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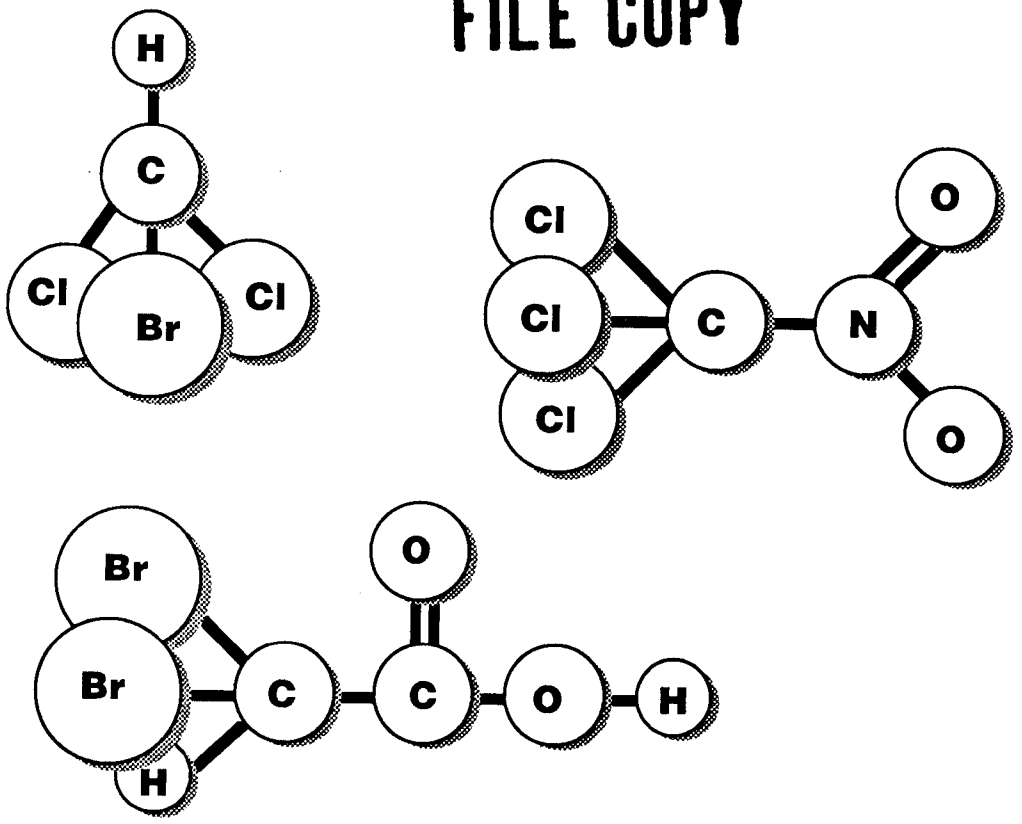


# United States Environmental Protection Agency
# Association of Metropolitan Water Agencies

*Final Report for*

## *Disinfection By-Products in United States Drinking Waters*

Volume 2 - Appendices

November 1989

JMM James M. Montgomery
Consulting Engineers, Inc.

Metropolitan Water District of Southern California

UNITED STATES ENVIRONMENTAL PROTECTION AGENCY

ASSOCIATION OF METROPOLITAN WATER AGENCIES

# DISINFECTION BY-PRODUCTS IN UNITED STATES DRINKING WATERS

## FINAL REPORT

## VOLUME 2- APPENDICES

November 1989

Metropolitan Water District of Southern California

James M. Montgomery, Consulting Engineers, Inc.

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# Appendix A

## *Questionnaire and Cover Letter*



# The Metropolitan Water District of Southern California

March 9, 1988

CERTIFIED MAIL

Contact Name
Utility Name
Utility Street Address
Utility City, State Zip Code

Dear Contact Name:

Increasing attention is being focused on the occurrence of disinfection by-products (DBPs) due to chlorination in drinking water treatment. These compounds include not only trihalomethanes, but also haloacetonitriles, haloketones, haloacids and chlorophenols, among others. The United States Environmental Protection Agency (EPA) will be developing regulations to control disinfection by-products as a result of the 1986 amendments to the Safe Drinking Water Act. Consequently, the Association of Metropolitan Water Agencies (AMWA), in cooperation with the EPA, is undertaking a study to assess the occurrence of disinfection by-products and the impact of treatment practices on DBP formation and control. The Metropolitan Water District of Southern California (MWD) and James M. Montgomery, Consulting Engineers, Inc. (JMM) will conduct the study.

The specific objectives of the project are: 1) to determine the baseline occurrence of DBPs at drinking water treatment facilities representing a broad range of source water qualities and treatment processes: and 2) to determine the effect of changes in treatment processes and/or disinfectants on the production of DBPs. Results of this study will be of value to the EPA in defining best available technology and costs in setting the new regulations. Results will also be of value to the water utility industry in deciding among treatment process alternatives to meet the new regulations.

The study will be conducted in two phases. Your involvement would focus on one of your utility's treatment plants. Participation in the first phase would include: 1) completing the enclosed written questionnaire and possibly a telephone interview, 2) collecting four sets of water quality samples over a period of one year (to be analyzed by MWD and JMM laboratories), 3) conducting pH and residual disinfectant measurements on the four sets of samples, and 4) providing some historical plant data regarding THM levels, chemical dosing and any previous process changes.

In the second phase of the project, a limited number of utilities will be selected to conduct bench, pilot or full-scale evaluations of the effect of process modifications on DPB production. If your treatment plant has the capability, such

modifications may include the use of ozonation and/or granular activated carbon adsorption, or a change of disinfectant. You may choose to participate in either the first phase or both phases of the project.

The identities of participating utilities would not appear in any published papers, presentations or press releases, but would be shared on a working basis with the CDHS.

All DBP data from the MWD and JMM laboratories pertaining to your utility will be provided to you. Such data may be useful in assessing your own treatment practices. You will also receive a copy of the executive summary of the final project report upon completion of the study.

The analytical methods for the DBPs studied under this project are the result of an extensive development effort by the U.S. Environmental Protection Agency, MWD and JMM laboratories. If you are interested in developing any of the methods in your own water quality laboratories, MWD and JMM will provide the methods to you. It is also possible to set up split samples if your laboratory would like to run quality control checks on the THM or any other DBP analysis conducted for this study.

The enclosed questionnaire is an integral part of this research effort. Please provide responses pertaining to **only one** of the water treatment facilities operated by your utility, preferably the facility producing the highest levels of THMs, or a facility producing high THMs that can also accomodate some type of process modification. If your utility participated in the previously conducted American Water Works Association Research Foundation THM survey, your responses on that survey form have been incorporated into the enclosed questionnaire form. Please double check these entries and make any necessary corrections or additions.

The results of this effort could influence the outcome of future regulations. Your input is very important. Please complete the enclosed questionnaire as soon as possible and return it in the enclosed postage-paid envelope by **March 23, 1988**. Thank you for your participation.

Very truly yours.

Michael J. McGuire, Ph.D.
Director of Water Quality

## DISINFECTION BY-PRODUCTS STUDY

## QUESTIONNAIRE

Please complete this questionnaire in its entirety. **All questions, with the exception of Questions 1 through 3, apply only to the specific water treatment facility where samples will be taken.** If certain information and/or data are not available, please indicate "Not Avail." If a question does not apply to your utility or water treatment facility, please mark "N/A" in the space provided. For questions that may require more space than is provided, please use a separate sheet of paper. **Handwritten responses are preferred** to avoid transcription errors during typing.

When completed, please return the questionnaire by **April 14, 1988**, in the enclosed postage-paid envelope to:

Dr. Joseph G. Jacangelo
James M. Montgomery, Consulting Engineers, Inc.
250 North Madison Avenue
P.O. Box 7009
Pasadena, California 91109-7009

Should you have any questions about the information requested, please contact either Joe Jacangelo or Nancy Patania at (818) 796-9141.

1. Utility name and address:

2. Contact person and telephone number:

3. Size of population served by utility:

| Direct retail: | Indirect Retail (Wholesale) |
|---|---|
| Connections_____ | Connections_____ |
| Population served_____ | Population served_____ |

4. Name and address of subject water treatment plant:

5. Source(s) of water supply to subject water treatment plant (please identify each source by name and whether the source is a flowing stream, groundwater, or lake/reservoir):

| Source Type | Name | Average % of supply to this facility |
|---|---|---|
| Flowing stream | _____ | _____ |
| Groundwater | _____ | _____ |
| Lake/reservoir | _____ | _____ |
| Purchased | _____ | _____ |

6. Design hydraulic capacity of plant (MGD):

7. Please attach or draw a schematic of the plant showing treatment processes and locations of chemical addition.

8. a. Chemical Application (i.e., oxidant, ozone, permanganate, coagulant, coagulant aid, powdered activated carbon, filter aid, disinfectant, etc.):

| Process | Chemical | Typical Dosage (ppm) | Typical Detention Time (min) |
|---|---|---|---|
| Pretreatment | | | |
| | | | |
| Rapid Mix | | | |
| | | | |
| Flocculation | | | |
| | | | |
| Sedimentation | | | |
| | | | |
| Filtration | | | |
| | | | |
| Disinfection | | | |
| | | | |
| Softening | | | |
| | | | |
| Other | | | |
| | | | |

b. Non-conventional treatment processes (if applicable):

| | | |
|---|---|---|
| Granular Activated Carbon: | Empty Bed Contact Time (min) | |
| Air Stripping: | Air-to-Water Ratio | |
| Ion Exchange: | Yes/No | |
| Reverse Osmosis: | Yes/No | |

9. Water Quality

| Parameter | RAW WATER QUALITY (1987 DATA) ------Measured Annual Concentration------ Average | Maximum | Minimum | TREATED WATER QUALITY (IMMEDIATELY AFTER FINAL DISINFECTION BUT BEFORE DISTRIBUTION) (1987 DATA) ------Measured Annual Concentration------ Average | Maximum | Minimum |
|---|---|---|---|---|---|---|
| pH (standard pH units) | | | | | | |
| Alkalinity (ppm as $CaCO_3$) | | | | | | |
| Turbidity (NTU) | | | | | | |
| Color (Standard color units) | | | | | | |
| Total Organic Carbon (ppm) | | | | | | |

10. Disinfection and Distribution System:

| Parameter | TREATED WATER QUALITY (**IMMEDIATELY AFTER FINAL DISINFECTION BUT BEFORE DISTRIBUTION**) (1987 DATA) Measured Annual Concentration | | | DISTRIBUTION SYSTEM CHARACTERISTICS (1987 DATA) Measured Annual Concentration | | |
|---|---|---|---|---|---|---|
| | Average | Maximum | Minimum | Average | Maximum | Minimum |
| Disinfectant Residual | | | | | | |
| Free Chlorine (ppm $Cl_2$) | | | | | | |
| Combined Chlorine (ppm $Cl_2$) | | | | | | |
| Chlorine Dioxide (ppm $ClO_2$) (if applicable) | | | | | | |
| Trihalomethanes | | | | | | |
| Total (**ppb**) | | | | | | |
| Chloroform (**ppb**) | | | | | | |
| Dichlorobromomethane (**ppb**) | | | | | | |
| Dibromochloromethane (**ppb**) | | | | | | |
| Bromoform (**ppb**) | | | | | | |
| Detention time (days) | | | | | | |

11. Has a pilot or bench study on control of THMs or DBPs ever been conducted at the plant? If yes, please provide information regarding study objectives. (MWD may request study results at a later time.)

_____

_____

_____

_____

_____

_____

Thank you very much for helping the Association of Metropolitan Water Agencies.

Return the questionnaire in the stamped, self-addressed envelope to:

Dr. Joseph G. Jacangelo
James M. Montgomery, Consulting Engineers, Inc.
250 North Madison Avenue
P.O. Box 7009
Pasadena, California 91109-7009

# Appendix B

## *Sampling Instructions and Sample Information Sheet*

To: Participants in Chlorination Disinfection By-Products Study

From: Stuart W. Krasner, Senior Chemist
Metropolitan Water District of Southern California

Subject: Instructions for Collection and Shipment of Water Samples

The samples you are about to collect are for an occurrence and control study of disinfection by-products which may be formed by the chlorination of your drinking water. These samples are very important and great care must be used when collecting and returning them.

Your sampling kit contains:

(1) 22 bottles to fill at the treatment plant clearwell effluent,

(2) 7 bottles (marked with red dots and in a separate bag) to fill at the influent to the treatment plant (i.e., "raw" water before the addition of disinfectant/oxidant, coagulant, lime, etc.), and

(3) 3 bottles (in a separate bag) to fill at the filter influent.

(4) Your sampling kit also contains 6 bottles labelled "TRAVEL BLANK". Do not open these bottles; just return them with the samples you collect.

Please measure the temperature, pH, and chlorine residual (free and total) at all three sample points and record the information on the attached SAMPLE INFORMATION SHEET. If chlorine dioxide is used, please measure its residual at the three sample points and record as well. Please fill out the remainder of the information sheet, **INCLUDING MARKING UP THE ATTACHED SCHEMATIC.**

Please collect the samples on _____, 19____.

SAMPLING INSTRUCTIONS

1. The sample bottles contained in the accompanying "sampling kit", and parameters to be analyzed from each bottle, are as follows:

| Parameter | # & Size of Sample Bottle |
|---|---|
| **CLEARWELL EFFLUENT SAMPLE BOTTLES:** | |
| Pent. Ext. DBPs* | 3 - 40 mL |
| Chloral Hydrate | 3 - 40 mL |
| Haloacids | 4 - 40 mL |
| Cyanogen Chloride | 4 - 40 mL |
| Formaldehyde | 3 - 40 mL |
| TOX | 2 - 250 mL |
| TOC | 3 - 60 mL |
| **PLANT INFLUENT (RAW) SAMPLE BOTTLES:** | |
| Formaldehyde | 3 - 40 mL |
| Bromide | 1 - 60 mL |
| TOC | 3 - 60 mL |
| **FILTER INFLUENT SAMPLE BOTTLES:** | |
| TOC | 3 - 60 mL |
| **ADDITIONAL BOTTLES IN KIT:** | |
| Travel Blanks | 6 - 40 mL |

* Pent. Ext. DBPs = pentane-extractable disinfection by-products, i.e., trihalomethanes, haloacetonitriles, haloketones, and chloropicrin.

2. If the faucet has an aerator, please remove it before collecting the sample. Let the water run freely from the tap for five minutes before you begin filling bottles, so you are taking water from the main and not water that has been settling in the pipes.

3. Slowly fill the sample bottles allowing the water to flow down into the bottles at a slight angle to reduce the possibility of aerating the sample. Remove each bottle from the tap when the water reaches the rim. **DO NOT RINSE THE BOTTLES BEFORE FILLING AND DO NOT OVERFILL, SINCE MOST OF THE BOTTLES CONTAIN A DECHLORINATION AGENT AND/OR PRESERVATIVE.**

4. Cap each bottle making certain that the hard shiny Teflon side of the septum is against the water. Do not overtighten since the caps break easily.

5. Invert each bottle to check for air bubbles. If air is present, re-open the bottle and add a few more drops of water. Reseal and check as before.

6. Put each bottle into a separate "bubble-pack" bag and seal the top. Put the bottles into the ice chest and add two frozen "Blue Ices". **(NOTE: THE "BLUE ICE" MUST BE PUT IN A FREEZER AT LEAST ONE DAY IN ADVANCE OF SAMPLING.)** Cover with styrofoam packing material so that the bottles will not bounce around during transit. Please return the SAMPLE INFORMATION SHEET and the marked-up schematic of your treatment plant in a sealed plastic bag and place in the ice chest. Close the ice chest and **SECURE WITH STRAPPING TAPE.**

7. It is essential that the samples are kept cold until we receive them, so ship the ice chest on the same day the samples are collected via Federal Express (guaranteed next day delivery). Metropolitan will pay all shipping costs. Use the enclosed Federal Express airbill. **YOU WILL NEED TO CALL FEDERAL EXPRESS EARLY IN THE DAY TO ARRANGE A PICK-UP TIME TO ENSURE OVERNIGHT DELIVERY.**

8. If you have any questions about these sampling and shipping instructions, please call Stuart Krasner, (714) 392-5083, or Cordelia Hwang, (714) 392-5126. If there are questions about the source of water or treatment plant operations for the sampling collection time, please call Joe Jacangelo or Nancy Patania, (818) 796-9141.

9. We will provide you with results of these measurements at the end of the project. Thank you very much for your assistance in this matter.

## SAMPLE INFORMATION SHEET

Name of water utility:

_____

_____

Name of water treatment plant:

_____

_____

Source of water at time of collection:

_____

_____

Sample collection date: _____
Time of Sampling:
Raw _____ Filter Influent _____ Clearwell Effluent _____

Name of sampler: _____

Total chlorine residual:
Raw _____ ppm, Filter Influent _____ ppm, Clearwell Effluent _____ ppm

Free chlorine residual:
Raw _____ ppm, Filter Influent _____ ppm, Clearwell Effluent _____ ppm

Chlorine dioxide residual:
Raw _____ ppm, Filter Influent _____ ppm, Clearwell Effluent _____ ppm

Water temperature:
Raw ___°F ___°C, Filter Influent ___°F ___°C, Clearwell Effluent ___°F ___°C

pH: Raw _____ Filter Influent _____ Clearwell Effluent _____

Plant flow at time of sample collection: _____

**PLEASE MARK THE DOSES AND POINTS OF ADDITION OF CHLORINE AND OTHER OXIDANTS/ DISINFECTANTS, PLUS COAGULANTS, USED ON THE SAMPLE COLLECTION DAY ON THE LINES BELOW AND ON THE ATTACHED SHEET, WHICH SHOWS A SCHEMATIC OF YOUR TREATMENT PLANT.** If chloramines are used as a disinfectant, include ammonia dosage and chlorine to ammonia-nitrogen ratio.

| | Dose | | | | |
|---|---|---|---|---|---|
| Location of Addition | Chlorine | Ammonia | Ozone | Others (Please Identify) | |
| _____ | _____ ppm | _____ ppm | _____ ppm | _____ | _____ ppm |
| _____ | _____ ppm | _____ ppm | _____ ppm | _____ | _____ ppm |
| _____ | _____ ppm | _____ ppm | _____ ppm | _____ | _____ ppm |
| _____ | _____ ppm | _____ ppm | _____ ppm | _____ | _____ ppm |
| _____ | _____ ppm | _____ ppm | _____ ppm | _____ | _____ ppm |
| _____ | _____ ppm | _____ ppm | _____ ppm | _____ | _____ ppm |
| _____ | _____ ppm | _____ ppm | _____ ppm | _____ | _____ ppm |

Alum dose _____ ppm
Name and dose of other coagulants and polymers used:

_____

_____

**DO NOT WRITE BELOW THIS LINE**

---

MWDSC sample no.: Raw _____ Filter Influent _____ Effluent _____
Date received _____ Time _____ Received by _____
TOC samples acidified by _____ Date _____ Time _____
TOX samples dechlorinated/acidified by _____ Date _____ Time _____

# Appendix C

## *Analytical Methods*



# ANALYSIS OF CHLORINATION DISINFECTION BY-PRODUCTS: MICRO PENTANE EXTRACTION

## 1. SCOPE AND APPLICATION

1.1 This method was developed to simultaneously analyze for the trihalomethanes, haloacetonitriles, chloropicrin, 1,1-dichloropropanone, and 1,1,1-trichloropropanone in drinking water.

1.2 The experimentally determined method detection limits were calculated (Table 1). The method has been shown to be useful for the trihalomethanes (THMs) over a range of 0.1 to 80 micrograms per liter ($\mu$g/L) and 0.02 to 20 $\mu$g/L for the other disinfection by-products (DBPs).

## 2. SUMMARY OF METHOD

2.1 Twenty milliliters (mL) of sample is extracted with 4 mL of pentane with a salting agent to increase the extraction efficiency. The analysis is conducted on a gas chromatograph (GC) with subambient temperature programming and a fused silica capillary column to obtain baseline resolution of all the analytes. Detection is performed with an electron capture detector (ECD). Aqueous calibration standards are extracted and analyzed in the same manner as the samples in order to compensate for extraction efficiency.

## 3. INTERFERENCES

3.1 Trihalomethane-grade pentane is used to minimize the contribution of interference from the extraction solvent.

3.2 Glassware, except volumetric flasks, is cleaned as follows:

3.2.1 Detergent washed.

3.2.2 Rinsed twice with tap water.

3.2.3 Rinsed twice with deionized water.

3.2.4 Rinsed twice with Millipore Super-Q System (Bedford, Mass.) water.

3.2.5 Baked in oven at 180$^{o}$C for one hour; however, septa are baked at 80$^{o}$C for one hour.

3.3 Cleaning procedure for volumetric flasks.

3.3.1 Immediately after use rinse three times with methanol.

3.3.2 Allow volumetric flasks to air dry in the ventilation hood for 3 hours.

3.3.3 These flasks are only reused for the preparation of "pentane-extractable" DBP standards.

4.4. SAFETY

4.1 Chloroform has been identified as a potential carcinogen and handling is minimized and performed under a ventilation hood. The toxicity of the other THMs and DBPs has not been precisely defined; each chemical is treated as a potential health hazard and handled under a ventilation hood.

4.2 All Occupational Safety and Health Association (OSHA) regulations regarding safe handling of chemicals and laboratory procedures are used in this method.

5. APPARATUS, EQUIPMENT AND MATERIALS

5.1 SAMPLE CONTAINERS - samples are collected in 40-mL screw-cap vials with Teflon/silicone septa closures.

5.2 EXTRACTION VIALS - Extraction vials are 30 mL (nominal 25 mL) with open-top screw cap and Teflon/silicone septa closure.

5.3 MICROLITER SYRINGES - 5, 10, 25, 50, 100 and 500 microliter ($\mu$L) sizes from Hamiliton Co., Reno, Nev., and a 20-mL syringe from Becton-Dickson Co., Rutherford, N. J.

5.4 VOLUMETRIC FLASKS - glass stoppered, 5-, 10- and 25-mL.

5.5 MECHANICAL SHAKER - For the pentane extraction process, a mechanical shaker table is used with the 30-mL vials. The vials are inserted into a custom-made wooden holding block (32-vial capacity). The shaker was purchased from the Eberbach Corp., Ann Arbor, Mich.

5.6 EXTRACT AND STANDARD SOLUTION STORAGE CONTAINERS - 1.5-mL clear-glass, 15-mL and 1-ounce (oz) amber-glass screw-cap vials with Teflon-lined septa.

