

Coulometric Study of the Redox Dynamics of Iron in Seawater

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Controlled potential coulometric analysis has long been recognized as one of the most sensitive electrochemical techniques but is limited in application by the lack of specificity of the method. One way of improving specificity is through electrochemical masking using strong, selective complexing agents. In this paper, a controlled potential coulometric procedure combined with a masking technique is developed and applied to the measurement of low concentrations of oxidizable Fe(II) species in seawater. The technique is particularly appropriate to studies of iron redox processes in seawater since the redox dynamics of the system under investigation are not greatly perturbed by the analytical procedure developed.

Iron exists in aqueous solution in either the ferrous [Fe(II)] or ferric [Fe(III)] form with the proportion of the total soluble iron present in each oxidation state under equilibrium conditions being governed by the electron activity (1, 2). For waters containing dissolved oxygen, where the electron activity is controlled by the O_2/H_2O couple (or, as suggested by Parsons (3), an intermediate redox couple such as O_2/H_2O_2), the proportion of soluble iron in the ferrous state will be much lower than that present in the ferric state. Due to the extremely insoluble nature of ferric oxyhydroxides, the total soluble iron concentration will thus be very low under oxic conditions. For example, in seawater the concentration of the major soluble iron species, $Fe(OH)_2^+$, is only $10^{-9.7}$ M. Only under anoxic conditions, where the electron activity is controlled by reduced sulfur or organic redox couples, do thermodynamic considerations predict significant equilibrium concentrations of soluble ferrous iron.

While thermodynamic considerations suggest that the concentration of reduced forms of iron will be very low in oxic waters, there is increasing evidence that nonequilibrium processes involving iron may lead to measurable concentrations of Fe(II) species in aquatic systems, even in the presence of oxygen. Thus, McMahon (4) observed the presence and diurnal variation of Fe(II) species in lake surface waters and attributed the observation to photochemically induced redox processes. Similar observations were made by Collienne (5) in studies of two acidic lakes in Belgium. Collienne demonstrated that the Fe(III) reduction process was essentially photochemical, promoted by the presence of organic matter and appropriate pH conditions. Miles and Brezonik (6) invoked a similar process in explaining the observation of low concentrations of dissolved oxygen in the surface waters of a highly colored lake. These authors proposed a reaction cycle in which Fe(III) compounds are photochemically reduced to Fe(II) compounds with the Fe(II) species then being oxidized back to Fe(III) species by dissolved oxygen. The concept of a dynamic reduction-oxidation cycle has also been suggested by Morgan and Stumm (7) and Theis and Singer (8).

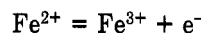
While information concerning iron speciation in freshwaters does appear to confirm that nonequilibrium redox processes may be occurring in some situations, very few data on seawater systems are available. It is thus difficult to draw conclusions regarding the existence or impact of such processes in the

marine environment. One reason for the scarcity of data on iron speciation in seawaters is that total iron concentrations rarely exceed 1–2 nM (9), thus estimation of total concentrations, let alone species concentrations, is very difficult. If measurement of net Fe(II) production were to be used as a means of investigating nonequilibrium iron redox processes in marine environments, the analytical technique implemented must clearly exhibit very high sensitivity. In addition the dynamics of the system of interest should either not be perturbed or be perturbed in a predictable manner by the investigative technique employed.

A variety of analytical techniques including colorimetry (10, 11) chemiluminescence (12), radioisotope dilution (13), and electrochemistry (14–20) have been used for the measurement of Fe(II) in aqueous systems. Of these techniques, electrochemistry—particularly the method of controlled potential coulometry—is the one most amenable to measurements of trace Fe(II) concentrations without major perturbation of the existing iron speciation. While exceptional sensitivity has often been reported, no attempt has been made to counter the major drawback of controlled potential coulometry—that of lack of specificity. Analyses have generally been performed on systems where the Fe(II)–Fe(III) current wave is the only signal of any significance in the voltage region of interest. The presence of additional redox couples responding in a voltage region similar to that of the Fe(II)–Fe(III) couple markedly limits the usefulness of the technique for iron specific analysis in complex media. In this paper one method of improving the specificity of the fixed potential coulometric procedure for the analysis of low concentrations of soluble Fe(II) and Fe(III) species is examined in detail and applied to the investigation of light-induced changes in the redox state of iron in marine waters.

