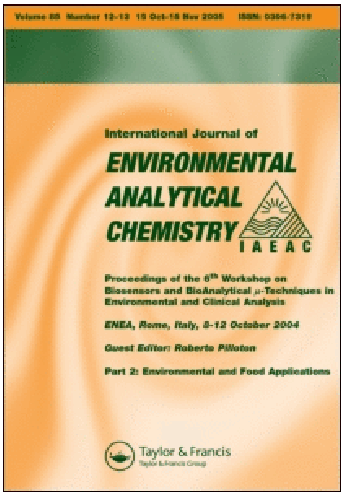

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Poly(Fe-4-Vinylpyridine) Modified Composite Graphite Paste Electrode for the Analysis of Iron(III)

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POLY(Fe-4-VINYLPYRIDINE) MODIFIED COMPOSITE GRAPHITE PASTE ELECTRODE FOR THE ANALYSIS OF IRON(III)

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An iron(III) selective electrode based on poly(Fe-4-vinylpyridine) modified composite graphite paste was investigated for its characteristics and mechanism of potential determining process. The electrode which was prepared through cathodic polymerization of the monomer 4-vinylpyridine and the Fe(III), showed Nernstian response towards Fe(III) in the 1.58×10^{-6} M to 6.3×10^{-3} M concentration range with slope 60±5 mV decade^{-1}, in solutions of pH 2.5 ±0.5 and in the presence of 0.1 M $NaClO_4$. The mechanism of the electrode's response appeared to follow a redox potential rather than an ion exchange. The steady state response was obtained in 15 s. The electrode was stable in temperature range of 35 ± 10°C. The drift in response was observed to be in the range of 3 ± 1 mV h^{-1}. The electrode displayed high selectivity towards Fe(III), even in the presence of Fe(II). Slight interferences were observed from Br^- and F^-. The electrode response showed good correlation with selected standard method, AAS, with coefficient, r, equal to 0.96. Experiments on industrial and waste waters, using t-test indicated no significance difference. The electrode remained stable after seventeen days of continued use.

Keywords: Ion selective electrode; iron; speciation

INTRODUCTION

To analyze iron(III), in the presence or absence of Fe(II), one would immediately consider either atomic or molecular absorption spectrophotometric techniques. However, samples preparation for these techniques remains time consuming so that they are not generally suitable for field work. By contrast, potentiometry with an ion selective electrode (ISE) making them relatively slower techniques compared to, if the electrode that sensitive and selective to Fe(III) is available. Apart from being a rather fast technique, the employment of ISE in ion measure-

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ment in solution is also non-destructive. Nonetheless, this technique is known to be susceptible to non-nernstian response and drift in measurement signals, especially, when multivalent ISE is used. This is reflected by the lack of multivalent ISE in the market.

The active materials in the sensing membrane are largely responsible for the performance of any ISE. In that respect, many hours of research have been spent in identifying active materials that can produce a sensitive yet selective response to the target analyte(s). In the fabrication of Fe(III)-ISE some active materials, such as metavanadate salt[1], montmorillonite clay[2], stannic arsenate[3], crown ether[4] and chalcogenides glasses[5] were reported used in have been incorporated into the sensing membrane, but this electrode requires frequent reactivation (by etching the surface). Moreover, electrode fabrication is tidious and components are expensive. An Iron(III) sensor comprising a heam-based of liquid membrane electrode with silicone rubber support has also been reported[6]. The sensitivity of this electrode was low and was also characterized by longer equilibration times. Cattrall and Chin-Poh[7] designed a tetrachloroferrate(III)-selective coated wire electrode (CWE) using tricaprylammonium (Aliquat 336 S) in PVC. For lower concentrations of the iron(III) complex, this electrode attained stable potential after 25 min. Later, Fung et. al.[8] presented a cupric ion-selective electrode for the determination of Fe(III), Chandravanshi[9] reported a tetrachloroferrate(III)-selective liquid membrane electrode encased in a PVC support, that was capable of detecting iron(III) down to 10^{-6} M but the responsiveness was −56 mV/decade increase in concentration and preparation of the membrane electrode was costly and time consuming. Cox et. al.[10] employed platinum electrodes modified with adsorbed adenosine-5-mono-phosphate for the extraction and subsequent determination of iron (III). Despite these many reports, a commercial Fe(III) selective electrode has yet to become available on the market.

