Analysis of Total Organic Halide

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

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Standard Operating Procedures

Analysis of Total Organic Halide

This guidance document was prepared to assist research assistants, post-docs and lab technicians in conducting total organic halide (TOX) analysis 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 and Angela Gonzalez 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 TOX analysis

Scope

This method has been used in the UMass Environmental Engineering Laboratory for analysis of TOX. 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.

It has been tested with standards of halogenated disinfection byproduct. The table below lists some observed recoveries.

Table 1: TOX Recoveries

Analyte	Recovery (%)		
	Dorhmann[1]	**Mitsubishi**	**Euroglass[2]**
Trihaloacetic Acids (THAA)			
Trichloroacetic Acid (TCAA)	97		100
Bromodichloroacetic Acid (BDCAA)			
Chlorodibromoacetic Acid (CDBAA)			
Tribromoacetic Acid (TBAA)			

[1] Data from Reckhow et al., 1990
[2] Data from von Stechow, 2002

Dihaloacetic Acids (DHAA)			
Dichloroacetic Acid (DCAA)	94		60
Bromochloroacetic Acid (BCAA)			
Dibromoacetic Acid (DBAA)			
Monohaloacetic Acids (MHAA)			
Monochloroacetic Acid (MCAA)	0		
Monobromoacetic Acid (MBAA)			
Trihalomethanes (THMs)			
Chloroform	79, 84, 89, 94	93	
Bromodichloromethane	98		
Chlorodibromomethane	86		
Bromoform	93, 98, 101, 111	93, 95	
Haloacetamides			
Dichloroacetamide			70
Trichloroacetamide			95
Halophenols			
2,4,6-Trichlorophenol	97, 98, 101	97	
2,4,6-Tribromophenol	91, 102		
Pentachlorophenol	93		

Other compounds tested with the Dohrmann instrument include a haloalkane (1-Chloro-2-Bromoethane; 106%), two haloalkenes (Dichloroethylene, 62% and tetrachloroethylene, 77%), a haloalcohol (chloroethanol, 20%), a haloether (bis(2-chloroethyl)ether, 92%), a haloketone (monochloroacetone, 90%), and three haloaromatics (bromobenzene, 95%; m-Dichlorobenzene, 107%; 3-Bromobenzoic Acid, 104%.

Dichloroacetic acid is prone to washout or breakthrough on both columns. Dichloracetamide shows a small amount of breakthrough (e.g., 25%) to the second column, so this only seems to account for a small amount of the incomplete recovery. Monochloroacetic acid has been reported to be weekly adsorbed on the GAC, whereas chloroethanol is desorbed by the nitrate wash[3].

[3] Takahashi et al., 1981

Method Overview

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

Table 2: Summary of Procedure for TOX Sample Analysis

1. **Prepare QC standards (Table 3 and Table 4)**
2. **Bring analytical samples to room temperature, and prepare calibration standards and QC samples**
3. **Acidify sample immediately prior to adsorption.**
4. **Rinse lines in Filtration Unit**
5. **Assemble adsorption system**
6. **Pass sample through carbon columns**
7. **Nitrate wash**
8. **Setup TOX Analyzer (see below) at the start of each day**
9. **Enter sample information into computer**
10. **Transfer carbon from first column into sample boat**
11. **Start pyrolysis sequence**
12. **Access results**
13. **Shut down analyzer at the end of the day (see below)**

Table 3. Typical Preparation of IX Spike Solution

1. **1. Add NaCl to Reagent Water**

Table 4. Typical Preparation of OX Spike Samples

1. **Add organic halide standard to water (primary standard)**
2. **Prepare Dilution (secondary standard)**
3. **Add to duplicate samples**

Detailed Procedures

Basis for Method

We use a protocol that is closely aligned with method 5320 of Standard Methods for the Examination of Water and Wastewater (APHA et al., 1999). Please refer to the latest version of this method (attached as Appendix 1) for all details.

For historical reasons and site-specific considerations, we have chosen to depart from method 5320 in several minor ways. The most substantial differences include:

- smaller volumes of sample, reagents, and solvents
- sodium arsenite sometimes used as a quench in place of ammonia
- addition of internal standard to solvent earlier in the procedure
- higher ratio of derivatizing agent to sample

Once again, the primary source for our TOX method is US EPA method 5320. Within this protocol, we use the microcolumn method (§ 4a). This should be consulted whenever questions arise. However, the analyst should keep in mind that we have made some specific modification. These are itemized below in Table 5.

