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Analytical Quantification of Electrochemical Ferrates for Drinking Water Treatments

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Abstract

Ferrate ions are a highly oxidizing and unstable species which are challenging to quantify and analyze. They are, however, becoming increasingly recognized as an excellent candidate for a number of applications such as for water treatment. A wider acceptance of ferrates requires an accurate assay of the produced ferrates. We report on four analytical methods (existing and new) for quantification of ferrates and discuss their advantages and disadvantages. These methods include titrimetric analysis, and spectrometric techniques such as direct colorimetric, measurements of ABTS or NaI colorimetric. In terms of accuracy, cost, simplicity and time required the modified indirect UV-Vis/NaI method is shown to be the most effective of all the four methods investigated.

KEYWORDS: ferrates, chemical, electrochemical, analytical quantification, titration, UV-Vis absorption, water treatment.

Graphical Abstract

1. Introduction

Currently, many remote and indigenous communities in Canada face inadequate access to drinking water. The NSERC-supported Res'eau WaterNET, is a nationally-funded strategic research network in Canada, which is dedicated to solving remote community drinking water challenges. The network activities include development of innovative treatment processes, water health assessment and monitoring, and governance/risk management. One of the technologies currently under investigation by the Res'EAU Network is the on-site electrosynthesis of ferrates for disinfection processes

Ferrate anions are very suitable for use in drinking water treatment. In particular, they have been shown to be very effective in the removal of Escherichia Coli, fecal coliform, sulphur and nitrogen containing contaminants¹ and toxins².

The suitability of ferrates is a consequence of their unique properties such as: a) a high standard half-cell reduction potential (2.20 V vs. SHE), b) non-toxic reduction byproducts (Fe^{3+}), and c) the simultaneous capacity to act as both an oxidant and coagulant agent³. Ferrate anions can exist in several oxidation states: $[\text{FeO}_4]^{2-}$ in the Fe (VI) state, $[\text{FeO}_4]^{3-}$ in the Fe (V) state or $[\text{FeO}_4]^{4-}$ in the Fe (IV)¹ state. The Fe (VI) state is known to be the most stable and common form, thus the terms ferrate and Fe (VI) are used interchangeably hereinafter. During an oxidation process, the ferrate (VI) ions reduce to Fe (III) ions or ferric hydroxide, hence generating a coagulant⁴. The redox potential of ferrate (VI) ions is greater than other commonly used oxidizing agents in water treatment such as chlorine (1.358 V vs. SHE) and ozone (2.076 V vs. SHE)⁵. Challenges with the use of traditional chlorination treatment processes include high dosages and long contact time, which lead to the formation of carcinogenic disinfection by-products (DBPs) such as trichloromethanes¹. Thus, alternative methods of water disinfection are

highly desired. Ozonation is an alternative disinfection method, but it is ineffective in alkaline conditions and may result in the formation of carcinogenic bromates when bromides ions are present in water¹. The high oxidation potential, disinfectant strength and coagulant properties of ferrates, make it a promising reagent for use in water purification⁶.

Traditional production of ferrates can be achieved by wet or thermal synthetic methods. However, there are a number of disadvantages associated with these methods^{7,8}. In the wet chemical method, chlorine gas is passed through an iron-containing concentrated strong alkaline solution (e.g., NaOH) to generate hypochlorite. Subsequently, iron (III) is oxidized into iron (VI) or ferrate. This process has a relatively low yield (10-15%) and additional reagents and further steps are required to further purify and separate the desired product, leading to high costs¹. On the other hand, dry thermal synthesis of ferrate (VI) is performed at elevated temperatures (370 °C), and is considered to be expensive because of high energy consumption, and it is dangerous due to potential detonation at high temperatures⁸. Since the stability of Fe (VI) is sensitive to temperature, elevated temperatures also increase the decomposition rate of ferrate species.

