Analysis of Haloacetic Acids

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

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Table of Contents

Standard Operating Procedures

Analysis of Haloacetic Acids

This guidance document was prepared to assist research assistants, post-docs and lab technicians in conducting haloacetic acid (HAA) 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 Allan Briggs, Melissa Brown, Amanda Keyes and Boning Liu for providing summaries of our revised practice since moving into our new research building. Please help keep this document current by alerting us to needs for long-term changes in methodology or equipment.

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Scope

This method has been used in the UMass Environmental Engineering Laboratory for all 9 haloacetic acids containing chlorine and bromine (HAA9; analytes listed in Table 1). 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.

Extension of this method to the 10 iodine-containing HAAs (Table 2) may be possible, however this has not been validated. Any use of this method for the iodinated species must be accompanied by appropriate disclaimers until the method can be fully validated.

Alternative methods for HAAs have employed LC/MS and microextraction with ESI-MS[1]. Many of these are still under investigation, and none are considered accepted methodologies.

Table 1: Standard HAA Analytes

Analyte	CAS Registry Number
Trihaloacetic Acids (THAA)	
Trichloroacetic Acid (TCAA)	76-03-9
Bromodichloroacetic Acid (BDCAA)	7113-314-7
Chlorodibromoacetic Acid (CDBAA)	5278-95-5
Tribromoacetic Acid (TBAA)	75-96-7

[1] Magnuson and Kelty, 2000 [Anal. Chem. 72, 2308]

Dihaloacetic Acids (DHAA)	
Dichloroacetic Acid (DCAA)	79-43-6
Bromochloroacetic Acid (BCAA)	5589-96-3
Dibromoacetic Acid (DBAA)	631-64-1
Monohaloacetic Acids (MHAA)	
Monochloroacetic Acid (MCAA)	79-11-8
Monobromoacetic Acid (MBAA)	79-08-3

Table 2: HAA Analytes Containing Iodine

Analyte	CAS Registry Number
Trihaloacetic Acids (THAA)	
Dichloroiodoacetic Acid (DCIAA)	
Bromochloroiodoacetic Acid (BCIAA)	
Dibromoiodoacetic Acid (DBIAA)	
Chlorodiiodoacetic Acid (CDIAA)	
Bromodiiodoacetic Acid (BDIAA)	
Triiodoacetic Acid (TIAA)	
Dihaloacetic Acids (DHAA)	
Chloroiodoacetic Acid (CIAA)	
Bromoiodoacetic Acid (BIAA)	
Diiodoacetic Acid (DIAA)	
Monohaloacetic Acids (MHAA)	
Monoiodoacetic Acid (MIAA)	64-69-7

Method Overview

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

Table 3: Summary of Procedure for HAA Sample Analysis

1. Prepare **calibration standards** (Table 4) and **QC samples** (Table 5)
2. Place 30 mL of sample/standard to be analyzed **into vial**.
3. If residual chlorine is present add approximately 40 mg of **NH_4Cl**
4. Add 20 µL of **surrogate** stock solution to each vial
5. Add 1.5mL concentrated **H_2SO_4** to each vial.
6. Add 3mL of the pre-mixed **MTBE** + internal standard.
7. Add approximately 15g of **Na_2SO_4**. (Use dispenser made by glass shop.)
8. **Shake** for 15 minutes.
9. Make a solution of acidic **methanol + 5% H_2SO_4**. Place 2mL of this solution into 20mL vials.
10. **Remove 1mL** from first extract and place into prepared 20mL vials.
11. Place in a 50°C **water bath** for 2 hours.
12. Make a saturated solution of **$NaHCO_3$**. Add 5 mL of this solution to each vial.
13. Add 1mL pure **MTBE (no IS)**.
14. **Shake** for 2 minutes.
15. Place extract into **autosampler** vials, freeze, and analyze.

Table 4. Typical Preparation of Calibration Standard

1. Prepare Stock II as needed: Add 150µL of a 2000µg/mL HAA stock (Supelco) and 300µL each of 1000 µg/mL Brominated stocks (Supelco) to a 10mL volumetric flask containing MTBE.
2. Prepare calibration standards: add 30mL of Super-Q to 7 vials. Add 0, 5, 10, 20, 30, 50, and 80 µL of stock II. Volumes of stock addition may be adjusted based on expected HAA concentration range and speciation.

Table 5. Typical Preparation of QC Samples

1. Prepare Spiked samples for determination of matrix recovery (laboratory fortified sample matrix). Select 10% of analytical samples and set aside an additional 30 mL aliquot of each. Add either 20, 30 or 50 µL of calibration stock II to each.
2. Prepare a continuing calibration check standard at the 50 µg/L level.
3. Prepare any other QC samples as needed (see Table 10, page 27).

Detailed Procedures

Basis for Method

We use a protocol that is closely aligned with the US EPA method 552.2, "Determination of Haloacetic Acids and Dalapon in Drinking Water by Liquid-Liquid Extraction, Derivatization and Gas Chromatography with Electron Capture Detection." Please refer to the latest version of this method (currently version 1.0, dated 1995; attached as Appendix 1) for all details.

For historical reasons and site-specific considerations, we have chosen to depart from method 552.2 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 HAA method is US EPA method 552.2. 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 6.