THEORETICAL SECTION

Consider the oxidation of Fe(II) to Fe(III) at an electrode. The half-reaction may be written



where Fe^{2+} and Fe^{3+} are in thermodynamic equilibrium with other solution iron species such that

$$[Fe(II)] = K_1(Fe^{2+})$$

and

$$[Fe(III)] = K_2(Fe^{3+})$$

where $[Fe(II)]$ and $[Fe(III)]$ represent the total concentration of soluble reduced and oxidized iron, respectively, and K_1 and K_2 are factors of proportionality. If the kinetics of electron transfer are rapid, the concentrations of Fe^{2+} and Fe^{3+} at the electrode surface can be assumed to be at their equilibrium values as governed by the Nernst equation

$$E = E^\circ + (RT/F) \ln [(Fe^{3+})_s / (Fe^{2+})_s] \quad (1)$$

where the subscript s indicates electrode surface concentrations and E° is the formal potential for the Fe^{3+}/Fe^{2+} couple ($E^\circ = 0.57$ V vs. an Ag/AgCl, saturated NaCl reference electrode). Since

$$(Fe^{3+})_s / (Fe^{2+})_s = K_1[Fe(III)]_s / K_2[Fe(II)]_s$$

the Nernst equation may be written

$$E = E^\circ + (RT/F) \ln [K_1/K_2] + (RT/F) \ln [\text{Fe(III)}]_s/[\text{Fe(II)}]_s \quad (2)$$

If $[\text{Fe(III)}]_s/[\text{Fe(II)}]_s$ is lower than the ratio expected from eq 2 for a given potential, then oxidation of Fe(II) species present in solution will occur in an attempt to reestablish equilibrium. Current will result from this oxidation reaction, the amount of which will be determined by the magnitude of the applied potential—at least up to a point where the incoming ions are oxidized as fast as they are transported across the concentration gradient set up at the electrode surface. In this “mass-transport limited” voltage region the current observed should be directly proportional to the concentration of oxidizable Fe(II) species in bulk solution. If Fe(III) species are initially absent from solution then, from classical electrochemical theory (21), eq 2 may be written in the form

$$E = E^\circ + (RT/F) \ln (K_1/K_2) - (RT/F) \ln (m_o/m_R) - (RT/F) \ln [(i - i_l)/i_l] \quad (3)$$

where m_o and m_R are the mass transfer coefficients for the oxidized and reduced species, respectively, i is the observed current, and i_l is the limiting current (the convention that currents are negative when the test electrode is an anode being adopted).

Under equilibrium conditions the position of the Fe(II)–Fe(III) wave will, of course, be dependent on the composition of the supporting electrolyte which governs the speciation of iron and hence the ratio K_1/K_2 . In some situations one of the oxidation states of iron may be stabilized to such an extent (for thermodynamic or kinetic reasons) that iron oxidation or reduction waves are no longer observable in the potential range of interest. Such “electrochemical masking” has proven to be a valuable tool in analytical chemistry (22, 23) and, provided selective masking agents are available, is a means by which the specificity of controlled potential coulometric measurements can be improved.

Consider, for example, the measurement of current at a fixed potential in the mass-transport limited region of the Fe(II) oxidation wave before and after addition of an Fe(II) specific masking agent—one that effectively inhibits Fe(II) oxidation at the electrode surface. Before masking agent addition, current will result from Fe(II) oxidation and from all other redox reactions proceeding at the chosen potential. After addition of the Fe(II) specific masking agent, current at the chosen potential may be expected to arise from reduction of certain Fe(III) species (i.e., those that become reducible as a result of the lowered Fe^{2+} activity) and from the same group of redox reactions as occurred prior to addition—assuming of course that addition of the masking agent perturbs only the speciation of iron. The difference in current before and after masking agent addition will then give the sum of the current due to oxidation of Fe(II) species and reduction of Fe(III) species. It is expected that under conditions typical of most marine waters, the reducible Fe(III) concentration will be very low and in fact, as will be verified later, below the detection limit of most analytical techniques since (i) the inorganic Fe(III) species will be kept at low concentrations by the formation of highly insoluble ferric oxyhydroxide precipitates, (ii) direct reduction of colloidal iron oxyhydroxides has been reported (24, 25) but occurs at potentials considerably more negative than that required for reduction of soluble Fe(III) hydroxy species, and (iii) if important Fe(III) organic species exist in seawater, they must be more stable than the oxyhydroxide solid and be reducible only at very negative potential, even in the presence of a strong Fe(II) complexing agent.

In this paper the electrochemical masking ability of the strong Fe(II) ligand 1,10-phenanthroline is studied. This agent

is then used in conjunction with controlled potential coulometry to investigate the properties of photochemically induced redox processes in seawater.