A means of employing dope the polymer with an ion binding species. Oyama and co-worker[11] reported that the PVP modified electrodes was capable of incorporating ions from solutions as dilute as 5×10^{-8} M, either by coordination to pyridine or by electrostatic binding to protonated PVP films. The result demonstrated the possibility of using metallo-PVP interactions for analytical purposes. Subsequently, have described the application of similar metallo-PVP complexes for the preparation of ion selective electrode[12,13]. But, these electrodes were used mostly for the determination of iron(II). The determination of Fe(III) using osmium(III)-PVP complex was, however, reported later in the speciation studies of iron(II) and iron(III)[14].

In this report we evaluate the capacity of a Fe(III)-PVP complex modified composite graphite paste electrode for the analysis of Fe(III) in aqueous solution.

We report its viability in various parameters tested with the objectives of achieving faster responses and a lower limit of detection (LOD).

EXPERIMENTAL

Apparatus

The deposition of poly(Fe-4-vinylpyridine) on the composite graphite paste electrode was performed using voltammograph CV-27 MF 9030 and RXY recorder MF-9004 (Bioanalytical System Inc., W. Laffayette, IN, USA) in conjunction with Ag/AgCl reference electrode (Russell pH Ltd, Fife, Scotland, UK) and a 1 cm^2 Pt foil (Johnson Matthey, Ward Hill, MA, USA) as counter electrode. The performance of the Fe(III)-PVP modified electrode was checked against external saturated calomel electrode (SCE) (Russell pH Ltd, Fife, UK) as reference and Orion pH/ISE meter 720A (Orion Research Inc., Boston, MA, USA) in tandem with IBM compatible PC, at room temperature (25 ± 2°C). An Orion combination pH electrode 81–72BN (Orion Research Inc., Boston, MA, USA) was used for all pH measurements. All measurements were made within 20–80 s after stirring the solution with a Teflon-coated stirring bar. The potential was considered constant if the drift was slower than 0.05 mV/min. Atomic absorption spectrophotometry was used as a reference method of analysis using IL-357 spectrophotometer (Instrumentation Laboratory Inc., Wilmington, MA, USA.).

Reagents and Materials

The sources of reagents used are recorded in parentheses; 4-vinylpyridine (VP) (~96%) (Fluka Chemika, Buch, Switzerland), tetraethylammonium tetrafluoroborate (Et_4NBF_4) (~99%) (Fluka Chemika, Buch, Switzerland), anhydrous iron(III) nitrate (BDH Ltd, Poole, England), acetonitrile (MeCN) (Ajax Chemicals, Auburn, NSW, Australia), methanol (R & M Chemicals, Essex, England), sodium perchlorate (~99%) (BDH Ltd, Poole, England), mineral oil (Sigma Chemical Co, St. Louis, MO, USA), Triton® X-100, i.e. polyethylene glycol tert-octylphenyl ether (PEG) (Boehringer Mannheim GMBH, Mannheim, Germany), ethylenediamnietetra-acetic acid (di-sodium salt) (EDTA) (Ajax Chemicals, Auburn, NSW, Australia) and 5-sulfosalicylic acid (BDH Ltd, Poole, England) were used as received. All other reagents were of analytical grade. The 0.01 M Fe(III) stock solution was standardized titrimetrically with 0.1 M EDTA and sulfosalicylic acid as indicator[15]. All solution was prepared using deionized water from Milli-Q plus (Millipore Corp., Bedford, MA, USA). Material for composite graphite paste was obtained from 2B pencil Mars Lumograph (Staedtler, Nurenberg, Germany).

Poly(Fe-4-vinylpyridine) membranes and cell assembly

The fabrication of a composite graphite paste electrode using 2B pencil has been reported elsewhere[16]. The poly(Fe-4-vinylpyridine) complex was then synthesized on the surface of the composite paste electrode using 0.01 M Fe^{3+}, 0.05 M 4VP in MeCN and 0.1 M Et_4NBF_4 at +0.12 V vs. Ag/AgCl and scan rate 50 mVs^{-1}. The electrodeposition on the composite paste disk, 1.5 mm, was continued until a steady state had been achieved. After the deposition time the electrode was removed from the solution and was washed with a mixture of MeCN and water containing successively increasing amounts of water. The poly(Fe-4-vinylpyridine) modified composite graphite paste was connected to the ion meter. All samples and standard solutions used were prepared in 0.1 M $NaClO_4$ as a total ionic strength adjuster buffer (TISAB). The standard Fe(III) solutions were prepared using nitrate salts instead of chloride as it was difficult to control the ionic strength if chloride was used.

