Analysis of Trihalomethanes

and Related Pentane-Extractable Organic Halides

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

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Standard Operating Procedures

Analysis of Trihalomethanes

and Related Pentane-Extractable Organic Halides

This guidance document was prepared to assist research assistants, post-docs and lab technicians in conducting trihalomethane (THM) 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 and Amanda Keyes for providing summaries of our revised practice since moving into Elab II. 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 THM analysis

Scope

This method has been used in the UMass Environmental Engineering Laboratory for all 4 trihalomethanes and all 3 dihaloacetonitriles containing chlorine and bromine, as well as several other chlorine-containing neutral compounds (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 some or all of the other halogenated analogues of these compounds (Table 2) may be possible, however this has not been validated at UMass. Any use of this method for compounds other than those in Table 1 must be accompanied by appropriate disclaimers until the method can be fully validated. Chloral hydrate has been found to be better recovered by ether extraction (e.g., MtBE), than by pentane. For this reason, it is sometimes analyzed separately using an alternative LLE/GC/ECD method, especially when low detection limits are desirable.

Table 1: Standard Neutral Extractable Analytes

Analyte	**CAS Registry #**
Trihalomethanes (THMs)	
Chloroform	67-66-3
Bromodichloromethane	75-27-4
Chlorodibromomethane	124-48-1
Bromoform	75-25-2
Dihaloacetonitriles (DHANs)	
Dichloroacetonitrile (DCAN)	3018-12-0
Bromochloroacetonitrile (BCAN)	83463-62-1
Dibromoacetonitrile (DBAN)	3252-43-5
Trihaloacetonitriles (THANs)	
Trichloroacetonitrile (TCAN)	545-06-2
Haloketones (HK)	
1,1,1-Trichloropropanone (TCP)	918-00-3
1,1-Dichloropropanone (DCP)	513-88-2
Chloropicrin (CP)	76-06-2
Chloral Hydrate (CH)	75-87-6

Table 2: Other Pentane Extractable Analytes

Analyte	**CAS Registry #**
Iodinated-Trihalomethanes (ITHMs)	
Dichloroiodomethane (DCIM)	
Bromochloroiodomethane (BCIM)	
Dibromoiodomethane (DBIM)	
Chlorodiiodomethane (CDIM)	
Bromodiiodomethane (BDIM)	
Iodoform (TIM)	
Iodinated-Dihaloacetonitriles (IDHAA)	
Chloroiodoacetonitrile (CIAN)	
Bromoiodoacetonitrile (BIAN)	
Diiodoacetonitrile (DIAN)	
Monohaloacetonitriles	
Chloroacetonitrile	
Bromoacetontrile	
Brominated Trihaloacetonitriles	
Bromodichloroacetonitrile	
Dibromochloroacetonitrile	
Tribromoacetonitrile	
Halopropanones	
1,3-Dichloropropanone	
1,1-Dibromopropanone	
1,1,3-Trichloropropanone	
1-Bromo-1,1-dichloropropanone	
1,1,1-Tribromopropanone	
1,1,3-Tribromopropanone	
1,1,1,3-Tetrachloropropanone	

1,1,3,3-Tetrachloropropanone	
1,1,3,3-Tetrabromopropanone	
Haloacetaldehydes	
Dichloroacetaldehyde	
Bromochloroacetaldehyde	
Tribromoacetaldehyde	
Halonitromethanes	
Chloronitromethane	
Bromonitromethane	
Dichloronitromethane	
Bromochloronitromethane	
Dibromonitromethane	
Bromodichloronitromethane	
Dibromochloronitromethane	
Bromopicrin	

Method Overview

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

Table 3: Summary of Procedure for THM Sample Analysis

1. Prepare **calibration standards** (Table 4) and **QC samples** (Table 5)
2. Place 20 mL of sample/standard to be analyzed **into vial**.
3. If residual chlorine is present add approximately 40 mg of **NH_4Cl**
4. Add 4mL of the pre-mixed **Pentane**[1] + internal standard.
5. Add approximately 15g of **Na_2SO_4** (Use dispenser made by glass shop.)
6. **Shake** for 15 minutes.
7. Transfer organic layer into **autosampler** vials
8. **Freeze** to remove water, and analyze.

Table 4. Typical Preparation of Calibration Standard

1. Prepare Stock II as needed: Add 100μL of 551A commercial mix and 20μL of the 551B commercial mix to a 10mL volumetric flask containing acetone.
2. Prepare calibration standards: add 20mL 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 20 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 26).

