Laboratory Chlorination

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

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Standard Operating Procedures

Laboratory Chlorination

This guidance document was prepared to assist research assistants, post-docs and lab technicians in conducting laboratory-scale chlorination tests 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 go to Caroline von Stechow for providing summaries of our existing practice. 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 Chlorination Tests

Scope

This method has been used in the UMass Environmental Engineering Laboratory for bench-scale chlorination aimed at assessing chemical impacts of addition of chlorine and related disinfectants. It has been found to meet data quality criteria with all raw and treated drinking for which it has been tested. This method should not be used for other media without further validation.

Method Overview

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

Table 2: Summary of Procedure for laboratory chlorination; single point precursor test

1. **Planning (bottles, blanks, buffers, verify UV absorbance is below threshold)**
2. **Prepare and calibrate chlorine stock**
3. **Buffer sample and adjust pH (not done for SDS)**
4. **Partially fill bottle with sample**
5. **Add chlorine and mix**
6. **Fill and cap, headspace-free**
7. **Store in darkness at desired temperature (usually 20 C)**
8. **After requisite incubation period (usually 3 days) remove bottle from incubator**
9. **Pour off subsamples for DBP analysis (these must be quenched)**
10. **Measure chlorine residual**
11. **Determine chlorine demand on samples and blanks and report these data**

Detailed Procedures

Basis for Method

There is no single, generally-accepted method for chlorinating and chloraminating water samples in the laboratory. Nevertheless there is significant precedent in the literature.

Elements of standard methods 2350 (Oxidant Demand) and 5710 (Formation of Trihalomethanes and other Disinfection Byproducts) can be found in this SOP. These published methods are included in the appendix of this document. They should be consulted by the analyst prior to running a chlorination test for the first time.

Types of Methods and Definitions

This document contains detailed protocols on several types of chlorination or chloramination tests. Before adopting one of these protocols, it is important to understand how the various tests should be used and to match the study objectives with the test protocol

Endpoint Measurements

The nature of chlorination or chloramination testing protocols will depend on the measurements that are to be made after treatment. Many of these tests involve the determination of disinfection byproducts as one of the endpoints. When these byproducts include volatile substances (e.g., THMs) as the often do, special precautions must be taken to minimize losses to the headspace. This most commonly calls for protocols with headspace-free vessels and procedures intended to minimize turbulence when headspace-free conditions cannot be met. Most of the following protocols assume that volatile byproducts are among the final analytes. If they are not, many of the specific directions intended to minimize volatilization may be relaxed.

Single point precursor tests versus kinetic tests

These are the most common types of laboratory chlorination tests. They are also the simplest and least labor-intensive.

Types of single point precursor tests

Fixed dose tests

Sometimes generically called "formation potential tests", these are the simplest and most robust of the single point precursor tests. They are distinguished from the others by use of a fixed chlorine dose that is far in excess of the sample's chlorine demand. It is simple, because only the crudest of demand assessments must be made. It is robust, because there is almost no risk of selecting an inappropriate dose. Small differences in residual (due to differences in demand) will have no substantial impact on the final results. It is therefore relatively insensitive to the presence of trace contaminants that consume chlorine.

Fixed dose tests are especially appropriate when the efficiency of treatment processes is to be assessed for precursor removal. They are also the preferred option when assessing precursor levels in untreated natural waters. Unless they are combined with kinetic tests, they should not be used for estimating DBP levels in distribution systems.

The fixed dose tests are the heirs to the original formation potential tests that were designed for maximum THM formation. Maximizing DBP formation is no longer a goal for these tests as the conditions that result in the highest levels of one DBP will not necessarily be the same for another.

At UMass, we use the following fixed dose conditions:

Table 1: Fixed Dose Conditions Used at UMass

Conditions	UMass Standard Method	Garvey, 2001	
Chlorine Dose (mg/L)	20 ±1		
Incubation Time (hr)	72 ±3	168	
Temperature (°C)	20.0 ±1.0		
pH	7.0 ±0.2		
Bromide (mg/L)	ambient		

Fixed residual tests

The fixed residual tests are more complicated than the fixed dose tests. They also require greater attention by the researcher/technician and are inherently less precise. However, they have the advantage of being useful (by themselves) for estimating DBP levels in distribution systems under a wide range of "what if" scenarios. Although a collection of protocols, the fixed-residual tests are sometimes generically referred to as "SDS-type" tests.