EMF measurements

The measurements were performed at room temperature, i.e. 25 ± 2°C. The required pH of solution was adjusted using concentrated HNO_3 and NaOH. Each membrane was conditioned in a buffered 0.1 M iron(III) solution overnight prior to use. Iron(III) concentration rather than activity were used in all measurements. This is because the activity of iron(III) strongly depends on the amount of formation of hydroxo and polynuclear complexes, hence the calculation of activity coefficients will become difficult. Selectivity coefficients were determined using IUPAC standard methods[17].

RESULTS AND DISCUSSION

Effect of ionic strength concentration

Sodium perchlorate was used as the total ionic strength adjustment buffer (TISAB) of its well-known for its weak tendency to form metallo-complexes. Concentration of sodium perchlorate over than 1×10^{-1} M had no effect on the electrode response for analyte concentrations in the range of 10^{-5}-10^{-3} M as presented in Figure 1. Since the measurements were made at low pH (between 2 and 3), all solutions were adjusted to constant ionic strength with 0.1 M sodium perchlorate. At concentration of 0.1 M $NaClO_4$ and above, the electrode response became virtually instantaneous.

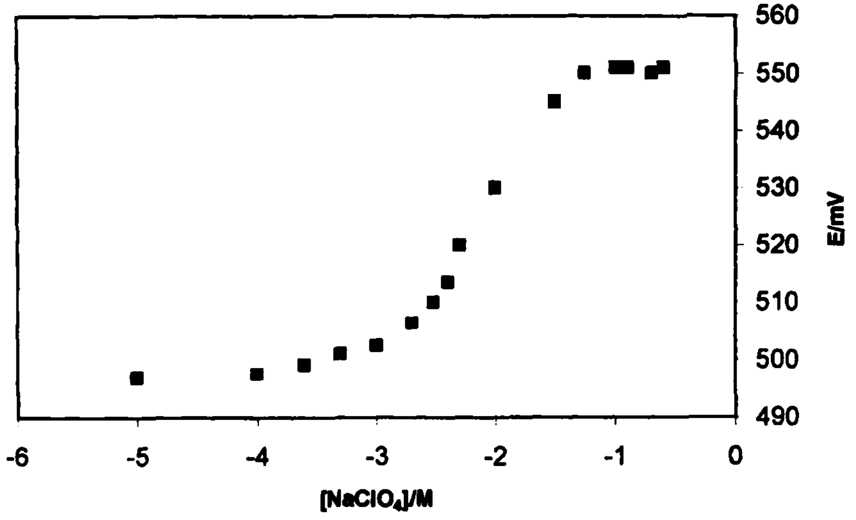

FIGURE 1 Effect of sodium perchlorate as total ionic strength adjustment buffer to the electrode response

PH Effect

The pH was adjusted by adding small volumes of 0.1 M HNO_3 or 0.01 M NaOH to the standard Fe(III) solution. The electrode potentials were recorded after their potentionmetric responses had stabilized, and were plotted as a function of pH values and Fe(III) concentration as shown in Figure 2. At higher pH, Fe(III) tends to form hydroxo complexes or precipitates as hydrous ferric oxide[18]; on the other hand, the interference of hydrogen ions is pronounced at very low pH. Thus, stringent control of pH of the sample solutions is essential to obtain a repeatable result. According to Figure 2, at pH values greater than 3 the electrode potential was decreased sharply. This is caused by the formation of Fe(III) hydroxo complexes that decreases the Fe(III) free ion activity in the electrolyte[19]. The function of the acid is to suppress hydrolysis of the iron(III) species so that this reaction will not compete with the complexation equilibrium. At pH values less than 2, the potential again decreased which might have been caused