Table 5. UMass Protocol Departures from US EPA Method 5320

§ from 5320	Step	5320 protocol	UMass protocol
1.c.	Sodium Sulfite	Used for quench	Currently we are using this protocol. For some studies we use arsenite

We typically use our Euroglass Analyzer for TOX analysis. This is equipped with an adsorption module. The second analyzer that can be used is the Dorhmann MX-20. A summary of the differences between the two instruments is shown below in Table 6.

Table 6. TOX Instrument Comparison

Component	Euroglass	Dohrmann
Carrier Gas	Oxygen	Carbon dioxide and oxygen
Flow generation for Adsorption	Peristaltic Pump	Gas Pressure on sample reservoir
Adsorption volume determination	Timed operation for pump	Optical sensor on receiving flask

Definitions

A number of method-specific terms are used in this document. Because the meaning of these terms is not always obvious, some are defined below:

- Titration cell: the enclosed vessel where halide detection/quantification takes place. It contains a stirring bar, four electrodes and a gas inlet and outlet.
- Acid Scrubber: is the vessel in the left compartment of the instrument. It contains concentrated sulfuric acid and its level should be kept at the black line (almost half of the volume of the column).
- Acid trap: this is between the acid scrubber and the titration cell. The acid trap also contains concentrated sulfuric acid!
- Boat: This is the quartz glass sample holder that slides into the oven.

UMass Detailed Procedures

Sample Preservation

1. **Add one of the following two quenches to 40mL clear vials.**
   - Add 250 µL of quenching solution (sodium arsenite solution 0.1 N, kept in refrigerator # 3)
   - Add at least 5 mg reagent-grade Sodium Sulfite (Na_2SO_3) crystals (Desiccator in 301 Elab II) per liter of sample using dispenser made by glass shop plus 4 drops of sulfuric acid

2. **Remove particulate matter prior to analysis**
   - Filter through a clean Whatman GF/F filter using a 50 mL glass syringe and syringe filter housing.[4]
   - Many samples will be sufficiently-free of particulate matter that filtration will be deemed unnecessary, and even unwanted (potential source of contamination, and analyte volatilization)
   - In some rare cases, it may be desirable to include particulate matter in the analysis of TOX. For these samples, particles must be broken up and re-dissolved prior to analysis. No standard methods have been developed for this.

3. **Add a biocide, if samples cannot be processed within 48 hours[5]**
   - ~50 µL of sodium azide solution to each 40-mL vial

4. **Acidify to pH 2 with nitric acid[6]**
5. **Place aqueous samples in a refrigerator until adsorption.**
   - Samples should be adsorbed and analyzed as soon after quenching as possible, but under no circumstances should more than 14 days be allowed to elapse.

Sample Adsorption and Preparation for Halide Analysis[7]

1. **Bring analytical samples to room temperature, and prepare calibration standards and QC samples**

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[4] Do not use a conventional vacuum filtration apparatus, as this will cause volatilization of THMs and other OX compounds.
[5] distribution system samples having a chlorine residual less than 0.5 mg/L should be treated with the biocide at the time of collection, regardless of when the sample is extracted.
[6] Some also use sulfuric acid, however nitric seems to work very well without interferences.
[7] Typical prep time is 4 hours for a run of 10 samples on the dual channel adsorption module

2. **Acidify sample immediately prior to adsorption.**
   - Add x ml of concentrated H_2SO_4 to the water sample using an Eppendorf pipette (location?)
   - May also use HNO_3 (causes additional loss of OX with sulfite?)

3. **Rinse lines in Filtration Unit**
   - Before you can use the rinsing stations, you need to rinse the lines for 2-3 minutes. (The filtration unit has 3 stations: 3 rinsing stations and 1 wash station.)
   - Use "escape" to reach the main menu. Use station 1 or 2. Press "enter".
   - Look for "start rinse" in the stations menu by pressing the arrow buttons.
   - Press "enter" to start the rinse. After 2-3 minutes press "enter" to stop the rinsing.

4. **Assemble adsorption system**
   - Poke holes in both ends of two pre-packed carbon columns and connect both columns with connector and connect to the station.
   - Use tubing to direct the sample into a graduated cylinder after it passes through the columns. Its volume should be around 100 mL. You should record the exact value and enter it into the program (analyzer window).
   - If it is much less or much more than 100ml, look for "calibrate" within the station's menu and use "calibrate" instead of "rinse" for your next sample. After the sample has passed through the columns, the display will ask for the actual value. Choose the actual value with the arrow buttons and press "enter".

