Chlorine Residual Determination

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

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Standard Operating Procedures

Chlorine Residual Determination

This guidance document was prepared to assist research assistants, post-docs and lab technicians in measuring residual chlorine 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. 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 Chlorine Residual Tests

Scope

This method has been used in the UMass Environmental Engineering Laboratory for measurement of chlorine 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:

- Chlorine dioxide (20% interference)
- Bromine and bromamine
- Iodine
- Ozone
- Permanganate

In addition, the presence of catalysts can accelerate the oxidation of DPD by chloramines, and thereby produce a positive bias for FRC at the expense of the combined forms. These catalysts include:

- Iodide

Method Overview

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

Table 1: Summary of Procedure for determination of chlorine residual

1. Add 5 mL of phosphate buffer to a 125 mL Erlenmeyer flask
2. Add 5 mL of DPD reagent to this
3. Add 100 mL of sample
4. Titrate rapidly with FAS until color is discharged (FRC)
5. Add one crystal of KI and titrate a 2nd time (MCA)
6. Add 1 g KI, hold for 2 minutes and titrate a 3rd time (DCA)

Detailed Procedures

Basis for Method

This SOP is based on standard methods #4500-Cl F (DPD ferrous titrimetric method). This published method is included in the appendix of this document. It should be consulted by the analyst prior to running a chlorine residual test for the first time.

Either chlorine or triiodide react with N,N-Diethyl-*p*-phenylene diamine (DPD) to form a relatively stable free radical species with an intense red color. This is then back titrated to the original colorless form with ferrous iron. The detection limit is about 18 ug/L. Oxidized manganese species will interfere. The DPD methods are the most widely used of the chlorine residual procedures (Gordon et al., 1988).

Free residual chlorine is measured first via direct reaction with DPD. Monochloramine will react slowly with DPD through a direct pathway at a rate of about 5% per minute depending on concentration. For this reason mercuric chloride ($HgCl_2$) is sometimes added as an integral constituent in the phosphate buffer. It apparently inhibits the reaction between monochloramine and DPD. Although the reaction mechanism isn't known, it is presumed to act by formation of an unreactive complex with monochloramine.

Combined residuals are measured after addition of iodide. Monochloramine will react quickly with trace quantities of iodide to form triiodide, which then reacts with the DPD. For dichloramine, the reaction is much slower, and relatively large amounts of iodide are needed for the reaction to go to completion. The presence of trichloramine requires some minor modifications of this method (see appendix). Both hydrogen peroxide and persulfate will also oxidize iodide, and can therefore interfere with the combined residual chlorine determination.

The DPD reagent is also subject to base catalyzed oxidation by atmospheric oxygen. For this reason it is kept in an acidified state, and replaced every month. Since the reaction with chlorine and triiodide is best when carried out at neutral pH, a neutral buffer is used and the DPD must be stored separately from the buffer and added at the last minute.

