A Simple Potentiometric Titration Method to Determine Concentration of Ferrate(VI) in Strong Alkaline Solutions

Dmitriy. A. Golovko a, Virender K. Sharma b, V. I. Suprunovich a, O. V. Pavlova a, I. D. Golovko a, Karel Bouzek c & Radek Zboril d

a Ukraine State Chemical Technological University, Dniepropetrovsk, Ukraine
b Chemistry Department, Florida Institute of Technology, Melbourne, Florida, USA
c Department of Inorganic Technology, Institute of Chemical Technology Prague, Prague, Czech Republic
d Nanomaterial Research Centre, Palacky University, Olomouc, Czech Republic

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Potentiometry

A SIMPLE POTENTIOMETRIC TITRATION METHOD TO DETERMINE CONCENTRATION OF FERRATE(VI) IN STRONG ALKALINE SOLUTIONS

Dmitriy. A. Golovko,¹ Virender K. Sharma,² V. I. Suprunovich,¹ O. V. Pavlova,¹ I. D. Golovko,¹ Karel Bouzek,³ and Radek Zboril⁴

¹Ukraine State Chemical Technological University, Dniepropetrovsk, Ukraine
²Chemistry Department, Florida Institute of Technology, Melbourne, Florida, USA
³Department of Inorganic Technology, Institute of Chemical Technology Prague, Prague, Czech Republic
⁴Nanomaterial Research Centre, Palacky University, Olomouc, Czech Republic

A new potentiometric titration method using a Pt wire as an indicator electrode was developed for quantitative determination of ferrate(VI) (Fe(VI)O₄⁴⁻) in the submillimolar to millimolar concentration range in a strong alkaline solution. A Ag/AgCl electrode was the reference electrode and the titrant used was chromium(III) hydroxide solution. The developed method is relatively simple and faster than the colorimetric titration technique. The method eliminates human error associated with the endpoint detection and increases accuracy of the results with respect to the colorimetric titration. The method was applied to study the decay of synthesized ferrate(VI) in alkaline solution.

Keywords: Accuracy; Oxyiron(VI); Potentiometry; Stability; Titration

INTRODUCTION

In recent years, there has been increasing interest in applications of ferrate(VI), which has the molecular formula Fe(VI)O₄⁴⁻, where iron exists in the +6 oxidation state to which four oxygen atoms are bonded covalently to give a tetrahedral...
structure (Hoppe, Schlemper, and Murmann 1983). Applications of ferrate(VI) include the “super iron” battery cathode, green chemistry synthesis oxidant, and non-chlorine oxidation/disinfection chemical for pollutant remediation (Licht, Wang, and Ghosh 1999; Delaude and Laszlo 1996; Sharma, Bloom, and Joshi 1998; Sharma 2004; Sharma et al. 2005; Yngard et al. 2008; He et al. 2009). Ferrate(VI) has the highest redox potential (+2.2 V in acid) of any oxidant used in water and wastewater treatment (Sharma 2002; Sharma 2010; Jiang 2002). Comparatively, ferrate(VI) can address the concerns of disinfectant by-products (DBPs) associated with currently used chemicals such as free chlorine, chloramines, and ozone (Richardson 2009). Fe(VI) also acts as a strong oxidant to degrade emerging contaminants such as estrogens, bisphenol-A, and pharmaceuticals present in water (Sharma 2008; Sharma et al. 2009; Sharma 2010; Li et al. 2008; Lee et al. 2009; Jiang 2007). Ferrate(VI) decomposition produces Fe(III), which itself is an excellent coagulant for removal of metals such as arsenic (Jain, Sharma, and Mbuya 2009; Sharma, Dutta, and Ray 2007).

Several studies with ferrate(VI) have been performed, which have examined production, stability, oxidation, and magnetic properties, all of which require determination of concentration of ferrate(VI) in solution (Márová et al. 2009; Márová, Bouzek, and Sharma 2010). The concentration of Fe$^{VI}O_4^{2-}$ in an aqueous sample can be determined by titrating it with chromium(III) or arsenite (Schreyer et al. 1950a, 1950b) (eqs. 1 and 2):

$$\text{Cr(OH)}_4^- + \text{FeO}_4^{2-} + 3\text{H}_2\text{O} \rightarrow \text{Fe(OH)}_3(\text{H}_2\text{O})_3 + \text{CrO}_4^{2-} + \text{OH}^- \quad (1)$$

$$3\text{AsO}_3^{3-} + 2\text{FeO}_4^{2-} + 9\text{H}_2\text{O} \rightarrow 2\text{Fe(OH)}_3(\text{H}_2\text{O})_2 + 3\text{AsO}_4^{3-} + 4\text{OH}^- \quad (2)$$

