledge of iron speciation and its behavior in the marine system. To this end a sensitive and species specific technique is required. Sample handling has to be minimized and ultraclean methods have to be used as the seawater sample is prone to contamination due to the low concentrations of iron. Furthermore, the sample needs to be preserved in its natural composition to give an accurate measurement of the iron speciation, i.e., the rapid oxidation of Fe^{II} at the natural pH of seawater needs to be inhibited prior to analysis.

Several spectrophotometric techniques exist to analyse Fe^{III} [16] and Fe^{II} [17] at nanomolar concentrations in seawater. However, in order to reach low detection limits samples have to be concentrated on a 8-quinolinol immobilized chelating resin at pH 3 [16] or between pH 5 and 6 [17] and eluted with acid. These pH adjustments lead to changes in the redox speciation [18]. Blain and Tréguer [19] present a method to determine Fe^{II} and Fe^{III} spectrophotometrically after preconcentration on a C-18 phase column impregnated with ferrozine and elution with methanol. Fe^{III} is reduced by an ascorbic acid solution prior to the preconcentration step. The limit of detection for Fe^{II} and Fe^{III} is 0.1 nM and 0.3 nM, respectively. Lower levels of Fe^{II} can be detected by chemiluminescence [4], by which a detection limit of 0.06 nM Fe^{II} in open ocean and 0.15 nM in coastal waters is achieved. The reducible iron concentration can be determined by reduction with sulfite.

Low levels of iron in water can be determined electrochemically by cathodic stripping voltammetry (CSV) preceded by adsorptive collection of complexes with catechol [20], solochrome violet RS [21], 1-nitroso-2-naphthol (NN) [22], salicylaldoxime (SA) [23] and *N*-benzoyl-*N*-phenylhydroxylamine (BPH) [24]. An important advantage of the voltammetric method is that it can be used to determine the chemical speciation of iron as well as its concentration.

The voltammetric sensitivity is greatly improved by including catalysis. Thus the sensitivity of CSV with NN and BPH is enhanced in the presence of H_2O_2 [1, 24]. The Fe^{III}-complexes with NN and BPH are adsorbed onto the mercury drop electrode and as the potential is scanned the iron is reduced to Fe^{II} and the reduction current is measured. Fe^{II} catalyzes the reduction of H_2O_2 and is reoxidized in the process, thus repeatedly contributing to the peak current. Fe^{II} is determined indirectly by masking with bipyridyl [9].

The catalytic CSV method using NN is more sensitive than the method using BPH. However, the determination of iron with NN suffers from interference by the background current of the added H_2O_2, which is suppressed by addition of a surfactant (sodium dodecyl sulphate, SDS). Thus the sensitivity is impaired and the SDS contributes to the reagent blank (the contamination of Fe in 1000 ppm SDS is 24 nM Fe/ml SDS). Furthermore, the sample needs to be heated to accelerate the complexation of iron by NN, which leads to extra handling of the sample and could lead to contamination.

Several oxidants were tested, such as nitrite, chlorate and bromate, to develop a more sensitive and convenient method. Chlorate (50 mM) and nitrite (100 mM) gave very low sensitivities and did not show a catalytic effect. Good sensitivity was achieved with bromate. The successful use of bromate with NN in the CSV determination of low iron concentrations as well as its redox speciation in seawater is described in this article.

2. Methodology

2.1. Instrumentation and Reagents

The voltammetric apparatus consisted of a μAutolab voltammeter (Ecochemie, Netherlands) with a static mercury drop

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electrode (Metrohm Model 663VA), a double-junction Ag/saturated AgCl reference electrode with a salt bridge filled with 3 M KCl, and a glassy carbon rod as a counter electrode.

Sample manipulations and reagent preparations were carried out under a laminar-flow clean hood with filtered air. The required quantity of Milli-Q (resistance 18.2 MΩ) was weighed on a Sartorius top loading balance to make up the reagents. A 0.01 M NN (1-nitroso-2-naphthol) solution in methanol was used without further cleaning.

The Fe contamination in the NN was determined by oxygen-plasma ashing in a Bio-Rad RF Plasma Barrel Etcher PT7150. Thereto 0.017 g NN was weighed out in duplicate in two acid-washed Teflon boats and ashed for 16 h, together with a blank. After the ashing the boats were rinsed off with 10 mL 0.1 M HCL, which was then neutralised with 50 % NH_3 and analysed by CSV. The iron contamination in this batch of NN was 0.050 ± 0.001 nM Fe/0.02 mL 0.01 M NN.