[1] MtBE must be used in place of pentane if chloral hydrate is to be analyzed.

Detailed Procedures

Basis for Method

We use a protocol that is closely aligned with the US EPA method 551.1, "Determination of Chlorination Disinfection Byproducts, Chlorinated Solvents and Halogenated Pesticides/Herbicides in Drinking Water by Liquid-Liquid Extraction and Gas Chromatography with Electron Capture Detection." Please refer to the latest version of this method (currently version 1.0, dated 1990; attached as Appendix 1) for all details.

For historical reasons and site-specific considerations, we have chosen to depart from method 551.1 in several minor ways. The most substantial differences include:

- Use of pentane; MtBE only used when chloral hydrate data are needed
- Smaller volumes of sample, reagents, and solvents
- Sodium arsenite sometimes used as a quench in place of ammonium chloride
- Addition of internal standard to solvent earlier in the procedure
- Volumetric rather than gravimetric determination of sample size

Once again, the primary source for our THM method is US EPA method 551.1. 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 551.1

§ from 551.1	Step or Material	551.1 protocol	UMass protocol
1.7	Solvent	MtBE	Pentane (MtBE is only used when chloral hydrate is to be quantified)
6.1	Sample Vials	60 mL size	40 mL size
7.1.7.1	Phosphate Buffer	99% KH_2PO_4 and 1% Na_2HPO_4	97.5% KH_2PO_4 and 2.5% Na_2HPO_4
7.3.6 and 7.4.2	Internal Standard	Bromofluorobenzene is added to pentane extracts	1,2-dibromopropane added to bulk solvent (300µg/L) prior to use for extraction
11.1.2	Aqueous sample handling	Removal of 10 mL from vial and gravimetric determination of remaining volume	Addition of sample by pipet to vial
11.1.2	Sample volume	50 mL	20 mL
11.2.2.1	Pentane volume	5.0 mL	4.0 mL
11.2.2.2	Sodium Sulfate	20 g	15 g

	addition		
11.2.2.3.1	Transfer to autosampler vial	Quantitative (necessary due to IS addition protocol)	Not quantitative

We use one of our Hewlett-Packard 6890 GCs for THM analysis. These are equipped with an HP 7673 autosampler. Our GC column and parameters are compared to method 551.1's column A (Table 1 in US EPA method) in Table 7 below.

Table 7. Instrument Parameters for THM Analysis

Step	551.1 protocol	UMass protocol
Analytical Column	DB-1	DB-5
Length	30 m	30 m
Internal Diameter	0.25 mm	0.25 mm
Film Thickness	1.0 µm	1.0 µm
Injection volume	2 µL	2 µL
Injection Type		Splitless
Split Flow		none
Carrier Gas	Helium	Zero-grade Nitrogen
Carrier Flow	Sufficient for 25 cm/sec linear velocity[2]	1.5 mL/min
Make-up Flow		30 mL/min
Injector Temp	200°C	175°C[3]
Detector Temp	290°C	275°C
Oven Program	Hold at 35°C for 22 min Ramp to 145°C at 10°C/min (11 min) Hold at 145°C for 2 min Ramp to 225°C at 20°C/min (4 min) Hold at 225°C for 15 min Ramp to 260°C at 10°C/min (3.5 min) Hold at 260°C for 30 min	Hold at 27°C for 10 min Ramp to 41°C at 3°C/min (4.67 min) Hold at 41°C for 6 min Ramp to 81°C at 5°C/min (8 min) No hold Ramp to 180°C at 25°C/min (3.96 min) Hold at 180°C for 6 min

[2] Evaluated at 35ºC
[3] May need to be lowered for analysis of some labile non-THMs (see Krasner et al., 2001)

UMass Detailed Procedures

Sample Preservation

1. **Add one of the following quenches to each 40mL amber vial[4].**
   - A. Add about 40 mg ammonium chloride (NH_4Cl) crystals (Desiccator in 301 Elab II) using dispenser made by glass shop (in drying cabinet above the desk)[5]
     - Converts free chlorine (FRC) to chloramines (CRC). Therefore, not recommended for DBPs that will form directly from reaction with chloramines (e.g., some dihalo compounds such as 1,1-DCP)
     - Can cause low recoveries for chloral hydrate[6] (EPA 551.1) and accelerate degradation of iodinated THMs (Gonzalez et al., 2000)
   - B. Alternatively, add 250 μL of sodium arsenite solution[7]
     - Not well studied, arsenite is toxic and must be handled with care
     - May not rapidly reduce combined chlorine
   - C. Alternatively, add an excess of ascorbic acid (e.g., 30 mg/L)[8]
     - Ascorbic acid can accelerate decomposition of brominated trihaloacetonitriles and brominated trihalonitromethanes (Krasner et al., 2001)

