CAPSULES
preliminary notes and applications from Bioanalytical Systems, Inc.

Determination of Fe^{2+} and Fe^{3+} Concentrations

Key Terms
Fe^{2+} Determination, Fe^{3+} Determination, Chronocoulometry, BAS 100A, Anson plot

Total iron content can be determined rather easily by a variety of methods. However, the determination of both Fe^{2+} and Fe^{3+} concentrations is difficult, but often of importance in natural water and plating bath studies. Electrochemical determinations can be developed to differentiate between the various oxidation states of a species. Pulse polarography has been used to determine Fe^{2+} and Fe^{3+} in process streams (1). A chronocoulometric method for both ferric and ferrous ions is outlined in this capsule.

The Fe^{2+}/Fe^{3+} couple is reversible; thus, the concentrations of Fe^{2+} [R] and Fe^{3+} [O] at the electrode surface are governed by the Nernst equation:

$$E = E^{o'} + \frac{RT}{nF} \ln \frac{[O]}{[R]} \qquad (1)$$

For a reversible couple the current-voltage curve obtained from a solution with both species present (Figure 1) is described by equation 2 (2).

$$E = E^{o'} - \frac{RT}{nF} \ln \frac{m_O}{m_R} + \frac{RT}{nF} \ln \left[\frac{i_{lc} - i}{i - i_{la}} \right] \qquad (2)$$

Where m_O and m_R are the mass transfer coefficients for Fe^{3+} and Fe^{2+} respectively. Figure 1 indicates that it should be possible to measure the Fe^{2+} and Fe^{3+} concentrations from the magnitude and sign of the current.

Difficulties with Fe^{2+} and Fe^{3+} determination arise with most potential-scan techniques because the initiation of the experiment begins at a potential which perturbs the concentration at the electrode surface. Figure 2 is a cyclic voltammogram of a mixture of Fe^{2+} and Fe^{3+}. Notice that the current is not zero at the beginning of the experiment due to reduction of Fe^{3+}. Therefore, the peak height is dependent upon both the Fe^{2+} and Fe^{3+} concentrations.

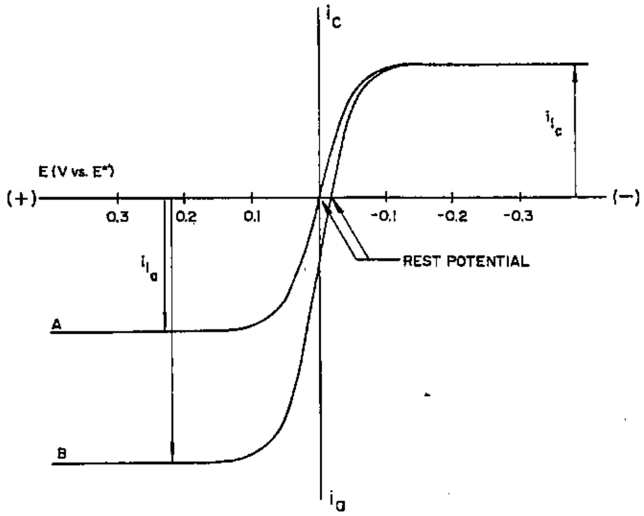

Figure 1. Current-potential curve for a reversible redox couple with both species present, $m_O = m_R$ a) [O] = [R]= a b) [O] = a, [R] = 2a.

At the rest potential, no net current flows; therefore, the concentrations of Fe^{2+} and Fe^{3+} at the electrode surface are the same as the bulk solution. The current which results from a positive potential step from the rest potential is due to oxidation of Fe^{2+}. The current from a negative potential is due to reduction of Fe^{3+}.

Thus, chronocoulometry initiated at the rest potential can be used to determine the concentration of the electroactive species. A plot of charge passed vs. $t^{1/2}$ (Anson plot) is linear with a slope of $2nFACD^{1/2}/\pi^{1/2}$. The BAS 100A can determine the

Table 1.

Solution	Rest Potential [mV vs. Ag/AgCl]	Slope Rest ---> 800 mV	Slope Rest ---> 200 mV
Sample	504	0.770 ± .012(8)	0.743 ± .015(5)
Sample + 3.78 mM Fe^{2+}	483	1.564 ± .012(4)	0.725 ± .015(4)

The number of determinations averaged is in parentheses.

rest potential of the system and the slopes of the Anson plots from the chronocoulometry experiments.

Results

The method was tested with a sample consisting of 3.71 mM Fe^{2+} and 4.5 mM Fe^{3+}. Table 1 (line 1) shows the rest potential and the resulting slopes of the Anson plots. If this were an unknown its concentration could be determined by addition of standard $FeCl_2$.

A decrease in rest potential is expected with the addition of Fe^{2+} (Figure 1). The midpoint of the curve is approximately $E^{o'}$. Therefore, upon addition of Fe^{2+}, the rest potential changes. The slope of the Anson plot resulting from a step from the rest potential to 800 mV is proportional to Fe^{2+} concentration. Therefore, the ratio of the slopes from the sample and the sample with the standard addition may be used to calculate the sample $[Fe^{2+}]$.

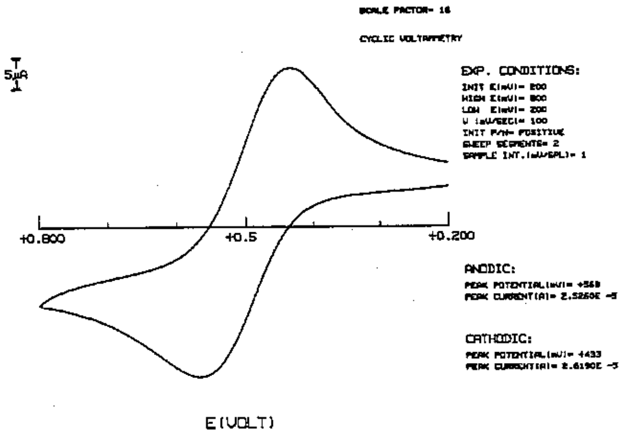

Figure 2. Cyclic voltammogram of 3.71 mM Fe^{2+} and 4.52 mM Fe^{3+} in 0.1 M KNO_3, pH 3 obtained with a platinum electrode at 100 mV s^{-1}.

$$\frac{[Fe^{2+}]_{\text{sample}}}{[Fe^{2+}]_{\text{sample}} + 3.78 \text{ mM } Fe^{2+}} = \frac{0.770}{1.564}$$

thus, $[Fe^{2+}]_{\text{sample}} = 3.67$ mM

The determined value is within 1.2% of the actual sample concentration. Notice that the slope of the Anson plot for the step from rest potential to 200 mV did not change since the Fe^{3+} concentration was unchanged. To determine Fe^{3+} concentration, a standard addition of Fe^{3+} must be performed. The relationship between the slope and concentrations differ with species, because the slope is also dependent upon the diffusion coefficient.

It is also possible to use chronocoulometry with a flow cell as an on-line monitor. The flow rate must be kept constant to get reproducible results. A cyclic voltammogram should also be performed to ensure that iR drop in the flow cell is not significant and to determine the step potentials.

References

1. *E.P. Parry and D.P. Anderson, Anal. Chem. 45 (1973) 458-463.*

2. *A.J. Bard and L.R. Faulkner, "Electrochemical Methods: Fundamentals and Applications," Wiley: New York, 1980.*