METHOD 552

DETERMINATION OF HALOACETIC ACIDS IN DRINKING WATER BY LIQUID-LIQUID EXTRACTION, DERIVATIZATION, AND GAS CHROMATOGRAPHY WITH ELECTRON CAPTURE DETECTION

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DETERMINATION OF HALOACETIC ACIDS IN DRINKING WATER BY LIQUID-LIQUID EXTRACTION, DERIVATIZATION, AND GAS CHROMATOGRAPHY WITH ELECTRON CAPTURE DETECTION

1.0 SCOPE AND APPLICATION

1.1 This is a gas chromatographic (GC) method[1-4,11] applicable to the determination of the listed halogenated acetic acids in drinking water, ground water, raw water and any intermediate treatment stage. In addition, the chlorinated phenols listed may be analyzed by this method.

Analyte	Chemical Abstract Services Registry Number
Monochloroacetic Acid	79-11-8
Dichloroacetic Acid	79-43-6
Trichloroacetic Acid	76-03-9
Monobromoacetic Acid	79-08-3
Bromochloroacetic Acid	5589-96-3
Dibromoacetic Acid	631-64-1
2,4-Dichlorophenol	120-83-2
2,4,6-Trichlorophenol	88-06-2

1.2 This method is applicable to the determination of these analytes over the concentration ranges typically found in drinking water[1,2,4], subject to the method detection limits (MDL) listed in Table 2. The detection limits observed may vary according to the particular matrix analyzed and the specific instrumentation employed. The haloacetic acids are observed ubiquitously in chlorinated supplies at concentrations normally within the spiking level ranges in Tables 2-5.

1.3 Tribromoacetic acid has not been included because of problems with extraction and chromatography by this method. The mixed bromochloroacetic acids have recently been synthesized. The bromochloroacetic acid is present in chlorinated supplies and method validation data are provided herein. However, neat material for this compound is not readily available. The mixed trihalogenated acids may also be present. These are not included because of current problems with sample purity and the chromatography for these two compounds.

1.4 The 2-chlorophenol has not been included as a method analyte in the above list, primarily because its realistic detection limit in environmental samples is likely to be above the odor threshold. Poor precision is usually obtained for this compound at even higher levels. In addition, this analyte displays

instability under the dechlorination/preservation conditions described herein. Nevertheless, some method validation data are given in Tables 2-7.

1.5 This method is designed for analysts skilled in liquid-liquid extractions, extract concentration techniques, derivatization procedures and the use of GC and interpretation of gas chromatograms.

1.6 When this method is used for the analyses of waters from unfamiliar sources, analyte identifications must be confirmed by at least one additional qualitative technique, such as GC/mass spectroscopy (MS) or by GC using dissimilar columns.

2.0 SUMMARY OF METHOD

2.1 A 100 mL volume of sample is adjusted to pH 11.5 and extracted with methyl-tert-butyl ether (MTBE) to remove neutral and basic organic compounds. The aqueous sample is then acidified to pH 0.5 and the acids are extracted into MTBE. After the extract is dried and concentrated, the acids are converted to their methyl esters with diazomethane (DAM). Excess DAM is removed and the methyl esters are determined by capillary GC using an electron capture detector (ECD). An alternative microextraction procedure is also offered in which a 30 mL sample is extracted without cleanup with a single 3 mL aliquot of MTBE for direct analysis by GC-ECD after methylation. Samples containing high concentrations of haloacetic acids and other disinfection byproducts, or other potentially interfering organic compounds, may require the sample cleanup.

3.0 DEFINITIONS

3.1 Internal Standard -- A pure analyte(s) added to a solution in known amount(s) and used to measure the relative responses of other method analytes and surrogates that are components of the same solution. The internal standard must be an analyte that is not a sample component.

3.2 Surrogate Analyte -- A pure analyte(s), which is extremely unlikely to be found in any sample, and which is added to a sample aliquot in known amount(s) before extraction and is measured with the same procedures used to measure other sample components. The purpose of a surrogate analyte is to monitor method performance with each sample.

3.3 Laboratory Duplicates (LD1 and LD2) -- Two sample aliquots taken in the analytical laboratory and analyzed separately with identical procedures. Analyses of LD1 and LD2 give a measure of the precision associated with laboratory procedures, but not with sample collection, preservation, or storage procedures.

3.4 Field Duplicates (FD1 and FD2) -- Two separate samples collected at the same time and place under identical circumstances and treated exactly the same throughout field and laboratory procedures. Analyses of FD1 and FD2 give a measure of the precision associated with sample collection, preservation and storage, as well as with laboratory procedures.

3.5 Laboratory Reagent Blank (LRB) -- An aliquot of reagent water that is treated exactly as a sample including exposure to all glassware, equipment, solvents, reagents, internal standards, and surrogates that are used with other samples. The LRB is used to determine if method analytes or other interferences are present in the labora-tory environment, the reagents, or the apparatus.

3.6 Field Reagent Blank (FRB) -- Reagent water placed in a sample container in the laboratory and treated as a sample in all respects, including exposure to sampling site conditions, storage, preservation and all analytical procedures. The purpose of the FRB is to determine if method analytes or other interferences are present in the field environment.

3.7 Laboratory Fortified Blank (LFB) -- An aliquot of reagent water to which known quantities of the method analytes are added in the laboratory. The LFB is analyzed exactly like a sample, and its purpose is to determine whether the methodology is in control, and whether the laboratory is capable of making accurate and precise measurements at the required method detection limit.

3.8 Laboratory Fortified Sample Matrix (LFM) -- An aliquot of an environmental sample to which known quantities of the method analytes are added in the laboratory. The LFM is analyzed exactly like a sample, and its purpose is to determine whether the sample matrix contributes bias to the analytical results. The background concentrations of the analytes in the sample matrix must be determined in a separate aliquot and the measured values in the LFM corrected for background concentrations.

3.9 Stock Standard Solution -- A concentrated solution containing a single certified standard that is a method analyte, or a concentrated solution of a single analyte prepared in the laboratory with an assayed reference compound. Stock standard solutions are used to prepare primary dilution standards.

3.10 Primary Dilution Standard Solution -- A solution of several analytes prepared in the laboratory from stock standard solutions and diluted as needed to prepare calibration solutions and other needed analyte solutions.

3.11 Calibration Standard (CAL) -- A solution prepared from the primary dilution standard solution and stock standard solutions of the internal standards and surrogate analytes. The CAL solutions are used to calibrate the instrument response with respect to analyte concentration.

3.12 Quality Control Sample (QCS) -- A sample matrix containing method analytes or a solution of method analytes in a water miscible solvent which is used to fortify reagent water or environmental samples. The QCS is obtained from a source external to the laboratory, and is used to check laboratory performance with externally prepared test materials.

4.0 INTERFERENCES

4.1 Method interferences may be caused by contaminants in solvents, reagents, glassware and other sample processing apparatus that lead to discrete artifacts or elevated baselines in gas chromatograms. All reagents and apparatus must be routinely demonstrated to be free from interferences under the conditions of the analysis by analyzing laboratory reagent blanks as described in Section 10.2. Subtracting blank values from sample results is not permitted.