Electrochemical generation of ferrates is an attractive alternative method of preparation, because it requires neither hazardous reagents nor high temperatures. Ferrate (VI) can be synthesized electrochemically by using either an inert electrode in a Fe (III) solution^{9,10}, or a dissolving iron anode¹¹. The sacrificial anode (dissolving iron anode) is the more widely studied approach. The process is conducted in a highly alkaline solution such as 10 M NaOH (or KOH), with an electric current serving to oxidize the iron to Fe (VI) according to following reaction:

The second approach uses inert high oxidation potential (HOP) anode electrodes to increase the current efficiency⁹. When dissolved Fe^{3+} is used as the source starting component, only three

electrons are necessary to achieve the required Fe^{+6} oxidation state^{3,7} according to the following reaction:

Although, electrochemical synthesis of Fe^{6+} is very promising for water treatment applications, the common quantification methods for the electrochemically-generated ferrates face a number of challenges such as high pH conditions, low concentration of ferrates (μM range), and the presence of Fe^{3+} . Most analytical techniques reported in the literature focus on the analysis of solid ferrates. In this case solid ferrate can be dissolved to make the optimum solution for each measurement method. In the case of electrochemical generated ferrate, the solution properties depend on the synthesis conditions, and in some cases are far from the optimal conditions for ferrate measurement using the conventional methods^{8,12,13}. Different ferrate measurement techniques include: i) the trimetric chromite method¹⁴, ii) amperometric-potentiometric titration^{15,16}, iii) spectrometric techniques such as direct colorimetric^{12,17}, iv) 2,2'-azino-bis(3-ethylbenzothiazoline-6-sulfonate) ABTS¹⁸, and v) iodide colorimetric^{6,8,15}. However, titrimetric analysis is time consuming, and requires at least 10 mL of solution, and it generates large amounts of chemical waste. Some of the challenges facing the colorimetric methods include the interference of colloidal Fe^{3+} oxides with the spectral measurements and poor response to low ($\sim \mu\text{M}$) iron concentrations^{12,13}. The ABTS method has a lower detection limit and is stable in several aqueous matrix systems including synthetic and natural water, however ABTS solution are unstable and must be used within 30 minutes after preparation^{12,13,18}. The conventional NaI method is only applicable for quantification of ferrate in the pH range of 5.5-9.3^{12,13}, making its application in high pH electrochemical ferrate solutions unsuitable. However, given NaI is just a

simple inorganic salt, in comparison with the more complex organic ABTS method, it would be advantageous to improve this technique for use over a wide range of pH for ferrate solutions.

The objectives of the research presented in this paper were: i) to test and modify appropriately different analytical techniques for ferrate quantification in solutions, and ii) to compare these ferrate quantification methods for their cost, accuracy, precision, time, and waste produced. The best quantification technique(s) for ferrate solutions with different pH conditions, in the presence of Fe (III) were determined, in terms of performance, ease of application and economic and environmental impact.

2. Experimental

For the generation of electrochemical ferrates, a two compartment glass cell was used as a bench-top electrochemical reactor to generate ferrates. The cathodic and anodic compartments were separated with a cation exchange membrane (Nafion NR-112). Carbon steel (AISI 1008, Metal Supermarket Vancouver) was used as the anode and stainless steel (SS 304 Metal Supermarket Vancouver) as the cathode. Both electrodes had dimensions of 1.50 cm × 5.0 cm. The cathodic and anodic compartments each had a volume of 80 mL and the electrolyte used was 14 M NaOH, in deionized water (DI) with 18 MΩ purity. The electrochemical experiments were performed galvanostatically at 10 mA cm⁻² for 24 hours, using a Solartron (Model 1470E) potentiostat.

For all the preparation and analytical methods the chemicals used were of analytical grade. Preparation of the required solutions and the sample preparation are discussed below.

For the titrimetric method three different solutions were used: a titrant solution, a standardized solution and the sample solution.