A 1 M HEPPS (*N*-2-hydroxylethylpiperazine-*N′*-3-propanesulphonic acid) buffer (pH 8.0) was made up in Milli-Q, and cleaned by equilibration with 50 μM MnO_2 [25] and filtration using an acid-washed membrane filter (Whatman, cellulose nitrate, 0.2 μm pore size). A 0.4 M bromate solution (potassium bromate, AnalaR) was prepared and cleaned in the same way.

For the determination of Fe^{III} a 2 mM Bp (2,2-bipyridyl) solution was prepared in 0.01 M HCl. Standard solutions of Fe^{III} chloride were made up in 0.01 M HCl. A Fe(II) standard (10^{-6} M) was prepared in 0.01 M HCl using ammonium ferrous sulfate hexahydrate ($FeH_8N_2O_8S_2x6H_2O$). Hydroxyl-ammonium hydrochloride (NH_2OH-HCl) (0.1 mM) was added to diluted Fe^{II} solutions for stabilisation. Hydrochloric acid, ammonia and methanol were purified by subboiling distillation using a quartz cold finger distillation unit. 0.4 μm filtered seawater from the North Atlantic was used for the development work.

2.2. Procedure to Determine Reactive and Total Iron

The concentration of reactive iron was determined without pretreatment of the seawater. The reactive iron concentration is defined by the iron which is bound within a period of 3 min by 20 μM NN added to pH 8 seawater. This fraction includes all inorganic iron (II and III) and part of the organically complexed iron.

The total (inorganic and organic) concentration of iron in seawater was determined after UV-digestion (3 h) at pH 2. The pH was brought back up to pH 7 by the addition of ammonia just before the measurement. 10 mL of seawater were pipetted into the cell and 20 μL NN (final concentration 20 μM), 100 μL HEPPS (final concentration 0.01 M) and 1 mL BrO_3^- (final concentration 40 mM) added. The solution was purged for 3 min with nitrogen gas prior to analysis. During the deposition time the solution was stirred with a Teflon-coated rotator. The deposition potential was set to -0.1 V for 60 s. After a quiescence time of 10 s, the potential scan was carried out from −0.2 to −0.7 V using sampled DC at a frequency of 10 Hz and a scan rate of 40 mVs^{-1}. The analyses were quantified by two standard additions of Fe^{III} of appropriate concentration.

2.3. Procedure to Determine Fe^{III}

Bipyridyl was added to the seawater to a final concentration of 10 μM Bp and left to equilibrate for 20–30 min. The HEPPS buffer (0.01 M), NN (20 μM) and BrO_3^- (40 mM) were added, and the reactive Fe^{III} concentration was determined as before. The concentration of reactive Fe^{II} was calculated from the difference between the concentration of the combined reactive iron and reactive Fe^{III}.

3. Results and Discussion

3.1. Effect of Bromate on the CSV Peak for Iron

Voltammetric scans for iron in seawater in the presence of 20 μM NN at pH 8 lead to a peak at −0.5 V. The peak height is greatly amplified when bromate is added. A comparison of scans using H_2O_2 as an oxidant with those using bromate (Fig. 1) show a much improved baseline and peak shape in the presence of bromate. It is therefore easier to integrate small peaks accurately and thus to determine lower iron concentrations. The baseline is reasonably flat next to the peak as the major distortion caused by H_2O_2 is no longer present. There is no need to add SDS (to suppress the diffusion current of H_2O_2), which eliminates one source of contamination.

Catalytic CSV in the presence of H_2O_2 required heating of the sample to accelerate a gradual increase in the peak height and to obtain stable peaks within a short time. To test the kinetics of the complexation of NN and the oxidation of Fe^{II} by BrO_3^-, repeated CSV scans of iron (1.49 ± 0.06 nM) in seawater were carried out over a period of 25 min. The baseline and the peak height were stable within the error of the measurements: the average peak height was 3.62 ± 0.11 nA (± 2.9 %, $n = 20$). It is therefore not necessary to microwave the solution to obtain stable peak heights as in the presence of hydrogen peroxide, which simplifies the procedure and reduces a possible source of contamination.

