ISSN 1430-4171
THE CHEMICAL EDUCATOR
http://journals.springer-ny.com/chedr

10.1007/s00897970134a

Laboratories and Demonstrations

Periodate Titration of Fe(II) in Acid Aqueous Solutions: An Environmentally Friendly Redox Reaction for the Undergraduate Laboratory

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The periodate ion, generated from the dissolution of sodium metaperiodate, is presented as an accurate and reproducible alternative….

An environmentally friendly redox laboratory for the determination of Fe(II) in an acid aqueous medium is presented. This laboratory exercise is an appropriate substitute for the traditional dichromate titration, which is environmentally problematic. This titration method uses the periodate ion as the oxidizing agent and yields results which are as accurate as the dichromate titration. Student success rate in quantitative analysis is better than 80% in two separate laboratory-based trials. This method requires a fairly high degree of operator skill to yield good results, making this a viable laboratory exercise at the sophomore or junior level.

ISSN 1430-4171
http://journals.springer-ny.com/chedr
S 1430-4171 (97) 04134-3

Introduction

Given the ever-increasing cost and concern associated with the use of hazardous chemicals and metals in the undergraduate laboratory, there exists the need to create new laboratories that continue to demonstrate traditional chemical principles but by more environmentally friendly means. The determination of Fe(II) in an unknown sample is a classic quantitative analysis laboratory, which has been performed using of the dichromate ion for generations [1]. Chromium is now considered to be one of the more hazardous metals for down-the-sink disposal, so more appropriate disposal methods must be used [2]. The authors acknowledge the existence of other oxidizing agents and procedures, which have also been in use for years. This would include both the permanganate method and the spectrophotometric EDTA titration of Fe(II) in the presence of salicylate. This paper presents a direct titration method for Fe(II) in acid aqueous solution that involves oxidation–reduction, the oxidizing agent being a nonmetal chemical species. The periodate ion, generated from the dissolution of sodium metaperiodate, is presented as an accurate and reproducible alternative as the oxidizing agent for the determination of Fe(II) [3, 4]. Present environmental concerns about metal-containing oxidizing agents, such as dichromate, chromate, permanganate, and cerate, can be avoided with the periodate method. In addition to the environmental advantages of periodate over chromate, this serves as an excellent example of the use of nonmetal oxidizing agents for quantitative analysis. The titration chemistry is

$$2Fe^{2+} + IO_4^{-} + 2H^{+} \rightarrow 2Fe^{3+} + IO_3^{-} + H_2O \tag{1}$$

The endpoint is determined with diphenylamine sulfonate. Phosphoric acid in the titration system forms complexes with Fe^{3+} so that the $Fe^{3/2+}$ half-cell potential is moved away from the indicator's half-cell potential. There is less chance of the indicator being oxidized before the Fe^{2+} ions are essentially completely oxidized.

The first part of this paper will be devoted to demonstrating the validity of using the periodate ion methodology in substitute of the dichromate ion methodology by directly comparing results of analogous determinations. Once the method is substantiated, a student procedure will be presented so that this method can be conveniently carried out in the undergraduate laboratory.

ISSN 1430-4171
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Experimental

The materials necessary for this laboratory are “Baker-Analyzed” Reagent sodium metaperiodate (label assay ($NaIO_4$) 99.9%), $Fe(NH_4)_2(SO_4)_2 \cdot 6H_2O$ (Thorn Smith Standard, label assay 99.45%), potassium dichromate (Thorn Smith Standard, label assay 100.01%), Fisher Scientific Co. diphenylamine-sulfonic acid sodium salt (0.28 g per 100 mL of water was the indicator), starch indicator, 5 M H_2SO_4, 85% H_3PO_4, potassium iodide (certified A.C.S).

It is necessary to determine the purity of the sodium metaperiodate because it can form a hydrate ($NaIO_4 \cdot 3H_2O$); the following method was used. Several 0.1-g samples of the sodium metaperiodate were weighed to four decimal places, dissolved in about 50 mL of water, and acidified with 12 mL of 5 M H_2SO_4. A 10-mL solution containing 3 g of KI was added. The resulting I_2 was titrated to a starch endpoint using standardized thiosulfate. The thiosulfate had been standardized against standard $K_2Cr_2O_7$ in acid solution (H_2SO_4) reacting with I^- from KI. The resulting I_2 was titrated to a starch endpoint.

The stoichiometric ratio of moles of Fe^{2+} to moles of IO_4^- in acid solution, shown in equation 1**,** was confirmed in the following manner. Assuming 100% purity, a mass of $NaIO_4$ was weighed to four decimal places, dissolved in water, and diluted to volume in a volumetric flask to give a 0.05 M solution. A volume of 5 mL of 85% H_3PO_4 and 5 mL of 5 M H_2SO_4 were diluted to about 50 mL with water. Several 1 g samples of standard $Fe(NH_4)_2(SO_4)_2 \cdot 6H_2O$, weighed to four decimal places, were dissolved in the acid mixture. Assuming 100% purity for the standard $Fe(NH_4)_2(SO_4)_2 \cdot 6H_2O$, a volume of the $NaIO_4$ solution, which was about 1 mL less than the expected endpoint volume, was run into the Fe^{2+} solution. This procedure was necessary due to nonreproducible color changes for the indicator when it added at the very beginning of the titration. A procedure to determine the approximate endpoint is described later. Eight drops of indicator were added and the titration rapidly completed drop-by-drop until the solution turned from essentially colorless to a relatively long-lived transparent violet color (we use “long-lived” to mean that the violet color persists for more than 30 s with vigorous swirling). Most but not all of the violet endpoints were preceded by the solution becoming faintly yellow or yellow-brown. The endpoint color change is best viewed through the side of the titration flask.