In the case of the chromite method (Schreyer et al. 1950a), the resulting chromate(VI) solution is acidified as dichromate and titrated with a standard solution of ferrous ion. A similar titration procedure has also been used in the reaction of ferrate(VI) with arsenic(III) (Schreyer et al. 1950b). Both methods determine concentrations only at the sub-molar to molar level of ferrate(VI). In addition, the volumetric titration steps are time consuming. To determine low concentrations of ferrate(VI) in aqueous samples, spectral methods can also be applied (J. D. Carr et al. 1985; Rush and Bielski 1986; Lee, Yoon, and van Gunten 2005; Noorhasan, Sharma, and Baum 2008). However, optical measurements of solutions require the use of buffer solution and a filtration step in order to avoid interferences from Fe(III) present in the solution. Moreover, the reagents used in spectral measurements are light sensitive and also need instrumentation (Lee et al. 2005; Noorhasan et al. 2008). Therefore, spectral methods are not always suitable. This prompted us to develop a simple potentiometric method to determine ferrate(VI) concentrations in aqueous samples.

The aims of the present paper were: (1) to develop the method by performing potentiometric titrations at various concentrations of ferrate(VI) and hydroxide ions; (2) to demonstrate that the developed method is simple and fast and has a better precision and accuracy than the chromite method; and (3) to apply the potentiometric method to observe decay of ferrate(VI) with time.
EXPERIMENTAL

Materials and Reagents

All solutions were prepared in double-distilled deionized water. Sodium hydroxide solutions at different ionic strength were prepared by dissolving solid NaOH (99.99% purity, Aldrich) into water. A stock solution of chromium(III) chloride (0.1 M) was prepared by dissolving solid crystals of CrCl$_3$·6H$_2$O in water. This solution was standardized by first oxidizing with hydrogen peroxide in alkaline media 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. The ferrate(VI) solutions at different concentrations were prepared in aqueous solutions of NaOH solutions using an electrochemical procedure. In this method, the current used was 60 mA and the anode was a low-carbon steel plate (40 mm × 25 mm). The electrolysis time varied from 2–24 hours depending on the desired ferrate(VI) concentration and all solutions were prepared fresh before performing titrations. The study of the decomposition kinetics of generated ferrate(VI) was carried out at 20°C by using a hermetically sealed Teflon vessel in order to avoid light.

Titration Procedure

Volumetric titrations were conducted using the chromite method (Schreyer et al. 1951a). Potentiometric titrations were performed in a 50 ml water-jacketed cell controlled at at 20±0.1°C with a circulating water bath (Ultra thermostat MLW U4). The Cr(III) solution was delivered to the cell by a microburet. The estimated accuracy of the burette was ±0.02 mL. The electrochemical cell was made of a Pt wire electrode and an Ag/AgCl reference electrode. Measurements of e.m.f. were made using the pH meter (millivoltmeter pH-150MA). The calculated accuracy was ±0.15 mV for e.m.f. readings. A computer program was applied to determine equivalence points of the titrations.

RESULTS AND DISCUSSION

Initially, potentiometric titrations were performed in 12.5 M NaOH solution using 4.34×10⁻³ M ferrate(VI) solution. Titrations were repeated thrice and the curves are shown in Figure 1A. The equivalence-points were determined using differential curves (Figure 1B). The calculated accuracy and precision of the titrations are given in Table 1. Titrations were then extended to lower concentrations of ferrate(VI) in 12.5 M NaOH solution. The lowest concentration used was approximately ten times lower than that of the initial titration concentration of ferrate(VI). The titration curves obtained at various concentrations are presented in Figure 2. The results obtained from the analysis of titration curves are given in Table 1.

The solutions at various concentrations of ferrate(VI) under the same conditions as stated previously were also titrated using the chromite method. The results of these titrations are also given in Table 1. It is very clear that the potentiometric method had a much better reproducibility than did the titration performed using the chromite method (Table 1). Furthermore $S_e$ of potentiometric titrations were
Table 1. Comparison of results obtained using two methods at different concentrations of FeO$_2^-$ in 12.5M NaOH (n = 5, p = 0.95)

<table>
<thead>
<tr>
<th>Sample No</th>
<th>Potentiometric Method</th>
<th>Chomite Method</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>[FeO$_2^-$] M</td>
<td>$S_t$</td>
</tr>
<tr>
<td>1</td>
<td>$(4.34 \pm 0.014) \times 10^{-3}$</td>
<td>0.00326</td>
</tr>
<tr>
<td>2</td>
<td>$(1.85 \pm 0.016) \times 10^{-3}$</td>
<td>0.00877</td>
</tr>
<tr>
<td>3</td>
<td>$(2.12 \pm 0.018) \times 10^{-3}$</td>
<td>0.00871</td>
</tr>
<tr>
<td>4</td>
<td>$(3.26 \pm 0.018) \times 10^{-3}$</td>
<td>0.00566</td>
</tr>
<tr>
<td>5</td>
<td>$(5.55 \pm 0.02) \times 10^{-3}$</td>
<td>0.00375</td>
</tr>
<tr>
<td>6</td>
<td>$(2.65 \pm 0.02) \times 10^{-3}$</td>
<td>0.0742</td>
</tr>
<tr>
<td>7</td>
<td>$(5.01 \pm 0.03) \times 10^{-4}$</td>
<td>0.0067</td>
</tr>
</tbody>
</table>

Figure 1. Reproducibility of potentiometric titrations: A – integral curves; B – differential curves. ([Cr(OH)$_4^-$] = 4.72 × 10$^{-3}$ M; [FeO$_2^-$] = 4.34 × 10$^{-3}$ M; [NaOH] = 12.5 M; 20°C.