Table 6. UMass Protocol Departures from US EPA Method 552.2

§ from 552.2	Step	552.2 protocol	UMass protocol
7.3.4	Ammonium Chloride	Used for quench	Currently we are using this protocol. For some studies we use arsenite
7.4.1	Acidic Methanol	10 % H_2SO_4	5 % H_2SO_4[2]
7.5.1	Internal Standard	1,2,3-trichloroproprane added as a concentrated stock to final derivatized extracts at §11.2.8	Either 1,2,3-trichloropropane or 1,2-dibromopropane added to bulk solvent (300µg/L) prior to use for extraction at §11.1.7
8.1.2	Quenching Agent	NH_4Cl at 100 mg/L-sample	NH_4Cl at 100 mg/L-sample. (With

[2] This change was made in the late 1990s based on a recommendation from US EPA. We may consider returning to 10% if methylation performance is low.

			some studies: Na_2AsO_2 at 75 mg/L-sample[3])
11.1.2	Sample volume	40 mL	30 mL
	Vial size	60 mL	40 mL
11.1.4	Sulfuric Acid addition	2 mL	1.5 mL
11.1.6	Sodium Sulfate addition	16 g	12 g
11.1.7	MTBE volume	4.0 mL	3.0 mL
11.2.1	MTBE transfer	3 mL	1 mL
11.2.2	Acidic Methanol volume	1 mL	2 mL
11.2.5	Sodium Bicarbonate addition	4 mL	5 mL
11.2.8	Point of addition of internal standard	After transfer of methylated extract to autosampler vial	Directly to MTBE added for extraction at §11.1.7

We use one of our Hewlett-Packard 5890 series II GCs for HAA analysis. These are equipped with an HP 7673 autosampler. Our GC column and parameters come closest to method 552.2's column B (Table 1 in US EPA method). The comparison is shown below in Table 7.

Table 7. Instrument Parameters for HAA Analysis

Step	552.2 protocol	UMass #1	UMass #2[4]
Analytical Column	DB-1701	DB-1701	DB-1
Length	30 m	30 m	30 m
Internal Diameter	0.25 mm	0.32 mm	
Film Thickness	0.25 µm[5]	0.25 µm	0.25 µm
Injection Type	Splitless with 0.50 min delay	Splitless with 0.47 min delay	
Split Flow	Not specified	77 mL/min	
Carrier Gas	Helium	Zero-grade Nitrogen	
Carrier Flow	25 cm/sec	23 mL/min	
Make-up Flow	Not specified	1 mL/min	
Injector Temp	200°C	157°C	
Detector Temp	260°C	297°C	
Oven Program	Hold at 35°C for 10 min Ramp to 75°C at 5	Hold at 37°C for 21 min Ramp to 136°C at 11 C/min (9 min)	

[3] This is typically done by adding 20µL of a 150 g/L sodium arsenite solution (1.5 g Na_2AsO_2 into 10 mL Super-Q water) to each vial prior to introduction of the sample. Arsenite is a very poisonous substance. Be careful when handling!
[4] On April 11, 2011 we began using method #2 due to logistical reasons, the DB-1701 had to be retired from regular use.
[5] MWH labs recommend a film thickness of 0.18µm for sharper peaks. They also use a DB-XLB for confirmation

	C/min Hold at 75°C for 15 min Ramp to 100°C at 5 C/min Hold at 100°C for 5 min Ramp to 135°C at 5 C/min	Hold at 136°C for 3 min Ramp to 236°C at 20 C/min (5 min) Hold at 236°C for 3 min	

UMass Detailed Procedures

Sample Preservation

1. **Add one of the following three quenches to each 40-mL clear vial.**[6]
   - A. ~40 mg NH_4Cl crystals (Desiccator in 301 Elab II) using dispenser made by glass shop[7]
   - B. ~250 µL of 0.1 N sodium arsenite solution[8]
   - C. ~60 mg $(NH_4)_2SO_4$ crystals[9]

2. **Add a biocide, if samples cannot be extracted within 24 hours**[10]
   - ~50 µL of sodium azide solution to each 40-mL vial

3. **Fill vial with fresh sample**
   - Turbulence will help mix in quench, but be careful not to lose quench in overflow

4. **Place aqueous samples in a refrigerator until extraction.**
   - Samples should be extracted and analyzed as soon after quenching as possible, but under no circumstances should more than 14 days be allowed to elapse.

Sample Extraction and Preparation for GC Analysis[11]

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

[6] Do not use sulfide, and avoid use of sulfite or thiosulfate, as these can cause degradation of HAAs. Ascorbic acid (1M/M, forming dehydro-accorbate) and hydrogen peroxide (1M/M, forming O_2 and H_2O) are also effective at reducing chlorine [Worley et al., 2003; JAWWA 95:3:109], but have not been adequately tested for HAA analysis.
[7] Newport News WW uses 100 mg in 60-mL vial
[8] kept in refrigerator # 3
[9] UNC uses 20 mg
[10] 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.
[11] Typical prep time is 4 hours for a run of 30 samples

2. **Place 30 mL of sample/standard to be analyzed into vial.**
   - Add 30 ml of the water sample using an Eppendorf pipette (Marcus 3D)

3. **Add 20 µL of surrogate (2,3-dibromopropionic acid) stock solution to each vial.**
   - Stock solution is stored in refrigerator #2
   - Use 25 µL glass syringe located in Marcus 3D syringe drawer

4. **Add 1.5mL concentrated H_2SO_4 to each vial.**
   - Make sure acid is not contaminated[12]
   - Use 10 mL glass pipet located in hood

5. **Add 3mL of the pre-mixed MTBE + internal standard.**
   - Use repeater pipet

6. **Add approximately 15g of anhydrous Na_2SO_4.**
   - One measure from the glass dispenser labeled HAA.
     - Dispenser (made by glass shop) is located in Marcus 3D cabinet above pH meter
     - Anhydrous sodium sulfate should be dried and purified by baking at 400ºC for 4 hr when new; care must be exercised not to introduce any contaminants into this reagent.

7. **Shake for 15 minutes.**
   - Place vials in rack
   - Secure rack with top into harness on New Brunswick G10 Gyrorotary shaker
   - Turn on and set speed to 250 rpm
   - Shake for 15 minutes.

8. **Make a solution of acidic methanol + 5% H_2SO_4. Place 2mL of this solution into 20mL vials.**

While shaking, prepare the acidic methanol solution and vials:

- Label 20-ml vials.
- Prepare a solution of Methanol + 5% H_2SO_4. (You'll need 2 ml of this solution per vial, so plan accordingly.)
- Place 2 ml of this solution into labeled 20-mL vials, using the repeater eppendorf pipette.