5. **Pass sample through carbon columns**

6. **Nitrate wash**
   - After the sample has passed through the columns, the columns will need to be washed with 15 mL of nitrate wash solution[8] in the wash station (to remove inorganic halide). Use the "esc" key to reach the main menu and look for "wash station" using the arrow buttons.
     - Pass 15 mL of nitrate wash solution through the column assembly, by pressing "rinse start". Then press "stop" when 15 mL of water has entered the graduated cylinder
   - After the carbon is washed, the samples are ready for the pyrolysis step[9].

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[8] Standard methods says 2-5 mL of a 5g/L solution; Euroglass recommends 25 mL of a ca. 1000 mg/L solution. Tests by Guanghui Hua indicate that 15 mL is sufficient to negate up to 1 g/L of inorganic chloride.
[9] Euroglass manual recommends use of a final distilled water rinse. This does not seem to be necessary based on 4/2003 results from Hua.

Analysis by Pyrolysis-Microcoulometry[10]

1. **Setup TOX Analyzer (see below) at the start of each day**

2. **Enter sample information into computer**
   a) Go to the "analyzer" window, and wait until baseline is stable.
   b) In the controller window:
      i. Go to Queue menu, to open a previously used queue
         - To create a new one, just type a new name and click OPEN, then OK to create.
      ii. Make sure that "Methods" has
      iii. Analysis: ECS
         - Evaluation: Absolute
         - Calibration: (empty, do not fill)
      iv. Include any comment or analyst name in the "Analyst/Remarks" box
      v. Using the ADD button to add samples into the queue
         - Change name
            - Size: volume of sample analyzed
         - Unit: Units of sample size
         - Type: SAMPLE (only samples will be used)
         - Pick dimensions for concentration
         - If you diluted your samples, include the dilution factor in the "Dilution Factor" box
         - Do not worry about vial, tolerance and density
         - When done, CHECK THE CHECK MARK BUTTON: ✓ otherwise, your sample will not be saved. The sample now should say *untreated*.
      vi. Click the "Analyze" button and wait for the "interactive sampler" window to show: "inject sample" (in red letters).

3. **Transfer carbon from first column into sample boat**
   - Remember to pyrolyse each column separately
   - Use special ejector tool to take of the end caps off of the columns and push the carbon into the boat insert (previously cleaned per section on: Pre-pyrolysis of boat and assembly). Do not touch the boat insert or the carbon.
   - Put boat insert into boat, make sure you close the lid very carefully because no gas should be allowed to escape the instrument without passing through the oven and titration cell.

[10] typically requires xx hours of GC time for a run of 30 samples

4. **Start pyrolysis sequence**
    - Do not click "OK" on the computer until the sample is loaded. After clicking "OK" you have only 15 seconds before the pyrolysis cycle begins
    - During a run, pyrolysis and integration time can be changed using the "measure time" box at the "analyzer" window:
        - If a longer time is needed increase "measure time"
        - If a shorter time is needed put the cursor on the "raw data" graph and click with the right mouse button at the time you want to stop.

5. **Access results**
    - After sample is done, click "evaluate" in the "controller" window to get concentration [you can reevaluate the concentrations after you change the units for it]
    - Arrows are to resort samples
    - To analyze or evaluate the whole queue go to Queue menu and click analyze or evaluate. Analyze or evaluate in the "controller" window analyzes only the sample highlighted.
    - If queue need to be repeated, use SAVE AS under queue menu, this will save the same queue with untreated samples

6. **Shut down analyzer at the end of the day (see below)**

Data Analysis & QC Reporting

1. **Data Analysis begins with cell setup.**
    - The analyst must inspect the first few integrations to see that the peak shapes are acceptable and that halide injections into the cell result in recoveries that are within tolerance limits.

2. **Carbon Blanks**

    The first full pyrolyzed column must come from a carbon blank. If it is not within tolerance, it must be repeated. If the second fails, corrective action must be taken. The analyst must report on the success or failure of these first few runs by email to the graduate QC officer or his/her designee if he/she is not available.
    - The message must also include the address of the Faculty QC officer in the "cc:" line (reckhow@ecs.umass.edu).
    - The subject line of this email message must simply read "QC report for TOX"
    - The report must also include the sample types (e.g., field samples from Stamford), field collection date, laboratory treatment date (if any), and analysis date

3. **<u>Column breakthrough should be monitored</u>**
   - When the breakthrough is excessive (>30%), it may be necessary to re-analyze the already processed aqueous sample (i.e., the GAC column effluent).

