Analysis of Cyanogen Halides

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

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Standard Operating Procedures

Analysis of Cyanogen Halides

This guidance document was prepared to assist research assistants, post-docs and lab technicians in conducting cyanogen halide (CNX) 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. Many thanks go to Dr. Jungsun Kim for helping to develop this SOP. 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 CNX analysis

Scope

This method has been used in the UMass Environmental Engineering Laboratory for the two cyanogen halides containing chlorine and bromine (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 iodinated analogue (Table 2) as well as to other neutral extractable compounds 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.

Table 1: Standard Cyanogen Halides

Analyte	**CAS Registry #**
Cyanogen Halides (CNX)	
Cyanogen Chloride (CNCl)	506-77-4
Cyanogen Bromide (CNBr)	506-68-3

Table 2: Other Neutral Extractable Analytes

Analyte	CAS Registry #
Cyanogen Iodide (CNI)	
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
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 CNX method for quick reference.

Table 3: Summary of Procedure for 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** and add 10 g Na_2SO_4
3. Add 3 mL of the pre-mixed **MTBE** + internal standard.
4. **Shake** for 10 minutes.
5. Transfer organic layer into **autosampler** vials
6. **Freeze** to remove water, and analyze.

Table 4. Typical Preparation of Calibration Standard

1. Prepare Stock II as needed: Add 20μL of commercial standard (1000 μg/mL) to a 10 mL 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 CNX 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 5.0 μg/L level.
3. Prepare any other QC samples as needed (see Table 10, page 25).

Detailed Procedures

Basis for Method

We use a protocol that is closely aligned with the LLE/GC-ECD method as used by MWD (Sclimenti et al., 1996). Please refer to this document (attached as Appendix 1) for all details.

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

Other methods include the headspace analysis (Xie and Reckhow, 1993, the purge and trap method (Flesch & Fair, 1988), and the membrane introduction mass spectrometry method (Yang and Shang, 2005). These other methods are not normally used at UMass because they either required specialized equipment or they require an especially high level of operator skill, and are therefore not as robust and the LLE method.

Once again, the primary source for our CNX method is the Sclimenti paper. 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 the MWD method

§ from Sclimenti et al., 1996	Step or Material	MWD protocol	UMass protocol

We use one of our Hewlett-Packard 6890N GCs for CNX analysis. This is equipped with an autosampler and sub-ambient LN_2 system. 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	MWD protocol	UMass protocol
Analytical Column	DB-624	Restek RTX-1701
Length	30 m	30 m
Internal Diameter	0.32 mm	0.25 mm
Film Thickness	1.8 µm	0.25 µm
Injection volume	1 µL	2 µL
Injection Type	Splitless	Splitless
Split Flow	none	none
Carrier Gas	Helium	Zero-grade Nitrogen
Carrier Flow	3.9 mL/min (xx cm/sec)[1]	2.6 mL/min
Make-up Flow	27 mL/min (N_2)	60 mL/min
Injector Temp	35°C ramped to 200°C	150°C[2]
Detector Temp		250°C
Oven Program	Hold at 25°C for 1 min Ramp to 120°C at 10°C/min (10.5 min) Hold at 120°C for 0 min Ramp to 190°C at 35°C/min (12.5 min) Hold at 190°C for 1 min (13.5 min)	Hold at 20°C for 1 min Ramp to 40°C at 2°C/min (11 min) No Hold Ramp to190°C at 35°C/min (15.3 min) Hold at 190°C for 1 min (16.3 min)

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

UMass Detailed Procedures

Sample Preservation

1. **Add ascorbic acid to each 40mL amber vial[3].**
    - ascorbic acid to achieve at least a 0.3 mM dose)[4]
        - Ascorbic acid can accelerate decomposition of brominated trihaloacetonitriles and brominated trihalonitromethanes (Krasner et al., 2001)

    a) Lab Method: Add ascorbic acid solution to achieve about 0.35 mM dose.[5]
        - Add 0.1 mL of a freshly prepared 0.142 M solution of ascorbic acid to each vial
        - This is probably better for lab sampling.

    b) Field Method: Add 4 mg of dry ascorbic acid to each vial [6].
        - For other volumes use 0.1 mg/ mL of sample.
        - This provides a dose of about 0.6 mM dose
        - This is probably better for field sampling.

2. **Add acid or buffer salts.**
    - It is recommended the pH adjustment be done on all samples for CNX analysis. If the pH is above 7, pH adjustment is absolutely required[7]. One of two methods can be used:

    a) Preferred: Add 0.2 mL of 1M H_2SO_4 to each vial.[8]

    b) Alternative: Using the marked spatula, add one measure of the phosphate buffer (~1g).
        - This may be best for field use
        - 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)
    - Make sure not to flush out preservative
    - Cyanogen chloride is quite volatile and easily lost to the air
    - This may not be necessary if sample is to be immediately extracted

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[3] clean, PTFE-faced septum capped glass 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.
[4] Ascorbic acid reacts at 1M/M stoichiometry forming dehydro-accorbate [Worley et al., 2003; JAWWA 95:3:109].
[5] This is the MWD protocol (Sclimenti et al., 1996).
[6] This is the ICR protocol.
[7] CNCl and CNBr are hydrolyzed by hydroxide at about the same rate. At pH 7 the half life is about 3 weeks at 25 C [Xie & Reckhow, 1992 WQTC]
[8] From Sclimenti et al., 1996

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[9].

