

Electrochemical technique to measure Fe(II) and Fe(III) concentrations simultaneously

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Abstract An electrochemical technique is presented to simultaneously determine the concentrations of Fe(II) and Fe(III) ions using a rotating disk electrode. The method consists of using a steady state polarization technique where the developed limiting currents are measured and related to the concentration of the cations present in solution. Two linear equations were derived which correlate the limiting currents with the concentrations of the pair cations. The equations are used to easily and simultaneously determine the concentrations of the multivalent species. The precision and accuracy of the technique were found to be comparable to other advanced methods for the quantification of cations, such as capillary zone electrophoresis and spectro-photometric sequential injection analysis.

Keywords Speciation · Fe(II) · Fe(III) · Rotating disk electrode · Sensors

Abbreviations

A	Surface area of the electrode (cm^2)
C	Concentration of the solution (mol cm^{-3})
$C_{\text{Fe(II)}}$	Concentration of Fe(II) (mM),
$C_{\text{Fe(III)}}$	Concentration of Fe(III) (mM)
C_{cal}	Calculated concentration (mM)
C_{st}	Concentration of standard solution (mM)
D	Diffusion coefficient ($\text{cm}^2 \text{s}^{-1}$)
E_{a}	Absolute error (mM)
F	Faraday's constant, 96485 C mol^{-1}
i_{l}	Limiting current (A)
i_{LL}	Lower limiting current (mA)

i_{LL}^0	Zero cathodic limiting current (mA)
i_{UL}	Upper limiting current (mA)
i_{UL}^0	Zero anodic limiting current (mA)
k_1	Constant of the equation for rotation rate
n	Number of electrons transferred
N	Number of sample solutions
ε	Relative error
ν	Kinetic viscosity of the solution ($\text{cm}^2 \text{s}^{-1}$)
ω	Angular velocity of the rotating electrode (rad s^{-1})
ω_{a}	Rotation rate of the rotating electrode (rpm)

1 Introduction

As one of the most common metal ions, iron ions play an important role in dominating many biogeochemical cycles which determine the trace element availability in the environmental system [1]. In addition, different oxidation states of iron ions play different roles. Therefore, simultaneous and accurate quantitative determination of the concentrations of Fe(II) and Fe(III) ions separately is of major significance not only in environmental chemistry [2–4] and biochemical engineering [5–7], but also in many scientific [8, 9] and industrial fields [10, 11]. Traditional techniques, such as atomic absorption spectroscopy (AAS), ion chromatography (IC), and colorimetric method have been generally known as analytical techniques for determining the concentrations of cations; however, these techniques can not distinguish the differences in metal valences. Since the early 1980s, a number of researchers have tried to extend these traditional techniques to measure the concentrations of different oxidation species of iron ions. The common procedure developed includes three steps: First, Fe(II) is complexed with a chelating agent and its

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concentration is measured by using one of the methods mentioned above (AAS, IC or colorimetric technique). Second, Fe(III) is reduced to Fe(II) and the total concentration of iron ions is determined similarly. Finally, the concentration of Fe(III) is determined by subtracting the concentration of Fe(II) from the total iron concentration [12]. The procedure described is complex, as it requires the use of chelating agents, it takes at least three steps to determine the concentration of Fe(II) and Fe(III) separately, and it requires the combination of different analytical techniques. Due to these complexities, researchers are working on modified methods [12].

Pozdniakova et al. [13] applied the capillary zone electrophoresis (CZE) method to determine the concentrations of Fe(II) and Fe(III) simultaneously using 1,10-phenanthroline and EDTA, which selectively form complexes with Fe(II) and Fe(III) ions, respectively. The detection limits (DL) are 1.0×10^{-6} M for Fe(II) and 2.0×10^{-6} M for Fe(III). Takagai and Igarashi [12] improved the CZE technique using different reagents: sulfonated bathophenanthroline to replace 1,10-phenanthroline and desferrioxamine B to replace EDTA. By doing this change, the detection limits were improved to 6.0×10^{-8} M for Fe(II) and 4.0×10^{-9} M for Fe(III).

Mulaudzi et al. [14] developed an analytical technique to determine the speciation of iron ions in solution based on spectro-photometric sequential injection analysis (SIA). In this method, the sample is separated into two streams and injected into two ports for analytical purposes. The DL were found to be 2.0×10^{-6} M and 3.0×10^{-6} M for Fe(II) and Fe(III), respectively. The SIA system can be fully computerized and is able to process 30 samples h^{-1} . The advantage of the CZE and SIA techniques is that they simplified the analytical procedure into one or two steps. However, those techniques still require the use of special reagents, pretreatment procedures, and relatively expensive instruments, which increase the analysis time and the operational costs.

An electrochemical technique to quantify iron ions was proposed by Ugo et al. [1, 15]. They described a method which applies cyclic and multiple square-wave voltammetry (CMSWV) techniques on a nafion coated electrode (NCE) to track iron species. The operability range of the method depends on the electroanalytical technique used to detect the cations. For example, it can be employed for determinations in the 10^{-6} M range when using simple cyclic voltammetry, and/or in the 10^{-9} M range when using multiple square-wave voltammetry. The advantages of the CMSWV method include: (1) The instrument used is not as expensive as AAS or IC; (2) The sample does not need to be specially treated; and (3) The DL is high. However, voltammetric measurements with the NCE provide only the overall iron concentration (not the speciation).