4. **<u>Evaluate all other QC data</u>**
   - This must be done as soon as possible, but no later than 24 hours from the end of the GC run. Send an email report as in #2 above, but this time include the following information:

   vii. Breakthroughs (average & SD)
   viii. Carbon Blanks
   ix. Super-Q Blanks
   x. OX Spike recoveries
   xi. IX Spike recoveries

5. **<u>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.</u>**

- Again, he subject line of this email message must simply read “QC report TOX”.
- This must be done as soon as possible, but no later than 24 hours from the time of receipt of the detailed QC report (per #4).

Data Interpretation

Normally, two carbon columns are used for each sample and each have to be loaded individually in the analyzer. These are compared to the carbon blanks:

TOX = TOX first column + TOX second column - 2*TOX blank

Daily Setup

<u>TOX Analyzer Set up</u>

1. Click on the “Controller” icon, on the desktop

2. Change Furnace temperatures.
    - Furnace 1: 1000C,
    - Furnace 2: 1000C,
    - Outlet: 300
    - Stirring: 95
    - Cooling: 100
3. Fill the scrubber buffer with concentrated H_2SO_4
4. Fill the scrubber absorber (the bottom of the container) from the acid up to the black line
5. Connect the scrubber to the splash trap
6. Turn on the oxygen tank, and check that flowmeter is at 50 psi.
7. Ensure that the titration cell is perfectly clean. Do NOT use any organic solvents just WATER to clean it!
8. Dry the cell and electrodes with kimwipes
9. If you took of the plastic lid of the titration cell, place the stirrer element in the cell
10. Fill titration cell with electrolyte solution: Acetic Acid solution (75% solution) to the red mark. It is not necessary to measure the volume of electrolyte precisely, however the electrolyte must cover the bundle of capillary tubes.
11. Use the gray bulb available to suck up electrolyte solution into the side leg containing the reference electrode until the liquid covers the reference electrode. Put in the electrode. Bubbles should NOT be in there!
12. Check that the electrode holder (gray cap) in the titration cell is properly installed: The indicator electrode (I) opening should be located immediately next to the side leg of the reference electrode (R)
13. IF YOU TOOK OUT THE PLASTIC COVER OF THE CELL, THE GRAY CAP WITH THE HOLES FOR THE ELECTRODES… PLEASE, apply a thin layer of silicon grease or acid free Vaseline to the O ring to prevent sticking.
14. Place the electrodes and the gas inlet tube into the holder.
15. Place the titration cell on the stirrer motor.
16. Insert the plugs of the coulometer cords into the electrodes. Make sure that the plugs are inserted into the right electrode:
    - I - black Indicator electrode
    - R - red Reference electrode
    - A - red (actually black) Anode

- C - black cathode

(NOTE: the anode and the indicator are the same electrodes, and exchangeable, actually for our instrument they both are black labeled)

17. Shut the titration compartment: THIS COMPARTMENT MUST BE KEPT SHUT, BECAUSE LIGHT AFFECTS THE TITRATION REACTION!.
18. Set the bias to –0.315 V. Go into the analyzer window, then SETUP, and then the second box is BIAS.
19. In the same SETUP window, turn the gain control to any value around 10 (9-12), and close the window.
20. Go to the analyzer window, and check the current. The current will drop slowly to zero. Wait until the current has fallen to virtually zero.
21. If the initial current is negative you might want to use a syringe to drop about 20 μl of the 1000 mg/L NaCl solution into the cell. You can do this by poking the syringe through the gas inlet in the electrode holder. A titration curve will now appear on the screen.
22. Check that current goes back to zero (± 1 uA). If the current does not go back to zero, clean the cell again, load new acetic acid solution. If that does not work, add some more NaCl solution.

Pre-pyrolysis of boat and assembly

Everyday before starting analysis, the boat and its assembly must be cleaned by extended pyrolysis in the furnace.

- In most cases it is good enough to make sure that the boat insert is in the boat during the cell test (see below).
- To heat up the boat independently from the cell test, go to the "analyzer" window, move the scroll of the manipulator to 180 or the position to 180, and then click " < ". The boat should start moving, let it inside the oven until the current goes back to zero, or close to zero. (Repeat this every time the dish is touch with fingers!)

Testing the cell

At the start of each day, you should run at least two NaCl tests to evaluate the cell performance.

- Set up the sample in the queue as “cell test”, including the sample volume (50 μL).
- Analyze and click OK. Wait a few seconds until current is stable.
- Inject 50 μl of a standard solution of 2mM NaCl, through the gas outlet opening in the electrode holder of the titration cell. Make sure the needle of the syringe is immersed in the liquid. Keep the gas inlet disconnected from the acid trap.
- After curve is done, evaluate the sample, and the concentration must correspond to 2 mM. Change the GAIN if titration takes too long or overshooting (See figure 8-10 in the Euroglass manual) is occurring. (Increasing the gain reduces analysis time and decreasing the gain can reduce overshooting). Connect gas inlet to the titration cell before your first analysis.