4.1.1 Glassware must be scrupulously cleaned[5]. Clean all glassware as soon as possible after use by thoroughly rinsing with the last solvent used in it. Follow by washing with hot water and detergent and thorough rinsing with tap water, dilute acid, and reagent water. Drain and heat in an oven or muffle furnace at 400°C for one hour. Do not heat volumetric ware. Thermally stable materials such as PCBs might not be eliminated by this treatment. Thorough rinsing with reagent grade acetone may be substituted for the heating. After drying and cooling, seal and store glassware in a clean environment to prevent any accumulation of dust or other contaminants. Store inverted or capped with aluminum foil.

4.1.2 The use of high purity reagents and solvents helps to minimize interference problems. Purification of solvents by distillation in all-glass systems may be required. The extraction solvent, MTBE, may need to be redistilled.

4.2 Whereas the 2,4,6-trichlorophenol is converted quantitatively to the corresponding anisole by the methylation procedure (Section 11.3), the 2,4 - dichlorophenol is only partially converted (10-20%). The 2,4 dichloroanisole partially coelutes with the 2,4,6-trichloroanisole on the DB-1701 primary column with the chromatographic conditions employed (Table 1). The 2,4-dichlorophenol is quantitated on the phenol peak. The extent of interference of the dichloroanisole with the 2,4,6-trichlorophenol analysis is insignificant (0.8%) when these compounds are present at equal concentrations. For samples in which the 2,4-dichlorophenol concentration appears significantly higher than that of the 2,4,6-trichlorophenol, e.g., greater than a factor of 15, analyses should be performed on the DB-210 confirmation column, on which these compounds are completely resolved.

4.3 The acid forms of the analytes are strong organic acids which react readily with alkaline substances and can be lost during sample preparation. Glassware and glass wool must be acid-rinsed with (1+9) hydrochloric acid,

and the sodium sulfate must be acidified (see Section 7.6) with sulfuric acid prior to use to avoid analyte losses due to adsorption.

4.4 Organic acids and phenols, especially chlorinated compounds, cause the most direct interference with the determination. The addition of base and subsequent extraction of the basic sample removes many neutral and basic chlorinated hydrocarbons and phthalate esters that might otherwise interfere with the electron capture analysis.

4.5 Interfering contamination may occur when a sample containing low concentrations of analytes is analyzed immediately following a sample containing relatively high concentrations of analytes. Routine between-sample rinsing of the sample syringe and associated equipment with MTBE can minimize sample cross contamination. After analysis of a sample containing high concentrations of analytes, one or more injections of MTBE should be made to ensure that accurate values are obtained for the next sample.

4.6 Matrix interferences may be caused by contaminants that are coextracted from the sample. The extent of matrix interferences will vary considerably from source to source, depending upon the water sampled. Positive identifications should be confirmed using the confirmation column specified in Table 1 or by the use of gas chromatography with mass spectrometric detection.

5.0 SAFETY

5.1 The toxicity or carcinogenicity of each reagent used in this method has not been precisely defined; however, each chemical compound must be treated as a potential health hazard. From this viewpoint, exposure to these chemicals must be reduced to the lowest possible level by whatever means available. The laboratory is responsible for maintaining a current awareness file of OSHA regulations regarding the safe handling of the chemicals specified in this method. A reference file of material data handling sheets should also be made available to all personnel involved in the chemical analysis. Additional references to laboratory safety are available and have been identified[6-8] for the information of the analyst.

5.2 Diazomethane is a toxic carcinogen and can explode under certain conditions, when produced in a purified or highly concentrated form. In this form, the following safety precautions must be followed.

5.2.1 Use only in a well ventilated hood. Do not breathe vapors.

5.2.2 Use a safety screen. Wear protective clothing and a shielded safety hood.

5.2.3 Use mechanical pipetting aides.

5.2.4 Do not heat above 90°C.

5.2.5 Avoid grinding surfaces, ground glass joints, sleeve bearings, glass stirrers.

5.2.6 Store away from alkali metals.

5.2.7 Solutions of diazomethane decompose rapidly in the presence of solid materials such as copper powder, calcium chloride, and boiling chips.

5.3 For the above reasons, the diazomethane generation apparatus used in the esterification procedure specified in this method[3] produces only micromolar amounts of diazomethane in very dilute solution (Section 11.3) to minimize safety hazards. In this form, the solution is not explosive. Nevertheless, the following precautions should be followed.

5.3.1 Use only in a well ventilated hood.

5.3.2 When handling the diazomethane solution, avoid contact with skin. If contact is made, immediately wash the exposed area with warm water.

5.3.3 Collect and store the diazomethane solution produced at 0°C to minimize losses due to decomposition.

5.4 The toxicity of the extraction solvent, MTBE, has not been well defined. Susceptible individuals may experience adverse affects upon skin contact or inhalation of vapors. For such individuals a mask may be required. Protective clothing and gloves should be used and MTBE should be used only in a chemical fume hood or glove box.

6.0 APPARATUS AND EQUIPMENT (All specifications in Sections 6.0 and 7.0 are suggested. Catalog numbers are provided for illustration only.)

6.1 Separatory Funnels -- 250 mL, with TFE fluorocarbon stopcocks, ground glass or TFE fluorocarbon stoppers.

6.2 Screw Cap -- 40 mL vials (Pierce #13219 or equivalent). Screw caps should have TFE fluorocarbon liners.

6.3 Balance -- Analytical, capable of weighing to 0.0001 g.

6.4 Diazomethane Generator -- The generator assembly is shown in Figure 1 along with the diazomethane collection vessel. There are some diazomethane generating kits commercially available. One is the Aldrich Diazald Kit, Part No. Z10,025-0; also see Aldrichim Acta, 1983, 16[1,3] for a review of the preparation and reactions of diazomethane.

6.5 Six or 12 Position Analytical Concentrator -- Organomation, N-EVAP Model #111/6917 or equivalent.

6.6 Gas Chromatograph -- Analytical system complete with gas chromatograph equipped for electron capture detection, split/splitless capillary injection, temperature programming, differential flow control, and with all required accessories including syringes, analytical columns, gases and strip-chart recorder. A data system is recommended for measuring peak areas. An autoinjector is recommended for improved precision of analyses. The gases flowing through the election capture detector should be vented through the laboratory fume hood system.

6.7 Vials -- Amber glass, 7-10 mL capacity with TFE-fluorocarbon lined screw cap.

6.8 Primary GC Column -- DB-1701 or equivalent bonded, fused silica column, 30m x 0.32mm ID, 0.25 µm film thickness.

6.9 Confirmatory GC Column -- DB-210 or equivalent bonded, fused silica column, 30 m x 0.32 mm ID, 0.50 µm film thickness.

6.10 Pasteur Pipets -- Glass disposable, 5¾" length wide bore diameter. (Baxter Scientific Products Giant-Pette-Pipets, Cat. No. P5240-1 or equivalent)

6.11 Volumetric Ware -- 5 mL.

6.12 pH Meter -- Wide range with the capability of accurate pH measurements in the 0-1 and 11-12 ranges. The use of separate glass pH electrode and calomel reference electrode facilitates this measurement.

7.0 REAGENTS AND CONSUMABLE MATERIALS

7.1 Glass Wool -- Acid washed, Heat to 400°C for one hour.

7.2 Reagent Water -- Reagent water is defined as a water in which an interference is not observed at the method detection limit of each parameter of interest.