Sample Extraction and Preparation for GC Analysis[10]

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

2. **Place 30 mL of sample/standard to be analyzed into vial.**
   - Add 30 ml of the water sample using an Eppendorf pipette[11]
   - 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 MTBE as soon as the sample is exposed to air, addition of sulfate and capping.

3. **Add 3mL of the pre-mixed MTBE + internal standard[12].**
   - Use repeater pipet

4. **Add approximately 10g of Na_2SO_4.**
   -

5. **Shake for 10 minutes.**
   - Cap vial
   - Place vials in rack
   - Wrap sample vials rack in bubble wrap and foam
   - Clamp sample vials in modified sieve shaker
   - Set timer to 10 minutes and start.

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[13].
   - Be certain to include necessary QC samples
     - See Table 10 (page 25) for a full listing of QC samples

[9] This is the MWD protocol (Sclimenti et al., 1994). Two days or ASAP is the ICR protocol [EPA 814-B-96-001]
[10] Typical prep time is 4 hours for a run of 30 samples
[11] 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.
[12] Internal standard (100 µg/L 1,2-dribromopropane) is for monitoring and controlling variable injection volume
[13] This is to help identify when excessive evaporation has occurred

- See Table 11 (page 26) for a typical sequence

7. **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

Analysis by Gas Chromatography[15]

GC Set up and Initiation of Run[16]

- Use Agilent 6890 near window. This one is equipped with cryogenics
- Make sure there is sufficient liquid nitrogen (NLL, not NLG) for sub-ambient operation of the column oven
- Use special program for this analysis (named: CNX ??)

See generic instructions for running Agilent 6890 gas chromatographs

Inspect the first few chromatograms

- Do this while they are coming off the integrator/recorder
- Make your first QC report by email (see "Data Analysis" below).

GC Shut-down procedure

See generic instructions for shutting down Agilent 6890 gas chromatographs

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
      - retention times of the analytes are within expected windows
      - the internal standard peak area that is within tolerance limits.

[14] since water is insoluble in MTBE, any water is present as a separate phase
[15] typically requires 20 hours of GC time for a run of 30 samples
[16] 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)

b) The analyst must report on the success or failure of these first few injections by email to the graduate QC officer, his/her designee if he/she is not available, or to the Faculty QC officer if there is no graduate QC officer.
   - If there is a graduate QC officer, the message must also include the address of the Faculty QC officer in the "cc:" line (reckhow@ecs.umass.edu).
   - The subject line of this email message must simply read "QC report"
   - The report must also indicate the sample types (e.g., field samples from Stamford CT), field collection date, laboratory treatment date (if any), and analysis date

2. Access the data stored in the computer

3. Preparation of Standard Curves

- We use generally 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. 19)
- 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 CNCl and CNBr)
ii. Internal standard average area
iii. 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 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 "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 DI water and leave them in the acid bath[17] overnight.
  - Then take them out, rinse them with laboratory DI water (3 times).
  - 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

Standard Solutions, Solvents and Supplies

[17] 5% H_2SO_4 is the UMass protocol; if desired may use 10% HNO_3 instead (UNC protocol)

Preparation of Calibration Standards[18]

1. **Prepare Stock II (2 mg/L) as needed.**
   a) Place about 5 mL of acetone[19] into a 10 mL volumetric flask
   b) To this add 20 μL of the CNX commercial mix (1000 μg/mL of the CNCl)[20]
   c) Add acetone to fill the volume.
   d) Transfer the solution to a heavy-walled extract vial (Supelco #3-3293) and store it in the container labeled CNX stocks in the refrigerator #2.

2. **Prepare calibration standards.**
   a) Add 20 mL of lab DI water to 7 vials
   b) Add a range of volumes to produce a standard curve that covers the concentration range of interest[21].
      i. Typical for finished drinking waters: 0, 5, 10, 20, 30, 50, and 80 μL of standards stock II for CNX. This gives a sequence of 0, 0.5, 1.0, 2.0, 3.0, 5.0, and 8.0 μg/L aqueous concentrations
      ii. Higher levels may be needed in some cases (e.g., some model compounds). For example, 0, 2.5, 5.0, 10.0, 15.0, 20.0, 35.0 μg/L may be a convenient range, and these can also be prepared from stock II.
   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 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 25).

Preparation of Internal Standard Stock Solution[22]

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:

[18] typically requires 20 minutes
[19] 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.
[20] e.g., from Fisher Scientific Spex CertiPrep S-1005, or Spectrum Chemical (800-813-1514) #CNCL-1000-M12
[21] Volumes and stock concentrations were selected so that one-tenth the number of μLs of Stock II added equals the concentration of the standard in μg/L.

$C_{ISstock}$ = (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 MTBE with Internal Standard[23]:

a) Rinse a dry 1-L volumetric flask with THM-grade or HPLC-grade MTBE (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 MTBE (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 MTBE
e) Place this into the bottle labeled THM + IS. The total volume should be about 1000 mL

Preparation of MtBE with Internal Standard[24]:

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.