9. **Remove 1mL from first extract and place into prepared 20mL vials.**
   - Use 1 mL glass pipets
   - Done in hood

[12] JT Baker seems to be reliable; EM Science may not always be (MWH)

10. Place in a 50°C water bath for 2 hours.

- Water bath is located on a shelf attached to the west wall of Marcus 3D
- Water level should be sufficient to cover samples

11. Make a saturated solution of $NaHCO_3$. Add 5 mL of this solution to each vial.

- Make a $NaHCO_3$ saturated solution.
  - In a beaker, add enough water (You'll need 5 ml of this solution per vial)
  - add sodium bicarbonate
  - warm it up to try to dissolve it.
  - Let it cool down, should have some no-dissolved solid in the bottom.
- Take the vials from the water bath
- Add 5 ml of the bicarbonate solution using the repeater eppendorf pipette

12. Add 1mL pure MTBE.

- With repeater pipet
- Done in hood

13. Shake for 2 minutes at 400 rpm.

- Use slow rotary table shaker located under water bath
- Sample tray is capped and fits sideways into clamp area and strapped down with bungee cord

14. Place extracts into autosampler vials.

- Use vials as supplied without further cleaning
- Fill using a Pasteur pipet and small rubber bulb
- Must be done in hood
- Place clean top on vial and use crimper to seal
- Vials are marked with ID
- When all are complete, approximate liquid level in each vial should be marked with a line using a permanent marker[13].
- Be certain to include necessary QC samples
  - See Table 10 (page 27) for a full listing of QC samples
  - See Table 11 (page 28) for a typical sequence

15. Freeze Samples to remove water[14]

- Store autosampler vials in freezer for at least 3 hours
  - Use refrigerator/freezer #2
- Inspect samples for ice
- Transfer organic phase of any samples with obvious ice particles into new autosampler vials
  - Label vial and cap
- Run GC analysis as soon as possible

[13] This is to help identify when excessive evaporation has occurred
[14] some water will always be present because of its solubility in MtBE, it may also be present as a separate phase

Analysis by Gas Chromatography[15]

GC Set up and Initiation of Run

1. **Check there is enough gas in the Nitrogen tank, if so, open Gas line for 5890**
2. **Turn on oven, detector, injector**
3. **Fill the rinsing vials with MTBE**
4. **Put no more than 5-15 samples in the autosampler trays at a time.**
   - See Table 11 (page 28) for typical vial sequence with QC samples
   - Avoid placing any more 5 at a time during the day and 15 during the night[16].
5. **Write down in the log book, vial number and sample identity**
6. **In the integrator press:**
   - SHIFT + LOAD
   - SHIFT + METHOD
   - write: JMCHAA
   - ENTER
   - SHIFT + EDIT
   - SHIFT + SEQ
   - write: 1
   - ENTER
   - Keep pressing enter up it gets to ask you about the FIRST BOTTLE which can be different and you may change depending on the number of your first bottle.
   - ENTER (keep pressing enter for the rest of the questions, until nothing more is asked)
   - SHIFT + SEQ
   - START
7. **Inspect the first few chromatograms**
   - Do this as they come off the integrator/recorder
   - At this point make your first QC report by email (see "Data Analysis & QC Reporting" §1b).
8. **Reload the next set of samples**
   - When it's time for a new set of samples to be place on the tray, remove 5 more vials from the freezer and place them in the next 5 positions
   - Remove the previous 5 vials, and estimate the amount of liquid remaining (% remaining based on original level) and record this for each vial
9. **Repeat step 8 until done.**
   - within 2 working hours of run completion
     - report on extract volume loss (see below: §2a)
   - within 24 hours of run completion

[15] typically requires 20 hours of GC time for a run of 30 samples
[16] intended to minimize volatilization losses during sample runs

- report on standard curves and other QC (see below: §5b)

GC Shut-down procedure

- Once the oven temperature is down to 30 C, turn off the oven, detector and injector in the front panel of the GC
- Close the gas valve

Data Analysis & QC Reporting

1. **Data Analysis begins with the first injection.**
   a) The analyst must inspect the first few injections to see that:
      - the solvent blank is free from extraneous peaks
      - the first standards have all of the peaks expected
      - the first standards exhibit good chromatography
      - the internal standard peak area is within tolerance limits.
      - retention times of the analytes are within expected windows (see Table 8)
        - Small differences in retention time are expected (from small changes in headloss through the column, temperature, leaking septa, etc.) from one run to the next. Because the retention factors are not as likely to change, retention times may be best re-estimated from them (see equation below). The mobile phase retention time (t_M) may be viewed directly (time for first peak to come off), calculated based on the observed retention time (t_R) from an easily identifiable solute peak (e.g., the internal standard), or from the column void volume (V_M) divided by the gas flow rate through the column.

$$t_R = t_m\left(k' + 1\right)$$

   b) The analyst must report on the success or failure of these first few injections 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 "HAA QC report"
      - 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

Table 8. Expected HAA Retention Times

Analyte	DB-1701		DB-1	
	Typical Retention Time, t_R (min)	**Retention Factor (k')**	**Typical Retention Time, t_R (min)**	**Retention Factor (k')**
Unretained Solutes	1.4 (t_M)	0	?? (t_M)	
Monochloroacetic Acid (MCAA)	6.71	3.8	20.29	
Internal Std: 1,2-dibromopropane (IS)	9.37	5.7	34.17	
Monobromoacetic Acid (MBAA)	10.98	6.8	28.00	
Dichloroacetic Acid (DCAA)	11.99	7.6	29.21	
Surrogate (Surr)	13.20	8.4		
Trichloroacetic Acid (TCAA)	17.88	11.8	34.80	
Bromochloroacetic Acid (BCAA)	22.77	15.3	34.46	
Bromodichloroacetic Acid (BDCAA)	25.57	17.3	39.25	
Dibromoacetic Acid (DBAA)	26.08	17.6	38.53	
Chlorodibromoacetic Acid (CDBAA)	27.92	18.9	43.40	
Tribromoacetic Acid (TBAA)	29.61	20.2	46.62	

