

Determination of submillimolar concentration of ferrate(VI) in alkaline solutions by amperometric titration

Short Communication

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Abstract: A new amperometric titration method was developed for quantitative determination of ferrate(VI) ($\text{Fe}^{\text{VI}}\text{O}_4^{2-}$) in the 7.06×10^{-5} – 5.73×10^{-3} M concentration range. Chromium(III) hydroxide solution was used as the titrant. The diffusion current (I_d) had a linear relationship with the concentration of ferrate(VI) and slopes were dependent on the concentration of NaOH. The amperometric titration could detect a lower concentration of ferrate(VI) than could potentiometric and colorimetric titrations. The method was applied successfully to determine concentrations of ferrate(VI), generated electrochemically, in strong alkaline solutions.

Keywords: Ferrate • Amperometric Titration • Electrochemical Analysis • Diffusion current • Chromite
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1. Introduction

The high-valent iron-based compound, ferrate(VI) (FeO_4^{2-}) is an emerging disinfectant and oxidant for treating water [1-7]. Ferrate(VI) is environmentally friendly and can address concerns associated with common treatment approaches. For example, ferrate(VI) does not produce bromate ion because of its non-reactivity with bromide ion [6]. Ferrate(VI) can also easily oxidize contaminants such as nitrogen- and sulfur-containing compounds, pharmaceuticals, and estrogens [8-14]. Another advantage of using ferrate(VI) is that in a single application it can act as an oxidant and a coagulant, which has been shown in removing metals and nutrients [15-21]. Ferrate(VI) is thus advantageous over other commonly used chemicals in the wastewater industry. Ferrate(VI) is also used in producing high-energy cathodes in batteries [22]. Because of these current and potential uses of ferrate(VI), numerous efforts are being made to synthesize ferrate(VI) efficiently [23-25].

Among the several known methods to synthesize ferrate(VI), an electrochemical approach seems promising for efficient and economical production [24]. This would require an understanding of the mechanism of the electrochemical synthesis, which is not fully understood [24,26]. The electrochemical processes occurring in the initial phase of the generation of ferrate(VI) at the anode must be known to make progress on synthesizing ferrate(VI) efficiently. In the initial phase of ferrate(VI), ferrate(VI) is produced at concentrations lower than millimolar and currently used methods are not suitable to detect such low levels under the conditions of electrochemical synthesis. Therefore, a method to determine low concentration of ferrate(VI) at submillimolar levels is critically needed.

Several methods, including volumetric titrations and spectrometric techniques, are known to determine concentration of ferrate(VI) in solution [27]. Volumetric titrations are not sensitive enough to detect less than millimolar concentrations of ferrate(VI) and are also associated with large volumes and human

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error, which increase the inaccuracy of the results. Spectrophotometric methods may quantify low concentrations of ferrate(VI), but electrochemically synthesized solutions of ferrate(VI) in high alkaline solutions produce bubbles and contain solid particles of Fe(III) hydroxide, which interfere strongly with spectral measurements, hence, colorimetric techniques are not appropriate. Recently, a potentiometric titration method was developed to determine low concentrations of ferrate(VI) in high alkaline solution [28], but this method is suitable only to quantify concentrations of ferrate(VI) greater than 10^{-3} M. This paper demonstrates for the first time an amperometric method to detect ferrate(VI) concentrations in submillimolar levels ($<10^{-4}$ M).

The objectives of the present paper are: (1) to describe the development of amperometric titrations at various concentrations of ferrate(VI) and hydroxide ions; (2) to demonstrate that the developed method has better precision and accuracy than the volumetric chromite method; and (3) to apply the developed method to determine submillimolar concentrations of ferrate(VI), generated electrochemically in 10-15 M NaOH solutions.

2. Experimental procedure

2.1 Materials and reagents

Sodium hydroxide solutions at different concentrations (10.0-15.0 M) were prepared by dissolving solid NaOH (99.99% purity, Aldrich) into doubly distilled water. Solid crystals of $\text{CrCl}_3 \cdot 6\text{H}_2\text{O}$ were dissolved in water to prepare a stock solution of a stock solution of chromium(III) chloride (0.1 M). The stock solution of Cr(III) was standardized by first oxidizing with hydrogen peroxide in alkaline medium and then titrating against standard ferrous ammonium sulfate solution. The Cr(III) solution as a titrant was prepared by diluting the stock solution with 12.5 M NaOH. An electrochemical procedure was used to generate ferrate(VI) solutions at different concentrations in NaOH solutions. The current used was 60 mA and the anode was a low-carbon steel plate (40×25 mm). The electrolysis time varied from 0.1-24 h and ferrate(VI) solutions were freshly synthesized fresh before performing titrations. In the case of preparing $\sim 10^{-5}$ - 10^{-4} M ferrate(VI), the electrolysis time was in the range of 10-30 min.