7.2.1 A Milli-pore Super-Q water system or its equivalent may be used to generate deionized reagent water. Distilled water that has been charcoal filtered may also be suitable.

7.2.2 Test reagent water each day it is used by analyzing according to Section 11.0.

7.3 Methanol -- Pesticide quality or equivalent.

7.4 Ethyl Ether -- Nanograde, redistilled in glass if necessary. Ethers must be free of peroxides as indicated by EM Quant test strips, available from EM Science, Gibbstown, NJ. Procedures recommended for removal of peroxides are provided with the test strips. Ethers must be periodically tested (monthly) for peroxide formation during use.

7.5 Methyl-Tert-Butyl Ether -- Nanograde, redistilled in glass if necessary. The same peroxide precautions as in Section 7.4 apply to this ether.

7.6 Sodium Sulfate -- ACS, granular, acidified, anhydrous. Heat in a shallow tray at 400°C for a minimum of four hours to remove phthalates and other interfering organic substances. Alternatively, extract with methylene chloride in a Soxhlet apparatus for 48 hours. Acidify by slurrying 100 g sodium sulfate with just enough ethyl ether to cover the solid. Add 0.1 mL concentrated sulfuric acid and mix thoroughly. Remove the ether under vacuum or allow to evaporate in a loosely covered beaker in a hood. Mix 1 g of the resulting solid with 5 mL of reagent water and measure the pH of the mixture. It must be below pH 4. Store at 130°C.

7.7 Sulfuric Acid Solution (1+1) -- Slowly add 50 mL H_2SO_4 (sp. gr. 1.84) to 50 mL of reagent water.

7.8 Sodium Hydroxide (NaOH), 1N -- Dissolve 4 g ACS grade in reagent water and dilute up to 100 mL in a 100 mL volumetric flask.

7.9 Potassium Hydroxide (KOH), 37% -- Dissolve 37 g of ACS grade in reagent water and dilute up to 100 mL in a 100 mL volumetric flask.

7.10 Carbitol -- (Diethylene glycol monoethyl ether), ACS. Available from Aldrich Chemical Co.

7.11 Diazald -- (N-methyl-N-nitroso-p-toluenesulfonamide), ACS. Available from Aldrich Chemical Co.

7.12 Diazald Solution -- Prepare a solution containing 10 g Diazald in 100 mL of a 50:50 by volume mixture of ethyl ether and carbitol. This solution is stable for one month or longer when stored at 4°C in an amber colored bottle with a Teflon-lined screw cap.

7.13 Silica Gel -- Chromatographic grade, nominal 100 mesh. Heat to 400°C for four hours. Store at 130°C.

7.14 Acetone -- ACS reagent grade or equivalent.

7.15 Ammonium Chloride -- ACS reagent grade or equivalent.

7.16 Sodium Sulfite -- ACS reagent grade or equivalent.

7.17 1,2,3-Trichloropropane -- Aldrich Chemical, 99+%.

7.18 3,5-Dichlorobenzoic Acid -- Aldrich Chemical, 99%.

7.19 Copper (II) Sulfate Pentahydrate -- ACS reagent grade or equivalent.

8.0 SAMPLE COLLECTION, PRESERVATION AND STORAGE

8.1 Grab samples must be collected in accordance with conventional sampling practices[9] using glass containers with TFE-lined screw-caps and capacities in excess of 100 mL.

8.1.1 Prior to shipment to the field, to combine residual chlorine, add crystalline ammonium chloride (NH_4Cl) to the sample container in an amount to produce a concentration of 100 mg/L in the sample. Alternatively, add 1.0 mL of a 10 mg/mL aqueous solution of NH_4Cl to the sample bottle for each 100 mL of sample bottle capacity immediately prior to sample collection. Granular ammonium chloride may also be added directly to the sample bottle.

8.1.2 After collecting the sample in the bottle containing the dechlorination reagent, seal the bottle and agitate for one minute.

8.1.3 Samples must be iced or refrigerated at 4°C and maintained at these conditions away from light until extraction. Holding studies performed to date have suggested that, in samples dechlorinated with NH_4Cl, the analytes are stable for up to 28 days. Since stability may be matrix dependent, the analyst should verify that the prescribed preservation technique is suitable for the samples under study.

8.1.4 Dried extract concentrates (Section 11.3.6) should be stored at 0-4°C away from light in glass vials with TFE-faced caps. Extracts should be analyzed within 48 hours following preparation.

9.0 CALIBRATION

9.1 Establish GC operating parameters equivalent to specifications in Table 1. The GC system must be calibrated using the internal standard (IS) technique.

9.2 Internal Standard Calibration Procedure -- This approach requires the analyst to select one or more internal standards which are compatible in analytical behavior with the method analytes. For the single laboratory precision and accuracy data reported in Tables 2-7, one internal standard (1,2,3-trichloropropane) was employed. The concentration of the internal standard used in obtaining these data was 0.4 µg/mL in the final 5.0 mL concentrate (Section 11.3.3).

9.2.1 Prepare separate stock standard solutions for each compound of interest at a concentration of 1-5 mg/mL in MTBE solvent. Method analytes may be obtained as neat materials or ampulized solutions (>99% purity) from a number of commercial suppliers.

9.2.2 Prepare primary dilution standard solutions by combining and diluting stock calibration standards with MTBE. The primary dilution standards are used to prepare calibration standards, which comprise at least three concentration levels (optimally five) of each analyte with the lowest standard being at or near the method detection limit of each analyte. The concentrations of the other standards should define a range containing the expected sample concentrations or the working range of the detector.

9.2.2.1 Calibration standards for 100 mL sample extraction (Section 11.1). These standards are prepared in the final 5 mL MTBE extract form and thus are not subject to the extraction procedure. These standards must be esterified according to the procedure beginning in Section 11.3.3. Thus, the individual calibration standards are initially prepared in approximately 4 mL MTBE to allow for the addition of diazomethane solution and the final dilution to 5.0 mL as called for in Section 11.3.3.2.

NOTE: The concentrations of the 5 mL calibration standards must be equivalent, after correction for the concentration factor, to aqueous standards which span the concentration range called for in Section 9.2.2.

9.2.2.2 Calibration standards for 30 mL (Microextraction) Samples (Section 11.2). In this procedure, aqueous standards are prepared by dilution of primary dilution standards with reagent water. These aqueous standards are treated and extracted in the same manner as the samples according to Section 11.2. The final 2 mL extract is esterified according to the procedure beginning in Section 11.3.4.

9.2.3 Include a surrogate analyte within the calibration standards prepared in Section 9.2.2. Both 3,5-dichlorobenzoic acid and 2,3-dichloropropanoic acid have been used as surrogate analytes in this method.

9.2.4 Inject 2 µL of each standard and calculate the relative response for each analyte (RR_a) using the equation:

$$RR_a = A_a / A_{is}$$

where: A_a = the peak area of the analyte.
A_{is} = the peak area of the internal standard.

9.2.5 Generate a calibration curve of RR_a versus analyte concentration of the standards expressed in equivalent µg/L in the original aqueous sample. The working calibration curve must be verified daily by measurement of one or more calibration standards. If the response for any analyte falls outside the predicted response by more than 15%, the calibration

check must be repeated using a freshly prepared calibration standard. Should the retest fail, a new calibration curve must be generated.

