

VOLATILE ORGANIC COMPOUNDS IN DRINKING
WATER OF STILLWATER, OKLAHOMA

By

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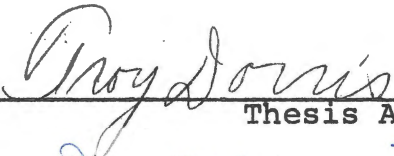
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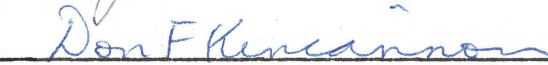
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Thesis Approved:



Thesis Adviser







Dean of the Graduate College

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PREFACE

(The objectives of the present study were to identify metabolites of actinomycetes and blue green algae which are responsible for periodic episodes of earthy, musty tastes and odors in the drinking water of Stillwater, Oklahoma, and to identify as many other volatile organic compounds as possible.)

Dr. Troy C. Dorris served as major adviser. Drs. Don Kincannon and Herb Bruneau served on the advisory committee and criticized the manuscript. Drs. Eisenbraun and Burks gave invaluable assistance with recommendations for chemical analysis. Mr. Keith Kenniberg and Mr. Ron Thomas assisted with analysis of organic compounds on the gas chromatograph-mass spectrometer. Ms. Penny Patty assisted with laboratory procedures. Mr. Chin Chi assisted with graphics. The assistance of all of these people is appreciated. Special thanks is due my husband, Mike, for his assistance with assembling and repairing the sampling equipment and for his support and encouragement throughout the study. Special thanks is due Versar, Inc. for financing the completion and publication of this manuscript and for making available laboratory facilities and providing haloform standards.

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CHAPTER I

INTRODUCTION

Periodic erosion of water quality by odorous metabolites of actinomycetes and blue-green algae is common in Southwestern impoundments, and in recent years earthy, musty tastes and odors have occurred in many U. S. waters (Rosen et al. 1970). The odorous metabolites are detectable in concentrations as low as 0.2 ppb (Henley et al. 1969). They are resistant to bacterial decomposition (Silvey and Roach 1964), and are resistant to and sometimes intensified by conventional water treatment methods (Silvey et al. 1972).

Geosmin (Gerber 1968), mucidone (Dougherty et al. 1966, Dougherty and Morris 1967), and 2-methyl isoborneol (Medsker et al. 1969) have been indirectly established as odor-causing metabolites. Direct identification from raw water has been reported by Rosen et al. (1970) and Henley (1970).

The present project was initiated to identify the taste and odor compounds in tap water of Stillwater, Oklahoma.

Review of Concentration Techniques

Various techniques effectively concentrate organic compounds from aqueous solutions, but each has certain limitations.

Freeze concentration inhibits bacterial degradation, reduces the loss of volatile compounds, and does not alter chemical structure of organic solutes (Baker 1965, Wilson et al. 1964, Shapiro 1961). Limiting requirements include slow freezing, fast mixing, and no more than a 10-fold volumetric concentration.

The advantages of ion exchange, as used by Burnham et al. (1972) and Junk et al. (1974), are that certain organic compounds can be selectively removed from water and from the resin. Efficiencies of concentration and elution, and compound interaction with the resin, are not well established, but the technique holds promise for future use.

Reverse osmosis has been used successfully to concentrate waterborne organics (Klein and Smith 1972, Deinzer et al. 1974, Tardiff and Deinzer 1973, and Kopfler et al. 1975). Except for possible membrane interactions, chemical alterations do not occur, and long periods of time are not required for organics concentration. This technique is potentially useful to trace organic analysis, but more research is needed.

Activated carbon has been used to concentrate organic compounds which cause tastes and odors in water supplies (Braus et al. 1951, Romano and Safferman 1963), and to con-

concentrate trace organic compounds in water prior to identification (Daniels et al. 1963, Booth et al. 1965, Rosen et al. 1963, Burks 1969). The carbon adsorption method (CAM) concentrates organics selectively, but complete elution is not possible (Goldin et al. 1956), and compound modification may occur. Volatile organics tend to be lost during the carbon drying step. During the concentration period selective adsorption and desorption may occur as characteristics of the water change, so that the compounds evidenced at the conclusion of sampling may not be representative of the compounds initially adsorbed.

Substituting flash evaporation for solvent extraction preferentially removes volatile organics which are collected in 0 °C and -30 °C condensers. Also temperature, length of heating time, decomposition and rearrangement reactions, and time for organic recovery are reduced.

Gas stripping has been used by Bellar and Lichtenberg (1974), and Rook (1972, 1974) to remove volatile organics from water. The air flow rate may be varied to maximize efficiency of removal. Since organic compounds encounter no adsorbents or elevated temperatures, no chemical rearrangements or decompositions occur.

X Analytical Techniques

The complex variety of organic compounds found in water samples has been a major obstacle to identification of individual compounds. Solubility separations are useful for partitioning a sample into less complex fractions. Final separations are generally performed by gas chromatography (Baker 1962, Cochran and Bess 1966, Collins 1966).

Compounds resolved by gas-liquid chromatography have been positively identified with mass spectrometry (GC-MS) (Hellar et al. 1975), infrared, nuclear magnetic resonance, or other analytical techniques. GC-MS, infrared, and nuclear magnetic resonance was used by Medsker et al. (1968) to identify geosmin from blue-green algae and actinomycetes. Infrared spectrometry has been used to identify compounds collected by the carbon adsorption method Rosen et al. (1963). GC-MS was used by Rook (1974) to positively identify haloforms in water.

The present study of organic metabolites in tap water utilized carbon adsorption-flash evaporation and air stripping techniques for compound collection. Gas-liquid chromatography-mass spectrometry was used for compound separation and identification.

CHAPTER II

DESCRIPTION OF WATER SOURCE

The original source of all drinking water samples was Lake Carl Blackwell (Fig. 1), a eutrophic impoundment (Ketelle and Uttormark 1971) located seven miles west of Stillwater, Oklahoma. Land use in the watershed is mainly grazing and agriculture. There are no industrial point source discharges. Primarily due to the overgrazed condition of the range and poor agricultural practices, erosion damage is evident on much of the land, and L. Carl Blackwell waters are turbid due to high concentrations of suspended clay particles. The sources of nutrients to support algae blooms include the septic system of a resort, influents from pastured land, fertilized fields in the watershed, and in situ nitrogen fixation. Intense clay turbidity favors development of thermophilic blue-green algae which can float or fix to substrates near the surface between June and September. Acute taste and odor problems in the local drinking water usually coincide with these periods of intense algal activity.