The fixed residual tests are often tailored to a specific full-scale drinking water system (city, treatment train, distribution system). In this case the conditions chosen will be based on the system being simulated. These site-specific tests are often called simulated distribution system tests (SDS). Because many studies are conducted without a well-defined system in mind, Summers and co-workers[1] developed a standardized non-specific SD-type test they called the "Uniform Formation Conditions" (UFC) test. At UMass we've used the following fixed residual conditions:

Table 1: Fixed Residual Conditions Used at UMass

Conditions	UFC Test	UNH study	SDS Test
Chlorine Residual[2] (mg/L)	1.0 ±0.4	1.0 ±0.4	Ambient
Incubation Time (hr)	24 ±1	24 ±1	Average[3]
Temperature (°C)	20.0 ±1.0	20.0 ±1.0	Ambient
pH	8.0 ±0.2	7.0 ±0.2	Ambient
Bromide (mg/L)	ambient	ambient	Ambient

Normalized dose tests

Normalized dose tests represent a compromise between the two types presented above. They often take the form of a TOC or DOC normalized test. Here the chlorine dose is linked to the organic carbon level (e.g., 2 mg Cl_2/mg-C).

[1] Summers RS, Hooper SM, Shukairy HM, Solarik G, Owen D. Assessing the Dbp Yield: Uniform Formation Conditions. Journal American Water Works Association 1996; 88: 80-93.
[2] At the end of the incubation time
[3] Representing the average residence time in the system under study

Methods of reagent addition for Chloramination

When using chloramines, two decisions must be made as to the specifics of application

- Chlorine/nitrogen ratio
- Order of addition

The chlorine to nitrogen ratio is very important as it determines the equilibrium oxidant speciation as well as the speed at which these equilibrium concentrations are reached. Ratios that are most commonly used range from 3 mg-Cl_2/mg-N (about 0.6 M/M) to 5 mg-Cl_2/mg-N (about 1 M/M) with 4 mg-Cl_2/mg-N being the most common. Beyond 5 mg-Cl_2/mg-N the breakpoint reactions result in loss of N from the system, and at about 8.5 mg-Cl_2/mg-N the theoretical breakpoint is reached.

The other decision involves the order of addition. There are at least 4 options here (below). With all methods of chloramination, it is important that there is excellent mixing at the time of chlorine addition. This helps to avoid problems of localized imbalances in chlorine to nitrogen ration and excessive nitrogen oxidation.

Pre-ammoniation

This is where ammonia is added first and the sample is thoroughly mixed prior to addition of chlorine. The exact contact time with ammonia prior to chlorination is not important as there is not expected to be any reaction between ammonia and the sample. The real contact time begins at the moment of addition of chlorine (under intense mixing).

Simultaneous Addition

As the name implies, simultaneous addition is when both chlorine and ammonia are added to a sample at the same time.

Pre-formed Chloramine Addition

Here chloramines are formed in a concentrated solution prior to addition to the sample. This mode of addition is intended to present the sample with fully-formed and stable chloramines only. It avoids exposure of precursors to the transient free chlorine that is always present during the early stages of chloramine formation. For this reason, it is expected to form the lowest concentrations of DBPs

Pre-chlorination

This is an option that is widely used in practice. It is essentially a sequential treatment where chlorine is added first for a well-defined free chlorine contact time, after which the residual is converted to chloramines by addition of ammonia. The amount of ammonia added is calculated to produce the desired Cl_2/N ratio, where the numerator in this fraction is the free chlorine residual at the time of ammonia addition. Note that this will be somewhat less than the original free chlorine dose due to the sample chlorine demand. Also, it is quite common to boost the total chlorine residual at this point by adding additional free chlorine In this case the ammonia dose must be adjusted to preserve the desired Cl_2/N ratio. Because there is a substantial free chlorine contact time, this method of chloramination always produces the highest level of THMs and HAAs.

UMass Detailed Procedures

Planning and Sample Volumes

Elements of the chlorination procedure and equipment used will depend on the sample size to be chlorinated. This decision itself depends on the experimental objectives (types of data desired).

1. **Decide on analyses to be performed on chlorinated sample**
   - Volumes needed per reaction time can be determined as follows:

Test	Volume needed per replicate (mL)		Typical # replicates
	Typical	Minimum	
Chlorine residual	100 for fixed resid. test 20-50 for fixed dose test	25 for fixed resid. test 5-10 for fixed dose test	1
THMs	40[4]	10	2
HAAs	30	15	2
TOX	50-100	25	2

   - Typical volume permits use of 300 mL BOD bottle for incubation vessel
   - Minimum volume or reduced analytical program usually permits use of 75 mL BOD bottle for incubation vessel
   - Septum-capped vials may also be used (volumes range from 40 mL to 1 L)
   - Headspace free incubation is needed if volatile analytes are concerned (e.g., THMs or TOX)

2. **Decide on single-point precursor test versus multi-point kinetic test**
   a) Most studies use single-point precursor tests, usually with incubation duplicates (i.e., two bottles of the same sample, incubated and analyzed separately
   b) More detailed DBP studies may require kinetic data for model simulations under a variety of system residence times and other conditions. These call for a multi-point kinetic test.
      - In its simplest form, a single sample is chlorinated and partitioned off into multiple incubation bottles for quenching and analysis after a range of contact times.
      - They may also call for parallel experiments at varying chlorine doses, and possibly pHs, temperatures, and bromide levels.