[22] The same IS stock is used for both THM and HAA analysis.
[23] This is the standard extraction solvent used whenever chloral hydrate quantification is not necessary
[24] This extraction solvent is normally only used when chloral hydrate is to be measured

Preparation of Buffer Salt Mix

e) Weigh out buffer chemicals in the ratio required[25].
   - 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

f) Mix and Store in an Erlenmeyer flask and cover with aluminum foil

g) Prepare a new mixture at least once a month

Supplies

Table 8. Summary of Supplies for CNX Analysis

Item	Catalog #	Approx. Price	Approx # used/run[26]
Pasteur Pipettes	Fisher: 13-678-20A	720/ $46	10
Autosampler Vials	Fisher: 03-340-51F	10 packs of 100 vials / $180	40
DIUF Water	Fisher: W2-20	$32 each	Not normally used
CNCl Standard	Fisher Scientific Spex CertiPrep S-1005		
	Spectrum Chemical (800-813-1514) #CNCL-1000-M12		
CNBr Standard			
Methanol	Fisher: A 454-4	Case of four 4L bottles/ $71	76 mL
MtBE	Fisher: E127-4	cs of four 4L bottles / $364	
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	

Table 9. Availability of Other Neutral Extractable Analytes

Analyte	**Source**

[25] Note: this differs slightly from EPA 551.1, which calls for a ratio of 99% and 1%

[26] Assuming about 30 samples analyzed

Iodinated-Trihalomethanes (ITHMs)	
Dichloroiodomethane (DCIM)	Agbar[27]
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[28]
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[29]
Haloacetaldehydes	
Dichloroacetaldehyde	TCI
Bromochloroacetaldehyde	UNC
Tribromoacetaldehyde	Aldrich
Halonitromethanes	
Chloronitromethane	Helix
Bromonitromethane	Aldrich
Dichloronitromethane	Helix
Bromochloronitromethane	Helix
Dibromonitromethane	Majestic[30]
Bromodichloronitromethane	Helix
Dibromochloronitromethane	Helix
Bromopicrin	Columbia, Helix

[27] Aigues of Barcelona (Spain)
[28] Synthesized at Univ. of North Carolina for USEPA study. These contained varying levels of other DBPs as impurities; see Krasner et al., 2001
[29] TCI America (Portland, OR)
[30] 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 CNX analysis must be kept in the dark, and in a refrigerator from the time of disinfectant quench until the start of analysis. Cyanogen halides are rather unstable, so analysis should be conducted as soon as possible after collection or quenching. Organic extracts (in MTBE 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 (MTBE 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 MTBE+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 standard. 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 CNX Analysis

General Analytical QC

Many types of QC procedures are recommended for CNX analysis. 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 CNX Analysis

Types of Samples or Standards	§	Purpose	Frequency	Timing	QC data
Solvent Blank		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)		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)		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)		To determine the lowest concentration level that the analyst can report	7 standards run		MDL and EDL
Laboratory Reagent Blank (LRB)		Test lab conditions and quench for interferents	1 per day	Beginning of day	Max peak size within analyte windows
Field Reagent Blank (FRB)		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)		To test analyte recovery in the sample matrix	1 for every 10 samples	Mixed throughout day	% recovery, mean and standard deviation
Calibration Standards[31]		To provide a basis for determining the concentrations in	7 levels including zero		Calibration curves (PAR vs. conc.), including slopes and

[31] 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)[32]		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

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

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

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

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 cyanogens halides. It is designed to be a double-blind test.

Procedure

h) The graduate QC officer prepares 100 mL volumes of five different aqueous solutions of the cyanogens halides (CNCl and CNBr) and places them in separate, labeled glass bottles.
i) These are given to the faculty QC officer or his designee along with 5 clean, empty standard sample vials (e.g., 40-mL septum vials).
j) The faculty QC officer (or designee) 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 or designee knows the identity of each.
k) The five IDC samples are passed on to the analyst for immediate analysis.
l) 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 13.

Method Detection Limit (MDL)

Procedure

a) Prepare a 500 mL of a 1 μg/L standard of all cyanogens halides.
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 22 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 Cyanogen Halides in Water

Analyte	MRL (µg/L)	MDL (µg/L)	
	Krasner et al., 1990	**Flesch & Fair, 1988**	**Krasner et al., 1990**
Cyanogen Halides (CNXs)			
Cyanogen Chloride	1	0.3	0.13
Cyanogen Bromide	0.1		0.13

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 13) 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 13 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 Elab II GC area (Rm 301). A duplicate set must be deposited with the faculty QC officer (D. Reckhow).

Table 13: 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	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

(LFM)				
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 RFD for replicate analyses ≤20%	❖ Re-run samples and/or discard outliers[35] 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

Literature Cited

Flesch, John J. and Fair, Patricia Snyder. The Analysis of Cyanogen Chloride in Drinking Water. Proceedings Water Quality Technology Conference; Advances in Water Analysis and Treatment St. Louis, MO , 465-474 1989.

Sclimenti MJ, Hwang CJ, Krasner SW. A Comparison of Analytical Techniques for Determining Cyanogen Chloride in Chloraminated Drinking Water. In: Minear RA, Amy GL, editors. Water Disinfection and Natural Organic Matter American Chemical Society, Washington DC, 1996, pp. 126-136.

Xie YF, Reckhow DA. A Rapid and Simple Analytical Method for Cyanogen Chloride and Cyanogen-Bromide in Drinking-Water. Water Research 1993; 27: 507-511.