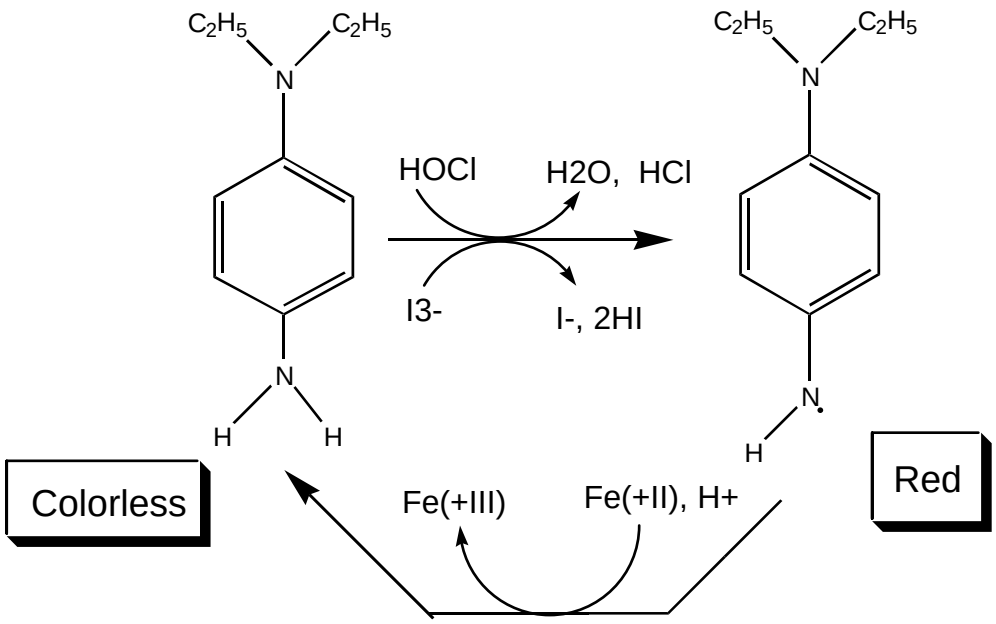


Figure 1
DPD Ferrous Titrimetric Determination of Chlorine

Types of Methods and Definitions

This document contains a detailed protocol for the standard DPD ferrous titrimetric method. In some cases it may be necessary to use a reduced volume test.

Standard Test

When possible the standard volume test should be used. This is widely tested, and is know to provide accurate and reproducible results. It is extremely robust. However, in order to use this test, one must have at least 100 mL of sample volume, and preferably 200 mL (for duplicate determinations). When residuals are expected to be greater than 5 mg/L, the sample must be diluted to bring it back below this value. In this way, less volume is needed for samples with a high chlorine residual. Sample dilution must be done immediately prior to addition of the diluted sample to the reagents. In addition, the highest quality dilution water (DI) must be used, as chlorine demand from even the best DI water can cause a negative bias.

Low Volume Tests

When sample volume is limiting, the test volumes may be scaled down. Most common is the 20% scale, where 20 mL of sample is added to 1 mL of each of the two reagents. This is then titrated in a microburet.

UMass Detailed Procedures

Planning and Sample Volumes

First step is to determine if a reduced volume test is necessary. This requires some planning if many tests are to be run on the same set of samples.

1. **Decide on necessity for sample dilution**
   - Sample must be diluted if residual is in excess of 5 mg/L
   - Extent of dilution is as needed to bring the expected value in the range of 2.5-5 mg/L

2. **Decide on sample volume to be used**
   - Standard test vs. low volume test
   - Depends on total sample volume and amounts of sample needed for other tests

Sample Preservation

Residual chlorine is reactive and therefore must be measured immediately. Do not attempt to store a sample for later residual determination if the intent is to know the residual at the time of collection

Standardization of Titrant[1]

1. **Titrate FAS against dichromate**
   - See section on Standard FAS Titrant (ca. 2.82 mM), page 11, for daily calibration of FAS titrant

Procedure[2]

1. **Prepare glassware**
   - Remove a 125-mL erlenmeyer flask and either a 100-mL graduated cylinder or a 100-mL volumetric flask from the chlorine bath
   - Rinse both three times with DI water

[1] Typical procedure is about 20 minutes
[2] Typical analysis time is about 30 minutes for a run of 10 samples

2. **Add reagents**
   - Add 5 mL of buffer solution to the Erlenmeyer flask
     - One measure from the dispenser
   - Add 5 mL of DPD indicator solution to the Erlenmeyer 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 Erlenmeyer flask.

4. **Titrate**

a) Free Chlorine titration
   i. Quickly titrate with standardized FAS until red color is gone[3]: This is the free chlorine titration (FAS volume A)
      - Volume of FAS added in this 1st step is recorded as volume "A"

b) Monocholoramine titration.
   i. Add one small crystal of KI and mix.
   ii. Quickly titrate until red color is again gone
      - Volume of FAS added in this 2nd step is recorded as volume "B"

c) Dicholoramine titration.
   i. Add about 1 g of KI crystals and mix.
   ii. Place flask in the dark for 2 minutes
   iii. Quickly titrate until red color is again gone
      - Volume of FAS added in this 3rd step is recorded as volume "C"

Data Analysis & QC Reporting

1. **Calculate concentration of chlorine species.**
   i. Standard volume test
      - Use titrant volumes (V_T) and FAS Standardization Factor (FASSF)
      - Multiply the appropriate volume from the table below by the FAS standardization factor to get the particular residual in mg/L
      - If sample was diluted, scale results back to the undiluted sample concentration (i.e., divide by fraction of original sample in diluted sample)