5.7 GAS CHROMATOGRAPH - A Varian model 3500 GC (Sunnyvale,

Calif.), equipped with split/splitless injector, subambient oven temperature control (with liquid $CO_2$), ECD, and model 8035 autosampler, is used for the analysis. See Table 2 for analytical conditions.

5.7.1 The analytical column is a fused silica DB-5 (J&W Scientific, Inc., Folsom, Calif.) with a 1.0 micron ($\mu$) film, internal diameter (ID) of 0.25 millimeters (mm) and 30 meters (m) in length.

5.7.2 A constant current pulse modulated Nickel 63 ECD with standard size cell is used for detection.

5.7.3 The carrier and make-up gases are high purity (99.999 percent) grade which pass through Drierite, molecular seive 5A, activated charcoal, and finally an oxygen purifying cartridge before entering the GC. Two-stage metal diaphragm high purity regulators are used at the compressed gas sources. Digital flow controllers regulate carrier gas flow and all gas lines are 1/8 inch copper tubing which have been acetone-rinsed and baked before use.

## 6. REAGENTS AND CONSUMABLE MATERIALS

### 6.1 REAGENTS

6.1.1 Extraction solvent is Burdick & Jackson (Muskegon, Mich.) THM analysis grade pentane.

6.1.2 Sodium sulfate is granular (12-60 mesh), "Baker Analyzed" reagent (Jackson, Tenn.), baked at 400°C overnight in a stainless steel pan and stored in a glass desiccator with Drierite.

6.1.3 Acetone for stock standard solutions is Baker Resi-Analyzed (Phillipsburg, N. J.).

6.1.4 The preservation agent is ammonium chloride, granular, "Baker Analyzed" reagent (Phillipsburg, N. J.).

### 6.2 STANDARD MATERIALS

6.2.1 See Table 3 for source and physical information.

6.2.2 The reference internal standard 1,2-dibromopropane is 98 percent pure (Chem Services, Inc., Westchester, Penn.). The internal standard is added at the 30 $\mu$g/L level in the pentane used for

extraction.

6.3 REAGENT WATER - Organic-pure water (OPW) is made in the laboratory by a Corning megapure all-glass distillation system (model MP3A, Corning, N. Y.). The source water for the MP3A is purified laboratory water (Super-Q), which has gone through several stages of cartridge-type purification to filter and demineralize the water and trap the organic compounds.

6.4 STANDARD STOCK SOLUTION

6.4.1 Stocks are prepared volumetrically in acetone from pure standards. Stock I is prepared at approximately 1000 $\mu$g/L for the four THMs and 280 $\mu$g/L for the other DBP components (haloacetonitriles, chloropicrin and halopropanones) as shown in Table 4. The appropriate volume of the pure standard (Table 4) is delivered by a 25-$\mu$L Hamilton gas-tight syringe into a 25-mL volumetric flask containing approximately 23 mL of acetone. A solvent flush technique is used for delivering the volume by first drawing up 0.5 $\mu$L of acetone and then 1.0 $\mu$L of air before measuring the volume of each component. The solution is diluted to final volume with acetone, stoppered and mixed by inverting the flask several times. Stock I is transferred into a clean 1-oz amber-glass storage bottle with Teflon-faced septa and screw cap and stored at 4$^{o}$C. Stock I is prepared fresh every 3 months.

6.4.2 A secondary stock standard (Stock II) is prepared by diluting 200 $\mu$L of Stock I into a 10-mL volumetric flask with acetone (Table 4). This results in concentrations of approximately 20 $\mu$g/L for the THMs and 5 $\mu$g/L for the other DBPs. The solvent flush technique with a gas-tight syringe is used. The solution is prepared each time a new set of calibration standards are prepared.

6.4.3 A spike solution is prepared by diluting 250 $\mu$L of a THM only stock (approximately 1000 mg/mL) and 250 $\mu$L of Stock I into a 5-mL volumetric flask with acetone (Table 5). The THM only stock is used to create a wider concentration differential between the THMs and the other DBPs in the spiked sample. The spike solution should have a concentration of approximately 100 $\mu$g/mL for the THMs and 14 $\mu$g/mL for the other DBPs. This will provide a spike sample concentration that is

similar to that which is found in the unspiked samples. The spike solution is prepared every 2 weeks.

## 7. SAMPLE COLLECTION, PRESERVATION, AND STORAGE

### 7.1 SAMPLE COLLECTION

7.1.1 Collect all samples in triplicate.

7.1.2 The sampling tap is allowed to flush for approximately 5 minutes to allow the water temperature to stabilize and the stagnant lines to be flushed.

7.1.3 Samples are collected in nominal 40-mL vials with Teflon-faced septa and screw caps. The sample vials are filled such that no air bubbles pass through the sample. The bottles are not rinsed before filling and are not allowed to overfill, since the bottles contain a preservative. The sample vials are sealed headspace free.

### 7.2 SAMPLE PRESERVATION

7.2.1 Ammonium chloride ($NH_4Cl$) is used as the preservative agent. The ammonium chloride acts as a preservative by forming monochloramine in the presence of free chlorine; monochloramine does not react with humic or fulvic acids to form the "pentane-extractable" DBPs during established holding times under refrigerated temperatures ($4^oC$).

7.2.2 Approximately 65 mg of crystalline $NH_4Cl$ is added to each vial prior to sampling.

### 7.3 SAMPLE STORAGE

7.3.1 Samples and sample extracts are stored at $4^oC$ until analysis. Analyses should be performed as soon as possible after collection and at least within 48 hours, as trichloroacetonitrile (TCAN) drops to approximately 50 and 40 percent of its initial value after 24 and 48 hours, respectively. The THMs are stable for 2 weeks.

## 8. CALIBRATION AND STANDARDIZATION

8.1 Aqueous calibration standards are prepared in OPW by injecting the correct amount of stock standard solution directly into water using the solvent flush technique.

8.2 Twelve different concentration levels (from 0.1 to 80 μg/L for the THMs and 0.02 to 20 μg/L for the other DBPs) are prepared in 160-mL crimp-top bottles containing 120 mL of OPW. Twenty-four mL of pentane, containing the internal standard, are placed on top of the OPW. Each bottle is spiked with the appropriate volume of the stock solutions (see Table 6). The spike volume should not exceed 5 μL per 20 mL of water because of possible solvent interference problems. Thirty grams of baked sodium sulfate are poured into each bottle from a plastic weigh boat and the bottle is sealed with a Teflon-lined septum crimp top. The bottle is laid on its side until ready for shaking. After all the levels have been prepared, the bottles are placed in a bottle holder and shaken for 15 minutes in a mechanical shaker. The pentane extract is transferred evenly between fourteen 1.5-mL vials using a disposable pasteur pipette.

8.3 The standards are prepared in batch (120-mL volume) as opposed to the individually prepared (20-mL volume) samples so standard extracts can be stored and do not have to be prepared every day. To verify that the batch prepared standards were equivalent to standards prepared individually, three concentrations of batch and individually prepared standards were compared. Table 7 shows a comparison of area counts obtained for the two methods of standard preparation. The results show that both methods of standard preparation are equivalent. The standards are prepared fresh at least every 21 days.

8.4 A set of standards in the range of 0.1 to 80 μg/L for the THMs and 0.02 to 20 μg/L for the other DBPs (see Table 6 for the actual concentrations) is analyzed by GC before the samples are analyzed. An external standard method is used to determine the concentration of the samples. The internal standard is not used in the quantitation but is used as a reference peak for peak identification and as an indicator of injection errors (see Section 9.2.3). A plot of area versus concentration (in μg/L) is prepared by using a point-to-point fit passing through zero. Calculations are made from only the linear portions of the curve. If the sample runs extend over 2 days, another set of standards are injected at the end of the run. Solvent blanks are run after the standards.

## 9. QUALITY CONTROL

### 9.1 MONITORING FOR INTERFERENCES

9.1.1 Laboratory reagent blanks - A laboratory reagent blank is analyzed each day to check for any interferences.

9.1.2 Travel blanks for each sampling location are prepared in the laboratory by filling 40-mL vials, as described above (see Section 7.2.2), with OPW. These are shipped to the sampling site and back to the laboratory with the sample bottles.

9.1.3 Each reagent bottle of pentane is analyzed before it is used.

9.2 QUALITY ASSURANCE/QUALITY CONTROL PROTOCOL

The Quality Assurance/Quality Control (QA/QC) protocol covers accuracy, precision, independent verification and the use of an internal standard. Accuracy is dependent on many factors, but the most important is the calibration curve. Accuracy is monitored by calculating the recoveries of samples which have been enhanced with known concentrations of the compounds of interest. Precision is another parameter that is dependent on more than one factor. The precision of a method is monitored by analyzing samples in duplicate and calculating the normalized difference between the two analyses. Independent verification of a method is done by analyzing QC check samples and interlaboratory calibration. The internal standard is used to insure that the GC makes consistent injections of samples and standards.

All of the above mentioned parameters are important in assuring that good quality data are produced. It is important to note that all portions of a QA/QC program must meet the established standards in order for an analysis to be considered in control.

9.2.1 Method Detection Limits

Initial calculations of the method detection limits (MDLs) are made according to the Code of Federal Regulations 40 part 136, July 1, 1987. A set of 7 standards are prepared in OPW at 1 to 5 times the estimated detection limit. Each standard is analyzed according to the method and the standard deviation of the 7 replicate measurements for each analyte is determined. The MDL is determined for each analyte as follows:

$$MDL = t\ (S)$$

t = 3.143 (student t value for 6 degrees of freedom and 99 percent confidence level)

S = standard deviation of the 7 replicate analyses

These MDLs are used as minimum reporting levels (MRLs), except where the instrumental detection limit has proved to be higher. Often, the MRLs correspond to the lowest level standard on the calibration curve.

9.2.2 Calibration Curves

Quantitation is done using an external standard calibration curve. Standards are prepared in OPW spiked with DBPs and extracted with the same solvent as that used for the samples (see Section 8). The extracted standards are used to compensate for the varying extraction efficiencies of the different compounds in the analysis. A 12-point calibration curve encompassing the 0.1 to 80 µg/L range for the THMs and 0.02 to 20 µg/L for the other DBPs are used and the 12 standards are analyzed each day prior to the analysis of the samples.

9.2.2.1 Acceptance/Rejection Criteria
The curve is determined acceptable if the fit is smooth. Also, the new calibration curve is compared to the previous curve to insure that they are comparable. The injection is determined to be acceptable if the internal standard is acceptable (see Section 9.2.3). All internal standard area counts (µV/seconds) should be within +/- 10 percent for all standards in the calibration curve.

9.2.2.2 QC Corrective Action
The problem is determined and corrected. The calibration curve is re-analyzed on the GC. If re-analysis does not produce a satisfactory curve, then a new set of calibration standards are prepared. The standards are re-analyzed until an acceptable curve is obtained. All sample extracts are re-analyzed from the last point where calibration curves were in control. The corrective action is documented in the DBP notebook and signed by the immediate supervisor and QC

officer.

9.2.3 Internal Standard
The internal standard (1,2-dibromopropane) is spiked directly into each new bottle of solvent at a concentration of 30 µg/L. The solvent is then used to extract both samples and calibration standards. The purpose of the internal standard is to monitor injections made by the autosampler.

9.2.3.1 Acceptance/Rejection Criteria
A sample injection is deemed acceptable if the area counts (µV/seconds) of the internal standard peak do not vary more than +/- 10 percent from other samples which are extracted using the same bottle of solvent on the same date. The internal standard areas of samples can not be compared to those of calibration standards when the samples and standards are prepared using extraction solvent from different bottles or on different days. The internal standard area can vary from bottle to bottle and day to day.

9.2.3.2 Corrective Action
The problem is determined and corrected. The sample extracts are re-analyzed. If reanalysis is not acceptable, then the samples are re-extracted and re-analyzed. If the re-extracted samples are not acceptable or the samples have exceeded the holding time, then the samples are re-sampled and re-analyzed or the results are recorded as suspect and out of control. Such data will not be entered into the database. The corrective action is documented in the DBP notebook and signed by the immediate supervisor and QC officer.

9.2.4 Spikes
Sample spikes are analyzed to monitor the extraction efficiency of specific analytes in sample matrices. This measures the accuracy of the method in a natural matrix. The spiked samples are analyzed at a frequency of at least 10 percent of the samples. The spike solution is prepared in acetone (Table 5). The samples are spiked with 4 µL of spike solution to acheive a

concentration of 20 µg/L for THMs and 3 µg/L for other DBPs, which are the levels that are typically found in samples. The spike volume must not exceed 5 µL per 20 mL of sample because of possible solvent interference problems. Data are entered into the QC table directly after the analysis. The QC charts are reviewed by the analyst and the immediate supervisor.

9.2.4.1 Acceptance/Rejection Criteria
All spike recoveries must fall within the upper and lower control limits to be acceptable. Initial control limits are defined by calculating the mean percent recovery from the most recent 50 sample spike data points. The 99 percent confidence interval is +/- three times the standard deviation. Warning limits are defined as +/- two times the standard deviation. If a sample recovery is above or below the warning limit this indicates there is a potential problem. The problem is determined and corrected before the analysis is out of control. Control limits and warning limits are re-calculated on a semiannual basis using the most recent 50 spiked sample percent recovery values. Data points that are out of control are not included in the re-calculation of new control limits. Control limits are re-calculated when any major changes are made in the analytical procedure (i.e. new type of column) and after at least 20 points have been collected.

9.2.4.2 QC Corrective Action
The problem is determined and corrected. The sample extracts and spiked sample extract are re-analyzed from the point where the last sample spike recovery was in control. If the spike recovery is still not acceptable, then the samples are re-extracted from the point where the last spike was in control and a sample is re-spiked and re-analyzed only for those analytes that are out of control. If the spike recovery is not acceptable or samples have exceeded the holding time, then the samples are re-sampled and re-analyzed from the point where the last

spike was in control. A sample is re-spiked and re-analyzed. If re-analysis is not possible the results are recorded as suspect for only those analytes that are out of control. Such data will not be entered into the database. The corrective action is documented in the DBP notebook and signed by the immediate supervisor and QC officer.

9.2.5 Duplicates

Sample duplicates are analyzed in order to monitor the precision of the method. Duplicates are analyzed on randomly selected samples at a frequency of at least 10 percent of the samples. Data are entered into the QC table within 24 hours after the analytical run is completed. The QC charts are reviewed by the analyst and the immediate supervisor.

9.2.5.1 Acceptance/Rejection Criteria

Control limits are determined by calculating the range as a function of the relative standard deviation (coefficient of variation) as specified in Standard Methods proposed method 1020B. The range (R) is calculated by taking the absolute difference of the duplicate values as follows:

$R = |x_1 - x_2|$ ($x_1$ and $x_2$ are the duplicate values)

The normalized range ($R_n$) is calculated by dividing the range (R) by the average of the duplicate values ($x_m$):

$$R_n = \frac{R}{x_m}$$

$$x_m = \frac{x_1 + x_2}{2}$$

A mean normalized range ($R_m$) is calculated for 50 pairs of duplicate data points:

$$R_m = \frac{\Sigma R_n}{n}$$

n = number of duplicate pairs

The variance ($s^2$) of the normalized ranges is calculated:

$$s^2 = \frac{\Sigma(R_n - R_m)^2}{n-1}$$

The standard deviation (s) is calculated as the square root of the variance.

The upper and lower control limits are defined as $R_m + 3s$ and zero, respectively. All duplicates must fall within the control limits to be acceptable. The upper warning limit is defined as $R_m + 2s$. If an $R_n$ is outside the warning limit, this indicates there is a potential problem. The problem is investigated before the analysis is out of control. Control limits are recalculated on a semiannual basis using the most recent 50 points. Data points that are out of control are not included in the recalculation of new control limits. Control limits are recalculated when any major changes are made in the analytical procedure (i.e. new type of column) and after at least 20 points have been collected.

9.2.5.2 QC Corrective Action

The problem is determined and corrected. The sample extracts and the duplicate extracts are re-analyzed from the point where the last sample duplicate was in control. If the duplicate is still not acceptable, then the samples are re-extracted from the point where the last duplicates were in control and a duplicate is re-analyzed only for those analytes that were out of control. If the duplicates are still unacceptable or the sample holding time has been exceeded, then the samples are re-sampled and re-analyzed from the point where the last duplicates were in control. A duplicate is re-analyzed. If this is not possible the results for only those analytes that were out of control are

recorded as suspect. Such data will not be entered into the database. The corrective action is documented in the DBP notebook and signed by the immediate supervisor and QC officer.

9.2.6 Check Samples

The check samples are used to provide an independent confirmation of the accuracy of the method. Check samples are only available for trihalomethanes (THMs) at the present time. There are many adequate sources of check samples, but the EPA is the best source. The mean, standard deviation, and 95 percent confidence interval for laboratories who have previously analyzed the samples are provided. This gives the added benefit of comparing the results against those of other laboratories. The THM check samples are analyzed quarterly.

9.2.6.1 Acceptance/Rejection Criteria

The 95 percent confidence interval that is provided by the EPA for each set of THM QC check samples is used as the acceptance limit. However, once enough data are accumulated on QC check samples analyzed in the laboratory, control limits will be established using the guidelines in section 9.2.4, based on at least 20 data points. All samples must be within control limits to be acceptable.

9.2.6.2 QC Corrective Action

The problem is determined and corrected. If the problem is determined to be with the check sample spiking and the sample spikes and duplicates are in control, it is only necessary to re-analyze the check sample extract. However, if the problem is more widespread, then it is necessary to re-analyze the check sample extract and those sample extracts which were analyzed with it. If the re-analysis is not acceptable then the check sample is re-analyzed until acceptable and the samples that were analyzed with the check sample are re-analyzed. If the check sample is still not in control or the holding time is exceeded for those sample extracts analyzed with the check sample,

then the samples are re-sampled and re-analyzed or the results for only those analytes that are out of control are recorded as suspect. Such data will not be entered into the database. The corrective action is documented in the DBP notebook and signed by the immediate supervisor and QC officer.

9.2.7 Interlaboratory Calibration
Samples will be split and sent to another laboratory that is experienced in DBP analysis when available. This will allow the comparison of results with another laboratory. This will provide another means of independent verification. When split samples are sent a QC check sample and DBP spiked sample will also be sent to verify the quality assurance of the other laboratory. Results will be recorded in the DBP notebook.

## 10. PROCEDURE

### 10.1 SAMPLE PREPARATION

10.1.1 Samples and standards are removed from storage and allowed to reach room temperature.

### 10.2 MICROEXTRACTION AND ANALYSIS

10.2.1 A 20-mL aliquot of sample water is withdrawn from the sample container by a 20-mL glass syringe and delivered to a 30-mL vial with Teflon-faced septum and screw cap.

10.2.2 A 4-mL volume of pentane (containing the internal standard) is added to the vial by a Brinkman Dispensette and the vial is capped.

10.2.3 After all the vials are filled, 5 gm of sodium sulfate is measured, using a custom-made "5 gm" stainless-steel scoop, and poured into each vial. The vial is capped immediately, shaken by hand for several seconds to break up the clumps of sodium sulfate.

10.2.4 After all the vials have been sealed and prepared for extraction, they are placed in a vial holder and shaken for 5 minutes in a mechanical shaker.

10.2.5 The vials are removed from the vial holder, placed upright and allowed to stand for 5

minutes. Equal volumes of extract are transferred into two 1.5-mL vials by a pasteur pipet.

10.2.6 At the beginning of each analytical run, a pentane solvent blank is injected to condition the GC and to verify that no interferences are present.

10.2.7 The data are collected on a Hewlett Packard model 300 microcomputer (Palo Alto, Calif.) with Nelson Analytical Xtrachrome chromatography software (Cupertino, Calif.). Autosampler information (rack# & vial#) is communicated to the data system for sample identification purposes. The data files are designated WFXXXXY where WF is a code designating the pentane-extractable DBP analysis, XXXX is the month and day in numbers and Y is a unique sequential cycle number assigned to each data file by the data system. The data files are archived to magnetic tape.

10.2.8 See Table 1 for retention times.

TABLE 1

METHOD DETECTION LIMITS (MDLs),
MINIMUM REPORTING LEVELS (MRLs),
AND RETENTION TIMES (RTs)

| Compounds | MDLs (µg/L) | MRLs (µg/L) | RTs (min) |
|---|---|---|---|
| Chloroform ($CHCl_3$) | 0.02 | 0.1 | 7.57 |
| Bromodichloromethane ($CHCl_2Br$) | 0.02 | 0.1 | 14.25 |
| Dibromochloromethane ($CHClBr_2$) | 0.02 | 0.1 | 22.81 |
| Bromoform ($CHBr_3$) | 0.01 | 0.1 | 26.68 |
| Trichloroacetonitrile (TCAN) | 0.01 | 0.03 | 11.55 |
| Dichloroacetonitrile (DCAN) | 0.02 | 0.03 | 15.77 |
| Bromochloroacetonitrile (BCAN) | 0.04 | 0.04 | 23.76 |
| Dibromoacetonitrile (DBAN) | 0.08 | 0.08 | 27.39 |
| 1,1-Dichloropropanone (1,1-DCP) | 0.03 | 0.03 | 17.61 |
| 1,1,1-Trichloropropanone (1,1,1-TCP) | 0.01 | 0.03 | 25.15 |
| Chloropicrin (CHP) | 0.01 | 0.03 | 22.13 |
| 1,2-Dibromopropane[a] | | | 25.59 |

[a]Internal standard.