EXPERIMENTAL SECTION

Apparatus. All electrochemical measurements (current–voltage curves and controlled potential coulometric studies) were made with an Environmental Sciences Associates (ESA) Model 3040 charge-transfer analyzer (CTA). The CTA was equipped with a hollow tubular pyrolytic graphite working electrode with an active inner surface of area $\approx 10 \text{ cm}^2$, a platinum wire counter-electrode, and an Ag/AgCl saturated NaCl reference electrode. Liquid was entrained into the working electrode by means of a spiral stirring propeller. The charge-transfer analyzer and electrode system have been described in detail by Matson et al. (26). Analyses were performed either in a 200-mL tall-form glass beaker attached to the electrode system by a threaded collet or in a 300-mL water-jacketed cylindrical glass vessel with quartz windows at either end and access ports into which the electrode system could be inserted.

When necessary, illumination of the analysis vessel was provided by a Schoeffel 1000-kW solar stimulator system. This system generated a reasonably well collimated, uniform beam exhibiting a spectral distribution similar to that of solar radiation at the earth's surface. An intensity of approximately 100 mW/cm^2 at the front window of the sample vessel was used.

Reagents. Either a solution containing 0.1 M NaCl and $2 \times 10^{-3} \text{ M NaHCO}_3$ or a synthetic ocean water (SOW) mixture was used as supporting electrolyte throughout this study. The preparative procedure and characteristics of the SOW mixture are described in detail by Morel et al. (27). The background concentration of total iron in these electrolytes was determined by using the cobalt coprecipitation method developed by Boyle and Edmond (28). The pH of solutions undergoing analysis was maintained by equilibration with a CO_2 /air mixture of appropriate CO_2 partial pressure. Essentially all studies were performed in electrolyte buffered to pH 6.5. At this pH the autooxidation of Fe(II) is relatively slow (compared to the time required for current measurement), thus complications due to change in $[\text{Fe(III)}]$ over the time of analysis were avoided.

Analytical reagent grade ferrous ammonium sulfate ($<0.01\% \text{ Fe(III)}$) was used to prepare the Fe(II) stock solutions and redistilled reagent grade HCl and Millipore Q-water were used throughout the study.

Procedure. Current–voltage curves for various supporting electrolytes containing micromolar concentrations of Fe(II) and Fe(III) were obtained by measuring the current generated as the potential of the working electrode was scanned from -0.2 V to $+1.0 \text{ V}$ at a rate of 5 mV/s . Current–voltage curves at lower Fe(II) concentrations were obtained by using “steady-state” voltammetric techniques similar to those described by Blaedel and Jenkins (29). Corrections were made for current due to non-mass-transport-limited phenomena (such as redox reactions of electrode surface functional groups and the reduction of oxygen adsorbed to the working electrode) by subtracting the response obtained under nonstirred conditions from that obtained while stirring (26). This was accomplished by using the multichannel facility of the charge transfer analyzer. This facility enables sequential operation under a variety of test electrode conditions (i.e., conditions of electrode potential, current integration time, and stirring) without the need for removal of the electrode from the solution of interest.

All calibration curves and controlled potential coulometric results were obtained by observing the response at a suitable potential in the mass transport limited region of the Fe(II) oxidation wave. The observed response represented the difference between the current integrated for 30 s with stirring and the current integrated for 30 s without stirring.

Investigations of light-induced changes in the iron oxidation state were made by using coastal seawater samples filtered through $0.2\text{-}\mu\text{m}$ Nuclepore membranes and spiked with nanomolar concentrations of ferric iron. The Fe(III) additions were made from acidified 10^{-6} M FeCl_3 stock solutions.

RESULTS AND DISCUSSION

Current–voltage curves obtained by linear-sweep voltammetry for micromolar amounts of Fe(II) in pH 6.5 buffered

