Ferrate Residual Determination

As performed at the University of Massachusetts, Environmental Engineering Research Laboratory

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Standard Operating Procedures

Ferrate Residual Determination

This guidance document was prepared to assist research assistants, post-docs and lab technicians in measuring residual ferrate in the UMass Environmental Engineering research laboratories. It aspires to outline our standard operating procedures, as they exist at the present time. It also emphasizes elements of quality control that are necessary to assure high quality data. Thanks to Jon Martin, Joe Goodwill and Yanjun Jiang for providing the initial draft. Please help me keep this document current by alerting me to any long-term changes in methodology or equipment.

Dave Reckhow

Faculty QC officer for Ferrate Residual Tests

Scope

This method has been used in the UMass Environmental Engineering Laboratory for measurement of ferrate residual. It has been found to meet data quality criteria with all drinking samples and model compound solutions for which it has been tested. This method should not be used for other media without further validation.

There are many potential sources of interference that the analyst should be aware of. The following list of oxidants can lead to a positive bias:

- TBD

In addition, the presence of catalysts can accelerate the oxidation of ABTS by other oxidants, and thereby produce a positive bias for residual ferrate. These catalysts include:

- Iodide??

Method Overview

Reproduced below for quick reference is a simple, step-by-step outline of our laboratory method for ferrate residual.

Table 1: Summary of Procedure for determination of ferrate residual

1. **Add 5 mL of phosphate buffer to a 25 mL Erlenmeyer flask**
2. **Add 1 mL of ABTS reagent to this**
3. **Add sample to the mark**
4. **Measure absorbance at 415 nm**

Detailed Procedures

Basis for Method

This SOP is based on the method published by Lee et al. 2005. The original publication is included in the appendix of this document. It should be consulted by the analyst prior to running a ferrate residual test for the first time.

Direct Measurement

In pure solutions one can measure the concentration of total ferrate (VI) by using direct spectrophotometry. Studies showed that ferrate (VI) has a peak absorbance at 510nm (Sharma 2010). The molar absorptivity of ferrate (VI) is highly dependent on pH (Lee et al. 2005). The molar absorptivity at pH 9.1 is $1150 M^{-1} cm^{-1}$ (Lee et al. 2005).

Standard solutions can be prepared from commercial, purified ferrate. Studies show that ferrate (VI) in water has the slowest reaction rate between a pH of 9.4 to 9.7 (Sharma 2002; 2010). The decomposition of ferrate (VI) in water is found to follow a first order reaction when the pH is below 9.0 and a second order reaction with a pH above 10.0 (Sharma 2010). The formation of iron hydroxide ($FeOH_3$) will also affect the reaction rate (Sharma 2010). When measuring ferrate (VI), borate and phosphate are often used to control the pH and prevent the formation of iron hydroxide particles (Lee et al. 2005). The 5mM phosphate/1mM borate buffer was prepared by placing 1.3396g of $Na_2HPO_4 \cdot 7H_2O$ and 0.0957g of $Na_2B_4O_7 \cdot 10H_2O$ into a one liter volumetric glass filled with Milli-Q water. After the buffer was mixed, the pH was checked and verified to be 9.2. All mass measurements were made using the analytical balance in the fume hood of Engineering Lab 2 room 301. Between tests, the buffer was stored in a temperature-controlled room set at 4°C. The pH was checked again before using it in the second test and found to be at 9.1.

A convenient target concentration of ferrate stock is 1mM because the theoretical maximum absorbance is $1.15 cm^{-1}$.