Cyclic voltammetry (CV) was used to investigate the electrochemistry of the reduction wave in the presence of bromate (Fig. 2). The forward scan shows the reduction current of the adsorbed iron plus the diffusion current. The peak for iron tails off at the end rather than showing a symmetric return to the baseline. This tail is ascribed to reduced iron continuing to be oxidized and contributing to the reduction current in the overlapping diffusion gradients of bromate and Fe^{II}. The returning scan shows the on-going background current due to this same effect, which is eliminated once the scan reaches potentials more positive than −0.5 V where the iron is no longer reduced.

Several scan modes were compared to optimize the sensitivity of the technique (Fig. 3). Filtered seawater with a reactive iron concentration of 0.55 ± 0.03 nM was analyzed with different scan modes at a deposition time of 60 s. The catalytic effect was negated when fast scanning waveforms such as square wave modulation >10 Hz or linear sweep mode > 0.1 V s^{-1} were used as the catalysis depends on diffusion of the oxidant to the electrode surface during the scan. Best sensitivities were therefore obtained using slow

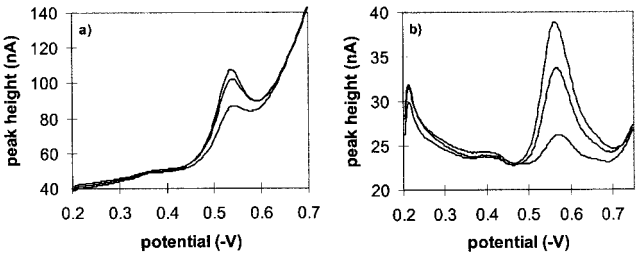

Fig. 1. Comparison of voltammetric scans for the determination of iron in seawater using a) hydrogen peroxide and b) bromate as oxidants, quantified by two standard additions of Fe^{III}. Conditions: a) 1.6 nM Fe, at pH 8.0, 1.8 mM H_2O_2, sensitivity 9.2 nA(nM min)$^{-1}$, deposition time 60 s; b) 0.5 nM Fe, at pH 8.0, 40 mM BrO_3^-, sensitivity 6.6 nA(nM min)$^{-1}$, deposition time 60 s.

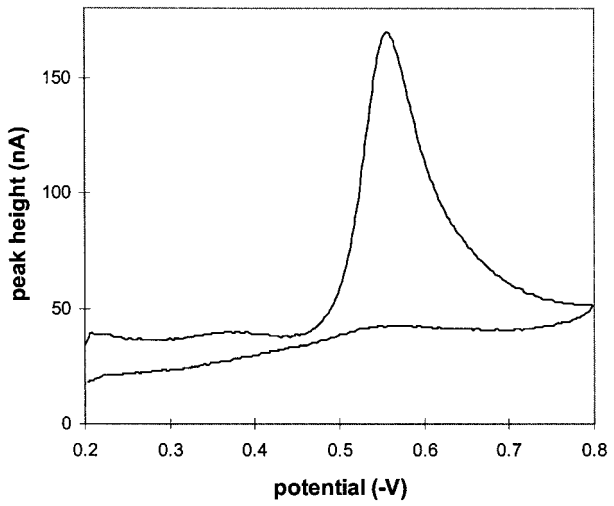

Fig. 2. Cyclic voltammetric scan of seawater containing 20 nM Fe. Conditions: 40 mM BrO_3^- at pH 7.7, deposition time 60 s, scan rate 0.1 Vs^{-1}.

waveforms. At a frequency of 10 Hz or a scan rate of 0.1 V s^{-1} the peak shapes and the sensitivities were optimal with sensitivities of 9.8 nA(nM min)$^{-1}$ and 12.7 nA(nM min)$^{-1}$, respectively.

The sensitivity of the differential pulse modulation was poor with a small modulation amplitude of 10 mV [$S = 1.3$ nA(nM min)$^{-1}$]. At a modulation amplitude of 50 mV the sensitivity was greater at 7.7 nA (nM min)$^{-1}$, but an unknown interference caused the detected iron concentration to be increased from 0.55 to 0.87 $\pm$ 0.09 nM. For this reason the sampled-DC mode was chosen for the analytical procedure, which had a sensitivity of 6.6 nA (nM s)$^{-1}$.