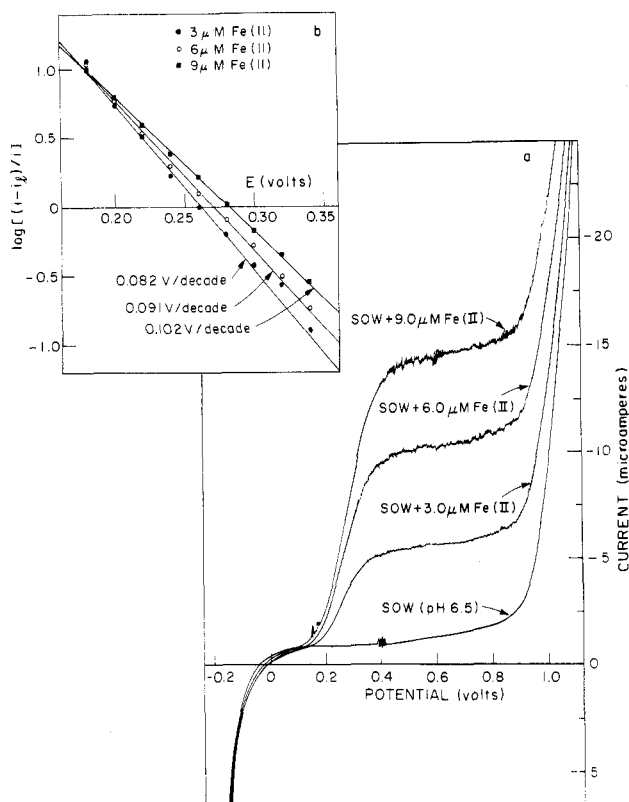
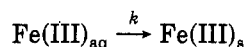
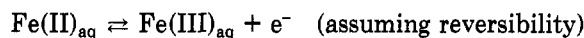


Figure 1. (a) Current-voltage curves for synthetic ocean water (buffered to pH 6.5) containing micromolar concentrations of iron. (b) Transformed data from the current-voltage curves in (a) plotted as $\log [(i - i_1)/i]$ vs. E . (The convention that currents are negative when the test electrode acts as an anode is used throughout.)

synthetic ocean water are shown in Figure 1a and demonstrate distinct plateau regions due to mass-transport limitation. While existence of this concentration-dependent plateau within a suitable voltage region is one of the two major criteria for success of this technique (the other being of course that this wave, if it exists, can be masked satisfactorily), additional information concerning the nature of the oxidation process can be verified by using these curves. For example, Fe(II) oxidation to the ferric state may be thought of as occurring in two stages: (a) oxidation of soluble Fe(II) species to soluble Fe(III) species at the electrode surface—the reversibility of this step being governed by the rate of electron transfer, and (b) formation of insoluble Fe(III) oxyhydroxides—the rate of this step being governed largely by the degree of oversaturation of the oxyhydroxides (30, 31). These steps may be represented as



The chemical (precipitation) reaction following the electrode reaction should not affect the height of the current plateau; however, the shape of the i - E curve leading up to the plateau region may be altered and will depend particularly on the relative rates of colloid formation, k , and scan rate, v , used to obtain the i - E curves (32). For small values of k/v , the i - E response should approximate reversible behavior while for large k/v , the observed response may resemble that of an irreversible electrode process. Plots of $\log [(i - i_1)/i]$ vs. E (Figure 1b) derived from the i - E data of Figure 1a (obtained at a constant scan rate, v) indicate non-Nernstian behavior at the higher Fe_T concentrations with an apparent reduction in irreversibility of the electrode reaction as Fe_T is lowered. These results most likely indicate a decreasing importance

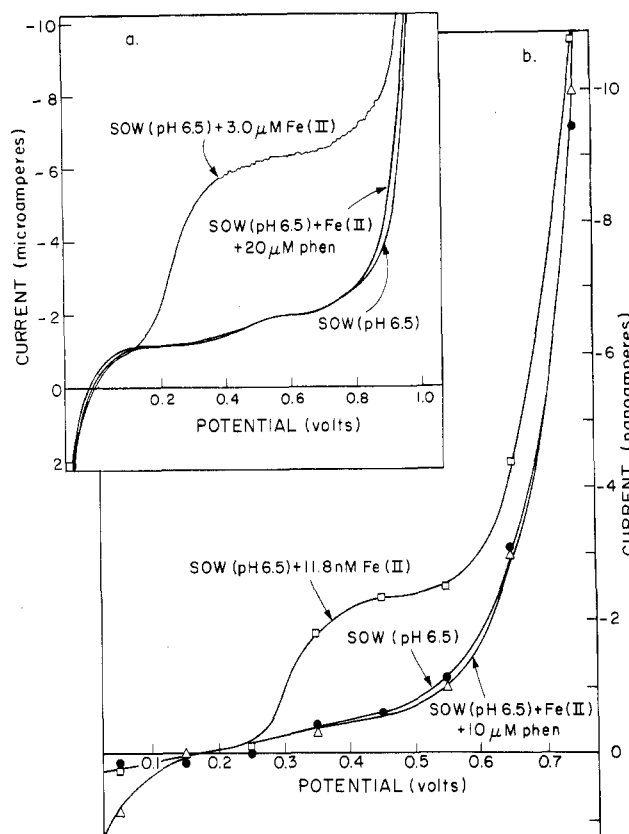


Figure 2. Effect of added excess 1,10-phenanthroline on the Fe(II) oxidation wave in synthetic ocean water (buffered to pH 6.5) containing (a) high (micromolar) and (b) low (nanomolar) concentrations of Fe(II). Current-voltage curves in (a) are obtained by continuously scanning the potential of the working electrode while curves in (b) are obtained by "steady-state" techniques (see text).