[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: MWD Method

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Chapter 9

A Comparison of Analytical Techniques for Determining Cyanogen Chloride in Chloraminated Drinking Water

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This study was undertaken to evaluate various analytical techniques for the determination of cyanogen chloride (CNCl) in chloraminated drinking water. CNCl will be included in the Federal Information Collection Rule and is a possible candidate for regulation in Stage 2 of the Disinfectants/Disinfection By-Products Rule. Analytical techniques for the measurement of CNCl include purge-and-trap (P&T)/gas chromatograph (GC)-mass spectrometer (MS) analysis, headspace/GC-electron capture detector (ECD) analysis, and micro-liquid/liquid extraction (micro-LLE) with GC-ECD analysis. Currently, the official U.S. Environmental Protection Agency method for CNCl is P&T/GC-MS analysis, although it is recognized that this method has its limitations. This research has demonstrated that the micro-LLE/GC-ECD, P&T/GC-MS, and headspace/GC-ECD methods were comparable analytical techniques for the determination of CNCl in chloraminated drinking water. Moreover, the micro-LLE/GC-ECD method is applicable for CNCl analyses in various matrix waters and should be usable in more laboratories in which GC-ECD equipment is more common. A cost comparison showed that the micro-LLE/GC-ECD method was the least expensive analytical technique compared to the P&T/GC-MS and headspace/GC-ECD methods.

Many utilities today use chloramines as an alternative to free chlorine as a secondary disinfectant in their distribution systems to minimize further formation of chlorination by-products. However, chloramines also form disinfection by-products (DBPs) of a different chemical nature. One chloramine DBP of interest is cyanogen chloride (CNCl), a highly volatile organic compound. The formation of CNCl has been shown to result from the chlorination of aliphatic amino acids in the presence of the ammonium ion (*1*). F. E. Sculley, Jr. ("Reaction Chemistry of Inorganic Monochloramine:

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Products and Implications for Drinking Water Disinfection," presented at the 200th ACS National Meeting, Washington, DC, 1990), and E. J. Pedersen et al. ("Formation of Cyanogen Chloride from the Reaction of Monochloramine and Formaldehyde," presented at the 210th ACS National Meeting, Chicago, IL, 1995) have shown CNCl formation to result from the reaction of formaldehyde--known to be an ozonation DBP--and monochloramine. CNCl was first reported as a chloramine DBP by Krasner and co-workers in a nationwide survey of 35 water utilities (*2*). This study found CNCl levels ranging from approximately 0.4 to 12 μg/L. CNCl is to be included in the Federal Information Collection Rule for systems using chloramines (*3*) and is a possible candidate for regulation in Stage 2 of the Disinfectants/DBP Rule.

This study was undertaken to evaluate various analytical techniques for the determination of CNCl in chloraminated drinking water. Analytical techniques for the measurement of CNCl include purge-and-trap (P&T) gas chromatograph (GC)/mass spectrometer (MS) analysis, headspace/GC-electron capture detector (ECD) analysis, and micro-liquid/liquid extraction (micro-LLE) with GC-ECD analysis. Currently, the official U.S. Environmental Protection Agency (USEPA) method for CNCl is P&T/GC-MS analysis, although it is recognized that this method has its limitations. Thus, the purpose of this research was to evaluate alternate analytical techniques for CNCl.

The P&T/GC-MS method utilizes a modification to USEPA Method 524.2, as described by Flesch and Fair (*4*). Method 524.2 is ideally suited for the analysis of many volatile organic compounds (VOCs), but it is difficult to obtain precise and accurate results for chemicals such as vinyl chloride and CNCl, which are gases at room temperature. In addition, because CNCl is a highly reactive compound, an all-glass system with inert or deactivated internal surfaces must be used. Xie and Reckhow developed a headspace/GC-ECD method that is more reliable (*5*). However, only 1 percent of the CNCl is recovered on an absolute basis by this headspace analysis. Xie and Reckhow estimated the Henry's Law constant of 0.9 atm-L/mol for CNCl, thus explaining the low absolute recovery. Also, this method is not easily automated without investment in a special headspace autosampler. A micro-LLE/GC-ECD technique was developed at the Metropolitan Water Distict of Southern California, using salted, methyl *tert*-butyl ether extraction with GC-ECD analysis (*6*). The micro-LLE/GC-ECD method recovers 14 percent of the CNCl on an absolute basis. Procedural calibration standards were used for all three methods to facilitate accurate quantitation in lieu of 100 percent absolute recoveries.

The analytical techniques available for CNCl determination are varied. The purpose of this study was to compare the three methods and evaluate each method simultaneously to determine whether or not there is equivalency between them. The need for an accurate and precise method for CNCl determination is important for regulatory purposes. In addition, ease of use and availability of equipment are important considerations.

Experimental Section

Reagents and Chemicals. Information on the analytical standards used in this research is provided in Table I. CNCl is a gas at room temperature and is highly toxic. Standards can be prepared by dissolving the pure gas into methanol. However, a

prepared standard can be purchased at concentrations up to 2000 µg/mL. The internal standard for the micro-LLE/GC-ECD and headspace techniques was 1,2-dibromopropane, and for the P&T/GC-MS technique the internal standard was fluorobenzene. The surrogate used for the P&T/GC-MS technique was 4-bromofluorobenzene.

Table I. Analytical Standards

Compound [CAS No.]	*Source*	*Purity (percent)*	*Molecular Weight (g/mole)*	*Boiling Point (°C)*	*Density (mg/mL)*
Cyanogen chloride[1] [506-77-4]	Island[2]	99.5	61.47	13.9	1.186
1,2-Dibromopropane[3] [78-75-1]	Aldrich[4]	99	201.90	140	1.9324
Fluorobenzene[5] [462-06-6]	Aldrich[4]	99	96.11	85.11	1.0225
4-Bromofluorobenzene[6] [460-00-4]	Aldrich[4]	99	175.01	152	1.4946

[1]CNCl is also available as a solution (concentration = 2000 µg/mL) from Protocol Analytical Supplies, Inc. (Middlesex, NJ).