Considering the advantages of electrochemical techniques, a simple technique to simultaneously determine Fe(II) and Fe(III) ions (or other multivalent cations) is proposed. The technique has been called EM2C2 (Electrochemical Measurement of Multivalent Cations Concentration). This paper describes the use of the EM2C2 technique to measure the concentrations of Fe(II) and Fe(III) ions simultaneously. The technique is based upon the electrochemical properties of the cations in solution.

2 Experimental setup

The EM2C2 method to measure iron ions consists of using a rotating disk electrode (RDE) in acidic media. While not discussed in this paper, determination of other cations may be more effective in an alkaline medium. The schematic representation of the RDE setup is given in Fig. 1. The RDE (working electrode) is a disk of Pt (with an exposed area of 0.2 cm^2) imbedded in a rod of Teflon (insulation material). The electrode is mounted to a rotator (Pine, AFM SRX) with a rotation rate controller. A coiled platinum foil (3N5 purity, 0.004" thick, 25 mm width, and 80 mm length, from ESPI) is used as the counter electrode. A saturated calomel electrode (from Fisher Scientific) is used as the reference electrode, and a luggin capillary is used to decrease the distance from the reference electrode to the working electrode. The luggin capillary was filled and kept wet with saturated KCl for better ion conductivity. All electrochemical measurements were performed with a Solartron potentiostat (1287A, 1281, and 1252A) at room temperature ($25 \text{ }^\circ\text{C}$) and ambient pressure.

ACS reagent-grade ferric sulfate (from Fisher Scientific, purity >95%), ferrous sulfate (from Fisher Scientific, purity >99%) and H_2SO_4 (from Fisher Scientific, purity 95.0–98.0%) were used to prepare the solutions described in this paper.

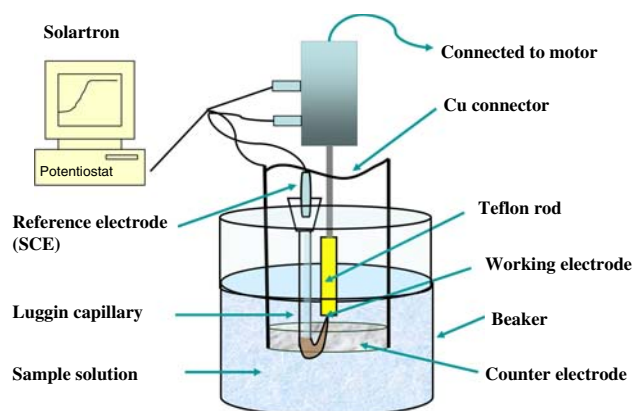
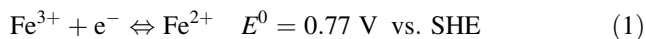


Fig. 1 Schematic diagram of the rotating disk electrode experimental setup

3 Results and discussion

3.1 Description of EM2C2 method

The EM2C2 method is based on the reduction/oxidation reaction of Fe(III) and Fe(II):



where Fe(III) is reduced to Fe(II) at potentials below 0.77 V vs. SHE, while Fe(II) is oxidized to Fe(III) at potentials above 0.77 V vs. SHE. A potentiostat is used to apply a potential wave change (from 0.2 to 1.2 V vs. SCE) between the working electrode and the reference electrode, and then the corresponding currents between the working electrode and the counter electrode are recorded. The working electrode consists of a Pt rotating disk electrode (RDE), with a rotating speed ranging from 500 to 3,000 rpm. This rotational motion sets up a well-defined flow of solution towards the surface of the RDE. The experimental results are generally plotted as a graph of current versus potential. A typical rotating disk voltammogram exhibits a sigmoidal shaped wave, where the height of this wave provides the analytical signal. The sigmoidal wave height is often called the limiting current or Levich current, which is described by Eq. 2:

$$i_l = 0.620nFAD^{2/3}\omega^{1/2}\nu^{-1/6}C \quad (2)$$

where, i_l is the limiting current of the redox Fe(III) and Fe(II) reactions (A), n is the number of electrons transferred, F is the Faraday's constant, $96,485 \text{ C mol}^{-1}$, A is the surface area of the electrode (cm^2), D is the diffusion coefficient ($\text{cm}^2 \text{ s}^{-1}$), ω is the angular velocity of the rotating electrode (rad s^{-1}), ν is the kinetic viscosity of the solution ($\text{cm}^2 \text{ s}^{-1}$), and C is the concentration of the solution (mol cm^{-3}).

A typical hydrodynamic voltammetry (HV) curve for a 1 M H_2SO_4 solution containing 30 mM Fe(II) and 30 mM Fe(III) ions under 1,000 rpm rotation rate and 50 mV potential scan rate is presented in Fig. 2. The upper limiting current (i_{UL}) is the analytical signal of Fe(II) ions, while the lower limiting current (i_{LL}) is the analytical signal of Fe(III) ions. The relationship between the analytical signal and the species' concentrations is expressed by Eq. 2, where i_l changes linearly with the species' concentrations. However, this equation is derived based on the following assumptions: (1) steady state; (2) laminar flow; and (3) mass-transfer-limited condition. Therefore, those assumptions need to be verified before applying this relationship to the EM2C2 technique.