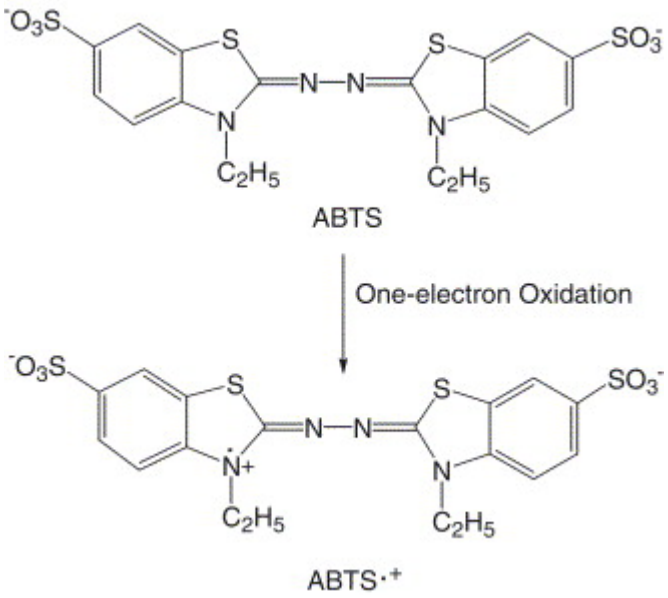

Figure 1. Oxidation of ABTS by ferrate (from Lee et al., 2005)

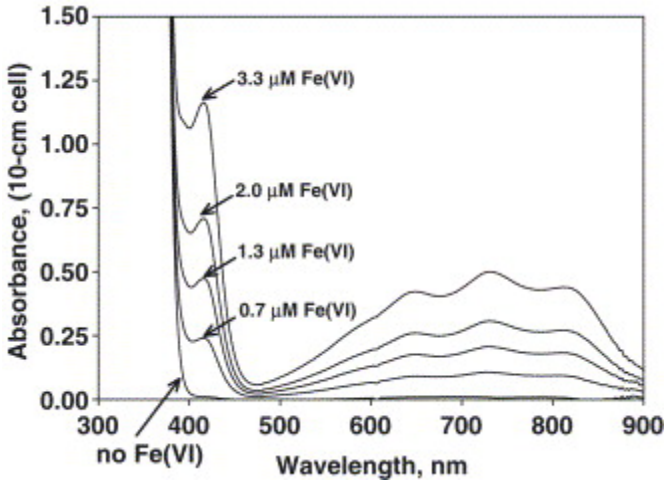

Figure 2. Absorbance Spectra from ABTS-Ferrate Reaction (from Lee et al., 2005)

ABTS Method

The preferred method for measuring ferrate (VI) in treated waters is the colorimetric procedure based on oxidation of 2,2'-azino-bis(3-ethylbenzothiazoline-6-sulfonate) (ABTS). Ferrate (VI) will oxidize ABTS creating a radical denoted as ABTS·+ (Lee et al. 2005). This radical form has a peak absorbance at 415nm. Lee and coworkers

determined that there is a 1:1 stoichiometric ratio between ferrate (VI) and $ABTS^{\cdot+}$. This conclusion allows the absorbance of a solution at 415nm to be directly correlated to the concentration of ferrate (VI) in that solution. The molar absorptivity of $ABTS^{\cdot+}$ is 34,000 (±500) $M^{-1}cm^{-1}$. This high molar absorptivity is responsible for the high level of sensitivity for the ABTS method and a substantially lower detection limit than others such as the triiodide (I_3^-) method (Luo et al. 2011).

The stoichiometric ratio of ferrate (VI) and ABTS in the overall reaction is 1:2. Ferrate (VI) reacts with two ABTS molecules, but produces only one $ABTS^{\cdot+}$.The study rationalized that ferrate (V), which is a product of the oxidation of ABTS with ferrate (VI), reacts with ABTS faster than ferrate (VI) and has the ability to react with different sites on ABTS that do not produce $ABTS^{\cdot+}$. Therefore, this method requires that ABTS be present in a greater than 2:1 molar ratio to the ferrate (VI) being measured.