[3] when using one of the chloramination scenarios, it is recommended that a stir bar be used to ensure proper mixing. In this case it is better to fill the bottle a bit more (e.g., ~90% prior to addition of reagents

$$Conc(mg - Cl_2 / L) = FASSF * V_T(mL)$$

ii. Reduced volume test
- Use titrant volumes (V_T), FAS Standardization Factor (FASSF), and sample volume (V_S)
- Multiply the appropriate volume from the table below by the FAS standardization factor and scale it down to get the particular residual in mg/L

$$Conc(mg - Cl_2 / L) = FASSF * V_T(mL) * \frac{100}{V_S(mL)}$$

Table 2. Assignment of Species to Titrant Volumes[4]

Species	Titrant Volume
HOCl + OCl^-	A
NH_2Cl	B-A
$NHCl_2$	C-B

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

At least one in every 15 titrated samples must be a laboratory water blank. If the measured chlorine 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 chlorine residual determination"

3. <u>Final Documentation of Chlorine 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, he subject line of this email message must simply read "QC report for chlorine 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).

[4] for cases where NCl_3 is not significant

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[5] 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

- FAS should not be left in the buret at the end of the day
- Dispose of any remaining FAS, **do not put it back into the FAS bottle**.
- Dispose of excess Potassium Dichromate solution into the Hazardous Waste bottle designated exclusively for this solution (located either in the hood or in the hazardous waste cabinet in the hallway).
- 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

DPD Indicator Solution (ca. 1 M)[6]

- Purchase DPD indicator solution, or
- Purchase DPD powder and prepare solution
    i. Dissolve 1 g N,N-diethyl-p-phenylenediamine oxalate in distilled water containing approximately 2 ml conc. H_2SO_4 and 200 mg Na_2EDTA dihydrate.
    ii. Make up to 1 liter, store in a brown glass-stoppered bottle.

Phosphate Buffer solution

A phosphate buffer is used instead to control pH at near to optimum level for obtaining a clear and stoichiometric endpoint. This buffer also includes EDTA to help control trace metal catalysis. We do not commonly add $HgCl_2$, for control of catalysis from trace levels of iodide. Instead we rely on use of high-purity reagents and scrupulously-clean glassware.

[5] use low temp oven (105 C) for volumetric glassware and high temp (180C) oven for non-volumetric borosilicate glassware
[6] do not keep DPD solutions for more than 2 months

a) In a 250-ml beaker dissolve 24 g of anhydrous Na_2HPO_4 and 46 g of anhydrous KH_2PO_4 in Super Q water.
b) In a 100-ml beaker dissolve 0.8 g of EDTA (disodiumethylenediamine tetraacetate dihydrated) in super-Q water
c) In a 1-L volumetric flask, add the phosphate and EDTA solutions.
d) Dilute to 1 L with Super Q water.
e) Store this solution in a properly labeled bottle in the refrigerator. NOTE: Do not store it in the volumetric flask!

1+5 H_2SO_4

Add one part H_2SO_4 and 5 parts Super Q by volume (i.e., 1:6 dilution). You should make at least 75 mL of this solution. Label the container with your initials and date and place in Refrigerator #5.

Standard FAS Titrant (ca. 2.82 mM)

FAS solution is typically purchased from a commercial supplier[7], however it may also be prepared in the laboratory. In either case it must be standardized the first time a new bottle is placed in use and every 3 weeks from that point. Once the remaining volume of standard FAS has dropped to about 20% of initial, the solution should be discarded[8] and a new one purchased or prepared to take its place. The peculiar concentration of this titrant was selected so that 1 mL will exactly react with 100 mL of a 1 mg/L chlorine solution[9].

1. **Preparation**[10]
   a) Using a clean 1-L volumetric flask, dissolve 1.106 g $Fe(NH_4)_2(SO_4)_2 \cdot 6H_2O$ in about 100 mL super Q water containing 1 ml of 1+3 H_2SO_4.
   b) Cap with ground glass stopper and swirl to mix
   c) Fill to mark with fresh Super-Q water
   d) Cap with ground-glass stopper and mix by inverting 5 times.
   e) Pour off top 10% and discard
   f) Save the remaining 90% for standardization and use in chlorine determination
   g) This solution may be kept in a refrigerator for up to 1 month

[7] e.g., Fisher Scientific Co.
[8] waste FAS in concentrated form must be disposed of as a hazardous waste
[9] note that each mole of residual chlorine reacts with two moles of FAS
[10] only needed if a commercial FAS titrant is not to be used.