Silvey et al. (1972) have proposed that taste and odor problems are related to seasonal fluctuations in populations of aquatic microorganisms (Fig. 2).

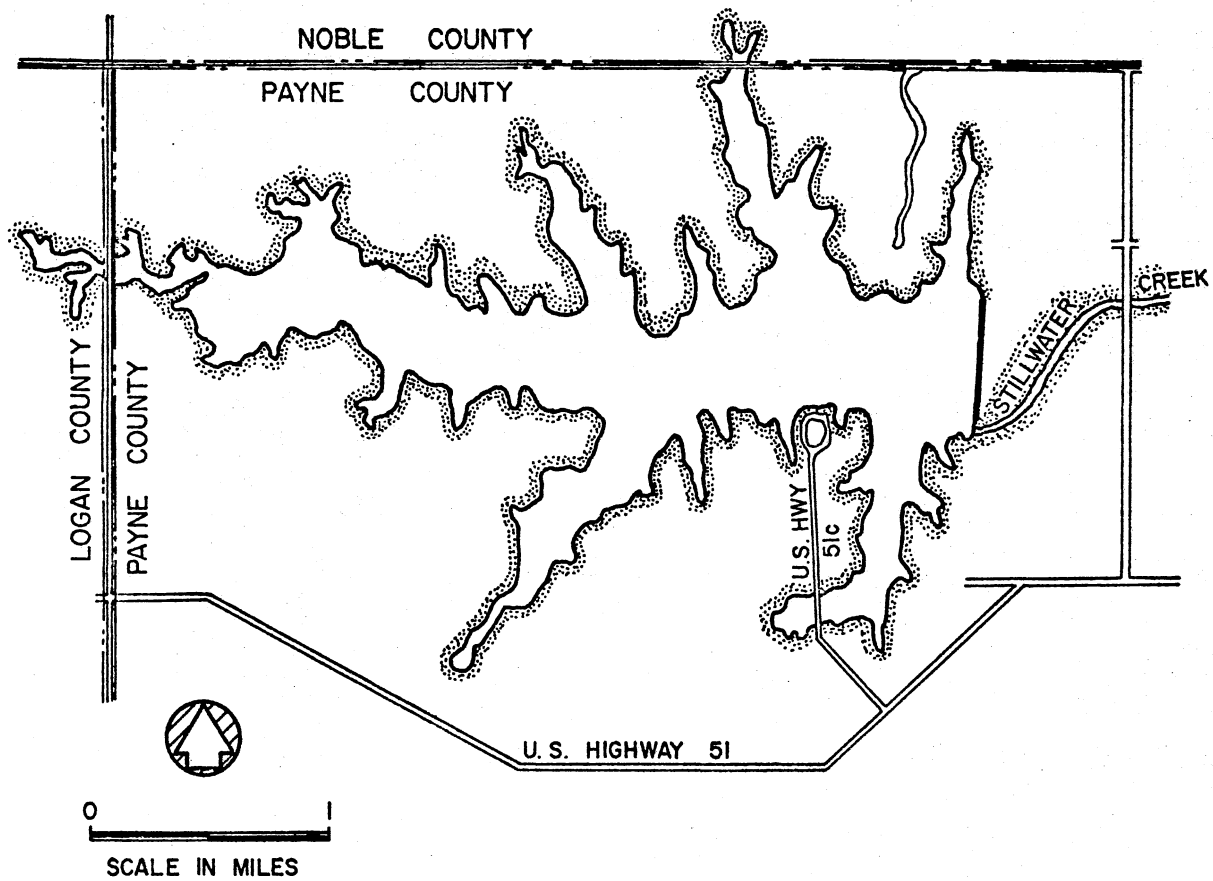


Figure 1. Lake Carl Blackwell, Payne County, Oklahoma. Water level at spillway, 944 ft above mean sea level.

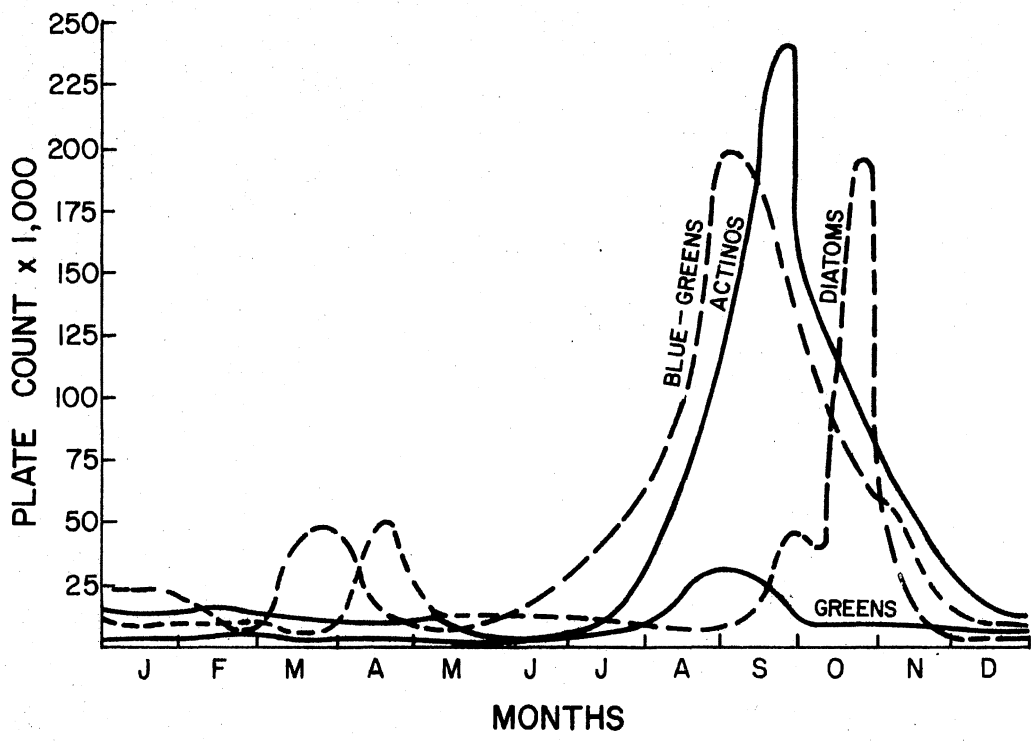


Figure 2. Relationship of Algae to Actinomycetes, Annual Cycle (Silvey et al 1972).