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The following method by which the expected endpoint volume could be estimated was developed for the Thorn Smith Fe^{2+}. Several 0.1-g samples of the Thorn Smith unknowns were weighed and dissolved in the previously described acid mixture. Eight drops of indicator were added and the titration rapidly completed drop-by-drop until the solution turned from essentially colorless to the relatively long-lived clear violet color. The yellow or yellow-brown coloration was more pronounced than previously described and so was the violet color.

The Thorn Smith unknowns were then titrated using 1-g samples. Five 1-g samples, weighed to four decimal places, were dissolved in the acid mixture. A volume of the $NaIO_4$ solution ten times that of the estimated endpoint volume less about 1 mL was run into the Fe^{2+} solution. Eight drops of indicator were added and the titration rapidly completed drop-by-drop until the solution turned from essentially colorless to the relatively long-lived clear violet color. The yellow or yellow-brown coloration was usually present.

To establish the accuracy of the procedure, titrations were carried out with standardized dichromate. The Thorn Smith Fe^{2+} unknowns were also titrated as 1-g samples weighed to four decimal places with standard dichromate in the acid mixture solution. Eight drops of indicator were added at the very beginning of a titration and the titration continued until one drop of the dichromate titrant caused the indicator to change color to violet-purple. The violet-purple was, of course, imposed over the light green of Cr^{3+} form by reduction of $Cr_2O_7^{2-}$.

Results and Discussion

The purity of sodium metaperiodate used was determined to be 98.81 ± 0.16 % (four determinations, the average value and standard deviation are reported for all measurements). The established stoichiometric ratio of Fe^{2+} to IO_4^- in an acid solution was found to be 1.990 ± 0.003 (five determinations) which is consistent with the stoichiometry of equation 1. Three different Thorn Smith Fe^{2+} unknowns were analyzed using the periodate titration and their results are shown in Table 1. Each Thorn Smith unknown was titrated five times by the periodate method. A comparison of the accuracy of the periodate method with the traditional dichromate titration was done and those results are also listed in Table 1. Three samples of the each of the three

ISSN 1430-4171
http://journals.springer-ny.com/chedr
S 1430-4171 (97) 04134-3

TABLE 1. Results of Comparative Titrations between periodate and dichromate ions.

Unknown#	Dichromate Titration Results (%)	$NaIO_4$ Results (%)	Thron Smith Certified Purity (%)
1	10.31 ± 0.01	10.36 ± 0.02	10.41
2	8.30 ± 0.01	8.31 ± 0.04	8.36
3	11.16 ± 0.01	11.18 ± 0.03	11.19

Thorn Smith unknowns were measured with the dichromate titration method. The $NaIO_4$ titration values were corrected for percent purity (98.81%).

This method was carried out several times over a two-year period in a quantitative analysis course. The rate of success of accurate analyses (within 2% of the known value) by students was better than 80%. Determinate error in the form of operator skill was the most frequent reason the analyses proved inaccurate. Aside from the normal mistakes due to inexperience, many students did not titrate rapidly enough prior to the degrading of the sample. With practice the titration proved to be an accurate and effective laboratory exercise.

Student Procedure

Materials needed

The materials necessary for this laboratory are “Baker-Analyzed” Reagent sodium metaperiodate (label assay ($NaIO_4$) 99.9%), $Fe(NH_4)_2(SO_4)_2 \cdot 6H_2O$ (Thorn Smith Standard, label assay 99.45%), Fisher Scientific Co. diphenylamine-sulfonic acid sodium salt (0.28 g per 100 mL of water was the indicator), starch indicator, 5 M H_2SO_4, 85% H_3PO_4, potassium iodide (certified A.C.S).

Determination of Approximate Equivalence Volume

Assuming 100% purity, a mass of $NaIO_4$ was weighed to four decimal places, dissolved in water, and diluted to volume in a volumetric flask to give a 0.05 M solution.

ISSN 1430-4171
http://journals.springer-ny.com/chedr
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1. Prepare the aqueous medium by mixing 5 mL of 85% H_3PO_4 and 5 mL of 5 M H_2SO_4. Dilute the mixture to about 50 mL with deionized water.

2. Weigh out about 0.1 g (to four decimal places) of ferrous ammonium sulfate unknown and dissolve the powder in the acid aqueous solution made in step 1.

3. Add exactly 8 drops of the diphenylamine sulfonate indicator and immediately titrate rapidly with $NaIO_4$ titrant to the violet endpoint.

4. Since the actual titration samples will be about 1 g, their endpoint volumes will be about 10 times that determined in step 3.

Titration Procedure

1. Prepare the aqueous medium by mixing 5 mL of 85% H_3PO_4 and 5 mL of 5 M H_2SO_4. Dilute the mixture to about 50 mL with deionized water.

2. Weigh out about 1 g (to four decimal places) of ferrous ammonium sulfate unknown and dissolve the powder in the acid aqueous solution made in step 1.

3. Run in a volume of $NaIO_4$ that is about 1 mL less than the expected endpoint volume.

4. Add exactly 8 drops of diphenylamine sulfonate indicator and immediately titrate drop-by-drop to the endpoint.

5. Repeat this procedure for two additional trials.

Conclusion

The comparison between the traditional dichromate titration and the periodate titration indicated that the periodate method is a valid substitute for the oxidizing agent for the determination of Fe(II) in unknown samples. Due to the complexity of the titration method, a fairly high degree of experience on the student’s part is necessary to carry out a successful determination. This makes this method most appropriate for quantitative analysis courses.

ISSN 1430-4171
http://journals.springer-ny.com/chedr
S 1430-4171 (97) 04134-3

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