Steady state can be achieved by performing multiple cycles. It was observed that the periodic and sustainable state was achieved after three cycles. Thus, the analytical signal for this technique is the stable limiting current

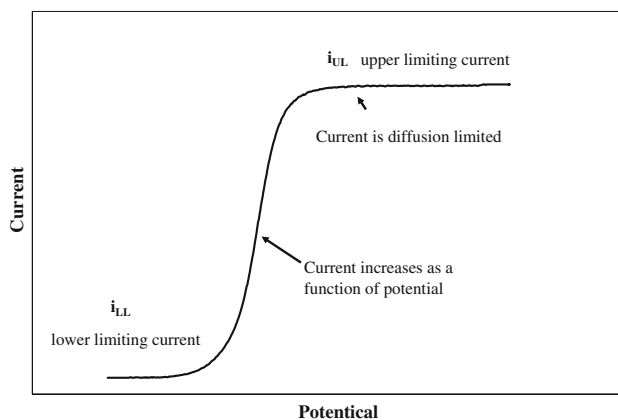


Fig. 2 Typical hydrodynamic voltammetry curve on rotating disk electrode for a 1 M H_2SO_4 solution including 30 mM Fe(II) and 30 mM Fe(III) ions (at 1,000 rpm and 50 mV s^{-1})

derived from the third cycle of the HV curve. Laminar flow can be achieved by controlling the rotation rate of the RDE. Mass-transfer-limited condition can be verified by the linear relationship between the limiting current and the ion concentration.

A number of experiments were carried out to test the linear relationship between the upper and lower limiting currents and the concentrations of Fe(II) and Fe(III) ions, respectively. A series of 1 M H_2SO_4 solutions with different Fe(II) concentrations and a series of 1 M H_2SO_4 solutions with different Fe(III) concentrations were tested using a HV program with a potential range from -0.2 to 1.2 V vs. SCE at 50 mV potential scan rate and $1,000 \text{ rpm}$ RDE rotation rate. The experimental matrix is shown in Table 1. Concentrations higher than 125 mM can also be determined by this method; however, higher concentrations of the pair ions can be easily determined by other simple analysis techniques with sufficient accuracy, such as titration. Therefore, concentrations higher than 125 mM were not analyzed in this paper. The higher and lower limiting currents were recorded in Table 1 in order to analyze the dependence of the limiting currents on the concentrations of Fe(II) and Fe(III) ions, respectively. All upper signals are the limiting currents at 1.0 V vs. SCE and lower signals are the limiting currents at 0 V vs. SCE . The experimental errors were derived by using error propagation considering the instrumental uncertainties. The experimental uncertainties for the concentration of the standard solutions (C_{st}) were calculated based on the instrumental error of the analytical balance and the volumetric glassware used for their preparation. The uncertainties of the limiting currents come from the potentiostat (Solartron) instrument, which are small ($1.0 \times 10^{-8} \text{ A}$), and can be neglected when carrying out the calculations.

The data in Table 1 indicate that the upper limiting current of the HV curve increases with Fe(II) concentration

Table 1 Experimental data and results for a series of 1 M H₂SO₄ solutions containing different concentrations of Fe(II) and Fe(III) ions

	$C_{st\ Fe(II)}$ mM	$C_{st\ Fe(III)}$ mM	i_{UL} mA	i_{LL} mA	$C_{cal\ Fe(II)}$ mM	$C_{cal\ Fe(III)}$ mM	ϵ (%)	E_a (mM)
Fe(II) ions	0.00	0.00	0.007 ^a	-0.122	0	0	-	0
	10.00 ± 0.01	0.00	0.851	-0.134	11.48 ± 0.11	0.27 ± 0.01	14.78	1.48
	20.00 ± 0.03	0.00	1.506	-0.136	20.39 ± 0.19	0.31 ± 0.01	1.93	0.39
	30.00 ± 0.05	0.00	2.312	-0.132	31.35 ± 0.30	0.22 ± 0.01	4.49	1.35
	40.00 ± 0.01	0.00	3.012	-0.132	40.87 ± 0.39	0.22 ± 0.01	2.17	0.87
	50.00 ± 0.08	0.00	3.563	-0.131	48.36 ± 0.46	0.20 ± 0.01	3.28	1.64
	60.00 ± 0.03	0.00	4.542	-0.128	61.68 ± 0.59	0.13 ± 0.00	2.79	1.68
	70.00 ± 0.04	0.00	5.281	-0.127	71.73 ± 0.69	0.11 ± 0.00	2.47	1.73
	80.00 ± 0.03	0.00	5.783	-0.132	78.55 ± 0.75	0.22 ± 0.01	1.81	1.45
	90.00 ± 0.08	0.00	6.712	-0.125	91.19 ± 0.87	0.07 ± 0.00	1.32	1.19
	100.00 ± 0.01	0.00	7.214	-0.122	98.02 ± 0.94	0	1.98	1.98
	110.00 ± 0.01	0.00	8.071	-0.121	109.67 ± 1.05	0.02 ± 0.00	0.30	0.33
	120.00 ± 0.02	0.00	8.843	-0.124	120.17 ± 1.15	0.04 ± 0.00	0.14	0.17
125.00 ± 0.05	0.00	9.176	-0.123	124.70 ± 1.19	0.02 ± 0.00	0.24	0.30	
Fe(III) ions	0.00	0.00	0.007	-0.122 ^b	0	0	-	0
	0.00	10.00 ± 0.01	0.104	-0.556	1.32 ± 0.01	9.72 ± 0.10	2.78	0.28
	0.00	20.00 ± 0.02	0.112	-0.926	1.43 ± 0.01	18.01 ± 0.18	9.95	1.99
	0.00	30.00 ± 0.05	0.115	-1.375	1.47 ± 0.01	28.07 ± 0.29	6.44	1.93
	0.00	40.00 ± 0.05	0.114	-1.845	1.46 ± 0.01	38.60 ± 0.40	3.51	1.40
	0.00	50.00 ± 0.08	0.123	-2.388	1.58 ± 0.02	50.76 ± 0.52	1.52	0.76
	0.00	60.00 ± 0.03	0.125	-2.859	1.60 ± 0.02	61.31 ± 0.63	2.18	1.31
	0.00	70.00 ± 0.04	0.124	-3.221	1.59 ± 0.02	69.42 ± 0.71	0.83	0.58
	0.00	80.00 ± 0.03	0.123	-3.627	1.58 ± 0.02	78.51 ± 0.81	1.86	1.49
	0.00	90.00 ± 0.08	0.132	-4.184	1.70 ± 0.02	90.99 ± 0.93	1.10	0.99
	0.00	100.00 ± 0.04	0.135	-4.553	1.74 ± 0.02	99.25 ± 1.02	0.75	0.75
	0.00	110.00 ± 0.01	0.138	-5.012	1.78 ± 0.02	109.54 ± 1.12	0.42	0.46
	0.00	120.00 ± 0.02	0.140	-5.435	1.81 ± 0.02	119.01 ± 1.22	0.82	0.99
	0.00	125.00 ± 0.02	0.141	-5.815	1.82 ± 0.02	127.52 ± 1.31	2.02	2.52