[4] this is needed to fill a 40-mL vial headspace-free, although only 20 mL of this are used for THM analysis.

3. **Select Reaction/Incubation Vessel Type**
   - For most tests (single point precursor), we use a 300 mL BOD bottle for both reaction and incubation
   - For kinetic tests we often use a properly-sized borosilicate glass vessel with a tap and Teflon stopcock for a reaction vessel, and standard 300 mL BOD bottles for incubation.
   - For tests not involving THM or TOX analysis, vials of almost any size can be used

Sample Preservation

1. **Refrigeration.**
   - Place samples for chlorination in a clean refrigerator designated for storage of drinking water samples
   -

2. **Acidification**
   - Add x ml of concentrated H_2SO_4 to the water sample using an Eppendorf pipette (location?)
   - May also use HNO_3

3. **Addition of biocide**
   - May be required of some protocols

Preliminary Sample Assessment[5]

Here is where judgments are made as to the need for sample dilution or the optimal disinfectant dose. This is a key and time-consuming step for fixed residual tests, but quite simple for the fixed dose tests.

For fixed dose tests: Possible Sample Dilution

a) If sample is well known from previous chlorination studies, follow prior, successful protocols
b) If sample is not well known, estimate demand from UV absorbance
   i. Measure sample UV absorbance
   ii. When using a 20 mg/L fixed chlorine dose, dilute sample if UV absorbance is above 0.30 cm^{-1} so that the final absorbance is about 0.15 cm^{-1}. This guidance comes from our experience with chlorine demands as shown in the figure below.
   iii. If other fixed doses are used, adjust absorbance criteria accordingly.

[5] Not usually necessary for kinetic tests

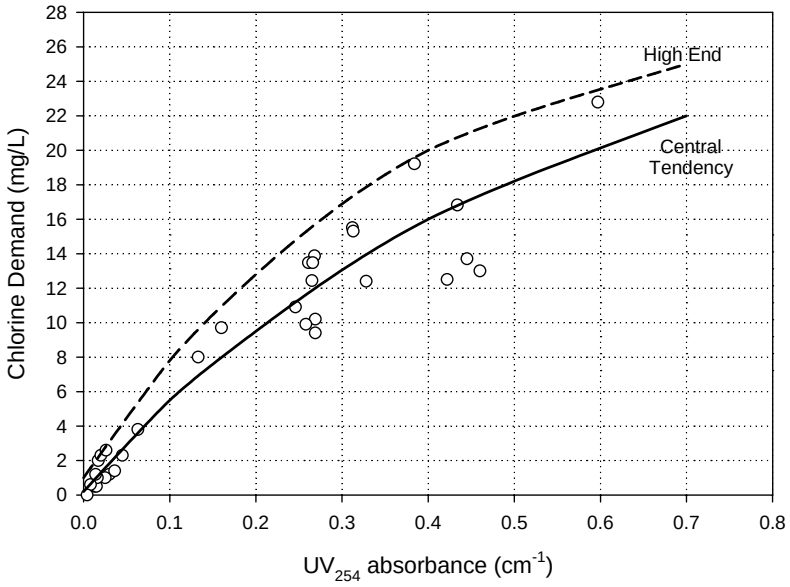


Figure 1: Typical Chlorine Demands under UMass Formation Potential Conditions (72 hrs, 20 mg/L dose, 20C, pH 7)

For fixed residual tests: Necessary Dose

a) Acquire an estimate of the sample's chlorine or chloramine demand
   - Best to use existing demand data for this sample
   - Otherwise use UV absorbance
     - Measure UV absorbance (1 cm pathlength)
     - Estimated demand (in mg/L) from the following equation