2. **Add buffer salts.**
   - Using the marked spatula, add one measure of the phosphate buffer (~1g)
     - This is used to adjust pH to 4.5-5.5, and it is prepared according to the section on: Preparation of Buffer Salt Mix (page 16)
     - A lower pH buffer (pH~ 3.5) should be used if iodinated THMs and certain HPs and HANs are to be measured (see: Gonzalez et al., 2000)

3. **Be sure that the vial is filled headspace-free.**
   - Fill to just overflowing and cap with Teflon-lined septum (be sure that septum doesn't have any holes and that the teflon side is down)
   - THMs are quite volatile and easily lost to the air
   - This may not be necessary if sample is to be immediately extracted

4. **Place vials with 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.

[4] clean, PTFE-faced septum capped vials; Hydrogen peroxide (1M/M, forming O_2 and H_2O) is also effective at reducing chlorine [Worley et al., 2003; JAWWA 95:3:109], but has not been adequately tested for THM analysis.
[5] UNC adds 20 mg of ammonium sulfate to each 40-mL vial; this is dropped to 4 mg for HAN & HK analysis
[6] sulfite can be used for analysis of chloral hydrate, but this is not recommended for most other DBPs.
[7] 0.1 N, kept in refrigerator # 3
[8] Ascorbic acid reacts at 1M/M stoichiometry forming dehydro-accorbate [Worley et al., 2003; JAWWA 95:3:109].

Sample Extraction and Preparation for GC Analysis[9]

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

2. **Place 20 mL of sample/standard to be analyzed into vial.**
   - Add 20 ml of the water sample using an Eppendorf pipette[10] (room 301)
   - It is critical that samples be treated to avoid volatilization of analytes
     - In our laboratory this is done by careful attention to quiescent sample transfer and rapid addition of pentane as soon as the sample is exposed to air, addition of sulfate and capping.

3. **Add 4mL of the pre-mixed Pentane[11] + internal standard.**
   - Use repeater pipet

4. **Add approximately 15g of Sodium Sulfate (Na_2SO_4)**
   - One measure from the glass dispenser labeled THM.
   - Dispenser is located in room 301 cabinet next to hood

5. **Shake for 15 minutes.**
   - Cap vial
   - 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.

6. **Transfer organic layer (top) to autosampler vials.**
   - Use pasteur pipets
   - 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[12].
   - Be certain to include necessary QC samples
     - See Table 10 (page 26) for a full listing of QC samples
     - See Table 11 (page 27) for a typical sequence

7. **Freeze Samples to remove water[13]**
   - Store autosampler vials in freezer for at least 3 hours

[9] Typical prep time is 4 hours for a run of 30 samples
[10] Samples are generally handled with a pipet designed for volatile liquids. We use an Eppendorf Maxipettor Model 4720 with "S" tips (Brinkmann Instruments Inc., Westbury, NY.
[11] Or MtBE if chloral hydrate is to be analyzed.
[12] This is to help identify when excessive evaporation has occurred
[13] since water is insoluble in pentane, any water is present as a separate phase

    - 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

Analysis by Gas Chromatography[14]

GC Set up and Initiation of Run[15]

1. **Check there is enough gas in the Nitrogen tank, if so, open Gas line for the 6890 GC**
2. **Turn on oven, detector, injector**
3. **Fill the rinsing vials with hexane**
4. **Put the samples in the autosampler trays.**
    - See Table 11 (page 27) for typical vial sequence with QC samples
5. **Write down in the log book, vial number and sample identity**
6. **Open the window for the appropriate instrument (#3 or #4) on the ChemStation Computer:**
    a) Fill in sample list
    b) Open method
    c) Check on directory for writing results
    d) Initiate run
7. **Inspect the first few chromatograms**
    - Do this while they are first showing up on the computer
    - Make your first QC report by email (see "Data Analysis" below).
8. **The GC will run until all your samples are done.**

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

[14] typically requires 20 hours of GC time for a run of 30 samples
[15] Note that the standard UMass GC method might have to be modified if certain thermally-labile non-THMs are to be analyzed (e.g., see Krasner et al., 2001)

- the first standards have all of the peaks expected
- the first standards exhibit good chromatography
- retention times of the analytes are within expected windows
- the internal standard peak area that is within tolerance limits.