All polarization experiments were performed at 1,000 rpm and 50 mV s⁻¹

^a Zero anodic limiting current

^b Zero cathodic limiting current

for the solutions containing only Fe(II) ions, while the lower limiting current remains constant with slight variations. Additionally, it was found that at zero concentration of Fe(II), there is a background current (or background noise) which is named as the zero anodic upper limiting current $i_{UL}^0 = 0.007$ mA (see Table 1). Similarly, there is a zero cathodic lower limiting current $i_{LL}^0 = -0.122$ mA (see Table 1). It is possible that the background currents are associated with the electrolyte–electrode interactions/interface. Therefore, the anodic analytical signal is defined as the current by subtracting the i_{UL}^0 from the upper limiting current, i_{UL} , while the cathodic analytical signal is defined as the current by subtracting the i_{LL}^0 from the lower limiting current, i_{LL} . Figure 3a shows the relationship between the anodic analytical signal and the concentration of Fe(II). The statistical analysis indicates that the anodic current follows a linear relationship with the concentration of

Fe(II) ions with a 95% confidence interval ($R^2 = 0.9998$ with F significance = 1.05×10^{-23}). The intercept of the line was set to zero because the analytical signal was corrected by the background noise (zero limiting currents). A similar analysis was performed between the cathodic analytical signal and the concentration of Fe(III) ions with a 95% confidence interval ($R^2 = 0.9997$ with F significance = 8.96×10^{-23}) and the results are shown in Fig. 3b. The results of the analysis can be summarized by Eqs. 3 and 4:

$$i_{UL} = (7.35 \pm 0.07) \times 10^{-2} C_{Fe(II)} + i_{UL}^0 \quad (3)$$

$$i_{LL} = -(4.46 \pm 0.05) \times 10^{-2} C_{Fe(III)} + i_{LL}^0 \quad (4)$$

where $C_{Fe(II)}$ is the concentration of Fe(II) (mM), $C_{Fe(III)}$ is the concentration of Fe(III) (mM), i_{UL} is the corresponding upper limiting current (mA), and i_{LL} is the corresponding

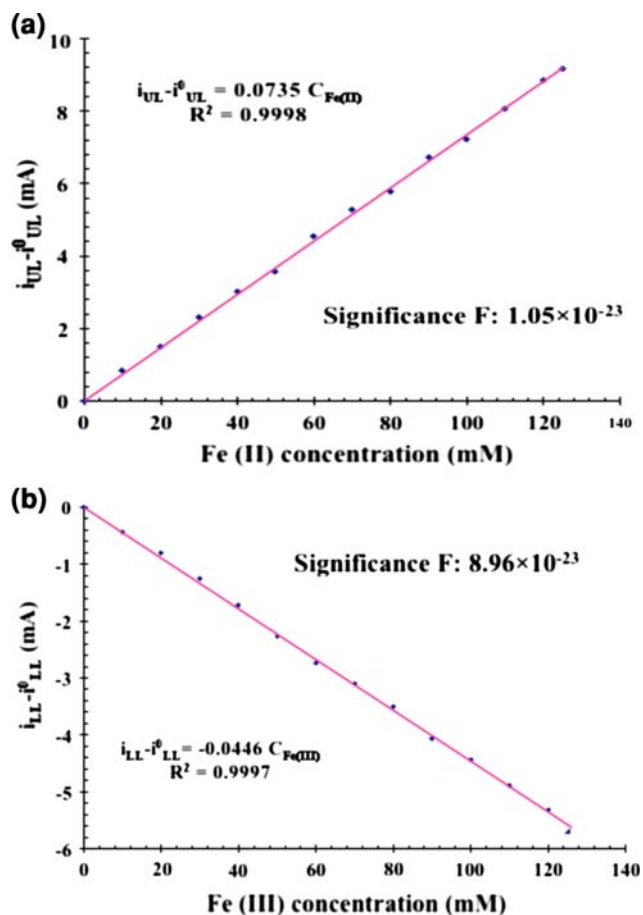


Fig. 3 Relationship of the anodic and cathodic limiting currents as a function of the Fe(II) and Fe(III) concentrations, respectively. Both anodic (a) and cathodic (b) limiting currents seem to follow the linear relationship (Eq. 2) with the concentrations of Fe(II) and Fe(III)