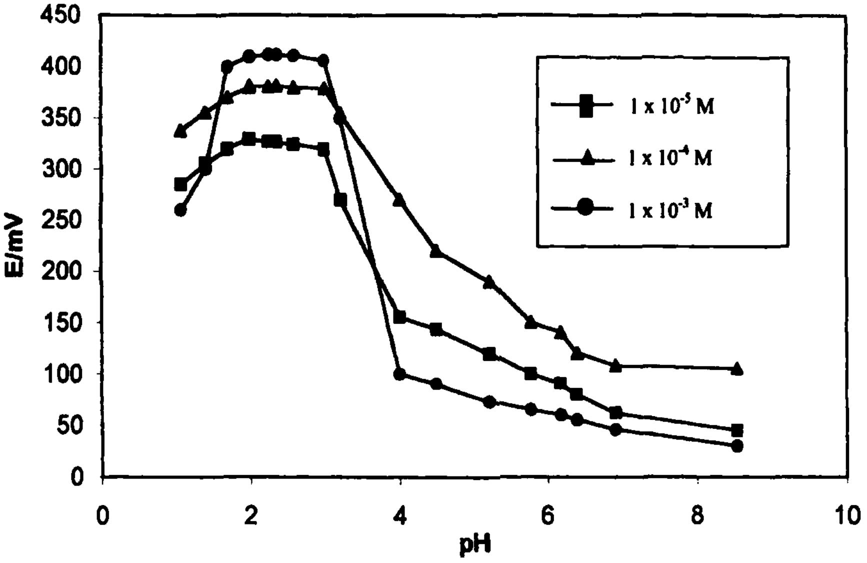

FIGURE 2 The influence of pH on the electrode response for a 10^{-5}, 10^{-4} and 10^{-3} M Fe(III) solutions

by reactions of the poly(Fe-4vp) membrane complex to form poly(H-4vp) or protonated poly-4-vinylpyridine. The pH range between 2 and 3 was optimal for 1×10^{-3}M Fe.

Potentiometric characteristics

The response times as defined by IUPAC[17] i.e. the time taken for the potential of the cell containing the electrode to reach a value 1 mV from the final equilibrium potential after a supposedly instantaneous change in determinant activity were found to be within 20 s for $> 1.0 \times 10^{-3}$ M and 20–90 s for lower concentrations of iron(III). The electrode responded to the complex anion for over two weeks, without significant change in slope (60.0 ± 5.0 mV/decade).

The response time of the electrode, though dependent on the age of the electrode, the stirring rate, the surface condition, and the direction of the activity change is found to be rapid for determinations of Fe(III). The dynamic behavior of the electrode was tested by changing the Fe(III) concentration from 10^{-6} to 10^{-3} M. the electrode potential rose sharply and reached the new value within 25s. The rate of equilibration varied from less than 1 min in concentration solution (10^{-3} M) to about 20 min in dilute ones (10^{-6} to 10^{-7} M). One drawback of the electrode was that the potential drifted between to 3–4 mV/h in a 10^{-3} Fe(III) solution. Hence they must be calibrated every 60 min in order to perform reliable measurements.

If a simple ion-exchange process determined to potential, one might have expected the slope of the calibration to have been 19 mV/decade increase since Fe^{3+}ions are three-fold positively charged. However, this electrode of Fe(III) selective electrodes based on metalo polymer report a slope of 60 mV/decade of higher. This suggests that single charged ions are involved in the potential controlling process. The potential of the metalated electrode versus a saturated calomel reference electrode for various concentration of Fe(III) solution (10^{-6} to 10^{-3} M) is presented in Figure 3. For Figure 3, the plot seems to indicate that there is no change in response below log[Fe(III)] = 5.2. The slope of the calibration plot amounts of 60 mV/decade for an electrode made from poly(Fe-vinylpyridine). It's indicating that the change in potential of the electrode with different concentrations of Fe(III) was from the couple of redox mechanism of Fe^{3+} in the solution towards Fe^{2+} in the membrane polymer poly(Fe-vinypyridine). Cathodic electropolymerization of 4-vinylpyridine and Fe(III) was produced Fe^{2+} in the membrane polymer and furthermore Fe-pyridine complexes more stable in Fe(II) forms[19]. The Nernst equation involved was as follows;

$$E = E_a + \frac{2.303RT}{F} \log \frac{[Fe^{3+}]}{[Fe^{2+}]}$$

With stirring, a steady state for 10^{-5} M was achieved within 20–30 min; without stirring, steady-state responses at 10^{-5} M were always quite long taking up to 60 min to reach steady-state (here steady state is defined as an electrode potential stable to within 0.1 mV/min[20]). At steady state the electrode potentials were independent of stirring rate, over the range of 0–275 rpm. At 10^{-5} M ferric ion, steady-state was achieved within 10–20 min with stirring.