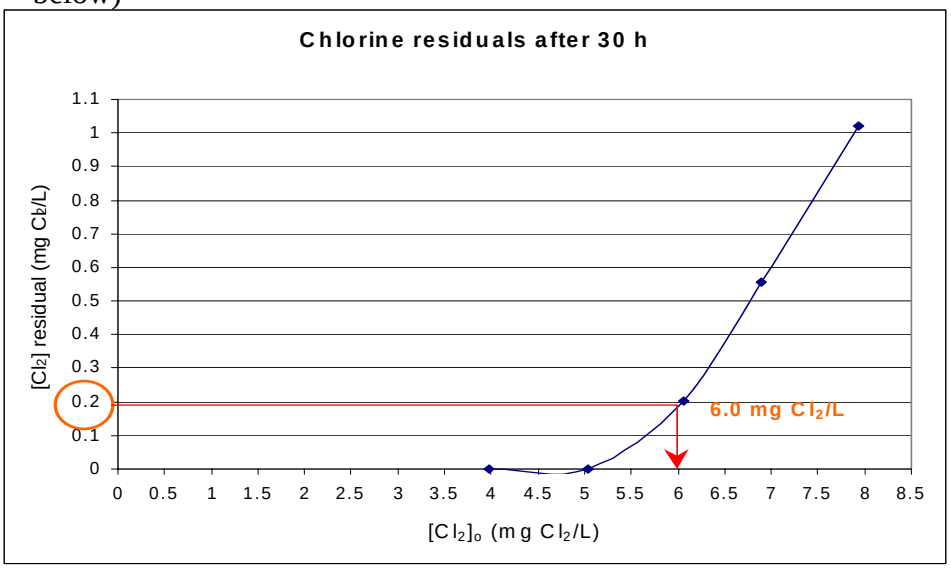
$$demand = 0.5 + 20(UVabs)(\text{incubation time (d)})^{0.4}$$

b) Select a range of doses for demand testing, depending on certainty of demand estimate
   - If estimate is based on existing data for sample, use as few as 3 bottles ranging from 60% to 150% of expected demand
   - If estimate is only based on UV absorbance, use as many as 7 dosed bottles ranging from 30% to 250% of expected demand

c) Conduct demand tests using incubation bottles of convenient size. Use incubation time and other conditions that will be used in the single point precursor test
   - 100 mL volumes of often chosen
   - bottles should be filled and sealed, but headspace-free conditions are not as important

d) After the end of the incubation time, measure only chlorine residual

e) Determine dose for fixed-residual test
- Plot residual versus dose for all bottles on a single set of axes
- Draw a smooth curve through the data
- Find dose point on curve that will the desired residual (see example graph below)



For normal

a) Meas
b) Calculate dose based on desired dose/TOC (or DOC) ratio

Sample Treatment and Incubation[6]

1. **Bring analytical samples to room temperature, and prepare stock solutions**
   - See section on Standard Hypochlorite Solution (ca. 1000 mg/L), page 18, for preparation and calibration of chlorine stock solution
   - See section on Ammonia Solution, page 19, for preparation of ammonia stock solution

2. **Add buffer solution**
   - Add 3.0 mL of buffer solution to each 300 mL bottle, select either:
     - Borate buffer (page 17), or
     - Phosphate buffer (page 18)
   - If final sample volume is not 300 mL, adjust buffer volume added accordingly. Either will result in a 1 mM concentration.

[6] Typical prep time is xx hours for a run of 10 samples

3. <u>Adjust pH to desired level</u>

- Make final pH adjustment with 1M H_2SO_4 or NaOH.

4. <u>Mix sample and disinfectants</u>

a) When the reaction is conducted in the incubation vessel (e.g., single point precursor tests)[7]:

i. Fill vessel about 60% with buffered, pH adjusted sample.[8]
ii. Quickly add the disinfectant reagents at the requisite dose based on the total amount of sample you intend to add (e.g. from part i and iii)
    - The quantity you add should be about 0.5-3% of the total sample volume so that mixing is quick, but the sample is not substantially diluted
    - It is recommended that you us a glass pipet with a repipet bulb (or similar device) that can be momentarily pressurized to rapidly expel the reagents into to the sample for best mixing.

iii. Fill to the top with remaining buffered, pH adjusted sample
iv. Cap so that there is no headspace nor any visible bubbles at the top
v. mix by hand using wrist-action shaking

b) When the reaction is conducted in a larger container and then distributed into separate incubation vessels (e.g., kinetic tests):

i. Fill reaction vessel about 60% with buffered, pH adjusted sample.
ii. Add magnetic stir bar Cap and mix slowly with stir plate
iii. Turn up mixing speed to near maximum and quickly add the disinfectant reagents at the requisite dose
    - The quantity you add should be about 0.05-1% of the total sample volume so that mixing is quick, but the sample is not substantially diluted
    - It is recommended that you us a glass pipet with a repipet bulb (or similar device) that can be momentarily pressurized to rapidly expel the reagents into to the sample for best mixing.

iv. Turn back to slow mix and fill to the top with remaining buffered, pH adjusted sample
v. Immediately start distributing sample to reaction vessels by means of the bottom spout and Teflon stopcock
    - The first ~100 mL must be wasted, as this represents sample that was trapped in the bottom drain and therefore incompletely chlorinated
vi. Fill each reaction vessel to the top and seal head-space free
vii. Often the first reaction vessel is immediately quenched and used as the first kinetic sample

[7] 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

[8]). If THMs or TOX are not to be measured as endpoint analytes, there is no need to avoid headspace-free conditions and those protocols that are intended to lead to headspace-free conditions (e.g., adding sample in two increments). However, you do want to avoid the addition of small volumes of reagent to a full bottle, as it may be lost in overflow.