2. **Standardization**[11]
   a) Use an Erlenmeyer flask from the chlorine bath, rinsed with super Q water. Add 10 ml of 1+5 H_2SO_4 and 5 ml of concentrated H_3PO_4, and 2 ml of 0.1% barium diphenylamine sulfonate indicator
   b) Add exactly 100 ml of FAS and a stirrer bar
   c) Titrate rapidly with the 0.10 N Potassium Dichromate solution (16.67 mM or 4.9035 g/L) kept in the refrigerator, to a violet end point that persists for 30 seconds. (Use the dedicated burette for $K_2Cr_2O_7$.)
   d) Calculate titer & standardization factor. If it differs by more than 10% from previous determination, repeat standardization
   e) If the two assessments of stock concentration are within 5% average them and use this value. If not, and if the second determination is within 10% of the value determined from the preceding day's test, use the titer from the second determination.

FAS Titer = mL of $K_2Cr_2O_7$ used (should be about 2.82)
FAS Standardization Factor = mL of $K_2Cr_2O_7$ used / 2.82 (should be about 1)

3. **Record Keeping & FAS 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.
   c) FAS titrant should be stored in the refrigerator. It is usually convenient to keep a 1-L disperser of FAS titrant in the refrigerator, and to use this for all standardizations and tests. This should be re-standardized when it is refilled.

Sample Bottles and other labware

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

[11] This relies on a stoichiometry of 6 moles of FAS reacting with one mole of dichromate (i.e., final products are ferric iron and manganese dioxide)

Cleaning of glassware

a) Acid wash by soaking in a covered acid bath[12]
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[13], and volumetric glassware in a low-temperature oven

Chlorine Baths

- 100 mg/L chlorine in DI water
- replaced every week

Supplies

Table 3. General Supplies

Item	Catalog #	Approx. Price	Approx # used/run[14]
Pasteur Pipettes	Fisher: 13-678-20A	720/ $46.10	10
FAS titrant	Fisher: LC145502		
DPD Indicator reagent	Fisher: LC137002		
DIUF Water	Fisher: W2-20	$32.29	Not normally used
Na_2HPO_3	Fisher: 3374-1		
KH_2PO_4	Fisher: P285-3		
Na_2EDTA	Fisher: 02793-500		
H_2SO_4	Fisher: A300-212		
H_3PO_4	Fisher: A242-500		
0.1% Barium diphenylamine sulfonate indicator	Fisher: LC116307		
Potassium dichromate	Fisher: SP170-1		

[12] may substitute overnight detergent (e.g, Fisher FL-70, 4%) soak
[13] preferably at 140 C or higher
[14] 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 Chlorine Residual Tests

General QC

Data quality objectives for chlorination and chlorine demand analysis is assured by: (1) use of blanks; (2) analysis of duplicates; (3) monitoring of FAS titer; and (4) monitoring of chlorine 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 chlorine determination (doubles with chlorination IDC)	One set of model compound chlorinations when first learning method, otherwise not done		Match to expected chlorine demands, 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 chlorine residual determination and laboratory chlorination. The analyst should record all details on solution preparation, chlorination, and residual determination in a permanent lab notebook. This should be done in such as way that it is understandable to other students and faculty.

1. **Conduct IDC lab experiment**
   a) Prepare 2 liters of a 1 mM solution of acetone in super-Q water and buffered at pH 7.0.
      - Acetone is a volatile liquid, so it should be measured out under a hood.
      - Do not use a hood where chlorination experiments are being done. I'd recommend the hood in the Marcus GC room.
      - Use a syringe or pipet to measure a volume.
      - Clean all labware thoroughly that comes in contact with acetone

   b) Prepare 1.5 liters of super-Q water buffered at pH 7.0
   c) From these assemble the following numbers of BOD bottles for incubation
      - 7 bottles for chlorinated acetone
      - 4 bottles for chlorinated buffered Super-Q
      - 2 bottles for chlorinated unbuffered Super-Q

   d) Chlorinate each under the standard UMass conditions for a single point precursor test. (20 C, 20 mg/L chlorine dose)
   e) However instead of incubating all for 72 hours, use the following timed program.