2.2 Titration procedure

Amperometric titrations were performed in a 50 mL water-jacketed cell controlled at $20 \pm 0.1^\circ\text{C}$ with a circulating water bath (Ultra thermostat MLW U4). A microburet having an estimated accuracy of ± 0.02 mL was used to

deliver the Cr(III) solution. The electrochemical cell was made of a platinum electrode and calomel electrode. The platinum electrode was made of platinum wire ($l = 8$ mm and $d = 0.5$ mm) and was rotated at a rate of 200-600 revolutions per minute. Measurements of e.m.f. (± 0.15 mV) were made using a pH meter (millivoltmeter pH-150MA). Current was recorded using a microampere meter after each addition of the titrant. In the titration procedure, 10 mL of ferrate(VI) in a strong alkaline solution was poured into the water jacketed cell and then titrated against freshly prepared, standardized Cr(III) solution. Currents were corrected for dilution introduced by adding the titrant. A computer program was used to determine equivalence points of the titrations. The chromite method was applied to perform volumetric titrations [29].

3. Results and discussion

Initially, an appropriate voltage for performing amperometric titrations of ferrate(VI) against Cr(III) solution was established by carrying out voltammetry of individual solutions of Cr(III), Cr(VI), Fe(III), and ferrate(VI) in 12.5 M NaOH. Cr(VI) and Fe(III) are formed from the reaction of Cr(III) and ferrate(VI) in alkaline solution (Eq. 1).



Voltammograms of solutions, shown in Fig. 1, suggest that ferrate(VI) ion is electrochemically active over a wide range of potentials and is reduced at $E < 0.2$ V. A voltammogram is not affected by other possible oxidation reactions of Cr(III) and OH^- ions ($\text{Cr(III)} \rightarrow \text{Cr(VI)} + 3e^-$ and $4\text{OH}^- \rightarrow \text{O}_2 + 2\text{H}_2\text{O} + 4e^-$).

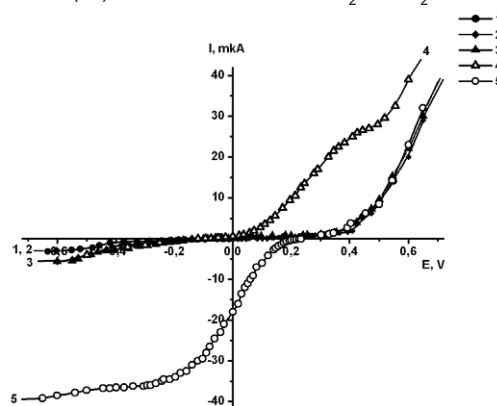


Figure 1. Voltammograms of: 1 - 12.5 M NaOH, 2 - 5.00×10^{-3} M CrO_4^{2-} ; 3 - 1.03×10^{-3} M $[\text{Fe}(\text{OH})_4]^-$; 4 - 6.35×10^{-4} M $[\text{Cr}(\text{OH})_4]^-$; 5 - 6.05×10^{-4} M FeO_4^{2-} in 12.5 M NaOH, 20°C .

Based on the results of Fig. 1 and negative effects of oxidation reactions on the voltammogram of ferrate(VI) ion, amperometric titrations were conducted by keeping E in the range of -0.2 – -0.4 V.

Next, diffusion currents of the reduction of ferrate(VI) ion under different concentrations of NaOH were determined. The relationship of I_d with the concentration of ferrate(VI) ion was found to be linear (Fig. 2). This linearity can thus be used for quantitative determination of ferrate(VI) ion. However, the calibration of I_d with respect to the concentration of NaOH should be performed under experimental conditions because slopes of linearity decrease with an increase in the concentration of NaOH. The dependence of current on the diffusion coefficient, which is inversely related to the viscosity of the NaOH solution [30], may explain the decrease in values of slopes with increasing concentration of NaOH from 10 – 15 M (Fig. 2).

Amperometric titrations were performed in 15 M NaOH solutions using varying concentrations of Cr(III) at constant [ferrate(VI)]. Titrations were repeated thrice and the curves are shown in Fig. 3. The results demonstrate the ease of finding the equivalence points of titrations at different concentrations of Cr(III).

