Laboratory Ozonation

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

File: ozonation SOP ver1
Last Modified: 9/5/2012 5:05:00 PM
Printed: 12/28/2012 10:51:00 AM

Prepared by:
David A. Reckhow 413-545-5392
18 Marston Hall reckhow@ecs.umass.edu
University of Massachusetts
Amherst, MA 01003

Table of Contents

Table of Contents 1
Scope 2
Method Overview 3
Detailed Procedures 4
Basis for Method 4
Types of Methods and Definitions 4
Methods of oxidant addition for Lab-Scale Ozonation 4
UMass Detailed Procedures 6
Planning and Sample Volumes 6
Sample Preservation 6
Sample Pre-Treatment 7
Set-up Contacting and Monitoring Equipment 7
Ozone Contacting 13
System Shut Down 15
Data Analysis & QC Reporting 16
Data Interpretation 16
Sample Bottles and other labware 17
Supplies 18
Quality Assurance/Quality Control 19
General Approach 19
Quality Assurance Objectives 20
General Procedures 20
Procedures specific to Ozonation Tests 21
General QC 21
Initial Demonstration of Capability (IDC) 22
QC Protocols after IDC 23
Sampling Custody 25
Sample Collection and Storage 25
Data Reduction, Validation and Reporting 25
Notes on the Analysis of Ozone and Related Oxidants 26
Standard Methods: 2350 & 4500-Ozone (APHA et al., 1999) 37

Standard Operating Procedures

Laboratory Ozonation

This guidance document was prepared to assist research assistants, post-docs and lab technicians in conducting laboratory-scale ozonation 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 David Pines and 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 Ozonation Tests

Scope

This method has been used in the UMass Environmental Engineering Laboratory for bench-scale ozonation aimed at assessing chemical impacts of addition of ozone and related advanced oxidants. 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 or matrices without further validation.

Method Overview

Because ozonation procedures are so variable, depending on the study objectives, it is not possible to present a simple, step-by-step outline of the method that can be followed in all cases. Therefore, we provide a set of decisions that must be made prior to development of the detailed protocol. These are presented below for quick reference.

Table 1: Planning summary for laboratory ozonation

1. **Decide on preferred method of addition (Batch, Semi, or Fully Continuous)**
2. **Determine best sample volumes given addition method and analytical plan**
3. **Determine need for initiators, scavengers and probe compounds**

Detailed Procedures

Basis for Method

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

Elements of standard methods 2350 (Oxidant Demand) and 4500-Ozone (Ozone Residual) 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 an ozonation test for the first time.

Types of Methods and Definitions

This document contains detailed protocols on several types of ozonation 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

Methods of oxidant addition for Lab-Scale Ozonation

Largely because ozone is a gas, there are three principal methods used for addition of ozone to water:

- Batch
- Semi-continuous
- Fully continuous

Batch Method

The batch method is the simplest of the three. It also permits the greatest accuracy in dosing. However, it can result in an unacceptable level of sample dilution at high doses, and it may not accurately reproduce conditions in full-scale systems that generally use continuous ozonation.

Batch ozonation involves the preparation of an aqueous ozone solution in high purity water (often acidified). This ozone solution is then added to the sample to be treated. Dose is determined by the stock concentration and the ratio of stock volume to

sample volume. Batch ozonation is most commonly used when low doses are applied to environmental samples (e.g., < 2 mg/L) or when synthetic samples (e.g., model compound solutions) are to be treated at doses of 15 mg/L or lower.

Semi-continuous Method

Most laboratory ozonation tests employ semi-continuous ozonation (also referred to as semi-batch ozonation). This method permits the application of any desired dose, although very low doses may be difficult to apply accurately. Semi-continuous dosing is more realistic of conditions used in most full-scale system, however, it requires more careful control (e.g., monitoring of gas concentrations).

Ozone is continuously bubbled through a contactor vessel containing the sample to be treated. During this period, the sample is static, although it may be agitated with a magnetic stirrer. Dose is determined by the ozone content in the gas stream, the gas flow rate, the sample volume and the bubbling time.

Fully Continuous Method

Fully-continuous ozonation requires a flow-through reactor where untreated sample is pumped or gravity fed on a continuous basis, and treated sample exits continuously. Ozone is bubbled though at the same time. The sample flow can either be co-current or counter-current with respect to the ozone bubble path.

This method is less suitable for laboratory work as it requires larger volumes of sample than is typically practical in this setting. However, continuous ozonation is the method of choice in pilot-scale testing.

UMass Detailed Procedures

Planning and Sample Volumes

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

1. **Decide on analyses to be performed on ozonated sample**

- Volumes needed per reaction time can be determined as follows:

Test	Volume needed per replicate (mL)		Typical # replicates
	Typical	Minimum	
Aldehydes	60	30	2
Keto-acids	80	40	2
Chlorination followed by: DBP analysis	400	100	2
COD	50	10	2
UV-Vis absorbance	10	5	1
TOC	20	5	1
PPCPs/EDCs	2000	500	1

- Typical volume needs permit use of 500 mL, 1 liter or 2 liter glass contacting vessels

2. Decide on method of application

a) Most studies use batch or semi-continuous method
b) Some applied tests may best use the fully-continuous method

3. Select Reaction/Incubation Vessel Type

a) Most studies use a 1-liter borosilicate glass reactor
b) Some process testing may require larger vessel

Sample Preservation

1. Refrigeration.

- Place low TOC samples for ozonation in a clean refrigerator or cold room designated for storage of drinking water samples
- Wastewater samples may be placed in non-drinking water refrigerators or suitable cold room

2. Acidification

- Each experimental protocol will be different with regard to sample acidification and general preservation. If needed, a protocol similar to the following could be adopted
  - Add 0.1 ml of concentrated H_2SO_4 to 1 liter water sample using a glass pipette
  - May also use HCl or HNO_3

3. Addition of biocide

- Usually not needed

Sample Pre-Treatment

1. Bring test samples to testing temperature, and prepare glassware

- Most ozonation tests are run at room temperature
- If other temperatures are needed, it may be necessary to use a jacketed reactor with a constant temperature circulating water bath

2. Add buffer solution or just adjust pH

- A buffer may or may not be necessary depending on the particular experimental objective
- If needed, we most often use 5 mM (diluted) concentrations of:
  - Phosphate (for pH 6.5-7.7)
  - Borate (for pH 7.7-8.5)
- Precise pH can be adjusted with small amounts of a strong acid or base (e.g., 1M HCl, 1M H_2SO_4 or 1M NaOH)

3. Add probe compound

- These are frequently used for monitoring hydroxyl radical exposure during ozonation of AOP treatment
- The compound of choice at UMass is *para*-chlorobenzoic acid (pCBA)
  - Typically at 0.5 µg/L initial diluted concentration

Set-up Contacting and Monitoring Equipment

General

1. Turn on UV spec to warm up instrument.

2. Turn on cooling water

- Lever to the left of the ozone generator

3. Turn on Oxygen (gas "J")

- Make sure oxygen cylinder is connected to gas "J" tubing
- Open value on oxygen cylinder all the way.
- Adjust pressure to between 7-8 psi (read pressure off of ozone generator and not the regulator on the cylinder) by using long thin handle on O_2 regulator.
- It may take some time to stabilize.
- Calibrate spec first because this will destabilize the pressure again.