2. **Examine samples at end of run**
   a) The analyst must report on status of the sample extracts and any observed problems 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 "HAA QC report"
      - The report must include the following information: (1) start date and time for run, (2) approximate average % volume loss for extracts, (3) maximum % volume loss observed; and (4) any other problems noted

3. **Access the data stored in the computer:**
   - Copy all your files (*.rpt) to a diskette.
     - Exit the peak program to DOS
     - cd..
     - cd peak
     - cd data 1
     - copy *.rpt b:
   - Use the Excel program to retrieve the data into an excel file. Remember to erase the files from this computer (use: del *.rpt)

4. **Preparation of Standard Curves**
   - We use least squares best linear fit of the standard peak area ratios (PARs) regressed against their known concentrations. Many people use an MS Excel that is re-used as a template. When using these types of files, be careful of the following:

- All standard data are being used for the standard curves. (this is a problem when standard data have been removed due to outliers, and not replaced in subsequent runs). Examine lines 12-18 in the "THM stds." worksheet.
- Reagent blanks are subtracted where appropriate, and not where inappropriate (see: Procedures specific to Chromatographic Analysis, pg. 21)

- Standard curves must also include the zero standard
- Standard curves must be visually inspected for non-linear behavior and the possible presence of outliers
  - When noted, an outlier may be excluded from the calibration curve, after consultation with the graduate QC officer. Removal of an outlier should:
  - Substantially improve the standard curve linearity or correlation
  - Improve agreement with the calibration check standard
  - Bring the regressed slope closer to the expected values based on recent data from the calibration slope control chart
- Be careful when removing an outlier in a spreadsheet that you remove it from the range used for graphing as well as from the range used for calculation of regression coefficients. Also be careful that you don't inadvertently replace it with a zero.

5. <u>Evaluation of standard curves and other QC data by the analyst</u>

a) This must be done as soon as possible, but no later than 24 hours from the end of the GC run. Compare with quantitative criteria in Table 9.

b) Send an email report as in #1b above, but this time include the following information:

i. Calibration curve slopes for all analytes (usually 9)
ii. Internal standard average area
iii. Surrogate peak area
iv. Spike recoveries

6. <u>Validation of QC data</u>

a) The graduate QC officer or his/her designee then must compile the analyst's data into the running QC data files, and examine the updated control charts.

b) The graduate QC officer or his/her designee then must send an email message to the faculty QC officer stating whether the QC data are within control limits, and if they are not, what actions will be taken.
   - Again, the subject line of this email message must simply read "HAA QC report".
   - 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 #3).

Clean Up

- Separate the organic phase from the water phase using the big separatory funnel in the hood. The water may be drained into the waste water bottles and

the organic phase must be disposed of in the properly labeled Hazardous Waste Container.

- All the vials, glassware, and other labware should be cleaned in the same fashion
  - First rinse with tap water.
  - Let them soak in soapy water (e.g., Alconox) overnight
  - Then rinse with RO water and leave them in the acid bath[17] overnight.
  - Then take them out, rinse them with distilled water (3 times) and once with super Q water.
  - Dry them:
    - Non-volumetric glassware in the oven at 180ºC.
    - The caps without septa, pipet tips and any volumetric glassware should be placed in the cooler oven at about 80ºC
    - Detachable septa and caps with fixed septa are dried at room temperature in the hood
- Syringes should be rinsed at least 5 times with acetone, before and after use.
- Acid baths must be cleaned and refreshed on a weekly basis

Standard Solutions, Solvents and Supplies

Preparation of Calibration Standards[18]

1. **Prepare Stock II as needed: Add 150 µL of a 2000 µg/mL HAA stock (Supelco) and 300 µL each of 1000 µg/mL Brominated stocks (Supelco) to a 10mL volumetric flask containing MTBE.**
   a) In a 10 mL volumetric flask containing some MTBE
   b) Add 150µL of a 2000µg/mL HAA stock (Supelco #4-8047) and
   c) Add 300µL each of 1000 µg/mL Brominated stocks (Supelco #4-7277, 4-7278 and 47729-U)
   d) Add MTBE to fill the volume.
   e) Transfer the solution to a heavy-walled extract vial (Supelco #3-3293) and store it in the container labeled HAA stocks in the refrigerator #2.

2. **Prepare calibration standards.**
   a) Add 30 ml of Super-Q water to 7 vials
   b) Add a range of volumes to produce a standard curve that covers the concentration range of interest[19].
      i. Typical for finished drinking waters: 0, 5, 10, 20, 30, 50, and 80 µL of standards stock II for HAA.
      ii. Higher levels (formation potential): 0, 25, 50, 100, 150, 200, 350 µL of standards stock II for HAA.

[17] 5% H_2SO_4, or 10% HNO_3 (UMass and UNC protocol)
[18] typically requires 20 minutes
[19] Volumes and stock concentrations were selected so that the number of µLs of Stock II added equals the concentration of the standard in µg/L.

c) These must be prepared fresh just before starting a GC run

Preparation of QC Samples

a) Prepare Spiked samples for determination of matrix recovery (laboratory fortified sample matrix). Select 10% of analytical samples and set aside an additional 30 mL aliquot of each. Add either 20, 30 or 50 μL of calibration stock II to each.
b) Prepare a continuing calibration check standard at the 50 μg/L level.
   - Dose from different stock solution vial
c) Prepare any other QC samples as needed (see Table 10, page 27).