Since ABTS is used to measure other oxidants (Pinkernell et al. 2000) such as bromine and chlorine, it is likely to be subject to positive bias when these oxidants are also present. Pinkernell et al. measured the absorbance at 405nm rather 415nm for chlorine or bromine species. Ferrate (VI) is still the most reactive oxidant in acidic conditions, seen in *Appendix A,* but other oxidants may react with excess ABTS, creating $ABTS^{\cdot+}$. The natural waters used by Lee et al. did not contain other oxidants. Researchers have not studied the measurement of ferrate (VI) in water that contains multiple oxidants.

Lee et al. also studied the kinetics of the reactions between ABTS and ferrate (VI). Results showed that ABTS at a concentration of 73µM reacted with ferrate (VI) within 0.1 seconds. They also determined that $ABTS^{\cdot+}$ can be a stable molecule, decreasing only 5% within 10hrs of being introduced to distilled water. Stability of $ABTS^{\cdot+}$ did decrease in natural waters, averaging less that 5% decrease over an hour. Their results indicated that the ABTS method is also less affected by the precipitation of ferric ions.

The ABTS method used at UMass follows the same procedure published by Lee and coworkers. Each water sample is mixed in a 25mL volumetric flask with 1mL of

dissolved ABTS and 5mLof 0.6M acetate/0.2M borate buffer solution. The buffer solution is a mixture of 34.3 mL of acetic acid (CH_3CO_2H), 21.3g of Na_2HPO_4, and 6.08g of KH_2PO_4 which was diluted with Milli-Q water into a one-liter volumetric flask. The buffer's pH is 4.3 immediately after mixing. Purified ABTS salt comes in a solid form that must be dissolved in water before use. A mass of 250 mg of diammonium-ABTS salt is dissolved into a 250mL volumetric glass with Milli-Q water.

Based on the experiments conducted by Lee et al., the ferrate stock concentration must be below 35μM. Therefore, 4.6 mg of potassium ferrate is dissolved into 500mL of 5mM phosphate/1mM borate buffer (the same buffer solution used in the previous two tests (pH=9.1)). The characteristics of the stock solution are summarized in *Appendix C*.

Once the ferrate stock solution is mixed, varying volumes (18, 15, 10, 5, 1mL) are distributed into the prepared 25mL volumetric flasks and diluted with Milli-Q water. Following the approach of Lee et al., the concentrations of ferrate (VI) forming the calibration curve ranged from 33.45μM-1.86μM. *Appendix C* shows each calculated concentration. *Figure 3* is an image taken of the five samples. The concentration of ferrate (VI) was determined using the absorbance at 415nm (Lee 2005). Both the calibration curve and the molar absorptivity were used to analyze the concentration of ferrate (VI) in each test. To compare the accuracy of ABTS measurement with direct absorbance (510nm), the absorbance of the ferrate stock without ABTS was measured at the same time as the 15mL of ferrate stock was added to ABTS/buffer solution.

UMass Detailed Procedures

Planning and Sample Volumes

Procedure[1]

1. **Prepare glassware**
   - Remove a 25-mL erlenmeyer flask and either a 25-mL graduated cylinder or a 25-mL volumetric flask from the chlorine bath
   - Rinse both three times with DI water

2. **Add reagents**
   - Add 5 mL of buffer solution to the Volumetriuc flask
     - One measure from the dispenser
   - Add 5 mL of ABTS solution to the Volumetric flask
     - One measure from the dispenser

3. **Add sample**
   - Measure out 100 mL of sample using either a 100-mL graduated cylinder of a 100-mL volumetric flask
     - If necessary, dilute the sample as planned and measure out 100-mL
   - Add the 100 mL sample (or diluted sample) and a stirrer bar to the Volumetric flask.