4. Verify gas flow at manifold

- Make sure dial between wall and O_3 generator is pointing toward the UV-spec.

5. Set up spec for measurement

- Once the UV-spec has stabilized at 750 nm, type "253.7" and hit "GOTO λ" button
- put the right cuvette holders in place.

Batch Method

1. Start Production of Ozone

- Start ozone generator by activating the ON switch
- Adjust voltage between 60-90 V.

2. Place Acidified Milli-Q Water in a contacting vessel

a) slightly acidify high purity lab water with about 0.1 mM HCl
b) cool to near freezing
c) add to a vessel of appropriate size (it need not have a ground glass joint to match the sparger)

Automated Semi-Continuous Method

1. Turn on UV spec to warm up instrument.

2. Turn on cooling water

- Lever to the left of the ozone generator

3. Turn on Oxygen

- open value on oxygen cylinder all the way.
- Adjust pressure to between 7-8 psi (read pressure off of ozone generator and not the regulator on the cylinder) by using long thin handle on O_2 regulator.
- It may take some time to stabilize.
- Calibrate spec first because this will destabilize the pressure again.

4. Verify gas flow at manifold

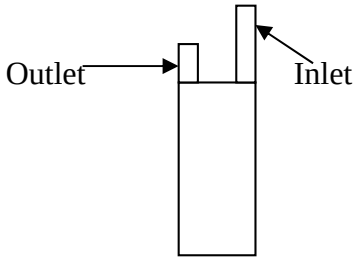
- Make sure dial between wall and O_3 generator is pointing toward the UV-spec.

5. Set up spec for measurement

- Once the UV-spec has stabilized at 750 nm, type "253.7" and hit "GOTO λ" button
- put the right cuvette holders in place.

6. Connect flow-through UV cells

- Hook up UV cells for ozone, with inlet ports on the right.
- Do NOT push the cells all the way down in the holder on the UV-spec, the pathlength is less than that of regular cells, so these cells need to be sticking up a couple of millimeters.
    a) Connect outlet tubing with tubing from generator marked "waste".
    b) Connect inlet tubing with flexible plastic tubing from the O_2 tank in order to zero UV-spec.
    c) Turn on oxygen with small black knob and push "AUTOZERO" on UV-spec, turn off oxygen
    d) Connect the inlet of the back cell with tube marked "O_3 reactor".
    e) Connect the inlet of the front cell with tube marked "O_3 generator".



7. Turn dial under the hood from "VENT" to "CHANNEL 1".

8. Generate flow calibration curve if necessary.

a) Make sure dial between wall and O_3 generator is pointing toward the hood.
b) Hook up inlet O_3 line (the one without the label) to tube on flowmeter.
c) Turn flowmeter on and make sure it is not reading split flow, but rather total flow. Add more water or soap to bulb if necessary.
d) Adjust flow by turning dial on flow regulator on the hood. You can judge it by the position of the upper ball.
e) For each adjustment, note position of upper ball and corresponding flowrate (for example, when upper ball is at 7, flowrate is approximately 115 mL/min). After several points are measured, a calibration curve can be created for future use.

9. Start Production of Ozone

- Start ozone generator by activating the ON switch
- Adjust voltage between 60-90 V.

10. Turn on computer

- Must wait for it to warm up.

11. Place sample in reactor

- Fill reactor with sample water to top and replace diffuser and thermometer
- turn on stirrer
- Note: reactor must always be filled with water, either sample water or Super-Q, to prevent electrode in the back from drying out.

12. Initiate Data Collection program on computer

a) On computer, launch the program by typing the following:
   - cd
   - cd qb45
   - qb /L c:\das800\std\d800qb45 cdm2
b) Go to run menu and choose start. Fill in data as follows:
   - Name the file
   - Time between data points (sec)→**10 or 15**
   - No. of data points→**1000**
   - Gas Flowrate (mL/min)→**whatever flow is set at (130, for example)**.
   - Water Volume (L)→**2.34 (or if using a different reactor, input that volume)** DO NOT PRESS ENTER AFTER ENTERING VOLUME!!!

13. Initialize off-gas system

a) Turn main manifold valve from "CHANNEL 1" to "VENT"
b) Connect gas inlet tube in hood (Teflon tube without label) directly to the gas outlet tube (teflon tube with red and white label) using a short piece of glass tubing
c) Turn main manifold valve from "VENT" to "CHANNEL 1"
d) Watch spectrophotometer reading
e) When it stabilizes, record that reading in your lab notebook
f) Turn main manifold valve from "CHANNEL 1" back to "VENT"
g) Remove connecting tube from inlet and outlet tubing

Manual Semi-Continuous Method

1. Turn on spectrophotometer to warm up instrument.

- There is an on-off switch on the back of the instrument on the right hand side
- Turn on the UV lamp switch on the front

2. Turn on cooling water

- Lever along the wall on the far right of the ozone generator. You should hear the water draining in the hood.

3. Turn on Oxygen

- Open value on oxygen cylinder all the way outside the room in the tank farm.
- Adjust pressure to between 3-8 psi (read pressure off of ozone generator and not the regulator on the cylinder) by using long thin handle on O_2 regulator. Once this is adjusted, don't change it as it affects ozone production rate
- It may take a few minutes for the gas flows to stabilize.