Finally, the concentrations of ferrate(VI) ion, generated electrochemically, in 15 M NaOH solution, were determined using amperometric titrations. The results are shown in Fig. 4. Equivalence points were very clear and the results are given in Table 1. The same ferrate(VI) solutions were also subjected to the volumetric titration method and the comparison of the calculated accuracy and precision of the two titration methods are given in Table 1. The lowest detection level of ferrate(VI) using the amperometric method was 7.0×10^{-5} M. At this level of ferrate(VI), application of the chromite method was not possible. The chromite method was not sensitive for ferrate concentrations lower than 5.6×10^{-4} M. Therefore, the amperometric method had much higher sensitivity than the chromite method. Furthermore, the amperometric method had much better reproducibility than did the chromite

method (Table 1). The dispersion (S_r) of amperometric titrations were also much better than the S_r calculated using the chromite method at all concentrations of ferrate(VI). Importantly, the value of S_r was quite low for low ferrate(VI) concentrations, which were at least two times better than the chromite method.

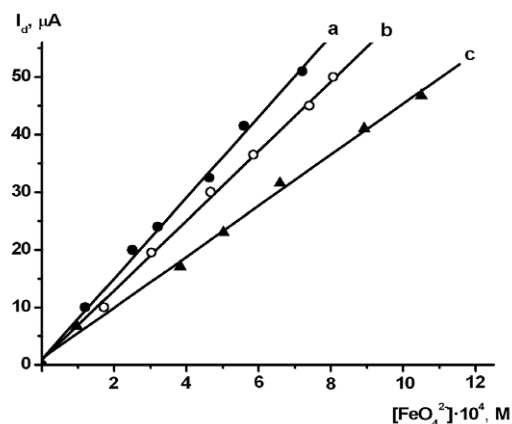


Figure 2. Dependence of diffusion current on the concentration of ferrate(VI) in different strength of NaOH solution at $E = -0.4$ V. a – 10.0 M NaOH; b – 12.5 M NaOH; c – 15.0 M NaOH

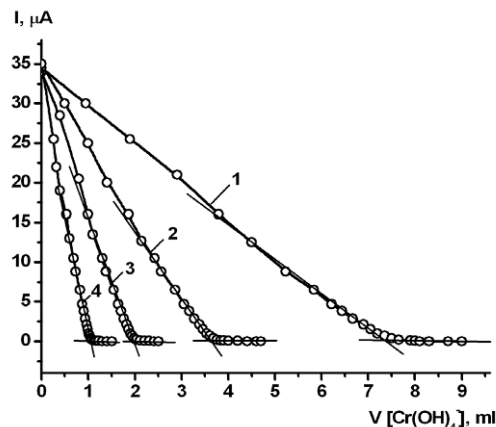


Figure 3. Amperometric titration curves of 10 mL 7.17×10^{-4} M ferrate(VI) solution using different $[\text{Cr}(\text{OH})_3]$: 1 – 9.85×10^{-4} M; 2 – 2.01×10^{-3} M; 3 – 3.73×10^{-3} M; 4 – 6.98×10^{-3} M. $[\text{NaOH}] = 15.0$ M; 20°C ; $E = -0.2$ V.

Table 1. Comparison of results obtained using chromite and amperometric methods in 15.0 M NaOH ($n = 5$, $p = 0.95$).

Simple №	Chomite method			Amperometric method		
	$[\text{FeO}_4^{2-}] \pm \delta$ M	Dispersion, σ^2	S_r	$[\text{FeO}_4^{2-}] \pm \delta$ M	Dispersion, σ^2	S_r
1	Determination is not possible			$(7.06 \pm 0.15) \times 10^{-5}$	1.47×10^{-12}	0.021
2	Determination is not possible			$(1.87 \pm 0.02) \times 10^{-4}$	3.83×10^{-12}	0.013
3	$(5.46 \pm 0.27) \times 10^{-4}$	4.59×10^{-10}	0.049	$(5.61 \pm 0.06) \times 10^{-4}$	2.36×10^{-11}	0.011
4	$(9.59 \pm 0.23) \times 10^{-4}$	3.34×10^{-10}	0.024	$(9.53 \pm 0.09) \times 10^{-4}$	5.13×10^{-11}	0.009
5	$(2.53 \pm 0.04) \times 10^{-3}$	1.04×10^{-9}	0.016	$(2.51 \pm 0.01) \times 10^{-3}$	1.26×10^{-10}	0.006
6	$(3.40 \pm 0.04) \times 10^{-3}$	1.28×10^{-9}	0.013	$(3.42 \pm 0.02) \times 10^{-3}$	3.54×10^{-10}	0.007
7	$(5.73 \pm 0.06) \times 10^{-3}$	2.60×10^{-9}	0.011	$(5.70 \pm 0.04) \times 10^{-3}$	1.00×10^{-9}	0.007