3.2. Reaction Mechanism

The dissolved Fe^{II} is oxidized to Fe^{III} upon addition of BrO_3^-. Fe^{III} forms a complex with NN [$Fe(NN)_3$] [26], which subsequently adsorbs on the HMDE during the deposition step. During the voltammetric scan the Fe^{III} in the complex is reduced to Fe^{II} which is then reoxidized to Fe^{III} by BrO_3^-. The reoxidized Fe^{III} then contributes again to the reduction current causing a greatly improved sensitivity. The potential of the catalytically enhanced peak is at the same location as that in the absence of bromate, indicating that the freshly reoxidized iron is complexed with NN as before. Fe^{III} is known to be complexed with 1-N-2-N [26]. For Fe^{II} this does not appear to be known. However, Fe^{II} is known to be complexed with 2-N-1-N [27]. It is therefore likely that Fe^{II} is also complexed with 1-N-2N. In view of the very short available reaction time (milliseconds in the diffusion layer close to the electrode surface), it is likely that the iron remains complexed with NN throughout the redox process. Therefore the following reaction mechanism is suggested:

$$Fe^{III} + 3NN \rightleftharpoons Fe^{III}(NN)_3$$

$$Fe^{III}(NN)_3 + Hg \rightleftharpoons Fe^{III}(NN)_{3\,ads}(Hg)$$

$$Fe^{III}(NN)_3 + e^- \rightarrow Fe^{II}(NN)_3$$

Catalytic cycle
Bromate

3.3. Effect of Varying Analytical Parameters

Variations of the bromate concentration between 10 mM and 40 mM showed that the sensitivity for iron increased with the bromate concentration (Fig. 4). Bromate is poorly soluble in water (the solubility is 0.48 M) restricting the maximum concentration which can be added to the cell without greatly diluting the sample. A concentration of 40 mM BrO_3^- (1 mL of 0.4 M BrO_3^- to 10 mL in the cell) was selected as a trade-off between increased sensitivity and sample dilution.

To test the effect of the pH, three different buffers were tested: PIPES (pH 6.8), HEPES (pH 7.7) and HEPPS (pH 8.0). At pH 6.8 the sensitivity was 0.7 nA(nM min)$^{-1}$ in comparison to 3.7 and 4.3 nA(nM min)$^{-1}$ at pH 8.0 and 7.7, respectively. For speciation analysis it is preferable to keep the seawater at its natural pH; therefore HEPPS pH 8.0 buffer was selected, even though greatest sensitivity was achieved using HEPES buffer at pH 7.7.

The deposition potential may affect the complex formation and adsorption of the complex as it may change the redox state of iron in the diffusion layer. Variation of the deposition potential between -0.05 V and -0.4 V had no effect on the peak height (Fig. 5a), whilst at potentials more negative than -0.4 V and more positive than -0.05 V the peak height decreased. It is likely that the decrease at potentials more negative than -0.4 V is due to diffusion of reduced Fe^{II} away from the electrode surface, suggesting that the Fe^{II} is not adsorbed. A deposition potential of -0.1 V was chosen in the present study.

Variations of the deposition time showed that the peak height increased linearly with increasing deposition time (Fig. 5b), doubling with a doubling of the deposition time over a tested range up to 480 s. The sensitivity can therefore be greatly increased by lengthening the deposition time.

Increasing the concentration of NN caused the peak height to increase up to an NN concentration of 150 μM; the increase levelled off at higher NN concentrations (Fig. 5c). However, the background current also increased with the NN concentration. A concentration of 20 μM NN was used in the present study in order to minimize the contamination due to iron from NN as well as the background current.

The linear range of the CSV response was established over a

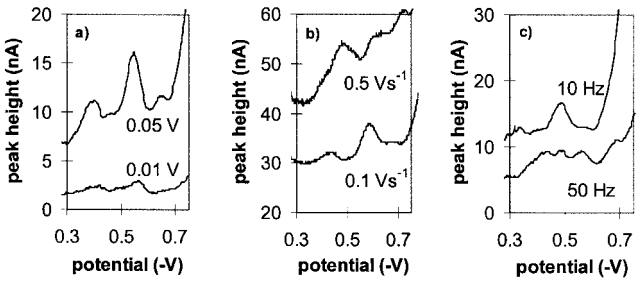

Fig. 3. Comparison of waveforms: a) differential pulse modulation, b) linear sweep modulation, c) square wave modulation. Conditions: 0.5 nM Fe, deposition time 60 s.