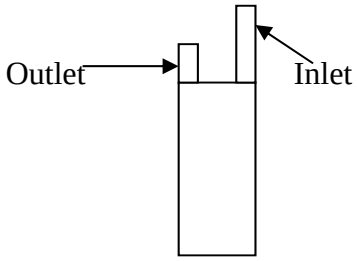
4. Set up spec for measurement

- Once the spectrophotometer has stabilized at 750 nm, type "253.7" and hit "GOTO λ" button
- put the 0.2 cm flow-through cuvette holders in place.

5. Connect flow-through UV cells

- Hook up UV cells for ozone, with inlet ports on the right.
- Do NOT push the cells all the way down in the holder on the UV-spec, the pathlength is less than that of regular cells, so these cells need to be sticking up a couple of millimeters.

a. Connect outlet tubing with tubing from generator marked "waste".
b. Connect inlet tubing with flexible plastic tubing from the O_2 tank in order to zero the spectrophotometer
c. Turn on oxygen with small black knob and push "AUTOZERO" on UV-spec, turn off oxygen
d. Connect the inlet of the back (reference) cell with tube marked "O_3 contactor".
e. Connect the inlet of the front (sample) cell with tube marked "O_3 generator".



7. Prepare Stabilization Contactor.

a. Fill one pyrex glass contactor as close to the top as possible with acidified Mill-Q water (minimize headspace, but don't allow carry-over of water to the outlet tube), and a large magnetic stir bar.
b. Place pyrex contactor on magnetic stir plate.
c. Connect contactor to inlet (CHANNEL 1) and outlet (to spec) tubing
d. Turn 4-way valve on manifold in hood from "VENT" to "CHANNEL 1"
e. Adjust flow rate by opening and closing the "BACK PRESSURE" needle valve in right-hand side of the gas manifold. Normally we keep the channel 1 needle valve (lower left side) completely on. By opening the back pressure valve, you increase the flow to vent and decrease the flow through the contactor. Once this valve is adjusted for a given test, you should not change it.
f. begin stirring

8. Generate flow calibration curve if necessary.

a. Verify that flowmeter valve is open and make sure it is not reading split flow, but rather total flow.
b. Adjust flow by turning back pressure valve on the hood. You can judge it by the position of the upper ball.
c. For each adjustment, note position of upper ball and corresponding flowrate (for example, when upper ball is at 7, flowrate is approximately 115 mL/min). After several points are measured, a calibration curve can be created for future use. However, it's important to check the flow rate calibration on a regular basis.

9. Start Production of Ozone and stabilize system

- a. Turn 4-way valve in hood manifold to the "VENT" position
- b. Start ozone generator by activating the ON switch
- c. Adjust voltage between 60-90 V.
- d. Watch the absorbance value increase until it appears to stabilize; record this value in "Ozone vs O_2" abs field in spreadsheet
- e. Switch 4-way valve in hood manifold to "CHANNEL 1". You should begin to see the absorbance drop as ozone enters the reactor headspace and flows to the reference cell

10. Prepare sample contactor

- a. Fill second pyrex glass contactor as close to the top as possible with the sample to be ozonated (minimize headspace, but don't allow carry-over of water to the outlet tube), and a large magnetic stir bar. Temperature of the water should be known and recorded
- b. Continue to monitor the spectrophotometer absorbance and note when it has reached a minimum. This should be close to zero. Record this value in the spreadsheet cell marked "stabilized abs"
- c. Once the system has stabilized, place this second pyrex contactor on magnetic stir plate.
- d. Carefully and quickly remove the Milli-Q contactor from the cap with diffuser and outlet tube, and place cap on sample contactor.
- e. As soon as the cap is tight, set the time to zero and start recording absorbance from the spectrophotometer
- f. Enter the times and absorbances in the spreadsheet as you are recording them. The column labeled "ozone transferred dose" will give you the calculated dose as you enter the numbers.
- g. Once the desired dose is reached, turn the 4-way valve to "VENT"

11. Measure aqueous residual ozone.

a. Quickly removed a small sample from the contactor and introduce it into the indigo flask for determination of aqueous ozone residual by the indigo method. Record the calculated concentration in the cell marked "final aqueous O_3 resid".

b. Repeat periodically on a small subsample until the ozone residual is gone. At this point you can record the conventional UV absorbance for NOM characterization.

Ozone Contacting

Batch Method

1. **Connect gas inlet tubing to sparger**
   - Inlet tube is the one without the label
   - Connect this to other inlet side of diffuser (side without the bubble trap)

2. **Start dissolving ozone**
   - Turn main manifold valve from "VENT" back to "CHANNEL 1"

3. **Continue until desired concentration is reached**
   - periodically measure ozone residual by direct UV absorbance (3000 cm^{-1} molar absorptivity)
   - the ozone solution is ready to use when the concentration reaches a steady state.
   - cool the generator if the concentration doesn't reach desired level

4. **Add ozone solution to sample**
   a) Fill a vessel with sample (this may or may not be an electrode-equipped contactor, depending on whether you wish to follow aqueous ozone residual with the electrode).
   b) Remove a small amount of sample as needed to adjust for addition of ozone stock
   c) If desired add scavenger (MTBE) and/or probe compound (e.g., 0.5 µM pCBA)
   d) If desired add initiator (e.g., H_2O_2)
   e) Quickly add ozone stock and stir (you might use a graduated cylinder or a large syringe for this).
   f) At this point you may acquire ozone residual data with the electrode. You may alternatively collect grab samples and measure with the indigo method at various times.
   g) You may also want to collect samples for assessment of probe compound and target compouds
   h) If desired, at the end of the test remove some sample and verify final electrode measurement by the indigo test.

Semi-Continuous Method

5. **Connect gas outlet tubing to reactor**
   - Connect gas outlet tube (Teflon tube with red and white label) to the side of the diffuser with the bubble trap.

6. **Connect gas inlet tubing to reactor**
   - Inlet tube is the one without the label
   - Connect this to other inlet side of diffuser (side without the bubble trap)

7. **Introduce scavengers/probes/initiators, if needed**
   - Add scavengers (e.g., MTBE)
   - Add probe compound (e.g., 5µM pCBA)
   - Add initiator (e.g., H_2O_2).

8. **Start contacting**
   - Turn main manifold valve from "VENT" back to "CHANNEL 1"
   - As quickly as possible, press "ENTER" on the computer to start program.

9. **Remove samples for Monitoring, if needed**
   - Ideally, use a vessel with syringe withdrawal and minimize volume of sample to be withdrawn
   - Upon withdrawal, either make ozone measurement or quench for later analysis of target compounds or probe compound.

