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TECHNICAL NOTES

Speciation of Iron(II) and Iron(III) Using a Dual Electrode Modified with Electrocatalytic Polymers

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Speciation of metal ions has received considerable attention in diverse areas such as ecotoxicology,¹ geology,² process analysis,³ and aquatic studies.⁴ Several approaches have been adopted for the speciation of Fe(II) and Fe(III). Electrochemical methods predominate in this type of analysis,²⁻⁴ but chromatographic⁵ and spectrometric^{6,7} methods have also been described. For the chromatographic and the spectrometric methods, interconversion from one redox state to another,⁸ the use of different chelating agents,⁹ or the use of more than one detection system⁶ is required to differentiate between the two redox states. Polarographic methods appear almost universal in the electrochemical approach, but as the Fe(II)/Fe(III) couple is reversible,¹⁰ the use of reagents to separate the half-wave potentials ($E_{1/2}$) for the oxidation and reduction processes is necessary. Several reports concerning the determination of Fe(II) and Fe(III) at solid electrodes have also appeared.^{11,12} However, the redox chemistry of the Fe(II)/Fe(III) couple is poor at glassy carbon,¹¹ and at platinum, electrode fouling is encountered.¹²

In this laboratory, the synthesis and characterization of polymer-bound electrocatalysts^{13,14} and their application as sensors in flow analysis^{15,16} have received considerable attention. In this technical note we demonstrate a novel amperometric sensor system for the flow injection speciation analysis of unbound Fe(II) and Fe(III) using a dual-electrode assembly using glassy carbon electrodes modified with the electrocatalysts [M(bpy)₂(PVP)₁₀Cl]Cl (M = Os, Ru; bpy = 2,2'-bipyridyl; PVP = poly(4-vinylpyridine)) to provide simultaneous detection of both Fe(II) and Fe(III) in a single-sample aliquot. The merits of this approach are discussed in relation to existing methods.

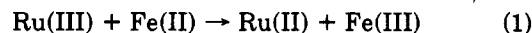
EXPERIMENTAL SECTION

Construction and Operation of the Dual Sensor. The detection system used consisted of an EG&G Princeton Applied Research (PAR) Model 400 electrochemical detector with dual-potentiostat function. The two working electrodes were glassy carbon (3 mm diameter) shrouded in a single teflon block. One electrode was modified with [Ru(bpy)₂(PVP)₁₀Cl]Cl, and the other with [Os(bpy)₂(PVP)₁₀Cl]Cl by droplet evaporation. These ma-

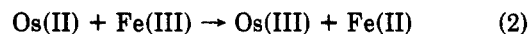
terials were synthesized as previously described.^{14,17} The structure of these polymers is shown in Figure 1. The working electrodes were placed in parallel in the thin-layer electrochemical flow cell. This parallel arrangement allows the sample plug to reach and be detected at each sensor simultaneously. This is represented in Figure 2. Detection of Fe(II) was achieved at the ruthenium polymer-modified electrode using an applied potential of 0.85 V vs SCE. The osmium polymer-modified electrode was used for the detection of Fe(III) at an applied potential of 0.12 V vs SCE. The simultaneous responses were recorded on a Philips PM8252 dual-pen recorder. The flow injection system was that previously described,¹⁸ connected to the detection system described above. The carrier electrolyte was 0.2 M Na₂SO₄ adjusted to pH 1.0 and a flow rate of 1.0 mL min⁻¹ was used. (NH₄)₂[Fe(SO₄)₂·6H₂O] and NH₄[Fe(SO₄)₂·12H₂O] were used to prepare solutions of Fe(II) and Fe(III), respectively. Deionized water obtained by passing distilled water through a Milli-Q water purification system was used. The recoveries of Fe(II) and Fe(III) from an acidified drinking water sample were determined from samples "spiked" with various ratios of [Fe(III)]/[Fe(II)].