4. **Measure Absorbance**
   - At 415 nm

Data Analysis & QC Reporting

1. **Calculate concentration of ferrate.**

$$[\mathrm{Fe(VI)}]_{\mathrm{sample}} = \frac{\Delta A_l^{415} V_{\mathrm{final}}}{\varepsilon l V_{\mathrm{sample}}},$$

[1] Typical analysis time is about 30 minutes for a run of 10 samples

where ΔA_l^{415} is the absorbance at 415 nm after correcting for blank in cell of path length l, ε=34,000(±500) M^{-1} cm^{-1}, l the path length of optical cell, V_{final} the final volume after addition of all reagents and buffer (25 mL), and V_{sample} the volume of original sample (1−19 mL).

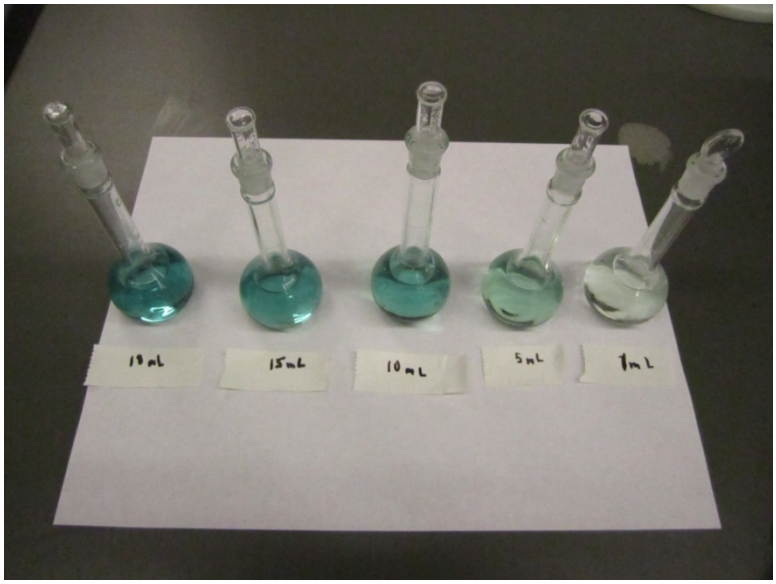

Figure 3: Solutions used to create a calibration curve (Martin 2011).

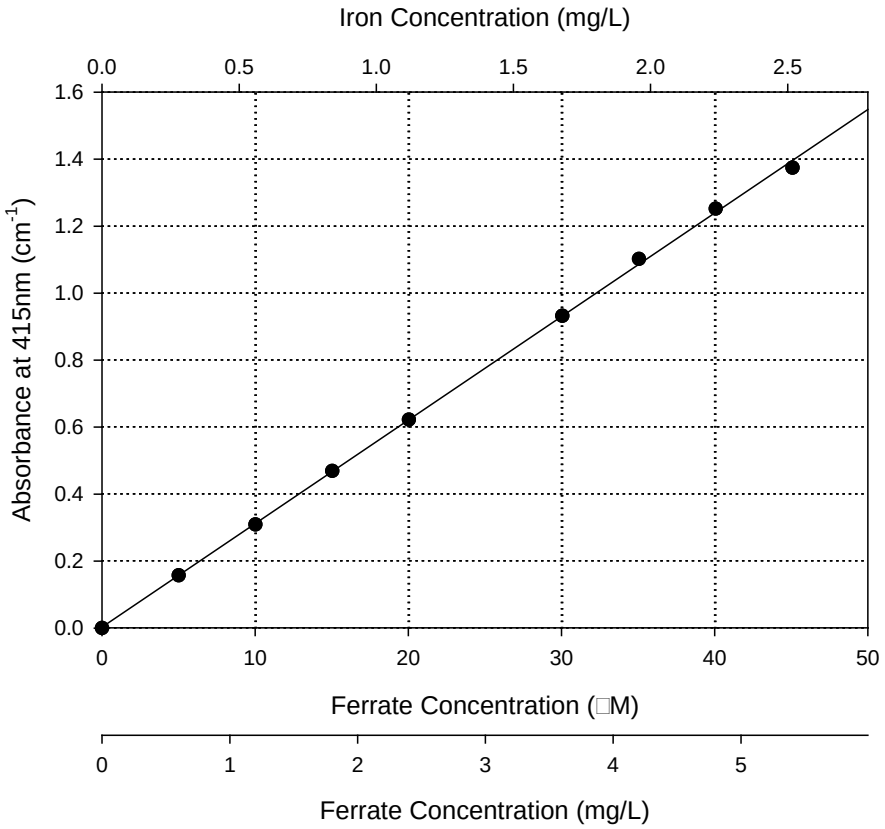

Figure 4. Typical Ferrate Calibration Curve (Jiang & Goodwill, 2013)