5. **Place all incubation vessels in a constant temperature incubator at the prescribed temperature**
   - 20°C for most standard single-point precursor tests
   - variable (2°C to 30°C) for multi-parameter kinetic tests

6. **remove and analyze at the prescribed reaction time**
   - 72 hours for most standard single-point precursor tests
   - variable (5 min to 1 week) for kinetic tests
     - with 8 bottles, a common set of times is: 20 min, 1h, 2h, 4h, 8h, 1d, 2d, 4d

Sample Quench and Residual Check

1. **Remove sample from incubator a few minutes before prescribed end of incubation period**
   - Have analytical vials (e.g., for THMs, HAAs, etc.) ready with quench before opening incubation vessel
   - Have chlorine residual materials ready for use

2. **At the prescribed time, open incubation vessel (if using BOD bottles, first pour off any standing water in water seal) and do the following:**
   a) Fill THM vials[9] and seal
   b) Fill HAA vials and seal
   c) Fill TOX vials or other vials and seal
   d) Pour off required volume for chlorine residual measurement and perform titration
   e) Pour off subsample for other measurement required (e.g., UV absorbance scans and pH)
   f) Fill an extra THM or HAA vial for about 20% of the samples (alternating between the two)[10]. This is to be used for determination of spike recoveries.

3. **Measure Chlorine Residual**
   - See SOP for Chlorine Residual

Data Analysis & QC Reporting

1. **Data Analysis begins with titration of chlorine stock.**
   - Record titer of stock

[9] Vials should have just been charged with the requisite quench and preservatives; based on analytical SOPs
[10] The extra volume needed for this should be available whenever dilution is needed for measuring chlorine residual. If dilution is not needed, some accommodation may be necessary for insuring adequate volume for spike recovery samples.

- Back-calculate the %age concentration of the commercial hypochlorite solution and record (see section on: Standard Hypochlorite Solution (ca. 1000 mg/L), page 18)

2. **Lab Water Blanks**
   At least one in every 10 incubated samples must be a laboratory chlorinated blank. If the chlorine demand is not within tolerance limits, corrective action must be taken. Results of lab water blanks and any proposed corrective action must be reported by email to the graduate QC officer (currently Guanghui Hua) 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 chlorination"

3. **Final Documentation of Chlorination QC**
   - The graduate QC officer or his/her designee then must send an email message to the faculty QC officer stating whether the QC data are 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 chlorination".
     - 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. **Evaluate all other QC data**
   - This must be done as soon as possible, but no later than 24 hours from the end of the analytical run. Send an email report in accordance with the analytical SOP.

Data Interpretation

Calculation of chlorine demand is quite simple mathematically. In principle it is just the difference between the chlorine dose and the chlorine residual. However, unwanted chlorine demands are sometimes introduced into laboratory experiments, and where possible these should be minimized. If they persist, they can be eliminated mathematically. This can be done by judicious use of chlorine blank values

When the only source of chlorine demand is believed to be the sample itself, we have the ideal situation where no corrections are needed. In this case we use the following equation:

Chlorine Demand = chlorine dose – sample chlorine residual

When there are chlorine demands arising from:

- Laboratory glassware
- Laboratory air
- Ambient Light energy

We may be able to justify the use of the lab water blank as a control:

Chlorine Demand = lab water blank chlorine residual – sample chlorine residual

When there are chlorine demands that also arise from the:

- Buffer chemicals
- Sample manipulation due to addition of the buffer
- Sample manipulation from measuring and adjusting pH

We would want to use the buffer blank as the control:

Chlorine Demand = buffer blank chlorine residual – sample chlorine residual

If we believe that there are substantial demands arising from impurities in the laboratory water itself, which overwhelm any minor demand from the glassware, laboratory air or light energy, we would want to avoid subtracting this out (unless the sample was actually diluted with the laboratory water). This requires that we further modify the control:

Chlorine Demand = chlorine dose – (lab water blank - buffer blank chlorine residual) – sample chlorine residual

Standard Solutions, Solvents and Supplies

Solutions

Concentrated Borate Buffer solution(ca. 1 M)