of the precipitation reaction as the degree of oversaturation (and hence the rate of colloid formation, k) is reduced. At the low iron concentrations of particular interest in this study, the behavior of the system approaches that of an ideal soluble system where both reductant and oxidant concentrations at the electrode surface depend principally on diffusion in the boundary layer, not on precipitation of an insoluble phase.

As can be seen in Figure 1, large currents at high and low positive potentials resulting from redox reactions in the supporting electrolyte obscure current contribution from the electrochemical activity of iron. The current observed at potentials more negative than about 0.06 V results from the reduction of dissolved oxygen while the current observed at potentials more positive than about 0.9 V results from the oxidation of water. While deoxygenation of the sample would eliminate the large background current at low potentials, such a step would be likely to alter the relative concentrations of Fe(II) and Fe(III) and should be avoided. Thus, in the presence of oxygen, a usable voltage region exists between about 0.06 and 0.9 V relative to the Ag/AgCl reference electrode.

It should be noted that, even in the absence of added Fe(II), a small background current does exist over the voltage range of interest. The magnitude of this background current was found to vary slightly from run to run and may be attributed to (a) slight imbalances in the stirred/nonstirred channel parameters (potential and integration time) and (b) current contributions from additional oxidizable species present in the supporting electrolyte. Because of the relatively arbitrary magnitude of this background current, current values are usually reported as the difference between an absolute current measurement and a measurement of the background current prior to Fe(II) addition.

Table I. Multiple Estimates of the Effect of Added Fe(III) on the Coulometric Responses and Subsequent Phenanthroline Masking of Fe(II) Added to 0.1 M NaCl, 2 mM NaHCO₃ Buffered to pH 6.5 (Working Electrode Potential = 0.5 V, [phen]_T = 10⁻⁵ M)

Fe(III) added, ^a nM	Δ current ^b (pA) after			
	Fe(III) addition	addition of 11.8 nM Fe(II)	phen addition	Δ , ^c pA
0		+1050	-80	1130
		+1000	-70	1070
		+1050	-80	1130
				(1110 ± 35) ^d
116	+90	+1010	-20	1030
	+90	+1080	-10	1090
				(1060 ± 30)
294	+140	+1160	-60	1220
	+160	+1360	+150	1210
	+200	+1180	-20	1200
				(1210 ± 10)
588	+280	+1260	-110	1370
	+310	+1310	-50	1360
	+330	+1310	-20	1330
				(1353 ± 17)

^a Total iron content of 0.1 M NaCl, 2 mM NaHCO₃ electrolyte approximately 20 nM. ^b Relative to response of electrolyte prior to any additions. ^c Δ = current after Fe(II) addition - current after phen addition. ^d Mean ± one standard deviation.

From the current-voltage curves of Figure 2 it is apparent that addition of 1,10-phenanthroline to a pH 6.5 synthetic ocean water medium containing Fe(II) and Fe(III) species eliminates the Fe(II) oxidation wave from the 0.06–0.9 V region over a wide range of Fe(II) concentrations, thus indicating that 1,10-phenanthroline is an excellent masking agent for soluble iron species—at least in well-defined synthetic ocean waters. Many of the problems and possibilities of this masking technique have been further elucidated by controlled potential coulometry in the mass transport limited region of the Fe(II) oxidation wave in a variety of electrolytes. The data presented in Figure 3 showing the current increase resulting from Fe(II) additions to the 0.1 M NaCl, 2 mM NaHCO₃ electrolyte and the subsequent decrease in current on masking the Fe(II) response by phenanthroline complexation confirmed the linear nature of the relationship between the observed response and bulk solution concentration of Fe(II) and the effectiveness of phenanthroline masking. Note that phenanthroline masking of the Fe(II) wave will not affect the bulk of the Fe(III) present when total ferric iron concentrations are in excess of approximately 10⁻¹⁰ M (at pH 6.5), since at these concentrations, kinetically inert iron oxyhydroxides will begin precipitating. Of course, the small current wave due to reduction of dissolved ferric species that are in equilibrium with the oxyhydroxide solid should be shifted by phenanthroline addition. In fact, a current decrease below the initial electrolyte reading (i.e., prior to Fe(II) addition) of 10–77 pA is apparent in Figure 3. If the reduction of dissolved ferric species produces a current approximately the same as oxidation of an equivalent amount of ferrous species, this decrease corresponds to a soluble Fe(III) concentration of 0.04–0.32 nM. Under these conditions of pH and ionic strength, a total soluble Fe(III) concentration in this range corresponds to an Fe(OH)₃ solubility product of 10^{-39.0}–10^{-38.1}, values which are consistent with those found for amorphous iron oxyhydroxides by other methods (33). Uncertainty introduced by current contributions from oxidation of Fe(III) species after phenanthroline addition places a lower limit on the precision of the technique, particularly at pH < 7. At high pH the total dissolved Fe(III) concentration will be very low (<10⁻¹⁰ M) and variability in current measurement becomes a more important factor in determining precision. A realistic estimate of the lowest Fe(II) concentration that can be reliably determined by using this technique is on the order of 10⁻⁹ M.