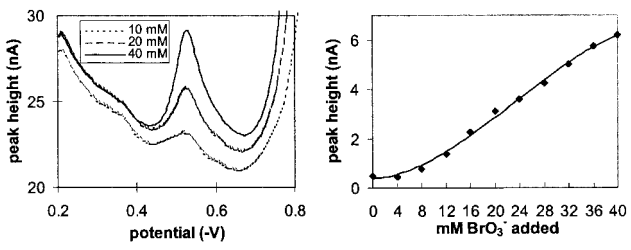

Fig. 4. Effect of varying the bromate concentration. Peak shape and peak height as a function of added bromate. Conditions: 0.8 nM Fe, pH 8.0, deposition time 60 s.

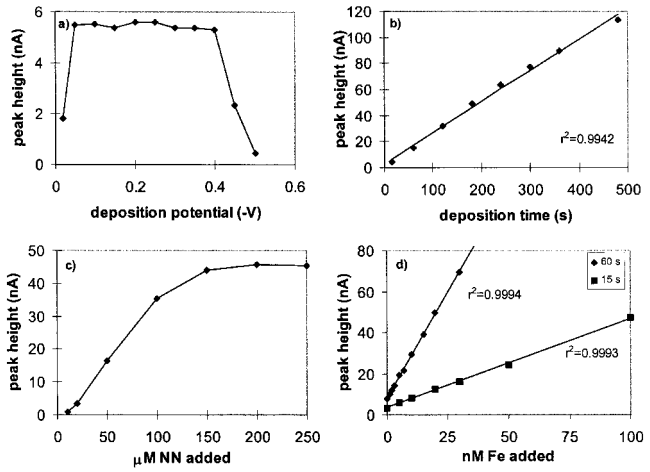

Fig. 5. a) Peak height as a function of the deposition potential; 0.9 nM Fe, pH 8.0, deposition time 60 s. b) Effect of increasing deposition time on the peak height and thus sensitivity; 3.9 nM Fe, 40 mM BrO_3^-, pH 7.7). c) Peak height as a function of NN concentration; 40 mM BrO_3^-, deposition time 60 s, pH 7.7). d) Peak height as a function of increased iron concentration; deposition time 15 s and 60 s, 20 µM NN, 40 mM BrO_3^-, pH 8.0.

concentration range of 1–100 nM iron in seawater (Fig. 5d). Using a deposition time of 60 s and 15 s the response was linear at least up to 30 nM and 100 nM Fe, respectively. The concentration was not increased any further as this range is ample for the iron concentrations found in seawater samples from oceanic and coastal waters.

3.4. Analysis of Total Dissolved Iron

Total dissolved iron was determined after UV-digestion of the seawater for 3 h at pH 2. Repeated CSV scans showed that the iron peak increased gradually before stabilizing after 20–30 min and was then stable within a standard deviation of less than ±2 % ($n = 22$). However, the iron peak (−0.56 V) was immediately stable if the UV-digested seawater was left overnight or if NH_2OH–HCl (final concentration of 0.05 mM) was added prior to the measurement. The peak instability might be due to HOCl, which is known to be formed during the UV irradiation at pH 2 and destroyed gradually at neutral pH or quickly by addition of NH_2OH–HCl [28].

The detection limit was calculated from 3× the standard deviation of four measurements of cleaned seawater (UV digested at pH 8 for 3 h and cleaned with MnO_2) using an adsorption time of 30 s. The total iron concentration was 0.784 ±0.0265 nM; calculation of the detection limit from 3× the standard deviation gives a value of 0.08 nM. This limit of detection can be lowered by a factor of 16 to an estimated 5 pM by extending the adsorption time to 480 s. At low iron concentrations the reagent blank (around 0.05 nM, predominantly due to that in NN) has to be taken into account by careful determination of the concentration of iron occurring in NN. Here the iron in the NN was determined by CSV after low temperature ashing off the NN (see Sec. 2).

