Determination of iron in water samples by adsorptive stripping voltammetry with a bismuth film electrode in the presence of 1-(2-piridylazo)-2-naphthol

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Abstract

An adsorptive stripping voltammetry method for the determination of iron has been developed. The procedure is based on the adsorptive collection of a complex of iron with 1-(2-piridylazo)-2-naphthol (PAN) on a bismuth-coated glassy carbon electrode (BiFE). Factors affecting the stripping performance, such as pH, PAN concentration (C_{PAN}), potential, accumulation time (E_{ads}, t_{ads}), and interference by other ions were also studied. The optimum conditions were obtained in a 0.1 mol L^{-1} acetate buffer at pH 4.0, C_{PAN} 5.0 μmol L^{-1}, t_{ads} 60 s, E_{ads} −400 mV, pulse height 4.0 mV, pulse amplitude 25 mV, and frequency 15 Hz. The detection limit was found to be 0.1 μg L^{-1} when a t_{ads} of 60 s was used, and the linear range was from 0.4 to 60.0 μg L^{-1}. The proposed procedure was validated by determining of Fe(III) in CRM-MFD, QCS-19 and CRM-SW certified reference materials and applied in seawater samples with satisfactory results.

Keywords: Adsorptive stripping voltammetry; Iron; 1-(2-Piridylazo)-2-naphthol (PAN); Seawater samples; Bismuth film electrode

1. Introduction

Total dissolved iron in surface waters of oceanic regimes can range from less than 0.05 to greater than 10 nmol L^{-1} [1–3]. However, in some beaches near populated or industrial areas iron concentration can be higher. The analysis of iron in seawater is difficult due to both the low concentrations and the seawater matrix. Therefore, shipboard determination of iron in seawater requires a sensitive analytical technique and trace-metal clean sample handling to obtain meaningful, oceanographically consistent results. The presence of iron in research vessels, laboratories and many manufactured materials poses a risk of contamination during sampling, filtration, storage and analysis. The first large-scale international intercomparison of analytical methods for the determination of dissolved iron in seawater was carried out between October 2000 and December 2002. The exercise was conducted as a rigorously "blind" comparison of seven analytical techniques by 24 international laboratories. For the complete dataset of 45 results (after excluding three outliers not passing the screening criteria), the mean concentration of dissolved iron in the ironages samples was 0.59 ± 0.21 nmol L^{-1}, with a coefficient of variation of 36% [4]. Higher values were found in acidified samples from Monterey Bay by a flow injection method combined with inductively coupled plasma sector field mass spectrometry (ICP-SFMS) using the NTA superflow resin in the preconcentration step (average 2.89 nmol L^{-1}) [5]. Iron can be determined by several methods such as inductively coupled plasma mass spectrometry (ICP-MS) [6], electrothermal atomization atomic absorption spectrometry (ETAAS) [7], cathodic stripping voltammetry (CSV) [8–10], luminescence [11], and spectrophotometry [12], preceded sometimes by column preconcentration. However, most of the sensitive and selective methods available are expensive to be used in routine analysis (ICP-MS and ETAAS). Electroanalytical techniques like anodic stripping voltammetry (ASV), cathodic stripping voltammetry (CSV),

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and adsorptive stripping voltammetry (AdSV) have important advantages including high sensitivity, accuracy and precision, as well as the low cost of instrumentation. AdSV is based on prior accumulation of the analyte on a suitable working electrode by potential controlled adsorption and subsequent electrochemical oxidation or reduction of the preconcentrated species. For decades, due to several electrochemical advantages, mercury electrodes have been widely used in stripping analysis. However, the well-known toxicity and handling inconveniences of mercury have recently declined considerably the popularity of mercury electrodes. The bismuth film electrode (BiFE) was introduced as an extremely promising alternative, based in that no present toxic character in relation to with those mercury electrodes [13–22]. BiFE has been used principally in anodic stripping voltammetry (Fe(III) [23]; Sn [24]; U [25]; Co [26–28]; Ni [29]; Mo [30]; Cr [31,32]; V [33]) and over the last years (2003–2007), a few selected application of AdSV on the BiFE have also been reported with promising results (Cr with DTPA [34]; Co-DMG [35–37]; Ni-DMG [38]; Co and Ni with DMG [39–41]; U-Cupferron [42]; Al-Cupferron [43]).