TABLE 2

GAS-CHROMATOGRAPHIC CONDITIONS

Column

| | |
|---|---|
| Type: | Fused silica capillary (Durabond-5, J&W Scientific, Folsom, Calif.) |
| Length: | 30 meters |
| Internal diameter: | 0.25 millimeters |
| Film thickness: | 1.0 micron |

Temperature program (subambient with liquid $CO_2$):

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| 17°C | ----------> | 29°C | ----------> | 110°C | ----------> | 204°C | |
| 1.11 min | 3°C/min | 13 min | 9°C/min | 0 min | 27°C/min | 2 min | |

Injector

| | |
|---|---|
| Injection volume: | 2 µL |
| Temperature: | 177°C |
| Splitless injection: | Split valve opened at 0.5 min |

Detector

| | |
|---|---|
| Type: | Electron capture |
| Temperature: | 272°C |

Gases

| | |
|---|---|
| Carrier: | Helium (99.999 percent purity) |
| Flow: | 1.5 mL/min at 25°C |
| Makeup: | Nitrogen (99.999 percent purity) |
| Flow: | 24 mL/min |

Autosampler Parameters - (for Varian model 8035 autosampler)

| | |
|---|---|
| Purge pulse pressure | 55 psi |
| Number of purge pulses | 1 |

TABLE 3

ANALYTICAL STANDARDS

| Compound | Source | Purity (percent) | Molecular Weight | Boiling Point (°C) | Density |
|---|---|---|---|---|---|
| $CHCl_3$ | Aldrich[a] | 99+ | 119 | 61 | 1.492 |
| $CHCl_2Br$ | Chem Svc[b] | 98.5 | 164 | 87 | 1.980 |
| $CHClBr_2$ | Chem Svc | 98+ | 208 | 119 | 2.451 |
| $CHBr_3$ | Chem Svc | 98 | 253 | 151 | 2.894 |
| TCAN | Pfaltz | | 144 | 86 | 1.4403 |
| DCAN | Pfaltz | 95 | 110 | 110-112 | 1.369 |
| BCAN | Columbia[c] | | 154 | 125-130 | 1.680 |
| DBAN | Pfaltz[d] | 95 | 199 | 70-72 | 2.369 |
| CHP | Kodak[e] | | 164 | 112 | 1.6483 |
| 1,1-DCP | Aldrich | 98 | 127 | 120 | 1.327 |
| 1,1,1-TCP | Aldrich | 99.4 | 161 | 149 | 1.435 |

[a]Aldrich Chemical Company, Inc., Milwaukee, Wisc.
[b]Chem Service, Inc., Westchester, Penn.
[c]Columbia Organic Chemical Company, Inc., Camden, S. C.
[d]Pfaltz & Bauer, Inc., Waterbury, Conn.
[e]Eastman Kodak Company, Rochester, N. Y.

TABLE 4

DBP STOCK SOLUTION CONCENTRATIONS

| Compound | Stock I ($\mu$L[a]) | Stock I (mg/L) | Stock II[b] (mg/L) |
|---|---|---|---|
| $CHCl_3$ | 17 | 1015 | 20.3 |
| $CHCl_2Br$ | 13 | 1030 | 20.6 |
| $CHClBr_2$ | 11 | 1078 | 21.6 |
| $CHBr_3$ | 9 | 1042 | 20.8 |
| TCAN | 5 | 288 | 5.76 |
| DCAN | 5 | 274 | 5.48 |
| BCAN | 4 | 269 | 5.38 |
| DBAN | 3 | 284 | 5.69 |
| CHP | 4 | 264 | 5.27 |
| 1,1-DCP | 5 | 265 | 5.31 |
| 1,1,1-TCP | 5 | 287 | 5.74 |

[a]Volume of pure compound spiked into 25 mL of acetone.
[b]200 $\mu$L of stock I spiked into 10 mL of acetone.

TABLE 5

SPIKE SOLUTION AND SAMPLE SPIKE CONCENTRATIONS

| Compound | THM* Stock mg/L | Spike Solution** Stock mg/L | Spike*** Sample µg/L |
|---|---|---|---|
| $CHCl_3$ | 1015 | 101 | 20.3 |
| $CHCl_2Br_3$ | 1030 | 103 | 20.6 |
| $CHClBr_2$ | 1078 | 108 | 21.6 |
| $CHBr_3$ | 1042 | 104 | 20.8 |
| TCAN | | 14.4 | 2.88 |
| DCAN | | 13.7 | 2.74 |
| BCAN | | 13.4 | 2.69 |
| DBAN | | 14.2 | 2.84 |
| CHP | | 13.2 | 2.64 |
| 1,1-DCP | | 13.3 | 2.65 |
| 1,1,1-TCP | | 14.4 | 2.87 |

---

* A THM stock is prepared in acetone with the same volumes of THMs as specified for Stock I (Table 4).

** Prepared by adding 250 µL of Stock I (Table 4) and 250 µL of THM stock to 5 mL of acetone. The THM stock is used to create a wider concentration differential between the THMs and the other DBPs in the spiked sample.

*** Add 4 µL of spike solution to 20 mL of sample.

TABLE 6

CONCENTRATION OF DBPs IN CALIBRATION STANDARDS ($\mu$g/L)

| | Stock II | | | | | Stock I | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Level: | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 | 10 | 11 | 12 |
| Stock volume[a] ($\mu$L): | 0.6[b] | 1.3[b] | 3.2[b] | 6.4[c] | 13[d] | 0.6[b] | 1.3[b] | 2.4[b] | 3.6[c] | 4.8[c] | 7.2[c] | 9.5[d] |
| Compound | | | | | | | | | | | | |
| $CHCl_3$ | 0.101 | 0.220 | 0.541 | 1.08 | 2.20 | 5.07 | 11.0 | 20.3 | 30.4 | 40.6 | 60.9 | 80.3 |
| $CHCl_2Br$ | 0.103 | 0.223 | 0.549 | 1.10 | 2.23 | 5.15 | 11.2 | 20.6 | 30.9 | 41.2 | 61.8 | 81.5 |
| $CHClBr_2$ | 0.108 | 0.234 | 0.575 | 1.15 | 2.34 | 5.39 | 11.7 | 21.6 | 32.4 | 43.1 | 64.7 | 85.4 |
| $CHBr_3$ | 0.104 | 0.226 | 0.556 | 1.11 | 2.26 | 5.21 | 11.3 | 20.8 | 31.3 | 41.7 | 62.5 | 82.5 |
| TCAN | 0.0288 | 0.0624 | 0.154 | 0.307 | 0.624 | 1.44 | 3.12 | 5.76 | 8.64 | 11.5 | 17.3 | 22.8 |
| DCAN | 0.0274 | 0.0593 | 0.146 | 0.292 | 0.593 | 1.37 | 2.97 | 5.48 | 8.21 | 11.0 | 16.4 | 21.7 |
| BCAN | 0.0269 | 0.0582 | 0.143 | 0.287 | 0.582 | 1.34 | 2.91 | 5.38 | 8.06 | 10.8 | 16.1 | 21.3 |
| DBAN | 0.0284 | 0.0616 | 0.152 | 0.303 | 0.616 | 1.42 | 3.08 | 5.69 | 8.53 | 11.4 | 17.1 | 22.5 |
| CHP | 0.0264 | 0.0571 | 0.141 | 0.281 | 0.571 | 1.32 | 2.86 | 5.27 | 7.91 | 10.6 | 15.8 | 20.9 |
| 1,1-DCP | 0.0265 | 0.0575 | 0.142 | 0.283 | 0.575 | 1.33 | 2.88 | 5.31 | 7.96 | 10.6 | 15.9 | 21.0 |
| 1,1,1-TCP | 0.0287 | 0.0622 | 0.153 | 0.306 | 0.622 | 1.44 | 3.11 | 5.74 | 8.61 | 11.5 | 17.2 | 22.7 |

[a]Volume of stock spiked into 120 mL of OPW.
[b]5-$\mu$L syringe used.
[c]10-$\mu$L syringe used.
[d]25-$\mu$L syringe used.

COMPARISON OF AREA COUNTS FOR BATCH-EXTRACTED VERSUS INDIVIDUALLY EXTRACTED STANDARDS

| | 0.5-µg/L Standard | | | 5-µg/L Standard | | | 20-µg/L Standard | | |
|---|---|---|---|---|---|---|---|---|---|
| Compound | Batch[a] | Ind[b] | % of Diff[c] | Batch | Ind. | % of Diff | Batch | Ind. | % of Diff |
| $CHCl_3$ | 7.5 | 7.2 | 4 | 83.9 | 83.9 | 6 | 433 | 392 | 10 |
| $CHCl_2Br$ | 57.5 | 57.3 | <1 | 5 | 805 | 6 | 2618 | 2623 | <1 |
| $CHClBr_2$ | 52.3 | 52.0 | 1 | 7 | 730 | 5 | 1846 | 1863 | 1 |
| $CHBr_3$ | 18.2 | 17.9 | 2 | 0 | 198 | 6 | 899 | 912 | 1 |
| TCAN | 114 | 114 | 0 | 2 | 1533 | 3 | 3562 | 3572 | <1 |
| DCAN | 46.0 | 47.4 | 3 | 0 | 564 | 1 | 2647 | 2686 | 1 |
| BCAN | 33.8 | 35.2 | 4 | 2 | 516 | 1 | 1520 | 1550 | 2 |
| DBAN | 28.5 | 30.2 | 6 | 1 | 430 | 3 | 1373 | 1405 | 2 |
| CHP | 109 | 108 | 1 | 36 | 1297 | 3 | 2779 | 2817 | 1 |
| 1,1-DCP | 29.5 | 30.7 | 4 | 24 | 318 | 2 | 1801 | 1838 | 2 |
| 1,1,1-TCP | 59.5 | 60.3 | 1 | 95 | 768 | 4 | 1782 | 1803 | 1 |

*Area counts in the thousands, i.e., area count of 7.5 is actually 7,500.
[a]Batch: GC area counts of batch-extracted standards.
[b]Individual: Average GC area counts of 20-mL individual extraction (three replicates).
[c]% of Diff: Percent of difference between batch and individual counts.

# ANALYSIS OF HALOACETIC ACIDS:
# tert-BUTYL METHYL ETHER EXTRACTION AND METHYLATION

## 1. SCOPE AND APPLICATION

1.1 This method was developed to simultaneously analyze for monochloroacetic acid, monobromoacetic acid, dichloroacetic acid, trichloroacetic acid, dibromoacetic acid, and 2,4,6-trichlorophenol in drinking water.

1.2 The experimentally determined method detection limits were calculated (Table 1). The method has been shown to be useful for the haloacetic acids (HAAs) over a working range of 0.5 to 30 micrograms per liter (µg/L) (1.0 to 30 µg/L for monochloroacetic acid) and 0.25 to 15 µg/L for 2,4,6-trichlorophenol. The calibration range can be extended depending on the compound and detector characteristics.

## 2. SUMMARY OF METHOD

2.1 Twenty milliliters (mL) of sample is extracted with 5 mL of tert-butyl methyl ether (tBME) at an acidic pH (in order to extract the nondissociated acid) and with a salting agent (to increase the extraction efficiency). The extract is subjected to esterification using diazomethane solution in order to produce chromatographable methyl ester derivatives. The analysis is conducted on a gas chromatograph (GC) with temperature programming and two fused silica capillary columns to obtain baseline resolution of all the analytes on an analytical and a confirmation column. Detection is performed with two electron capture detectors (ECDs). Aqueous calibration standards are extracted, esterified, and analyzed in the same manner as the samples in order to compensate for extraction efficiency.

## 3. INTERFERENCES

3.1 HPLC-grade tBME is used to minimize the contribution of interference from the extraction solvent.

3.2 All glassware, except volumetric flasks and diazomethane generators, use the following cleaning procedure.

3.2.1 Detergent wash (Liquinox detergent, Alconox, Inc., New York, N. Y.).

3.2.2 Rinse twice with tap water.

3.2.3 Acid rinse (except for sample collection vials) with 1:10 hydrochloric acid (HCl).

3.2.4 Rinse twice with deionized water.

3.2.5 Rinse twice with Millipore Super-Q System (Bedford, Mass.) water.

3.2.6 Bake in annealing oven at 400°C for 30 minutes (cover tops and openings with aluminum foil before baking); however, bake sample collection vials in an oven at 180°C for one hour.

3.3 Cleaning procedure for diazomethane generators.

3.3.1 Immediately after use rinse inner tube twice with 5.0 N sodium hydroxide (NaOH), then rinse twice with tap water.

3.3.2 Immediately after use add 1 gm of silica gel to the outside tube to quench any residual diazomethane solution, then rinse twice with methanol and twice with tap water.

3.3.3 Subsequently, rinse both inner and outside tubes twice with 5.0 N NaOH.

3.3.4 Rinse with deionized water.

3.3.5 Rinse twice with 25% HCl solution.

3.3.6 Rinse with deionized water 3 times.

3.3.7 Bake at 130°C for at least 2 hours in a clean, forced-air convection oven.

3.4 Cleaning procedure for volumetric flasks.

3.4.1 Immediately after use rinse three times with methanol. Invert them to drain on a rack.

3.4.2 Allow volumetric flasks to air dry in the ventilation hood for 3 hours.

3.4.3 These flasks are reserved for the preparation of haloacetic acid standards only.

3.5 Cleaning procedure for all caps, septa, and Teflon stopcocks.

3.5.1 Rinse with acetone once.

3.5.2 Rinse with hexane once.

3.5.3 Rinse with acetone once.

3.5.4 Bake at 80°C for not more than 1 hour in a clean, forced-air convection oven.

## 4.0 SAFETY

4.1 The toxicity and carcinogenicity of all the chemicals used in this method have not been fully identified; therefore, each chemical is treated as a potential health hazard. Thus any exposure to these chemicals is minimized, and they are only used in a properly operating ventilation hood.

4.2 All Occupational Safety and Health Association (OSHA) regulations regarding safe handling of chemicals and laboratory procedures are used in this method.

4.3 MNNG (1-methyl-3-nitro-1-nitrosoguanidine) is carcinogenic.

4.3.1 The MNNG is stored in plastic containers containing activated carbon in a refrigerator used only for chemical storage.

4.3.2 Spatulas and glassware for the handling of MNNG are stored in specially labelled plastic containers and only used for that purpose.

4.4 Diazomethane is toxic, carcinogenic and an explosion hazard. Special precautions must be followed whenever handling this material.

4.4.1 Use only in a properly operating fume hood - do not breath vapors.

4.4.2 Transfer solutions using only mechanical pipetting techniques.

4.4.3 Do not heat above 90°C to avoid explosions.

4.4.4 Do not use glassware with grinding surfaces (e.g., ground glass joints, sleeve bearings) or glass stirrers to avoid explosions. Special glassware for diazomethane generation and handling, as well as screw-cap volumetric flasks, are commercially available.

4.4.5 A safety shield must be used when generating diazomethane.

4.4.6 Excess diazomethane must always be quenched with silica gel.

4.5 Safety requirements for ether.

4.5.1 Store ether in tightly-closed, amber bottles in an explosion-safe or -proof refrigerator.

4.5.2 Store only with compatible chemicals.

4.5.3 Ether is extremely flammable; all sources of ignition shall be eliminated. Keep away from heat, sparks and flames.

4.5.4 Ether can cause eye irritation and dermatitis; handle only in a hood and avoid direct physical contact.

4.5.5 Ether can cause headaches, dizziness, nausea or unconsciousness - do not breathe vapors.

4.5.6 Spills or leaks require evacuation of area, then ventilate and absorb on vermiculite or similar material. Wear appropriate OSHA equipment before entering spill area.

4.6 Explosion-safe or -proof refrigerator/freezer.

4.6.1 Ether extracts with diazomethane solution (during esterification step, see Section 10.4.4) must be stored in an explosion-safe or -proof refrigerator.

4.6.2 Ether extracts must be stored in an explosion-safe or -proof freezer.

4.6.3 Most laboratory refrigerator/freezers are not explosion-safe or -proof; although, explosion-safe and -proof units are commercially available.

## 5. APPARATUS, EQUIPMENT AND MATERIALS

5.1 SAMPLE CONTAINERS - samples are collected in 40-mL screw cap vials with Teflon/silicone septa closures.

5.2 EXTRACTION VIALS - Extraction vials are 40-mL volume with open-top screw cap and Teflon/silicone septa closure (same as sample containers).

5.3 MICROLITER SYRINGES - 5, 10, 25, 50, 100, 500 and 1000 microliter ($\mu$L) sizes from Hamiliton Co., Reno, Nev., and a 20-mL all-glass syringe (Becton-Dickson Co., Rutherford, N. J.).

5.4 MICRO VOLUMETRIC FLASKS - Teflon-lined screw-cap: 2-mL, 5-mL and 10-mL (Kontes Scientific Glassware, Vineland, N. J.).

5.5 MECHANICAL SHAKER - For the tBME extraction process, a mechanical shaker table is used with the 40-mL vials. The vials are inserted into a custom-made wooden holding block (20 vial capacity). The shaker was purchased from the Eberbach Corp., Ann Arbor, Mich.

5.6 EXTRACT AND STANDARD SOLUTION STORAGE CONTAINERS - 1.8-mL clear glass, 7- and 14-mL amber glass screw-cap vials with Teflon-lined septa.

5.7 GAS CHROMATOGRAPH - A Varian model 3400 GC equipped with split/splitless injector (using a straight open bore insert), two ECDs, and model 8035 autosampler, is used for the analysis. See Table 2 for analytical conditions.

5.7.1 The analytical column is a fused silica DB-1701 (J&W Scientific, Inc., Folsom, Calif.) with a 0.25 micron ($\mu$) film, internal diameter of 0.25 millimeters (mm) and 30 meters (m) in length. The confirmation column is a fused silica DB-5 (J&W Scientific, Inc.) with a 0.25 $\mu$ film, internal diameter of 0.25 mm and 30 m in length.

5.7.2 A constant current pulse modulated Nickel 63 ECD with standard size cell is used for detection.

5.7.3 The carrier and make-up gases are high purity (99.999 percent) grade which pass through Drierite, molecular seive 5A, activated charcoal, and finally an oxygen purifying cartridge before entering the GC. Two-stage metal diaphragm high purity regulators are used at the compressed gas sources. Digital flow controllers regulate carrier gas flow and all gas lines are 1/8 inch copper tubing which have been acetone-rinsed and baked before use.

## 6.0 REAGENTS AND CONSUMABLE MATERIALS

### 6.1 REAGENTS

6.1.1 Extraction solvent is Aldrich HPLC-grade 99+% tert-butyl methyl ether (Milwaukee, Wisc.)

6.1.2 Sodium sulfate is granular, "Baker Analyzed" reagent, suitable for pesticide analysis (Jackson, Tenn.). Heat treat at 400°C overnight in a shallow stainless steel pan covered with pierced aluminum foil. Store in a 1-L glass

bottle with Teflon-lined polypropylene cap (Wheaton, Millville, N. J.).

6.1.3 Acidified sodium sulfate - Weigh out 1000 gm of baked sodium sulfate and add enough methylene chloride (~375-400 mL) to make a slurry. While stirring continuously, add slowly 3 mL of concentrated sulfuric acid and leave in a well-ventilated hood, allowing the solvent to evaporate completely with occasional stirring. Test for acidity by mixing 1 gm of salt with 5 mL of distilled water and measure the pH of the mixture to ensure that it is below 4. After checking the pH level, dry the acidified salt in a 130°C oven overnight. Store in a 1-L glass bottle with a Teflon-lined polypropylene cap.

6.1.4 Methanol for stock standard solutions is Baker Resi-Analyzed (Phillipsburg, N. J.).

6.1.5 The preservation agent is ammonium chloride, Fischer Scientific (Pittsburg, Penn.), USP/FCC grade.

6.1.6 Sodium hydroxide solution - Prepare a 20% solution using ACS low carbonate grade pellets. Dissolve 200 gm into 800 mL of distilled water.

6.1.7 MNNG (1-methyl-3-nitro-1-nitrosoguanidine), Aldrich Chemical Co. (Milwaukee, Wisc.)

6.1.8 Silica gel #15, Alltech 35/60 mesh (Deerfield, Ill.). Activate at 180°C and store in a dessicator.

6.1.9 Sulfuric acid - Use ACS grade concentrated acid.

6.1.10 Copper (II) sulfate pentahydrate - ACS reagent grade.

6.1.11 Silanized glass wool (J&W Scientific, Inc.)

6.2 STANDARD MATERIALS

6.2.1 See Table 3 for source and physical information.

6.2.2 The reference internal standard 1,2-dibromopropane is 98% pure (Chem Services, Westchester, Penn.).

6.2.3 The surrogate 2,3-dibromopropionic acid is 99% pure (Aldrich Chemical Co., Milwaukee, Wisc.).

6.3 REAGENT WATER - Organic-pure water (OPW) is made in the laboratory by a Corning megapure all-glass distillation system (model MP3A, Corning, N. Y.). The source water for the MP3A is purified laboratory water (Super-Q), which has gone through several stages of cartridge-type purification to filter and demineralize the water and trap the organic compounds.

6.4 HALOACETIC ACID STANDARD STOCK SOLUTIONS

6.4.1 Individual haloacetic acid stock solutions - Prepare the 5 individual haloacetic acids and the trichlorophenol stock solutions as follows: Weigh on an analytical balance ~0.15 gm of each analyte. Dilute each standard in methanol to 10 mL in a screw-top volumetric flask. Transfer each stock standard solution to a separate clean 14-mL amber vial and store in a freezer at -11°C. The stock standards are used for six months.

6.4.2 Multicomponent haloacetic acid spiking solution.

6.4.2.1 Prepare a 6 component spiking solution using the individual haloacetic acid stock solutions (Section 6.4.1). Dilute ~16.7 $\mu$L of each stock standard into a 10-mL volumetric flask containing 9 mL of methanol, except use ~8.4 $\mu$l of the 2,4,6-trichlorophenol solution. After all the stock solutions have been added, dilute to volume with methanol to achieve ~25 ppm of each analyte, except ~12.5 ppm for the 2,4,6-trichlorophenol. The spiking solution is used for three months.

6.4.2.2 The microliter volumes are measured with a gas-tight syringe (Hamilton Corp.) using the solvent flush delivery technique. The solvent flush can be performed with a 25-$\mu$L syringe by first drawing up 2.5 $\mu$L of solvent and then drawing the syringe plunger to the 5 $\mu$L mark with air. From the 5 $\mu$L mark measure the amount of stock solution desired and then deliver the entire contents to the volumetric flask.

6.5 HALOESTER STANDARD STOCK SOLUTIONS

6.5.1 Individual haloester stock solutions - Prepare

the 6 individual methyl ester stock solutions as follows: Weigh on an analytical balance ~0.1 gm of each commercially-available methyl ester (see Table 1) in a 10-mL volumetric flask and dilute each standard with methanol. Prepare the methyl ester for dibromoacetic acid by derivatizing 1 mL of a ~20,000 ppm solution of the acid (Section 6.4.1) and 100 µL of methanol (follow derivatization steps in Section 10.5.1 through 10.5.6), except substitute dibromoacetic acid stock solution and methanol for tBME in step 10.5.3). After derivatizing, transfer the ester quantitatively to a 2-mL volumetric flask with a Teflon-lined screw-cap and dilute to the mark with tBME. The stock standards are used for six months.

6.5.2 Multicomponent haloester spiking solution - Prepare a 6 component spiking solution by diluting ~10 µL of each haloester stock standard, except use ~5 µL of the 2,4,6-trichloroanisole (methyl ester of the phenol), in a 10-mL volumetric flask and bring to volume using methanol. This will yield a mixture containing appoximately 10 ppm of each analyte, except for the 2,4,6-trichloroanisole which will be approximately 5 ppm. The spiking solution is used for three months.