1) Preparation of Fe (VI) containing solution

It was prepared using 10 mL of a solution of 720 g NaOH in 1 liter of water, 5 mL of a solution of 25 g of CrCl_3 in 150 mL of deionized (DI) water, 5 mL DI water and 5 mL Fe (VI) solution

2) Preparation of the sample solution:

25 mL of Fe (VI) solution (for standardization of 25 mL of $\text{K}_2\text{Cr}_2\text{O}_7$ solution), 60 mL of a solution prepared using 20 mL (95-97%) H_2SO_4 and 80 mL water 150 mL DI water 15 mL of an acidic solution containing 150 mL 85% H_3PO_4 were mixed with 60 ml 95% H_2SO_4 and 240 mL water.

3) Preparation of indicator:

For the indicator, 0.32 g of sodium diphenylamine sulfonate were dissolved in 100 mL of DI water.

4) Preparation of titrant:

33.36 g of $(\text{NH}_4)_2\text{Fe}(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$ were dissolved in 1 L of deionized water (about 0.085 N). The precise value for normality of the $(\text{NH}_4)_2\text{Fe}(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$ was determined by using this solution to titrate a known sample solution containing $\text{K}_2\text{Cr}_2\text{O}_7$. The $\text{K}_2\text{Cr}_2\text{O}_7$ solution was prepared by dissolving 1.042 g of the solid per 250 mL of DI water. From the titration of the $\text{K}_2\text{Cr}_2\text{O}_7$ solution using $(\text{NH}_4)_2\text{Fe}(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$, the precise normality was then determined from the volume of $\text{Fe}(\text{NH}_4)_2(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$ titrant required to yield a color change from dark red to green yellowish.

For the ABTS colorimetric method the following solutions are used:

1) Preparation of stock solutions

The stock solution of 2,2'-azino-bis(3-ethylbenzothiazoline-6-sulfonate) (ABTS) reagent was prepared by dissolving 0.1 g ABTS in 100 mL distilled water and stored at 4 °C. The pH 4.1 buffer solution was prepared by dissolving 3.43 mL of CH₃COOH, 0.69 g of NaH₂PO₄, and 2.67 g of Na₂HPO₄ in 100 mL of distilled water to yield 0.6 M acetate and 0.2 M phosphate. The Na₂HPO₄/Borate buffer solution was prepared by dissolving 0.01454 g H₃BO₃ and 0.777 g Na₂HPO₄ in 250 mL distilled water.

2) Preparation of samples for absorbance measurement

5 mL of 4.1 buffer solution, 1 mL ABTS reagent and a ferrate sample volume between 5 µl -25 µl were added to a 25 mL volumetric flask. The Na₂HPO₄/Borate buffer solution was then added until the volume of the solution in the flask is 25 mL. The solution changes color to green due to the formation of ABTS⁺.

For the sodium iodide method, a pH 9 buffer was prepared by combining of 995 mL of 0.1 M Na₂HPO₄ and 45 mL of 0.1 M HCl. A 0.1 M solution using anhydrous NaI (Alfa Aesar) was then prepared with this buffer.

Absorption measurements for the direct UV-VIS, ABTS and NaI methods were performed at 505 nm, 415 nm and 351 nm, respectively, with a Cary 100 spectrophotometer using 1 cm quartz UV cells. The methodologies for all of the different quantification techniques are schematically shown in Figure 1.

3. Results and discussion

3.1. Chemical Titrimetric Fe (VI) Analysis (chromite)

The titrimetric method proposed by Schreyer *et al.* (J. M. Schreyer, G. W. Thompson', 1950) is considered the most accurate method for quantification of ferrates, and has been used as a

standard procedure to bench mark other methods. In this titration method, dissolved ferrates oxidize chromite Cr^{3+} to chromate Cr^{6+}

The generated chromate is then titrated with ferrous ammonium sulphate solution, using sodium diphenylamine sulfonate ($\text{C}_{12}\text{H}_{10}\text{NNaO}_3\text{S}$) as an indicator:

Oxidation reaction

Reduction reaction

In our approach, the Schreyer's titration method for solutions of ferrates has been modified, because the standard procedure measurement for high pH ($\text{pH} > 12$) solutions is not compatible with the indicator (diphenylamine sulfonate). For solid ferrate quantification these changes were not necessary.