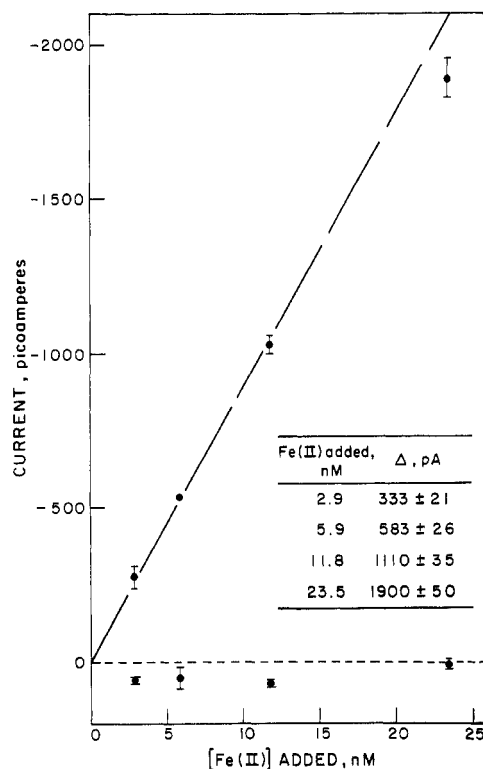


Figure 3. Response observed at a working electrode potential of 0.5 V on addition of Fe(II) to 0.1 M NaCl, 2 mM NaHCO₃ buffered to pH 6.5. The effect of adding 1,10-phenanthroline ([phen]_T = 10⁻⁵ M) is also shown. The plotted current represents the response observed relative to the response of the electrolyte prior to any additions and Δ represents the difference in current before and after phenanthroline addition.

While very high background iron concentrations might be expected to lower the rate of charge transfer through adsorption of ferric oxyhydroxide colloids to the working electrode and hence lowering of the effective electrode surface area, the effects of background total iron concentrations up to about 600 nM appear to be minor (Table I). The most noticeable effect of increasing total iron content is a small increase in the concentration of oxidizable species (see column 2 of Table I)—possibly due to the Fe(II) contamination of the

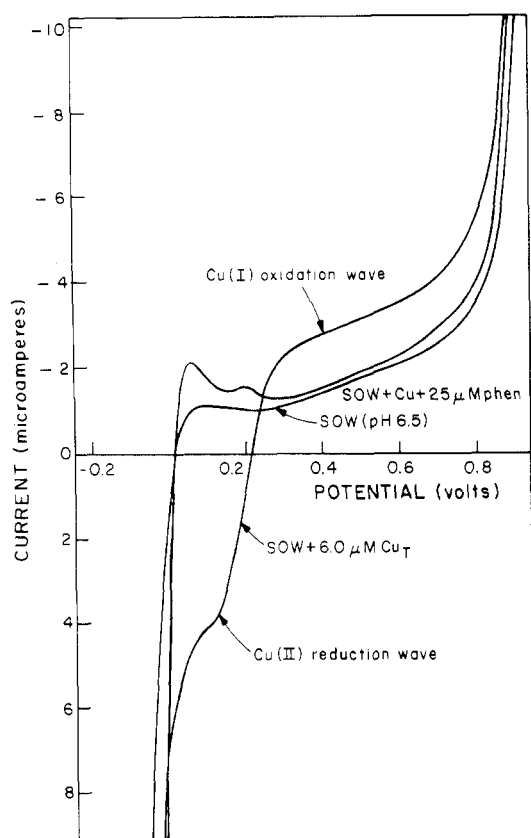


Figure 4. Current-voltage for synthetic ocean water containing micromolar concentrations of Cu(I) and Cu(II) before and after the addition of excess 1,10-phenanthroline. Cu(I) was generated by electrolysis at -200 mV for ≈ 10 min.