6.5.3 Direct injection standards.

6.5.3.1 Prepare direct injection standards using the 10 ppm multicomponent haloester spiking solution, a 30 ppm internal standard spiking solution, and a 10 ppm methanol solution of methyl-2,3-dibromopropionate (surrogate ester; see Section 6.8.2). Prepare direct injection standard by diluting the appropriate volumes of the multicomponent haloester spiking mix, internal standard spiking solution, and surrogate ester solution with enough tBME to give a final volume of 1.0 mL.

6.5.3.2 For example, measure 970 µL of tBME into a 1.8-mL vial and add 5.0 µL of the multicomponent haloester spiking solution, plus 10 µL of the internal standard spiking solution and 10 µL of the methyl-2,3-dibromopropionate

spiking solution, to yield a 50 ppb direct injection haloester standard (25 ppb of 2,4,6-trichloroanisole, 300 ppb of internal standard, and 100 ppb surrogate ester).

6.6 INTERNAL STANDARD STOCK SOLUTIONS

6.6.1 Internal standard stock solution - Prepare an internal standard (IS) stock solution by weighing approximately 50 mg of 1,2-dibromopropane into a 10-mL volumetric flask and bring to volume with methanol. This will yield approximately a 5000 ppm stock solution. Stock standards are used for six months.

6.6.2 Internal standard spiking solution - Make a 30 ppm IS spiking solution by delivering approximately 60 $\mu$L of IS stock solution into a 10-mL volumetric flask and dilute to volume with methanol. Divide this solution evenly among six 1.8-mL vials and store at -11°C. The spiking solution is used for three months.

6.6.3 Internal standard addition to extracts - Add 20 $\mu$L IS spiking solution to each 2 mL extract (see Section 10.4.2), yielding IS at the 300 ppb level.

6.7 SURROGATE STOCK SOLUTIONS

6.7.1 Surrogate stock solution - Make a 20,000 ppm surrogate (SUR) stock solution by weighing approximately 0.2 gm of 2,3-dibromopropionic acid into a 10-mL screw-cap volumetric flask and dilute to the mark with tBME. Stock solutions are used for six months.

6.7.2 Surrogate spiking solution - Make a 10 ppm SUR spiking solution by delivering approximately 5 $\mu$L of SUR stock solution into a 10-mL volumetric flask and dilute to volume with methanol. Divide this solution evenly among six 1.8-mL vials and store at -11°C. Spiking solutions are used for three months.

6.7.3 Surrogate addition to sample aliquots - Add 20 $\mu$L SUR spiking solution to each 20-mL aliquot of sample (see Section 10.2.2), yielding SUR at the 10 ppb level (which will equal 100 ppb after extraction and concentration to 2 mL).

6.8 ESTERIFIED SURROGATE STOCK SOLUTIONS

6.8.1 Surrogate ester stock solution - Prepare a 10,000 ppm SUR ester stock solution by derivatizing 1 mL of the SUR stock solution and 100 µL of methanol (follow derivatization steps in Section 10.5.1 through 10.5.6, except substitute SUR stock solution and methanol for tBME in step 10.5.3). After derivatizing, transfer the ester quantitatively to a 2-mL volumetric flask with a Teflon-lined screw-cap and dilute to the mark with tBME. Stock solutions are used for six months.

6.8.2 Surrogate ester spiking solution - Make a 10 ppm SUR ester spiking solution by delivering approximately 10 µL of SUR ester stock solution into a 10-mL volumetric flask and dilute to volume with methanol. Spiking solutions are used for three months.

6.8.3 Surrogate ester addition to direct standards - Add 10 µL SUR ester spiking solution to each (1 mL of) direct injection standard (see Section 6.5.3), yielding SUR ester at the 100 ppb level.

## SAMPLE COLLECTION, PRESERVATION, AND STORAGE

7.1 SAMPLE COLLECTION

7.1.1 Samples are collected in quadruplicate.

7.1.2 The sampling tap is allowed to flush for approximately 5 minutes to allow the water temperature to stabilize and the stagnant lines to be flushed.

7.1.3 Samples are collected in nominal 40-mL vials with Teflon-faced septa and screw caps. The sample vials are filled such that no air bubbles pass through the sample. The bottles are not rinsed before filling and are not allowed to overfill, since the bottles contain a preservative. The sample vials are sealed headspace free.

7.2 SAMPLE PRESERVATION

7.2.1 Ammonium chloride ($NH_4Cl$) is used as the preservative agent. The ammonium chloride acts as a preservative by forming monochloramine in the presence of free chlorine; monochloramine

does not react with humic or fulvic acids to form the haloacetic acids during established holding times under refrigerated temperatures (4°C). Likewise, monochloramine does not react with phenol to form 2,4,6-trichlorophenol during established holding times under refrigerated temperatures.

7.2.2 Approximately 65 mg of crystalline $NH_4Cl$ is added to each vial prior to sampling.

7.3 SAMPLE STORAGE

7.3.1 Samples are stored at 4°C and sample extracts are stored at -11°C until analysis. Analyses should be performed as soon as possible after collection; however, the samples can be held for 9 days. Sample extracts can be held for 21 days.

## 8. CALIBRATION AND STANDARDIZATION

8.1 Aqueous calibration standards are prepared in OPW by injecting a measured amount of the multicomponent haloacetic acid solution directly into water using the solvent flush technique.

8.2 Five different concentration levels from 0.5 to 30 µg/L for the HAAs and 0.25 to 15 µg/L for 2,4,6-trichlorophenol are prepared in 40-mL Teflon-lined screw-top bottles containing 20 mL of OPW. The same extraction/esterification procedure is used for both the standards and samples. The calibration standards are extracted and analyzed along with the samples using the same batch of diazomethane solution.

8.3 A five-point calibration plot is constructed using a 0.5, 5, 10, 20, and 30 µg/L extracted set of standards (the trichlorophenol calibration standards are at half of the HAA levels). A point-to-point calibration curve passing through zero is generated from the plotted points for each analyte using chromatography software (XTRACHROME II, Nelson Analytical, Cupertino, Calif.). The internal standard quantitation method is used to determine unknown concentrations using the fitted curves.

## 9. QUALITY CONTROL

9.1 MONITORING FOR INTERFERENCES

9.1.1 Laboratory reagent blanks - A laboratory reagent blank is analyzed each day to check for any

interferences.

9.1.2 Travel blanks for each sampling location are prepared in the laboratory by filling 40-mL vials, as described above (Section 7.1.3), with OPW. These are shipped to the sampling locations and back to the laboratory with the sample bottles.

9.1.3 Each reagent bottle of tBME is analyzed on the GC before it is used.

9.2 QUALITY ASSURANCE/QUALITY CONTROL PROTOCOL

The Quality Assurance/Quality Control (QA/QC) protocol covers accuracy, precision, independent verification, internal standard, and the use of a surrogate. Accuracy is dependent on many factors, but the most important is the calibration curve. Accuracy is monitored by calculating the recoveries of samples which have been enhanced with known concentrations of the compounds of interest. Precision is another parameter that is dependent on more than one factor. The precision of a method is monitored by analyzing samples in duplicate and calculating the normalized difference between the two analyses. Independent verification of a method is done by interlaboratory calibration. The internal standard is used to insure that the GC makes consistent injections of samples and standards. A surrogate compound is added to samples and standards to insure that the water is sufficiently acidified prior to extraction and that the derivatization reaction was successful.

All of the above mentioned parameters are important in assuring that good quality data are produced. It is important to note that all portions of a QA/QC program must meet the established standards in order for an analysis to be considered in control.

9.2.1 Method Detection Limits

Initial calculations of the method detection limits (MDLs) are made according to the Code of Federal Regulations 40 part 136, July 1, 1987. A set of 7 standards are prepared in OPW at 1 to 5 times the estimated detection limit. Each standard is analyzed according to the method and the standard deviation of the 7 replicate measurements for each analyte is determined. The method detection limit is determined for each

analyte as follows:

MDL = t (S).

t = 3.143 (student t value for 6 degrees of freedom and 99 percent confidence level).

S = standard deviation of the 7 replicate analyses.

These MDLs are used as minimum reporting levels (MRLs), except where the instrumental detection limit has proved to be higher. Often, the MRLs correspond to the lowest level standard on the calibration curve.

9.2.2 Calibration Curves

Quantitation is done using an external standard calibration curve with internal standard referencing (relative areas). Standards are prepared in OPW water spiked with haloacetic acids and trichlorophenol and extracted with the same solvent and derivatized with the same diazomethane as that used for the samples. The extracted standards are used to compensate for the varying extraction efficiencies of the different compounds in the analysis. A five-point calibration curve encompassing 0.5 to 30 µg/L range, except 2,4,6-trichlorophenol which is from 0.25 to 15 µg/L, is analyzed each day prior to analysis of samples. Samples with levels greater than the highest standard analyzed are reanalyzed with dilution. When a sample is reanalyzed, only the analytes that were at levels higher than the calibration curve will have their values obtained from the dilution; the other analytes use the values obtained from analysis of the original sample.

9.2.2.1 Acceptance/Rejection Criteria
The curve is determined acceptable if the fit is smooth. Also, the new calibration curve is compared to the previous curve to insure that they are comparable. The injection is determined to be acceptable if the internal standard is acceptable (see Section 9.2.3). All internal standard area counts (µv/seconds) should be within +/- 10 percent for all standards

in the calibration curve. A standard extract with a surrogate area that is outside +/- 15 percent of the average standard surrogate area will not be used to set up the calibration plots.

9.2.2.2 QC Corrective Action
The problem is determined and corrected. The calibration curve is reanalyzed on the GC. If reanalysis does not produce a satisfactory curve, then a new set of calibration standards are prepared. The standards are reanalyzed until an acceptable curve is obtained. All sample extracts analyzed with an out-of-control calibration curve are reanalyzed. The corrective action is documented in the HAA notebook and signed by the immediate supervisor and QC officer.

9.2.3 Internal Standard

The internal standard (1,2-dibromopropane) is added to each extract. The purpose of the internal standard is to monitor injections made by the autosampler, it is used as a reference peak for peak identification by establishing relative retention times, and it is used in the calculation of unknown samples. Also, the internal standard corrects for any deviation in sample volume injected.

9.2.3.1 Acceptance/Rejection Criteria
A sample injection is deemed acceptable if the area counts ($\mu$v/seconds) of the internal standard peak do not vary more than +/- 10 percent from other samples which are analyzed using the same batch of diazomethane.

9.2.3.2 Corrective Action
The problem is determined and corrected. The out-of-control sample extracts are reanalyzed on the GC. If reanalysis is not acceptable, then the out-of-control samples are reextracted and reanalyzed. If the reextracted samples are not acceptable or the samples have exceeded the holding time, then the out-of-control samples are

resampled and reanalyzed or the results are recorded as suspect and out of control. Such data will not be entered into the database. The corrective action is documented in the HAA notebook and signed by the immediate supervisor and QC officer.

9.2.4 Surrogate

9.2.4.1 The surrogate (2,3-dibromopropionic acid) is spiked directly into all water samples prior to acidification and extraction. If the surrogate area is low or absent, there has been a derivatization problem (e.g., water in extract) or extraction problem (e.g., water insufficiently acidified).

9.2.4.2 Acceptance/Rejection Criteria
An extract is deemed acceptable if the area counts of the surrogate peak do not vary more than +/- 15 percent from other samples that have been analyzed using the same batch of diazomethane.

9.2.4.3 Corrective Action
The problem is determined and corrected. The out-of-control sample extracts are reanalyzed on the GC. If reanalysis is not acceptable, then those samples are reextracted and reanalyzed. If the reextracted samples are not acceptable or the samples have exceeded the holding time, then the out-of-control samples are resampled and reanalyzed or the results are recorded as suspect and out of control. Such data will not be entered into the database. The corrective action is documented in the HAA notebook and signed by the immediate supervisor and QC officer.

9.2.4 Spikes

Sample spikes are analyzed to monitor the extraction efficiency of specific analytes in sample matrices. This measures the accuracy of the method in a natural matrix. Randomly selected spiked samples are analyzed at a

frequency of at least 10 percent of the samples. The spike solution is prepared in methanol. Typically samples are spiked with 4 µL of haloacetic acid spiking solution to achieve a concentration of 5 µg/L for HAAs and 2.5 µg/L for the 2,4,6-trichlorophenol. Higher spike levels may be needed when sample levels are above 10 µg/L. Data are entered into the QC table directly after the analysis. The QC charts are reviewed by the analyst and the immediate supervisor.

9.2.4.1 Acceptance/Rejection Criteria
All spike recoveries must fall within the upper and lower control limits to be acceptable. Initial control limits are defined by calculating the mean percent recovery from the most recent 20 sample spike data points. Control limits for HAAs are defined as +/- two times the standard deviation. Warning limits for HAAs are defined as +/- one time the standard deviation. If a sample recovery is above or below the warning limits, this indicates there is a potential problem. The problem is determined and corrected before the analysis is out of control. Control limits and warning limits are recalculated on a semiannual basis using the most recent 50 spiked sample percent recovery values. Data points that are out of control are not included in the recalculation of new control limits. Control limits are recalculated when any major changes are made in the analytical procedure (i.e. new type of column) and after at least 20 points have been collected.

9.2.4.2 QC Corrective Action
The problem is determined and corrected. The sample extracts and spiked sample extract are reanalyzed from the point where the last sample spike recovery was in control. If the spike recovery is still not acceptable, then the samples are reextracted from the point where the last spike was in control and a sample is respiked and reanalyzed only for those analytes that

are out of control. If the spike recovery is not acceptable or samples have exceeded the holding time, then the samples are resampled and reanalyzed from the point where the last spike was in control. A sample is respiked and reanalyzed. If reanalysis is not possible the results are recorded as suspect for only those analytes that are out of control. Such data will not be entered into the database. The corrective action is documented in the HAA notebook and signed by the immediate supervisor and QC officer.

9.2.5 Duplicates

Sample duplicates are analyzed in order to monitor the precision of the method. Duplicates are analyzed on randomly selected samples at a frequency of at least 10 percent of the samples. Data are entered into the QC table within 24 hours after the analytical run is completed. The QC charts are reviewed by the analysts and the immediate supervisor.

9.2.5.1 Acceptance/Rejection Criteria
Control limits are determined by calculating the range as a function of the relative standard deviation (coefficient of variation) as specified in Standard Methods proposed method 1020B. The range (R) is calculated by taking the absolute difference of the duplicate values as follows:

$R = |x_1 - x_2|$ ($x_1$ and $x_2$ are the duplicate values)

The normalized range ($R_n$) is calculated by dividing the range (R) by the average of the duplicate values ($x_m$):

$$R_n = \frac{R}{x_m}$$

$$x_m = \frac{x_1 + x_2}{2}$$

A mean normalized range ($R_m$) is calculated for 20 pairs of duplicate data points initially and 50 pairs of points semiannually:

$$R_m = \frac{\Sigma R_n}{n}$$

n = number of duplicate pairs

The variance ($s^2$) of the normalized ranges is calculated:

$$s^2 = \frac{\Sigma(R_n - R_m)^2}{n-1}$$

The standard deviation (s) is calculated as the square root of the variance.

The upper and lower control limits are defined as $R_m$ + 3s and zero, respectively. All duplicates must fall within the control limits to be acceptable. The upper warning limit is defined as $R_m$ + 2s. If an $R_n$ is outside the warning limit, this indicates there is a potential problem. The problem is investigated before the analysis is out of control. Control limits are recalculated on an annual basis using the most recent 20 points. Data points that are out of control are not included in the recalculation of new control limits. Control limits are recalculated when any major changes are made in the analytical procedure (i.e. new type of column) and after at least 20 points have been collected.

9.2.5.2 QC Corrective Action

The problem is determined and corrected. The sample extracts and the duplicate extracts are reanalyzed from the point where the last sample duplicate was in control. If the duplicate is still not acceptable, then the samples are reextracted from the point where the last duplicates were in

control and a duplicate is reanalyzed only for those analytes that were out of control. If the duplicates are still unacceptable or the sample holding time has been exceeded, then the samples are resampled and reanalyzed from the point where the last duplicates were in control. A duplicate is reanalyzed. If this is not possible the results for only those analytes that were out of control are recorded as suspect and out of control. Such data will not be entered into the database. The corrective action is documented in the HAA notebook and signed by the immediate supervisor and QC officer.

9.2.6 Check Samples

Check samples are used to provide an independent confirmation of the accuracy of the method. Check samples are not available for haloacetic acids at the present time; therefore an interlaboratory calibration is used instead.

9.2.7 Interlaboratory Calibration

Samples will be split and sent to another laboratory that is experienced in HAA analysis when available. This will allow the comparison of results with another laboratory. This will provide a means of independent verification. When split samples are sent a spiked sample will also be sent to verify the quality assurance of the other laboratory. Results will be recorded in the HAA notebook.

## 10. PROCEDURE

### 10.1 SAMPLE PREPARATION

10.1.1 Samples and standards are removed from storage and allowed to reach room temperature.

### 10.2 MICROEXTRACTION

10.2.1 A 20-mL aliquot of sample water is withdrawn from the sample container by a 20-mL glass syringe and delivered to a 40-mL vial with Teflon-faced septum and screw cap.

10.2.2 Add 20 $\mu$L of surrogate spiking solution (10 ppm 2,3-dibromopropionic acid in methanol) to each sample including standards and blanks. Any addition of haloacetic acid spiking solution is done at this stage.

10.2.3 Take one vial at a time and add the following in sequence: 1 mL of concentrated sulfuric acid from a 2-mL size Brinkman dispensette (to lower pH to < 0.5), 5 mL of tBME from a 5-mL size Brinkman dispensette, 3 gm of copper sulfate (one scoop using a custom made "3 gm" stainless steel measure), and 6 gm of baked sodium sulfate (two scoops). Immediately cap the vial and shake by hand to break up any salt clumps and place in vial holder.

10.2.4 Continue to the next sample vial repeating step 10.2.3 for each vial before proceeding to the next sample.

10.2.5 After all the sample vials have been prepared, place the vial holding block containing the sample vials onto the mechanical shaker. Shake the vials at fast speed for 7 minutes.

10.2.6 The vials are removed from the vial holder, placed upright and allowed to stand for 3 minutes.

10.3 SEPARATION AND CONCENTRATION

10.3.1 Separate the ether layer using an empty glass chromatography colunm (22 x 300 mm with Teflon stopcock, not glass). Pour the entire contents of one sample vial into a clean column. Drain about half of the blue water layer back into the extraction vial and pour through the column again as a rinse. Drain the bottom water layer to waste. The presence of the copper sulfate enhances visualization of the phase separation of the ether and salted water.

10.3.2 Prepare a conical funnel by using a small amount of silanized glass wool to plug the bottom of the funnel and then add two 3 gm scoops of acidified baked sodium sulfate to the funnel. Drain the ether layer from the column through the drying funnel into a 10-mL graduated concentration tube.

10.3.3 Rinse the column 3 times with ~1 mL tBME each

time, draining through and washing the sodium sulfate, with enough ether to give a final volume of 8 mL.

10.3.4 Concentrate the dried extract to 0.8 mL using a moderate stream of nitrogen blowing on the extract while in a water bath set at 40°C. Apply the nitrogen to the sample before heating the sample in a water bath. (The blowdown takes ~15-20 min.)

10.4 DERIVATIZATION

10.4.1 Quantitatively transfer the extract (avoiding aeration) using a disposable pasteur pipette to a 2-mL volumetric flask with a Teflon-faced-septum screw top. Do at least a 0.5- and 0.2-mL rinse; final volume must be less than 1.7 mL.

10.4.2 Add 20 µL of 30 ppm 1,2-dibromopropane (the internal standard) in methanol. Place extracts in a -11°C explosion-safe freezer for 3 min to cool extracts before adding diazomethane.

10.4.3 Add 250 µL of cold diazomethane/tBME solution (see Section 10.5 for preparation of diazomethane), using a pasteur-pipette-tipped Eppendorf pipetter, to each volumetric flask. Cap immediately with a Teflon-lined screw cap; mix gently by inverting once. Then go on to next sample.

10.4.4 Allow the samples to esterify for 15 minutes at 4°C in an explosion-safe or -proof refrigerator.

10.4.5 Add approximately 0.01 gm of silica gel to each autosampler (1.8-mL) vial to quench any excess diazomethane.

10.4.6 After the 15 minutes, allow extracts to stand another 15 minutes until they reach room temperature, then dilute to the mark with tBME. Transfer each extract evenly between two autosampler vials prepared above (Section 10.4.5). Each extract should be in contact with diazomethane for approximately the same of amount of time before quenching.

10.5 PREPARATION OF DIAZOMETHANE

10.5.1 Add ~133 mg of MNNG to the inside tube of the

diazomethane generator.

10.5.2 Add 0.5 mL of OPW to the MNNG and tighten the cap and septum.

10.5.3 Add 2 mL of tBME to the outside tube of the generator.

10.5.4 Place the butyl-o-ring in the glass joint and clamp with the pinch clamp.

10.5.5 Place the generator and its contents in an ice bath. Bath must contain enough ice to keep diazomethane at 0°C until used.

10.5.6 Add 600 µL of 5.0 N NaOH with a 1-mL syringe. The syringe needle is placed through the septum on the top of the generator tube (check that the syringe needle is on the opposite side of the vapor exit hole). Add the NaOH at a rate of 1 drop per 5 seconds.

10.5.7 Allow the derivatization process to continue for 30 min after addition of all the NaOH and use immediately. Provide enough ice to keep the solution at 0°C while standing.

10.5.8 If more diazomethane is needed, prepare two or more batches and combine just before use.

10.6 ANALYSIS

10.6.1 At the beginning of each analytical run, two tBME solvent blanks are injected to condition the GC and to verify that no interferences are present.

10.6.2 The data are collected on a Hewlett Packard model 300 microcomputer (Palo Alto, Calif.) with Nelson Analytical Xtrachrome chromatography software (Cupertino, Calif.) Autosampler information (rack# & vial#) is communicated to the data system for sample identification purposes. The data files are designated KAXXXXY and KBXXXXY where KA and KB are the codes designating the HAA analysis on the analytical and confirmation columns, XXXX is the month and day in numbers and Y is a unique sequential cycle number assigned to each data file by the data system. The data files are archived to magnetic tape.