A borate buffer is often used instead of the more common phosphate or carbonate buffer. Both of the latter can form precipitates in some samples. Furthermore, carbonate is volatile and may result in pH drift and formation of bubbles. Since borate has a pKa of about 9.2, it does not provide as strong a buffer intensity at neutral pH as phosphate.

a) To 1 liter of Super-Q water, add about 61.8 grams of anhydrous boric acid (H_3BO_3)
b) Heat to a boil while stirring
c) Cool to room temperature
d) Pour off solution if any precipitate exists
e) Add 40% sodium hydroxide solution very carefully until pH is about 7.0 (may require about 6 mL)

Concentrated Phosphate Buffer solution (ca. 1 M)

A phosphate buffer may be used instead of borate if the water is low in divalent cations. Some waters, especially those high in calcium and magnesium can precipitate phosphates when used with these buffers. There is then a danger that organic precursors will precipitate too. However, if this does not happen, phosphate buffers are a better choice than borate at neutral pH. This is because the pKa is at 7.2 (versus 9.2) and therefore provides much greater buffer intensity at neutrality.

a) To 1 liter of Super-Q water, add about 138 grams of sodium phosphate monobasic, monohydrate ($NaH_2PO_4 \cdot H_2O$) [CAS# 10049-21-5]
b) Stir to dissolve
c) Add 40% sodium hydroxide solution until pH is about 7.0 (may require about 20 mL)
d) Store this solution in the dark, and under refrigeration. It should be inspected carefully for any greenish tinge indicating algal growth and discarded if any is detected.

Standard Hypochlorite Solution (ca. 1000 mg/L)

This must be prepared fresh daily and standardized the morning of use.

1. **Preparation**
   a) Half fill a clean 250 mL volumetric flask with Super-Q water
   b) To this add 5.0 mL of the freshest-available Fisher Hypochlorite solution (nominally 5-6%)
   c) Cap with ground glass stopper and swirl to mix
   d) Fill to mark with Super-Q water
   e) Cap with ground-glass stopper and mix by inverting 5 times.
   f) Pour off top 10% and discard
   g) Save the remaining 90% for standardization and chlorination of samples
2. **Standardization**
   a) With a volumetric pipet, remove 1 mL and add it to a 250 mL volumetric flask half filed with super-Q water
   b) Cap and mix by swirling
   c) Fill to mark with super-Q water
   d) Cap with ground-glass stopper and mix by inverting 5 times.
   e) Pour off top 10% and discard
   f) Pour off 100 mL and titrate for residual chlorine
   g) Pour off a second 100 mL and titrate for residual chlorine
   h) Take the average and calculate the stock concentration
   i) Repeat the above procedure, but this time add 1 mL of the stock to 500 mL of super-Q water
   j) If the two assessments of stock concentration are within 5% average them.
   k) If not repeat one of these standardization tests until two agree within 5%.
   l) The calculated stock concentration is then the average of the two retained determinations

3. **Record Keeping**
   a) Back calculate the %age concentration in the commercial hypochlorite reagent
   b) Record this number with the date and your name in the log
   c) Discard the commercial reagent when it reaches its expiration date, or when its titer falls 10% below its original value, whichever comes first.

Ammonia Solution (10,000 mg-N/L)

- Add 19.19 g of reagent grade ammonium chloride (NH_4Cl) to 500 mL of super-Q water

Pre-formed chloramine solution

1. **Add 250 mL of the stock hypochlorite solution to a 1 L Erlenmeyer flask**
2. **buffer at pH 8.5**
3. **Chill to near freezing**
4. **Add stir bar and mix rapidly**
5. **Slowly add the requisite volume of 10,000 mg-N/L NH_4Cl solution, with intense mixing; keep on ice;**
6. **Standardize in accordance with the hypochlorite procedure above**

Sample Bottles and other labware

All glassware must be rendered free from contamination by chlorine demanding substances. In many cases, they are also used for subsequent analysis of DBPs, and must therefore be free from trace halogenated contaminants. Because many OX compounds are volatile, incubation bottles must be filled headspace-free. When volumes of around 300 mL are conventient, standard BOD bottles should be used. For volumes of about 75 mL, mini-BOD bottles may be used. Otherwise septum-capped vials (volumes of 60 mL and below) or larger borosilicate glass bottles can be used.

Cleaning of bottles and other glassware

a) Acid wash by soaking in a covered acid bath[11]
b) rinse thoroughly with Super-Q water
c) place overnight in a covered chlorine bath
d) rinse thoroughly with Super-Q water
e) dry in a high-temperature oven.[12]

Cleaning of septa

- Septa must be washed with detergent, rinsed with Super-Q water, wrapped in aluminum foil and dried in 100ºC oven.