10.0 QUALITY CONTROL

10.1 Minimum quality control (QC) requirements are initial demonstration of laboratory capability, determination of surrogate compound recoveries in each sample and blank, monitoring internal standard peak area or height in each sample and blank, analysis of laboratory reagent blanks, laboratory fortified blanks, laboratory fortified sample matrices, and QC samples. Additional quality control practices are recommended.

10.2 Laboratory Reagent Blanks (LRB) -- Before processing any samples, the analyst must analyze at least one LRB to demonstrate that all glassware and reagent interferences are under control. In addition, each time a set of samples is extracted or reagents are changed, a LRB must be analyzed. If within the retention time window (Section 11.4.4) of any analyte, the LRB produces a peak that would prevent the determination of that analyte, determine the source of contamination and eliminate the interference before processing samples.

10.3 Initial Demonstration of Capability

10.3.1 Select a representative fortified concentration for each of the target analytes. Concentrations near Level 3 (Table 4) are recommended. Prepare a laboratory control (LC) sample concentrate in methanol 1000 times more concentrated than the selected concentration. With a syringe, add 100 µL of the LC sample concentrate to each of four to seven 100 mL aliquots of reagent water. Analyze the aliquots according to the method beginning in Section 11.0 and calculate mean recoveries and standard deviation for each analyte.

10.3.2 Calculate the mean percent recovery (R) and the standard deviation of the recovery (S_R). For each analyte, the mean recovery values for all must fall in the range of R ±30% (or within R ±3S_R if broader) using the values for R and S_R for reagent water in Table 4. The standard deviation should be less than ±30% or 3S_R, whichever is larger. For those compounds that meet these criteria, performance is considered acceptable and sample analysis may begin. For those compounds that fail these criteria, this procedure must be repeated using a minimum of five fresh samples until satisfactory performance has been demonstrated.

10.3.3 The initial demonstration of capability is used primarily to preclude a laboratory from analyzing unknown samples via a new, unfamiliar method prior to obtaining some experience with it. It is expected that as laboratory personnel gain experience with this method, the quality of data will improve beyond those required here.

10.3.4 The analyst is permitted to modify GC columns, GC conditions, detectors, extraction techniques, concentration techniques (i.e., evaporation techniques), internal standard or surrogate compounds. Each time such method modifications are made, the analyst must repeat the procedures in Section 10.3.1.

10.4 Assessing Surrogate Recovery

10.4.1 When surrogate recovery from a sample or method blank is <70% or >130%, check (1) calculations to locate possible errors, (2) standard solutions for degradation, (3) contamination, and (4) instrument performance. If those steps do not reveal the cause of the problem, reanalyze the extract.

10.4.2 If the extract reanalysis fails the 70-130% recovery criterion, the problem must be identified and corrected before continuing.

10.4.3 If the extract reanalysis meets the surrogate recovery criterion, report only data for the analyzed extract. If sample extract continues to fail the recovery criterion, report all data for that sample as suspect.

10.4.4 Develop and maintain control charts on surrogate recovery as described in Section 10.6.2. Charting of surrogate recoveries is an especially valuable activity, since these are present in every sample and the analytical results will form a significant record of data quality.

10.5 Assessing the Internal Standard

10.5.1 When using the internal standard calibration procedure, the analyst is expected to monitor the IS response (peak area or peak height) of all samples during each analysis day. The IS response for any sample chromatogram should not deviate from daily calibration standard's IS response by more than 30%.

10.5.2 If >30% deviation occurs with an individual extract, optimize instrument performance and inject a second aliquot of that extract.

10.5.2.1 If the reinjected aliquot produces an acceptable internal standard response, report results for that aliquot.

10.5.2.2 If a deviation of greater than 30% is obtained for the reinjected extract, analysis of the samples should be repeated beginning with Section 11.0, provided the sample is still available. Otherwise, report results obtained from the reinjected extract, but annotate as suspect.

10.5.3 If consecutive samples fail the IS response acceptance criterion, immediately analyze a calibration check standard.

10.5.3.1 If the check standard provides a response factor (RF) within 20% of the predicted value, then follow procedures itemized in Section 10.5.2 for each sample failing the IS response criterion.

10.5.3.2 If the check standard provides a response factor which deviates more than 20% of the predicted value, then the analyst must recalibrate, as specified in Section 9.0.

10.6 Laboratory Fortified Blank (LFB)

10.6.1 The laboratory must analyze at least one LFB sample with every 20 samples or one per sample set (all samples extracted within a 24-hour period), whichever is greater. Fortified concentrations near Level 3 (Table 4) are recommended. Calculate accuracy as percent recovery (R). If the recovery of any analyte falls outside the control limits (see Section 10.6.2), that analyte is judged out of control, and the source of the problem should be identified and resolved before continuing analyses.

10.6.2 Prepare control charts based on mean upper and lower control limits, $R \pm 3\ S_R$. The initial demonstration of capability (Section 10.3) establishes the initial limits. After each four to six new recovery measurements, recalculate R and S_R using all the data, and construct new control limits. When the total number of data points reach 20, update the control limits by calculating R and S_R using only the most recent 20 data points. At least quarterly, replicates of LFBs should be analyzed to determine the precision of the laboratory measurements. Add these results to the ongoing control charts to document data quality.

10.7 Laboratory Fortified Sample Matrix

10.7.1 The laboratory must add known concentrations of analytes to a minimum of 10% of the routine samples or one concentration per sample set, whichever is greater. The concentrations should be equal to or greater than the background concentrations in the sample selected for fortification. Ideally, the concentration should be the same as that used for the laboratory fortified blank (Section 10.6). Over time, samples from all routine sample sources should be fortified.

10.7.2 Calculate the mean percent recovery, R, of the concentration for each analyte, after correcting the total mean measured concentration, A, from the fortified sample for the back-ground concentration, B, measured in the unfortified sample, i.e.:

$$R = 100 (A - B) / C,$$

where: C = the fortifying concentration.

Compare these values to control limits appropriate for reagent water data collected in the same fashion (Section 10.6).

10.7.3 If the analysis of the unfortified sample reveals the absence of measurable background concentrations, and the added concentrations are those specified in Section 10.6, then the appropriate control limits would be the acceptance limits in Section 10.6.

10.7.4 If the sample contains measurable background concentrations of analytes, calculate mean recovery of the fortified concentration, R, for each such analyte after correcting for the background concentration.

$$R = 100 (A - B)/C$$

Compare these values to reagent water recovery data, R*, at comparable fortified concentrations from Tables 3-5. Results are considered comparable if the measured recoveries fall within the range,

$$R^* \pm 3S_c,$$

where S_c = the estimated percent relative standard deviation in the measurement of the fortified concentration.

By contrast to the measurement of recoveries in reagent water (Section 10.6.2) or matrix samples without background (Section 10.7.3), the relative standard deviation, S_c, must be expressed as the statistical sum of variation from two sources, the measurement of the total concentration as well as the measurement of background concentration. In this case, variances, defined as S^2, are additive and S_c can be expressed as,

$$S_c^2 = S_a^2 + S_b^2$$

$$\text{or } S_c = (S_a^2 + S_b^2)^{1/2},$$

where S_a and S_b = the percent relative standard deviations of the total measured concentration and the background concentration respectively.