Odor intensifies as the actinomycete (or blue-green algae) population increases; the peak of odor intensity generally occurs during the actinomycete decline phase when actinomycetes die, lyse, and release their contents. Fritsche (1945), Lund (1959), and Fogg (1969) established the relationship of hypolimnetic de-oxygenation to taste and odor production. Actinomycetes grow abundantly in the anaerobic hypolimnetic sediments where copious quantities of odorous metabolites are released. Mixing of lake waters after periods of stratification brings hypolimnetic water laden with odorous metabolites to the surface and into water supply intakes.

Lake Carl Blackwell was the sole source of drinking water for Stillwater, Oklahoma while the study was in progress. Raw water purification included the rapid mix addition of alum as a coagulant to reduce alkalinity and turbidity. A slow mix step followed after which the floc particles are settled out. The water polishing step involved passage through a dual media filter of anthracite coal and sand. Fluorides were added immediately before chlorination, after which the water was pumped to a storage tank. From the tank water was released to the water distribution system. During taste and odor episodes potassium permanganate and small amounts of activated carbon were added to the slow mixing step.

CHAPTER III

METHODS

Carbon Adsorption/Evaporation Technique

Concentration, recovery, and sample preparation steps detailed below are summarized in Figure 3. Three portable organic adsorption sampling units (Fig. 4) based on the Robert A. Taft Sanitary Engineering Center design (Public Health Service 1965) were installed on tap water lines, and a carbon column was installed on a raw water line at the Stillwater municipal water treatment plant.

Pyrex glass cylinders 7.6 cm ID by 45.7 cm long were containers for the activated carbon. A 40 mesh stain less steel screen neoprene gasket retained the carbon. Endplates were constructed of 0.64 cm thick brass or plexiglass. Teflon tape was used to seal all joints; teflon tubing was used for water supply lines. The pyrex tubes were filled with 30 mesh activated carbon without tamping. Water flow rate was normally 2 liters/minute. The liquid level control was calibrated to dump the volumetric measuring tank at 1800 ml (+ 5 ml) and actuate a digital counter.

The one week carbon adsorption periods were staggered so that a 7-day sample was obtained every one to three

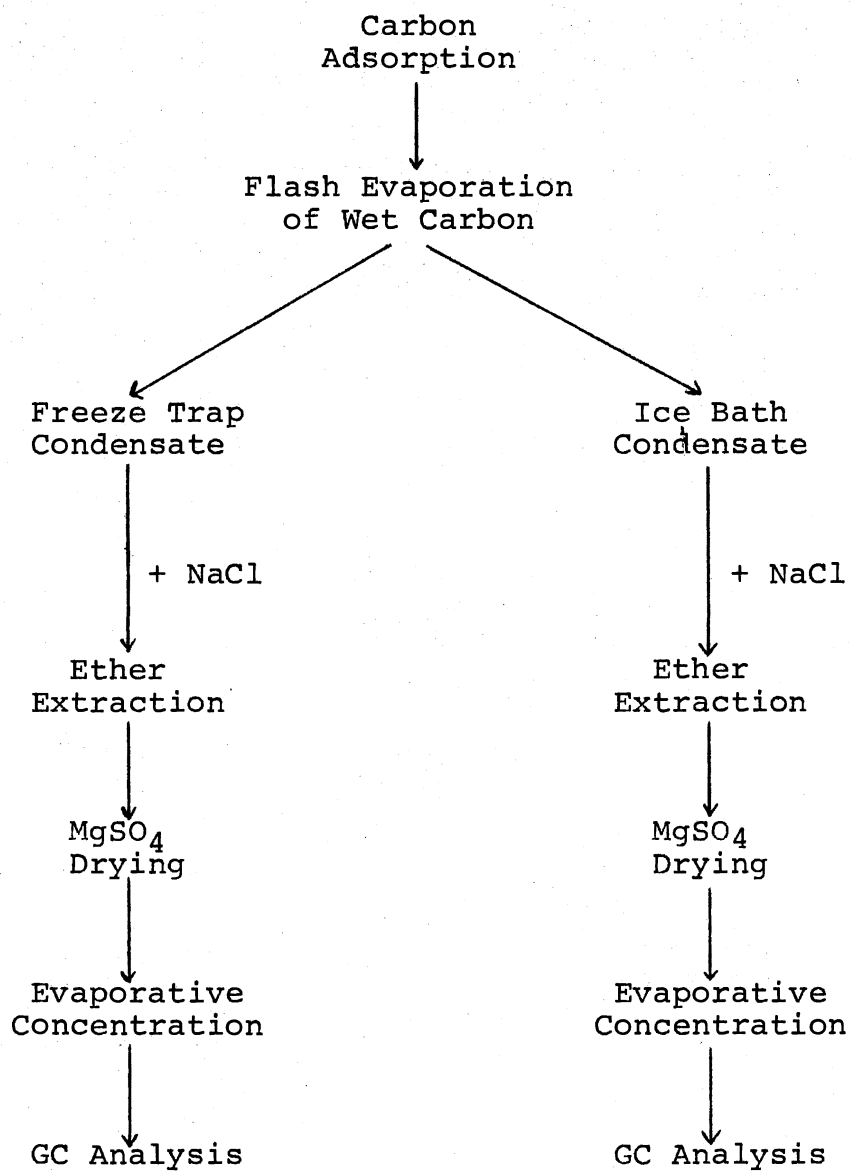
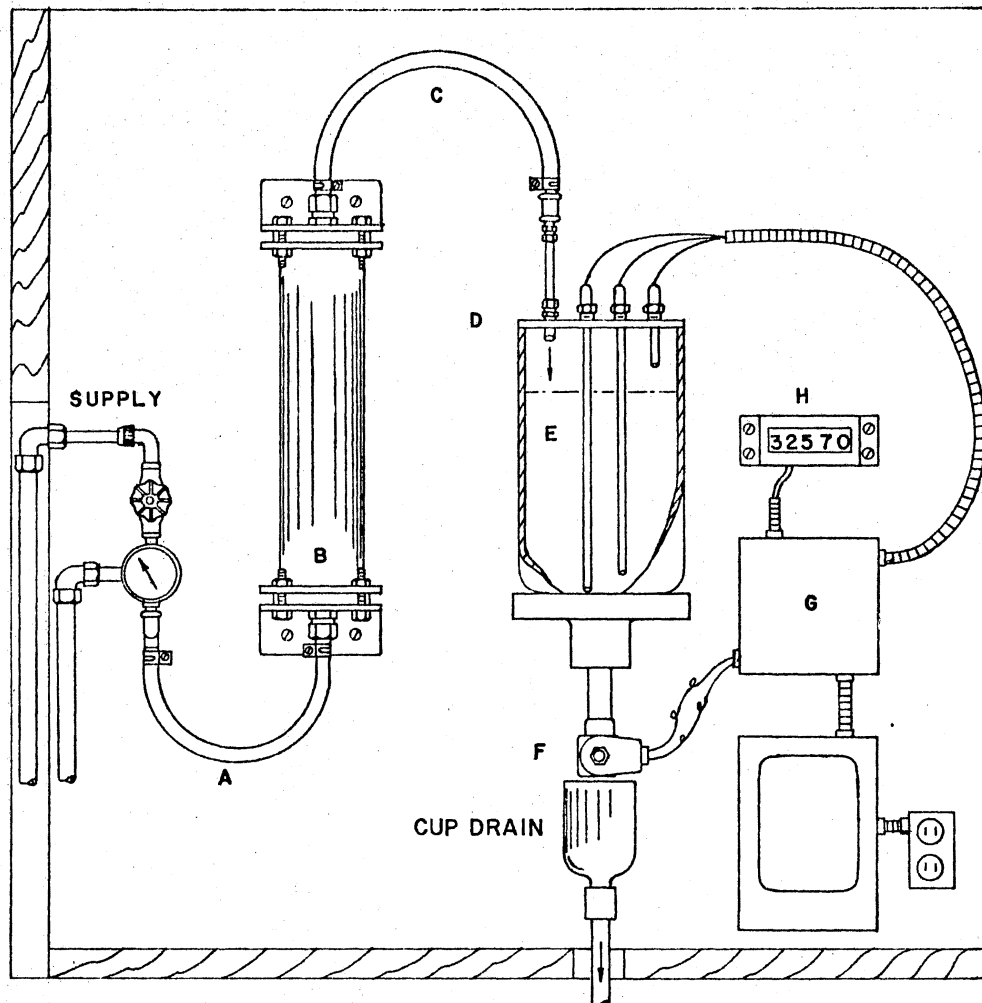