lower limiting current (mA). Equations 3 and 4 can be modified to yield the concentrations of Fe(II) and Fe(III), respectively:

$$C_{Fe(II)} = (13.60 \pm 0.13)(i_{UL} - i_{UL}^0) \quad (5)$$

$$C_{Fe(III)} = -(22.40 \pm 0.23)(i_{LL} - i_{LL}^0) \quad (6)$$

The results show that if a solution contains only one of the species either Fe(II) or Fe(III), the concentration of the ions can easily be determined by inserting the experimental values of the limiting currents into Eqs. 5 or 6. It is worth mentioning that the constants in those equations may change according to different experimental conditions such as: temperature, pressure, working electrode, rotation rate, electrolyte type, and electrolyte concentrations.

3.2 Interaction between Fe(II) and Fe(III) ions

When the solution contains both Fe(II) and Fe(III) ions, the interaction between Fe(II) and Fe(III) ions should be

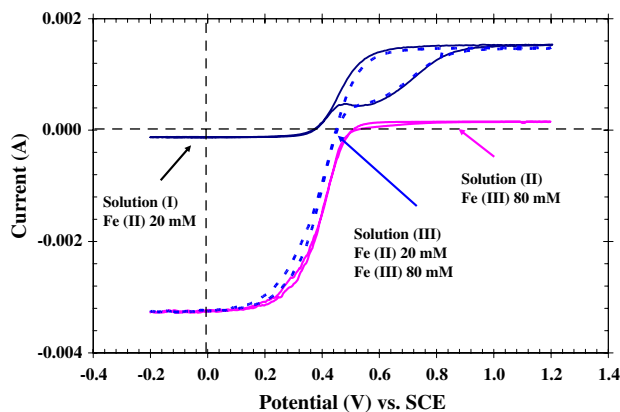


Fig. 4 Hydrodynamic voltammetry curves of different solutions: Solution (I): 20 mM Fe(II), Solution (II): 80 mM Fe(III), and Solution (III): a mixed of 20 mM Fe(II) and 80 mM Fe(III) (1 M H₂SO₄ electrolyte, 1,000 rpm and 50 mV s⁻¹). The results indicate that the presence of Fe(II) does not affect the analytical signals (lower limiting current) associated with the concentrations of Fe(III) ions and vice versa

considered, which directly affects the method to quantify the concentrations of Fe(II) and Fe(III) ions in the same solution. In order to analyze the interaction, hydrodynamic voltammetry experiments were performed to different solutions containing 20 mM Fe(II) ions (Solution I), 80 mM Fe(III) ions (Solution II), and a mixed of 20 mM Fe(II) and 80 mM Fe(III) ions (Solution III) under the same analytical conditions as described in Sect. 3.1. The results of the comparison are shown in Fig. 4. The data indicate that the presence of Fe(II) does not affect the cathodic limiting current associated with the concentrations of Fe(III) and vice versa.

In order to further analyze the interaction between Fe(II) and Fe(III) ions, different ratios of Fe(II) and Fe(III) were tested and the results are reported in Table 2. When compared with the results shown in Table 1 (single cations in solution) it can be observed that there are no significant differences between the limiting currents of solutions with mixed cations (Table 2) and single cations (Table 1). The results indicate that there is no interaction between Fe(II) and Fe(III) ions. Therefore, the concentration of each of these cations can be quantified by using Eqs. 5 and 6.

3.3 Accuracy and reproducibility

Calculated concentration values using Eqs. 5 and 6 are presented in Tables 1 and 2 and compared to the standard solutions used. Eqs. 7 and 8 were used to evaluate the accuracy of the technique:

$$\varepsilon = \frac{|C_{st} - C_{cal}|}{C_{st}} \times 100\% \quad (7)$$

$$E_a = |C_{st} - C_{cal}| \quad (8)$$

Table 2 Application of EM2C2 technique to five standard solutions containing both Fe(II) and Fe(III) ions

$C_{st\ Fe(II)}$ (mM)	$C_{st\ Fe(III)}$ (mM)	i_{UL} (mA)	i_{LL} (mA)	$C_{cal\ Fe(II)}$ (mM)	$C_{cal\ Fe(III)}$ (mM)	$E_a\ Fe(II)$ (mM)	$E_a\ Fe(III)$ (mM)
20.00 ± 0.01	80.00 ± 0.04	1.504	-3.620	20.35 ± 0.20	78.36 ± 0.80	0.35	1.64
40.00 ± 0.01	40.00 ± 0.01	3.020	-1.872	40.98 ± 0.40	39.20 ± 0.40	0.98	0.80
80.00 ± 0.03	20.00 ± 0.01	5.785	-0.964	78.58 ± 0.75	18.86 ± 0.20	1.42	1.14
5.00 ± 0.02	80.00 ± 0.03	0.418	-3.619	5.59 ± 0.05	78.33 ± 0.80	0.59	1.67
80.00 ± 0.03	5.00 ± 0.01	5.859	-0.356	79.58 ± 0.76	5.24 ± 0.05	0.42	0.24

The results indicate that there is no interaction when measuring the concentrations of Fe(II) and Fe(III) ions separately in the same solution. The data also indicate that the absolute errors reported by the method are small for the concentration range used

where ε is the relative error, E_a is the absolute error, C_{st} is the standard solution concentration and C_{cal} is the calculated concentration (using Eqs. 5 and 6).