The value of S_a may be estimated from the mean measurement of A above or from data at comparable concentrations from Tables 3-5. Likewise, S_b can be measured from repetitive measurements of the background concentration or estimated from comparable concentration data from Tables 2-5.

10.7.5 If the recovery of any such analyte falls outside the designated range, and the laboratory performance for that analyte is shown to be in control (Section 10.6), the recovery problem encountered with the fortified sample is judged to be matrix related, not system related. The result for that analyte in the unfortified sample is labeled suspect/matrix to inform the data user that the results are suspect due to matrix effects.

10.8 Quality Control Sample (QCS) -- At least quarterly, analyze a QCS from an external source. If measured analyte concentrations are not of acceptable accuracy, check the entire analytical procedure to locate and correct the problem source.

10.9 The laboratory may adapt additional quality control practices for use with this method. The specific practices that are most productive depend upon the needs of the laboratory and the nature of the samples. For example, field or laboratory duplicates may be analyzed to assess the precision of the environmental measurements or field reagent blanks may be used to assess contamination of samples under site conditions, transportation and storage.

11.0 PROCEDURE

11.1 Sample Preparation -- 100 mL sample. This procedure employs a sample cleanup step, serial extraction with MTBE, extract concentration and drying prior to esterification (Section 11.3.3). In this procedure, sample standards are prepared in the final 5 mL extract form prior to esterification.

11.1.1 Remove the samples from storage (Section 8.1.3) and allow to equilibrate to room temperature.

11.1.2 Transfer 100 mL of sample with a pipet to a 250 mL separatory funnel. Add 1 mL of 1.0 N NaOH solution. Remove an aliquot and measure pH, which should be approximately 11.5.

11.1.3 Optional -- Add 100 µL of surrogate fortifying solution (5 µg/mL of 3,5-dichlorobenzoic acid or 2,3-dibromo-propanoic acid in methanol) to each sample including standards and blanks.

11.1.4 Return the aliquot to the separatory funnel.

NOTE: If sufficient sample is available, use a separate 100 mL sample to measure the basic pH and to determine the amount of H_2SO_4 required.

The measurement of pH should be done with the wide range pH meter described in Section 6.12. Add 30 mL MTBE. Extract the sample one time by vigorously shaking the funnel for two minutes with periodic venting to release excess pressure. Allow the organic layer to separate

from the water phase for a minimum of 10 minutes. If the emulsion interface between layers is more than one-third the volume of the solvent layer, the analyst must employ mechanical techniques to complete the phase separation. The optimum technique depends upon the sample, but may include stirring, filtration of the emulsion through glass wool, centrifugation, or other physical methods. Discard the organic phase and return the aqueous phase to the 250 mL separatory funnel.

11.1.5 Add sufficient 1:1 H_2SO_4 in reagent water (ca. 15-20 mL) to adjust the pH to pH ≤0.5. Add 15 mL of MTBE and extract for two minutes as in Section 11.1.3. Allow the phases to separate for 10 minutes. If an emulsion persists employ the same procedures for separation as in Section 11.1.3. Separate the phases and collect the MTBE phase in a 40 mL screw cap vial (Section 6.2). Add 15 mL of MTBE to the sample and repeat the extraction a second time. Combine the extracts in the 40 mL vial.

11.1.6 Extract concentration -- Evaporate the solvent at room temperature to a volume of 1-2 mL under a gentle stream of dry nitrogen. Under these conditions the sample cools during evaporation and some condensation will be observed on the outside of the vial. Alternately place the vials in a water bath maintained at 35°C and concentrate to a minimum volume of 2 mL. The method validation data in Tables 2-7 were obtained with the former technique. These gentle concentration conditions are necessary because of the volatility of the monohaloacetic acids.

11.1.7 Extract drying technique

11.1.7.1 Prepare sodium sulfate drying tubes by inserting a small piece of acid washed glass wool into the bottom, restricted, end of a wide bore, Pasteur pipet (Section 6.10).

11.1.7.2 Add a column of approximately 5 cm acidified sodium sulfate. Tap pipet gently to pack sodium sulfate.

11.1.7.3 Immediately, using another Pasteur pipet, transfer the 1-2 mL MTBE extract from the 40 mL vial into the top of the drying tube. A small amount of separated water phase will likely be present in the bottom of the 40 mL vial. Avoid transferring any of the water phase. Examine the lower portion of the Pasteur pipet to see whether a separate water phase is present. Collect dried extract in a 5.0 mL volumetric flask.

11.1.7.4 Rinse sides of 40 mL sample tube with approximately 0.7 mL of clean MTBE. Transfer this MTBE into the drying tube using the same pipet as in Step 3.

11.1.7.5 Repeat Step 4 until the volumetric flask contains 3.8-4.0 mL.

11.2 Sample Preparation -- 30 mL sample. Without employing any sample cleanup, a 30 mL aliquot is salted and extracted with a single aliquot of MTBE. The extract is esterified directly, without a prior drying step. Aqueous standards are also processed through the complete procedure[11].

11.2.1 Remove the samples from storage and allow them to equilibrate to room temperature.

11.2.2 Transfer 30 mL sample or standard with a pipet to a 40 mL vial equipped with a Teflon-faced screw cap. A slightly larger vial might be more suitable.

11.2.3 Optional -- Add 30 µL of surrogate spiking solution (10 µg/mL 2,3-dibromopropanoic acid in methanol) to each sample including standards and blanks.

11.2.4 Add 1.5-3.0 mL concentrated sulfuric acid to lower the pH to less than 0.5. The analyst must verify that the pH is less than 0.5.

11.2.5 Add accurately 3.0 mL methyl tertiary butyl ether (MTBE) using a pipet.

11.2.6 Add 3 g copper (II) sulfate pentahydrate, followed by 12 g acidified sodium sulfate, carefully to prevent splashing the MTBE. The blue color of the copper sulfate solution facilitates observation of the phase interface when the organic extract is transferred in Section 11.2.10.

11.2.7 Cap all vials immediately, and shake by hand to break up clumps. Vent, recap, and lay vials on their sides until all vials have been shaken. Clumps of undissolved salt will cause loss of analytes.

11.2.8 Place vials in a mechanical shaker and shake for approximately 30 minutes. Required shaking time will vary from shaker to shaker. Shaking by hand is perfectly acceptable. The required time for this will have to be established during the initial demonstration of capability.

11.2.9 Remove vials from shaker and allow to stand for five minutes for phase separation.

11.2.10 Transfer exactly 2.0 mL of the ether extract (top layer) using a pipet into a 2.0 mL volumetric flask.

Be careful to not include any water.

11.2.11 Using a stream of clean, dry nitrogen, evaporate approximately 0.3 mL of MTBE from the flask to make room for the addition of diazomethane and internal standard (Section 11.3.4.2).

11.3 Esterification of Acids

11.3.1 Assemble the diazomethane generator shown in Figure 1 in a hood. The collection vessel is a 10-15 mL vial, equipped with a Teflon-lined screw cap and maintained at 0-5°C. It is perfectly acceptable to use a commercially available diazomethane generator in place of the one shown in Figure 1.