This trend of decreasing response time with increasing iron(III) concentration did not persist above 10^{-4} M; generally 20 min were required to reach steady state, as defined, and stirring had little effect. The stability of the electrode is 17 days.

Interference studies

These were carried out according to the mixed solution methods were employed to evaluate the selectivity coefficients, Kij, of the potentiometric sensor. The Kij values in Table I suggest that most of the ions tested would not pose a serious interference for the determination of iron in diverse samples.

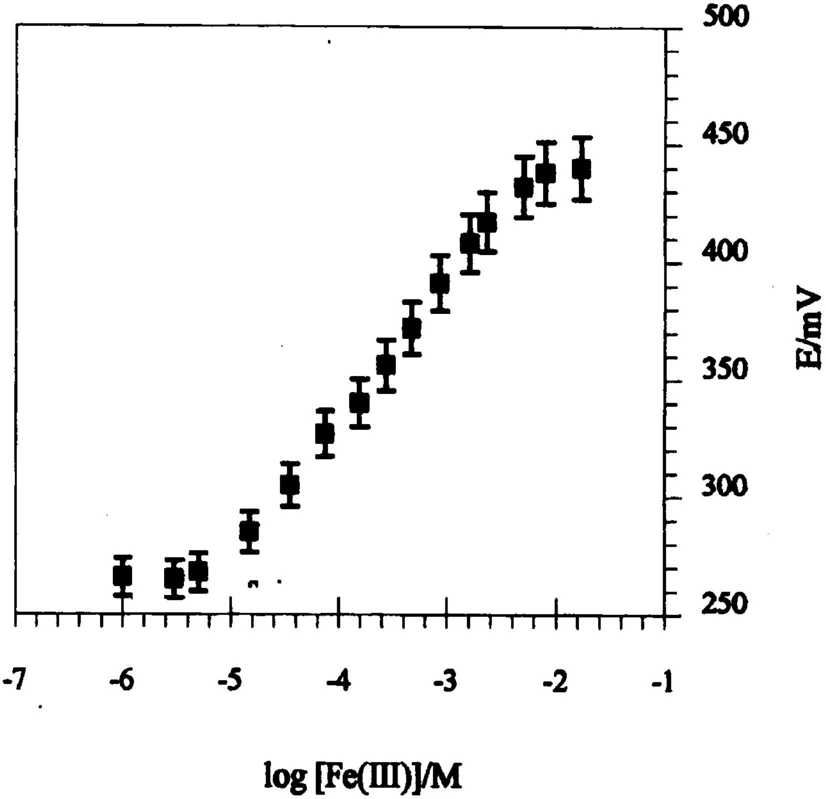

FIGURE 3 Calibration curve for Fe(III) in 0.1 M NaClO4 and pH 2–3

Mixed solution experiments to evaluate the interference of Na^+, K^+, Ca^{2+}, Mg^{2+}, Ba^{2+}, Pb^{2+}(0.1 M) indicated that interference due to these ions arose when the iron(III) concentration is less than 6×10^{-5} M. The concentration of the interfering ion was generally fixed to 0.1 M while the total concentration of iron(III) was varied between 10^{-6} to 10^{-3} M by dilution of a standard ferric nitrate solution and the selectivity coefficients were evaluated. Fe^{2+} was checked by separate solution method. The mixed solution method was only applied study the interference of different cations and anions of Fe(III) determination. The concentration of Fe(III) (10^{-4} M), ionic strength (0.1 M sodium perchlorate), and pH (2.5) of the solution were maintained constant and the concentration of interferent was varied. The selectivity ratio was estimated from the intercept of the two extrapolated straight lines of the normal and deviated parts of the E vs. [interference] curve. The selectivity ratios for some common cations are summarized in

Table I. Fe(II) has no interfering effect on electrode potential even up to 600 times Fe(III) concentration (Figure 4). That feasible to measure Fe^{3+}ions in present of Fe^{2+} ions which had been equilibrate with Fe^{3+}in the environment water system. In the speciation study of iron in environmental water system, either Fe^{3+} or Fe^{2+} has to be measure immediately because $Fe^{2+}$is unstable in axic conditions and easily to form Fe^{3+}. This problem can be solved with the ISEs that were fabricated in this study. A trace amount of iodide (10^{-7} M) will interfere with the electrode response in a 10^{-4}m Fe(III) solution, which is caused by the reducing power of iodide. The behavior of fluoride ion was quite different from others ions presented in Table I. It is because silver fluoride is soluble in water and fluoride forms a stable complex with Fe(III). The results of the potentiometric assays are generally in good agreement with the amounts certified or analyzed by standard methods I.e., AAS (error ≤ 3.3 %).