2. <u>Lab Water Blanks</u>

At least one in every 15 titrated samples must be a laboratory water blank. If the measured ferrate residual is not within tolerance limits, corrective action must be taken. Results of non-complying lab water blanks and any proposed corrective action must be reported by email to the graduate QC officer or his/her designee if he/she is not available.

- The message must also include the address of the Faculty QC officer in the "cc:" line (reckhow@ecs.umass.edu).
- The subject line of this email message must simply read "QC report for ferrate residual determination"

3. <u>Final Documentation of Ferrate residual QC</u>

- If there is a problem with the lab water blanks, the graduate QC officer or his/her designee then must send an email message to the faculty QC officer stating whether the QC data have been brought within control limits, and if they are not, what actions will be taken.
  - Again, the subject line of this email message must simply read "QC report for ferrate residual determination".

- This must be done as soon as possible, but no later than 24 hours from the time of receipt of the analyst's QC report (per instructions on Lab Water Blanks above).

Clean up

1. Labware

- Any glassware should be rinsed three times with RO water, and once with Super Q water, then placed in a chlorine bath for 24 hours prior to final Super-Q rinse and drying in an oven[2] or immediate use without drying.
    - Glassware in contact with especially contaminated water can be soaked in soapy water overnight prior to rinsing and the chlorine bath
- Rinse the dichromate burette with Super Q water 2 times and leave it on the bench
- Rinse the stirrer bars with super Q water.

2. Reagents

- Dispose of any remaining ABTS, **do not put it back into the bottle**.
- Dispose of any excess solutions/acids and the contents of the Erlenmeyer flask into its corresponding hazardous waste bottle in the hood

Standard Solutions, Solvents and Supplies

Solutions

ABTS Solution

- Purchase ABTS solution, or
- Purified ABTS salt comes in a solid form that must be dissolved in water before use. A mass of 250 mg of diammonium-ABTS salt is dissolved into a 250mL volumetric glass with Milli-Q water.Purchase DPD powder and prepare solution

Phosphate Buffer solution

The buffer solution is a mixture of 34.3 mL of acetic acid (CH_3CO_2H), 21.3g of Na_2HPO_4, and 6.08g of KH_2PO_4 which was diluted with Milli-Q water into a one-liter volumetric flask. The buffer's pH is 4.3 immediately after mixing.

[2] use low temp oven (105 C) for volumetric glassware and high temp (180C) oven for non-volumetric borosilicate glassware

Figure 5: Photo of potassium ferrate in a buffer solution just after mixing (Martin 2011).

3. **Record Keeping & ABTS Management**
   a) Record the new titer along with the date and your name in the log
   b) Discard the commercial reagent when it reaches its expiration date (3 months after purchase), or when its titer falls 20% below its original value, whichever comes first.

Sample Bottles and other labware

All glassware must be rendered free from contamination by ferrate or chlorine demanding substances.