10. **Stop contacting when desired ozone transfer is reached**
    - Turn main manifold valve from "CHANNEL 1" back to "VENT" and note time from start of contacting
    - Quickly disconnect inlet and outlet tubes from reactor
    - Re-connect them directly using the straight glass tube
    - Turn main manifold valve from "VENT" back to "CHANNEL 1"
    - Monitor return of ozone off gas concentration and dissipation of aqueous ozone residual from the computer.
    - Note final spectrophotometer reading as it stabilizes

System Shut Down

11. **Turn off ozone generator**
    - flip the switch to off.

12. **Stop computer program if used**
    - with "CTRL-Break".

13. **Empty reactor and clean apparatus**
    - When not in use, reactor should be filled with Super-Q to keep electrode wet.

14. **Return system to "VENT"**
    - After spec indicates that ozone has been flushed from the system turn dial from "CHANNEL 1" back to "VENT".

15. **After 15 minutes shut down flows and equipment**
    - Turn off O_2 flow at cylinder
    - turn off cooling water
    - turn off computer
    - turn off UV-spec.
    - Disconnect and put away UV cells.

Data Analysis & QC Reporting

16. **Data Analysis begins with the first spec measurements.**
    - Absorbance of ozone generator product gas (determine % ozone composition from this)
        - Not important with batch method
    - Compare with absorbance of gas when bypass connector is in place of contactor
        - Not applicable to batch method
    - Record this information along with physical parameters (room temperature, generator voltage, gas flow rate) in the ozone generator log book
    -
17. **Lab Water Blanks**
    - At least one in every 10 ozonated samples must be a laboratory water blank. This water is mildly acidified with 0.1 mM HCl. If the ozone demand and ozone decay rate 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 or his/her designee if he/she is not available.

18. **Electrode Validation against Direct UV**
    This may be done by ozonating a laboratory water blank as above. Ozone residual is monitored with the electrode and samples are periodically removed for analysis by direct UV (254 nm). The UV absorbance is plotted against the concentration as measured by the electrode. If the slope (absorptivity) does not fall within the tolerance limits, calibration of the electrode must be re-visited.

Data Interpretation

Calculation of ozone demand in a semi-continuous test is quite simple mathematically. In principle it is just the difference between the ozone absorbed dose and the ozone residual (usually zero). However, unwanted ozone 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 ozone blank values

When the only source of ozone 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:

Ozone Demand = Ozone applied – ozone in off gas – sample ozone residual

When there are ozone 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:

Ozone Demand = Ozone applied – ozone in off gas – sample ozone residual – blank ozone demand

When there are ozone demands that also arise from the:

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

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

Ozone Demand = Ozone applied – ozone in off gas – sample ozone residual – buffer blank ozone demand

In a batch test, ozone demand is simply the dose minus the aqueous residual. Eventually the residual is lost and the demand and the dose are the same.

Ozone Demand = Ozone added –sample ozone residual

Sample Bottles and other labware

All glassware must be rendered free from contamination by ozone demanding substances. In many cases, they are also used for subsequent analysis of DBPs, and must therefore be free from trace organic contaminants.

Cleaning of bottles and other glassware

a) Acid wash by soaking in a covered acid bath[1]
b) rinse thoroughly with Super-Q water
c) soak for several hours in a bath of Super-Q water containing an ozone residual, alternatively fill with super-Q water and use as an ozone contactor for a "dummy" ozonation test.
d) rinse thoroughly with Super-Q water
e) dry in a high-temperature oven.[2]

Cleaning of septa

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

Supplies

Item	Catalog #	Approx. Price	Approx # used/test
Pasteur Pipettes	Fisher: 13-678-20A	720/ $46.10	10
Indigo Trisulfonate			
DIUF Water	Fisher: W2-20	$32.29	Not normally used
HCl			
Sodium Sulfate	Fisher: S 415-1	cs of 6/ $112.83	
Sodium Bicarbonate	Fisher: S233-500	$25.05	
H_2SO_4	UMass Stockroom		
H_2O_2			
p-chlorobenzoic acid			
MTBE			

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

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 Ozonation Tests

General QC

Data quality objectives for ozonation and ozone demand analysis is assured by: (1) use of blanks; (2) analysis of duplicates; (3) analysis of a matrix standard; and (4) monitoring of ozone generator output.

Three types of blanks should be run by all analysts: (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., acetaldehyde) 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 Ozonation and Analysis of Ozone 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 ozonations	One set of model compound ozonations when first learning method, otherwise not done		Match to expected ozone 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 Laboratory	To test analyte recovery in the sample	1 for every 10 samples	Mixed throughout	% recovery, mean and standard

Fortified Sample Matrix (LFM)	matrix		day	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 ozonation. The analyst should record all details on solution preparation, ozonation, 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. Either the Model Compound Method or the Dual Contacting Method may be selected, per agreement with faculty QC officer.

Model Compound Method

19. Conduct IDC lab experiment

a) Prepare 2 liters of a 1 mM solution of acetaldehyde in super-Q water and buffered at pH 7.0.
   - Acetaldehyde 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 acetaldehyde

b) Prepare 2 liters of super-Q water buffered at pH 7.0
c) Ozonate each under standard semi-continuous conditions. (room temperature)
d) Apply ozone until an absorbed dose of 25 mg/L is reached or until the bubbling time reaches 2 hours, whichever comes first.
e) After stopping ozonation monitor residual for the next 60 minutes.