The new catalytic method was compared with the earlier noncatalytic version to verify whether the same iron concentration is detected. UV-digested and cleaned seawater was thereto analyzed by CSV in the presence of NN but without addition of oxidant [22] and by the new bromate method. The detected iron concentration was 0.45 ± 0.05 nM [sensitivity 1.77 nA(nM min)$^{-1}$] without bromate, and 0.38 ± 0.04 nM [sensitivity 6.16 nA(nM min)$^{-1}$] in the presence of bromate. Thus, the addition of 40 mM bromate to the sample caused a three and a half fold increase in sensitivity and no significant difference in the iron concentration.

Table 1. Addition of Fe^{II}- and Fe^{III}-standards, which were mixed with Bp, to seawater samples. Fe^{II} was masked by Bp and did not contribute to the CSV response. However, Fe^{III} contributed to the CSV response as it was not masked by Bp.

Sample	*Addition*	*Result*
1.6 ± 0.1 nM	6.25 nM Fe^{II} in 1.25 µM Bp	1.7 ± 0.03 nM
	12.5 nM Fe^{II} in 2.5 µM Bp	1.8 ± 0.05 nM
1.9 ± 0.04 nM	1.25 nM Fe^{III} in 2.5 µM Bp	3.17 ± 0.5 nM

3.5. Indirect Detection of Fe^{II}

Fe^{II} was added to seawater to investigate whether both Fe^{II} and Fe^{III} contribute to the CSV response. Addition of 2 nM Fe^{II} to seawater containing an initial reactive iron concentration of 1.5 ± 0.1 nM caused the detected concentration to increase to 3.5 ± 0.07 nM (indicating an analytical recovery of all added Fe^{II}). It is therefore likely that the bromate addition oxidizes all reactive iron to Fe^{III} causing the combined reactive iron concentration to be measured by this method.

It was attempted to determine Fe^{III} specifically by masking Fe^{II} using a specific Fe^{II} binding ligand, bipyridyl (Bp) [9]. The selective masking of Fe^{II} by Bp was tested by adding Fe^{II}- and Fe^{III}-standards, which were previously complexed with Bp for several hours, to seawater (Table 1). CSV of seawater to which 6.25 nM Fe^{II} plus 1.25 µM Bp or 12.5 nM Fe^{II} plus 2.5 µM Bp were added indicated that the added Fe^{II} was masked from the analysis. However, Fe^{III} was not masked by Bp as the addition of 1.25 nM Fe^{III} plus 2.5 µM Bp was found to increase the detected reactive iron concentration from 1.9 ± 0.04 nM to 3.17 ± 0.5 nM. The addition of the mixtures showed that Bp retained Fe^{II} specifically, and did not bind any Fe^{III}. The addition of Bp therefore allows the differentiation between the two redox species.

The concentration of Bp was varied to optimise its concentration. Increasing concentrations of 0 to 20 µM Bp were allowed to react for 30 min with 2 nM Fe^{II}, at an initial reactive iron concentration of 1.4 ± 0.02 nM (Fig. 6a). No Fe^{II} was originally detected in that seawater, which had been stored in the fridge for several months prior to the analyses. The added Fe^{II} was fully measured as combined reactive iron in the absence of Bp. Increasing the concentration of Bp increased the degree of masking of 2 nM Fe^{II} from 70 % at 2 µM Bp to 100 % at 10 µM Bp after 30 min equilibration time. This level of Bp is greater than that used previously in the presence of H_2O_2 [9], and the difference may reflect a greater oxidizing power of bromate. Unexpectedly the CSV sensitivity increased with increasing concentrations of Bp up to 4 µM, after which the sensitivity decreased. This change in sensitivity was also observed when Bp was not equilibrated with

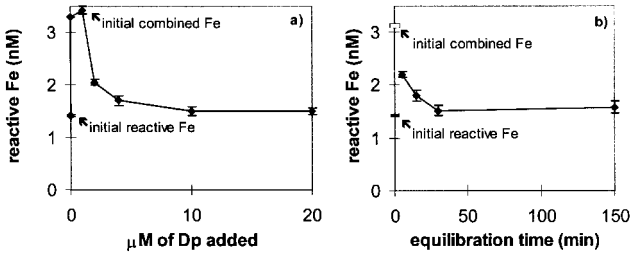

Fig. 6. a) Effect of increasing the Bp concentration on the complexation of Fe^{II} (2 nM), error bars indicate ± standard deviation. b) Effect of increasing the equilibration time on the complexation of Fe^{II} by Bp (2 nM Fe^{II} added in 10 µM Bp), error bars indicate ± standard deviation; initial reactive iron concentration of 1.4 ± 0.02 nM.

the sample and can thus be explained as a surfactant effect of Bp at the mercury drop.