11.3.2 Add a sufficient amount of ethyl ether to Tube 1 to cover the first impinger. Add 5 mL of MTBE to the collection vial. Set the nitrogen flow at 5-10 cm^3/min. Add 2 mL Diazald solution and 1.5 mL of 37% KOH solution to the second impinger. Connect the tubing as shown and allow the N_2 flow to purge the diazomethane from the reaction vessel into the collection vial for 30 minutes. Cap the vial when collection is complete and maintain at 0-5°C. When stored at 0-5°C this diazomethane solution may be used over a period of 48 hours.

11.3.3 Esterification of 100 mL Extract (from Section 11.1.7.5)

11.3.3.1 Fortify the sample (Section 11.1.7.5) and standard (Section 9.2.2.1) extracts with identical volumes of the internal standard(s). The appropriate amount of internal standard is dependent on the calibration range. As a general rule, the internal standard response should be approximately equal to the response produced by the middle trichloroacetic acid calibration standard. For the validation data in Table 3-7, 20 µL of a 100 µg/mL internal standard solution in MTBE were added to the 5.0 mL concentrate to yield a concentration of 0.4 µg/mL.

11.3.3.2 Add 100 µL methanol and 500 µL of cold diazomethane solution (Section 11.3.2). A persistent pale yellow color after the addition of diazomethane indicates that an excess was available for esterification of the analytes. If this is not obtained, continue adding successive 50 µL aliquots of diazomethane solution until the persistent yellow color is obtained. Dilute to a final volume of 5.0 mL with MTBE.

11.3.4 Esterification of 30 mL extract (from Section 11.2.11).

11.3.4.1 Add 20 µL of a 20 µg/mL solution of 1,2,3-trichloropropane in methanol as the internal standard to the extract from aqueous standards or samples (Section 11.2.11).

11.3.4.2 Add 250 µL of cold diazomethane solution (Section 11.3.2). A persistent yellow color representing excess diazomethane should be observed in the solution. The final extract volume should be 2.0 mL.

11.3.5 Allow the sample from Section 11.3.3.2 or 11.3.4.2 to remain in contact with dizaoamethane for 30 minutes. Remove any unreacted diazomethane by addition of 0.2 g silica gel. Effervescence due to nitrogen evolution is a further indication that excess diazomethane is present. Mix gently by inverting once.

11.3.6 After a contact time of 15-20 minutes, transfer a portion of the extract solution to an appropriate vial for injection into the GC. A duplicate GC vial may be filled from excess sample extract, if desired. Analyze the samples as soon as possible. Alternatively, the sample extract, after removal from the silica gel, may be stored for 48 hours at 0-4°C away from light in glass vials with TFE-lined caps.

11.4 Gas Chromatography

11.4.1 Table 1 summarizes the recommended operating conditions for the GC. Included in Table 1 are the retention times observed using this method. An example of the separation achieved using these conditions is shown in Figure 2. Other GC columns, chromatographic conditions, or detectors may be used if the requirements of Section 10.3 are met.

11.4.2 Calibrate the system daily as described in Section 9.0. The standards and extracts must be in MTBE.

11.4.3 Inject 2 µL of the sample extract. Record the resulting peak size in area units.

11.4.4 The width of the retention time window used to make identifications should be based upon measurements of actual retention time variations of standards over the course of a day. Three times the standard deviation of a retention time can be used to calculate a suggested window size for a compound. However, the experience of the analyst should weigh heavily in the interpretation of chromatograms.

11.4.5 If the response for the peak exceeds the working range of the system, dilute the extract and reanalyze.

12.0 CALCULATIONS

12.1 Calculate analyte concentrations in the sample from the response for the analyte relative to the internal standard (RR_a) using the equation in Section 9.2.4.

12.2 For samples processed as part of a set where recoveries falls outside of the control limits established in Section 10.0, results for the affected analytes must be labeled as suspect.

13.0 PRECISION AND ACCURACY

13.1 In a single laboratory (EMSL-Cincinnati), recovery and precision data were obtained at four concentrations in reagent water (Tables 2-5). Tables 6 and 7 give representative recovery and precision data for fortified tap water, which had been chlorinated. The Method Detection Limit (MDL)[10] data are given in Table 2, and Tables 3-5 illustrate instrument range. These method validation data were obtained by the 100 mL sample extraction procedure. In the calculation of MDL's, the mean observed concentrations were not corrected for recovery. Method detection limits using the microextraction sample preparation were determined from eight replicate analyses of fortified reagent water. The data showed they were not significantly different from those listed in Table 2, obtained using the large sample preparation procedure. Also, data obtained from replicate analyses of a variety of drinking water samples using the microextraction sample preparation procedure were found to be essentially equivalent to the 100 mL procedure. The data indicate that both sample preparation procedures presented for the haloacetic acids provide good analytical results under routine use for finished drinking waters. However, the microextraction procedure has not been tested on samples from formation potential tests in which the total concentration of haloacetic acids may exceed 100 µg/L. In these cases, the cleanup steps presented in this method may be necessary to eliminate interferences.

14.0 REFERENCES

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TABLE 1. RETENTION DATA AND CHROMATOGRAPHIC CONDITIONS

Analyte	Retention Time (min) Column A	Column B
Monochloroacetic Acid	5.77	10.97
Monobromoacetic Acid	8.70	13.03
Dichloroacetic Acid	9.40	12.72
Trichloroacetic Acid	12.20	14.37
1,2,3-Trichloropropane[a]	13.28	13.87
Bromochloroacetic Acid	13.52	15.11
Dibromoacetic Acid	16.00	16.83
2-Chlorophenol	16.65	18.32
2,4-Dichlorophenol	20.70	19.27
2,4,6-Trichlorophenol	21.94	22.08
3,5-Dichlorobenzoic Acid[b]	23.06	23.95

Column A: DB-1701, 30 m x 0.32 mm i.d., 0.25 µm film thickness, Injector Temp. = 200°C, Detector Temp. = 290°C, Helium Linear Velocity = 27 cm/sec, Splitless injection with 30 second delay

Program: Hold at 50°C for 10 minutes, to 210°C at 10°C/min. and hold 10 minutes.

Column B: DB-210, 30 m x 0.32 mm i.d., 0.50 µm film thickness, Injector Temp. = 200°C, Detector Temp. = 290°C, Linear Helium Flow = 25 cm/sec, splitless injection with 30 second delay.

Program: Hold at 50°C for 10 minutes, to 210°< at 10°C/min and hold 10 minutes.

[a]Internal Standard.
[b]Surrogate Acid.

TABLE 2. ANALYTE RECOVERY AND PRECISION DATA AND METHOD DETECTION LIMITS[a]

LEVEL 1 IN REAGENT WATER

Analyte	Fortified Conc. (µg/L)	Mean Meas. Conc. (µg/L)	Std. Dev. (µg/L)	Rel. Std. Dev. (%)	Mean Recovery (%)	Method Detection Limit (µg/L)
Monochloroacetic Acid	0.050	0.037	0.014	38	74	0.052
Monobromoacetic Acid	0.050	0.029	0.002	7	58	0.0074
Dichloroacetic Acid	0.050	0.042	0.004	10	84	0.015
Trichloroacetic Acid	0.050	0.039	0.023	59	78	0.085
Bromochloroacetic Acid	0.100	0.150	0.063	41	150	0.14
Dibromoacetic Acid	0.050	0.029	0.004	14	58	0.015
2-Chlorophenol	0.200	0.123	0.038	31	61	0.14
2,4-Dichlorophenol	0.250	0.147	0.085	58	59	0.32
2,4,6-Trichlorophenol	0.050	0.033	0.006	18	66	0.022

[a]Produced by analysis of seven aliquots of fortified reagent water (Reference 10).