Preparation of Internal Standard Stock Solution[20]

a) Place a 10 mL volumetric flask partially filled with MtBE in an analytical balance
b) Zero out the weight
c) Add 7 drops of *1,2,3-trichloropropane*[21] and RECORD the weight ($Mass_{IS}$)
d) Fill to the mark with MTBE
e) The concentration of the Internal Standard Stock solution is determined by:

$$C_{IS_{stock}}(mg/mL) = \frac{Mass_{IS}(g)}{10mL}\left(\frac{1000mg}{g}\right)$$

- The concentration ($C_{ISstock}$) should be around 10 mg/mL.
- Place the unused portion of this solution in a heavy-walled extract vial (Supelco #3-3293), label it with your initials, the date, the IS compound and the IS concentration and store it in the refrigerator #2.

Preparation of MTBE with Internal Standard:

a) Rinse a dry 1-L volumetric flask with methanol (once) and with MTBE (twice). Dispose the rinse solutions in the waste bottle in the hood.
b) Fill the flask up to ~2/3 with MTBE
c) Calculate the amount of 1,2,3-trichloropropane ("x" mLs) necessary to prepare a 1500 μg/L solution:

$$x(mL) = \frac{1500\mu g/L}{C_{IS_{stock}}(mg/mL)}\left(\frac{1L}{1000\mu g/mg}\right)$$

[20] The same IS stock is used for both THM and HAA analysis.
[21] The pure compound is stored in the extraction hood. Be careful. This is a flammable and irritating chemical. Use gloves. Prior to February 2003, we commonly used 1,2-dibromopropane. This compound can still be used as an IS, but it may be subject to chromatographic interference in some samples.

d) Add "x" mL of the standard solution to the MTBE and fill to the mark with MTBE.
   - There is a dedicated 250 mL syringe for pipeting the 1,2,3-trichloropropane into the MTBE

Preparation of Surrogate Stock Solution

a) Partially fill a 10 mL volumetric flask with MtBE
b) Add 100 µL of *2,3-dibromopropionic acid surrogate standard* (1000µg/mL in MtBE)
c) Fill to the mark with MTBE
d) Transfer to two heavy-walled extract vials (Supelco #3-3293) and label with your name and date
e) Surrogate stock solution is stored in refrigerator #2:

Preparation of Sodium Azide Preservative[22]

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

Table 9. Summary of Supplies for HAA Analysis

Item	Catalog #	Approx. Price	Approx # used/run[23]
Pasteur Pipettes	Fisher: 13-678-20A	720/ $46.10	10
Autosampler Vials	Fisher: 03-340-51F	10 packs of 100 vials / $209.10	40
Septa for the 40 ml vials	Fisher 03-34-04H	$85/a case of 144 septa	
Sept for vials	Fisher 03-377-42	$80/pk of 100	
Integrator Paper	Fisher: 07-684-60	cs of 4 / $96.12	
Ink Cartridges	Fisher: 07-684-61	$15.20 each	
DIUF Water	Fisher: W2-20	$32.29	Not normally used
Methanol	Fisher: A 454-4	Case of four 4L bottles/ $178	76 mL
MtBE	Fisher: E127-4	cs of four 4L bottles / $364.84	
Sodium Sulfate	Fisher: S 415-1	cs of six 1Kg bottles/ $112.83	600 g
Sodium Bicarbonate	Fisher: S233-500	500 g/$25.05	

[22] Only necessary for field sampling, or if aqueous samples are to be held for more than 24 hours
[23] Assuming about 30 samples analyzed

HAA6 mix[24]	Sigma: 4-8047	1ml / $58 (4/11)	
BDCAA[25]	Sigma: 4-7278	1ml / $34.10	
CDBAA[25]	Sigma: 4-7277	1ml / $34.10	
TBAA[25]	Supelco: 4-7729-U	1ml / $33.30	
2,3-Dibromopropionic Acid in MtBE[25]	Supelco: 4-7789	1 ml/ $34.80	
Sodium Azide	Aldrich: 43,845-6		
H_2SO_4	UMass Stockroom		34 mL
Dichloroiodoacetic Acid (DCIAA)			
Bromochloroiodoacetic Acid (BCIAA)			
Dibromoiodoacetic Acid (DBIAA)			
Chlorodiiodoacetic Acid (CDIAA)			
Bromodiiodoacetic Acid (BDIAA)			
Triiodoacetic Acid (TIAA)			
Chloroiodoacetic Acid (CIAA)			
Bromoiodoacetic Acid (BIAA)			
Diiodoacetic Acid (DIAA)			
Monoiodoacetic Acid (MIAA)	Sigma: I4386 (99%)	$13 for 10g	
Iodoacetic Acid Methyl Ester	Fluka: 57850 (98%)		
Heavy-walled vials	Supelco #3-3293		
Small HAA vials	Fisher: 03-393D		40
1,2-Dibromopropane			

[24] includes TCAA, DCAA, BCAA, DBAA, MCAA, MBAA all prepared at 2000 µg/mL
[25] 1000 µg/mL

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. Emphasis must be given throughout one's lab work to incorporate the plan into the research project by all research personnel.

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, unavailable standards 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 release. 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 an SOP, and any departures or clarifications), instrument and conditions of analysis, failed experiments, etc. Data output will be archived.

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 review. 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.

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 Chromatographic Analysis

Quantitative chromatographic analyses must always be standardized by the use of carefully prepared solutions of known standards. In general, non-aqueous primary stocks are kept in a -10^{o}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 GC analysis is assured by: (1) use of blanks; (2) use of an internal standard;

(3) analysis of duplicates; (4) determination of spike recovery; (5) analysis of a matrix standard; (6) monitoring of response factors; and (7) monitoring for spurious peaks.