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 Staff and Faculty QC officers in the "cc:" line (lkramer@ecs.umass.edu and reckhow@ecs.umass.edu).
   - The subject line of this email message must simply read "QC report"
   - The report must also indicate the sample types (e.g., field samples from Monroe, MI), field collection date, laboratory treatment date (if any), and analysis date

2. <u>Access the data stored in the computer:</u>

- Save all your integration data to a thumb drive. Remember to record the directory on the ChemStation computer where your data are stored
- Use the Excel program to retrieve the data into an excel file.

3. <u>Preparation of Standard Curves</u>

- 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).
  - Reagent blanks are subtracted where appropriate, and not where inappropriate (see: Procedures specific to Chromatographic Analysis, pg. 20)
- Standard curves must also include the zero standard (sometimes called the laboratory reagent blank)
- 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.

4. **Evaluation of standard curves and other QC data by the analyst**
   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 4 THMs, 2 HANs & 2 HKs; may also include CP and CH). These are called the PAR slopes.
      ii. Internal standard (IS) average area for the calibration standards
      iii. Calibration slope multiplied by the average IS area (above). These are called the raw slopes
      iv. Spike recoveries

5. **Validation of QC data**
   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 staff and faculty QC officers 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 "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, pipet tips 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[16] 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.
- Caps are soaked in Super-Q water, rinsed and dried in low temp oven.
- Acid baths must be cleaned and refreshed on a weekly basis

[16] 5% H_2SO_4 is the UMass protocol; if desired may use 10% HNO_3 instead (UNC protocol)

Standard Solutions, Solvents and Supplies

Preparation of Calibration Standards[17]

1. **Prepare Stock II (20 or 4 µg/mL) as needed from fresh commercial standard.**
   a) Place about 5 mL of acetone[18] into each of a set of nine 10 mL volumetric flasks
   b) Open the sealed ampule of the 551A[19] commercial mix (2000µg/mL of the THMs; Supelco #4-8045) and add 100 µL to each of the nine volumetric flasks
   c) Open the sealed ampule of the 551B commercial mix (2000 µg/mL of DCAN, BCAN, DBAN, TCAN, CP, DCP & TCP; Supelco #4-8046)and add 20µL to each of the nine volumetric flasks
   d) Add acetone to fill each flask to the mark.
   e) Transfer each of the solutions to separate heavy-walled extract vials (Supelco #3-3293) and store them in the container labeled THM stocks in the freezer compartment of refrigerator #2. Each should be labelled with the date prepared and a unique identifying number (e.g., 1-9).

2. **Prepare aqueous calibration standards.**
   a) Remove two vials of Stock II from the freezer
   b) Add 20 ml of Milli-Q water to each of 8 large extraction vials
   c) Using one of the two Stock II vials, add a range of volumes to each vial resulting in a 7-point standard curve that covers the concentration range of interest[20].
      i. Typical for finished drinking waters: 0, 5, 10, 20, 30, 50, and 80 µL of standards stock II for THM.
      ii. Higher levels (formation potential): 0, 25, 50, 100, 150, 200, 350 µL of standards stock II for THM.
   d) From the second Stock II vial, prepare a duplicate high level standard using the remaining 8th aqueous sample vial. This will serve as a "calibration check" in the event that one of the Stock II solutions becomes degraded.
   e) Indicate in your notebook, which stock II vials you used.
   f) These aqueous standards 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

[17] typically requires 20 minutes
[18] Acetone is extremely volatile and quite soluble in water. Because it is also a THM precursor, it's use near aqueous samples can result in contamination and elevated DBP levels upon chlorination. Minimize volatilization of acetone, by keeping all acetone-containing vessels capped or isolated under a hood.
[19] Usually kept in the refrigerated compartmentof refrigerator #16
[20] 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 for the THMs. Non-THMs are at 1/5th of this level.

additional 20 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 26).