RESULTS AND DISCUSSION

Principle of Operation. The dual sensor is based on the use of two polymer-bound electrocatalysts for electrode modification with half-wave potentials which envelop the formal potential of the Fe(II)/Fe(III) redox couple. The $E_{1/2}$ of the ruthenium and osmium centers in the electrolyte used here are 0.75 and 0.25 V vs SCE, respectively, and the formal potential of the Fe(II)/Fe(III) couple is 0.46 V vs SCE.¹⁹ This produces electrochemical driving forces of 0.21 V for the reduction of Fe(III) and 0.29 V for the oxidation of Fe(II). The ruthenium electrocatalyst with an $E_{1/2}$ more positive than the formal potential of the analytes is capable of the electrocatalytic oxidation of Fe(II) via the mediated cross reaction given in reaction 1. The osmium electrocatalyst with an $E_{1/2}$ less



positive than the analyte formal potential can mediate the reduction of Fe(III) via reaction 2. It has been observed that



the ruthenium polymer can mediate the reduction of Fe(III)¹⁹ as a result of negative shifting of the wave toward the formal potential of the Fe(II)/Fe(III) couple. However, the high

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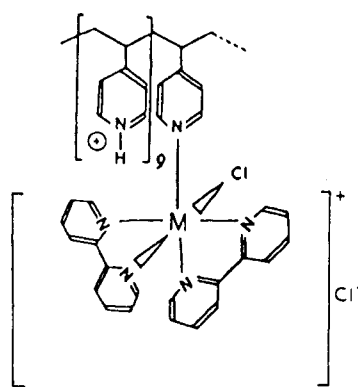


Figure 1. Structure of redox polymers where $M = \text{Os}, \text{Ru}$. Note that the PVP is protonated in electrolyte at pH 1.0.

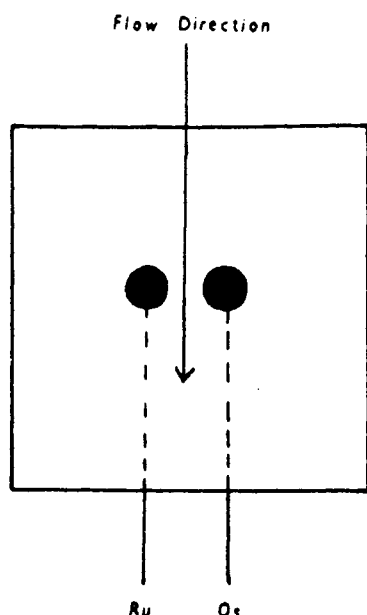


Figure 2. Schematic representation of carrier electrolyte flow direction in relation to the Fe(III) and Fe(II) sensor position.

selectivity of each sensor for its corresponding redox species is assured when the sensors are operated at applied potentials such that the oxidation states of the electroactive centers are Ru(III) and Os(II) . In order for the mediated cross reactions (1) and (2) to occur selectively and with maximum response and minimum background currents, optimum applied potentials were found to be 0.85 V vs SCE for the Fe(II) sensor and 0.12 V vs SCE for the Fe(III) sensor.

It was found for both sensors that increasing the surface coverage of the polymer films resulted in an increase in response when placed in the thin-layer electrochemical flow cell. This indicates that mediation is occurring through the polymer layer. This is not surprising as it has been shown previously for rotating-disk electrodes that the mediated cross reactions (1) and (2) occur in considerable portions of the polymer films.^{19,20} The modified electrodes are therefore operating as a three-dimensional arrangement of electroactive centers and exhibit homogeneous electrocatalytic behavior with rapid analyte penetration of the films and rapid charge-transfer kinetics. The three-dimensional nature of the electrocatalysts, along with the electrochemical driving forces, allows efficient electrocatalysis of the oxidation and reduction reactions examined here.