The aim of this study was to optimize the determination of iron using the bismuth film electrode. The metal was accumulated as the Fe(III)-1-(2-piridylazo)-2-naphthol (PAN) complex. This ligand has been widely used as chomophore reagent in spectroscopic techniques for the determination of several metal ions at trace level, but there are no reports on adsorptive stripping voltammetry with BiFE. The method was validated using certified reference material (CRM-MFD mixed food diet and QCS-19 standard solution) and was applied to the analysis of seawater samples obtained from five beaches in highly populated zones.

2. Experimental

2.1. Instruments

Square wave adsorptive stripping voltammograms (SWAdSV) were obtained with a CV50W Voltammetric analyzer (Bioanalytical Systems, Inc., BAS, USA). A 10 mL capacity cell was equipped with Ag/AgCl/KCl 3 mol L^{-1} reference electrode, a glassy carbon working electrode (3-mm diameter, BAS, USA) and auxiliary platinum electrode. A mechanical mini-stirrer, and a capillary to supply an inert gas were also used. An Orion pH meter was used to determine the pH of the solutions.

2.2. Reagents

All solutions were prepared with ultra pure water from a Millipore Milli-Q system (Milford, MA, USA). Bismuth and iron standard solutions (1000 mg L^{-1}) were obtained from Merck (Darmstadt, Germany). Acetic acid buffers (pH 3.0–6.0) were prepared by mixing 5.7 mL of acid and diluting to 1 L with water. The pH was adjusted with sodium hydroxide solution. A 1 mmol L^{-1} solution of PAN (Sigma) was prepared by dissolving 0.2493 g of solid compound in 100 mL of ethanol. ASTM D 665 synthetic seawater was obtained from Aldrich. Certified reference material of seawater (CRM-SW), trace metals in mixed food diet (CRM-MFD) reference materials, and quality control standards (QCS-19) obtained from high-purity standards (Charleston, SC, USA) were used for validation measurements.

2.3. Preparation of BiFE electrode

The glassy carbon electrode (GCE) was polished with 0.3-μm alumina powder, then, washed with deionized water in an ultrasonic bath. Bismuth was deposited on the GCE from 10.0 mL of a 100 mg L^{-1} Bi(III) solution containing 0.1 mol L^{-1} of acetate buffer (pH 5.0) at an applied potential of −1000 mV *vs.* Ag/AgCl for 5 min with stirring. The modified electrode was rinsed with water and was ready for use.

2.4. Procedure

All bottles and containers used for standards and samples were thoroughly cleaned with 5% nitric acid before use. Filtration was done through 0.45-μm membrane filters. Seawater samples were obtained from five different beaches of Viña del Mar (Chile) in a highly populated zone and near copper and oil industries.

All voltammetric measurements were carried out in 0.10 mol L^{-1} acetate buffer solution (pH 4.0) at room temperature (23 ± 2 °C) containing 5.0 μmol L^{-1} PAN as complexing agent. The solution was purged with nitrogen for at least 5 min. A deposition potential of −400 mV *vs.* Ag/AgCl was applied to the working electrode. During the deposition step, the solution was stirred, and after an equilibration period of 10 s the voltammogram was recorded by applying a negative-going potential scan between −300 and −1100 mV. Square wave voltammograms were obtained with an amplitude of 25 mV, a frequency of 15 Hz, and a potential step of 4 mV.