Three types of blanks should be run daily or with each set of samples: (1) reagent blanks, composed of the extracting solvent(s) and internal standard; (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". Peaks co-eluting with the analyte may appear in either the reagent blanks or the laboratory water blanks. Efforts must be made to minimize these (e.g., use of highest quality reagents, avoidance of possible sources of contamination). Some small interfering peaks or background analyte contamination may be unavoidable. If the evidence suggests that contamination is from the reagents (solvent & internal standards), the concentrations measured in the reagent blank should be subtracted from the concentrations determined for the analytical samples. If the source is unclear (possibly from the laboratory environment), it should not be subtracted. If the laboratory water blank shows higher apparent analyte concentrations than the reagent blank, there is probably some contamination from the laboratory water. This additional contaminant level should not be subtracted from analytical samples, unless those samples were prepared with laboratory water.

An internal standard is used to control for solvent evaporation and variable injection volume. Most samples will be run in duplicate. If they differ by more than the acceptable range, additional GC or LC injections will be made. If there still exists a significant problem, either the original sample will be re-extracted or the data will be discarded.

Spike recoveries are determined for each analyte/method. With some DBP studies, precursor matrix standards may be prepared and analyzed for the full suite of analytes. These are generally test-specific, but it is also traditional in our laboratory to make use of a bulk sample of raw Wachusett Reservoir water. This would be treated with the oxidant of interest under well-defined conditions. Control charts are prepared and continually updated for matrix spikes and standards. Data falling outside of the control limits require that the method be re-tested in order to bring it back under control. Calibration response factors will be monitored and compared from one day to the next. Significant changes in either these response factors or in the spike recoveries will be considered cause for method re-evaluation. Finally, general QA requires that all chromatograms be manually inspected for spurious 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. General maintenance activities must be documented here (e.g., new septa, cleaning of injection liner). 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.

Data Quality Indicators

A wide range of data quality indicators are normally calculated for the purpose of assessing method performance. Some of these are defined below.

Precision

Precision may be expressed as the relative percent difference (RPD) from duplicate measurements (C_1 and C_2) of the same sample:

$$RPD = \frac{|C_1 - C_2| x100\%}{(C_1 + C_2)/2}$$

When three or more replicates are available, the relative standard deviation (RSD) should be used:

$$RSD = \left(\frac{s}{\bar{y}}\right) x100\%$$

where the standard deviation (s) is determined from:

$$s = \sqrt{\sum_{i-1}^{n} \frac{(y_i - \bar{y})^2}{n-1}}$$

Accuracy

Accuracy is best assessed by analysis of a standard reference material (SRM) prepared in the matrix of interest. It is quite rare that such materials are available, so two possible compromise may be used instead. These are the laboratory-prepared matrix spikes, and the independent SRM prepared in a standard matrix. One or both may be analyzed and the percent recovery (%R) calculated as a measure of accuracy.

$$\%R = \left(\frac{S - U}{C_{sa}}\right) x100\%$$

where:

S = measured concentration in spiked aliquot

U = measured concentration in unspiked aliquot

C_{sa} = actual concentration of spike added

$$\%R = \left(\frac{C_m}{C_{srm}} \right) x100\%$$

and:

C_m = measured concentration of SRM

C_{srm} = actual concentration of SRM

Method Detection Limit (MDL)

The method detection limit (MDL) will be defined as:

$$MDL = s_7 \bullet t_{(n-1,1-\alpha=0.99)}$$

where:

s_7 = standard deviation of 7 replicate analyses where the mean is no more than 10 times the MDL

$t_{(n-1,1-\alpha=0.99)}$ = Students' t-value for a one-sided 99% confidence level and a standard deviation estimate with n-1 degrees of freedom.

Linearity

The calibration curve linearity (L) is defined as the ratio of the slope using the highest standards (S_U) divided by the slope determined from the lowest standards (S_L) as follows:

$$L = \frac{S_U}{S_L}$$

The highest standards shall be all those that fall within the top 50% of the calibration range including the 50% standard if it is used. If only one standard falls within that range, the S_U shall be calculated based on the top two standards. The lowest standards are all those that fall within the bottom 50% of the calibration range including the 50% standard if it is used. Least squares linear regression is used to determine slopes.

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 150ºC oven.

Samples for HAA analysis must be kept in the dark, and in a refrigerator from the time of disinfectant quench until the start of analysis. HAAs are biodegradable, so a biocide must be added if the samples are to be kept for more than 2 days prior to extraction. Organic extracts (in MtBE) can be kept in a freezer (~-10C) for up to 14 days. The liquid level must be marked on all vials at the time of capping, so that solvent loss can be noted.

Handling and Storage of Standards and Reagents

Solvent used for extraction (MtBE) is purchased from Aldrich Chemical Company as a Pesticide-Grade product. They are mixed as needed with the internal standard in batches of 1-L. This MtBE+IS is then stored in the original solvent bottle, but clearly marked as having been fortified with the IS. It is used until the volume reaches 20 % of the original. At this point the MtBE+IS is discarded (due to concern over excessive volatilization and changes in the IS concentration). Whenever new MtBE+IS is mixed, the IS peak are is evaluated by injection of a solvent blank. If this falls outside of the control limits (±30 of the long term average), the MtBE+IS is discarded and a new one is prepared.

Calibration stock II is prepared as needed from the commercial HAA stocks. This is stored in a 5-mL heavy-walled extraction vial (Supelco # 3-3293) in a freezer for up to 1 month. After this time it is used for preparation of the calibration check standard for 1 additional month before being discarded.