The dual sensor is constructed with two modified glassy-carbon electrodes placed in parallel in a planar electrochemical flow cell. The electrochemical oxidation of Fe(II) and reduction of Fe(III) does not give rise to any defined waves at

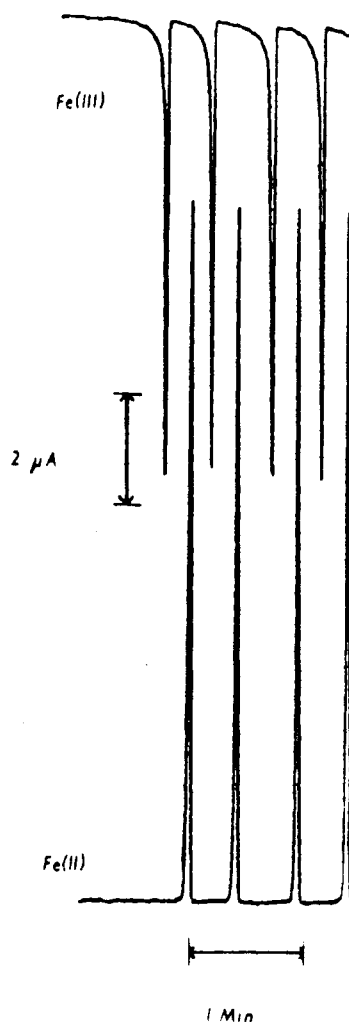


Figure 3. Typical recorder traces of detector responses. The concentrations of Fe(II) and Fe(III) are $1.0 \times 10^{-3} \text{ mol dm}^{-3}$. The electrolyte was $0.2 \text{ mol dm}^{-3} \text{ Na}_2\text{SO}_4$ adjusted to pH 1.0 at a flow rate of 1.0 mL min^{-1} . Surface coverages were $1.0 \times 10^{-9} \text{ mol cm}^{-2}$ for each polymer.

glassy carbon, but with the use of these polymer-bound electrocatalysts the redox chemistry is significantly improved in terms of lowering of activation overpotential, enhanced response, and absence of electrode fouling. Typical sensor responses can be seen in Figure 3. It can be seen that rapid and reproducible responses can be obtained from the dual sensor.

Operational Performance of the Dual Sensor. The straightforward approach upon which the dual sensor is based allows simple operation in practice. There is no requirement for potential scanning or elaborate pulsed techniques to be used. As each sensor is selective for its corresponding iron redox species, there is no requirement either for interconversion from one redox species to another or for the use of complexing agents, nor for reagents to separate the $E_{1/2}$ potentials for the oxidation-reduction processes. For both sensors it was found that variation in pH of the carrier electrolyte over the range pH 1 to pH 4 did not affect the current response of the sensors (higher pH electrolytes were not examined to avoid Fe(III) hydroxide formation). Rigorous control of pH is therefore unnecessary for the speciation analysis whereas chromatographic⁵ spectrometric^{6,7} and polarographic¹⁰ methods require precise pH control. These attributes simplify the analysis in terms of reagent use and the time required per analysis.

With the use of a flow injection procedure, only small sample aliquots ($20 \mu\text{L}$) are required for satisfactory sensor

response. The effect of carrier flow rate on sensor responses was assessed, and it was found that, for both sensors, responses increased with increasing flow rate, optimum performance being obtained at about 1.0 mL min⁻¹. Such flow rates allow a high analytical throughput with 180 determinations per hour. There is also no need for any in-line separation process, and only one detection system is used. Flow injection systems are easily automated, and the system used here is no exception. These attributes are of considerable advantage compared to electrochemical methods currently in use, which require relatively large sample sizes and operate using batch type operator intensive procedures.