Standardization of ferrous ammonium sulphate, following the original Schreyer titration method^{9,10} uses 5 mL of dichromate mixed with 150 mL of H_2O , 60 mL of sulphuric acid solution, and 15 mL of phosphoric acid solution in a 500 mL flask. A drop of the indicator is then used in the stirred solution, which turns the solution color to purple. The standardization of ferric ammonium sulphate is then achieved by titrating it against a known concentration of $\text{Cr}(\text{VI})$ from a solution of dichromate, after which the purple solution turns green.

In the original methodology proposed by Schreyer¹⁴ (Figure 1), when a ferrate solution is analyzed instead of solid ferrate, 5 mL of ferrate solution must be mixed in a solution containing 20 mL of 10 M NaOH, 5 mL of CrCl_3 solution and 5 mL of water. However, the pH is now very

high and out of the range where the indicator works. For the solution to be titrated, a pH range of 0 to 1 is needed to reach the optimum potential of the indicator which is 0.85 V vs SHE in 1M sulfuric acid. For this reason, we avoided using NaOH solution in order to keep the pH low (between 0 to 1) and therefore in the optimal range for the indicator. We refer to this method as the “modified Schreyer method”.

In the modified Schreyer method the solution to be titrated is prepared by first mixing 5 mL of ferrate solution generated at high pH ($\text{pH} > 12$) with 2 mL of chromic chloride solution in a 500 mL flask. Once mixed, 150 mL of DI H_2O , 60 mL of sulphuric acid solution, and 15 mL of phosphoric acid solution are all added to the flask. The previously standardized titrant is now used to determine the concentration of the ferrate solution. At least two trials were performed, and if repeatable results were not achieved, a third measurement was attempted. The following equation was used to calculate the ferrate concentration in the solution:

$$[\text{FeO}_4^{2-}] = (N_t \times V_t) / (3 \times V_f) \quad (7)$$

Where V_t and N_t are the volume and normality of the ferrous ammonium sulphate, 3 is the number of equivalents (number of electrons to reduce Cr^{6+} to Cr^{3+}) per Fe^{6+} and V_f is the volume of ferrate.

Although the titration method (such as the conventional Schreyer method or the modified Schreyer method) is very accurate, it is not the most convenient method, particularly if a high frequency of measurements is required. We find that these titrations take on average about 40 minutes to complete. In addition, this method requires at least 5 mL of ferrate solution for a single measurement, thus making it difficult to do multiple quantifications with small samples, and it involves hazardous chemicals like acids and toxic Cr (VI) ions. The cost of consumables involved for this method is estimated to be about \$30 USD per trial. Therefore, an analytical

technique, which uses a smaller sample size, is accurate, low cost, safe, and environmentally friendly is still highly desired.

3.2. Direct Ferrate UV-VIS (Direct colorimetric method)

In this method absorbance of ferrates in 14M NaOH is measured in the range wavelength between 300 to 700 nm. The absorbance curves were measured for a number of different ferrate concentrations ranging from 0 to 692 μM . Each sample was prepared by adding a 20 μL aliquot of concentrated 0.0173 M ferrate solution to a blank solution of 14 M NaOH.

Figure 2 shows the absorption spectra of the samples with different ferrate concentrations. The ferrate spectra show a maximum at 505 nm and two minima at 390 nm and 670 nm in close agreement with previous studies¹³. The shape of the adsorption curve was not affected by the ferrate concentration.

Figure 3 shows the ferrate absorbance peaks at 505 nm versus the ferrate concentration. The data were corrected for the blank absorbance by subtracting the 14 M NaOH absorbance from the data. Error bars for the absorbance represent the standard deviation calculated from 3 or more measurements.