20. Evaluate IDC data

- tabulate ozone demand and residual data
- graph residual decay data after contacting is stopped
- calculate a decay rate constant
- report this to the faculty QC officer (David Reckhow) in an MS excel spreadsheet

21. 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

Dual Contacting Method

22. Apply ozone in semi-continuous and batch system

a) Collect about 4 liters of a surface water having a moderate to high absorbance
   - e.g., UV_{254} absorbance of between 0.100 and 0.500 cm^{-1}.

b) Split the sample into identical 2 L aliquots

c) Dose one of the aliquots in a semi-continuous reactor
   - Use a dose range of about 0-10 mg/L
   - Collect small samples (e.g., 10 mL) at 5 or more intermediate points during ozonation
   - Record the point at which the samples were collected so that absorbed ozone dose at that point can be calculated
   - Allow each sample to react (e.g., >30 min) and measure absorbance at 254 nm for each of the samples

d) Use the remaining 2 liters of this water for batch ozone dosing
   - Use a dose range of about 0-10 mg/L
   - Divide 2 L sample into at least 5 subsamples
   - Select ozone doses across the range so that an even distribution is adopted
   - Allow each sample to react (e.g., >30 min) and measure absorbance at 254 nm for each of the samples

23. Evaluate IDC data

- Calculate, tabulate and graph UV absorbance vs. absorbed ozone dose for both sets of experiments
- Calculate corrected UV absorbance and corrected absorbed ozone dose for the batch data, taking into account dilution
- Plot this on the same set of axes
- report this to the faculty QC officer (David Reckhow) in an MS excel spreadsheet

24. 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 multiple laboratory ozonation experiments. The blank 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 Ozonation Sequence

Sample #	Sample type	QC objectives
1	Lab Water Blank	To check for gross contamination of water or lab environment, and establish background
2-4	**Analytical Samples**	
5	Buffered Water Blank	Background ozone loss
6-10	**Analytical Samples**	
11	Lab Water Blank	Background ozone loss
12-16	**Analytical Samples**	
17	Buffered Water Blank	Background ozone loss

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 16). 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. All summarized QC data (tabular and graphical) must be kept in a notebook in the Marcus Hall ozone generator area (Rm 5). 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	❖ Replicates = ±10%

		run	

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 ozonation and subsequent analysis must be kept in the dark, and in a refrigerator from the time of collection until the start of analysis. Some organic solutes are biodegradable, so a biocide must be added if the samples are to be kept for more than 2 days prior to analysis.

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 1

Notes on the Analysis of Ozone and Related Oxidants

A. Ozone: Gas phase

1. Direct UV Absorption

Commercial gas phase ozone monitors are based on the direct measurement of ultraviolet absorbance. With bench-scale studies, it is often convenient to use a laboratory UV-Vis spectrophotometer equipped with a flow-through quartz cell (0.1-0.2 cm pathlength) as a substitute for a dedicated ozone gas monitor. The ozone concentration may be calculated based on Beer's Law and the Ideal Gas Law.

$$conc.(\%-by-volume) = \frac{100\%}{\alpha_o}\frac{T_a}{293}\frac{760}{P}\frac{Abs}{L} \qquad (1.1)$$

where α_o is the absorptivity in $atm^{-1}cm^{-1}$ of ozone at the wavelength of measurement, Ta is the absolute temperature of the gas being measured, P is the pressure in mm Hg of the gas, and L is the cell pathlength in cm. At 253.7 nm, the absorptivity of ozone in the gas phase (at 760 torr, 293^{o}K or 20^{o}C) is 134 $atm^{-1}cm^{-1}$ (Inn & Tanaka, 1959; Hearn, 1961; DeMore & Patapoff, 1976). There is quite a bit of fine structure to ozone's broad UV absorbance band in the gas phase. For this reason, narrow band widths are preferable. When expressed as mass per volume, the terms for pressure and temperature drop out and one gets equation 1.2a.

$$conc.(mg/L) = \frac{1}{\alpha_o}\frac{48{,}000}{22.4}\frac{Abs}{L} \qquad (1.2a)$$

which for a wavelength of 253.7 nm and a pathlength of 0.2 cm reduces to equation 1.2b.

$$conc.(mg/L) = 80\,Abs \qquad (1.2b)$$

Use of equations 1.1 and 1.2 is more convenient in the laboratory. If necessary, one can convert back to percent-based concentrations by equation 17.34c.

$$conc.(\%-by-volume) = 0.04667\frac{T_a}{293}\frac{760}{P}conc(mg/L) \quad (1.2c)$$

2. Iodometric Methods

Gas phase concentrations of ozone are also easily measured iodometrically. Wet chemical analysis of ozone in the gas phase is less convenient, however, it allows one to calibrate or check spectrophotometric analyzers. Also, the wet chemical tests measure mass flow rather than concentration directly. If there are uncertainties in the gas flow rate, the wet chemical methods may provide greater accuracy in estimating mass ozone application rates.

Many variations on the classic iodometric method have been proposed, Basically, a portion of the gas stream is directed to a gas bubbler filled with 2% KI solution for an exact period of time. Ozone reacts stoichiometrically to form an equivalent amount of iodine. In the presence of excess iodide, the triiodide ion (I_3) is formed.

$$O_3 + 2KI + H_2O \text{ ---------> } I_2 + O_2 + 2OH^- + 2K^+ \quad (1.3)$$

$$I_2 + I^- \text{ <---------> } I_3^- \quad (1.4)$$

The iodine formed is then titrated with sodium thiosulfate using starch as an indicator to accentuate the endpoint (APHA et al., 1985). Phosphate buffered KI solutions are to be avoided, as the phosphate anions appear to catalyze the formation of hydrogen peroxide (Flamm, 1977). This can lead to a shifting endpoint and unpredictable stoichiometry. Flamm (1977) reports that a borate buffered modification of the standard KI procedure has shown excellent agreement with direct gas-phase UV absorption. He measured the triiodide by spectrophotometry (352 nm). Calibration of this method requires the spectrophotometric analysis of standard triiodide solutions. These solutions are prepared by oxidation of iodide using standard iodate solutions (equation 1.5). The stoichiometry of this reaction is preserved when conducted in 0.1 to 1.0 N acid. The direct preparation of triiodide from iodine crystals and iodide is less accurate.

$$\tfrac{1}{3}IO_3^- + \tfrac{8}{3}I^- + 2H^+ \rightarrow I_2 + I^- + H_2O \leftrightarrow I_3^- + H_2O \quad (1.5)$$

From equations 1.3 and 1.5, one concludes that one mole of iodate liberates the same amount of iodine/triiodide as three moles of ozone. Since iodine or triiodide has two equivalents of oxidizing potential, ozone also has two, and iodate has six.

a. Procedure

1. Bubble ozone gas through a gas washing bottle containing a convenient volume of BKI solution (usually 250-500 mL). Record the bubbling time and gas flow rate or settings. A sample of the original (time zero) BKI solution should be saved for determination of UV blank. For low-level measurements, it is recommended that the BKI solution be very slightly preozonated. This removes small amounts or reducing materials that are invariably present in commercial potassium iodide.
2. At the end of the ozone trapping period, disconnect the gas washing bottle, and pour a small sample (e.g., 10 mL) into a 50 mL beaker.
3. Measure absorbance of the ozonated BKI at 352 nm after 1 minute (Abs_S). If the absorbance is greater than 1.2, the sample must be diluted. The final absorbance value must then be corrected for this dilution.
4. Obtain a blank measurement by determining the absorbance at 352 nm of an aliquot of the same BKI solution that was present in the gas washing bottle at time zero (Abs_b).
5. Calculate concentration with equation #8. Obtain the calibration factor, β_1, by the standardization procedure in "b".

$$\text{Ozone Concentration (mg/L as } O_3) = (Abs_S - Abs_b)/\beta_1 \qquad (1.6)$$

b. Standardization

1. Prepare a set of standard triiodide solutions. This is done by first cleaning a series of 100 mL volumetric flasks, and half filling them with the Acidic KI solution. Add aliquots ("V" mL) of the Standard Potassium Iodate Solution to each and fill to the mark with additional acidic KI solution. Each mL of iodate will be roughly equivalent to 1.5 mg/L ozone.