Simultaneous calibration of the sensors was made using mixed calibration solutions. The calibration solutions were stable for at least 24 h. No interconversion from one redox state to another was evident. This observation is important as the reagents used do not affect the relative proportions of Fe(II) and Fe(III) in solution. This is significant, as it is recognized that many speciation procedures affect the concentration of individual chemical species considerably.²¹ The linear dynamic range for both sensors extended from 1×10^{-7} to 1×10^{-2} mol dm⁻³ with limits of detection of 5×10^{-8} mol dm⁻³. Such linear ranges are impressive compared to existing electrochemical and spectroscopic procedures. Typical calibration curves for the Fe(III) sensor over this range had correlation coefficients of 0.9999 and slopes of 3.080 ± 0.004 μ A mmol⁻¹. The calibration slopes were found to be constant between different modified electrodes. The slope for the Fe(II) calibration curve was found to be 6.419 μ A mmol⁻¹, which is larger than that for the Fe(III) sensor. This increased sensitivity is most likely due to the larger driving force for oxidation compared to the driving force for reduction. The precision of response for each sensor was very good, having relative standard deviations of 0.52% and 1.32% for the Fe(III) sensor ($n = 8$) and the Fe(II) sensor ($n = 7$), respectively.

No memory effects were encountered for both sensors. The electron-transfer reactions proceed cleanly without adsorption or accumulation of electrolytic products within the film. These observations are consistent with purely outer-sphere electron-transfer processes with fast diffusion of reactant and products within the film.

Cross Talk. Two possible sources of electrode "cross talk" have been identified with the dual sensor demonstrated here. Firstly and most importantly, "electronic cross talk" is observed. This behavior occurs as the reference and counter electrode employed are common to both sensors. When a large depolarization of a sensor occurs with respect to the adjacent sensor a shift in background current at the adjacent sensor occurs. This behavior becomes important when the ratio $[\text{Fe(III)}]/[\text{Fe(II)}]$ is larger than 1000 and less than 0.001. At less extreme concentration ratios the shift in base line is insignificant compared to the magnitude of response, typically less than 0.1% of the current response for the lower concentration redox species. This behavior limits the safe use of the dual sensor demonstrated here to concentration ratios of $\text{Fe(III)}/\text{Fe(II)}$ in the region 100–0.01. So, samples with Fe(III) and Fe(II) concentrations within 2 orders of magnitude of each other can be applied to this detection system. In situations where the relative concentrations of both redox species are very different, splitting of the sample plug followed by detection at individual thin-layer cells would circumvent this limitation. Secondly, "chemical cross talk" may occur. It is recognized that the electrolytic product formed at each sensor is capable of producing a response at the adjacent electrode. It was conceived that this may be a source of chemical cross talk between the sensors. However, it was found that at flow rates as low as 0.1 mL min⁻¹ (where diffusion in the flow cell

Table I. Analytical Recoveries (SDs in Parentheses) for Various Concentration Ratios of Fe(II) and Fe(III) from "Spiked" Drinking Water Samples^a

ratio [Fe(III)]/ [Fe(II)]	[Fe(II)], mol dm ⁻³		[Fe(III)], mol dm ⁻³	
	anal.	recovered	anal.	recovered
100	1.0×10^{-6}	1.05×10^{-6} ($\pm 5 \times 10^{-8}$)	1.0×10^{-4}	1.04×10^{-4} ($\pm 3 \times 10^{-6}$)
0.01	1.0×10^{-4}	1.02×10^{-4} ($\pm 2 \times 10^{-6}$)	1.0×10^{-6}	1.0×10^{-6} ($\pm 2 \times 10^{-8}$)
1	1.0×10^{-6}	1.0×10^{-6} ($\pm 2 \times 10^{-8}$)	1.0×10^{-6}	1.0×10^{-6} ($\pm 2 \times 10^{-8}$)
1	1.0×10^{-4}	9.8×10^{-5} ($\pm 2 \times 10^{-6}$)	1.0×10^{-4}	1.0×10^{-4} ($\pm 2 \times 10^{-6}$)
1	1.0×10^{-2}	9.98×10^{-3} ($\pm 3 \times 10^{-4}$)	1.0×10^{-2}	1.01×10^{-2} ($\pm 3 \times 10^{-4}$)