If integrated value and peak shape (e.g., no overshooting) are correct, the titration cell is ready for use and should in principle not require any further attention during the day. However make sure that

- The titration compartment is kept shut
- The GAIN control remains on the same value
- The stirrer motor is NOT turned off.

Daily Shut-down & Cleanup

Analyzer Shut-down procedure

This procedure has to be done everyday:

a) Disconnect the gas supply to the titration cell
b) Place a beaker under the scrubber (the one with H_2SO_4) and drain the sulfuric acid in the absorber into it. Dispose the sulfuric acid in waste bottle under the hood.
c) Leave the stirrer motor on
d) Set GAIN to zero (in the Analyzer window, the GAIN is in the SETUP in that same window, and into IOC, the third box is the GAIN!)
e) Shut the main gas supply valve, at the tank. Do not turn off the gas supply at the flowmeters!
f) Check the temperature setting and the "temperature" of the oven. In the analyzer window, set Furnace 1 = 300,   Furnace 2 = 300 C
g) Set the temperature of the gas outlet to 100. In the analyzer window set Outlet = 100
h) Take out all the electrodes, and dry them with kimwipes
i) Drain the acetic acid solution from the titration cell.
j) Close all the windows and quit the program.

Once a week, it will be necessary to change the sulfuric acid in the trap before the titration cell. It contains sulfuric acid concentrated and should be fill to the black line, or just bellow the white patch.

Titration Cell Cleanup

The titration cell will require cleaning after a series of measurements. Furthermore, the electrodes should be stored dry overnight and when not in use.

1. Set the gain to 0 (in the "analyzer" window: in the SETUP window, IOC folder) –
The gain should always be 0 when the electrodes are disconnected! -
2. Remove the contact pins from the electrodes
3. Disconnect the cell from the gas supply.
4. Dispose of the liquid in the cell and rinse thoroughly with water. DO NOT USE ORGANIC SOLVENTS.

If there is a grayish white coating on the walls of the cell:

5. Fill the cell with a concentrated solution of ammonia (Ammonium hydroxide)
6. Allow to stand for about 20 minutes
7. Dispose of the ammonia and rinse thoroughly with water. DO NOT USE ORGANIC SOLVENTS.

The electrodes should be cleaned when measurements need to use higher GAIN values (larger than 20). To clean the electrodes use soft tissue paper: kimwipes.

The platinum cathode will become gray to black with time. Immerse the cathode in a concentrated solution of ammonia (ammonium hydroxide) for a short while. Rinse thoroughly with water.

Filtration Unit

The filtration unit is not usually turned off (possible loss of calibration data?) after use.

Lines are normally flushed before every sample (as described above), and especially when carbon blanks are abnormally high. This may be done at the end of the day as well. Flushing of the lines is especially important if they come into contact with an organic solvent.

Standard Solutions, Solvents and Supplies

Preparation of Inorganic Halide Spike Solution[11]

k) Prepare a 1000 mg/L chloride solution (1 µL = 1 µg Cl^-)
   - Dissolve 0.1648 g NaCl in about 50 mL of Super-Q water.
   - Quantitatively transfer this to a 100 mL volumetric flask
   - Fill to the mark with Super-Q water

l) Store this in a stoppered reagent bottle

Preparation of OX Spike Solution

a) Primary OX Stock: Prepare a 10 g-Cl/L stock solution of the desired DOX standard.
   - Add the requisite amount of the pure compound (see table below) to Super-Q water and dilute to 100 mL

DOX compound	Quantity	Notes
Trichlorophenol	1.856 g	
Trichloroacetic Acid	1.534 g	Must be dry crystals

[11] Typically requires 10 minutes

b) Secondary OX Stock: Prepare a 100 mg-Cl/L stock solution of the desired DOX standard.
   - Add 1 mL of the primary OX stock to a 100-mL volumetric flask and dilute to the mark with Super-Q water.

c) Spiked samples for determination of matrix recovery (laboratory fortified sample matrix). Select 10% of analytical samples and set aside an additional 50 mL aliquot of each. Add 20 - 50 µL of secondary OX stock solution to each, and record the exact volume.
   - Each µL of secondary stock added, corresponds to 2 µg/L OX concentration

Nitrate Wash Solution

Stock Nitrate Solution

Weigh out 16.3g of sodium nitrate (KNO_3). Transfer the weighed material to a 1000ml-measuring flask and add 800ml deionized water.
Pipette sufficient concentrated nitric acid (HNO_3) into the measuring flask to drop the pH to 2 (usually requires about 0.6 mL) and top up the solution to 1000ml.