Table 5: Suggested Sampling Schedule for IDC

Incubation time	Sample type
20 min	Super-Q blank
1 hr	Buffer Blank
1.5 hr	Acetone sample
3 hr	Acetone sample
6 hr	Acetone sample
24 hr	Acetone sample
26 hr	Super-Q blank
48 hr	Acetone sample
50 hr	Buffer Blank
72 hr	Acetone sample
74 hr	Buffer Blank
96 hr	Acetone sample
98 hr	Buffer Blank

2. **Evaluate IDC data**
   - Report chlorine residual data to the faculty QC officer (David Reckhow) in an MS excel spreadsheet
   - Include determination of chlorine demand
   - Perform a kinetic analysis and estimate the chlorine consumption rate

3. **Compare with data quality criteria**
   - The faculty QC officer will check the data and compare with the quality objectives for this tests
   - Depending on the results, you may be asked to re-do the test

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 Chlorine 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 8). 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. Chlorine 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 DPD 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 DPD 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[15] until precision can be brought under control

Direct UV Absorbance for DPD Validation

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

The direct absorbance approach can also be used for diluted chlorine residuals, provided that the absence of other absorbing substance (e.g., NOM) can be assured. When several chlorine species are likely to be present, the overlapping spectra can be easily de-convoluted by taking absorbance measurements at several wavelengths. There are many ways of doing this. For example, Mitch and colleagures (2005; [Env. Eng. Sci, 22:6:882]) used molar absorptivities determined by Valentine et al (1986) at 245 nm and 295 nm to estimate concentrations of monochloramine and dichloramine in pre-formed stocks.