The direct colorimetric method provides more accurate measurements for concentrations higher than 100 μM . For example for a 17.3 ± 0.1 mM concentration using the titration method, the value for direct UV-Vis measurement was 16.9 ± 0.4 mM, which is in reasonable agreement. This method also requires larger concentrations of ferrate to reach the same levels of absorbance as the indirect spectral methods because the molar absorptive of Fe (VI) at 505 nm is low ($1.5 \times 10^3 \text{ M}^{-1} \text{ cm}^{-1}$, $R^2 = 0.99976$)¹³. In addition, the ferrate solution tends to decompose to yield colloidal Fe (III) oxides, which can interfere with the spectral measurements¹⁹. This problem can

be avoided by centrifuging the sample prior to the adsorption measurement. The cost of consumables involved for this method is low and estimated to be about \$0.1 USD per test.

3.3. Indirect ABTS UV- VIS method

In this method, colorless ABTS reacts with Fe (VI) to form the green radical cation ABTS⁺. The reaction of Fe (VI) with ABTS has a 1:1 stoichiometry in the presence of an excess of ABTS²⁰.

The procedure used by Lee et. al²⁰ involves adding, 5 mL of a pH 4.1 buffer solution, 1 mL of ABTS reagent and a ferrate sample volume between 5 µL and 25 µL to a 25 ml volumetric flask. The Na₂HPO₄/Borate buffer pH 9.1 solution is then added until the volume of the solution in the flask is 25 ml. The solution will change color to green due to the formation of the ABTS⁺ radical. The absorbance of the blank solution and the ferrate solution are measured. Ferrate solutions with different concentrations were chosen to cover a wide range of absorbance.

Figure 4 shows the absorption spectra of ABTS⁺ for different ferrates concentrations. The maxima of the spectra for ABTS occur at about 415 nm in agreement with the results reported by Lee et. al²⁰. However, a small difference in the shape of the absorption curves can be noticed with the presence of a small peak at 390 nm. This may be due to differences in the procedure that were used, Lee et. al²⁰ used solid ferrate dissolved in a pH 9 buffer solution, whereas we used a high pH ferrate solution without a buffer for our experiments.

Figure 5 shows the absorbance peaks obtained at 415 nm for different ferrate concentrations. Error bars for the absorbance represent the standard deviation calculated from 3 or more measurements. The data has been corrected by subtraction of the blank absorbance. The ABTS method leads to highly accurate measurements for low ferrate concentrations as compared with

the titration method. For example, for a 17.3 ± 0.1 mM ferrate concentration (using the titration method) the value for ABTS method was 17.32 ± 0.03 mM.

The ABTS^+ radical has a higher molar absorptivity than ferrate, allowing for better sensitivity and more accurate results with low ferrate concentrations. The molar absorptivity is $3.7 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$ ($R^2=0.99858$) for ABTS. A ferrate solution of $700 \mu\text{M}$ has an absorption value of around 1, whereas ABTS^+ reaches the same value of absorption with a much smaller ferrate concentration of only $35 \mu\text{M}$. This is more than an order of magnitude enhancement in the sensitivity.

One of the major drawbacks of the ABTS method is the instability of the solution. After about 30 minutes, at room temperature, the ABTS solution begins to decompose changing its blank absorption values. When the ABTS solution has a slightly higher blank absorption than 0.02 at 415 nm and in a 10 cm path length (about 0.2 in 10 cm path length) it must be replaced¹⁸. If this decomposition reaction occurs significantly before mixing with ferrate, the technique will not give an accurate reading for ferrate. Therefore, it is essential to use fresh ABTS solutions for accurate determination of the ferrate concentrations. Furthermore, analyzing multiple samples is time consuming and generates a lot of organic chemical waste coming from ABTS. The cost of consumables involved for this method is estimated to be about \$3 USD per trial.