Figure 2. Potentiometric titration curves at different concentrations of FeO$_2^-$ ions using [Cr(OH)$_4^-$] = 1.00 × 10$^{-3}$ M; [NaOH] = 12.5 M; 20°C. A – integral curves; B – differential curves. (1 – 1.52 × 10$^{-3}$ M; 2–1.10 × 10$^{-3}$ M; 3–7.81 × 10$^{-4}$ M; 4–6.01 × 10$^{-4}$ M; 5–4.01 × 10$^{-4}$ M; 6–2.61 × 10$^{-4}$ M.
at least three times 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 $5.01 \times 10^{-4}$ M ferrate(VI) concentration. The better precision of the potentiometric titration compared to the titration conducted using the chromite method can be seen in the dispersion ($S^2$) values (Table 1). In some cases, $S^2$ of the potentiometric titrations was an order of magnitude lower than that of the volumetric titrations using the chromite method. This further suggested the superiority of potentiometric titration method over the colorimetric titration.

Next, a comparison of potentiometric and chromite methods was conducted at different concentrations of hydroxide ion (10.5–14.5 M). The results are presented in Table 2. The reproducibility of potentiometric titrations was about 3–9 times better than that of the chromite titrations. It appears that the reproducibility varies without any relationship to hydroxide concentration. Similar results were observed for the values of $S_r$ (Table 2).

Finally, the developed method was tested to study the stability of ferrate(VI) in solution and to monitor the concentration of electrochemically generated ferrate(VI) under different conditions. In the stability study, the decay of ferrate(VI) was followed for several days (Figure 3). The initial concentrations of ferrate(VI) in solution decreased by 90% in 20 days. Interestingly, the decay was slow initially, followed by a fast decay (Figure 3). This observation is similar to results obtained in the decomposition of potassium ferrate ($K_2FeO_4$) in humid air (Machala et al. 2009).

Iron(III) hydroxide obtained in the decay of ferrate(VI) ion is in the amorphous iron oxide form. It seems that the large surface of this hydrous iron oxide accelerate the catalytic decomposition of ferrate(VI) ion. This process has also been suggested in the decomposition of ferrate(VI) as a function of pH (J. Carr 2008).

The concentration of electrochemically generated ferrate(VI) under different hydroxide concentration at different time intervals of the synthesis is shown in Figure 4. The results show that the amount of generated ferrate(VI) increased with the concentration of hydroxide ions in the solution. The ferrate(VI) concentration increased more than doubled when the concentration of hydroxide increased from 10.0 to 15.0 M NaOH. This agrees with previous studies, which also suggest that

$$2FeO_4^{2-} + 5H_2O \rightarrow 2Fe(OH)_3 + 3/2O_2 + 4OH^-$$  \hspace{1cm} (3)
electrochemically generated ferrate(VI) production is highly dependent on the concentration of hydroxide ion (Márová et al. 2009). Significantly, the results demonstrate that the developed method is suitable to monitor electrochemically generated ferrate(VI).

**Figure 3.** The change in concentrations of $\text{FeO}_2^-$ with time in 12.5 M NaOH. Initial: $1.13 \times 10^{-3}$ M; 2 – after 2 days: $1.04 \times 10^{-3}$ M; 3 – after 4 days: $9.25 \times 10^{-4}$ M; 4 – after 7 days: $7.24 \times 10^{-4}$ M; 5 – after 10 days: $5.25 \times 10^{-3}$ M; 6 – after 15 days: $2.82 \times 10^{-4}$ M; 7 – after 20 days: $1.07 \times 10^{-4}$ M.

**Figure 4.** The monitoring of ferrate(VI) concentration as a function of time under different conditions at 20°C. 1 – 10.0 M NaOH; 2 – 12.5 M NaOH; and 3 – 15.0 M NaOH.
CONCLUSION

A new potentiometric method for the quantitative determination of ferrate(VI) was developed and was also tested in the monitoring of the decay of ferrate(VI) and production of ferrate(VI) in an alkaline solution. The method is simple, fast, and highly accurate with good reproducibility. The method is superior to widely used chromite volumetric method and is suitable for analysis of dilute ferrate(VI) solutions in the $10^{-4}$–$10^{-3}$ M concentration range.

REFERENCES