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

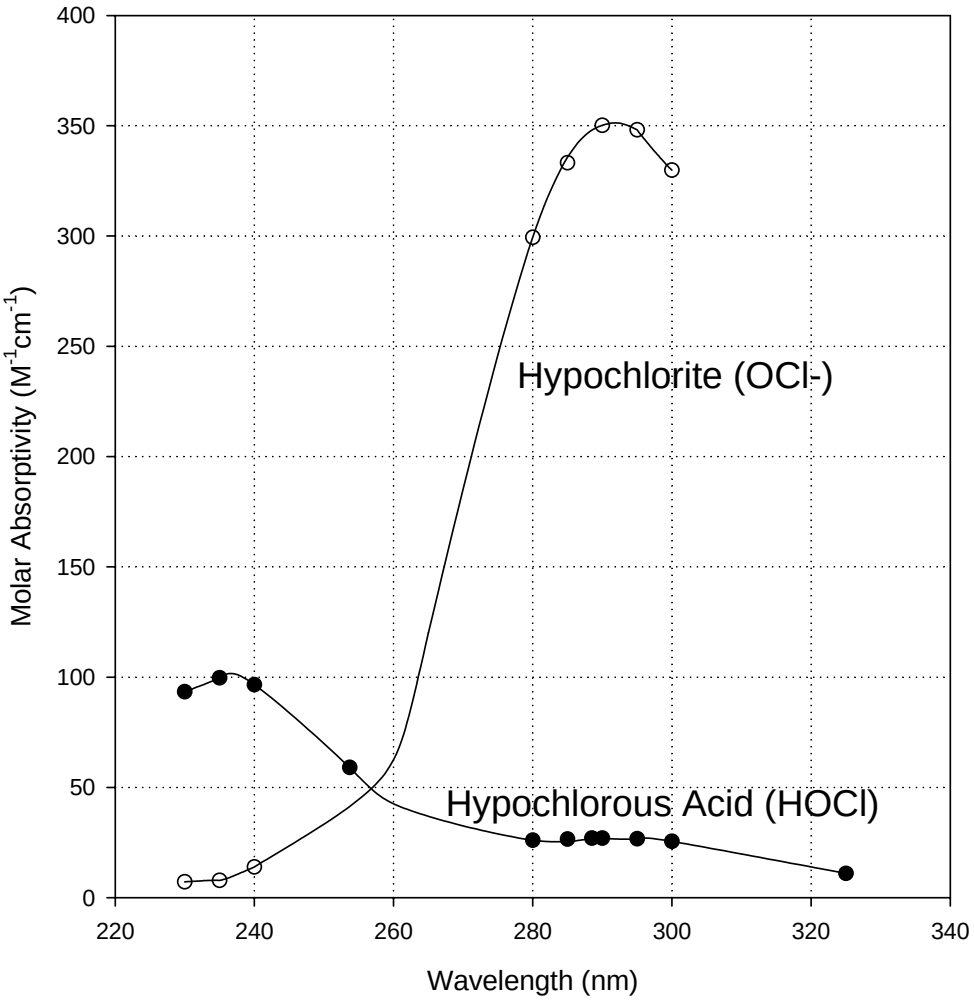


Figure 1. Free Chlorine Absorptivity at 20 C

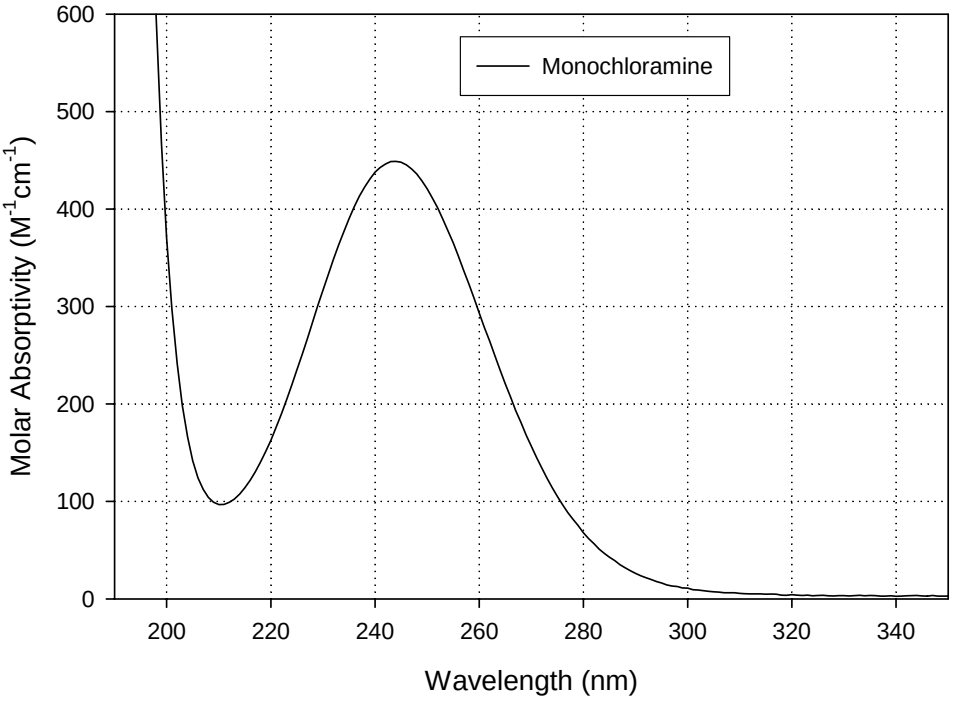
Table 9. Molar Absorptivities of Chlorine Species ($M^{-1}cm^{-1}$) at 20 C[16]

Wavelength (nm)	HOCl	OCl^-	NH_2Cl	$NHCl_2$	ClO_2
203			199	2120	
220			163	67.5	
230	93.4	7.2	317		
235	99.7	7.8	390		
240	96.6	13.9	438		
243			449	245	
245			448 (445)[17]	(208)	
253.7	59.0		378		
257			337	135	
262			264	112	
265			220	110	

[16] Monochloramine by Guanghui Hua, unless otherwise indicated
[17] Values in parentheses are from: Valentine et al., 1986

278			81.5	182	
280	26.0	299.4	67.9		
285	26.55	333.2	42.7		
288.5	27.0		30.4		
290	26.95	350.2	26.2		
294			17.8	276	
295	26.65	348.15	16.1 (14)	(267)	
297			13.1	265	
300	25.5	329.85	11.1	293	
325	11.0		3.5		
335			3.5	73	
345			3.0	39	
360			2.5		1250

Refer to: Hand and Margerum, 1983, for more [Inorg. Chem. 22(10)1449].



Furman and Margerum (1998) [*Inorg. Chem.* 37(17)4321] have confirmed that the molar absorptivity of hypochlorite is 362 $M^{-1}cm^{-1}$ at the 292 nm local maximum. This is probably the most reliable measurement as it was obtained by two different methods.

In the presence of small amounts of bromide, there will be some formation of hypobromite and bromamines. One should be cognizant of this possibility. Some absorptivities of bromine species are shown below.

Table 10. Molar Absorptivities of Bromine Species ($M^{-1}cm^{-1}$) at 20 C

Wavelength (nm)	HOBr	OBr^-	NH_2Br	$NHBr_2$	
232			82	2000 (max)	
278			425 (max)	715	
329		332 (max)			

Hypobromite datum is from Troy & Margerum, 1991 [Inorg. Chem. 30:3538]
Bromamine data are from Lei et al., 2004 [ES&T 38:2111]

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 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

Chlorine stock solutions that are not made fresh daily must be kept in a refrigerator and away from storage of volatile organic chemicals.

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

Standard Methods: 4500-Cl F.

(APHA et al., 1999)