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 HAA Analysis

General Analytical QC

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 10. Summary of QC Elements as Applied to HAA Analysis

Types of Samples or Standards	§ in 552.2	Purpose	Frequency	Timing	QC data
Solvent Blank	None	Assess general GC operation, cleanliness of column, and possible ghost peaks	1 for every 25 samples	Beginning of each day and scattered throughout	
Laboratory Performance Check Standard (LPC)[26]	9.2	To establish basic GC performance for separation and sensitivity	1 standard per day	Beginning of each day	S/N, peak gaussian factor (PGF), Resolution
Initial Demonstration of Capability (IDC)	9.3	To show that an analyst's technique and equipment are adequate for HAA analysis	4-7 standards when first learning method, otherwise not done	Not done unless learning	Mean % recovery and standard deviation
Analysis of HAA methyl esters	None	To determine the analyte-specific esterification efficiency	3 levels of HAA methyl esters run directly in MtBE	Only done as a trouble-shooting measure	% conversion to MEs
Method Detection Limit (MDL)	9.4	To determine the lowest concentration level that the analyst can report	7 sandards run	Usually done once per year	MDL and EDL
Laboratory Reagent Blank (LRB)[27]	9.5	Test lab conditions and quench for interferents	1 per day, if no FRB	Near Beginning of day	Max peak size within analyte windows
Field Reagent Blank (FRB)[28]	None	Test all field conditions for interferents	1 per day, if sampling occurred outside of the lab	Near end of day	Max peak size within analyte windows

[26] usually one of the calibration standards serves this purpose
[27] laboratory water treated exactly as a field sample (e.g.,buffering, chlorination, quenching, etc.)
[28] laboratory water transported to field, transferred to sampling bottle and then treated exactly as a field sample

Spiked sample, or Laboratory Fortified Sample Matrix (LFM)	9.7	To test analyte recovery in the sample matrix	1 for every 10 samples	Mixed throughout day	% recovery, mean and standard deviation
Calibration Standards[29]	10.1	To provide a basis for determining the concentrations in unknowns	≥ 6 levels including zero	At beginning of day, and re-checked later	Calibration curves (PAR vs. conc.), including slopes and intercepts; surrogate PARs; mean IS areas
Continuing Calibration Check Standards (CCC)[30]	10.2	To verify the accuracy of the calibration standards	At least 1 per day	Usually mid-day	
Unchlorinated blank		Evaluate contaminants in background water	1 per run	mid-day	Interfering peak areas; surrogate recovery
Positive chlorination control		Evaluate all conditions including chorination & quench	1 per run	mid-day	Recovery based on known yield
Unknowns or "samples"		This is what you really want to measure	As many as desired	Mixed throughout day	Surrogate recoveries vs. calibration standards, IS areas
		Laboratory Replicates	As many as 1 per sample, depending on study	Throughout	Analytical Precision
		Field Replicates	As many as 1 per sample, depending on study	Throughout	Aggregate sampling handling, treatment and analytical precision

Table 11 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 11: Typical Vial Sequence for a 30-sample Run

Vial #	Sample type	QC objectives
1	Solvent Blank	To check on GC condition
2	Zero Standard	To check for gross contamination of water or lab environment
3-7	Remaining calibration standards	Calibration
8	Laboratory Reagent Blank	Contamination
9-13	**Analytical Samples (5)**	
14	Calibration check standard	Check on accuracy of calibration samples

[29] Prepared from the currently-used calibration stock II (less than 1 month old)
[30] Prepared from the previously-used calibration stock II

15-19	**Analytical Samples (5)**	
20	Spiked sample	Spike recovery
21-25	**Analytical Samples (5)**	
26	Field Blank/Lab Blank	Contamination
27	Spiked sample	Spike recovery
28	Positive Chlorination Control	Recovery
29-33	**Analytical Samples (5)**	
34	Unchlorinated sample	Check on interferences
35-39	**Analytical Samples (5)**	
40	Spiked sample	Spike recovery
41-45	Analytical Samples (5)	
46-48	Calibration standards (0, highest, and one intermediate)	Final check to verify that calibration hasn't changed during run

Special QC Tests

The following are "special" tests that are not part of the normal QC protocol. They are used when first learning this analytical method (e.g., IDC), and they may be used when there are suspected problems or there is a need for method performance evaluation.

Initial Demonstration of Capability (IDC)

This is normally performed by each analyst when he/she is first learning to measure haloacetic acids. It is designed to be a double-blind test.

Procedure

a) The graduate QC officer prepares 100 mL volumes of five different aqueous solutions of HAAs and places them in separate, labeled glass bottles.
b) These are given to the faculty QC officer along with 5 clean, empty standard sample vials (e.g., 40-mL septum vials).
c) The faculty QC officer uses the solutions and bottles to prepare a set of 5 standards that are labeled A, B, C, D and E. Only the faculty QC officer knows the identity of each.
d) The five IDC samples are passed on to the analyst for immediate analysis.
e) Results for each are returned to the faculty QC officer for determination of accuracy.

Performance

IDC results are expected to meet the LFM QC criteria from Table 14.

Analysis of Esterification Efficiency

Analysis of commercial esters can be used to determine "absolute recovery". This is a measure of the overall efficiency of extraction and methylation. This is

commonly done when there are concerns over data quality, and the underlying problem is not evident.

Procedure

a) Add 100, 250 and 1000 µL of HAAME stock II to three volumes of 30 mL of MtBE
b) Analyze with samples. If "absolute recovery" is 100%, these will be quantified as 33.3 µg/L, 83.3 µg/L, and 333 µg/L, respectively

Preparation of HAAME individual stock I solutions (10 g-acid/L)

- Measure out enough HAAME (taking into account the density and MW) with a microliter syringe to account for 0.1 g of each as the acid:

$$volume(mL) = \frac{0.1g}{density(g/mL)}\left(\frac{MW_{HAAME}}{MW_{HAA}}\right)$$

- Add it to a 10 mL volumetric flask with 5 mL MtBE
- Dilute to volume with MtBE
- Usable for 6 months if saved at –10 C

Preparation of multicomponent HAAME stock II (10 mg-acid/L):

- Add 10 µL of each stock standard into a 10-mL volumetric flask containing about 5 mL MtBE.
- Dilute to volume with MtBE
- Usable for 3 months when stored at –10 C

Performance

- Low recoveries have been documented for monochloroacetic acid, using both the acidic methanol procedure (Cancho et al., 1999)[31] and the diazomethane procedure (Chen & Weisel, 1998)[32].