^a The concentrations recovered are an average of five repeat determinations. The carrier electrolyte was 0.2 mol dm⁻³ Na₂SO₄ adjusted to pH 1.0 with a flow rate of 1.0 mL min⁻¹. The surface coverages were 1.0×10^{-9} mol cm⁻² for each polymer.

may be problematic) no detection of electrolytic products at adjacent sensors was apparent. This observation is not surprising as the parallel arrangement of electrodes allows simultaneous measurements in the sample plug and the continuous forward flow of the electrolyte ensures that the electrolytic products are swept from the cell. In addition to the cell design, the physical constraints on diffusion would prevent diffusional processes from causing chemical cross talk. Under the assumption of the worst case situation where the system is under static conditions, the diffusion coefficient of Fe(III) and Fe(II) is 2.0×10^{-6} cm² s⁻¹, there is total consumption of all iron species reaching the electrode surface, and the peak width is 8 s, then the diffusional layer thickness at each electrode would be 7×10^{-3} cm, which is smaller by a factor of 14 compared to the interelectrode distance of 0.1 cm. Under these conditions, the time interval required for the diffusion of product from one sensor to the adjacent sensor would be on the order of 1600 s. It is obvious that the design of the thin-layer cell used here along with constraints on diffusion prevent chemical cross talk even at very low flow rates.

Recoveries and Interferences. In order to test the applicability of the sensors for the analysis of aquatic samples, the recoveries of Fe(II) and Fe(III) from spiked drinking water samples were examined. Due to the presence of electronic cross talk only solutions with $[\text{Fe(III)}]/[\text{Fe(II)}]$ ratios in the range 100–0.01 were examined. The results are shown in Table I. It can be seen that good recoveries of Fe(III) and Fe(II) were obtained over the range 1×10^{-4} to 1×10^{-6} mol dm⁻³ at different concentration ratios. It can also be seen that solutions of equal concentration of both redox species show good recoveries over the concentration range 1×10^{-2} to 1×10^{-6} mol dm⁻³. Calibration with mixed solutions or with individual solutions did not affect recoveries.

In the interference study, oxygen was found not to affect detection at both sensors; consequently, deoxygenation of sample solutions or the electrolyte carrier was not required. For the Fe(II) sensor the following cations did not produce a response even at millimolar concentrations: K(I), Na(I), Li(I), Ca(II), Pb(II), Ni(II), Mg(II), Cu(II), Hg(II), Zn(II), Al(III), Cr(III). At the Fe(III) sensor the above cations were found not to interfere, with the exception of Cu(II). The results for Cu(II) interference are given in Table II. It was found that the response for Cu(II) decreased with increasing surface coverage. It can be seen that selectivity for Fe(III) with respect to Cu(II) can be controlled by control of the polymer layer thickness, increased surface coverage favoring Fe(III) reduction. It was also found that higher flow rates

Table II. Effect of Surface Coverage on Fe(III) Sensor Response to Fe(III) and Cu(II)^a

surface coverage, mol cm ⁻²	<i>i</i> _p , μA ⁻¹		ratio of responses
	Fe(II)	Cu(II)	
1.0 × 10 ⁻¹⁰	37.6	10.0	3.8
1.0 × 10 ⁻⁹	43.2	9.2	4.7
1.0 × 10 ⁻⁸	52.3	8.9	5.9

^aThe concentrations of Fe(III) and Cu(II) are 1.0 × 10⁻³ mol dm⁻³. The conditions are as in Table I.

avored the response for Fe(III) reduction. Optimum selectivity was therefore obtained at thick polymer films and high flow rates.

CONCLUSIONS

In this technical note we have demonstrated that a sensor system can be constructed from redox polymer-modified electrodes to carry out speciation analysis of Fe(II) and Fe(III) in flowing streams. This approach has considerable advantages over existing methods with regard to simplicity and speed and operational performance. It is possible that this approach may also be applied to the speciation analysis of other redox couples. Using arrays of modified electrodes with synthetically controlled $E_{1/2}$ values, the simultaneous analysis of several redox species may also be possible in the future.

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