3. Results and discussion

3.1. Cyclic voltammetry

Two successive cyclic voltammograms of a solution containing PAN in the presence and absence of Fe(III) are shown in Fig. 1 (scan between −300 and −1250 mV). In the absence of Fe(III) a cathodic peak was obtained at −470 mV (solid line in Fig. 1), attributed to the reduction of free PAN. In the presence of Fe(III) the voltammograms show two peaks at −470 and −670 mV (dotted line in Fig. 1). The second peak is attributed to the reduction of the Fe(III)–PAN complex. In the back scan no peaks were observed, suggesting that the reduction of the free PAN and the reduction of the complex are irreversible processes.

3.2. Effect of pH

The formation of the complexes and their stability are strongly dependent on the pH of the solution. The influence of pH on the peak current of the Fe(III)–PAN complex was

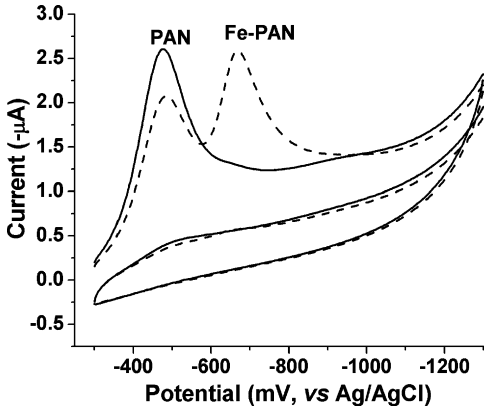

Fig. 1. Cyclic voltammograms of a solution containing 10.0 μmol L^{-1} PAN (solid line) plus 20.0 μg L^{-1} Fe(III) (dotted line) in 0.1 mol L^{-1} acetate buffer, pH 4.0, with E_{ads} −400 mV, t_{ads} 60 s, and a scan rate of 100 mV s^{-1}.

studied in the range of pH 3.0–6.0 in acetate buffer media (Fig. 2). It was found that at pH 4.0 the peak current of the Fe(III)–PAN complex was maximum. At higher pH values the peak current decreases and then remains constant. This profile indicates that about pH 4.0 offers the most favorable performance, and this value was used in all succeeding measurements.

3.3. Effect of adsorptive potential

The adsorption of a complex on BiFE depends strongly not only on the potential at which the accumulation process is carried out, but also on both the complex and the electrode charge. Complexes with positive charge will be adsorbed strongly on surfaces with a negative charge. The effect of adsorptive potential on the peak current of the Fe(III)–PAN complex was studied in the range between −300 and −1100 mV (Fig. 3). The peak current due to the Fe–PAN complex increased from −300 to −400 mV and then decreased to zero. The peak current was obtained at about −400 mV, and this value was used in all later measurements.

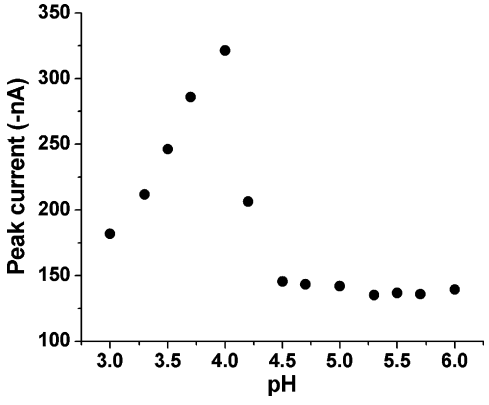

Fig. 2. Effect of pH on the peak current of the Fe–PAN complex. Conditions: Fe(III), 10.0 μg L^{-1}; PAN, 5.0 μmol L^{-1}; supporting electrolyte, 0.1 mol L^{-1} acetate buffer; E_{ads} −400 mV; t_{ads} 60 s; amplitude 25 mV; frequency 15 Hz; step potential 4 mV, and stirring speed in the accumulation step 700 rpm.