10.6.3 See Table 1 for retention times.

TABLE 1A

METHOD DETECTION LIMITS (MDLs)
AND MINIMUM REPORTING LEVELS (MRLs)

| Compounds | MDLs (µg/L) | MRLs (µg/L) |
|---|---|---|
| Monochloroacetic acic (MCAA) | 0.6 | 1.0 |
| Monobromoacetic acid (MBAA) | 0.4 | 0.5 |
| Dichloroacetic acid (DCAA) | 0.6 | 0.6 |
| Trichloroacetic acid (TCAA) | 0.6 | 0.6 |
| Dibromoacetic acid (DBAA) | 0.6 | 0.6 |
| 2,4,6-Trichlorophenol (TCP) | 0.4 | 0.4 |

TABLE 1B

RETENTION TIMES (RTs)

| Compounds[a] | RTs (min) DB-1701 Column | DB-5 Column |
|---|---|---|
| Methyl chloroacetate (MeCA) | 8.68 | 5.01 |
| Methyl bromoacetate (MeBA) | 14.50 | 8.00 |
| Methyl dichloroacetate (MeDCA) | 15.96 | 8.73 |
| Methyl trichloroacetate (MeTCA) | 22.79 | 16.37 |
| Methyl dibromoacetate (MeDBA) | 27.48 | 24.72 |
| 2,4,6-Trichloroanisole (TCAn) | 33.52 | 32.88 |
| 1,2-Dibromopropane (IS)[b] | 12.40 | 9.33 |
| Methyl-2,3-dibromopropionate (SUR ester)[c] | 29.58 | 27.94 |

[a]These compounds are the methyl ester derivatives of the haloacetic acids, trichlorophenol, and surrogate.
[b]Internal Standard
[c]Surrogate ester

TABLE 2

GAS-CHROMATOGRAPHIC CONDITIONS

Analytical Column

| | |
|---|---|
| Type: | Fused silica capillary (Durabond-1701, J&W Scientific, Folsom, Calif.) |
| Length: | 30 meters |
| Internal diameter: | 0.25 millimeters |
| Film thickness: | 0.25 micron |

Confirmation Column

| | |
|---|---|
| Type: | Fused silica capillary (Durabond-5, J&W Scientific, Folsom, Calif.) |
| Length: | 30 meters |
| Internal diameter: | 0.25 millimeters |
| Film thickness: | 0.25 micron |

Temperature program:

| | | | | |
|---|---|---|---|---|
| 37°C | ----------> | 136°C | ----------> | 236°C |
| 21 min | 11°C/min | 3 min | 20°C/min | 3 min |

Injector

| | |
|---|---|
| Injection volume: | 2 μL |
| Temperature: | 157°C |
| Splitless injection: | Split valve opened at 0.47 min |
| Split Flow: | 77 mL/min |

Detectors

| | |
|---|---|
| Type: | Electron capture |
| Temperature: | 297°C |

Gases

| | |
|---|---|
| Carrier: | Helium (99.999 percent purity) |
| Flow: | 1.0 mL/min at 37°C |
| Makeup: | Nitrogen (99.999 percent purity) |
| Flow: | 23 mL/min |

Autosampler Parameters - (for Varian model 8035 autosampler)

| | |
|---|---|
| Purge pulse pressure | 33 psi |
| number of purge pulses | 2 |

TABLE 3

ANALYTICAL STANDARDS

| Compound | Source | Purity (percent) | Molecular Weight | Boiling Point (°C @ mm)[a] |
|---|---|---|---|---|
| MCAA | Aldrich[b] | 99 | 94.5 | 61 |
| MBAA | Aldrich | 99+ | 138.95 | 87 |
| DCAA | Aldrich | 99+ | 128.94 | 119 |
| TCAA | Aldrich | 98 | 163.39 | 151 |
| DBAA | Pfaltz[c] | 99 | 217.86 | 125-130 |
| TCP | Chem Svc[d] | 95 | 197.45 | 246 |
| IS | Aldrich | 95 | 201.9 | 140-142 |
| SUR | Aldrich | 99 | 231.88 | 160 @ 20 |
| MeCA | Aldrich | 99+ | 108.52 | 130 @ 740 |
| MeBA | Aldrich | 98 | 152.98 | 51 @ 15 |
| MeDCA | Aldrich | 99+ | 142.97 | 143 |
| MeTCA | Aldrich | 99 | 177.42 | 152-153 |
| MeDBA | MWDSC[e] | | | |
| TCAn | Aldrich | 99 | 211.48 | 132 @ 28 |
| SUR ester | MWDSC[e] | | | |

[a]Degrees centigrade at reduced pressure in millimeters of mercury.
[b]Aldrich Chemical Company, Inc., Milwaukee, Wisc.
[c]Pfaltz & Bauer, Inc., Waterbury, Conn.
[d]Chem Service, Inc., Westchester, Pa.
[e]Derivatize acid at Metropolitan Water District laboratory.

# ANALYSIS OF CHLORAL HYDRATE: MICRO METHYL t-BUTYL ETHER EXTRACTION

## 1. SCOPE AND APPLICATION

1.1 This method was developed to analyze for chloral hydrate in drinking water.

1.2 The experimentally determined method detection limit was calculated (Table 1). The method has been shown to be useful for chloral hydrate over a range of 0.05 to 30 micrograms per liter ($\mu$g/L).

## 2. SUMMARY OF METHOD

2.1 Twenty milliliters (mL) of sample is extracted with 4 mL of methyl t-butyl ether (MTBE) with a salting agent to increase the extraction efficiency. The analysis is conducted on a gas chromatograph (GC) with temperature programming and a fused silica capillary column to obtain baseline resolution of chloral hydrate from other disinfection by-products (see Table 1). Detection is performed with an electron capture detector (ECD). Aqueous calibration standards are extracted and analyzed in the same manner as the samples in order to compensate for extraction efficiency.

## 3. INTERFERENCES

3.1 The highest grade methyl t-butyl ether is used to minimize the contribution of interference from the extraction solvent.

3.2 Glassware, except volumetric flasks, is cleaned as follows:

3.2.1 Detergent washed.

3.2.2 Rinsed twice with tap water.

3.2.3 Rinsed twice with deionized water.

3.2.4 Rinsed twice with Millipore Super-Q System (Bedford, Mass.) water.

3.2.5 Baked in oven at 180°C for one hour; however, septa are baked at 80°C for one hour.

3.3 Cleaning procedure for volumetric flasks.

3.3.1 Immediately after use rinse three times with methanol.

3.3.2 Allow volumetric flasks to air dry in the ventilation hood for 3 hours.

3.3.3 These flasks are only reused for the preparation of chloral hydrate standards.

## 4. SAFETY

4.1 Chloral hydrate is a controlled substance determined to be poisonous and corrosive; each chemical is treated as a potential health hazard and handled under a ventilation hood.

4.2 All Occupational Safety and Health Association (OSHA) regulations regarding safe handling of chemicals and laboratory procedures are used in this method.

## 5. APPARATUS, EQUIPMENT AND MATERIALS

5.1 SAMPLE CONTAINERS - samples are collected in 40-mL screw-cap vials with Teflon/silicone septa closures.

5.2 EXTRACTION VIALS - Extraction vials are 30 mL (nominal 25 mL) with open-top screw cap and Teflon/silicone septa closure.

5.3 MICROLITER SYRINGES - 10, 25, 50, 500 and 1000 microliter ($\mu$L) sizes from Hamiliton Co., Reno, Nev., and a 20-mL syringe from Becton-Dickson Co., Rutherford, N. J.

5.4 VOLUMETRIC FLASKS - glass stoppered, 2 and 5 mL.

5.5 MECHANICAL SHAKER - For the ether extraction process, a mechanical shaker table is used with the 30-mL vials. The vials are inserted into a custom-made wooden holding block (32-vial capacity). The shaker was purchased from the Eberbach Corp., Ann Arbor, Mich.

5.6 EXTRACT AND STANDARD SOLUTION STORAGE CONTAINERS - 1.5-mL clear and amber glass, 15-mL and 1-ounce (oz) amber-glass screw-cap vials with Teflon-lined septa.

5.7 GAS CHROMATOGRAPH - A Varian model 3500 GC (Sunnyvale, Calif.), equipped with split/splitless injector, ECD, and model 8035 autosampler, is used for the analysis. See Table 2 for analytical conditions.

5.7.1 The analytical column is a fused silica DB-1 (J&W Scientific, Inc., Folsom, Calif.) with a 1.0 micron ($\mu$) film, internal diameter (ID) of 0.25 millimeters (mm) and 30 meters (m) in length.

5.7.2 A constant current pulse modulated Nickel 63 ECD with capillary size cell is used for detection.

5.7.3 The carrier and make-up gases are high purity (99.999 percent) grade which pass through Drierite, molecular seive 5A, activated charcoal, and finally an oxygen purifying cartridge before entering the GC. Two-stage metal diaphragm high purity regulators are used at the compressed gas sources. Digital flow controllers regulate carrier gas flow and all gas lines are 1/8 inch copper tubing which have been acetone-rinsed and baked before use.

## 6. REAGENTS AND CONSUMABLE MATERIALS

### 6.1 REAGENTS

6.1.1 Extraction solvent is EM Science "OmniSolv" t-butyl methyl ether (Cherry Hill, N. J.).

6.1.2 Sodium sulfate is granular (12-60 mesh), "Baker Analyzed" reagent (Jackson, Tenn.), baked at 400°C overnight in a stainless steel pan and stored in a glass desiccator with Drierite.

6.1.3 Acetone for stock standard solutions is Baker Resi-Analyzed (Phillipsburg, N. J.).

6.1.4 The dechlorination agent is L-(+)-ascorbic acid, powder, "Baker Analyzed" biochemical grade (Phillipsburg, N. J.).

### 6.2 STANDARD MATERIALS

6.2.1 A 1000 mg/L chloral hydrate (99.3 percent purity) solution is obtained from the USEPA, Repository for Toxic and Hazardous Materials, Cincinnati, Ohio.

6.2.2 The reference internal standard 1,2-dibromopropane is 98 percent pure (Chem Services, Inc., Westchester, Penn.). The internal standard is added at the 30 $\mu$g/L level in the ether used for extraction.

6.3 REAGENT WATER - Organic-pure water (OPW) is made in the laboratory by a Corning megapure all-glass distillation system (model MP3A, Corning, N. Y.). The source water for the MP3A is purified laboratory water (Super-Q), which has gone through several stages of cartridge-type purification to filter and demineralize the water and trap the organic compounds.

6.4 STANDARD STOCK SOLUTION

6.4.1 A 500 mg/L Stock I of chloral hydrate is prepared in a 2-mL volumetric flask containing <1 mL acetone. A 1000-$\mu$L volume of a 1000 mg/L (USEPA) solution is delivered by a 1000-$\mu$L gas tight syringe. A solvent flush technique is used for delivering the volume by first drawing up 0.5 $\mu$L of acetone and then 1.0 $\mu$L of air before measuring the volume of chloral hydrate solution. The solution is then brought up to final volume with acetone, stoppered and mixed by inverting the flask several times. The solution is then split evenly between two 1.5-mL amber-glass screw-cap vials (with Teflon-faced septa), using a disposable pasteur pipette, and stored at 4°C. This stock solution is prepared fresh once a month.

6.4.2 A secondary stock standard of 25 mg/L (Stock II) is prepared in a 5-mL volumetric flask by diluting 250 $\mu$L of Stock I into 5 mL of acetone. The solvent flush technique with a gas-tight syringe is used. This solution is prepared each time a new set of calibration standards are prepared.

6.4.3 A tertiary stock standard of 2 mg/L (Stock III) is prepared in a 5-mL volumetric flask by diluting 20 $\mu$L of Stock I into 5 mL of acetone. The solvent flush technique with a gas-tight syringe is used. This solution is prepared each time a new set of calibration standards are prepared.

6.4.4 A spike solution of 15 mg/L is prepared in a 5-mL volumetric flask by diluting 150 $\mu$L of Stock I into 5 mL of acetone. Typically, 4 $\mu$l of spike solution is added to a 20-mL sample, yielding a spike concentration of 3 $\mu$g/L. This will provide a spike sample concentration that is similar to that which is found in many unspiked samples. Since samples should be spiked at concentrtations approximately 60 to 150 percent of concentrations present in the unspiked sample, higher spike levels are needed when sample levels are above 6

μg/L. The spike solution is prepared every 2 weeks.

## 7. SAMPLE COLLECTION, PRESERVATION, AND STORAGE

### 7.1 SAMPLE COLLECTION

7.1.1 Collect all samples in triplicate.

7.1.2 The sampling tap is allowed to flush for approximately 5 minutes to allow the water temperature to stabilize and the stagnant lines to be flushed.

7.1.3 Samples are collected in nominal 40-mL vials with Teflon-faced septa and screw caps. The sample vials are filled such that no air bubbles pass through the sample. The bottles are not rinsed before filling and are not allowed to overfill, since the bottles contain a preservative. The sample vials are sealed headspace free.

### 7.2 SAMPLE PRESERVATION

7.2.1 Ascorbic acid is used as the dechlorination agent. The ascorbic acid acts as a preservative by reducing the free chlorine or chloramines.

7.2.2 Approximately 20 mg of powdered ascorbic acid is added to each vial prior to sampling.

### 7.3 SAMPLE STORAGE

7.3.1 Samples and sample extracts are stored at 4°C until analysis. Analyses should be performed as soon as possible after collection. Chloral hydrate is stable for 21 days.

## 8. CALIBRATION AND STANDARDIZATION

8.1 Aqueous calibration standards are prepared in OPW by injecting the correct amount of stock standard solution directly into water using the solvent flush technique.

8.2 Standards are prepared at the time samples are extracted. Six different concentration levels (from 0.05 to 30 μg/L) are prepared in 30 mL vials with Teflon-faced septa and screw caps, containing 20 mL of OPW. Each vial is spiked with the appropriate volume of the appropriate stock solution (see Table 3). The aqueous calibration standards are extracted in the same

manner as the samples (see Section 10.2.2-10.2.5).

8.3 A set of standards in the range of 0.05 to 30 µg/L (see Table 3) is analyzed by GC before the samples are analyzed. An external standard method is used to determine the concentration of the samples. The internal standard is not used in the quantitation but is used as a reference peak for peak identification and as an indicator of injection errors (see Section 9.2.3). A plot of area versus concentration (in µg/L) is prepared by using a point-to point fit passing through zero. Calculations are made from only the linear portions of the curve. If the sample run extends over 2 days of GC injections, then another set of standards are injected at the end of the run. Solvent blanks are run after the standards.

## 9. QUALITY CONTROL

### 9.1 MONITORING FOR INTERFERENCES

9.1.1 Laboratory reagent blanks - A laboratory reagent blank is analyzed each day to verify any interferences.

9.1.2 Travel blanks for each sampling location are prepared in the laboratory by filling 40-mL vials, as described above (see Section 7.2.2), with OPW. These are shipped to the sampling site and back to the laboratory with the sample bottles.

9.1.3 Each reagent bottle of MTBE is analyzed before it is used.

### 9.2 QUALITY ASSURANCE/QUALITY CONTROL PROTOCOL

The Quality Assurance/Quality Control (QA/QC) protocol covers accuracy, precision, independent verification and the use of an internal standard. Accuracy is dependent on many factors, but the most important is the calibration curve. Accuracy is monitored by calculating the recoveries of samples which have been enhanced with known concentrations of the compounds of interest. Precision is another parameter that is dependent on more than one factor. The precision of a method is monitored by analyzing samples in duplicate and calculating the normalized difference between the two analyses. Independent verification of a method is done by analyzing QC check samples and interlaboratory calibration. The internal standard is used to insure that the GC makes consistent injections of samples and

standards.

All of the above mentioned parameters are important in assuring that good quality data are produced. It is important to note that all portions of a QA/QC program must meet the established standards in order for an analysis to be considered in control.

9.2.1 Method Detection Limits

Initial calculations of the method detection limits (MDLs) are made according to the Code of Federal Regulations 40 part 136, July 1, 1987. A set of 7 standards are prepared in OPW at 1 to 5 times the estimated detection limit. Each standard is analyzed according to the method and the standard deviation of the 7 replicate measurements for each analyte is determined. The MDL is determined for chloral hydrate as follows:

MDL = t (S)

t = 3.143 (student t value for 6 degrees of freedom and 99 percent confidence level)

S = standard deviation of the 7 replicate analyses

These MDLs are used as minimum reporting levels (MRLs), except where the instrumental detection limit has proved to be higher. Often, the MRLs correspond to the lowest level standard on the calibration curve.

9.2.2 Calibration Curves

Quantitation is done using an external standard calibration curve. Standards are prepared in OPW spiked with chloral hydrate and extracted with the same solvent as that used for the samples (see Section 8). The extracted standards are used to compensate for the extraction efficiency of chloral hydrate in this analysis. A six-point calibration curve encompassing the 0.05 to 30 $\mu$g/L range for chloral hydrate is used, and the six standards are analyzed each day prior to the analysis of the samples.

9.2.2.1 Acceptance/Rejection Criteria
The curve is determined acceptable if the fit is smooth. Also, the new calibration curve is compared to the previous curve

to insure that they are comparable. The injection is determined to be acceptable if the internal standard is acceptable (see Section 9.2.3). All internal standard area counts (μV/seconds) should be within +/- 10 percent for all standards in the calibration curve.

9.2.2.2 QC Corrective Action
The problem is determined and corrected. The calibration curve is re-analyzed on the GC. If re-analysis does not produce a satisfactory curve, then a new set of calibration standards are prepared. The standards are re-analyzed until an acceptable curve is obtained. All sample extracts are re-analyzed from the last point where calibration curves were in control. The corrective action is documented in the chloral hydrate notebook and signed by the immediate supervisor and QC officer.

9.2.3 Internal Standard

The internal standard (1,2-dibromopropane) is spiked directly into each new bottle of solvent at a concentration of 30 μg/L. The solvent is then used to extract both samples and calibration standards. The purpose of the internal standard is to monitor injections made by the autosampler.

9.2.3.1 Acceptance/Rejection Criteria
A sample injection is deemed acceptable if the area counts (μV/seconds) of the internal standard peak do not vary more than +/- 10 percent from other samples which are extracted using the same bottle of solvent on the same date. The internal standard areas of samples can not be compared to those of calibration standards when the samples and standards are prepared using extraction solvent from different bottles or on different days. The internal standard area can vary from bottle to bottle and day to day.

9.2.3.2 Corrective Action
The problem is determined and corrected. The sample extracts are re-analyzed. If

reanalysis is not acceptable, then the samples are re-extracted and re-analyzed. If the re-extracted samples are not acceptable or the samples have exceeded the holding time, then the samples are re-sampled and re-analyzed or the results are recorded as suspect and out of control. Such data will not be entered into the database. The corrective action is documented in the chloral hydrate notebook and signed by the immediate supervisor and QC officer.

9.2.4 Spikes

Sample spikes are analyzed to monitor the extraction efficiency of chloral hydrate in sample matrices. This measures the accuracy of the method in a natural matrix. The spiked samples are analyzed at a frequency of at least 10 percent of the samples. Typically, the samples are spiked with 4 $\mu$L of spike solution to achieve a concentration of 3 $\mu$g/L for chloral hydrate, which is the level that is typically found in samples. Since samples should be spiked at concentrtations approximately 60 to 150 percent of concentrations present in the unspiked sample, higher spike levels are needed when sample levels are above 6 $\mu$g/L. The spike volume must not exceed 5 $\mu$L per 20 mL of sample because of possible solvent interference problems (the spike solution is prepared in acetone). Thus, a different concentration of spike solution may need to be prepared. Data are entered into the QC table directly after the analysis. The QC charts are reviewed by the analyst and the immediate supervisor.

9.2.4.1 Acceptance/Rejection Criteria
All spike recoveries must fall within the upper and lower control limits to be acceptable. Initial control limits are defined by calculating the mean percent recovery from the most recent 50 sample spike data points. The 99 percent confidence interval is +/- three times the standard deviation. Warning limits are defined as +/- two times the standard deviation. If a sample recovery is above or below the warning limit this indicates there is a potential problem. The

problem is determined and corrected before the analysis is out of control. Control limits and warning limits are re-calculated on a semiannual basis using the most recent 50 spiked sample percent recovery values. Data points that are out of control are not included in the re-calculation of new control limits. Control limits are re-calculated when any major changes are made in the analytical procedure (i.e. new type of column) and after at least 20 points have been collected.

9.2.4.2 QC Corrective Action
The problem is determined and corrected. The sample extracts and spiked sample extract are re-analyzed from the point where the last sample spike recovery was in control. If the spike recovery is still not acceptable, then the samples are re-extracted from the point where the last spike was in control and a sample is re-spiked and re-analyzed. If the spike recovery is not acceptable or samples have exceeded the holding time, then the samples are re-sampled and re-analyzed from the point where the last spike was in control. A sample is re-spiked and re-analyzed. If re-analysis is not possible the results are recorded as suspect and out of control. Such data will not be entered into the database. The corrective action is documented in the chloral hydrate notebook and signed by the immediate supervisor and QC officer.

9.2.5 Duplicates

Sample duplicates are analyzed in order to monitor the precision of the method. Duplicates are analyzed on randomly selected samples at a frequency of at least 10 percent of the samples. Data are entered into the QC table within 24 hours after the analytical run is completed. The QC charts are reviewed by the analyst and the immediate supervisor.

9.2.5.1 Acceptance/Rejection Criteria
Control limits are determined by

calculating the range as a function of the relative standard deviation (coefficient of variation) as specified in Standard Methods proposed method 1020B. The range (R) is calculated by taking the absolute difference of the duplicate values as follows:

$R = |x_1 - x_2|$ ($x_1$ and $x_2$ are the duplicate values)

The normalized range ($R_n$) is calculated by dividing the range (R) by the average of the duplicate values ($x_m$):

$$R_n = \frac{R}{x_m}$$

$$x_m = \frac{x_1 + x_2}{2}$$

A mean normalized range ($R_m$) is calculated for 50 pairs of duplicate data points:

$$R_m = \frac{\Sigma R_n}{n}$$

n = number of duplicate pairs

The variance ($s^2$) of the normalized ranges is calculated:

$$s^2 = \frac{\Sigma(R_n - R_m)^2}{n-1}$$

The standard deviation (s) is calculated as the square root of the variance.

The upper and lower control limits are defined as $R_m + 3s$ and zero, respectively. All duplicates must fall within the control limits to be acceptable. The upper warning limit is defined as $R_m + 2s$. If an $R_n$ is outside the warning limit, this indicates there is a potential problem. The problem is

investigated before the analysis is out of control. Control limits are recalculated on a semiannual basis using the most recent 50 points. Data points that are out of control are not included in the recalculation of new control limits. Control limits are recalculated when any major changes are made in the analytical procedure (i.e. new type of column) and after at least 20 points have been collected.