For solutions with single cations (Table 1), it can be seen that the relative error drops with an increase in the iron concentration, while the absolute errors are randomly distributed. Therefore, from a statistical standpoint, the absolute error is more appropriate to evaluate the accuracy of the technique. It can be seen that most of the relative errors are less than 2.5% and absolute errors are less than 2 mM for Fe(II) and Fe(III) in the concentration range of 10–125 mM. Similar results were observed for the solutions containing both iron ions (Table 2), indicating that the technique can measure concentrations of iron ions as low as 5 mM with absolute errors under 1 mM.

Reproducibility is an important criterion for an analytical technique. Five samples containing 1 M H_2SO_4 and 80 mM Fe(II) ions were tested at the same conditions described in Sect. 3.1 and the results are shown in Fig. 5. The results indicate that there is no significant difference among the analytical signals with a relative standard deviation (RSD) of 0.04% which justifies the reproducibility of this technique for 80 mM Fe(II) solutions. The

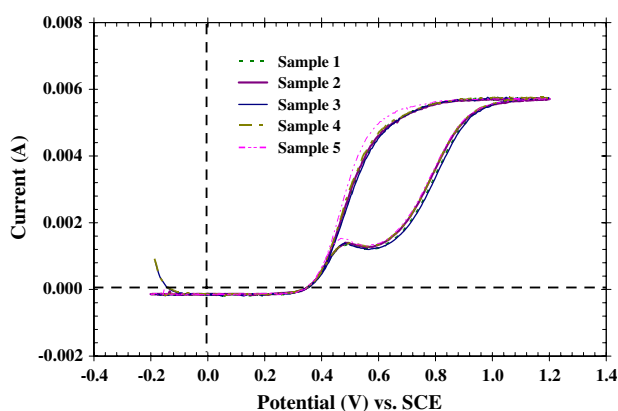


Fig. 5 Hydrodynamic voltammetry curves of five samples containing 80 mM Fe(II) ions (1 M H_2SO_4 electrolyte, 1,000 rpm and 50 $mV\ s^{-1}$). The analytical signals of the samples are overlapped demonstrating the reproducibility of the method

reproducibility of the technique was also evaluated for solutions containing different concentrations of both ions and the relative standard deviations of these results are shown in Table 3. The maximum relative standard deviations observed were 0.13% for Fe(II) and 0.38% for Fe(III) solutions in the ion concentration range from 1 to 100 mM. The RSD values are small and justify the reproducibility of the method within the given concentration range.

3.4 Effect of potential scan rate

Without stirring or rotating, the potential scan rate will affect the height of the peak in a polarization curve due to diffusion limitations. However, Eq. 2 indicates that the limiting current is independent of the potential scan rate for the RDE system. In order to validate this relationship and minimize the operating time, the effect of the potential scan rate on the analytical signal was tested. Solutions containing different concentrations of Fe(II) and Fe(III) were tested at different potential scan rates (10, 30, 40, 50 and

Table 3 Reproducibility of the method for different concentrations of Fe(II), Fe(III), and combinations of Fe(II) and Fe(III)

	$C_{st\ Fe(II)}$ (mM)	$C_{st\ Fe(III)}$ (mM)	Reproducibility RSD (%)
Fe(II) or Fe(III)	1.00 ± 0.01	0.00	0.05
	5.00 ± 0.02	0.00	0.12
	20.00 ± 0.03	0.00	0.12
	40.00 ± 0.01	0.00	0.07
	100.00 ± 0.03	0.00	0.06
	0.00	1.00 ± 0.02	0.11
	0.00	5.00 ± 0.03	0.09
	0.00	20.00 ± 0.02	0.38
	0.00	40.00 ± 0.05	0.20
	0.00	100.00 ± 0.03	0.14
Both Fe(II)/Fe(III)	20.00 ± 0.01	100.00 ± 0.04	0.13/0.13
	40.00 ± 0.01	40.00 ± 0.01	0.08/0.16
	100.00 ± 0.03	20.00 ± 0.01	0.06/0.35

The relative standard deviations among the different samples are small

Table 4 Effect of the potential scan rate on the analytical signals for different concentrations of Fe(II) and Fe(III) ions

	$C_{st\ Fe(II)}$ (mM)	$C_{st\ Fe(III)}$ (mM)	RSD at different potential scan rates (%)
Fe(II) or Fe(III)	1.00 ± 0.01	0.00	0.21
	5.00 ± 0.02	0.00	0.12
	20.00 ± 0.03	0.00	0.26
	40.00 ± 0.01	0.00	0.12
	100.00 ± 0.03	0.00	0.17
	0.00	1.00 ± 0.02	0.36
	0.00	5.00 ± 0.03	0.28
	0.00	20.00 ± 0.02	0.41
	0.00	40.00 ± 0.05	0.24
	0.00	100.00 ± 0.03	0.18
Both Fe(II)/Fe(III)	20.00 ± 0.01	100.00 ± 0.04	0.28/0.15
	40.00 ± 0.01	40.00 ± 0.01	0.16/0.25
	100.00 ± 0.03	20.00 ± 0.01	0.20/0.40

80 mV s⁻¹) and the RSD for those analytical signals are shown in Table 4. The maximum RSD value is 0.28% for Fe(II) and 0.41% for Fe(III) within the ion concentration range (1–100 mM). This demonstrates that the potential scan rate does not affect the analytical signal and Eqs. 5 and 6 are valid in the potential scan rate range of 10–80 mV s⁻¹. The independence of the potential scan rate on the limiting current provides flexibility for changing the potential scan rate according to analysis requirements. By using 80 mV s⁻¹, the results can be derived within 1 minute, which is much faster than other techniques.