Cleaning of glassware

a) Acid wash by soaking in a covered acid bath[3]
b) rinse thoroughly with DI water
c) place overnight in a covered chlorine bath
d) rinse thoroughly with DI water
e) dry non volumetric glassware in a high-temperature oven[4], and volumetric glassware in a low-temperature oven

Supplies

Table 3. General Supplies

Item	Catalog #	Approx. Price	Approx # used/run[5]
Pasteur Pipettes	Fisher: 13-678-20A	720/ $46.10	10
ABTS reagent			
Phosphate Buffer	Fisher: 5805-32	$22/1L	
DIUF Water	Fisher: W2-20	$32.29	Not normally used
Na_2HPO_3	Fisher: 3374-1		
KH_2PO_4	Fisher: P285-3		

[3] may substitute overnight detergent (e.g, Fisher FL-70, 4%) soak
[4] preferably at 140 C or higher
[5] Assuming about 10 samples analyzed

Quality Assurance/Quality Control

General Approach

Quality assurance is an essential and integral part of a research study. The purpose of any QA plan is to insure that valid and reliable procedures are used in collecting and processing research data. The procedures outlined are designed to eliminate or reduce errors in experiments, sample preparation and handling, and analytical methods. Attention must be paid throughout one's lab work to incorporating the QA plan into all ongoing research projects.

Any equipment and experimental procedures that are used to provide numerical data must be calibrated to the accuracy requirements for its use. Records are to be kept of all calibrations. Calibration schedules are generally established for all aspects of physical and chemical measurements and these must be strictly followed. Physical standards and measuring devices must have currently valid calibrations, traceable to national standards. Most chemical standards are acquired from commercial suppliers, and they should be of the highest purity available. When necessary, standards unavailable from commercial suppliers should be synthesized using the best methodology available.

As a general rule, experiments should be replicated to assure reproducibility. All data reported should include a statement of its uncertainty, and the means for the determination and assignment of such limits. Standard reference materials are used for this purpose where possible. Statistically established confidence limits and an analysis of sources of systematic error are to be used in the absence of experimental demonstration of limits of inaccuracy.

All data will be subject to review by the faculty QC officer before being formally accepted. The analysts involved will certify reports as well as all who review them. All analysts and QC officers must attest that the data and associated information contained in the report are believed to be correct and that all quality assurance requirements have been fulfilled, unless exceptions are approved and noted. Careful and detailed laboratory records will be maintained by each analyst, including source of reagents, meticulously detailed procedures (referring to a traceable SOP, and any departures or clarifications), instrumentation and conditions of analysis, failed experiments, etc.

Regular meetings will be held to review the results and project progress, and to plan further experiments. The results will be analyzed promptly and summarized by means of internal reports or formal reports for external distribution. The experimental and analytical procedures will be reviewed for their performances and changes will be made as necessary. The quality assurance program as described in this document must be strictly observed.

Quality Assurance Objectives

Precision, accuracy and repeatability are evaluated to the extent possible, and where there are existing protocols, held within the control limits set forth in the accepted references (e.g.,APHA et al., 1999; USEPA-EMSL, 1990; ASTM, 1994). In addition to the analysis of sample replicates, a minimum of 10 percent of the time is typically involved in experimentation that is devoted to quality control. The precision or reproducibility of each process test is determined through analysis of sample replicates. These are commonly presented in the form of control charts (e.g. Section 1020B of APHA et al., 1999).

Data generated by the QA program will be incorporated into a Quality Control (QC) archive that is used to monitor the fluctuations in precision and accuracy so that chance or assignable causes of error can be determined. Control charts such as X-charts for simple successive samples or cumulative sum techniques may be employed to record both precision and accuracy data (Taylor, 1987).

General Procedures

General sample collection and handling will be in accordance with the guidelines of Section 1060 of Standard Methods (APHA et al., 1999). All previously established analytical methods used in laboratory research will follow approved methods in the standard compilations (e.g., ,APHA et al., 1999; USEPA-EMSL, 1990, or ASTM, 1994).

Reagent grade chemicals or higher quality when needed will be used throughout the research. Super-Q water (purified by reverse osmosis, deionization, and carbon adsorption) will be used for preparation of reagents, sample blanks, and dilution water. Where necessary, this water will be further purified using batch UV irradiation. All glassware used in the experiments and in analytical analyses will be thoroughly cleaned with a chromium-free sequence of detergent, oxidant and acid to prevent interferences from trace contaminants.