Figure 3. Carbon Adsorption/Evaporation Technique. Summary of Concentration, Recovery, and Sample Preparation Procedures.



- | | |
|---------------------------|-----------------------------|
| A-TEFLON TUBING | E-VOLUMETRIC MEASURING TANK |
| B-ACTIVATED CARBON COLUMN | F-SOLENOID VALVE |
| C-RUBBER HOSE | G-LIQUID LEVEL CONTROL |
| D-PROBE HOLDER | H-DIGITAL COUNTER |

Figure 4. Model LF-2 Low Flow Rate Organics Sampler for Water.

days. Samples were taken from August to December, 1971, and during August, 1972. Detailed sampling data is given in Table I of the Appendix.

At the end of the sampling period the wet carbon was placed in a Buchler model FE-2 flash evaporator and evaporated to dryness. Most moisture and organics were collected in a 2000 ml condenser whose temperature was maintained at 0 °C by partial immersion and continual rotation in an ice bath. All remaining compounds were crystallized in a 50 ml dry ice/acetone freeze trap. Figure 5 illustrates the flash evaporation and condensation apparatus utilized.

The condensates were extracted twice with volumes of anhydrous ethyl ether equal to one tenth of the condensate volume. Reagent grade NaCl was added as needed to break up emulsions. The extracts were combined, dried with magnesium sulfate and concentrated in a modified Kuderna-Danish concentrator (Fig. 6) fitted with a 3-bulb Snyder column. (Use of this concentrator allowed immersion of the flask in hot water up to the level of solvent inside the flask without immersion of a ground glass joint.) After evaporation to about 5 mls the sample was slowly evaporated to about 1 ml before quantitative transfer to a 1 ml vial and further concentration to 0.1 ml. The sample was sealed and stored at approximately 5 °C prior to chromatographic analysis.