2. Measure the absorbance of each of the standard triiodide solutions at 352 nm. Plot absorbance vs equivalent ozone concentration.

$$Abs = \beta_1 (\text{Equiv. Conc.}) \qquad (1.7)$$

where the equivalent concentration is given by:

$$Equiv.Conc.\left(\frac{mg}{L} - as - O_3\right) = M_{IO3}\left(\frac{V}{100}\right)\left(\frac{3Mole - O_3}{1Mole - IO_3}\right)\left(\frac{48{,}000mg - O_3}{Mole - O_3}\right) = 1{,}440 M_{IO3} V \qquad (1.8)$$

Note that M_{IO3} is the exact molar concentration of the Standard Potassium Iodate Solution. Try to work only in the linear range, or the range from 0-1.2 absorbance units.

c. Reagents

1. BKI Reagent (0.1 M Boric Acid, 1% Potassium Iodide): Add 6.2 g H_3BO_3 and 10.0 g KI to 1 liter of distilled water. Stir to dissolve.

2. Standard Potassium Iodate Solution: Dry the primary standard at 120^{o}C for 2 hours. Then, weigh out about 0.021 g of the dried material. Record the exact weight to 4 significant figures. Dissolve in distilled water in a 100 mL volumetric flask and fill to the mark. Calculate exact molar concentration:

$$M_{IO3} = \text{wt in grams} / 21.402 \quad (1.9)$$

3. Acidic KI Solution (1% potassium iodide in 0.1N acid): Add 5.6 mL of concentrated H_2SO_4 to a 1 liter volumetric flask. Slowly fill the flask about half-way with distilled water and stir. Then add 10 g KI, stir, and fill to the mark with distilled water.

Strictly speaking, all of these iodometric methods are non-selective. That is, they measure a wide range of oxidants, not just ozone. For this reason, they should not be used to measure aqueous ozone concentrations. Because ozone is by far the major oxidant species produced by corona ozone generators, and because ozone is far more easily stripped from water, the measurement of ozone in the gas phase is not subject to significant problems with interferences. Thus, iodometric methods may be used in this case without reservation.

B. Ozone: Aqueous Phase

1. Direct UV Method

Aqueous ozone concentrations in pure (e.g., distilled) water may be conveniently determined by direct spectrophotometric measurement at 260 nm.

$$C_{O3} \text{ (mg/L as } O_3) = 14.59*(\text{Abs @260 nm}) \quad (1.10)$$

Equation 1.10 is based on a molar absorptivity of 3290 $M^{-1}cm^{-1}$ (Hart et al., 1983). Unfortunately, most solutes will interfere at this wavelength, so with actual environmental

samples another method must be used. Since the iodometric method is too nonspecific for aqueous determinations, the indigo method of Bader and Hoigne (1981) is recommended.

2. Indigo Method

This colorimetric procedure uses solutions of indigo trisulfonate (Bader & Hoigne, 1981). Ozone will stoichiometrically bleach this intense blue dye, and the loss in absorbance at 600 nm may be translated directly into an ozone concentration. The reaction product is relatively unreactive to further ozonation. The reaction is best carried out at low pH to minimize ozone decomposition, and preserve the 1:1 stoichiometry. Bader and Hoigne (1981) report a sensitivity factor or apparent absorptivity for indigo trisulfonate of 20,000 $M^{-1}cm^{-1}$. This is based on an aqueous ozone molar absorptivity of 2900 $M^{-1}cm^{-1}$. If one adopts the higher value reported by Hart et al. (i.e., 3290 $M^{-1}cm^{-1}$), the sensitivity factor for indigo trisulfonate becomes 22,700 $M^{-1}cm^{-1}$.

This method is quite selective, however, it is subject to a few notable interferences. The presence of residual chlorine will cause a positive bias. Addition of 500 mg/L malonic acid to the Indigo Reagent solves this problem by out-competing the indigo for the chlorine. Oxidized manganese species will also result in bleaching of the indigo. Here it is recommended that duplicate samples be analyzed, one according to the standard procedure, and one following addition of glycine. The glycine selectively reduces residual ozone without affecting oxidized manganese species. The true ozone concentration may then be estimated from the difference of these two measurements.

a. Procedure

1. Prepare an indigo blank by adding 1 mL of the Standard Indigo Stock to a 25 mL volumetric flask and filling to the mark with Phosphate Buffer. Stopper and mix. Measure the absorbance of this solution at 600 nm (Abs_I). When the Indigo Stock is new, it should be about 0.650. With time this value will drop. When it falls below 80% of the original value, prepare a new Indigo Stock and repeat procedure. If low ozone concentrations are anticipated (i.e., < 0.3 mg/L) prepare a Secondary Indigo Stock by adding 20 mL of the Standard Indigo Stock to a 100 mL volumetric flask and diluting to the mark with Super-Q water.
2. Soak a series of volumetric pipets in a dilute ozone solution for several minutes. These pipets are to be used to transfer the solution to be measured to the indigo-containing flasks. They must therefore be rendered ozone-demand-free. The capacities of the pipets will depend on the range of anticipated ozone concentrations (see table below).
3. Assemble a series of clean, glass-stoppered 25 mL or 50 mL volumetric flasks (see table below) and fill each with 1.00 mL of Standard Indigo Stock (25 mL flasks) or Secondary Indigo Stock (50 mL flasks) using a volumetric pipet. Wash this down from the inner surfaces of the neck with about 10 mL of Phosphate Buffer.