9.2.5.2 QC Corrective Action
The problem is determined and corrected. The sample extracts and the duplicate extracts are re-analyzed from the point where the last sample duplicate was in control. If the duplicate is still not acceptable, then the samples are re-extracted from the point where the last duplicates were in control and a duplicate is re-analyzed. If the duplicates are still unacceptable or the sample holding time has been exceeded, then the samples are re-sampled and re-analyzed from the point where the last duplicates were in control. A duplicate is re-analyzed. If this is not possible the results are recorded as suspect and out of control. Such data will not be entered into the database. The corrective action is documented in the chloral hydrate notebook and signed by the immediate supervisor and QC officer.

9.2.6 Check Samples

The check samples are used to provide an independent confirmation of the accuracy of the method. Check samples are not available for chloral hydrate at the present time.

9.2.7 Interlaboratory Calibration
Samples will be split and sent to another laboratory that is experienced in chloral hydrate analysis when available. This will allow the comparison of results with another laboratory. This will provide a means of independent verification. When split samples are sent a chloral hydrate spiked sample will also be sent to verify the quality assurance of the other

laboratory. Results will be recorded in the chloral hydrate notebook.

## 10. PROCEDURE

### 10.1 SAMPLE PREPARATION

10.1.1 Samples and standards are removed from storage and allowed to reach room temperature.

### 10.2 MICROEXTRACTION AND ANALYSIS

10.2.1 A 20-mL aliquot of sample water is withdrawn from the sample container by a 20-mL glass syringe and delivered to a 30-mL vial with Teflon-faced septum and screw cap.

10.2.2 A 4-mL volume of MTBE (containing the internal standard) is added to the vial by a Brinkman Dispensette and the vial is capped.

10.2.3 After all the vials are filled, 5 gm of sodium sulfate is measured, using a custom-made "5 gm" stainless-steel scoop, and poured into each vial. The vial is capped immediately, shaken by hand for several seconds to break up the clumps of sodium sulfate.

10.2.4 After all the vials have been sealed and prepared for extraction, they are placed in a vial holder and shaken for 5 minutes in a mechanical shaker.

10.2.5 The vials are removed from the vial holder, placed upright and allowed to stand for 5 minutes. Equal volumes of extract are transferred into two 1.5-mL clear-glass vials by a pasteur pipet.

10.2.6 At the beginning of each analytical run, a MTBE solvent blank is injected to condition the GC and to verify that no interferences are present.

10.2.7 The data are collected on a Hewlett Packard model 300 microcomputer (Palo Alto, Calif.) with Nelson Analytical Xtrachrome chromatography software (Cupertino, Calif.). Autosampler information (rack# & vial#) is communicated to the data system for sample identification purposes. The data files are designated XOXXXXY where XO is a code designating the chloral

hydrate analysis, XXXX is the month and day in numbers and Y is a unique sequential cycle number assigned to each data file by the data system. The data files are archived to magnetic tape.

10.2.8 See Table 1 for retention times.

TABLE 1

METHOD DETECTION LIMITS (MDLs),
MINIMUM REPORTING LEVELS (MRLs),
AND RETENTION TIMES (RTs)

| Compounds | MDLs (µg/L) | MRLs (µg/L) | RTs (min) |
|---|---|---|---|
| Chloroform | | | 7.57* |
| Bromodichloromethane | | | 11.91* |
| Chloral Hydrate | 0.03 | 0.05 | 12.78 |
| Dibromochloromethane | | | 21.38* |
| Bromoform | | | 27.66* |
| 1,2-Dibromopropane[a] | | | 26.35 |

*Retention times for trihalomethanes presented for information purposes.
[a]Internal standard.

TABLE 2

GAS-CHROMATOGRAPHIC CONDITIONS

Column

| | |
|---|---|
| Type: | Fused silica capillary (Durabond-1, J&W Scientific, Folsom, Calif.) |
| Length: | 30 meters |
| Internal diameter: | 0.25 millimeters |
| Film thickness: | 1.0 micron |

Temperature program:

| | | | | | | |
|---|---|---|---|---|---|---|
| 35°C | ——— | 41°C | ——— | 81°C | ——— | 181°C |
| 10 min | 1°C/min | 6 min | 5°C/min | 0 min | 25°C/min | 1 min |

Injector

| | |
|---|---|
| Injection volume: | 2 μL |
| Temperature: | 177°C |
| Splitless injection: | Split valve opened at 0.5 min |

Detector

| | |
|---|---|
| Type: | Electron capture |
| Temperature: | 272°C |

Gases

| | |
|---|---|
| Carrier: | Helium (99.999 percent purity) |
| Flow: | 1.5 mL/min at 25°C |
| Makeup: | Nitrogen (99.999 percent purity) |
| Flow: | 24 mL/min |

Autosampler Parameters - (for Varian model 8035 autosampler)

| | |
|---|---|
| Purge pulse pressure | 30 psi |
| Number of purge pulses | 2 |

TABLE 3

CONCENTRATION OF CHLORAL HYDRATE IN CALIBRATION STANDARDS

| | Stock III* | | | Stock II# | | |
|---|---|---|---|---|---|---|
| Level: | 1 | 2 | 3 | 4 | 5 | 6 |
| Stock volume[a] (μL): | 0.5[b] | 2.5[b] | 10[c] | 4[b] | 12[c] | 24[d] |
| Chloral Hydrate Level (μg/L) | 0.05 | 0.25 | 1.0 | 5.0 | 15 | 30 |

*2 mg/L stock solution.
#25 mg/L stock solution.
[a]volume of stock spiked into 20 mL of OPW.
[b]10-μL syringe used.
[c]25-μL syringe used.
[d]50-μL syringe used.

# ANALYSIS OF CYANOGEN CHLORIDE: PURGE-AND-TRAP METHOD

## 1. SCOPE AND APPLICATION

1.1 This method was developed to analyze for low parts-per-billion (ppb) levels of cyanogen chloride (CNCl) in drinking water. The method is also used to monitor the formation of cyanogen chloride in drinking water treatment pilot plant studies.

1.2 The method detection limit (MDL) has been determined to be 0.02 microgram per liter ($\mu$g/L); the minimum reporting level (MRL) has been set at 0.1 $\mu$g/L. The method has been shown to perform well for the analysis of cyanogen chloride over a concentration range of 0.1 to 10 $\mu$g/L in a drinking water matrix.

## 2. SUMMARY OF METHOD

2.1 This method is a modification of the United States Environmental Protection Agency (USEPA) Method 524.2. This method describes a purge-and-trap technique using a gas chromatograph/mass spectrometer (GC/MS). Cyanogen chloride is extracted from 25 milliliters (mL) of a water sample by bubbling (purging) with helium gas. The CNCl is trapped onto a Tenax trap. When the purging process is completed, the Tenax trap is heated and backflushed with helium to remove (desorb) the trapped CNCl. The CNCl is cryofocussed onto an uncoated capillary pre-column prior to being flash heated onto a narrow bore capillary column. The column is temperature programmed to separate CNCl from other chemical components. Cyanogen chloride is then detected with a mass spectrometer that is interfaced with the gas chromatrograph. Aqueous calibration standards are purged and trapped and analyzed in the same manner as the samples in order to compensate for purging efficiency.

## 3. INTERFERENCES

3.1 The purge-and-trap method often transfers significant amounts of water and air into the analytical system. The transfer of water and air results in interferences to early eluting compounds. Since cyanogen chloride elutes extremely early chromatographically, caution must be taken to ensure minimization of water and air transfer into the analytical system.

3.2 Glassware is cleaned as follows:

3.2.1 Detergent washed.

3.2.2 Rinsed twice with tap water.

3.2.3 Rinsed twice with deionized water.

3.2.4 Rinsed twice with Millipore Super-Q System (Bedford, Mass.) water.

3.2.5 Baked in oven at 180°C for one hour; however, septa are baked at 80°C for one hour, while volumetric glassware are rinsed twice with reagent-grade acetone and air-dried.

## 4. SAFETY

4.1 Cyanogen chloride in its pure form is a highly toxic gas that needs special attention and care whenever it is being handled in order to prevent unsafe incidents from occurring. **Only trained personnel that are familiar with the health effects, hazards and safe handling of cyanogen chloride are allowed to work directly with this gas.** Always work in well ventilated fume hoods whenever working with cyanogen chloride. **Read the attached Material Safety Data Sheet (MSDS) for cyanogen chloride** for detailed information and procedures for handling this chemical.

4.2 **An internal laboratory protocol should be established.** All Occupational Safety and Health Association (OSHA) regulations and laboratory procedures for the safe handling of chemicals are used in this method.

## 5. APPARATUS, EQUIPMENT AND MATERIALS

5.1 SAMPLE CONTAINERS - samples are collected in 40-mL screw-cap vials with Teflon/silicone septa closures.

5.2 MICROLITER SYRINGES - 5, 10, 25, 50, and 1000 microliter ($\mu$L) sizes from Hamiliton Co., Reno, Nevada, and a 25 mL syringe from Tekmar Co., Cincinnati, Ohio.

5.3 VOLUMETRIC FLASKS - glass stoppered, 10, 50, and 100 mL.

5.4 STANDARD SOLUTION STORAGE CONTAINERS - 2-mL and 15-mL amber glass screw-cap vials with Teflon-lined septa.

5.5 GC/MS - The GC/MS is a Finnigan 4021 (San Jose, Calif.) equipped with Tekmar LSC-2 purge-and-trap apparatus and Tekmar 1000 capillary cryofocussing interface module.

5.5.1 The analytical column is a fused silica DB-5 (J&W Scientific, Inc., Folsom, Calif.) with a 1.0 micron ($\mu$) film, internal diameter (ID) of 0.25 millimeters (mm) and 30 meters (m) in length.

5.5.2 The precolumn is an uncoated, deactivated, fused silica megabore column (0.53 mm ID), approximately 0.5 m in length (J&W Scientific, Inc.).

5.5.3 The trap is Tekmar trap #1 containing Tenax only.

5.5.4 The carrier gas is an ultrahigh purity (99.999 percent) grade which passes through Drierite, molecular seive 5A, activated charcoal, and finally an oxygen purifying cartridge before entering the GC. A two-stage metal diaphragm high purity regulator is used at the compressed gas source. Pressure controllers regulate carrier gas flow and all gas lines are 1/8 inch copper tubing which have been acetone-rinsed and baked before use.

## 6. REAGENTS AND CONSUMABLE MATERIALS

### 6.1 REAGENTS

6.1.1 Methanol for stock standard solutions is Purge & Trap High Purity Grade by Baxter (Burdick & Jackson, Muskegon, Mich.).

6.1.2 Dechlorinating agent is L-(+)-ascorbic acid, powder, "Baker Analyzed" biochemical grade (Phillipsburg, N. J.).

### 6.2 STANDARD MATERIALS

6.2.1 The pure cyanogen chloride gas is available at Solkatronic Chemical Inc., 30 Two Ridge Road, Fairfield, N. J. 07006, (201) 882-7900.

6.2.2 A 1% cyanogen chloride standard (the balance is nitrogen) is available at Scott Specialty Gases, 2600 Cajon Blvd., San Bernadino, Calif. 92411, (714) 887-2571. At this time, the concentration of the cyanogen chloride is not certified; however, evaluation of one cylinder indicated that one was quantitative.

6.2.3 The internal standard fluorobenzene is 99+% (Chem Service, Westchester, Penn.)

6.3 REAGENT WATER - Organic-pure water (OPW) is made in the laboratory by a Corning megapure all-glass distillation system (model MP3A, Corning, New York). The source water for the MP3A is purified laboratory water (Super-Q), which has gone through several stages of cartridge-type purification to filter and demineralize the water and trap the organic compounds.

6.4 STANDARD STOCK SOLUTIONS

6.4.1 Preparation of cyanogen chloride stock standard from 1% cyanogen chloride gas in nitrogen:

6.4.1.1 The stock solution is prepared by transferring a known volume (V) of gas volumetically with a gas-tight syringe through a septum into 10 mL of methanol in a closed, screw-cap, 40-ml vial. After all gas is transferred, the bottle is shaken and stored in freezer overnight before using. This process will help keep the gas absorbed in the solvent.

6.4.1.2 The volume of a known concentration of cyanogen chloride gas to be transferred into a known volume of solvent can be determine by using the following equation:

$$V = (C \times v)/(10 \times d \times m)$$

where,

V = Volume of cyanogen chloride gas mixture to be transferred into the solvent in units of mL.

C = Concentration of cyanogen chloride stock solution to be prepared in units of $\mu g/mL$ (or ppm).

v = Volume of solvent to be used in units of mL.

m = % cyanogen chloride in gas mixture.

d = Density of cyanogen chloride (CNCl) gas, where:

$$d = \frac{\text{molecular weight CNCl}}{\text{molar volume}} \times \frac{T_{std}}{T_{actual}} \times \frac{P_{actual}}{P_{std}}$$

$$d = \frac{61.48}{22.41} \times \frac{273}{273+T(^{o}C)} \times \frac{P\ (mm\ Hg)}{760}$$

where P = atmospheric pressure and
T = room temperature at laboratory.
(This corrects for variations in one's laboratory from standard temperature, pressure conditions.)

6.4.1.3 Therefore, to make a 100 µg/mL stock solution, at 1 atmosphere (pressure 760 mm Hg) and 22°C room temperature, transfer 39.39 mL of 1% cyanogen chloride gas mixture to 10 mL methanol.

6.4.1.4 This 100 µg/mL stock solution is good (stable) for approximately three months.

6.4.2 Preparation of cyanogen chloride stock standard from pure gas:
**NOTE: Follow proper safety precautions; cyanogen chloride is extremely toxic.**

6.4.2.1 In a fume hood the cyanogen chloride gas cylinder is fitted with a pressure regulator, on/off valve, and approximately 1 m length of megabore fused silica precolumn. In order to remove any air that may be present, the line is minimally flushed by turning on the gas cylinder valve while the pre-column is submerged in a beaker of methanol. The valve is shut and the methanol solution is disposed of in a safe manner. Care should be taken not to bleed the line into the open air as some cyanogen chloride may be released into the fume hood.

6.4.2.2 Eight milliliters of methanol are placed in a 10-ml volumetric flask. The alcohol-wetted glass surfaces are allowed to air dry and the flask is stoppered and weighed. The flask is unstoppered, the megabore column is submerged into the methanol, and the cyanogen chloride gas is bubbled into

the methanol for 0.5 to 1 minute. Then the flask is stoppered and reweighed. If necessary, the bubbling is repeated until at least 50 mg of cyanogen chloride have been added. The volume is adjusted beyond 10 mL, if necessary, with the addition of an appropriate amount of methanol using a syringe to yield a final concentration of cyanogen chloride of 5.0 mg/mL (5000 ppm).

6.4.2.3 The stock solution is transferred to a 14-mL Teflon-lined screw-cap vial and stored in an explosion-safe freezer. This solution is good (stable) for approximately three months.

6.4.3 Preparation of internal standard stock solution:

6.4.3.1 Nine milliliters of methanol are placed in a 10-mL volumetric flask. The alcohol-wetted glass surfaces are allowed to air dry and the flask is stoppered and weighed to the nearest 0.1 mg. Fluorobenzene is added dropwise into the methanol without contacting the neck of the flask until at least 50 mg have been added. The flask is stoppered and reweighed. The stock stolution is adjusted to the appropriate volume to yield a concentration of 5.0 mg/mL. The flask is stoppered and inverted three times to mix.

6.4.3.2 The solution is transferred to a 14-mL Teflon-lined screw-cap vial and stored in an explosion-safe freezer. This solution is good (stable) for approximately six months.

6.5 SPIKING SOLUTIONS

6.5.1 A working spiking solution of 5 µg/mL cyanogen chloride is prepared daily by diluting 50 µL of the 100 µg/mL stock standard (Section 6.4.1) with 950 µL methanol in a 2-mL gas-tight vial.

6.5.2 Alternatively, a working spiking solution of 5 µg/mL cyanogen chloride is prepared daily by diluting the 5.0 mg/mL stock standard (Section 6.4.2):

6.5.2.1 Dilute 10 µL of the 5.0 mg/mL stock standard with 990 µL of methanol in a 2-mL gas-tight vial to yield a concentration of 50 µg/mL. This secondary dilution standard is prepared daily and can also be used as the working spiking solution for the preparation of high-level calibration standards (to minimize the volume of methanol delivered to the sample).

6.5.2.2 Dilute 100 µL of the 50 µg/mL secondary dilution standard solution with 900 µL of methanol in a 2-mL gas-tight vial to yield a concentration of 5 µg/mL. This working spiking solution is prepared daily.

6.5.3 Preparation of internal standard spiking solution:

6.5.3.1 Dilute 10 µL of the 5.0 mg/mL stock standard (Section 6.4.3) with 990 µL of methanol in a 2-mL gas-tight vial to yield a concentration of 50 µg/mL. This secondary dilution standard solution is stable for approximately one week.

6.5.3.2 Dilute 100 µL of the 50 µg/mL secondary dilution standard solution with 900 µL of methanol in a 2-mL gas-tight vial to yield a concentration of 5 µg/mL. This working spiking solution is stable for approximately two days.

6.5.3.3 The addition of 5 µL of the working spiking solution to a 25-mL sample will yield an internal standard concentration of 1.0 µg/L.

## 7. SAMPLE COLLECTION, PRESERVATION, AND STORAGE

### 7.1 SAMPLE COLLECTION

7.1.1 Samples are collected in quadruplicate.

7.1.2 The sampling tap is allowed to flush for approximately 5 minutes to allow the water temperature to stabilize and the stagnant lines to be flushed.

7.1.3 Samples are collected in nominal 40-mL vials with Teflon-faced septa and screw caps. The sample vials are filled such that no air bubbles pass through the sample. The bottles are not rinsed before filling and are not allowed to overfill, since the bottles contain a dechlorination agent. The sample vials are sealed headspace free.

7.2 SAMPLE PRESERVATION

7.2.1 Approximately 20 mg of ascorbic acid is added to each 40-mL sample bottle prior to sample collection. The acorbic acid is used as a dechlorination agent.

7.3 SAMPLE STORAGE

7.3.1 Store the samples at 4°C until time of analysis. Analyses should be performed as soon as possible after collection and receipt at the laboratory, as cyanogen chloride slowly degrades in an ascorbic-acid-preserved sample.

## 8.0 CALIBRATION AND STANDARDIZATION

8.1 Quantitation is performed using an external calibration curve, with the peak area of cyanogen chloride m/z of 61 relative to the internal standard m/z of 96 peak. Calibration standards are prepared in OPW spiked with cyanogen chloride. Standards are purged, trapped, and analyzed with the same methodology as that used for the samples.

8.2 Initial 6-point standard calibration: An initial 6-point standard calibration is established by analyzing 6 cyanogen chloride standards at varying concentrations ranging between 0.1 µg/L and 10 µg/L. The response factors are calculated with the use of an internal standard. For a small working range, fewer calibration standards are analyzed, as long as the shape of the curve is adequately characterized.

8.3 Daily on-going standard calibration: At the beginning of each day of analysis, a daily cyanogen chloride standard at 5 µg/L is analyzed and its response factor calculated. Typically, 2-3 runs of the standard are made to ensure that the instrument is stable. If the response factor has changed significantly, a new calibration curve is generated (see Section 9.2.3).

## 9. QUALITY CONTROL

### 9.1 MONITORING FOR INTERFERENCES

9.1.1 Laboratory Reagent Blanks - A laboratory reagent blank is analyzed each day to verify any interferences.

9.1.2 Travel blanks for each sampling location are prepared in the laboratory by filling 40-mL vials, as described above, with OPW. These are shipped to the sampling site and back to the laboratory with the sample bottles.

### 9.2 QUALITY ASSURANCE/QUALITY CONTROL PROTOCOL

The Quality Assurance/Quality Control (QA/QC) protocol covers accuracy, precision, independent verification and the use of an internal standard. Accuracy is dependent on many factors, but the most important is the calibration curve. Accuracy is monitored by calculating the recoveries of samples which have been enhanced with known concentrations of the compounds of interest. Precision is another parameter that is dependent on more than one factor. The precision of a method is monitored by analyzing samples in duplicate and calculating the relative difference between the two analyses. Independent verification of a method is done by interlaboratory calibration. The internal standard is used to quantitatively compensate for variations in the GC/MS response.

All of the above mentioned parameters are important in assuring that good quality data are produced. It is important to note that all portions of a QA/QC program must meet the established standards in order for an analysis to be considered in control.

9.2.1 Method Detection Limits

Initial calculations of the method detection limit (MDL) are made according to the Code of Federal Regulations 40 part 136, July 1, 1987. A set of 7 standards are prepared in OPW at 1 to 5 times the estimated detection limit. Each standard is analyzed according to the method and the standard deviation of the 7 replicate measurements for cyanogen chloride is determined. The MDL is determined for each analyte as follows:

MDL = t (S)

t = 3.143 (student t value for 6 degrees of freedom and 99 percent confidence level)

S = standard deviation of the 7 replicate analyses

This MDL is used as the minimum reporting level (MRL), except where the instrumental detection limit has proved to be higher. Often, the MRL corresponds to the lowest level standard on the calibration curve.

9.2.2 Initial Calibration Curve

Quantitation is done using an external standard calibration curve, with peak areas relative to an internal standard. Standards are prepared in OPW at 6 different concentration levels that encompass a range between 0.1 and 10 µg/L. For a smaller working range, fewer calibration standards are analyzed, as long as the shape of the curve is adequately characterized. The CNCl standard calibration curve is established prior to the analysis of samples.

9.2.2.1 Acceptance/Rejection Criteria
The acceptance criteria requires that the response factors for each point on the calibration must agree to within 10 percent relative standard deviation (RSD). RSD less than or equal to 10 percent will define the concentration range analyzed to be linear and, therefore, the average response factor can be used for quantitation. RSD greater than 10 percent indicates non-linearity and, therefore, quantitation must be based upon a best quadratic fit for the multi-point standard calibration curve. The curve is determined to be acceptable if the fit is smooth. Also, the response factors are compared to the previous calibration curve to ensure that they are comparable.

9.2.2.2 QC Corrective Action
The problem is determined and corrected. If re-analysis does not produce a satisfactory curve, then a new set of calibration standards are prepared or the

mass spectrometer is retuned. The standards are re-analyzed until an acceptable curve is obtained. If the curve is plateauing above one of the calibration standard levels, the working range will be limited by the highest level standard that characterizes a smooth, unplateaued section of the curve. No samples are analyzed until the calibration curve is in control. The corrective action is documented on the CNCl daily worksheet and signed by the immediate supervisor and QC officer.