Procedures specific to Ferrate Residual Tests

General QC

Data quality objectives for ferrate demand analysis is assured by: (1) use of blanks; (2) analysis of duplicates; (3) monitoring of ABTS purity; and (4) monitoring of ferrate stock titer.

Two types of blanks may be run daily, where appropriate with each set of samples: (1) laboratory water blanks; and (2) field blanks. This second type of blank is prepared by transporting laboratory reagent to the study site, and transferring it to a labeled sample vial at the time of general sample collection and analysis. In some laboratory experimentation, the laboratory water blank can also serve as a “field blank”.

This outlines our general QA philosophy for process tests. Many specific details relating to the individual procedures may be found in the cited references, and other particulars will have to be adopted as new methods are developed.

Many types of QC procedures are required as indicated in the preceding text. The guidelines below are prepared assuming that samples are run in groups, whereby a "daily" frequency refers to once every day that the analytical method is being used.

Table 4. Summary of QC Elements as Applied to Analysis of Chlorine Residual

Types of Samples or Standards	Purpose	Frequency	Timing	QC data
Laboratory Water Blank	Check for excessive pre-oxidation of DPD or presence of other oxidants	1 for every 15 samples	Beginning of each day and scattered throughout	
Initial Demonstration of Capability (IDC)	To show that an analyst's technique and equipment are adequate for ferrate determination	One set of ferrate solutions when first learning method, otherwise not done		Match to expected ferrate loss, in terms of rate constant and individual sample agreement
Field Reagent Blank (FRB)	Test all field conditions for interferents or contaminants	1 per day, if sampling occurred outside of the lab	mid day	
Spiked blank, or Laboratory Fortified water blank (LFB)	To test analyte recovery in the sample matrix	1 for every 15 samples	Mixed throughout day	% recovery, mean and standard deviation
Unknowns or "samples"	This is what you really want to measure	As many as desired	Mixed throughout day	Reproducibility

Initial Demonstration of Capability (IDC)

This should be done whenever a new student or technician is first learning the procedure for ferrate residual determination and laboratory chlorination. The analyst should record all details on solution preparation, ferrate treatment, and residual determination in a permanent lab notebook. This should be done in such a way that it is understandable to other students and faculty.

1. **<u>Conduct IDC lab experiment</u>**

Under development

QC Protocols after IDC

Table 6 shows a recommended sequence for a typical run of about 30 samples. The first two samples require immediate attention, as they are simple indicators of unacceptable QC. When these show abnormal values, the operator must intervene before proceeding. The problem must be diagnosed, solved and the sequence restarted at sample #1.

Table 6: Typical Ferrate Residual Sequence for a set of 30 samples

Sample #	Sample type	QC objectives
1	Lab Water Blank	To check for gross contamination of water or lab environment, and establish background
2	Laboratory Fortified Water Blank	Contamination and calibration problems
3-17	**Analytical Samples & Duplicates**	
18	Lab Water Blank	Contaminant check
19	Field Reagent Blank	Field contamination
20-34	**Analytical Samples & Duplicates**	
35	Laboratory Fortified Water Blank	Contamination and calibration problems

Quality control data must be analyzed as soon as possible. The best practice is to have the QC data tabulated and evaluated as the run is underway. However, it is recognized that there will be times when this is impossible (e.g., for some complex experiments). QC and calibration data must always be analyzed and reported within 24 hours of completion of a run (see section on Data Analysis & QC Reporting, page 9). Quantitative criteria (Table 7) must be applied, and violations must be immediately reported to the faculty QC officer. The graduate and faculty QC officer along with the analyst will then work out a plan for returning the analysis to acceptable levels of QC.