In order to investigate the kinetics of the complexation between Fe^{II} and Bp, seawater with added Fe^{II} was equilibrated with Bp for different lengths of time. Figure 6b summarizes the results obtained by equilibrating 2 nM Fe^{II} with 10 μM Bp (initial reactive iron concentration of 1.4 ± 0.02 nM). After an equilibration time of 5 min (time required to purge the solution) only 60 % of the Fe^{II} was masked. After 30 min 100 % of the Fe^{II} was complexed and this was stable for at least 2.5 h.

3.6. Interferences

Other trace metals may interfere if they form a complex with NN, which adsorbs on the mercury drop and is reduced at a potential similar to that of iron. Several metals were added to evaluate possible interferences. The concentrations of the added metals were considerably higher than in natural seawater. 200 nM Mn^{II} showed no interference in the determination of reactive iron or Fe^{III}. 150 nM Zn (natural oceanic concentrations <10 nM) reduced the sensitivity of the reactive iron measurement by 30 %, but had no effect on the detection of Fe^{III}. Co showed a peak at −0.517 V after the addition of Bp, which interfered with the iron peak at −0.555 V. However, in the analysis without Bp, Co did not cause any interferences. The interference was caused by 50 nM Co indicating that this interference is unlikely to be important as the natural Co concentration is about a thousand times lower. The addition of 100 nM Cu^{II} was found to interfere with the determination of Fe^{II} as it masked the difference between the combined reactive iron and Fe^{III}. A possible explanation is that Cu^{II} oxidizes Fe^{II} in seawater [4].

3.7. Definition of Reactive Iron

Seawater is known to contain 0.2–10 nM organic ligands [23, 29], which complex iron with values for the conditional stability constant ($K'_{Fe^{3+}L}$) of $10^{18.8}$–$10^{21.8}$ [29] or $10^{21.4}$–$10^{23.1}$ [23]. The values of Rue and Bruland [23] were converted to $K'_{Fe^{3+}L}$ values by multiplication with the value for $\alpha_{Fe'}$ (10^{10}) used by them. The α-coefficient for nM levels of these natural complexes, α_{FeL}, is $10^{10.5}$–$10^{13.7}$ [29, 30] or $10^{12.1}$–$10^{13.7}$ [23, 31]. The α-coefficient of the most stable complexes is similar to that for $Fe(NN)_3$, which has a value of $\alpha_{FeNN3} = 10^{13.7}$ in the presence of 20 μM NN. If α_{FeL} is lower than α_{FeNN3} most of the iron is bound by the added NN, and only a small amount is masked by the natural organic complexing ligands. However, if the α_{FeL} is similar to α_{FeNN3} the competition between the natural organic complexing ligands and the added NN is significant, and the reactive iron concentration is lowered. It is therefore important to take natural organic complexes into account when the reactive iron concentration in natural waters is analyzed.

4. Conclusions

The established procedure to determine iron in seawater by CSV was improved by using bromate instead of hydrogen-peroxide as oxidant. The new procedure can be used successfully at pH 8.0 using HEPPS as pH buffer and a BrO_3^- concentration of 40 mM. The reagent blank was reduced by eliminating the addition of SDS to the sample, whereas BrO_3^- is purified relatively easy. Stable peak heights were obtained when the reagents were added to seawater, indicating that it is not necessary to heat the sample (as required when hydrogen-peroxide was used), which minimizes the sample handling. The absence of hydrogen-peroxide improved the baseline, which facilitated the integration of the peak and decreased the standard deviation.

Fe^{III} is determined specifically by masking of Fe^{II} with 10 μM Bp (reaction time of 30 min) against oxidation by the added bromate. This can be used to determine the redox speciation of iron in seawater. Interferences by other trace metals in uncontaminated seawater were insignificant. However, natural organic complexing ligands interfere with the added NN by masking some of the dissolved iron. The calculated α-coefficient of the iron-NN complex is similar to that of the most stable natural organic complexes of iron known to occur in seawater, indicating that it is likely that a significant fraction of the iron is masked from the NN. This effect can be taken advantage of to determine the organic speciation of iron. The organic matter can be removed by UV-digestion of the seawater.

5. Acknowledgements

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