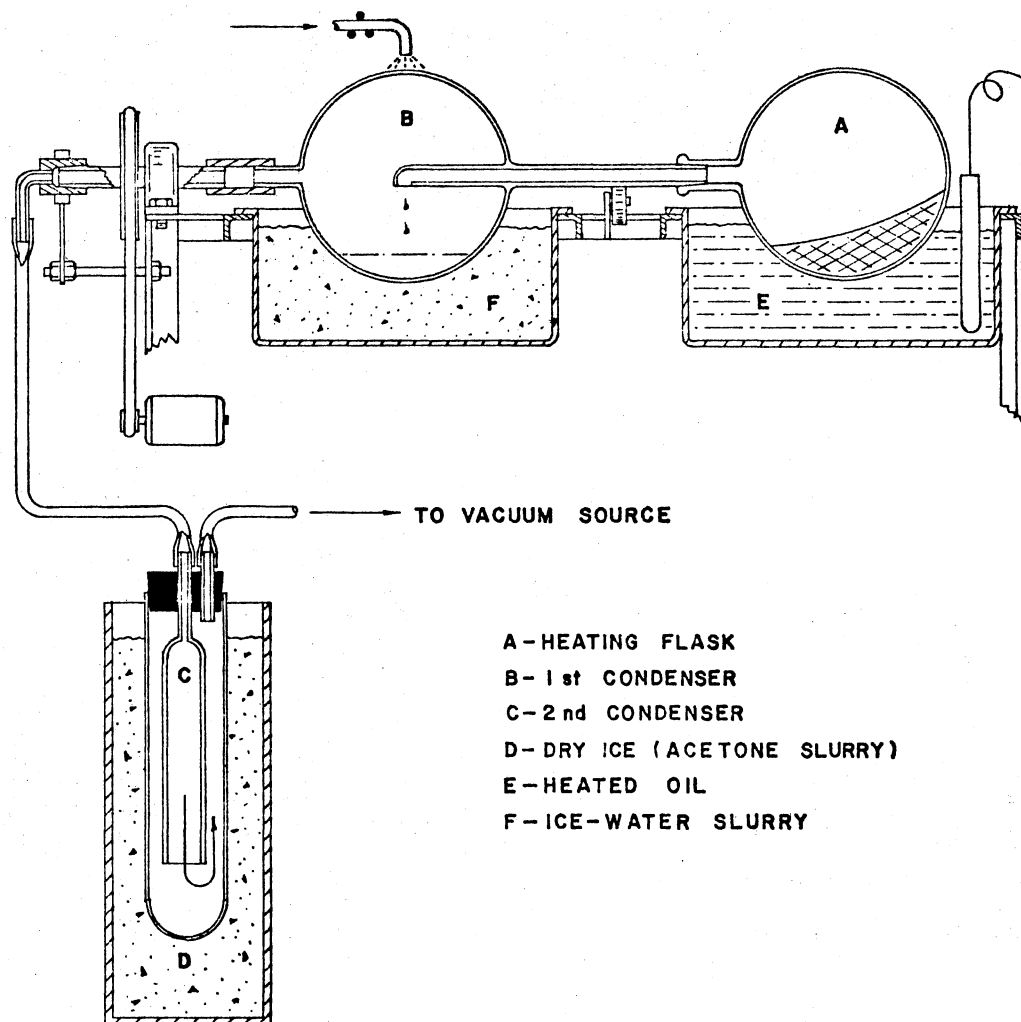


Figure 5. Flash Evaporation Apparatus.

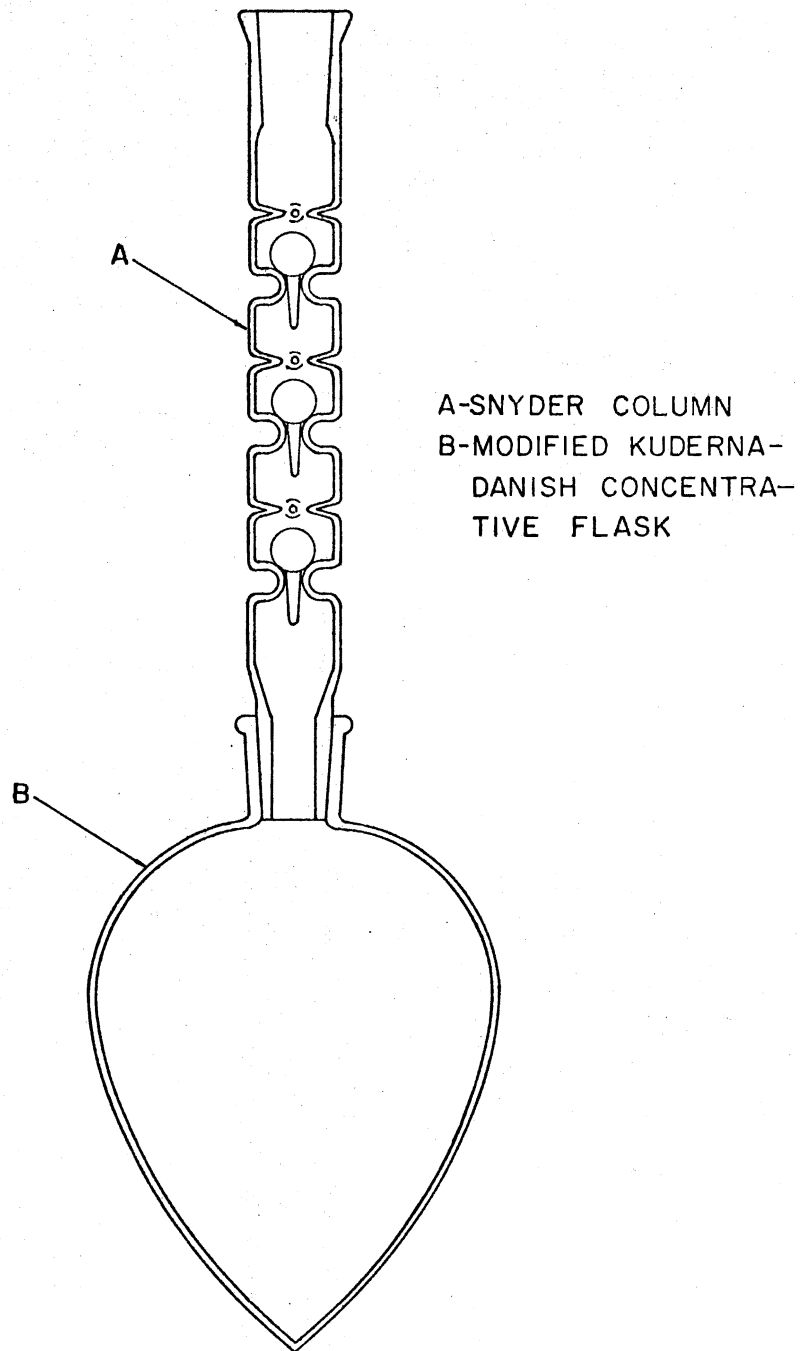


Figure 6. Modified Kuderna-Danish Evaporative Concentrator Apparatus.

Air-Stripping Technique

Figure 7 summarizes the steps required for concentration, recovery and sample preparation. These steps are detailed below.

An air stripping column (Fig. 8) was constructed of plexiglas tubing 4 ft long by 3 in ID. The air stream, after passing through an activated carbon filter, entered the column through a gas diffusion tube at the bottom of the column and exited from the top of the column to the freeze concentrators. Hot tap water flowed downward counter-current to the airflow.

The water flow rate was 2 gal/min (\pm 10%); the air flow rate was 60-100 ml/min. Each sampling period was 24 hours. Detailed sampling data is given in Table II of the Appendix.

The procedure for adding air and water to the column proved to be important to successful sampling. Air was metered to the column first, followed by water. The water level was maintained in two ways: 1) by adjusting the flow of water, and 2) by adjusting the diameter of the exit port.