Fe(III) salt since the increase in current is masked by phenanthroline addition.

There are two types of species which may interfere in the analysis of iron by coulometry and masking: (a) species that are electrochemically active in the voltage region of interest and interact with the masking agent and (b) species that become electrochemically active in the voltage region of interest upon addition of the masking agent. From inspection of reported standard electrode potentials for a wide range of redox couples, it is clear that the number of species in these categories is not large, but some interferences do exist. Consider, for example, a marine system containing Cu(I) species. The Cu(I)–Cu(II) half-wave potential in seawater lies at about 0.20 V [vs. Ag–AgCl as corrected from Waite and Morel (34)]; thus current measurements at potentials more positive than this may include a contribution from oxidizable Cu(I) species that are present. As can be seen from Figure 4 the height of the Cu(I) oxidation wave is significantly reduced on addition of 1,10-phenanthroline. It thus appears that, like Fe(II), the Cu(I)–phenanthroline complex is not oxidizable in the potential range of interest. While no direct evidence for the existence of Cu(I) species in marine waters exists, a variety of formation pathways have been postulated (35).

A good example of a species that becomes electroactive in the voltage region of interest only after masking agent addition is provided by cobalt. In aqueous solution in the absence of complexing agents the reduced state of cobalt, Co(II), is thermodynamically stable over the pH range of interest (the electrode potential for Co(II)–Co(III) in aqueous solution $E_0 = +1.64$ V vs. Ag–AgCl). In the presence of nitrogen-containing ligands such as ethylenediamine and bipyridyl (and 1,10-phenanthroline), the ligand field stabilization energy is considerably larger for Co(III) than for Co(II) leading to a preferential stabilization of the oxidized state (36) (the elec-

Table II. Effect of Co(II) on the Controlled Potential Coulometric Response at a Working Electrode Potential of 0.5 V before and after Addition of 1,10-Phenanthroline to Synthetic Ocean Water Buffered to pH 6.5 ($[\text{phen}]_T = 10^{-5}$ M)

	Δ current, pA	
	SOW (pH 6.5)	SOW (pH 6.5) + 11.8 nM Co(II)
before Fe(II) or phen addition ^a	0 ± 10	-15 ± 5
after adding 11.8 nM Fe(II) ^a	930 ± 10	945 ± 5
after adding excess phen ^a	-110 ± 30	615 ± 15
Δ^b	1040 ± 30	330 ± 10

^a Relative to response of electrolyte prior to any additions. ^b Δ = current after Fe(II) addition – current after phen addition.

trode potential for Co(II)–Co(III) in the presence of excess bipyridyl is $E_0 = +0.11$ V vs. Ag–AgCl). Thus, addition of excess phenanthroline to a solution containing Co(II) results in the observation of current due to Co(phen)_3^{2+} oxidation in the voltage region of interest. Such a “negative interference” is apparent from the data shown in Table II in which the current before and after phenanthroline addition is recorded for pH 6.5 buffered synthetic ocean water samples containing Fe(II) in the absence and presence of ≈ 12 nM Co(II). Investigation of the influence on the controlled potential coulometric and masking procedures of a range of additional species that may be present in marine systems (nitrate, phosphate, Cd(II), Zn(II), Mn(II), and Mo(VI)) confirmed that no complicating effects should arise.

All studies discussed above have been performed in synthetic ocean water or NaCl, NaHCO_3 electrolytes buffered to pH 6.5. At this pH, the loss of Fe(II) from solution as a result of oxidation (by oxygen) is relatively slow; thus examination of the electrochemical response of these species is possible. While a great deal of information can be obtained from such buffered systems, lowering of the pH is certain to alter the iron speciation significantly—possibly in an unpredictable manner. For this reason, it would be desirable to be able to apply this analytical technique at the natural pH of the sample of interest. This should be possible provided the response to added Fe(II) does not change significantly with variation in pH.

In order to investigate the effect of pH on system response, the oxidation of Fe(II) added to a number of synthetic ocean water mixtures buffered to different pH has been followed in time. Extrapolation back to time zero allows estimation of the current corresponding to the known initial (added) Fe(II) concentration at each pH considered. Examples of the decrease in current over time due (presumably) to the oxidation of Fe(II) species at pH 6.5, 7.6, and 8.2 are shown in Figure 5. The time zero currents estimated by extrapolation for an added $[\text{Fe(II)}] = 117.6$ nM at the three different pH values are also given. These results appear to indicate a slight decrease in system responsiveness to added Fe(II) at pH 8.2; however, the effect is not major and measurements at pH 8.2 should give reasonable estimates of Fe(II) concentration.