Preparation of Internal Standard Stock Solution[21]

a) Place a 10 mL volumetric flask partially filled with MtBE in an analytical balance
b) Zero out the weight
c) Add 6-7 drops of *1,2-dibromopropane* and RECORD the weight
d) Fill to the mark with MTBE
e) The concentration of the Internal Standard Stock solution is determined by:

$C_{ISstock}$ = (weight IS (g) / 10 ml) * (1000 mg/g)

- The concentration 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 you name and the IS concentration and store it in the refrigerator #2.

Preparation of Pentane with Internal Standard[22]:

a) Rinse a dry 1-L volumetric flask with THM-grade or HPLC-grade Pentane (1x). Dispose of this rinse solution into the waste bottle in the hood
b) Fill the flask to about 2/3rd capacity with THM-grade pentane (Aldrich)
c) Calculate the amount of 1,2-dibromopropane stock necessary to prepare a 300 µg/L solution:

("x" mL / 1000 mL) * ($C_{ISstock}$ mg/mL) * (1000 mL/L) * (1000 µg/mg) = 300 µg/L

d) Add "x" ml of the standard solution to the pentane
e) Place this into the bottle labeled THM + IS. The total volume should be about 1000 mL

[21] The same IS stock is used for both THM and HAA analysis.
[22] This is the standard extraction solvent used whenever chloral hydrate quantification is not necessary

Preparation of MtBE with Internal Standard[23]:

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 dibromopropane necessary to prepare a 300 μg/L solution:

("x" ml / 1000 ml) * ($C_{ISstock}$ mg/ml) * (1000ml/L) * (1000 μg/mg) = 300 μg/L

d) Add "x" ml of the standard solution to the MTBE and fill to the mark with MTBE.

Preparation of Buffer Salt Mix

a) Weigh out buffer chemicals in the ratio required[24].
   - 97.5% KH_2PO_4 by weight
   - 2.5% Na_2HPO_4 by weight
   - For example you would weigh out 97.5 g KH_2PO_4 and 2.5 g Na_2HPO_4 to make 100 g total mixture
   - This is designed to achieve a pH of 4.5-5.5
b) Mix and Store in an Erlenmeyer flask and cover with aluminum foil
c) Prepare a new mixture at least once a month

Supplies

Table 8. Summary of Supplies for THM Analysis

Item	Catalog #	Approx. Price	Approx # used/run[25]
Pasteur Pipettes	Fisher: 13-678-20A	720/ $46	10
Autosampler Vials	Fisher: 03-340-51F	10 packs of 100 vials / $180	40
Integrator Paper	Fisher: 07-684-60	cs of 4 / $96	
Ink Cartridges	Fisher: 07-684-61	$15 each	
DIUF Water	Fisher: W2-20	$32 each	Not normally used
THM standards: 551A	Sigma: 48045	1ml / $34.80	
Other standards: 551B	Sigma: 48046	1ml / $34.80	
Methanol	Fisher: A 454-4	Case of four 4L bottles/ $71	76 mL
MtBE	Fisher: E127-4	cs of four 4L bottles / $364	

[23] This extraction solvent is normally only used when chloral hydrate is to be measured
[24] Note: this differs slightly from EPA 551.1, which calls for a ratio of 99% and 1%
[25] Assuming about 30 samples analyzed

Sodium Sulfate	Fisher: S 415-1	cs of six 1Kg bottles/ $94	600 g
1,2-Dibromopropane			
Septa for the 40 ml vials	Fisher 03-34-04H.	$64/a case of 144 septa	
septa for the vial caps	03-377-42	pack of 100 for $76.16	

Table 9. Availability of Other Neutral Extractable Analytes

Analyte	**Source**
Iodinated-Trihalomethanes (ITHMs)	
Dichloroiodomethane (DCIM)	Agbar[26]
Bromochloroiodomethane (BCIM)	Agbar
Dibromoiodomethane (DBIM)	Agbar
Chlorodiiodomethane (CDIM)	Agbar
Bromodiiodomethane (BDIM)	Agbar
Iodoform (TIM)	Aldrich
Iodinated-Dihaloacetonitriles (IDHAA)	
Chloroiodoacetonitrile (CIAN)	
Bromoiodoacetonitrile (BIAN)	
Diiodoacetonitrile (DIAN)	
Monohaloacetonitriles	
Chloroacetonitrile	Aldrich
Bromoacetontrile	Aldrich
Brominated Trihaloacetonitriles	
Bromodichloroacetonitrile	UNC[27]
Dibromochloroacetonitrile	UNC
Tribromoacetonitrile	UNC
Halopropanones	
1,3-Dichloropropanone	Aldrich
1,1-Dibromopropanone	Helix
1,1,3-Trichloropropanone	Fluka
1-Bromo-1,1-dichloropropanone	UNC
1,1,1-Tribromopropanone	Helix
1,1,3-Tribromopropanone	Helix
1,1,1,3-Tetrachloropropanone	Helix
1,1,3,3-Tetrachloropropanone	Helix
1,1,3,3-Tetrabromopropanone	TIC[28]
Haloacetaldehydes	
Dichloroacetaldehyde	TCI
Bromochloroacetaldehyde	UNC
Tribromoacetaldehyde	Aldrich
Halonitromethanes	