3.4. Indirect NaI UV- VIS method

This is a very promising spectrophotometric method that has been developed for quantification of ferrates. The method uses sodium iodide (NaI) solution to determine concentrations of Fe (VI) at low ($< 10 \mu\text{M}$) concentrations levels in water^{12,13}. It is thus ideally suited for applications of ferrates for water treatment. The method relies on the reaction of the ferrate solution with an excess amount of NaI. Upon reaction the purple color of Fe (VI) disappears instantaneously and a yellow solution appears indicating the formation of I_3^- ions:

308 This method is generally applicable for a pH range of 5.5 to 9.3¹². However, for testing at pH
309 higher than 9 no I_3^- peak was observed. To expand the range of operating pH conditions, we
310 modified the methodology by using a phosphate-based buffer with a pH=9. We used this
311 particular buffer to keep the pH constant, because phosphates stabilizes Fe (III) avoiding the
312 formation of hydroxides that can interfere in the UV-VIS reading¹⁸.

313 In the original methodology, solid ferrate is dissolved only in the NaI solution. In this modified
314 methodology NaI was dissolved to a 0.1M concentration in a buffer solution prepared with 955
315 mL of 0.1 M disodium hydrogen phosphate and 45 mL 0.1 M HCl. A 25 mL volume of this
316 buffer solution is then dosed with aliquots of the ferrate solution to reach concentrations between
317 2 to 30 μM and the UV-VIS spectra were then recorded. Figure 6 shows the absorption spectra
318 for a number of different ferrate concentrations with the maximum absorption peak at about 351
319 nm, in agreement with previous studies¹³. The shape of the absorption curves for I_3^- is not
320 affected by the Fe (VI) dosage range.

321 Figure 7 shows the peak maxima of the absorbance curves versus the ferrate concentration (0 -
322 28.52 μM). The blank absorbance has been subtracted from the data points. The increase in the
323 absorbance peak at 351 nm is linear with respect to the concentration of Fe (VI). The molar
324 absorptivity at 351 nm is 0.0396 $\mu\text{M cm}^{-1}$ ($R^2=0.9972$). This value is slightly higher than the
325 reported value of 0.0291 $\mu\text{M cm}^{-1}$ ^{12,13}. Discrepancies may be attributed to the different
326 experimental conditions such as the higher pH and the use of the buffer solution to keep the pH
327 constant. Nevertheless, the modified NaI method gives an accurate measurement of the ferrate
328 concentration. For example, for a 17.3 ± 0.1 mM ferrate concentration (using titration), the value
329 for the NaI method was 17.27 ± 0.08 mM.

Similar to the ABTS method, the NaI method has been developed due to the higher molar absorptivity of the I_3^- ion compared to ferrate, allowing for higher precision as well as more accurate readings at low concentrations of ferrate. The NaI method requires a 27 μ M solution of ferrate for an absorbance around 1, compared to the 700 μ M concentration required by direct UV-Vis ferrate spectrophotometry. Compared to the ABTS indirect method, the NaI holding solution can be left for extended periods of time without degrading or reacting which makes it feasible method for use in multiple samples requiring more time. The NaI method can also be carried out using just 4 mL of a 0.1 M NaI buffer pH 9 solution, decreasing the quantity of generated waste. The cost of consumables involved for this method is estimated to be about \$0.1 USD per trial.

3.5. Impact of Fe (III) on ferrate solutions quantification.

The impact of Fe (III) on quantification of electrochemically generated ferrate was also studied.

We waited 24 hours keeping the samples at 21° C in order to reduce Fe (VI) to Fe (III) and then study the effect of naturally produce Fe (III) on ferrate degradation. After this period of time, some samples were centrifuged for 20 minutes at 2000 rpm. Centrifuged and non-centrifuged samples were quantified by the chemical titration method as well as by spectrophotometry. The ferrate concentrations of the centrifuged and non-centrifuged samples, using the chemical titration method, were 1.25 mM and 1.11 mM, respectively. The difference between centrifuged and non- centrifuged data could partially be explained by the fact that the non- soluble Fe (III) compounds, which are suspended in the non- centrifuged sample and which

do not react during titration, will be pipetted, thus occupying volume that would otherwise be ferrate solution.