The exiting water- and organic- saturated air was passed through three condensers (Fig. 9). Condenser A, designed to remove the moisture, consisted of a two neck, 2000 ml flask which was cooled with dry ice flakes. Condensers B and C were cooled by dry ice-acetone slurries.

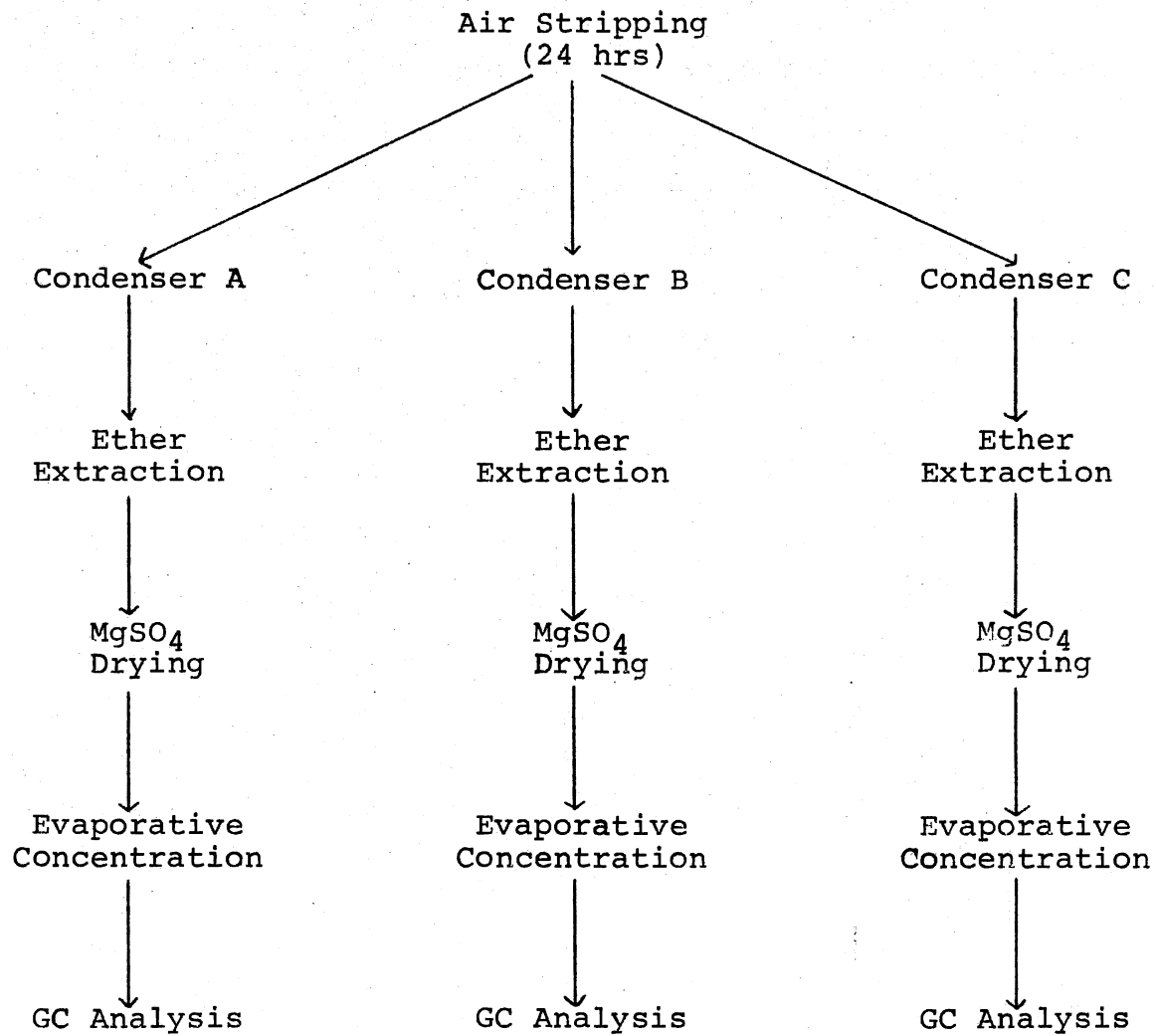


Figure 7. Air Stripping Technique. Summary of Concentration, Recovery, and Sample Preparation Procedures.