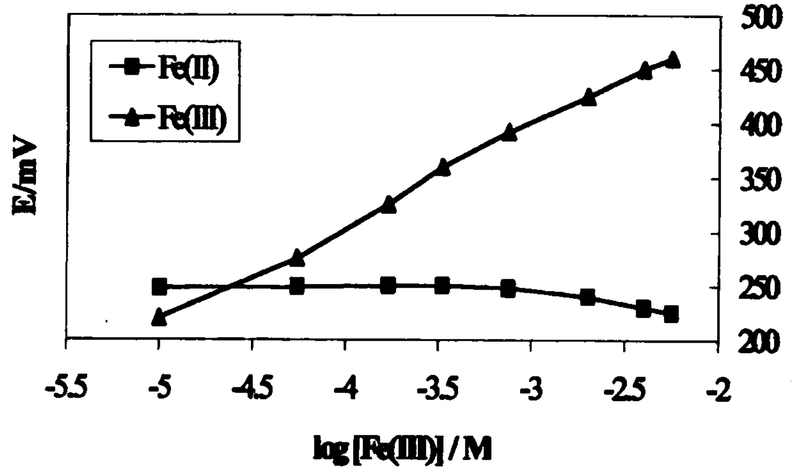

FIGURE 4 The comparison of electrode response to Fe^{3+} and Fe^{2+}

Analysis of lake and industrial waste waters

The ISE-Fe(III) was applied to the determination of the Fe^{3+} ion in lake and industrial waste water. The values with ISE-Fe(III) are good correlation with those with AAS ($r^2 = 0.986$) (Table II). The t-test showed that no significant different between ISE-Fe(III) and AAS method in the analysis of Fe(III) in lake and industrial waste water. It is clear that the present Fe(III) ion-selective electrode was useful for the simple and speedy control of Fe(III) ion in the industrial waste water with sufficient sensitivity compared with AAS.

TABLE I Selectivity coefficient, $K^{pot}_{Fe,M}$, some cathion and anion to ISI-Fe(III)

Ion	*Selectivity coefficient, $K^{pot}_{Fe,M}$*
Na^+	6.15×10^4
K^+	9.81×10^{-4}
NH_4^+	2.26×10^{-4}
Ca^{2+}	4.60×10^{-5}
Mg^{2+}	7.12×10^{-5}
Ba^{2+}	3.92×10^{-5}
Cu^{2+}	3.90×10^{-5}
Pb^{2+}	3.13×10^{-5}
Fe^{2+}	7.37×10^{-3}
Al^{3+}	1.57×10^4
F^-	0.43
Cl^-	0.05
Br^-	0.071
I^-	0.048
ClO_4^-	1.20×10^{-5}
NO_3^-	3.12×10^{-5}
SO_4^{2-}	3.65×10^{-3}

TABLE II The t-test for ISE-Fe(III) and AAS method in the analysis of Fe(III) in lake and industrial waste water

	Fe(III)-ISE	*AAS*
Mean	2.2235	2.2247
Variance	3.7619	3.7137
Obseration	27	27
Differential mean hypothesis	0	
Degree of freedom	16	
t	–0.2310	
P(T<=t), 1-tail	0.4101	
1-tail critical t	1.7459	
P(T<=t) 2-tail	0.8202	
2-tail critical	2.1199	

CONCLUSION

The equilibration time of the electrode, though dependent on the age of the electrode, the stirring rate, the surface condition, and the direction of the activity change was found to be rapid in the determination of Fe(III). The advantages are that the working range remains reasonably wide (10^{-5} – 10^{-3} M); the method is rapid and selective for Fe^{3+}. The determination of multivalent cations such as Fe^{3+} by exploiting the activities of complexed species with charge less than the corresponding free metal cation will impart greater sensitivity to the determination. This is because of the larger potential change per decade change in activity. The potential response to ferric ion is a normal 60 mV/decade concentration change, indicative of a one-electron process rather than the expected three-electron process (20 mV/decade). This approach has considerable advantages over existing methods with regards to simplicity and speed and operational performance.

Acknowledgements

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