[2]Island Pyrochemical Industries (Great Neck, NY).

[3]Internal standard used for micro-LLE and headspace/GC analyses.

[4]Aldrich Chemical Company, Inc. (Milwaukee, WI).

[5]Internal standard for P&T/GC-MS analysis.

[6]Surrogate used for P&T/GC-MS analysis.

The extraction solvent used for the micro-LLE/GC-ECD technique was "Omnisolv"-grade methyl *tert*-butyl ether from EM Science (Gibbstown, NJ). The salt used in the micro-LLE/GC-ECD technique was sodium sulfate (Na_2SO_4) from J. T. Baker, Inc. (Jackson, TN).

The sulfuric acid used for sample preservation was Fisher Scientific Co. (Pittsburgh, PA) A.C.S. reagent grade. The dechlorinating/dechloraminating agent, L-ascorbic acid, was obtained from Sigma Chemical Co. (St. Louis, MO). Samples were preserved in the same manner for all three analytical techniques. Preservation included the addition of 2.5 mg of ascorbic acid to a 40-mL sample plus 0.2 mL of a 1*M* sulfuric acid solution. Sample pH was ~3-3.5, which minimized base-catalyzed hydrolysis. With these preservatives, samples could be held for up to 14 days (*6*).

Analytical Methods.

Sample Preservation. Samples were collected in nominal 40-mL vials with Teflon-faced polypropylene septa and screw caps (I-Chem Research, Inc., Hayward, CA). The sample vials were filled so as to ensure that no air bubbles passed through the sample, thus minimizing aeration. Approximately 0.1 mL of a freshly prepared 0.142*M* ascorbic acid solution and 0.2 mL of 1*M* sulfuric acid were added to each vial prior to sampling. It was important that the ascorbic acid solution be fresh, as it had a very short shelf life. The volume of acid was adjusted as needed to achieve the desired pH of ~3-3.5. The bottles were not rinsed before filling and were not allowed to overfill, since the bottles contained preservatives. The sample vials were sealed headspace-free. Ascorbic acid and sulfuric acid were employed as dechlorinating/dechloraminating and preservation agents, respectively. The ascorbic acid reduced any free chlorine or monochloramine residual present, thus preventing further production of CNCl. The 1*M* sulfuric acid reduced the pH of the sample to ~3-3.5. Samples were stored in a refrigerator at 4°C. All samples were brought up to room temperature prior to analysis.

The GC conditions used in this comparison are outlined in Table II. A brief summary of each method used is given below.

Micro-LLE/GC-ECD Analysis. Samples were first brought up to room temperature prior to extraction. A 30-mL aliquot of sample was extracted by addition of 10 g of Na_2SO_4 and 4 mL of methyl *tert*-butyl ether containing 100 µg/L internal standard, 1,2-dibromopropane. The purpose of the salt was to increase the extraction efficiency by increasing the ionic strength of the sample matrix, thus reducing the solubility of the CNCl in water, and the purpose of the internal standard was simply to monitor the autosampler injections for constancy. The sample was then shaken in a mechanical shaker for 10 min. The methyl *tert*-butyl ether layer was transferred between two 1.5-mL autosampler vials. The second vial was used as a backup extract in the event that reanalysis became necessary. The analysis was conducted on a GC (model 3600; Varian Instrument Group, Sunnyvale, CA) with a ^{63}Ni ECD and a fused-silica capillary column (DB-624, 30-m length, 1.8-µm film thickness, 0.32-mm internal diameter; J&W Scientific, Folsom, CA) to obtain baseline resolution of CNCl from vinyl chloride.

P&T/GC-MS Analysis. Samples were first brought up to room temperature prior to analysis. A 25-mL gas-tight syringe was filled with sample from a 40-mL vial. Internal standard and surrogate were then added to this aliquot. The aliquot was then transferred to a fritted sparger attached to a P&T concentrator (Tekmar LSC2000; Rosemount Analytical, Inc., Tekmar Co., Cincinnati, OH). Connections were made with all glass-lined tubing because CNCl is highly reactive and can be degraded very easily on hot metal surfaces. The sample was then sparged for 4 min with helium onto a Tenax #1 cartridge trap (Enka Research Institute, Arnhem, Netherlands) where CNCl was retained. The analyte was then desorbed from the trap by heating, and the desorbed gas was cryofocused (Tekmar Cryofocusing Module; Rosemount Analytical) prior to injection onto the GC and analysis on the MS. The GC was a model HP 5890 (Hewlett-Packard Co., Avondale, PA)--with a fused-silica capillary column (DB-5,