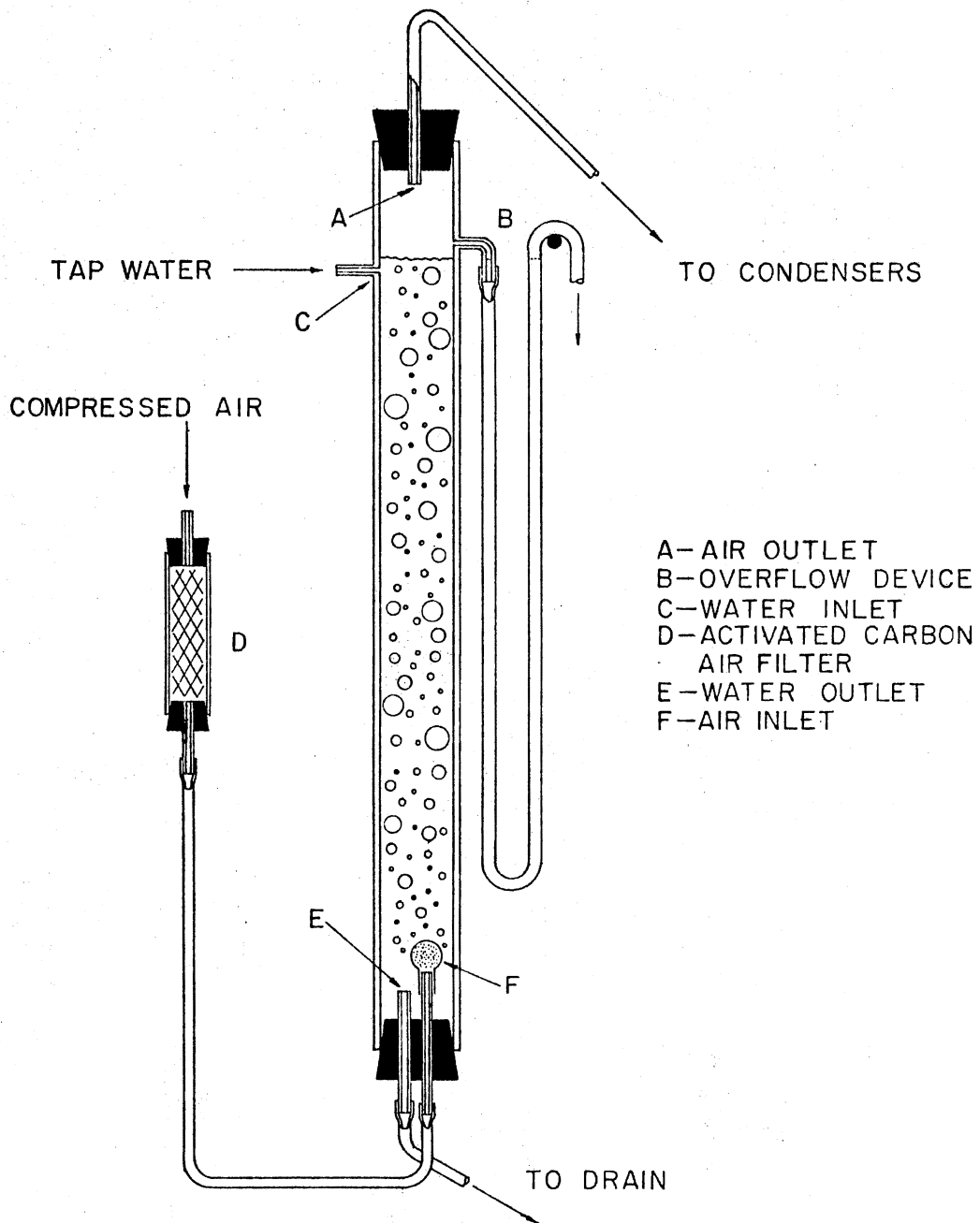
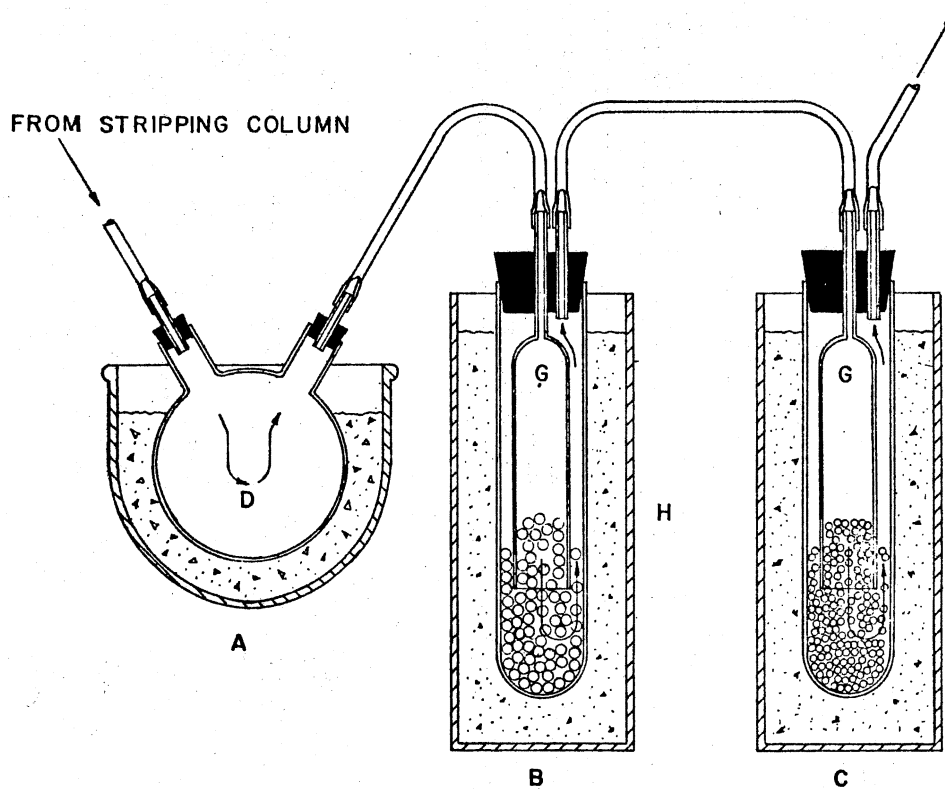


Figure 8. Air Stripping Column.



- A-CONDENSER 1 (DRY ICE FLAKES)
- B-CONDENSER 2 (DRY ICE-ACETONE SLURRY)
- C-CONDENSER 3 (DRY ICE-ACETONE SLURRY)
- D-TWO-NECK FLASK, 2000 ml
- E-DRY ICE
- F-DRY ICE-ACETONE SLURRY
- G-AIR FLOW CONTROL TUBE
- H-4mm GLASS BEADS
- I-2mm GLASS BEADS

Figure 9. Condenser System Used with Air Stripping Column.

The configuration of condensers B and C fragmented and slowed the air stream allowing deposition of frozen material without restricting flow. Most volatile organics were collected in condenser B. Very few crystals were deposited in condenser C.

Condensates were extracted three times with ether, dried with magnesium sulfate, concentrated in a modified Kuderna-Danish evaporator, and stored at 5 °C prior to analysis by gas chromatography.

Separation and Identification of Volatile Components

An F&M Model 810 Gas Chromatograph equipped with a hydrogen flame ionization detector was used to separate and detect the components of each sample. A six foot by one-eighth inch copper column packed with 10 per cent SE-30 on Diatoport S, 60-80 mesh, was used to resolve the volatile compounds. The maximum temperature used in the study was 300 °C; the chromatographic column was preconditioned at 25-50 °C above the anticipated maximum operating temperature. Because the percentage of liquid phase was reduced by "bleed-off", the actual percentage of liquid phase was less than reported. Other operating conditions are given in Table I.

Odor characterization of samples was accomplished by olfactory detection. After obtaining good resolution for a sample, the flame detector was extinguished. An

observer was stationed at the exit port, and an aliquot of the sample was reinjected. After the solvent peak was noted each observed odor was described and its retention time determined with a stopwatch. Identification of odorous peaks was accomplished by matching retention times of observed odors with peak retention time data obtained previously with the same sample.