TABLE 3. ANALYTE RECOVERY AND PRECISION DATA[a]

LEVEL 2 IN REAGENT WATER

Analyte	Fortified Conc. (µg/L)	Mean Meas. Conc. (µg/L)	Std. Dev. (µg/L)	Rel. Std. Dev. (%)	Mean Recovery (%)
Monochloroacetic Acid	1.0	0.81	0.065	8	81
Monobromoacetic Acid	1.0	0.61	0.046	8	61
Dichloroacetic Acid	2.5	2.53	0.15	6	101
Trichloroacetic Acid	0.50	0.30	0.032	11	60
Bromochloroacetic Acid	0.50	0.51	0.041	8	103
Dibromoacetic Acid	1.25	0.81	0.033	4	65
2-Chlorophenol	2.50	1.79	0.62	35	72
2,4-Dichlorophenol	1.00	0.74	0.072	10	74
2,4,6-Trichlorophenol	0.50	0.43	0.032	7	86

[a]Produced by the analysis of seven aliquots of fortified reagent water.

TABLE 4. ANALYTE RECOVERY AND PRECISION DATA[a]

LEVEL 3 IN REAGENT WATER

Analyte	Fortified Conc. (µg/L)	Mean Meas. Conc. (µg/L)	Std. Dev. (µg/L)	Rel. Std. Dev. (%)	Mean Recovery (%)
Monochloroacetic Acid	5.0	3.47	0.25	7	69
Monobromoacetic Acid	5.0	2.85	0.13	5	57
Dichloroacetic Acid	12.50	11.84	0.25	2	95
Trichloroacetic Acid	2.50	2.18	0.083	4	87
Bromochloroacetic Acid	1.00	0.90	0.059	7	90
Dibromoacetic Acid	2.50	1.84	0.11	6	74
2-Chlorophenol	6.25	5.66	0.34	6	91
2,4-Dichlorophenol	5.00	5.12	0.47	9	102
2,4,6-Trichlorophenol	2.50	2.47	0.054	2	99

[a]Produced by the analysis of seven aliquots of fortified reagent water.

TABLE 5. ANALYTE RECOVERY AND PRECISION DATA[a]

LEVEL 4 IN REAGENT WATER

Analyte	Fortified Conc. (µg/L)	Mean Meas. Conc. (µg/L)	Std. Dev. (µg/L)	Rel. Std. Dev. (%)	Mean Recovery (%)
Monochloroacetic Acid	10.0	7.08	0.16	2.3	71
Monobromoacetic Acid	10.0	7.62	0.18	2.4	76
Dichloroacetic Acid	25.0	24.1	0.41	1.7	96
Trichloroacetic Acid	5.00	5.70	0.11	1.9	114
Bromochloroacetic Acid	5.00	4.66	0.22	4.7	93
Dibromoacetic Acid	5.00	5.35	0.096	1.8	107
2-Chlorophenol	12.50	12.7	0.66	5.2	102
2,4-Dichlorophenol	10.00	11.0	0.57	5.2	110
2,4,6-Trichlorophenol	5.00	5.18	0.072	1.4	104

[a]Produced by the analysis of seven aliquots of fortified reagent water.

TABLE 6. ANALYTE RECOVERY AND PRECISION DATA[a]

LEVEL 1 IN TAP WATER

Analyte	Back-ground Conc. (µg/L)	Fortified Conc. (µg/L)	Mean[b] Meas. Conc. (µg/L)	Std. Dev. (µg/L)	Rel. Std. Dev. (%)	Mean Recovery (%)
Monochloroacetic Acid	1.83	3.60	2.23	0.19	8	62
Monobromacetic Acid	0.32	1.20	1.36	0.11	8	113
Dichloroacetic Acid	32.3	36.0	26.0	2.4	9	72
Trichloroacetic Acid	5.4	10.0	10.7	0.83	8	107
Dibromoacetic Acid	10.6	15.0	19.2	1.4	7	128
2-Chlorophenol	11.5	45.0	41.6	8.5	20	92
2,4-Dichlorophenol	0	10.0	12.0	1.2	10	120
2,4,6-Trichlorophenol	0	2.00	28.8	0.23	8	144

[a]Produced by the analysis of seven aliquots of fortified tap water.
[b]Background level subtracted.

TABLE 7. ANALYTE RECOVERY AND PRECISION DATA[a]

LEVEL 2 IN TAP WATER

Analyte	Back-ground Conc. (µg/L)	Fortified Conc. (µg/L)	Mean[b] Meas. Conc. (µg/L)	Std. Dev. (µg/L)	Rel. Std. Dev. (%)	Mean Recovery (%)
Monochloroacetic Acid	1.44	10.0	6.45	0.26	40	64
Monobromacetic Acid	0.27	4.00	3.85	0.20	5	96
Dichloroacetic Acid	27.9	72.0	61.0	2.9	5	85
Trichloroacetic Acid	49.2	20.0	20.7	1.0	5	104
Dibromoacetic Acid	11.0	30.0	34.1	0.89	3	114
2-Chlorophenol	11.0	60.0	69.8	6.0	9	116
2,4-Dichlorophenol	0	30.0	26.9	1.5	55	90
2,4,6-Trichlorophenol	0	10.0	10.7	0.27	2	107

[a]Produced by the analysis of seven aliquots of fortified tap water.
[b]Background level subtracted.

FIGURE 2A

Spiked Reagent Water

1) Monochloracetic Acid - 6.25 µg/L
2) Monobromacetic Acid - 6.25 µg/L
3) Dichloroacetic Acid - 6.25 µg/L
4) Trichloroacetic Acid - 1.6 µg/L
5) Internal Standard - 20 µg/L
6) Dibromoacetic Acid - 1.0 µg/L
7) 2-Chloro-Phenol - 6.25 µg/L
8) 2,4-Dichlorophenol - 6.25 µg/L
9) 2,4,6-Trichorophenol - 1.6 µg/L

FIGURE 2B

Representative Tap Water Sample

1) Monochloracetic Acid - Background + 5 µg/L Spike
2) Monobromacetic Acid - Background + 5 µg/L Spike
3) Dichloroacetic Acid - 13.4 µg/L
4) Trichloroacetic Acid - 3.7 µg/L
5) Internal Standard - 20 µg/L
6) Dibromoacetic Acid - 2.0 µg/L