Chlorine Baths

- 100 mg/L chlorine in super-Q water
- replaced every week

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

Supplies

Item	Catalog #	Approx. Price	Approx # used/run[13]
Pasteur Pipettes	Fisher: 13-678-20A	720/ $46.10	10
DIUF Water	Fisher: W2-20	$32.29	Not normally used
Methanol	Fisher: A 454-4		
MtBE	Fisher: E127-4	cs of 4 / $364.84	
Sodium Sulfate	Fisher: S 415-1	cs of 6/ $112.83	
Sodium Bicarbonate	Fisher: S233-500	$25.05	
HAA mix	Supelco: 4-8407	1ml / $32.98	
BDCAA	Supelco: 4-7278	1ml / $31.10	
CDBAA	Supelco: 4-7277	1ml / $31.10	
TBAA	Supelco: 4-7729-U	1ml / $30.35	
H_2SO_4	UMass Stockroom		
Small HAA vials	Fisher: 03-393D		

[13] 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).

Process tests generally involve a measurable outcome (e.g., chemical demand, dose vs. response relationship). The accuracy of some process tests can be determined by testing samples that have been fortified with a standard having a known and measurable influence on the test. Recovery is then calculated as the incremental effect of the presence of this standard as compared to the sample when it is absent. The recovery will be calculated and will be considered acceptable it falls within the control limits determined for the particular test. For new methods developed at UMass or for modifications of existing methods, we will have to establish criteria on acceptable control limits. Where possible, external performance standards will also be run. This serves as a measure of accuracy both for the analysis and for standard preparation. When this is not possible or practical, independently prepared standards will be used instead (e.g., standards prepared by different analysts at different times using different reagents & equipment. These are sometimes referred to as "calibration check" standards).

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 Chlorination Tests

General QC

Data quality objectives for chlorination and chlorine demand analysis is assured by: (1) use of blanks; (2) analysis of duplicates; (3) analysis of a matrix standard; (5) monitoring of commercial hypochlorite titer.

Three types of blanks should be run daily or with each set of samples: (1) buffer blanks; (2) laboratory water blanks; and (3) field blanks. This last 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. In some laboratory experimentation, the laboratory water blank can also serve as a "field blank". Matrix standards (e.g., acetone) are prepared and analyzed by each new RA or technician.

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 7. Summary of QC Elements as Applied to Chlorination and Analysis of Chlorine Demand

Types of Samples or Standards	Purpose	Frequency	Timing	QC data
Laboratory Water Blank	Assess cleanliness of water, reagents, and glassware	1 for every 10 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 laboratory chlorinations	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 sample, or	To test analyte	1 for every 10	Mixed	% recovery, mean

Laboratory Fortified Sample Matrix (LFM)	recovery in the sample matrix	samples	throughout day	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 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.

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 8 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 abnormally elevated demands, the operator must intervene before proceeding. The problem must be diagnosed, solved and the sequence restarted at sample #1.

Table 8: Typical Chlorination Sequence

Sample #	Sample type	QC objectives
1	Lab Water Blank	To check for gross contamination of water or lab environment, and establish background
2	Buffered water Blank	Contamination from buffer
3-10	**Analytical Samples**	
11	Buffered Water Blank	Background chlorine loss
12-21	**Analytical Samples**	
22	Lab Water Blank	Background chlorine loss
23-32	**Analytical Samples**	
33	Buffered Water Blank	Background chlorine loss
34-43	**Analytical Samples**	
44	Lab Water Blank	Background chlorine loss

45-54	**Analytical Samples**	
33		

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 15). Quantitative criteria (Table 9) 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 must be monitored by means of appropriate control charts. Chlorine stock titers, laboratory water blanks and buffer blanks are documented over time 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 9: Quantitative Criteria for Judging Data Acceptability

Types of Samples or Standards	Frequency	Timing	QC data Acceptance Criteria
			❖
Laboratory Water Blanks	1 for every 10 samples		❖ Average value of demand ≤2 mg/L ❖ Max value ≤3 mg/L
Unknowns or "samples"	As many as desired	Mixed throughout day	❖ Replicates = ±10%

Special Check on Chlorine Standardization

When there are concerns that the chlorine standardization 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 figure or table below. Using the molar absorptivities and the pKa for FRC if appropriate, one can determine an approximate concentration.