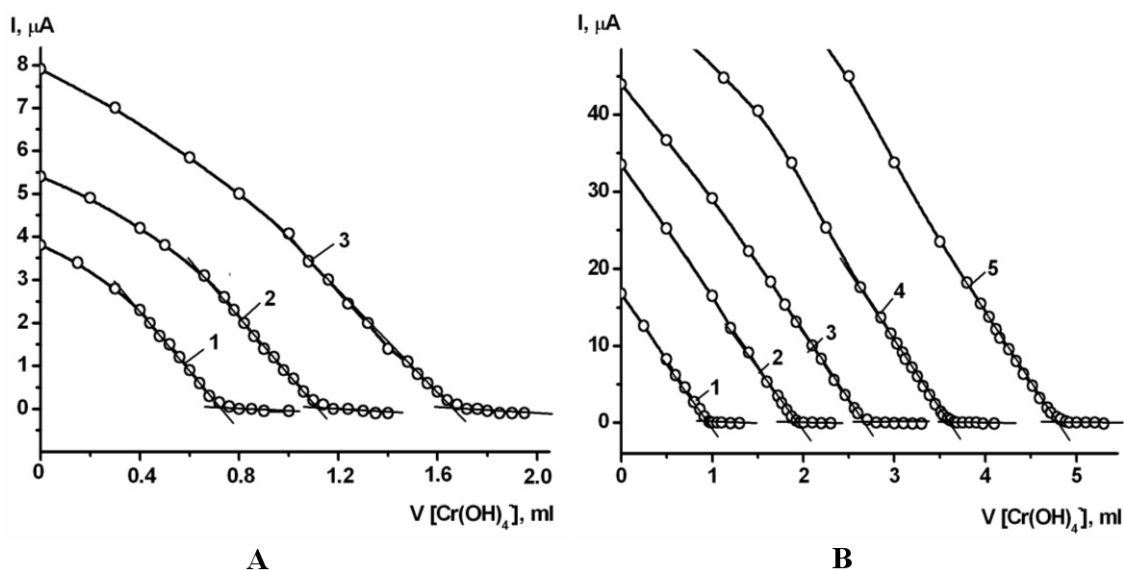


Figure 4. Amperometric titration curves of 10 ml at different concentrations of FeO_4^{2-} ions ($[\text{NaOH}] = 15.0 \text{ M}$; 20°C ; $E = -0.2 \text{ V}$). A: 1 - $7.06 \times 10^{-5} \text{ M}$; 2 - $1.07 \times 10^{-4} \text{ M}$; 3 - $1.60 \times 10^{-4} \text{ M}$. $[\text{Cr}(\text{OH})_4] = 9.62 \times 10^{-4} \text{ M}$ B: 1 - $3.44 \times 10^{-4} \text{ M}$; 2 - $7.20 \times 10^{-4} \text{ M}$; 3 - $1.01 \times 10^{-3} \text{ M}$; 4 - $1.34 \times 10^{-3} \text{ M}$; 5 - $1.80 \times 10^{-3} \text{ M}$. $[\text{Cr}(\text{OH})_4] = 3.74 \times 10^{-3} \text{ M}$

Table 2. Comparison of results obtained using chromite and amperometric methods in different concentrations of NaOH ($n = 5$, $p = 0.95$).

[NaOH], M	Chomite method [8]		Amperometric method	
	$[\text{FeO}_4^{2-}] \pm \delta$ $\text{M} \times 10^3$	S_r	$[\text{FeO}_4^{2-}] \pm \delta$ $\text{M} \times 10^3$	S_r
10.0	1.29 ± 0.02	0.013	1.27 ± 0.01	0.009
12.5	1.40 ± 0.02	0.013	1.41 ± 0.01	0.010
15.0	1.17 ± 0.02	0.017	1.18 ± 0.01	0.007

The amperometric method was also tested for electrochemically generated ferrate(VI) at different concentrations of NaOH and results were compared with the chromite method (Table 2). The superior precision of the amperometric titration compared to the chromite method can be seen in the accuracy and S^2 values (Table 2). In some cases, the S^2 of the potentiometric titrations was an order of magnitude lower than that of the volumetric titrations using the chromite method. This further suggests the superiority of the amperometric titration method over the colorimetric titration method.

4. Conclusions

A new amperometric method uses small volumes and is simple and fast for the quantitative determination of ferrate(VI). The method is also highly accurate with good reproducibility. The developed method was also

tested successfully in determining the concentrations of electrochemically generated ferrate(VI) in strong alkaline solutions. The amperometric method could determine concentrations of ferrate(VI) at a level of $7.06 \times 10^{-5} \text{ M}$ which is much lower than that of either the potentiometric or volumetric titration method.

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