The effect of Fe (III) on quantification of ferrate solutions was also tested using spectrophotometric techniques. For the direct colorimetric method the concentration of the centrifuged ferrate solution was 1.22 mM while the non-centrifuged solution had a concentration of 1.08 mM. The NaI and ABTS methods measure the absorbance of the I_3^- and $ABTS^+$ ions, respectively, which are generated as a result of chemical reactions with ferrate. This allows for the ability to account only for the presence of ferrate while any Fe (III) ions are left unreacted. In addition, the indirect methods used a phosphate buffer were used. Phosphates stabilize Fe (III) by surface complexation²¹, avoiding the formation of hydroxides that interfere in the UV-VIS reading¹⁸.

The NaI and ABTS methods were tested using 5, 15 and 25 μ L concentration aliquots of ferrate. Figure 8 shows the effects of centrifuging on the concentration of ferrate quantified, using the NaI and ABTS methods.

In the case of NaI (Figure 8a) for 5 μ L, the centrifuged ferrate solution resulted in an absorbance of 0.170, compared to the non-centrifuged value of 0.120, corresponding to 4.2 μ M and 3.1 μ M respectively. A similar effect was obtained with the ABTS method, i.e., an absorbance of 0.140 (3.5 μ M) and 0.120 (2.9 μ M) for the centrifuged and non-centrifuged ferrate solutions, respectively.

The impact of centrifuging on the absorbance for the ABTS method here is less pronounced than for the NaI method, however in both cases the difference between centrifuged and non-centrifuged was lower than 1 μ M.

Centrifuging the ferrate solution in the presence of Fe (III) helps in physical separation of insoluble species from the solution and leads to higher absorbance values.

3.6. Comparison of the various different quantification techniques.

Table 1 shows a summary of the four different ferrate quantification methods investigated here.

Parameters considered were as follows : 1) *Preparation Time*: the time necessary for preparing all the solutions required for the quantification method, 2) *Test Time*: the time required to quantify a sample, 3) *Waste per Sample*: chemical waste generated per sample, 4) *Toxicity*: the degree of toxicity for the waste generated, 5) *Stability*: the stability of each solution used in the quantification methods, 6) *Accuracy*: accuracy of the measurement (as compared to the titration method which is considered to be the most accurate method), 7) *Precision*: precision of the measurement (defined as the repeatability of the measurement), 8) *Range*: the range of ferrate concentration over which the quantification method works well, and 9) *Cost per sample*: the cost of all the consumables used per sample measurement, (based on Fisher Scientific's prices).

The following summary points can be made about the different ferrate quantification methods:

1) The chemical titration method for quantification is very accurate, but the method requires large amounts of acid and uses toxic Cr (VI). This method produces large amounts of chemical wastes (chromium, sulphuric acid and phosphoric acid) that are hazardous. The method is also time consuming and inefficient for a) the measurement of multiple samples in a short time period and for b) low ferrate concentration samples.

2) The direct ferrate UV-Vis technique provides adequate accuracy and moderate precision. Due to its low molar absorptivity, it is not possible to quantify samples with concentrations smaller than 70 μM of Fe (VI) by the direct UV-Vis colorimetric method.

3) The indirect ABTS-based spectrophotometric method is a very simple, efficient, and a highly accurate method. However, the ABTS solution is not stable and degradation of the ABTS solution will lead to erroneous results. For longer-time ferrate quantification, a stable solution is necessary.

4) The indirect NaI UV-Vis method is a very good option because it is stable, easy to make, environmentally benign, and does not lead to harmful wastes. For UV-Vis measurements, smaller concentrations of ferrate are required resulting in smaller concentrations of ferrate that can be detected, thus making it ideal for water treatment applications. NaI can be left for extended periods of time without any degradation, making it ideal for ferrate quantification. Furthermore, the costs associated with this technique, compared to the ABTS method, are significantly lower. The cost of NaI is about \$1 USD per gram whereas that of ABTS is about \$60 USD per gram. The waste generated from this method is also significantly less hazardous than that of other quantification methods.