3.5 Effect of the rotation rate

Equation 2 indicates that the limiting current (i_l) changes linearly with the angular velocities of the rotation rate ($\omega^{1/2}$), so higher rotation rates would generate higher analytical signals. A series of HV tests were performed for 80 mM Fe(II) solution under different rotation rates and the results are shown in Section (I) of Table 5. The results show that the limiting current increases with the rotation rate. These results may have a positive impact when measuring low concentrations. Based on the experimental results, the relationship $i_{UL} = k_1 \cdot \omega_a^{1/2}$ ($k_1 = 0.182$ with R square 0.998) was derived for the limiting current at different rotation rates. This relationship can be incorporated into Eqs. 3 and 4 to generate new equations for this technique. Although the analytical signal can be improved by increasing the rotation rate, rotation rates higher than 3,000 rpm cannot guarantee the laminar flow and thus cannot be used for this technique. Therefore, the range of rotation rate recommended for the method is from 500 to

Table 5 Effect of rotation rate and electrolyte concentration on the limiting currents

Section (I) effect of rotation rate					
Rotation rate (rpm)	500	800	1,000	2,000	3,000
i_{UL} (mA)	4.121	4.952	5.783	8.154	9.950
Section (II) effect of sulfuric acid concentration					
Sulfuric acid (mol/L)	0.1	0.2	1	2	4
i_{UL} (mA)	5.651	5.804	5.783	5.654	4.891

The concentration of Fe(II) ions was kept constant at 80 mM

3,000 rpm. The rotation rate may have an impact on the detection limit of the technique; this topic will be discussed in Sect. 3.7.

3.6 Effect of electrolyte concentration

The effect of the concentration of electrolyte H₂SO₄ on the analytical signal was also determined and the results are presented in Section (II) of Table 5. The results show that the limiting current for the 80 mM Fe(II) solution increased with the electrolyte concentration changing from 4 to 1 M H₂SO₄, remained constant in the range from 1 to 0.2 M H₂SO₄, and dropped when the H₂SO₄ concentration was less than 0.2 M. A possible explanation for this effect is that the interaction between the cations and the electrolyte became stronger when increasing the electrolyte concentration above 1 M, which decreased the mobility (or diffusion coefficient) of the cations in the medium; while the ion conductivity is low at concentrations less than 0.2 M. Therefore, 0.2 M H₂SO₄ can be used to determine higher ion concentrations (above 1 mM), while 1 M H₂SO₄ is recommended when measuring trace ion concentrations (below 1 mM).

3.7 Detection limit and comparison with other techniques

In order to determine the detection limit DL, solutions containing low concentrations (ppm) of iron ions were analyzed under different operating conditions. Due to the low concentrations, the limiting current signals are not horizontal lines and they are difficult to distinguish from the blank solution. In order to minimize this problem, the potential range was extended to -0.2 to 1.5 V vs. SCE. Solutions of 1 M H₂SO₄ containing 0, 0.02, and 0.1 mM Fe(II) ions were tested at the rotation rate of 1,000 rpm and potential scan rate of 50 mV s⁻¹. The results are shown in Fig. 6. The rapid increase of the current after 1.4 V is due to the oxidation of water, which does not affect our results and can be avoided when narrowing the polarization potential range. From this figure, it can be observed that

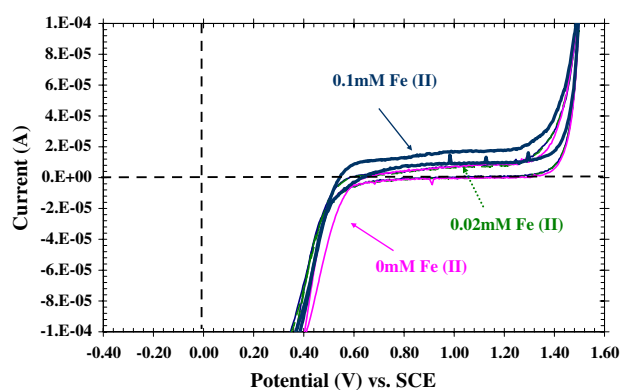


Fig. 6 Hydrodynamic voltammograms for solutions containing 0, 0.1, and 0.02 mM Fe(II) ions (1 M H₂SO₄ electrolyte, 1,000 rpm and 50 mV s⁻¹). Only limiting currents of 0.1 mM Fe(II) solutions can be distinguished from the blank solution, which indicates that the detection limit of the technique at the given conditions is 0.1 mM

only the limiting current (1.72×10^{-5} A) of the solution containing 0.1 mM Fe(II) can be distinguished from the limiting current (6.75×10^{-6} A) of the blank solution (1 M H₂SO₄ electrolyte solution without Fe(II) ions). The limiting current (6.79×10^{-6} A) of the solution containing iron ion concentrations lower than 0.1 mM almost overlaps the limiting current (6.75×10^{-6} A) of the blank solution. Therefore, it can be concluded that the DL for the method is 0.1 mM (5 ppm) for Fe(II) at the rotation rate of 1,000 rpm. A similar result was derived from the analysis of the Fe(III) ions (the DL is 0.1 mM Fe(III)).