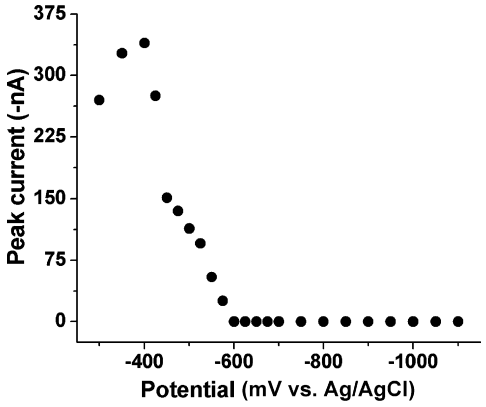

Fig. 3. Effect of accumulation potential on the peak current of the Fe–PAN complex. Conditions: Fe(III) 10.0 μg L^{-1}; PAN 5.0 μmol L^{-1}; supporting electrolyte 0.1 mol L^{-1} acetate buffer, pH 4.0; t_{ads} 60 s; amplitude 25 mV; frequency 15 Hz; step potential 4 mV, and stirring speed in the accumulation step 700 rpm.

3.4. Effect of accumulation time

The effect of accumulation time on the Fe(III)–PAN complex peak current was studied in the 0–400 s range in solutions containing 0.5, 0.9 and 10.0 μg L^{-1} of Fe, as illustrated in Fig. 4. It is seen that the peak current of the Fe(III)–PAN complex increases linearly as accumulation time increases, up to 80 s (10.0 μg L^{-1}), 120 s (0.9 μg L^{-1}), and 200 s (0.5 μg L^{-1}). At longer times the peak current for higher concentration (10.0 μg L^{-1}) decreased notoriously and for 0.5 and 0.9 μg L^{-1} concentration became almost constant, probably due to saturation of the film electrode. For succeeding studies an accumulation time of 60 s was chosen.

3.5. Effect of PAN concentration

PAN concentration affects greatly the voltammetric peak height. Fig. 5 shows the effect when PAN concentration was varied from 1.0 to 17.0 μmol L^{-1}. The peak current of the complex was maximum between 3.8 and 5.0 μmol L^{-1} of ligand concentration; for higher values a significant decrease was seen due to

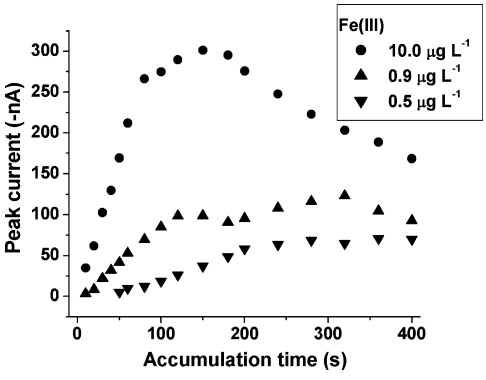

Fig. 4. Effect of accumulation time on the peak current of the Fe–PAN complex. Conditions: Fe(III) 0.5, 0.9, and 10.0 μg L^{-1}; PAN 5.0 μmol L^{-1}; supporting electrolyte 0.1 mol L^{-1} acetate buffer, pH 4.0; E_{ads} −400 mV; amplitude 25 mV; frequency 15 Hz; step potential 4 mV, and stirring speed in accumulation step 700 rpm.

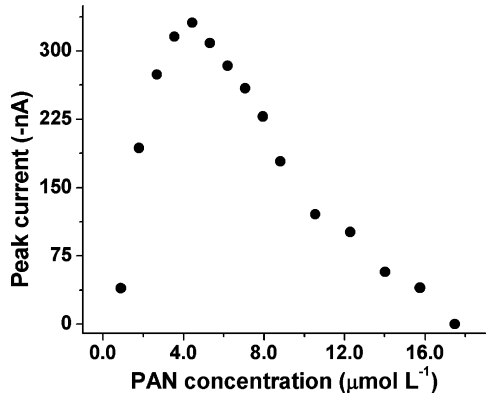

Fig. 5. Effect of PAN concentration on the peak current of 10.0 μg L^{-1} Fe(III). Conditions: supporting electrolyte 0.1 mol L^{-1} acetate buffer, pH 4.0; E_{ads} −400 mV; t_{ads} 60 s; amplitude 25 mV; frequency 15 Hz; step potential 4 mV and stirring rate in accumulation step 700 rpm.

competitive adsorption between free PAN and the Fe(III)–PAN complex on the electrode. A PAN concentration of 5.0 μmol L^{-1} was used in all succeeding measurements.