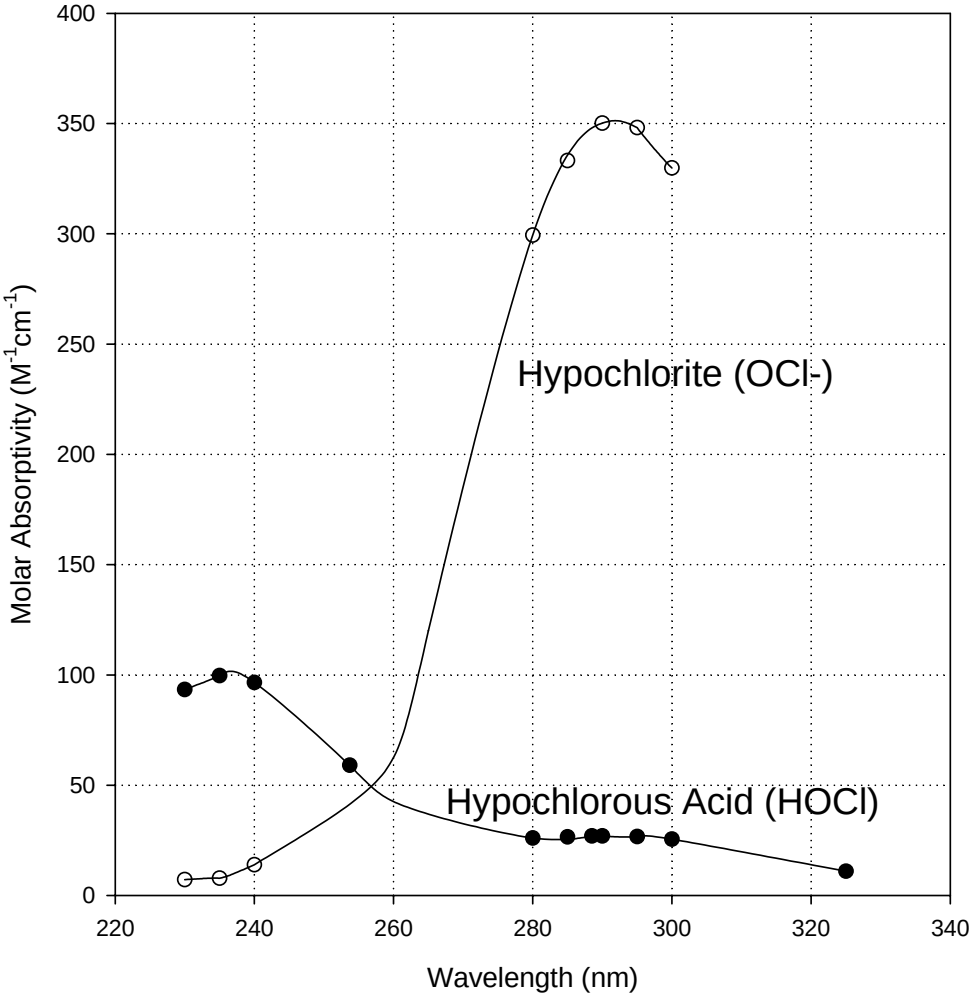


Figure 1. Free Chlorine Absorptivity at 20 C

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

Wavelength (nm)	HOCl	OCl^-	NH_2Cl	$NHCl_2$	ClO_2
203				2120	
220			1200	67.5	
230	93.4	7.2			
235	99.7	7.8			
240	96.6	13.9			
243			445	245	
245			416 (445)[14]	(208)	
253.7	59.0				
257			400	135	
262			423	112	
265			414	110	

[14] Values in parentheses are from: Valentine et al., 1986

278			91	182	
280	26.0	299.4			
285	26.55	333.2			
288.5	27.0				
290	26.95	350.2			
294			27	276	
295	26.65	348.15	(14)	(267)	
297				265	
300	25.5	329.85	25	293	
325	11.0				
335				73	
345				39	
360					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.

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.

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 immediately upon return from the field or after preparation of samples in the laboratory. Problems with sample custody are minimized, because the same people who receive (or sometimes, collect) the samples also analyze them. In general sample collection, handling, and preservation will be in accordance with the guidelines of Section 1060 of Standard Methods (APHA et al., 1999). All samples must be fully labeled with the sample identity, date, and name of researcher.

Sample Collection and Storage

Samples are collected and stored in clean borosilicate (e.g., Pyrex, Kimax) glass containers. Containers must be capped with either Teflon-lined septa or ground glass stoppers. Exceptions are made for large volume samples which may be stored and shipped in clean polyethylene carboys. Glass containers are cleaned with detergent, followed by 5% sulfuric acid soak, and final rinsing with reagent-grade water. These containers are dried in a 150 C oven.

Samples for laboratory chlorination and subsequent analysis must be kept in the dark, and in a refrigerator from the time of disinfectant quench until the start of analysis. Some DBPs and precursors are biodegradable, so a biocide must be added if the samples are to be kept for more than 2 days prior to analysis.

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. Our laboratory has several personal computers that can be used for this purpose.

Appendix

Standard Methods: 2350 & 5710

(APHA et al., 1999)