9.2.3 Daily On-Going Standard Calibration

9.2.3.1 Acceptance/Rejection Criteria
If the true value of cyanogen chloride for the daily standard agrees with the calculated value from the initial multi-point standard calibration curve to within 10 percent difference, then real samples can begin to be analyzed.

9.2.3.2 QC Corrective Action
If the true value is greater than 10 percent different from the calculated value, then a new multi-point standard calibration must be established before analyzing real samples. Note, if the first daily standard analyzed has a much different response factor than the subsequent ones, it is rejected as reflecting that the instrument was not stabilized yet for that day. The corrective action is documented on the CNCl daily worksheet and signed by the immediate supervisor and QC officer.

9.2.4 Internal Standard

The internal standard (fluorobenzene) is spiked directly into the 25-mL sample syringe prior to purging a sample. The purpose of the internal standard is to quantitatively compensate for variability in the GC/MS response.

9.2.4.1 Acceptance/Rejection Criteria
A GC/MS analysis is deemed acceptable if the area counts of the internal standard peak do not vary more than +/- 20 percent

from other samples which are analyzed that same day.

9.2.4.2 Corrective Action
The problem is determined and corrected. The samples that fail the internal standard acceptance criteria are re-analyzed. If re-analysis is not acceptable, then these samples are re-analyzed again. If all the sample aliquots are used up, then the samples with out-of-control internal standard areas are re-sampled and re-analyzed or the results are recorded as suspect and out of control. Such data will not be entered into the database. The corrective action is documented on the cyanogen chloride daily worksheet and signed by the supervisor and the QC officer.

9.2.5 Spikes

Sample spikes are analyzed to monitor the purging efficiency of cyanogen chloride in sample matrices. This measures the accuracy of the method in a natural matrix. The spiked samples are analyzed at a frequency of at least 10 percent of the samples. The samples are spiked at concentrations approximately 60 to 150 percent of concentrations present in the unspiked sample. Data are entered into the QC table directly after the analysis. The QC charts are reviewed by the analyst and the immediate supervisor.

9.2.5.1 Acceptance/Rejection Criteria
All spike recoveries must fall within the upper and lower control limits to be acceptable. Initial control limits are defined by calculating the mean percent recovery from the most recent 50 sample spike data points. The 99 percent confidence interval is +/- three times the standard deviation. Warning limits are defined as +/- two times the standard deviation. If a sample recovery is above or below the warning limit this indicates there is a potential problem. The problem is determined and corrected before the analysis is out of control. Control limits and warning limits are re-

calculated on a semiannual basis using the most recent 50 spiked sample percent recovery values. Data points that are out of control are not included in the re-calculation of new control limits. Control limits are re-calculated when any major changes are made in the analytical procedure (i.e. new type of column) and after at least 20 points have been collected.

9.2.5.2 QC Corrective Action
The problem is determined and corrected. Another sample is spiked and analyzed. If the spike recovery is still not acceptable, then the purge-and-trap system and GC/MS must be trouble-shot until the problem is determined and corrected. If the spike recovery is not acceptable or samples have exceeded the holding time, then the samples are re-sampled and re-analyzed from the point where the last spike was in control. A sample is re-spiked and re-analyzed. If re-analysis is not possible the results are recorded as suspect and out of control. Such data will not be entered into the database. The corrective action is documented on the cyanogen chloride daily worksheet and signed by the immediate supervisor and QC officer.

9.2.6 Duplicates

Sample duplicates are analyzed in order to monitor the precision of the method. Duplicates are analyzed on randomly selected samples at a frequency of at least 10 percent of the samples. If a set of samples is expected to not contain cyanogen chloride, then duplicate spike analyses are performed. Data are entered into the QC table within 24 hours after the analytical run is completed. Duplicate spike data are entered into the duplicate QC table and as two separate entries in the spike QC table. The QC charts are reviewed by the analysts and the immediate supervisor.

9.2.6.1 Acceptance/Rejection Criteria
Control limits are determined by calculating the range as a function of the relative standard deviation

(coefficient of variation) as specified in Standard Methods proposed method 1020B. The range (R) is calculated by taking the absolute difference of the duplicate values as follows:

$R = |x_1 - x_2|$ ($x_1$ and $x_2$ are the duplicate values)

The normalized range ($R_n$) is calculated by dividing the range (R) by the average of the duplicate values ($x_m$):

$$R_n = \frac{R}{x_m}$$

$$x_m = \frac{x_1 + x_2}{2}$$

A mean normalized range ($R_m$) is calculated for 50 pairs of duplicate data points:

$$R_m = \frac{\Sigma R_n}{n}$$

n = number of duplicate pairs

The variance ($s^2$) of the normalized ranges is calculated:

$$s^2 = \frac{\Sigma(R_n - R_m)^2}{n-1}$$

The standard deviation (s) is calculated as the square root of the variance.

The upper and lower control limits are defined as $R_m + 3s$ and zero, respectively. All duplicates must fall within the control limits to be acceptable. If duplicate spikes are analyzed, both spikes must fall within the spike control limits to be acceptable. The upper warning limit for duplicates is defined as $R_m + 2s$. If an $R_n$ is outside the warning limit, this

indicates there is a potential problem. The problem is investigated before the analysis is out of control. Control limits are recalculated on a semiannual basis using the most recent 50 points. Data points that are out of control are not included in the recalculation of new control limits. Control limits are recalculated when any major changes are made in the analytical procedure (i.e. new type of column) and after at least 20 points have been collected.

9.2.6.2 QC Corrective Action
The problem is determined and corrected. Another sample is analyzed in duplicate. If the duplicate is still not acceptable, then the purge-and-trap system and GC/MS must be trouble-shot until the problem is determined and corrected. If the duplicates are still unacceptable or the sample holding time has been exceeded, then the samples are re-sampled and re-analyzed from the point where the last duplicates were in control. A duplicate is re-analyzed. If this is not possible the results are out of control and recorded as suspect. Such data will not be entered into the database. The corrective action is documented on the cyanogen chloride daily worksheet and signed by the immediate supervisor and QC officer.

9.2.7 Check Samples

Check samples are currently not available.

9.2.7.1 Acceptance/Rejection Criteria
These criteria cannot be established at this time.

9.2.7.2 QC Corrective Action
This section does not apply at this time.

9.2.8 Interlaboratory Calibration

Samples will be split and sent to another laboratory that is experienced in cyanogen chloride analysis when available. This will

allow the comparison of results with another laboratory. This will provide a means of independent verification. When split samples are sent a cyanogen chloride spiked sample will also be sent to verify the quality assurance of both laboratories. Results will be recorded in the cyanogen chloride notebook.

## 10. PROCEDURE

### 10.1 INSTRUMENT PREPARATION

10.1.1 At the beginning of each day of analysis, a system blank is analyzed to verify that no interferences are present and also to evaluate instrumental conditions.

### 10.2 PURGE-AND-TRAP ANALYSIS

10.2.1 25 mL of the sample is placed in a 25-mL gas-tight syringe. 1 $\mu$g/L of flurobenzene internal standard is added through the tip of the sample syringe. The sample is placed in the glass sparger of the Tekmar LSC-2 unit and purged for 6 minutes.

10.2.2 When the purge cycle has completed, the cooling cycle of the Tekmar 1000 cryofocussing unit is started. The parameters on the Tekmar 1000 unit are set at -150°C and 4-second heating time. The liquid nitrogen tank must be set at 50 psi pressure to operate proper cooling of the cryo-interface cross connector. A 1/4 inch copper tubing is used at the liquid nitrogen exit end of the cross connector. This is to help provide for faster cooling of the cross connector.

10.2.3 When the cross connector has reached the proper temperature, the sample is desorbed onto the cryo-interface for 1½ minutes. The Tenax trap is then baked for 5 minutes.

10.2.4 Acqusition is started when the heat cycle on the Tekmar 1000 is completed.

10.2.5 See Table 1 for GC/MS operating conditions.

## 11. IDENTIFICATION

Identification is made by comparison of cyanogen chloride and fluorobenzene spectrum in the samples with those in the

standard. The ion abundances for ions given in Table 1 must agree within 10% absolute with the daily standard. For example, if an ion has a relative abundance of 30 percent in the standard spectrum, its abundance in the sample spectrum should be in the range of 20 to 40 percent.

TABLE 1

GAS CHROMATOGRAPH/MASS SPECTROMETER
OPERATING CONDITIONS

GC Column

| | |
|---|---|
| Type: | DB-5 fused silica capillary |
| Length: | 30 meters |
| Internal diameter: | 0.25 millimeters |
| Film thickness: | 1.0 micron |
| Pre-column: | 1 m x 0.32 mm ID fused silica |

Temperature program:

$10^{o}C$ ----------> $184^{o}C$
2 min $20^{o}C$/min

Injector

| | |
|---|---|
| Temperature: | $185^{o}C$ |

Gases

| | |
|---|---|
| Carrier: | Helium (99.999 percent purity) |
| Flow: | 2 mL/min |

Mass Spectrometer

| | |
|---|---|
| Interface temperature: | $185^{o}C$. |
| Manifold temperature: | $100^{o}C$. |
| Ionizer temperature setting: | $270^{o}C$. |
| Electron energy: | 70 eV |
| Acquisition: | 700 scans at 0.6 sec/scan: |

| Int # | Low Mass (m/z) | High Mass (m/z) | Time |
|---|---|---|---|
| 1 | 34.510 | 39.512 | 0.008 |
| 2 | 40.512 | 43.513 | 0.005 |
| 3 | 44.513 | 300.590 | 0.419 |

GC/MS Values

| | |
|---|---|
| Cyanogen chloride: | |
| Retention time: | 1.5 min |
| Mass spectrum: | m/z 61 (100%), m/z 63 (22%) |
| Fluorobenzene: | |
| Retention time: | 5.6 min |
| Mass spectrum: | m/z 96 (100%), m/z 70 (19%), m/z 50 (9%) |

# ANALYSIS OF FORMALDEHYDE/ACETALDEHYDE: MICRO PENTANE EXTRACTION

## 1. SCOPE AND APPLICATION

1.1 This method was developed to simultaneously analyze for formaldehyde and acetaldehyde in drinking water.

1.2 The experimentally determined method detection limits were calculated (Table 1). The method has been shown to be useful for formaldehyde and acetaldehyde over a range of 1 to 40 micrograms per liter ($\mu$g/L).

## 2. SUMMARY OF METHOD

2.1 Twenty milliliters (mL) of sample is derivatized with 1 mL of O-(2,3,4,5,6-pentafluorobenzyl)hydroxylamine (PFBOA) and allowed to sit for 2 hours. The sample is then quenched with concentrated sulfuric acid ($H_2SO_4$) and extracted with 4 mL of pentane. The analysis is conducted on a gas chromatograph (GC) with temperature programming and a fused silica capillary column to obtain baseline resolution of all the analytes. Detection is with an electron capture detector (ECD). Aqueous calibration standards are derivatized, extracted and analyzed in the same manner as the samples in order to compensate for extraction efficiency.

## 3. INTERFERENCES

3.1 Glassware, except volumetric flasks, is cleaned as follows:

3.1.1 Detergent washed.

3.1.2 Rinsed twice with tap water.

3.1.3 Rinsed twice with deionized water.

3.1.4 Rinsed twice with Millipore Super-Q System (Bedford, Mass.) water.

3.1.5 Baked in oven at 180°C for one hour; however, septa are baked at 80°C for one hour.

3.2 Cleaning procedure for volumetric flasks.

3.2.1 Immediately after use rinse several times with methanol.

3.2.2 Allow volumetric flasks to air dry in the

ventilation hood for 3 hours.

3.2.3 These flasks are only reused for the preparation of aldehyde standards.

3.3 Polypropylene caps from I-Chem Research, Inc. (Hayward, Calif.) are used instead of the Bakerlite caps that normally come with the vials. Bakerlite caps are made from phenol and formaldehyde and are a potential contaminant.

3.4 Formaldehyde and acetaldehyde are air pollutants, and data have indicated that their concentrations are increased when oxygenated fuels are used in automobiles. In addition, formaldehyde in the air can be traced to the presence of certain insulation materials. Therefore, a laboratory reagent blank is analyzed each day to determine if the laboratory air is contaminated. Also, travel blanks are used to identify contamination during sampling and shipping of the samples. Unfortunately, though, travel blanks can become contaminated during the shipment and storage of ice chests prior to sampling (typically a two-week period), so the interpretation of aldehyde data is more problematic.

## 4. SAFETY

4.1 The toxicity of formaldehyde and acetaldehyde has not been precisely defined; each chemical is treated as a potential health hazard and handled under a ventilation hood.

4.2 All Occupational Safety and Health Association (OSHA) regulations regarding safe handling of chemicals and laboratory procedures are used in this method.

## 5. APPARATUS, EQUIPMENT AND MATERIALS

5.1 SAMPLE CONTAINERS - samples are collected in 40-mL screw-cap (polypropylene, I-Chem Research, Inc.) vials with Teflon/silicone septa closures.

5.2 EXTRACTION VIALS - Extraction vials are 30 mL (nominal 25 mL) with open-top screw cap (polypropylene, I-Chem Research, Inc.) and Teflon/silicone septa closure.

5.3 MICROLITER SYRINGES - 5, 10, 25, 50, 100 and 500 microliter ($\mu$L) sizes from Hamiliton Co., Reno, Nev., and a 20-mL syringe from Becton-Dickson Co., Rutherford, N. J.

5.4 VOLUMETRIC FLASK - glass stoppered, 10 mL.

5.5 MECHANICAL SHAKER - For the pentane extraction process, a mechanical shaker table is used with the 30-mL vials. The vials are inserted into a custom-made wooden holding block (28-vial capacity). The shaker was purchased from the Eberbach Corp., Ann Arbor, Mich.

5.6 EXTRACT AND STANDARD SOLUTION STORAGE CONTAINERS - 1.5-mL clear glass, 15-mL and 1-ounce (oz) amber-glass screw cap vials with Teflon-lined septa.

5.7 GAS CHROMATOGRAPH - A Varian model 3500 GC (Sunnyvale, Calif.), equipped with split/splitless injector, ECD, and model 8035 autosampler, is used for the analysis. See Table 2 for analytical conditions.

5.7.1 The analytical column is a fused silica DB-5 (J&W Scientific, Inc., Folsom, Calif.) with a 1.0 micron ($\mu$) film, internal diameter (ID) of 0.25 millimeters (mm) and 30 meters (m) in length.

5.7.2 A constant current pulse modulated Nickel 63 ECD with capillary size cell is used for detection.

5.7.3 The carrier and make-up gases are high purity (99.999 percent) grade which pass through Drierite, molecular sieve 5A, activated charcoal, and finally an oxygen purifying cartridge before entering the GC. Two-stage metal diaphragm high purity regulators are used at the compressed gas sources. Digital flow controllers regulate carrier gas flow and all gas lines are 1/8 inch copper tubing which have been acetone-rinsed and baked before use.

## 6. REAGENTS AND CONSUMABLE MATERIALS

### 6.1 REAGENTS

6.1.1 Extraction solvent is Burdick & Jackson (Muskegon, Mich.) THM analysis grade pentane.

6.1.2 O-(2,3,4,5,6-Pentafluorobenzyl)hydroxylamine hydrochloride (PFBOA) is from Aldrich Chemical Co. (Milwaukee, Wisc.).

6.1.3 Sulfuric acid is Fisher Scientific (Pittsburg, Penn.) A.C.S. reagent grade.

6.1.4 The "dechlorinating agent" is ammonium chloride,

granular, "Baker Analyzed" reagent (Phillipsburg, N. J.).

6.1.5 The preservative is mercuric chloride, "Baker Analyzed" reagent.

6.2 STANDARD MATERIALS

6.2.1 See Table 3 for source and physical information.

6.2.2 The reference internal standard 1,3-dibromopropane is 98 percent pure (Chem Services, Inc., Westchester, Penn.). The internal standard is added at the 180 $\mu$g/L level in the pentane used for extraction.

6.3 REAGENT WATER - Organic-pure water (OPW) is made in the laboratory by a Corning megapure all-glass distillation system (model MP3A, Corning, N. Y.). The source water for the MP3A is purified laboratory water (Super-Q), which has gone through several stages of cartridge-type purification to filter and demineralize the water and trap the organic compounds. The OPW should be prepared when needed, as storage can increase the opportunity for contamination.

6.4 STANDARD STOCK SOLUTION

6.4.1 Stocks are prepared gravimetrically in OPW from pure standards. Separate stock solutions are prepared for formaldehyde and acetaldehyde. The syringe and the volumetric flask used for acetaldehyde should be placed in the freezer for about 10 minutes before preparing this standard due to the volatility of the compound. The pure standard is weighed into a tared, 10-mL volumetric flask, so that the final concentration is between 2 to 6 mg/mL. Since formaldehyde is commercially-available as a 37 weight percent solution in water, the concentration must take into account this dilution factor. The stock solutions are diluted to final volume with OPW, stoppered and mixed by inverting the flasks several times. The stock solutions are transferred into clean, 1-oz amber-glass storage bottles with Teflon-faced septa and screw caps, and they are stored at 4°C. The formaldehyde stock is prepared fresh every 3 months. The acetaldehyde stock is prepared fresh every month.

6.4.2 A spike solution is prepared by diluting the

appropriate amount of each stock solution into 10 mL of OPW so that the resulting concentration of each aldehyde is approximately 20 mg/L. The solvent flush technique with a gas-tight syringe is used. The spike solution is prepared every two weeks.

## 7. SAMPLE COLLECTION, PRESERVATION, AND STORAGE

### 7.1 SAMPLE COLLECTION

7.1.1 Collect all samples in triplicate.

7.1.2 The sampling tap is allowed to flush for approximately 5 minutes to allow the water temperature to stabilize and the stagnant lines to be flushed.

7.1.3 Samples are collected in nominal 40-mL vials with Teflon-faced septa and screw caps (polypropylene, I-Chem Research, Inc.). The sample vials are filled such that no air bubbles pass through the sample. The bottles are not rinsed before filling and are not allowed to overfill, since the bottles contain a preservative. The sample vials are sealed headspace free.

### 7.2 SAMPLE PRESERVATION

7.2.1 Ammonium chloride ($NH_4Cl$) and mercuric chloride ($HgCl_2$) are used as the preservative agents. The ammonium chloride acts as a preservative by forming monochloramine in the presence of free chlorine; monochloramine does not react with natural organic material in the samples to form these aldehydes during established holding times under refrigerated temperatures (4°C). The mercuric chloride prevents the bacterial degradation of the aldehydes.

7.2.2 Approximately 65 mg of crystalline $NH_4Cl$ is added to each vial prior to sampling.

7.2.3 Approximately 40 µL of 10 mg/mL $HgCl_2$ is added to each vial prior to sampling. The concentration of $HgCl_2$ in the sample will be approximately 10 mg/L.

### 7.3 SAMPLE STORAGE

7.3.1 Samples and sample extracts are stored at 4°C until analysis. Analyses should be performed as

soon as possible after collection due to the instability of the formaldehyde. Typically, these samples are derivatized and extracted upon receipt at the laboratory.

## 8. CALIBRATION AND STANDARDIZATION

8.1 Aqueous calibration standards are prepared in OPW by injecting the appropriate amount of spike solution directly into water using the solvent flush technique.

8.2 Eight different concentration levels (from 0.5 to 40 µg/L) are prepared in 30-mL screw-cap (polypropylene, I-Chem Research, Inc.) vials with Teflon/silicone septa containing 20 mL of OPW. An extraction blank is also included in the standard curve. The standards are then analyzed in the same manner as the samples. The entire calibration curve is analyzed every 7 days. Two standards (5 and 20 µg/L levels) are analyzed daily and compared against the established curve. If the results of the latter standards are not within +/- 10 percent, the complete standard curve is rerun before calculating the values of samples (see Section 9.2.3).

8.3 A set of standards in the range of 0.5 to 40 µg/L is analyzed by GC weekly. Two standards are analyzed each day prior to the analysis of the samples. These daily standards are used to verify the accuracy of the calibration curve. An external standard method is used to determine the concentration of the samples, utilizing the current calibration curve. The internal standard is not used in the quantitation but is used as a reference peak for peak identification and as an indicator of injection errors (see Section 9.2.4). A plot of area versus concentration (in µg/L) is prepared by using a point-to point fit passing through zero. Calculations are made from only the linear portions of the curve. Solvent blanks are run after the standards.

8.4 PFBOA forms a cis and trans oxime with acetaldehyde. The trans oxime is used for quantitation.

## 9. QUALITY CONTROL

### 9.1 MONITORING FOR INTERFERENCES

9.1.1 Laboratory reagent blanks - A laboratory reagent blank is analyzed each day to verify any interferences.

9.1.2 Travel blanks for each sampling location are

prepared in the laboratory by filling 40-mL vials, as described above (Section 7.1.3), with OPW. These are shipped to the sampling site and back to the laboratory with the sample bottles.

9.1.3 Each reagent bottle of pentane is analyzed before it is used.

## 9.2 QUALITY ASSURANCE/QUALITY CONTROL PROTOCOL

The Quality Assurance/Quality Control (QA/QC) protocol covers accuracy, precision, independent verification and the use of an internal standard. Accuracy is dependent on many factors, but the most important is the calibration curve. Accuracy is monitored by calculating the recoveries of samples which have been enhanced with known concentrations of the compounds of interest. Precision is another parameter that is dependent on more than one factor. The precision of a method is monitored by analyzing samples in duplicate and calculating the normalized difference between the two analyses. Independent verification of a method is done by interlaboratory calibration. The internal standard is used to insure that the GC makes consistent injections of samples and standards.

All of the above mentioned parameters are important in assuring that good quality data are produced. It is important to note that all portions of a QA/QC program must meet the established standards in order for an analysis to be considered in control.

### 9.2.1 Method Detection Limits

Initial calculations of the method detection limits (MDLs) are made according to the Code of Federal Regulations 40 part 136, July 1, 1987. A set of 7 standards are prepared in OPW at 1 to 5 times the estimated detection limit. Each standard is analyzed according to the method and the standard deviation of the 7 replicate measurements for each analyte is determined. The MDL is determined for each analyte as follows:

$$MDL = t\ (S)$$

t = 3.143 (student t value for 6 degrees of freedom and 99 percent confidence level)

S = standard deviation of the 7 replicate analyses

These MDLs are used as minimum reporting levels (MRLs), except where the instrumental detection limit has proved to be higher. Often, the MRLs correspond to the lowest level standard on the calibration curve.