Table II. GC Conditions and Parameters

	Micro-LLE/ GC-ECD	*P&T/GC-MS*	*Headspace/ GC-ECD*
Injector/ sample introduction	Septum-equipped, programmable temperature injector (Varian model 1093)	P&T concentrator with cryofocusing unit	Split/splitless injector (Varian model 1077); split ratio set at 50:1
Injector/ sample introduction programming	Hold at 35°C for 0 min, ramp 180°C/min to 200°C, hold for 12.59 min	Purge 4.0 min Desorb preheat = 175°C Desorb 1.5 min at 180°C Capillary cooldown = -150°C Inject 0.85 min at 220°C Bake 2.0 min at 220°C	Isothermal, set at 150°C
Column temperature program	25°C, 1 min; 10°C/min; 120°C, 0 min; 35°C/min; 190°C, 1 min	10°C, 4 min; 20°C/min; 184°C, 3 min	25°C, 0.5 min; 8°C/min; 89°C, 0 min; 15°C/min; 150°C, 3 min
Total run time	13.5 min	15.7 min	15.56 min
Gases: Carrier (He) Detector make-up (N_2) Purge (He) Headspace (N_2)	 3.9 mL/min 27 mL/min NA NA	 1.5 mL/min NA 40 mL/min NA	 1.5 mL/min 30 mL/min NA 10 mL
Autosampler/ sample volume	Varian model 8100 Injection volume: 1 µL Solvent plug volume: 0.5 µL Injection rate: 5.0 µL/sec Injection time: 0.05 min	Purge sample volume = 25 mL	Injection volume = 400 µL of headspace volume
Other		GC inlet temperature = 200°C Source temperature = 180°C MS resolution = 500 Multiplier volts = 1400 eV EI voltage = 70 eV	

NA = Not applicable

30-m length, 1.0-μm film thickness, 0.25-mm internal diameter; J&W Scientific)--coupled to a medium-resolution, electron-impact, magnetic-sector MS (model TS-250; VG Tritech Ltd., Wythenshawe, Manchester, England). The MS was set up to monitor full-scan for CNCl as well as the internal standard and surrogate.

Headspace/GC-ECD Analysis. The method of Xie and Reckhow (*5*) was utilized with some modifications. Briefly, after the sample was brought up to room temperature, the internal standard (1,2-dibromopropane) was added to the sample. Then 10 mL of sample liquid was displaced by nitrogen gas to create a headspace. This was accomplished by first piercing the vial septum with a bare syringe needle and then forcing the needle of a syringe containing 10 mL of nitrogen through the same septum. As the nitrogen was forced into the vial, an equivalent amount of liquid was displaced through the bare needle, thus creating the desired headspace. The syringe and bare needle were removed after the required volume had been displaced. The vial was then shaken for 30 seconds. Next, using a 500-μL gas-tight syringe, 400 μL of the headspace volume was injected onto a split/splitless injector (in splitless mode). The analysis was conducted on a GC (Varian model 3600) with a ^{63}Ni ECD and a fused-silica capillary column (DB-1701, 30-m length, 1.0-μm film thickness, 0.25-mm internal diameter; J&W Scientific) to obtain baseline resolution of CNCl.

Water Samples. In order to directly compare each of the analytical techniques, samples were split and analyzed by the three methods. Several different sample matrix waters were obtained from various facilities nationwide, including two pilot plants and five full-scale water treatment plants. These locations were chosen on the basis of bromide ion concentration, total organic carbon concentration, pH, and chlorine-to-ammonia-nitrogen ratio (American Water Works Association Research Foundation [AWWARF], *Factors Affecting Disinfection By-Products Formation During Chloramination*, final report; AWWA and AWWARF, Denver, CO; in press). Table III outlines the range of water quality parameters for the samples used in this comparison. CNCl values ranged from 0.9 to 4.6 μg/L, with one pilot-plant sample representing an extreme condition (pH = 6) measuring as high as 12 μg/L.

Table III. Water Quality Parameters

Water Quality Parameter	*Range*
Bromide ion concentration	7 to 857 μg/L
Total organic carbon	1.4 to 8.9 mg/L
pH	6.7 to 9.2
Chlorine-to-ammonia nitrogen ratio	3:1 to 4.6:1
UV absorbance @ 254 nm	0.028 to 0.21

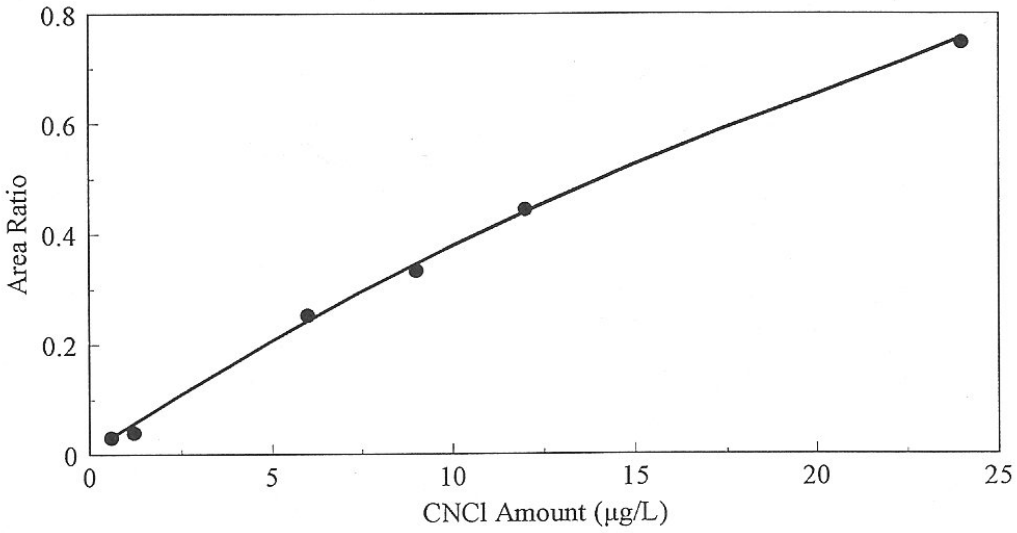

Figure 1. CNCl Calibration Curve for the P&T/GC-MS Method.
(Area ratio = [CNCl area/Internal standard area].)