In order to improve the detection limit, experiments were performed at higher rotation rates. 1 M H₂SO₄ electrolyte solutions containing 0, 0.02, and 0.1 mM Fe(II) ions were tested at 3,000 rpm under the same conditions described above. The results are shown in Fig. 7. It can be

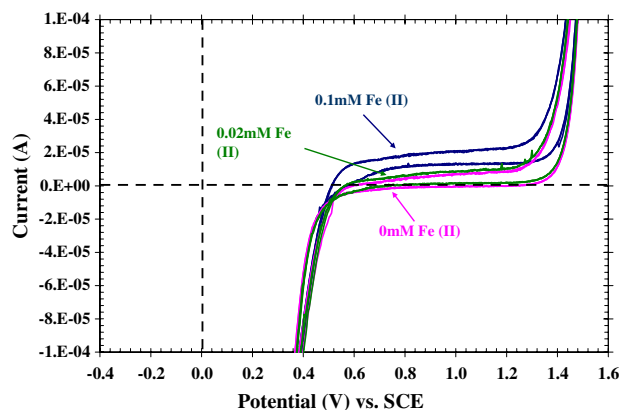


Fig. 7 Hydrodynamic voltammograms for solutions containing 0, 0.1, and 0.02 mM Fe(II) ions (1 M H₂SO₄ electrolyte, 3,000 rpm and 50 mV s⁻¹). The limiting current of 0.02 mM Fe(II) solution can be distinguished from the blank solution, which indicates that the detection limit is 0.02 mM

seen that the limiting current (8.66×10^{-6} A) of the solution containing 0.02 mM Fe(II) can be distinguished from the limiting current (7.14×10^{-6} A) of the blank solution. This indicates that the DL is 0.02 mM (1 ppm) at 3,000 rpm rotation rate. Therefore, the DL is improved by increasing the rotation rate. However, as discussed before, rotation rates higher than 3,000 rpm cannot be used, so other techniques may be required to further lower the DL and broaden the applications of this technique.

Table 6 presents a comparison of the EM2C2 method with the CZE and SIA techniques. The EM2C2 technique has the advantages of low cost, simple and fast operation. The costs of these techniques only include the instrumental cost and the cost of the EM2C2 technique includes a potentiostat (1×10^{-6} A DL is required for 1 ppm DL and most commercial potentiostat instruments can satisfy this requirement) and a rotating disk electrode system. The accuracy of the method is in the same order of magnitude with the SIA technique, while the reproducibility is better than the SIA and CZE techniques. However, the DL is higher than other techniques; therefore, this technique is applicable for processes in which the Fe(II) and Fe(III) concentrations are above 0.02 mM (1 ppm). Other techniques are required to quantify ion concentrations lower than 0.02 mM. However, this technique still has the potential to lower its DL by increasing the operating temperature or by changing the electrode materials (e.g., a plated Pt electrode may provide higher DL due to larger surface area when compared to Pt foil).

One of the applications of this technique can be found in Jin and Botte [16], where it was applied to determine the concentrations of Fe(II) and Fe(III) ions in a coal slurry solution before and after coal electrolysis. The iron ion species have an influence on the electrolysis of coal. Those results are important to study the mechanism of coal electrolysis and help to determine the coal conversion efficiency.

4 Conclusions

The EM2C2 technique described herein has significantly simplified the analysis procedure to determine the concentrations of Fe(II) and Fe(III) ions separately and reduced the instrumental cost. The precision and accuracy of this technique is comparable with CZE and SIA techniques. The detection limit is 0.1 mM (5 ppm) under 1,000 rpm rotation rate, while the detection limit can be improved to 0.02 mM (1 ppm) by increasing the rotation rate to 3,000 rpm. The detection limit may be increased by testing other working electrode materials or operating this technique at higher temperatures. Experimental data show that rotation rate and electrolyte concentration affect the

Table 6 Comparison of EM2C2 technique with CZE and SIA methods

Technique	Cost (\$)	Procedure/testing time	Detection limit Fe(II)/Fe(III)/mM	ε (%) Fe(II)/Fe(III)	Reproducibility (%)
CZE	~25,000 (2008)	Pretreatment + one step/3 min	$6 \times 10^{-5}/4 \times 10^{-6}$	–	7.98/0.75
SIA	~22,000 (2008)	Pretreatment + one step/2 min	0.002/0.003	0.8/1.3	0.8/1.3
EM2C2	~7,000 (2008) (Pine Instr.)	One step/1 min	0.02/0.02	<2.5/<2.5	0.43/0.52

analytical signal of the regression analysis, while the potential scan rate does not affect the analytical signal, which gives the advantage of fast operation (1 sample min^{-1}).

It is proposed that this technique can be applied to other metal ions, so this is a promising beginning to explore the use of this electrochemical analysis method to measure the concentrations of other multivalent cations, such as As(III)/As(V), Se(IV)/Se(VI), Cr(VI)/Cr(III), and Sb(III)/Sb(V).

When compared to other techniques, the developed procedures for the EM2C2 method can be summarized as: (1) Establish the RDE setup and generate equations. This step includes choosing the appropriate operating conditions, such as: potential range, electrolyte, electrolyte concentration, potential scan rate, rotation rate, and operating temperature. Performing CV experiments (identify the steady-state condition) for serials of standard solutions, and then generating the equations. (2) Perform CV experiments for sample solutions; and (3) Predict the concentrations of Fe(II) and Fe(III) by using the analytical signals and the equations derived in step (1). In addition, the RDE can be made as small as needed (for example, it could have the dimensions of a portable electric screw driver). Mathematical modeling could help to generate the equations for

different operating conditions and lower ion concentrations in order to decrease the experimental time.

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