[26] Aigues of Barcelona (Spain)
[27] Synthesized at Univ. of North Carolina for USEPA study. These contained varying levels of other DBPs as impurities; see Krasner et al., 2001
[28] TCI America (Portland, OR)

Chloronitromethane	Helix
Bromonitromethane	Aldrich
Dichloronitromethane	Helix
Bromochloronitromethane	Helix
Dibromonitromethane	Majestic[29]
Bromodichloronitromethane	Helix
Dibromochloronitromethane	Helix
Bromopicrin	Columbia, Helix

[29] Majestic Research; synthesized by George Majetich, Univ. of Georgia (Athens, GA)

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 THM analysis must be kept in the dark, and in a refrigerator from the time of disinfectant quench until the start of analysis. Some analytes in the THM method are biodegradable, so a biocide must be added if the samples are to be kept for more than 2 days prior to extraction, and if the non-THM neutral extractables are to be quantified. Organic extracts (in Pentane or MtBE) can be kept in a freezer (~-10ºC) 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 (Pentane or MtBE) is purchased from Aldrich Chemical Company as a THM-Grade product. They are mixed as needed with the internal standard in batches of 1-L. This Pentane+IS (or MtBE+IS) is then stored in a dedicated bottle, which is clearly marked as having been fortified with the IS. It is used until the volume reaches 10 % of the original. At this point the solvent+IS is discarded (due to concern over excessive volatilization and changes in the IS concentration). Whenever new solvent+IS is mixed, the IS peak is evaluated by injection of a solvent blank. If this falls outside of the control limits (±30 of the long term average), the solvent+IS is discarded and a new one is prepared.

Calibration stock II is prepared as needed from the commercial THM 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 THM Analysis

General Analytical QC

Many types of QC procedures are required as indicated under US EPA method 551.1. 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 THM Analysis

Types of Samples or Standards	§ in 551.1	Purpose	Frequency	Timing	QC data
Solvent Blank	None	Assess general GC operation, cleanliness of column, and possible ghost peaks	1 for every 15 samples	Beginning of each day and scattered throughout	
Laboratory Performance Check Standard (LPC)	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		Mean % recovery and standard deviation
Method Detection Limit (MDL)	9.4	To determine the lowest concentration level that the analyst can report	7 standards run		MDL and EDL
Laboratory Reagent Blank (LRB)	9.5	Test lab conditions and quench for interferents	1 per day	Beginning of day	Max peak size within analyte windows
Field Reagent Blank (FRB)	None	Test all field conditions for interferents	1 per day, if sampling occurred outside of the lab	mid day	Max peak size within analyte windows
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[30]	10.1	To provide a basis for determining the concentrations in	7 levels including zero		Calibration curves (PAR vs. conc.), including slopes and

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

		unknowns			intercepts; surrogate PARs; mean IS areas
Continuing Calibration Check Standards (CCC)[31]	10.2	To verify the accuracy of the calibration standards			
Positive chlorination control		Evaluate all conditions including chlorination & 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 Autoinjector

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
3-8	Remaining calibration standards	Calibration
9-13	**Analytical Samples**	
14	Spiked sample	Spike recovery
15-19	**Analytical Samples**	
20	Field Blank/Lab Blank	Contamination
21-25	**Analytical Samples**	
26	Calibration check standard	Check on accuracy of calibration samples
27-31	**Analytical Samples**	
32	Positive Chlorination control	Recovery
33-37	**Analytical Samples**	
38	Spiked sample	Spike recovery
39-43	**Analytical Samples**	
44-46	Calibration standards (0, highest, and one intermediate)	Final check to verify that calibration hasn't changed during run

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

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 trihalomethanes. It is designed to be a double-blind test.