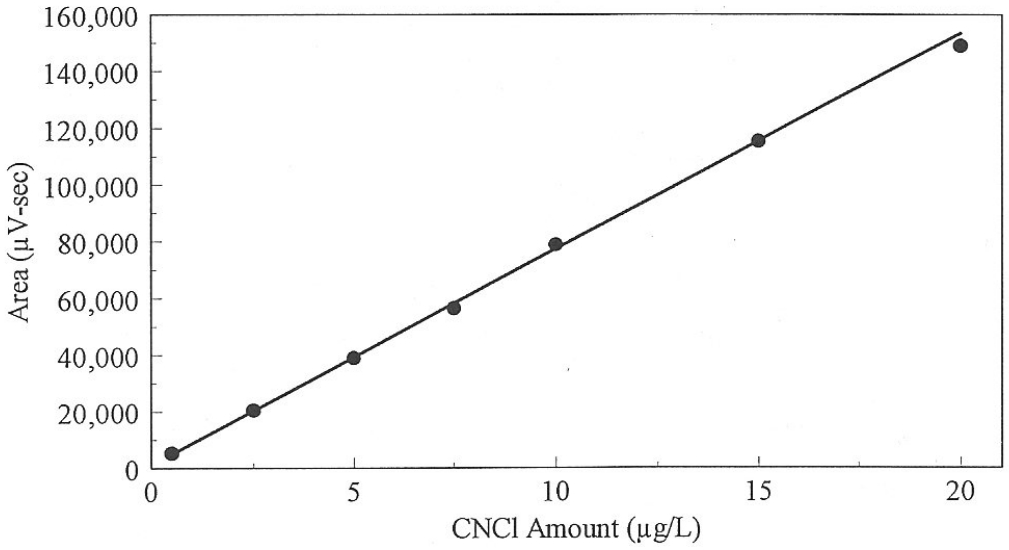

Figure 2. CNCl Calibration Curve for the Micro-LLE/GC-ECD Method.

Results and Discussion

Calibration and Quality Control. Calibration standards were analyzed in the same manner as the samples to compensate for less than 100-percent extraction or purge efficiency. The instruments were calibrated prior to sample analysis. Figures 1-3 show the calibration curves for the three analytical techniques. The P&T/GC-MS calibration curve (Figure 1) was curvilinear (second-order polynomial), whereas the micro-LLE/GC-ECD (Figure 2) and headspace/GC-ECD (Figure 3) techniques yielded linear calibration curves. Procedural standards led to accurate quantitation for these methods, each of which could detect CNCl concentrations as low as ~0.5 μg/L.

Quality control samples, including both accuracy (matrix spike) and precision (replicate) samples, were also analyzed in this comparison. Mean matrix-spike recoveries (±1 standard deviation) for CNCl were 98 ± 6.3 percent for the micro-LLE/GC-ECD method, 96 ± 18 percent for the P&T/GC-MS method, and 107 ± 14 percent for the headspace/GC-ECD method. The precision (±1 standard deviation) for CNCl was 3.7 ± 3.9 percent for the micro-LLE/GC-ECD method, 14.2 ± 9.5 percent for the P&T/GC-MS method, and 10.7 ± 7.3 percent for the headspace/GC-ECD method. The three methods demonstrated comparable accuracy; however, precision was best for the micro-LLE/GC-ECD technique.

Analytical Methods Comparison. The analyses were performed within the established 14-day holding period for CNCl. When the comparisons were performed, samples were analyzed within 24 h of each other.

Figure 4 compares the micro-LLE/GC-ECD and P&T/GC-MS methods. Typically, the micro-LLE/GC-ECD method produced CNCl results within ± 20 percent of the values determined by the P&T/GC-MS technique. In this limited data set, there somewhat higher results appear to have been produced by the micro-LLE/GC-ECD method. This difference may be partially a result of the calibration curves generated for each analysis. Figure 5 compares the headspace/GC-ECD and micro-LLE/GC-ECD methods. Once again, the micro-LLE/GC-ECD method produced CNCl results within ± 20 percent of the values determined by the headspace/GC-ECD method. Because of sampling limitations, no direct comparison was made between the headspace/GC-ECD and P&T/GC-MS methods. An indirect comparison could be made between these two methods based on the previous comparisons, as similar results were obtained for all three analytical techniques.

An advantage of the micro-LLE/GC-ECD method is that an expensive GC-MS system is not required. A comparison of the costs of the analyses in Southern California showed that a typical LLE/GC-ECD analysis (for other VOCs) ranged from $65 to $100, whereas the cost of a P&T/GC-MS analysis ranged from $150 to $260. Headspace analyses ranged from $150 to $300, in part because of uncommon usage. In addition, downtime on a GC-ECD system is significantly less than for the GC-MS.