Nitrate Washing Solution

Pour 50 ml of the stock nitrate solution into a 500ml measuring flask and fill to 500ml with deionized water.

Sample Bottles

Sample bottles must be rendered free from TOX contamination. In many cases, they are also used for laboratory chlorination, and must therefore be free from chlorine reactive substances. Because many OX compounds are volatile, these 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.

- These bottles must be acid washed, rinsed with Super-Q water and dried in a high-temperature oven.
- Septa must be washed with detergent, rinsed with Super-Q water, wrapped in aluminum foil and dried in 100ºC oven.

Preparation of Sodium Azide Preservative (80 g/L)[12]

a) Add 800 mg of NaN_3 (99.9+% purity) to a 10-mL volumetric flask
b) Fill flask to mark with Super-Q water
c) Cap and invert 5 times to dissolve
d) Transfer this solution to a septum-capped vial and store in a refrigerator
e) Solution should be prepared fresh every 2 months

Supplies

Item	Catalog #	Approx. Price	Approx # used/run[13]
Pasteur Pipettes	Fisher: 13-678-20A	720/ $46.10	10
TOX Columns[14]	CPI #634-004E		28
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	
TCAA			
BDCAA			
CDBAA			
TBAA			
H_2SO_4	UMass Stockroom		
Small HAA vials	Fisher: 03-393D		

[12] Only necessary for field sampling, or if aqueous samples are to be held for more than 48 hours
[13] Assuming about 10 samples analyzed
[14] CPI International, 800-878-7654 (FAX: 707-545-7901), part #634-004E, prepacked glass columns, 3x6x47 mm, Euroglass type

Alternative Methodology: Halide-Specific Detection

Background

Recently methodologies have been developed for measuring TOCl, TOBr and TOI as separate fractions of the TOX. This may be done by trapping the HX vapor in the pyrolysis tube gases, and subjecting these to inorganic halide analysis by ion chromatography. This approach has been used by a small number of researchers over the past 20 years. However, Minear is one of the few to actually publish a specific methodology (e.g., see: Echigo et al., 2000[15]). They used a heated transfer line, which was also flushed after each sample. The Euroglass TOX analyzer does not use a CO_2 auxiliary gas, which should prove to be an advantage over the Dohrmann instrument (used by Minear) as carbon dioxide will interfere with halide analysis by IC.

Inorganic halide analysis is conducted with the Dionex ion chromatograph located in 301 Elab II, near the TOX analyzers. This instrument uses chemical suppression technology, and is equipped a data system. There is a separate SOP for halide analysis by IC.

Table 1. Recovery of TOCl & TOBr from Direct Application to Sample Boat[16]

Compound	Boat Injection		Full Method	
	Recovery (%)	SD (%)	Recovery (%)	SD (%)
Dichloroacetic Acid	88.0	4.0	83.6	6.8
Dibromoacetic Acid	84.5	3.7	76.4	7.2
Bromoform	90.2	3.1	82.6	5.4
2,4,6-Trichlorophenol	91.6	2.8	84	5.9

Instrument Configuration

- Furnace is connected to a test tube through a bubble diffuser
- Transfer line must be heated with heating tape
- Test tube contains 10 mL distilled water
- Possibly lower gas flow rates to minimize splashing

[15] Echigo, Shinya; Zhang, Xiangru; Minear, Roger A.; and Plewa, Michael J. Differentiation of Total Organic Brominated and Chlorinated Compounds in Total Organic Halide Measurement: A New Approach with an Ion-Chromatographic Technique, in Natural Organic Matter and Disinfection Byproducts: Characterization and Control in Drinking Water, Barrett, S.E., Krasner, S.W. and Amy, G.L. editors, ACS Symp. #761, American Chemical Society, Washington (2000)
[16] using a Dohrmann instrument, 10 µg injection; 4 replicates each; from Echigo et al., 2000.

Operation

- Gas transfer line is flushed with 3 mL Super-Q water after combustion to remove condensed halides and this is added to 10 mL in test tube
- Total water volume adjusted to 15 mL prior to IC analysis
- Sample must be sparged with nitrogen gas (5 psi) for 5 min to remove excess carbon dioxide
- Sample is analyzed by IC with chemical suppression and conductivity detection

Analyzer Maintenance

Initial Conditions

These conditions were setup by Roger Curtis on June 25, 1999.