The results presented in Figure 5 are a good illustration of the applicability of the controlled potential coulometric procedure to kinetic studies involving low concentrations of oxidizable Fe(II) species. The high sensitivity and ability to perform “in situ” analyses without the need for removal of subsamples are major advantages of this technique. The rate data presented confirm that the oxidation of Fe(II) under these conditions is first order with respect to time. The value

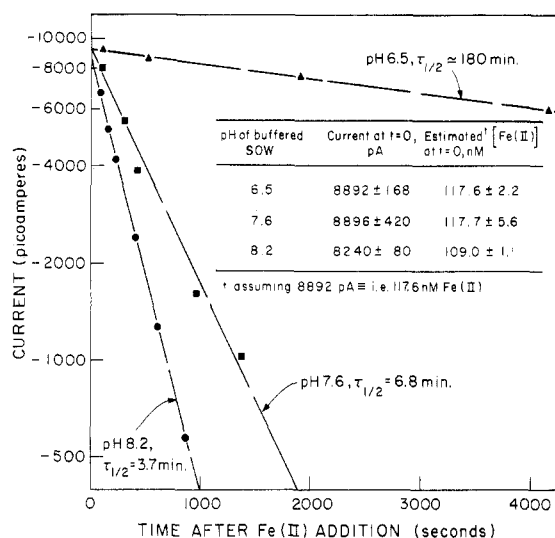


Figure 5. Decrease in oxidative current with time after addition of 117.6 nM Fe(II) to synthetic ocean water medium buffered to various pH. The average zero-time extrapolated values (± 1 standard deviation) obtained from triplicate studies are also shown. (Working electrode potential = 0.5 V.)

Table III. Application of Coulometric Analysis with Phenanthroline Masking to the Determination of the Concentration of Oxidizable Fe(II) Species Produced on Illumination of a Coastal Seawater (pH Buffered to 6.5, Working Electrode Potential = 0.5 V, [phen]_T = 10^{-5} M)

[Fe(III)] added, nM	Δ current (pA) after			[Fe(II)] formed, ^c nM
	275 min illumi- nation ^a	phen addition ^a	Δ , ^b pA	
0	432	28	404	4.2
42	856	-12	868	9.1
84	1376	28	1348	14.0

^a Relative to response of electrolyte before illumination.

^b Δ = current after illumination - current after phenanthroline addition. ^c 1 nM Fe(II) = 96 pA.

of $\tau_{1/2} = 3.7$ min obtained for Fe(II) added to synthetic ocean water at pH 8.2 is consistent with the half-life obtained for Fe(II) oxidation in seawaters by other workers (for example, Murray and Gill (37) report a $\tau_{1/2} = 3.9$ min for Fe(II) in Puget Sound seawater).

As a further example of application of this coulometry/masking technique, an investigation of the light-induced production of Fe(II) species in a coastal seawater sample has been performed. The results of this study for a seawater sample buffered to pH 6.5 are summarized in Table III and indicate that an increase in oxidative current on illumination of the seawater sample occurs. This increase in current is related to the amount of Fe(III) present. The produced response for all Fe(III) additions is effectively masked by phenanthroline addition, providing reasonable confirmation that the light-induced increase in current is due to the formation of oxidizable Fe(II) species. No significant change in current on illumination of a seawater sample at natural pH is observed. The absence of observable concentrations of oxidizable Fe(II) species at this pH may reflect the low steady-state concentrations of Fe(II), which exist as a result of rapid reoxidation, or may be indicative of a decrease in the concentration of photolabile Fe(III) species with increasing pH. (More detailed studies of the effects of light on the redox state of iron in natural waters are in progress.)

In summary it is clear that very low concentrations of oxidizable Fe(II) species can be measured by controlled potential coulometry in the mass transport limited region of the Fe(II)

oxidation wave. Sensitivity is significantly improved by correction for non-mass-transport-limited currents. Current masking using the strong Fe(II) complexing agent 1,10-phenanthroline enables estimation of the proportion of observed current that may be attributed to Fe(II) oxidation. While interfering species do exist (such as Cu(I) and Co(II)), the number of such species is limited. The technique should find particular use in studies on relatively well-defined media (such as the synthetic ocean water mixture used extensively here) in which some information is available on possible interfering components.

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Registry No. Fe, 7439-89-6; H₂O, 7732-18-5; phen, 66-71-7.

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