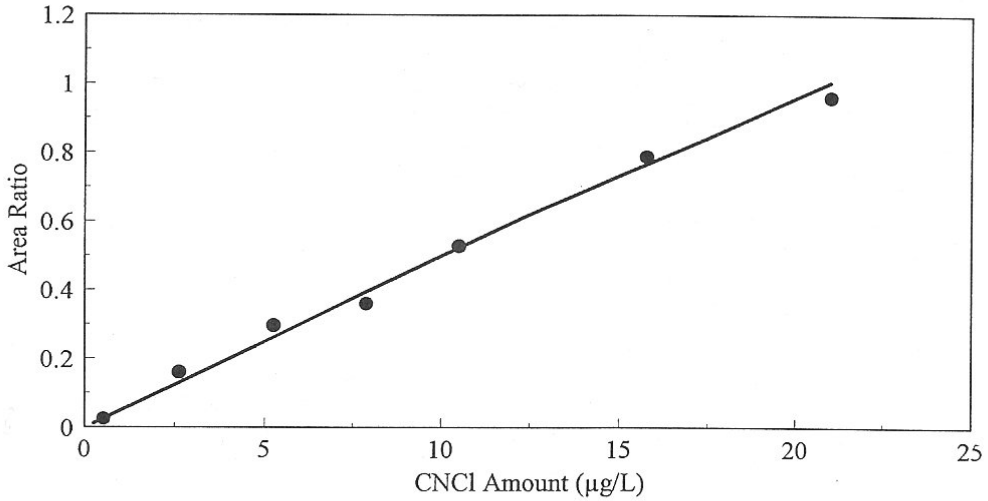

Figure 3. CNCl Calibration Curve for the Headspace/GC-ECD Method. (Area ratio = [CNCl area/Internal standard area].)

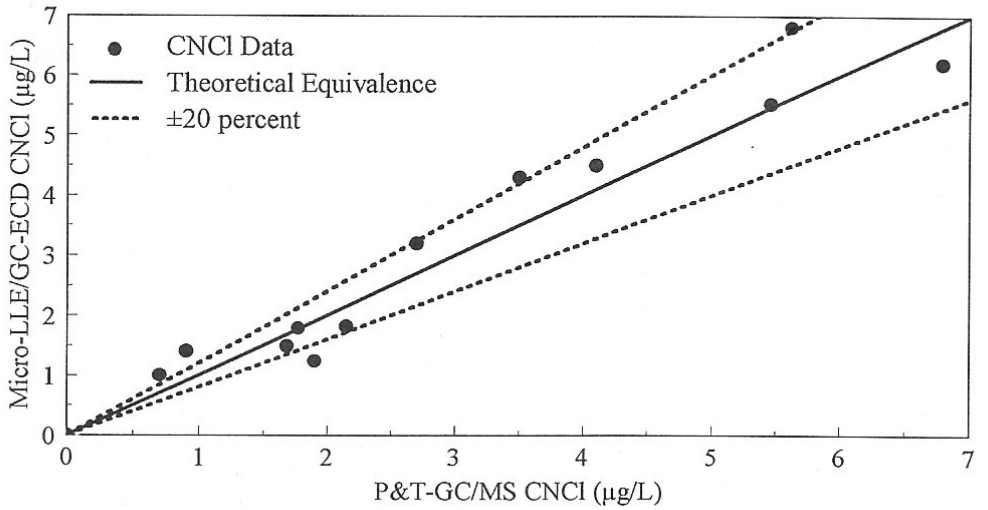

Figure 4. Analytical Methods Comparison Between the P&T/GC-MS and Micro-LLE/GC-ECD Methods.

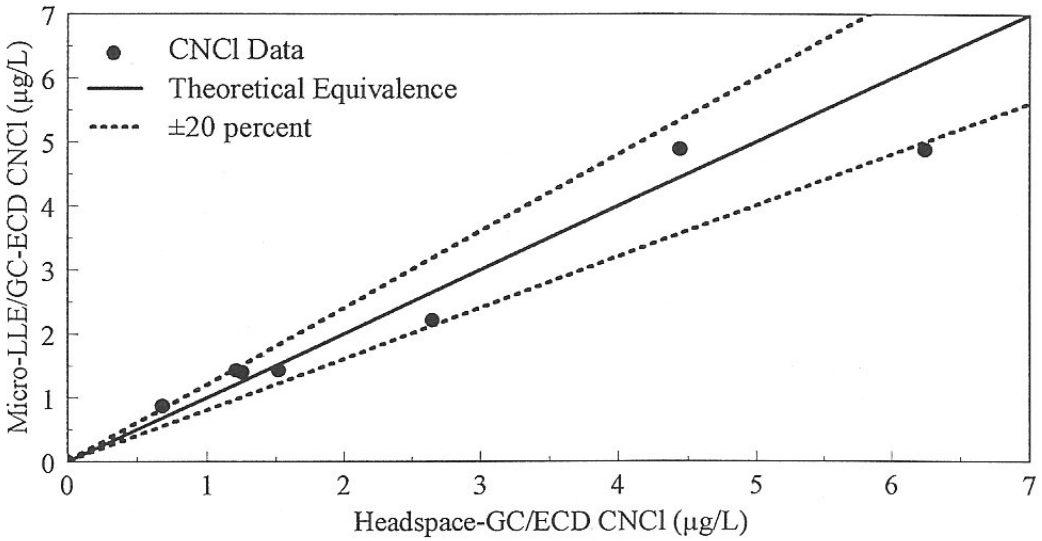

Figure 5. Analytical Methods Comparison Between the Headspace/GC-ECD and Micro-LLE/GC-ECD Methods.

Conclusions

As the comparisons show, the micro-LLE/GC-ECD, P&T/GC-MS, and headspace/GC-ECD methods are comparable analytical techniques for the determination of CNCl in drinking water. The accuracies of the three methods were comparable, and the micro-LLE method was the most precise. The results of split samples typically agreed to within ±20 percent. The cost comparison showed that the micro-LLE technique was the least expensive of the three analytical techniques. The comparative data presented here can provide a basis for acceptance of the micro-LLE/GC-ECD method as an alternative to the P&T/GC-MS and headspace/GC-ECD methods.

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