In several cases, quantitative criteria are based on long term trends, and these may be monitored by means of appropriate control charts. Ferrate stock titers, FAS titers, laboratory water blanks and fortified water blanks are documented over time and may be plotted in this way. All summarized QC data (tabular and graphical) must be kept in a notebook in the Marcus Hall chlorination room (Rm 5D). A duplicate set must be deposited with the faculty QC officer (D. Reckhow).

Table 7: Quantitative Criteria for Judging Data Acceptability

Types of Samples or Standards	Frequency	Timing	QC data Acceptance Criteria	Typical Corrective Action
Spiked sample, or Laboratory Fortified Sample Matrix (LFM)	1 for every 15 samples	Mixed throughout day	Recovery = ±20% of long-term average	❖ Re-run matrix spikes ❖ Re-examine entire run for errors ❖ Possibly change SOP
Super-Q Water Blanks	1 for every 10 samples	Beginning of each day and scattered throughout	Average value ≤0.05 mg/L Maximum value ≤0.10 mg/L	❖ 1. Replace ABTS solution ❖ 2. Check & correct operation of Super-Q system
Field Reagent Blanks (FRB)	1 per day, if sampling occurred outside of the lab	mid day	Average value ≤0.05 mg/L Maximum value ≤0.10 mg/L	❖ 1. Replace ABTS solution ❖ 2. Check for possible contamination from oxidants
Unknowns or "samples"	As many as desired	Mixed throughout day	RSD or RFD for replicate analyses ≤10%	❖ Re-run samples and/or discard outliers[6] until precision can be brought under control

Direct Absorbance for Ferrate Validation

When there are concerns that the ABTS method is in error, direct absorbance measurements can be used as a guide. Diluted ferrate stock solutions can be analyzed for direct absorbance and compared to the figures or table below. Using the molar absorptivities and the pKa for ferrate if appropriate, one can determine an approximate concentration of these stocks.

The direct absorbance approach can also be used for diluted ferrate residuals, provided that the absence of other absorbing substance (e.g., NOM) can be assured.

Sampling Custody

In most cases analyses will be performed by the same person who collected the sample. In any case, the two functions are never greatly separated as chlorine residual must be performed immediately upon collection. Problems with sample custody are therefore, minimized. In general sample collection, handling, and preservation will be in

[6] using Dixon's Q Test, or some logic test (e.g., monotonic increase with timed data series).

accordance with the guidelines of Section 1060 of Standard Methods (APHA et al., 1999).

Sample Collection

Samples are collected in clean borosilicate (e.g., Pyrex, Kimax) glass containers. Containers must be capped with either Teflon-lined septa or ground glass stoppers. Glass containers are cleaned with detergent, followed by 5% sulfuric acid soak, and final rinsing with reagent-grade water. They must then be rendered chlorine-demand-free by soaking in a chlorine bath (see section on glassware cleaning).

Handling and Storage of Standards and Reagents

Ferrate stock solutions must be made fresh immediately before calibration.

Data Reduction, Validation and Reporting

To ensure the accuracy and permanency of collected data, all research data are recorded with permanent ink in bound notebooks and all QC data (precision, accuracy) are recorded in instrument log notebooks. Summary QC graphs and tables are reviewed at least quarterly by the Faculty QC officer to observe noteworthy trends or inconsistencies. These are maintained in loose leaf notebooks for subsequent use in preparing progress reports, final reports, and theses. Major concerns and conclusions are reported to the external Project Officer via the progress reports.

Pages from the laboratory data books are regularly duplicated so that a file copy of raw data can be placed in safe storage in the event that the book is lost or destroyed. At the end of the project, all bound data books and any loose leaf data will be stored by the project team for at least ten years. Summary data files will be put on magnetic media so that statistical analysis of the data can be done. The UMass Environmental Engineering laboratories have several personal computers that can be used for this purpose.

Appendix

Lee, Y., J. Yoon, and U. von Gunten. 2005. Spectrophotometric determination of ferrate (Fe(VI)) in water by ABTS. Water Research 39:1946-1953.