Procedure

d) The graduate QC officer prepares 100 mL volumes of five different aqueous solutions of the neutral extractables (THMs and others DBPs in Table 1) and places them in separate, labeled glass bottles.
e) These are given to the staff QC officer along with 5 clean, empty standard sample vials (e.g., 40-mL septum vials).
f) The staff 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 staff QC officer knows the identity of each.
g) The five IDC samples are passed on to the analyst for immediate analysis.
h) Results for each are returned to the staff QC officer for determination of accuracy.

Performance

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

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 23 of this document)

Performance

There are no firm performance criteria for MDL. Some typical values are listed in Table 12.

Table 12. Reported MDLs for Standard Neutral Extractables in Water

Analyte	**MRL** (µg/L)	**MDL** (µg/L)	
	Krasner et al., 2001	**Gonzalez et al., 2000**	**EPA 551.1**
Trihalomethanes (THMs)			
Chloroform	0.1	0.07	0.080
Bromodichloromethane	0.1	0.12	0.068
Chlorodibromomethane	0.1-0.19	0.07	0.008
Bromoform	0.1-0.6	0.14	0.020
Dihaloacetonitriles (DHANs)			
Dichloroacetonitrile (DCAN)	0.1	0.06	0.022
Bromochloroacetonitrile (BCAN)	0.1	0.09	0.005
Dibromoacetonitrile (DBAN)	0.1-0.17	0.09	0.005
Trihaloacetonitriles (THANs)			
Trichloroacetonitrile (TCAN)	0.1	0.12	0.004
Haloketones (HK)			
1,1,1-Trichloropropanone (TCP)	0.1	0.10	0.005
1,1-Dichloropropanone (DCP)	0.1-0.11	0.05	0.006
Chloropicrin (CP)	0.1	0.10	0.006
Chloral Hydrate (CH)	0.1-0.2	ND[32]	ND

Table 13. Reported MDLs for Non-Standard Neutral Extractables in Water

Analyte	**MDL** (µg/L)
	Gonzalez et al., 2000
Iodinated-Trihalomethanes (ITHMs)	
Dichloroiodomethane (DCIM)	0.09
Bromochloroiodomethane (BCIM)	0.19
Dibromoiodomethane (DBIM)	ND
Chlorodiiodomethane (CDIM)	0.13
Bromodiiodomethane (BDIM)	ND
Iodoform (TIM)	0.23
Iodinated-Dihaloacetonitriles (IDHAA)	
Chloroiodoacetonitrile (CIAN)	
Bromoiodoacetonitrile (BIAN)	
Diiodoacetonitrile (DIAN)	
Monohaloacetonitriles	
Chloroacetonitrile	0.10
Bromoacetontrile	0.14
Brominated Trihaloacetonitriles	
Bromodichloroacetonitrile	

[32] Method can be used to quantify this analyte, but MDL was not determined

Dibromochloroacetonitrile	
Tribromoacetonitrile	ND
Halopropanones	
1,3-Dichloropropanone	0.03
1,1-Dibromopropanone	
1,1,3-Trichloropropanone	0.02
1-Bromo-1,1-dichloropropanone	
1,1,1-Tribromopropanone	
1,1,3-Tribromopropanone	
1,1,1,3-Tetrachloropropanone	
1,1,3,3-Tetrachloropropanone	0.16
1,1,3,3-Tetrabromopropanone	
Haloacetaldehydes	
Dichloroacetaldehyde	0.20
Bromochloroacetaldehyde	ND
Tribromoacetaldehyde	ND
Halonitromethanes	
Chloronitromethane	
Bromonitromethane	0.21
Dichloronitromethane	
Bromochloronitromethane	
Dibromonitromethane	ND
Bromodichloronitromethane	0.10
Dibromochloronitromethane	ND
Bromopicrin	ND

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 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 Elab II room 301. A duplicate set must be deposited with the staff or faculty QC officer.

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 = 80%-120%	❖ Re-run matrix spikes ❖ Re-examine entire run for errors ❖ Possibly change SOP
Calibration Standards[33]	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)[34]			❖ Calculated Conc. = ±20% 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 IS area for a run = ±30% of long-term average	❖ Prepare new solvent & IS
			❖ 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[35] 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 new set of standards ❖ If within 150% of max standard, concentrations may be flagged as tentative

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

Appendix

USEPA Method 551.1:

(Revision 1.0)