3.6. Construction of calibration curves and determination of detection limits and linear range

For the evaluation of the analytical parameters, a study of the influence of the concentration of the Fe(III)–PAN complex was made in aqueous solution under the optimal conditions mentioned above. Measurements were made with successive additions of aliquots of Fe(III) solution, with increments of about 0.9 μg L^{-1}. An accumulation time of 60 s and an accumulation potential of −400 mV were applied. Fig. 6(A) shows the voltammograms and Fig. 6(B) calibrate curve obtained. The peak current increased linearly with metal concentration in the range of 0.9–60.0 μg L^{-1} ($Y = 3.591x + 11.138$; $R^2 = 0.998$). The detection limit was 0.10 μg L^{-1} as Fe(III) [44]. A series of repetitive measurements with 20.0 μg L^{-1} of Fe(III) solution produced a very stable response with a relative standard deviation of 3.8% (t_{ads} 60 s). These results were obtained without an electrochemical cleaning period, using the same bismuth electrode surface, indicative of total desorption of the complex.

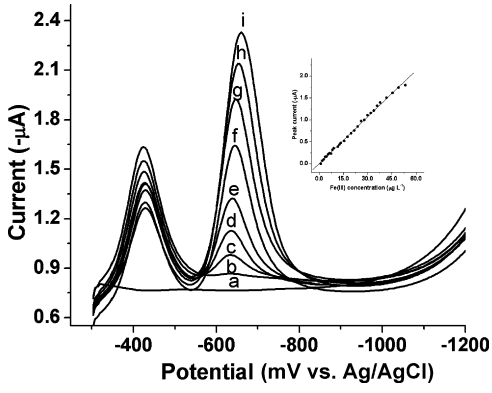

Fig. 6. (A) Adsorptive voltammograms of PAN solution in the presence of increasing amounts of Fe(III). Conditions: E_{ads} −400 mV; t_{ads} 60 s; amplitude 25 mV; frequency 15 Hz; step potential 4 mV, and stirring speed in accumulation step 700 rpm (a) supporting electrolyte 0.1 mol L^{-1} acetate buffer, pH 4.0; (b) PAN 5 μmol L^{-1}; (c–i) Fe(III) 10.0, 20.0, 29.9, 39.8, 49.8, 59.6 and 69.5 μg L^{-1}. (B) Dependence of peak current of Fe(III)–PAN complex on Fe(III) concentration.

Table 1
Analytical results of Fe determination in synthetic seawater, in certified reference material and in seawater samples

Sample	Fe found (μg L^{-1})	Fe certified (μg L^{-1})
Synthetic seawater[a]	11.0 ± 1.0	10.0 spiked
Synthetic seawater[a]	41.0 ± 2.5	40.0 spiked
CRM-MFD mixed food dietary[a]	823.0 ± 0.3	800.0
QCS-19 quality control[a]	109.3 ± 4.0 mg L^{-1}	100.0 mg L^{-1}
CRM-SW[a]	23.0 ± 1.2	20.0
1[b]	58.0 ± 1.9	60.0 ± 0.2[c]
2[b]	41.0 ± 1.3	40.0 ± 0.2[c]
3[b]	6.0 ± 0.8	5.0 ± 0.2[c]
4[b]	42.0 ± 1.5	40.0 ± 0.2[c]
5[b]	ND	ND[c]

[a] $n = 8$.
[b] $n = 3$.
[c] Values obtained with ICP-MS.