9.2.2 Calibration Curves

Quantitation is done using an external standard calibration curve. Standards are prepared in OPW spiked with the aldehydes and extracted with the same solvent as that used for the samples (see section 8). The extracted standards are used to compensate for the varying extraction efficiencies of the different compounds in the analysis. An eight-point calibration curve encompassing the 0.5 to 40 µg/L range is used, and two standards are analyzed each day prior to the analysis of the samples (see Section 9.2.3).

9.2.2.1 Acceptance/Rejection Criteria
The curve is determined acceptable if the fit is smooth. Also, the new calibration curve is compared to the previous curve to insure that they are comparable. The injection is determined to be acceptable if the internal standard is acceptable (see Section 9.2.4). All internal standard area counts (µV/seconds) should be within +/- 10 percent for all standards in the calibration curve.

9.2.2.2 QC Corrective Action
The problem is determined and corrected. The calibration curve is reanalyzed on the GC. If reanalysis does not produce a satisfactory curve, then a new set of calibration standards are prepared. The standards are reanalyzed until an acceptable curve is obtained. All sample extracts are reanalyzed from the last point where calibration curves were in control. The corrective action is documented in the formaldehyde notebook and signed by the immediate supervisor and QC officer.

9.2.3 Daily Standards

The current calibration curve is verified daily using the two standards (5 and 20 µg/L levels)

analyzed with the sample set.

9.2.3.1 Acceptance/Rejection Criteria
The calculated values of both of the two daily standards (using the current calibration curve) must agree to within +/- 10 percent of their true values.

9.2.3.2 QC Corrective Action
The problem is determined and corrected. The daily standards are reanalyzed on the GC. If reanalysis does not produce satisfactory results, then a new set of calibration standards are prepared. The new calibration standards must meet the criteria in Section 9.2.2. All sample extracts analyzed with an out-of-control set of daily standards are recalibrated utilizing the new calibration curve that is in control. The corrective action is documented in the formaldehyde notebook and signed by the immediate supervisor and QC officer.

9.2.4 Internal Standard
The internal standard (1,3-dibromopropane) is spiked directly into each new bottle of solvent at a concentration of 180 $\mu g/L$. (Note, this is not the same internal standard that is used for the other disinfection by-product analyses; the 1,2-dibromopropane presents interference problems for this method.) The solvent is then used to extract both samples and calibration standards. The purpose of the internal standard is to monitor injections made by the autosampler.

9.2.4.1 Acceptance/Rejection Criteria
A sample injection is deemed acceptable if the area counts ($\mu V$/seconds) of the internal standard peak do not vary more than +/- 10 percent from other samples which are extracted using the same bottle of solvent on the same date. The internal standard areas of samples can not be compared to those of calibration standards when the samples and standards are prepared using extraction solvent from different bottles or on different days. The internal standard area can vary from bottle to bottle and day to day.

9.2.4.2 Corrective Action
The problem is determined and corrected. The sample extracts are reanalyzed. If reanalysis is not acceptable, then the samples are reextracted and reanalyzed. If the reextracted samples are not acceptable or the samples have exceeded the holding time, then the samples are resampled and reanalyzed or the results are recorded as suspect and out of control. Such data are not entered into the database. The corrective action is documented in the formaldehyde notebook and signed by the immediate supervisor and QC officer.

9.2.5 Spikes
Sample spikes are analyzed to monitor the extraction efficiency of specific analytes in sample matrices. This measures the accuracy of the method in a natural matrix. The spiked samples are analyzed at a frequency of at least 10 percent of the samples. The spike solution is prepared in OPW (Section 6.4.2). The samples are spiked with 10 $\mu$L of spike solution to achieve a concentration of 10 $\mu$g/L of each aldehyde, which are the levels that are typically found in ozonated waters. Data are entered into the QC table directly after the analysis. The QC charts are reviewed by the analyst and the immediate supervisor.

9.2.5.1 Acceptance/Rejection Criteria
All spike recoveries must fall within the upper and lower control limits to be acceptable. Initial control limits are defined by calculating the mean percent recovery from the most recent 50 sample spike data points. The 99 percent confidence interval is +/- three times the standard deviation. Warning limits are defined as +/- two times the standard deviation. If a sample recovery is above or below the warning limit this indicates there is a potential problem. The problem is determined and corrected before the analysis is out of control. Control limits and warning limits are recalculated on a semiannual basis using the most recent 50 spiked sample percent recovery values. Data points that are

out of control are not included in the recalculation of new control limits. Control limits are recalculated when any major changes are made in the analytical procedure (i.e. new type of column) and after at least 20 points have been collected.

9.2.5.2 QC Corrective Action
The problem is determined and corrected. The sample extracts and spiked sample extract are reanalyzed from the point where the last sample spike recovery was in control. If the spike recovery is still not acceptable, then the samples are reextracted from the point where the last spike was in control and a sample is respiked and reanalyzed only for those analytes that are out of control. If the spike recovery is not acceptable or samples have exceeded the holding time, then the samples are resampled and reanalyzed from the point where the last spike was in control. A sample is respiked and reanalyzed. If reanalysis is not possible the results are recorded as suspect for only those analytes that are out of control. Such data are not entered into the database. The corrective action is documented in the formaldehyde notebook and signed by the immediate supervisor and QC officer.

9.2.6 Duplicates
Sample duplicates are analyzed in order to monitor the precision of the method. Duplicates are analyzed on randomly selected samples at a frequency of at least 10 percent of the samples. Data are entered into the QC table within 24 hours after the analytical run is completed. The QC charts are reviewed by the analysts and the immediate supervisor.

9.2.6.1 Acceptance/Rejection Criteria
Control limits are determined by calculating the range as a function of the relative standard deviation (coefficient of variation) as specified in Standard Methods proposed method 1020B. The range (R) is calculated by taking the absolute difference of the

duplicate values as follows:

$R = |x_1 - x_2|$ ($x_1$ and $x_2$ are the duplicate values)

The normalized range ($R_n$) is calculated by dividing the range (R) by the average of the duplicate values ($x_m$):

$$R_n = \frac{R}{x_m}$$

$$x_m = \frac{x_1 + x_2}{2}$$

A mean normalized range ($R_m$) is calculated for 50 pairs of duplicate data points:

$$R_m = \frac{\Sigma R_n}{n}$$

n = number of duplicate pairs

The variance ($s^2$) of the normalized ranges is calculated:

$$s^2 = \frac{\Sigma(R_n - R_m)^2}{n-1}$$

The standard deviation (s) is calculated as the square root of the variance.

The upper and lower control limits are defined as $R_m + 3s$ and zero, respectively. All duplicates must fall within the control limits to be acceptable. The upper warning limit is defined as $R_m + 2s$. If an $R_n$ is outside the warning limit, this indicates there is a potential problem. The problem is investigated before the analysis is out of control. Control limits are recalculated on an annual basis using the most recent 50 points. Data points that are out of control are not included in the recalculation of new control limits.

Data points below the detection limit should not be used either. Control limits are recalculated when any major changes are made in the analytical procedure (i.e. new type of column) and after at least 20 points have been collected.

9.2.6.2 QC Corrective Action
The problem is determined and corrected. The sample extracts and the duplicate extracts are reanalyzed from the point where the last sample duplicate was in control. If the duplicate is still not acceptable, then the samples are reextracted from the point where the last duplicates were in control and a duplicate is reanalyzed only for those analytes that were out of control. If the duplicates are still unacceptable or the sample holding time has been exceeded, then the samples are resampled and reanalyzed from the point where the last duplicates were in control. A duplicate is reanalyzed. If this is not possible the results for only those analytes that were out of control are recorded as suspect. Such data are not entered into the database. The corrective action is documented in the formaldehyde notebook and signed by the immediate supervisor and QC officer.

9.2.7 Interlaboratory Calibration
Samples will be split and sent to another laboratory that is experienced in formaldehyde/acetaldehyde analysis when available. This will allow the comparison of results with another laboratory. This will provide another means of independent verification. When split samples are sent a formaldehyde/acetaldehyde spiked sample will also be sent to verify the quality assurance of the other laboratory. Results will be recorded in the formaldehyde notebook.

## 10. PROCEDURE

### 10.1 SAMPLE PREPARATION

10.1.1 Samples and standards are removed from storage and allowed to reach room temperature.

10.2 DERIVATIZATION, MICROEXTRACTION AND ANALYSIS

10.2.1 A 20-mL aliquot of sample water is withdrawn from the sample container by a 20-mL glass syringe and delivered to a 30-mL vial with Teflon-faced septum and screw cap (polypropylene, I-Chem Research, Inc.).

10.2.2 A 1-mL volume of freshly prepared 2 mg/mL PFBOA is added to each vial by a Brinkman Dispensette, capped, and swirled. The sample sits at room temperature for 2 hours +/- 5 minutes.

10.2.3 The sample is quenched by adding 0.05 mL (approximately 2 drops) of concentrated $H_2SO_4$ and swirled. A 4-mL volume of pentane (containing the internal standard) is added to the vial by a Brinkman Dispensette and the vial is then capped.

10.2.4 After all the vials have been sealed and prepared for extraction, they are placed in a vial holder and shaken for 5 minutes in a mechanical shaker.

10.2.5 The vials are removed from the vial holder, placed upright and allowed to stand for 5 minutes. Equal volumes of extract are transferred into two 1.5-mL autosampler vials by a pasteur pipet.

10.2.6 At the beginning of each analytical run, a pentane solvent blank is injected to condition the GC and to verify that no interferences are present.

10.2.7 The data are collected on a Hewlett Packard model 300 microcomputer (Palo Alto, Calif.) with Nelson Analytical Xtrachrome chromatography software (Cupertino, Calif.). Autosampler information (rack# & vial#) is communicated to the data system for sample identification purposes. The data files are designated ZSXXXXY where ZS is a code designating the formaldehdye/acetaldehyde analysis, XXXX is the month and day in numbers and Y is a unique sequential cycle number assigned to each data file by the data system. The data files are archived to magnetic tape.

10.2.8 See Table 1 for retention times.

TABLE 1

METHOD DETECTION LIMITS (MDLs),
MINIMUM REPORTING LEVELS (MRLs),
AND RETENTION TIMES (RTs)

| Compounds | MDLs (μg/L) | MRLs (μg/L) | RTs (min) |
|---|---|---|---|
| 1,3-Dibromopropane[a] | | | 10.54 |
| Formaldehyde (HCHO) | 0.87 | 1.0 | 11.85* |
| Acetaldehyde$_{cis}$ ($CH_3CHO_{cis}$)# | 0.55 | 1.0 | 15.23* |
| Acetaldehyde$_{trans}$ ($CH_3CHO_{trans}$)# | 0.64 | 1.0 | 15.62* |

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[a]Internal standard.
*These are the retention times of the derivatized oximes formed by the PFBOA.
#Acetaldehyde forms cis and trans oximes with the PFBOA.

TABLE 2

GAS-CHROMATOGRAPHIC CONDITIONS

Column

| | |
|---|---|
| Type: | Fused silica capillary (Durabond-5, J&W Scientific, Folsom, Calif.) |
| Length: | 30 meters |
| Internal diameter: | 0.25 millimeters |
| Film thickness: | 1.0 micron |

Temperature program :

| | | | | |
|---|---|---|---|---|
| 50°C | ----------> | 122°C | ----------> | 245°C |
| 1 min | 8°C/min | 7 min | 30°C/min | 2 min |

Injector

| | |
|---|---|
| Injection volume: | 2 µL |
| Temperature: | 150°C |
| Splitless injection: | Split valve opened at 0.5 min |

Detector

| | |
|---|---|
| Type: | Electron capture |
| Temperature: | 272°C |

Gases

| | |
|---|---|
| Carrier: | Helium (99.999 percent purity) |
| Flow: | 1.5 mL/min at 25°C |
| Makeup: | Nitrogen (99.999 percent purity) |
| Flow: | 24 mL/min |

Autosampler Parameters - (for Varian model 8035 autosampler)

| | |
|---|---|
| Purge pulse pressure | 55 psi |
| number of purge pulses | 1 |

TABLE 3

ANALYTICAL STANDARDS

| Compound | Source | Purity (percent) | Molecular Weight | Boiling Point (°C) | Density |
|---|---|---|---|---|---|
| Formaldehyde | Aldrich[a] | * | 30.03 | 96 | 1.083 |
| Acetaldehyde | Chem Svc[b] | | 44.05 | 21 | 0.788 |

---

[a]Aldrich Chemical Company, Inc., Milwaukee, Wisc.
[b]Chem Service, Inc., Westchester, Pa.
*Formaldehyde available as a 37 weight percent solution in water.

# Appendix D

## *Correlation Matrices*



# CORRELATION ANALYSES

| | | THMs | | |
|---|---|---|---|---|
| | | CHCl3 | CHCl2Br | CHBr2Cl |
| THMs | CHBr3 | -0.305 | 0.032 | 0.578 |
| | CHBr2Cl | 0.001 | 0.659 | |
| | CHCl2Br | 0.606 | | |

| | | THMs | | | |
|---|---|---|---|---|---|
| | | CHCl3 | CHCl2Br | CHBr2Cl | CHBr3 |
| HAAs | TCAA | 0.802 | 0.397 | -0.131 | -0.314 |
| | DCAA | 0.860 | 0.538 | -0.030 | -0.326 |
| | MCAA | 0.649 | 0.519 | 0.050 | -0.192 |
| | MBAA | -0.054 | 0.414 | 0.767 | 0.608 |
| | DBAA | -0.222 | 0.229 | 0.785 | 0.816 |

| | | THMs | | | |
|---|---|---|---|---|---|
| | | CHCl3 | CHCl2Br | CHBr2Cl | CHBr3 |
| HANs | TCAN | 0.343 | 0.183 | -0.088 | -0.106 |
| | DCAN | 0.740 | 0.508 | 0.017 | -0.241 |
| | BCAN | 0.341 | 0.833 | 0.770 | 0.244 |
| | DBAN | -0.250 | 0.227 | 0.756 | 0.880 |

# CORRELATION ANALYSES

| | | THMs | | | |
|---|---|---|---|---|---|
| | | CHCl3 | CHCl2Br | CHBr2Cl | CHBr3 |
| HKs | 1,1-DCP | 0.330 | 0.084 | -0.260 | -0.397 |
| | 1,1,1-TCP | 0.520 | 0.124 | -0.195 | -0.286 |

| | | THMs | | | |
|---|---|---|---|---|---|
| | | CHCl 3 | CHCl2Br | CHBr2Cl | CHBr3 |
| MISC | CHP | 0.491 | 0.253 | -0.130 | -0.305 |
| | CH | 0.846 | 0.657 | 0.129 | -0.236 |
| | CNCl | 0.046 | 0.084 | -0.025 | -0.160 |

| | | THMs | | | |
|---|---|---|---|---|---|
| | | CHCl3 | CHCl2Br | CHBr2Cl | CHBr3 |
| ALDs | FRM | 0.150 | 0.159 | 0.099 | -0.095 |
| | ACETAL | 0.223 | 0.377 | 0.251 | -0.052 |

# CORRELATION ANALYSES

| | | THMs | | | |
|---|---|---|---|---|---|
| | | CHCl3 | CHCl2Br | CHBr2Cl | CHBr3 |
| INFLUENT PARAMETERS | TOC | 0.502 | 0.513 | 0.189 | -0.087 |
| | UV | 0.436 | 0.403 | 0.178 | -0.067 |
| | $Cl^-$ | -0.246 | -0.006 | 0.289 | 0.629 |
| | $Br^-$ | -0.250 | -0.073 | 0.180 | 0.566 |

| | | HAAs | | | |
|---|---|---|---|---|---|
| | | TCAA | DCAA | MCAA | MBAA |
| HAAs | DBAA | -0.277 | -0.233 | -0.099 | 0.818 |
| | MBAA | -0.122 | -0.056 | 0.079 | |
| | MCAA | 0.591 | 0.726 | | |
| | DCAA | 0.854 | | | |

| | | HAAs | | | | |
|---|---|---|---|---|---|---|
| | | TCAA | DCAA | MCAA | MBAA | DBAA |
| HANs | TCAN | 0.575 | 0.426 | 0.355 | -0.038 | -0.142 |
| | DCAN | 0.762 | 0.616 | 0.502 | -0.065 | -0.171 |
| | BCAN | 0.213 | 0.265 | 0.312 | 0.565 | 0.516 |
| | DBAN | -0.306 | -0.280 | -0.132 | 0.739 | 0.850 |

# CORRELATION ANALYSES

| | | HAAs | | | | |
|---|---|---|---|---|---|---|
| | | TCAA | DCAA | MCAA | MBAA | DBAA |
| HKs | 1,1-DCP | 0.508 | 0.559 | 0.441 | -0.259 | -0.387 |
| | 1,1,1-TCP | 0.770 | 0.659 | 0.369 | -0.142 | -0.284 |

| | | HAAs | | | | |
|---|---|---|---|---|---|---|
| | | TCAA | DCAA | MCAA | MBAA | DBAA |
| MISC | CHP | 0.397 | 0.536 | 0.385 | -0.160 | -0.273 |
| | CH | 0.660 | 0.741 | 0.594 | 0.040 | -0.114 |
| | CNCl | 0.115 | 0.184 | 0.283 | 0.058 | -0.104 |

| | | HAAs | | | | |
|---|---|---|---|---|---|---|
| | | TCAA | DCAA | MCAA | MBAA | DBAA |
| ALDs | FRM | 0.070 | 0.210 | 0.333 | 0.107 | -0.016 |
| | ACETAL | 0.126 | 0.301 | 0.422 | 0.234 | 0.076 |

# CORRELATION ANALYSES

| | | HAAs | | | | |
|---|---|---|---|---|---|---|
| | | TCAA | DCAA | MCAA | MBAA | DBAA |
| INFLUENT PARAMETERS | TOC | 0.278 | 0.578 | 0.560 | 0.132 | 0.046 |
| | UV | 0.222 | 0.488 | 0.589 | 0.152 | 0.079 |
| | $Cl^-$ | -0.273 | -0.259 | -0.110 | 0.476 | 0.668 |
| | $Br^-$ | -0.272 | -0.267 | -0.076 | 0.389 | 0.600 |

| | | HANs | | |
|---|---|---|---|---|
| | | TCAN | DCAN | BCAN |
| HANs | DBAN | -0.103 | -0.174 | 0.517 |
| | BCAN | 0.163 | 0.469 | |
| | DCAN | 0.504 | | |

| | | HANs | | | |
|---|---|---|---|---|---|
| | | TCAN | DCAN | BCAN | DBAN |
| HKs | 1,1-DCP | 0.456 | 0.392 | -0.041 | -0.417 |
| | 1,1,1-TCP | 0.671 | 0.496 | 0.032 | -0.288 |

# CORRELATION ANALYSES

| | | HANs | | | |
|---|---|---|---|---|---|
| | | TCAN | DCAN | BCAN | DBAN |
| MISC | CHP | 0.218 | 0.277 | 0.048 | -0.293 |
| | CH | 0.452 | 0.619 | 0.449 | -0.140 |
| | CNCl | 0.173 | 0.330 | 0.096 | -0.159 |

| | | HANs | | | |
|---|---|---|---|---|---|
| | | TCAN | DCAN | BCAN | DBAN |
| ALDs | FRM | -0.028 | 0.153 | 0.066 | -0.067 |
| | ACETAL | 0.108 | 0.256 | 0.321 | 0.047 |

| | | HANs | | | |
|---|---|---|---|---|---|
| | | TCAN | DCAN | BCAN | DBAN |
| INFLUENT PARAMETERS | TOC | 0.105 | 0.264 | 0.323 | -0.008 |
| | UV | 0.041 | 0.279 | 0.351 | 0.012 |
| | $Cl^-$ | -0.066 | -0.164 | 0.210 | 0.587 |
| | $Br^-$ | -0.100 | -0.178 | 0.119 | 0.485 |

# CORRELATION ANALYSES

| | | HKs |
|---|---|---|
| | | 1,1-DCP |
| HKs | 1,1,1-TCP | 0.595 |

| | | HKs | |
|---|---|---|---|
| | | 1,1-DCP | 1,1,1-TCP |
| MISC | CHP | 0.373 | 0.355 |
| | CH | 0.279 | 0.528 |
| | CNCl | 0.471 | -0.021 |

| | | HKs | |
|---|---|---|---|
| | | 1,1-DCP | 1,1,1-TCP |
| ALDs | FRM | 0.380 | 0.009 |
| | ACETAL | 0.352 | -0.009 |

| | | HKs | |
|---|---|---|---|
| | | 1,1-DCP | 1,1,1-TCP |
| INFLUENT PARAMETERS | TOC | 0.340 | 0.096 |
| | UV | 0.280 | 0.052 |
| | Cl | -0.311 | -0.238 |
| | Br | -0.298 | -0.256 |

| | | MISC | |
|---|---|---|---|
| | | CHP | CH |
| MISC | CNCl | 0.289 | -0.045 |
| | CH | 0.503 | |

| | | MISC | | |
|---|---|---|---|---|
| | | CHP | CH | CNCl |
| ALDs | FRM | 0.348 | 0.174 | 0.319 |
| | ACETAL | 0.416 | 0.328 | 0.592 |

# CORRELATION ANALYSES

| | | MISC | | |
|---|---|---|---|---|
| | | CHP | CH | CNCl |
| INFLUENT PARAMETERS | TOC | 0.353 | 0.360 | 0.338 |
| | UV | 0.243 | 0.259 | 0.308 |
| | $Cl^-$ | -0.226 | -0.178 | -0.112 |
| | $Br^-$ | -0.218 | -0.210 | -0.103 |

| | | ALDs |
|---|---|---|
| | | FRM |
| ALDs | ACETAL | 0.638 |

| | | ALDs | |
|---|---|---|---|
| | | FRM | ACETAL |
| INFLUENT PARAMETERS | TOC | 0.237 | 0.352 |
| | UV | 0.298 | 0.303 |
| | $Cl^-$ | -0.134 | -0.062 |
| | $Br^-$ | -0.109 | -0.072 |

| | | INFLUENT PARAMETERS | | |
|---|---|---|---|---|
| | | TOC | UV | $Cl^-$ |
| INFLUENT PARAMETERS | $Br^-$ | 0.054 | 0.064 | 0.967 * |
| | $Cl^-$ | 0.057 | 0.042 | |
| | UV | 0.793# | | |

* without Utility 10, r = 0.857

\# without Utility 30, 4th qurter, r = 0.872