4. Quickly pipet the recommended sample volume to an indigo-containing volumetric flask (see table below). Be sure that the tip of the pipet is below the meniscus. Fill the flask to the mark with Phosphate Buffer, cap and invert several times to mix.

Anticipated Ozone Concentration	(V_S) Recommended Sample Volume	(V_t) Recommended Total Volume	(L) Recommended Pathlength
0 - 0.2 mg/L	25 mL	50 mL *	10 cm
0.1 - 0.3 mg/L	15 mL	50 mL *	10 cm
0.2 - 0.5 mg/L	10 mL	50 mL *	10 cm
0.3 - 2.0 mg/L	15 mL	25 mL	1 cm
1.5 - 3.0 mg/L	10 mL	25 mL	1 cm
1.8 - 3.5 mg/L	8 or 9 mL	25 mL	1 cm
2.3 - 4.5 mg/L	6 or 7 mL	25 mL	1 cm
3 - 6 mg/L	5 mL	25 mL	1 cm
4 - 7 mg/L	4 mL	25 mL	1 cm
5 - 10 mg/L	3 mL	25 mL	1 cm
7 - 15 mg/L	2 mL	25 mL	1 cm
15 - 30 mg/L	1 mL	25 mL	1 cm

*Secondary Indigo Stock must be used with 10 cm pathlength cells

5. Measure absorbance (Abs_f) of each sample at 600 nm using cells of the indicated pathlength (L). Concentration is calculated from a slope or calibration factor determined by calibration against the direct UV method (see b. Calibration).

$$\text{Ozone Conc. (mg/L as } O_3) = V_t(Abs_i - Abs_f)/fV_sL \quad (1.11)$$

b. Calibration

1. Prepare a series of aqueous ozone standards in slightly acidified (0.1 mM HNO_3) Super-Q water. This is generally done by first bubbling ozone gas through about 500-1000 mL of the acidified water until near saturation (~1 hour). Under optimal conditions for high ozone output (i.e., high voltage, low gas flow, low temperature) this should result in aqueous concentrations of about 10 mg/L. Then, aliquots of this water are removed and diluted with varying amounts of un-ozonated, acidified Super-Q water. The degree of dilution will depend on the range of ozone concentrations anticipated in the samples of interest.

2. One-by-one measure each of these diluted solutions by the indigo method above and by the direct UV method (equation 1.10). Use the same sample volume, V_S, for all standards.
3. Plot absorbance (from indigo method) versus aqueous ozone concentration (from direct UV method). The slope of this line multiplied by V_t/V_S gives fL (see equation 1.12). Based on the presumed sensitivity factor[3] for indigo trisulfonate of 20,000 $M^{-1}cm^{-1}$, the calibration factor, f, should be about 0.42 abs/cm per mg-O_3/L.

$$Abs_f = Abs_i - (fLV_S/V_t)(\text{Ozone Conc.}) \qquad (1.12)$$

Note that the calibration factor, f, is in theory equal to the real molar absorptivity divided by the factor: 48,000 mg-O_3/mole. In a non-ideal system this becomes:

$$f = \frac{a_{ITS}}{48{,}000\ {}^{mg-O_3}\!/_{mole-O_3}}\left(\frac{moles-ITS}{moles-O_3}\right)$$

The actual values of "f" can vary from 0.43 to 0.37 depending on the supplier[4]. Indigo trisulfonate will slowly degrade even in a dry form, so that older bottles may produce even lower "f" values.

c. Reagents

1. Standard Indigo Stock (1 mM in 20 mM phosphoric acid): Dissolve 1.36 mL conc. H_3PO_4 in 1 liter of super-Q water and mix. To this add 0.6 g indigo trisulfonate, mix and store in a brown glass bottle.
2. Phosphate Buffer (pH 2): Dissolve 28 g $NaH_2PO_4 \cdot H_2O$ and 20.6 mL (35 g) conc. H_3PO_4 in Super-Q water and dilute to 1 liter.

C. Aqueous Total Oxidant Concentration

Ozone reacts in aqueous solution to give a variety of oxidant species. These may include simple inorganic oxygen-containing free radicals, hydrogen peroxide, organic free radicals, and organic peroxides. The iodometric method of Flamm (1977) coupled with the use of a catalyst (Taube & Bray, 1940) is sufficiently non-specific to be useful for the determination of total oxidant concentration.

[3] molar absorptivity is thought to be 22,700 to 23,800 $M^{-1}cm^{-1}$, but this is not exactly equal to the sensitivity factor due to possible impurities and non ideal stoichiometry

[4] Gordon, Walters and Bubnis, 2000; IOA Conference Proceedings, Orlando Conference.

a. Procedure

1. Place between 1 and 9 mL of BKI reagent in a 10 mL volumetric flask.
2. Add 1 mL of the Molybdate Catalyst solution.
3. Quickly add sample to the mark, stopper and invert several times to mix.
4. Measure absorbance at 352 nm after 1 minute (Abs_S)
5. Repeat steps 1-4 substituting distilled water for the sample (Abs_b)
6. Calculate total oxidant concentration:

$$\text{Total Oxidant Concentration (mg/L as } O_3) = b_1*(Abs_S-Abs_b)/V_S \quad (1.13)$$

Follow the procedure in part "b" using iodate standards to get the calibration factor, b_1. Experience indicates that it should be about 21.6 mg/L as O_3 per mL of sample per cm pathlength.

b. Standardization

1. Prepare a set of standard triiodide solutions. Clean a series of 100 mL volumetric flasks, and half fill them with the Acidic KI solution. Add aliquots ("V" mL) of the Standard Potassium Iodate Solution to each and fill to the mark with additional acidic KI solution. Each mL of iodate will be roughly equivalent to 1.5 mg/L ozone.
2. Measure the absorbance of each of the standard triiodide solutions at 352 nm. Plot absorbance vs equivalent ozone concentration.

$$Equiv.Conc.\left(\frac{mg}{L}-as-O_3\right) = M_{IO3}\left(\frac{V}{100}\right)\left(\frac{3Mole-O_3}{1Mole-IO_3}\right)\left(\frac{48{,}000mg-O_3}{Mole-O_3}\right) = 1{,}440M_{IO3}V \quad (1.14)$$

Try to work only in the linear range, or the range from 0-1.2 absorbance units.

c. Reagents

1. BKI Reagent (0.1 M Boric Acid, 1% Potassium Iodide): Add 6.2 g H_3BO_3 and 10.0 g KI to 1 liter of distilled water. Stir to dissolve.
2. Molybdate Catalyst Solution: Add 0.9 g Ammonium Molybdate to 10 mL distilled water and stir to dissolve.
3. Standard Potassium Iodate Solution: Dry the primary standard at 120^{o}C for 2 hours. Then, weigh out about 0.021 g of the dried material. Record the exact weight to 4 significant figures. Dissolve in distilled water in a 100 mL volumetric flask and fill to the mark. Calculate exact molar concentration:

$$M_{IO3} = \text{wt in grams} / 21.402 \quad (1.15)$$

4. Acidic KI Solution (1% potassium iodide in 0.1N acid): Add 5.6 mL of concentrated H_2SO_4 to a 1 liter volumetric flask. Slowly fill the flask about half-way with distilled water and stir. Then add 10 g KI, stir, and fill to the mark with distilled water.