3.7. Interferences

High sensitivity and reproducibility are coupled with high selectivity. The possible interference of various trace metals was investigated to test for selectivity. When a solution containing Ag(I), Al(III), As(III), Bi(III), Cu(II), Cd(II), Cr(III), Mo(VI), Ni(II) and Zn(II) at 100 μg L^{-1} concentration contains 20.0 μg L^{-1} of Fe(III) in the presence of 5.0 μmol L^{-1} of PAN (pH 4.0), the peak current of the Fe(III)–PAN complex was not affected. This agrees with literature reports, because these metals form complexes with PAN at pH higher than 4.0, and their reduction peaks were not observed in this potential zone.

3.8. Validation of the methodology

The usefulness of the present method was evaluated by examining the analysis of Fe(III) in CRM-MFD mixed food diet, seawater CRM-SW certified reference material, and QCS-19 quality control standards using an ex situ plated bismuth film electrode. A standard addition method was used for Fe(III) quantitation. Three replicate analyses were carried out for each sample. The results are given in Table 1, indicating that the proposed method is applicable to the analysis of seawater samples containing more than 0.1 μg L^{-1} of Fe(III). The proposed method was successfully applied to the determination of iron in synthetic seawater (ASTM D665) spiked with 10.0 and 40.0 μg L^{-1} of Fe(III).

3.9. Application of the proposed method

Direct measurements of the samples were not possible due to lack of reproducibility. For that reason, 10.0 mL aliquots of the samples were previously digested with concentrated nitric acid and warmed on a hot plate almost to dryness. The pH was then adjusted to 4.0, the volume was made up to 10.0 mL with

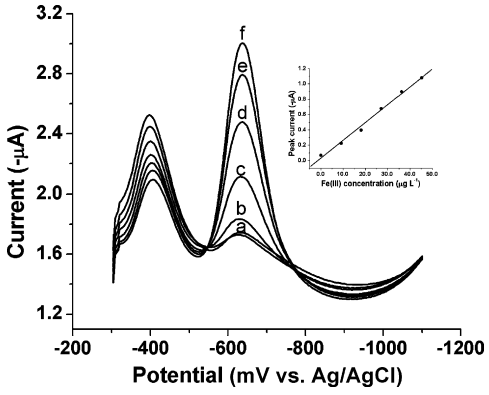

Fig. 7. (A) Typical voltammograms for the determination of Fe(III) contents in a seawater sample by the standard addition method. Conditions: E_{ads} −400 mV; t_{ads} 120 s; amplitude 25 mV; frequency 15 Hz; step potential 4 mV, and stirring speed in accumulation step 700 rpm (a) sample in 0.1 mol L^{-1} acetate buffer, pH 4.0; (b) (a) plus 9.1; (c) (a) plus 18.1; (d) (a) plus 27.2; (e) (a) plus 36.2 and (f) (a) plus 45.2 μg L^{-1} of Fe(III), respectively. (B) Dependence of peak current of the Fe(III)–PAN complex in a seawater sample in the presence of increasing amounts of Fe(III).

deionized water, and Fe(III) was determined. Iron concentration was obtained using the standard addition method. Adsorptive voltammograms of a digested seawater sample are shown in Fig. 7(A) and calibrate curve in Fig. 7(B). The data obtained with spiked and real samples were compared with those obtained by inductively coupled plasma spectrometry (ICP) in a service laboratory. The results obtained by both methods were compared (Table 1), showing that there are no significant differences between them.

4. Conclusion

The optimized method has been successfully applied to the determination of Fe(III) in seawater samples with good accuracy and precision. The proposed method is inexpensive and fast. The detection limit of 0.10 μg L^{-1} can be lowered further by increasing accumulation time. Acceptable agreement was found between the results obtained and the values of certified reference material.

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