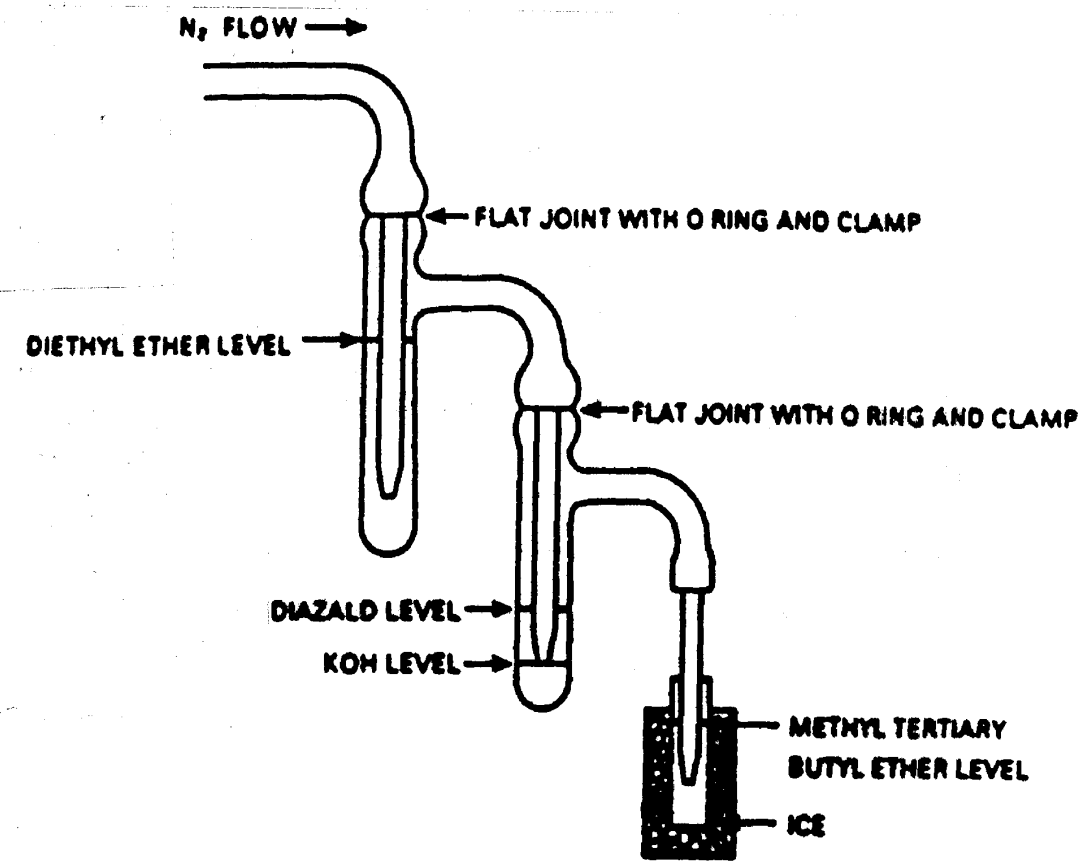

FIGURE 1. DIAZOMETHANE GENERATOR

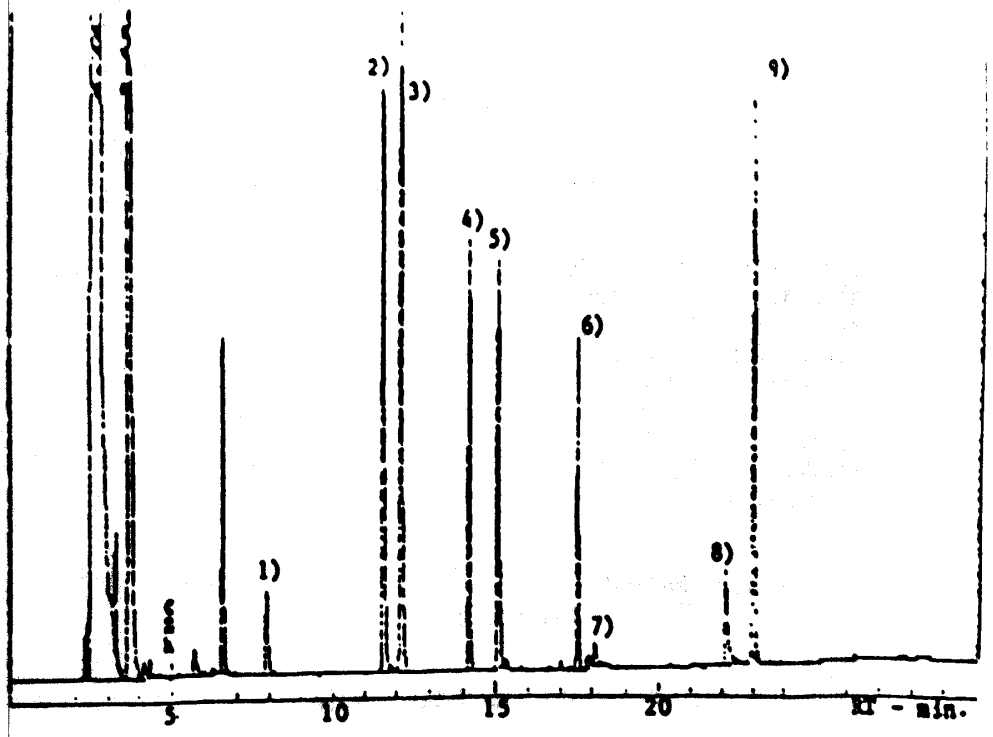

FIGURE 2A

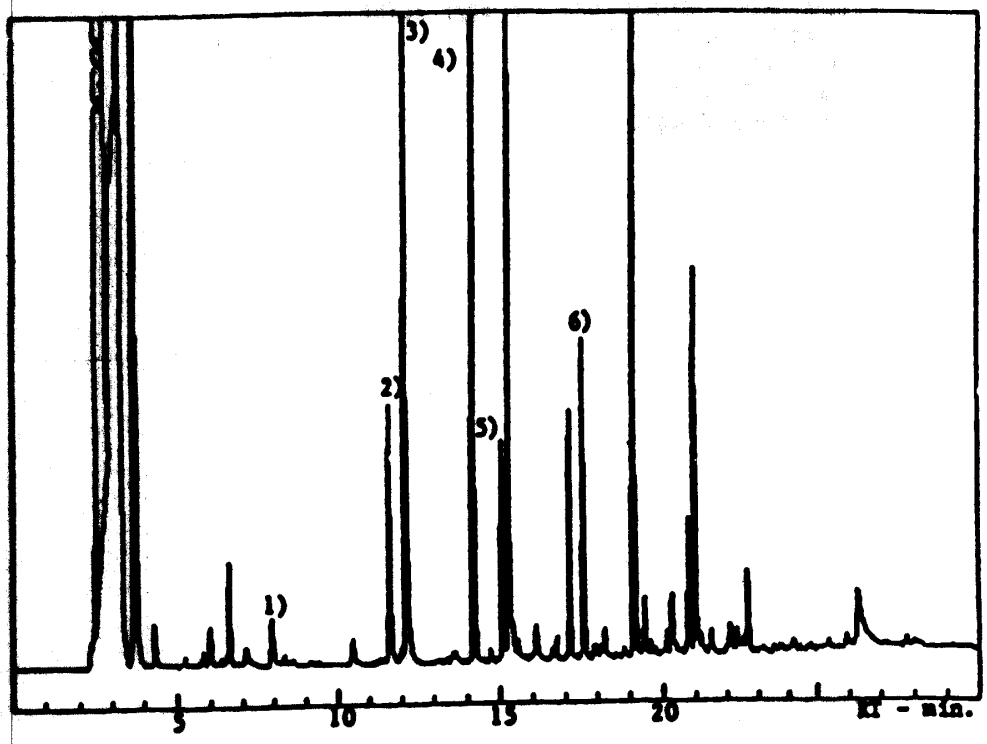

FIGURE 2B