D. Hydrogen Peroxide

Hydrogen peroxide is one of the secondary oxidants produced by the action of ozone. It may be produced as a byproduct of aqueous ozone decomposition. It is also an important byproduct of the reaction of ozone with unsaturated organic compounds. Hydrogen peroxide is also important, because it may be added to waters undergoing ozonation for the purposes of accelerating the formation of hydroxyl radicals. These radical species are capable of oxidizing many types of organic structures that are not affected by molecular ozone. The two preferred methods for hydrogen peroxide analysis involve the formation of heavy metal complexes (Parker, 1928; Masschelein et al., 1977). Both are susceptible to interference from aqueous ozone. Therefore, ozone must first be purged. The titanium method (Parker, 1928) is recommended here.

a. Procedure

1. Sparge sample to remove residual ozone as necessary.
2. Pipet 1 mL of the Titanium Reagent into a 10 mL volumetric flask.
3. Add sample to the mark, stopper and invert several times.
4. Measure absorbance at 415 nm.
5. Calculate concentration from a calibration curve prepared as below.

b. Standardization

1. Prepare two serial dilutions of the commercial 30% solution. Add 1 mL of the commercial solution to a 500 mL volumetric flask and dilute to the mark with distilled water. This is the concentrated peroxide stock solution. In a second 500 mL volumetric flask dilute 5 mL of the concentrated stock to 500 mL with distilled water. This is the dilute peroxide stock.
2. Standardize the dilute peroxide stock using the BKI spectrophotometric method for total oxidants. In this case the standard curve is most conveniently based on equivalent hydrogen peroxide concentrations in mg/L.

$$Equiv.Conc.(mg-H_2O_2/L) = M_{IO_3}\left(\frac{V}{100}\right)\left(\frac{3mol-H_2O_2}{Mole-IO_3}\right)\left(\frac{34{,}000mg-H_2O_2}{Mole-H_2O_2}\right)$$

$$Equiv.Conc.(mg-H_2O_2/L) = 1{,}020M_{IO_3}V \qquad (1.16)$$

Equiv. Conc. (mg/L as H_2O_2) = 0.708 Equiv. Conc. (mg/L as O_3) (1.17)

3. Into a series of 10 mL volumetric flasks, place 1 mL of the Titanium Reagent. Add varying amounts of the dilute peroxide standard, and

fill to the mark with distilled water. Measure the absorbance at 415 nm. Plot concentration versus absorbance. The data should be linear with a slope of about 57 mg/L per absorbance unit per cm.

c. Reagents

1. Titanium (IV) Reagent: Place 10 mL of 6N HCl in a beaker on a crushed ice bath under a fume hood. Place $TiCl_4$ in an ice bath and allow both to cool. Carefully add 10 mL of the $TiCl_4$ dropwise to the chilled HCl. Allow the mixture to stand in the ice bath until the solids that form dissolve. Transfer this mixture to a 1 liter volumetric flask using 6N HCl. Dilute to the mark with additional HCl.
2. 30% Hydrogen Peroxide Solution (Commercially available).
3. BKI Reagent: (This is the same solution prepared for ozone gas phase analysis and the total oxidant analysis; 0.1 M Boric Acid, 1% Potassium Iodide): Add 6.2 g H_3BO_3 and 10.0 g KI to 1 liter of distilled water. Stir to dissolve.
4. Molybdate Catalyst Solution: (This is the same solution prepared for the total oxidant analysis) Add 0.9 g Ammonium Molybdate to 10 mL distilled water and stir to dissolve.
5. Standard Potassium Iodate Solution: (This is the same solution prepared for ozone gas phase analysis and the total oxidant analysis) Dry the primary standard at 120^{o}C for 2 hours. Then, weigh out about 0.021 g of the dried material. Record the exact weight to 4 significant figures. Dissolve in distilled water in a 100 mL volumetric flask and fill to the mark. Calculate exact molar concentration:

$$M_{IO3} = \text{wt in grams} / 21.402 \qquad (1.18)$$

6. Acidic KI Solution (1% potassium iodide in 0.1N acid; This is the same solution prepared for the ozone gas phase analysis and the total oxidant analysis): Add 5.6 mL of concentrated H_2SO_4 to a 1 liter volumetric flask. Slowly fill the flask about half-way with distilled water and stir. Then add 10 g KI, stir, and fill to the mark with distilled water.

REFERENCES

Bader, H.; Hoigne, J. Wat. Res. **1981**, 15:449-456.
DeMore, W.B.; Patapoff. M. Environ. Sci. Technol. **1976**, 10:897.
Flamm, D.L. Environ. Sci. Technol. **1977**, 11:10:978-983.
Hart, E.J.; Sehested, K.; Holcman, K. Anal. Chem. **1983**, 55:46.
Hearn, A.G. Proc. Phys. Soc. **1961**, 78:932.

Inn, E.C.Y.; Tanaka, Y. In Ozone Chemistry and Technology **1959**, ACS Advances in Chemistry Series #21, ACS, Washington, pp.263-268.

Masschelein, W.J.; Denis, M.; Ledent, R. Wat. Sewage. Wrks. **1977**, August, 69-72.

Parker, G.A. In Colorimetric Determination of Nonmetals, **1928**, Boltz, D.R.; Howell, J.A., Eds. Wiley, New York, pp.301-303.

Taube, H., Bray, W.C. J. Am. Chem. Soc. **1940**, 62:3357.

Appendix 2

Standard Methods: 2350 & 4500-Ozone

(APHA et al., 1999)