- In the "Controller" window, go to the Options menu:
  - Analysis
    - Description folder:
      - Method name ECS
      - Chem. Elem.: Cl
      - Method: AOX
    - Parameters folder:
        - With ECS 3000 Analyzer
      - Cool Forced: 100
      - Cool Norm: 100
      - Meas. Time: 1800
      - Stirring: 95
      - Tfurn1: 1000
      - Tfurn2: 1000
      - Toulet: 300
        - With NONE Sampler
          - Sample name YES
          - Sample size YES
          - Vial No YES

      This conditions can be changed in the "Analyzer" window, but those are temporal, this are the conditions for the actual analysis.
    - Manipulator folder:
      - STBY 0 20 15
      - EVAP 80 10 30
      - COMB 170 5 180
      - HOME 0 15 0

This characteristics can be changed depending on the amount of carbon left over, if it is too much, may be you should change the time the comb is in (180)

- Evaluation:
  - Method name: Absolute
  - Calibration order: None
  - Time window: 5s
  - Threshold: 5%
  - Threshold 1: 0.001
  - Threshold 2: 0.001

- Setup:
  - ECS 3000 analyzer
  - Sampler: None

Troubleshooting the TOX Analyzer

1. **Some useful notes**
   - Titration curve may have more than one peak. This is normal with certain compounds that are not easily pyrolyzed.
   - When high concentrations are used, the signal may show a flat top. This is normal and the integration should be OK.
   - If the voltage goes up or down to an extreme and it stays there for more than a day, check out the electrodes. The anode and the indicator are silver electrodes and there should be a shining silver tip in the bottom of the electrode, if this is not the case ask for help!
   - We're using an old software version. It has had problems with data file buildup (Interbase data files). These need to be backed up on occasion, and then the files can be deleted from the Interbase Server. If this isn't done, the error message, "Interbase setting not correct" may appear.
   - For other concerns, consult the EUROGLASS manual for TOX analysis

2. **If you need more help**
   - Representatives in the US
     - David J. Scott (dscott@ptsltd.com)
     - Lindsey Pyron (lpyron@estanalytical.com)
   - Technician at Euroglass (they are usually only contacted by US reps)
     - Frans Heijstraten (fheijstraten@euroglas.nl)
   - If you call the US representative you may need to present the following information
     - Instrument was installed by Mr. Roger Curtis.

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

The precision, accuracy and method detection limits will be evaluated, and where there are existing methods, 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 analytical determinations that are devoted to quality control. The precision of each 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).

The accuracy of each analysis will be determined by measuring spike recoveries in the matrix of interest. The relative errors will be calculated and will be considered acceptable if they fall 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. In general, a test will not be deemed useful if its precision or accuracy is found to be equal to or greater than 20% of the highest values observed. 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.

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 TOX analysis must be kept in the dark, and in a refrigerator from the time of disinfectant quench until the start of analysis. Some TOX compounds 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

Standard solutions and reagents are generally kept under refrigeration. Specifics of their handling is included in the method protocol.

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.

Procedures specific to TOX Analysis

General QC

Quantitative organic analyses must always be standardized or validated by the use of carefully prepared solutions of known standards. In general, non-aqueous primary stocks are kept in a -10°C freezer and discarded after two months. Duplicate primary stocks are prepared regularly, as a check against degradation of the primary stock. Data quality objectives for TOX analysis is assured by: (1) use of blanks; (2) analysis of duplicates; (3) determination of spike recovery; (4) analysis of a matrix standard; (5) monitoring of response factors; and (6) monitoring for unusual peak shape.

Three types of blanks should be run daily or with each set of samples: (1) carbon blanks; (2) laboratory water blanks or a zero standard; 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".

Spike recoveries are determined for each selected OX compounds. Matrix standards will be prepared and analyzed with each run. Finally, general QA requires that all instrument output be manually inspected for non-standard peaks. When such peaks are observed, potential sources must be investigated. If the problem cannot be corrected, the data may have to be discarded.