4. Conclusions

We have investigated four different analytical methods for quantification of ferrates with particular attention to the use of ferrates for water treatment applications. These four methods include: 1) chemical titrimetric analysis, 2) and the spectrometric techniques of direct ferrate UV-Vis, 3) indirect UV-Vis ABTS, and 4) indirect UV-Vis NaI. These techniques were initially developed for chemical ferrates which can be dissolved to form the optimal solution concentration for each measurement method. In the research reported here, we have evaluated

the suitability of these “chemical ferrate” methods for “electrochemical ferrates” and made modifications where necessary. The key for successful measurement of electrochemically generated ferrate appears to be the modification of these techniques to keep the pH at the optimum value for each quantification method.

The advantages and disadvantages of each quantification method and their respective modified version(s) were discussed. Although the commonly used ABTS approach is very simple, efficient and highly accurate, the ABTS solution is not stable, which poses a problem for ferrate quantification. For a quantification procedure with a longer required time span, a stable solution is necessary. The modified indirect NaI UV-Vis method is an ideal approach, because it is stable, easy to prepare, it does not lead to harmful or significant waste, it is low cost, and it has high accuracy and precision, and it is suitable for low (μM) ferrate concentrations. In the presence of Fe (III), the additional step of sample centrifuging was shown to be an important step for improving measurement accuracy.

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475 **Figures and Captions**

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(a) Titrimetric Analysis

(b) Direct Ferrate UV-Vis method

(c) Indirect ABTS UV-Vis method

(c) Indirect ABTS UV-Vis method

Figure 1. Flow diagrams for different quantification techniques (a) Titrimetric Analysis, (b) Direct UV-Vis method, (c) Indirect ABTS UV-Vis method, and (d) Indirect NaI UV-Vis method.

Figure 2. Absorption spectra for different concentrations of ferrate in 10 mL of a 14 M NaOH solution, using a 1 cm path length cell.

Figure 3. 505 nm absorbance of ferrate at different concentrations in a 14 M NaOH solution, using a 1 cm path length cell.

Figure 4: Absorption spectra of ABTS⁺ for different concentrations of ferrates using a 1 cm path length cell.

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499 **Figure 5:** 415 nm absorbance of ABTS^+ for different concentrations of ferrate solution, using a 1
500 cm path length cell.

Figure 6: Absorption spectra for different concentrations of ferrate in 0.1 M NaI solution buffered to pH 9, using a 1 cm path length cell.

Figure 7: Absorbance obtained at 351 nm for different concentrations of ferrate in 0.1 M of NaI solution buffered to pH 9 using a 1cm path length cell.

Figure 8: The effects of centrifuging on the concentration of ferrate, quantified using the NaI and ABTS methods.

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Table 1: Comparison of ferrate quantification methods.

<i>Parameter</i>		Chemical Modified Titration	Direct Ferrate UV-VIS	Indirect NaI Modified UV-VIS	Indirect ABTS UV-VIS
<i>Preparation time</i>		1h	15 min	20 mins	30 min
<i>Test Time</i>		30 min	1 min	3 min	5 min
<i>Generated Waste per sample</i>		1L (chromium / acid)	4 to 10 mL NaOH	4 to 25 mL NaI	25 mL ABTS (Organic waste)
<i>Toxicity</i>		High	low	Medium	Medium
<i>UV- Vis</i>	<i>Peak λ</i>	NA	505 nm	351 nm	415 nm
	<i>Molar Absorptivity</i>	NA	$1.5 \times 10^3 \text{ M}^{-1} \text{ cm}^{-1}$	$4.1 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$	$3.7 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$
<i>Stability</i>		low	moderate	high	low
<i>Accuracy</i>		Very good	Moderate	Very good	Very Good
<i>Precision</i>		Very good	Moderate	Good	Good
<i>Range $[\text{FeO}_4]^{2-}$</i>		> 0.2 mM	> 70 μM	>0.25 μM	>0.03 μM
<i>Cost per sample (consumables)</i>		\$30 USD	\$0.1 USD	\$3 USD	\$0.5 USD

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