Table 12. Reported Absolute Recoveries of HAA MEs

Analyte	Absolute Recovery (%)		
	Diazomethane Methods		Acidic MeOH
	Standard Methods. 1999	Brophy et al., 2000[33]	Brophy et al., 2000
Trihaloacetic Acids (THAA)			
Trichloroacetic Acid (TCAA)	92.7	~100	~100

[31] Bull. Environ. Contam. Toxicol. 63:610-617.
[32] J. AWWA 90:151-163.
[33] With MgSO4 drying step, from Barrett et al. ACS Symp Series 761

Bromodichloroacetic Acid (BDCAA)		~90	~90
Chlorodibromoacetic Acid (CDBAA)		~100	~25
Tribromoacetic Acid (TBAA)		~100	~30
Dihaloacetic Acids (DHAA)			
Dichloroacetic Acid (DCAA)	110	~100	~100
Bromochloroacetic Acid (BCAA)	98	~100	~100
Dibromoacetic Acid (DBAA)	116	~100	~100
Monohaloacetic Acids (MHAA)			
Monochloroacetic Acid (MCAA)	78.9	~100	~100
Monobromoacetic Acid (MBAA)	70.6	~100	~100

Method Detection Limit (MDL)

Procedure

a) Prepare a 500 mL of a 1 μg/L standard of all HAAs.
b) Separate this into 7 aliquots of 30 mL each.
c) Analyze each on the same day.
d) Determine MDL based on the standard deviation of these 7 sets of measurements (refer to section on: MDL calculations on page 24 of this document)

Performance

There are no firm performance criteria for MDL. Some typical values are listed in Table 13.

Table 13. Reported MDLs for HAA Analysis in Water

Analyte	**MDL** (μg/L)		
	Standard Methods, 1999	**Chen & Weisel, 1998**	**Brophy et al., 2000**[34]
Trihaloacetic Acids (THAA)			
Trichloroacetic Acid (TCAA)	0.054	0.38	0.34
Bromodichloroacetic Acid (BDCAA)			0.34
Chlorodibromoacetic Acid (CDBAA)			0.30
Tribromoacetic Acid (TBAA)			0.19
Dihaloacetic Acids (DHAA)			
Dichloroacetic Acid (DCAA)	0.054	0.75	0.15
Bromochloroacetic Acid (BCAA)	0.04		0.10

[34] using diazomethane with MgSO4 drying step, from Barrett et al. ACS Symp Series 761

Dibromoacetic Acid (DBAA)	0.065	0.28	0.25
Monohaloacetic Acids (MHAA)			
Monochloroacetic Acid (MCAA)	0.082	17.0	0.26
Monobromoacetic Acid (MBAA)	0.087	0.63	0.11

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 13). Quantitative criteria (Table 14) 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. Table 14 lists some typical corrective action, however the actions taken may differ depending on the particular circumstances. Excursions from QC criteria can be quite complex, and many analytical characteristics and conditions must be considered before a decision can be made on the most effective steps to be taken.

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 Marcus Hall GC room (Rm 5C). A duplicate set must be deposited with the faculty QC officer (D. Reckhow).

Table 14: Quantitative Criteria for Judging Data Acceptability

Types of Samples or Standards	Frequency	Timing	QC data Acceptance Criteria	Typical Corrective Action
Spiked sample, or Laboratory Fortified Sample Matrix (LFM)	1 for every 10 samples	Mixed throughout day	Mean % recovery = 85%-115%, for DHAAs and THAAs, 70%-130% for MHAAs	❖ Re-run matrix spikes ❖ Re-examine entire run for errors ❖ Possibly change SOP
Calibration Standards[35]	7 levels including		Calibration slopes (PAR vs. conc.), = ±30% of long-term average for	❖ Run new set of standards ❖ Prepare new HAA stock

[35] Prepared from the currently-used calibration stock II (less than 1 month old)

	zero		DHAAs and THAAs, = ±50% of long-term average for MHAAs	❖ Examine GC for problems, needed maintenance
			Calibration linearity must not fall below 0.5	❖ Use a lower calibration range until L≥0.5, and dilute samples if necessary ❖ Perform maintenance on column and other components
			Average Surrogate area for a run = ±30% of long-term average	❖ Examine chromatograms ❖ Re-run standards, with special attention to derivatization conditions
Continuing Calibration Check Standards (CCC)[36]			Calculated Conc. = ±25% of expected value	❖ 1. Prepare new calibration check standard ❖ 2. Prepare new standard curve based on new stock
Unknowns or "samples"	As many as desired	Mixed throughout day	Average Surrogate area for a run <70% of long-term average	❖ Examine derivatization procedure ❖ Examine surrogate area for matrix spikes & standards ❖ Re-run some samples with more severe methylation
			Average IS area for a run = ±30% of long-term average	❖ Prepare new solvent & IS
			Surrogate area for a sample = ±50% of entire-run average	❖ Re-run samples
			IS area for a sample = ±25% of entire-run average	❖ Inspect samples for possible evaporation ❖ Inspect chromatograms for interfering peaks or poor integration ❖ Re-calculate based on peak areas only ❖ Re-run samples
			RSD or RPD for laboratory replicate analyses ≤20% or AD ≤5 µg/L, whichever is less restrictive	❖ Re-run samples and/or discard outliers[37] until precision can be brought under control
			RSD or RPD for laboratory replicate analyses ≤30% or AD ≤10 µg/L, whichever is less restrictive	❖ Re-evaluate sampling and field protocols until precision can be brought under control
			Estimated concentration in unknowns must not exceed highest standard	❖ Re-run samples with higher level standards ❖ Dilute and re-run samples ❖ If within 150% of max standard, concentrations may be flagged as tentative

[36] Prepared from the previously-used calibration stock II

Appendix

USEPA Method 552.2:

(Revision 1.0)

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