Instrument usage must be monitored by means of instrument log books. A sign-up book or calendar is advisable for scheduling purposes. However, once an instrument is to be used, the analyst must document this use in an instrument-dedicated log book. The exact dates, times (starting and ending) and approximate number and type of samples must be recorded. The analyst should also indicate any irregularities in the instrument's operation or in the physical environment (e.g., high room temperature)

This outlines our general QA philosophy for chromatographic and other methods. 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 under US EPA method 552.2. 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 TOX Analysis

Types of Samples or Standards	§ in 5320	Purpose	Frequency	Timing	QC data
Carbon Blank (nitrate washed)	5e2	Assess general operation and halide content of carbon	1 for every 15 samples	Beginning of each day and scattered throughout	
Initial Demonstration of Capability (IDC)		To show that an analyst's technique and equipment are adequate for TOX analysis	4-7 standards when first learning method, otherwise not done		Mean % recovery and standard deviation
Method Detection Limit (MDL)		To determine the lowest concentration level that the analyst can report	7 standards run		MDL and EDL
Laboratory Reagent Blank (LRB)	5e1	Test lab conditions and quench for interferents	1 per day	Beginning of day	
Field Reagent Blank (FRB)		Test all field conditions for interferents	1 per day, if sampling occurred outside of the lab	mid day	
Spiked sample, or Laboratory Fortified Sample Matrix (LFM)		To test analyte recovery in the sample matrix	1 for every 10 samples	Mixed throughout day	% recovery, mean and standard deviation
Sample spiked with 10x matrix concentration in Cl^- and Br^-		To test for inorganic halide rejection	1 for every new batch of PAC or new analyst or new sample type		
Compound Challenge		To verify the recovery of poorly adsorbing and volatile analytes in matrix			% recovery of DCAA and Chloroform
Unknowns or "samples"		This is what you really want to measure	As many as desired	Mixed throughout day	Breakthrough

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 chromatograms show abnormally elevated noise levels or drifting baseline, the operator must intervene before proceeding. The problem must be diagnosed, solved and the sequence restarted at vial #1.

Table 8: Typical TOX Analytical Sequence

Sample #	Sample type	QC objectives
1	Carbon Blank	To check on carbon conditions
2	Lab Water Blank	To check for gross contamination of water or lab environment, and establish background
3-8	Analytical Samples	
9	Spiked sample	Analyte recovery
10-14	Analytical Samples	
15	Carbon Blank	Background
16-20	Analytical Samples	
21	Spiked sample	Analyte recovery
22-26	Analytical Samples	
27	Carbon Blank	Background
28-32	Analytical Samples	
33		

Quantitative QC Criteria

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., when injections are being made overnight by the autosampler). 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 11). 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. Standard slopes, % analyte recoveries, calibration check controls and mean surrogate recoveries are documented over time in this way. All summarized QC data (tabular and graphical) must be kept in a notebook in the Elab II organic analysis room (Rm 301). 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	Typical Corrective Action
OX Spiked sample, or Laboratory Fortified Sample Matrix	1 for every 15 samples	Mixed throughout day	DCAA and chloroform recovery = ±30% of long-term average Trichlorophenol = ±20% of real value	❖ Re-run matrix spikes ❖ Re-examine entire run for errors ❖ Possibly change SOP

(LFM)				
Direct halide injections	1 for every 10 samples	Mixed throughout day	Mean % recovery = 95%-100% Acceptable peak shape	❖ Clean electrodes and titration cell
Carbon Blanks	1 for every 10 samples		Average value ≤1 μg Max value ≤2 μg	❖ Try another carbon batch
Super-Q Water Blanks			Average value ≤10 μg/L	❖ 1. Check & correct operation of Super-Q system ❖ 2. Use alternative high-purity water source
Calibration Standards[17]	7 levels including zero		Calibration slopes (PAR vs. conc.), = ±30% of long-term average	❖ Run new set of standards ❖ Prepare new THM stock ❖ Examine GC for problems, needed maintenance
Continuing Calibration Check Standards (CCC)[18]			Calculated Conc. = ±25% of expected value	❖ 1. Prepare new calibration check standard ❖ 2. Prepare new standard curve based on new stock
X Spiked samples			Halide interference ≤5 μg/L	❖ 1. verify nitrate wash effectiveness ❖ 2. look for alternative carbon source that solves problem
Unknowns or “samples”	As many as desired	Mixed throughout day	2nd column ≤15% of total	❖ Run effluent through 2 more columns & analyze
			RSD or RFD for replicate analyses ≤25%	❖ Re-run samples and/or discard outliers[19] until precision can be brought under control
			Sample tailing	❖ 1. verify that furnace is working properly ❖ 2. clean furnace tube ❖ 3. use longer program

[17] Prepared from the currently-used calibration stock II (less than 1 month old)
[18] Prepared from the previously-used calibration stock II
[19] using Dixon’s Q Test, or some logic test (e.g., monotonic increase with timed data series).

Appendix

Standard Method 5320:

(APHA et al., 1999)