TABLE I
GC OPERATING CONDITIONS

Detector Temperature:	320 °C
Injector Temperature:	275 °C
Temperature Program:	
Initial Column Temperature:	155 °C
Initial Isothermal Period:	none
Rate of Temperature Increase:	4 °C/min
Final Isothermal Temperature:	270 °C
Bridge Current:	150 mv
Carrier Gas:	helium
Carrier Gas Flow Rate:	40 ml/min

An LKB Model 9000 magnetic sector combination GC-MS

instrument (Waller 1968) was utilized for compound identification; operating conditions are given in Table II. After tentative identification based on mass spectral fragmentation pattern and molecular weight, confirmation was accomplished by obtaining mass spectra from the appropriate pure compounds, and comparing these with the water constituent.

TABLE II
GC-MS OPERATING CONDITIONS

Ion Source Temperature:	250 °C
Ionizing Energy:	70 ev
Trap Current:	20 ua
Ion Accelerating Voltage:	3.5 Kev
Oscillograph Chart Speed:	4 ips
Temperature Program:	
Initial Column Temperature:	80 °C
Initial Isothermal Period:	15 min
Rate of Temperature Increase:	6 °C/min
Final Isothermal Temperature:	200 °C
Carrier Gas:	helium
Carrier Gas Flow Rate:	34 ml/min

CHAPTER IV

RESULTS

Over one hundred distinctly identifiable peaks were obtained by GC/MS analysis (Figures 10, 11, 12, 13, 14). The air stripping samples consistently showed a greater number of peaks than the CA/E samples even though greater volumes of water were extracted with the CA/E technique.

Regardless of concentrative technique, each chromatogram was similar. During the first ten minutes there was generally a flat baseline and relatively good compound separation, but at the end of this period each tracing showed a very large area in which peaks were incompletely resolved. This was probably due to the presence of large numbers of compounds with similar retention times under the chromatographic conditions utilized.

Olfactory detection of chromatographically separated compounds was completed on three samples. The tracing of the most significant sample is shown in Figure 15. The earthy, musty peak (D) was detected 7.0 min after the solvent. Based on subsequent mass spectrometric analysis (Fig. 16) 1-secbutyl-3,7-dimethyl-6-hydroxy-bicyclo-dec-2-ene has been proposed as a possible compound identity. The structural formula of this compound is shown in Figure

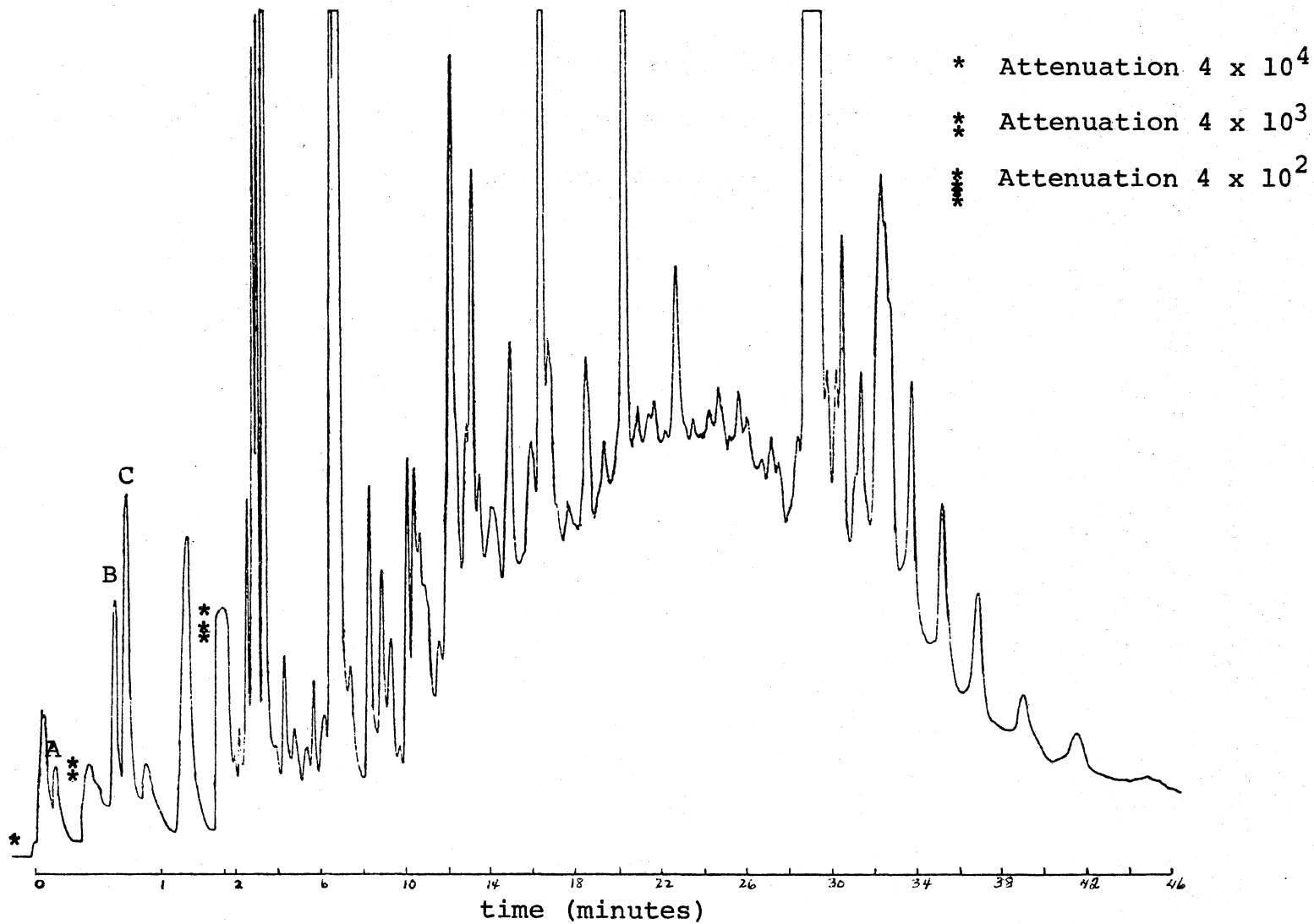


Figure 10. Chromatogram of Organics in Water Concentrate - Condenser B, Air Stripping. Peaks A, B, and C -subsequently identified as haloforms.

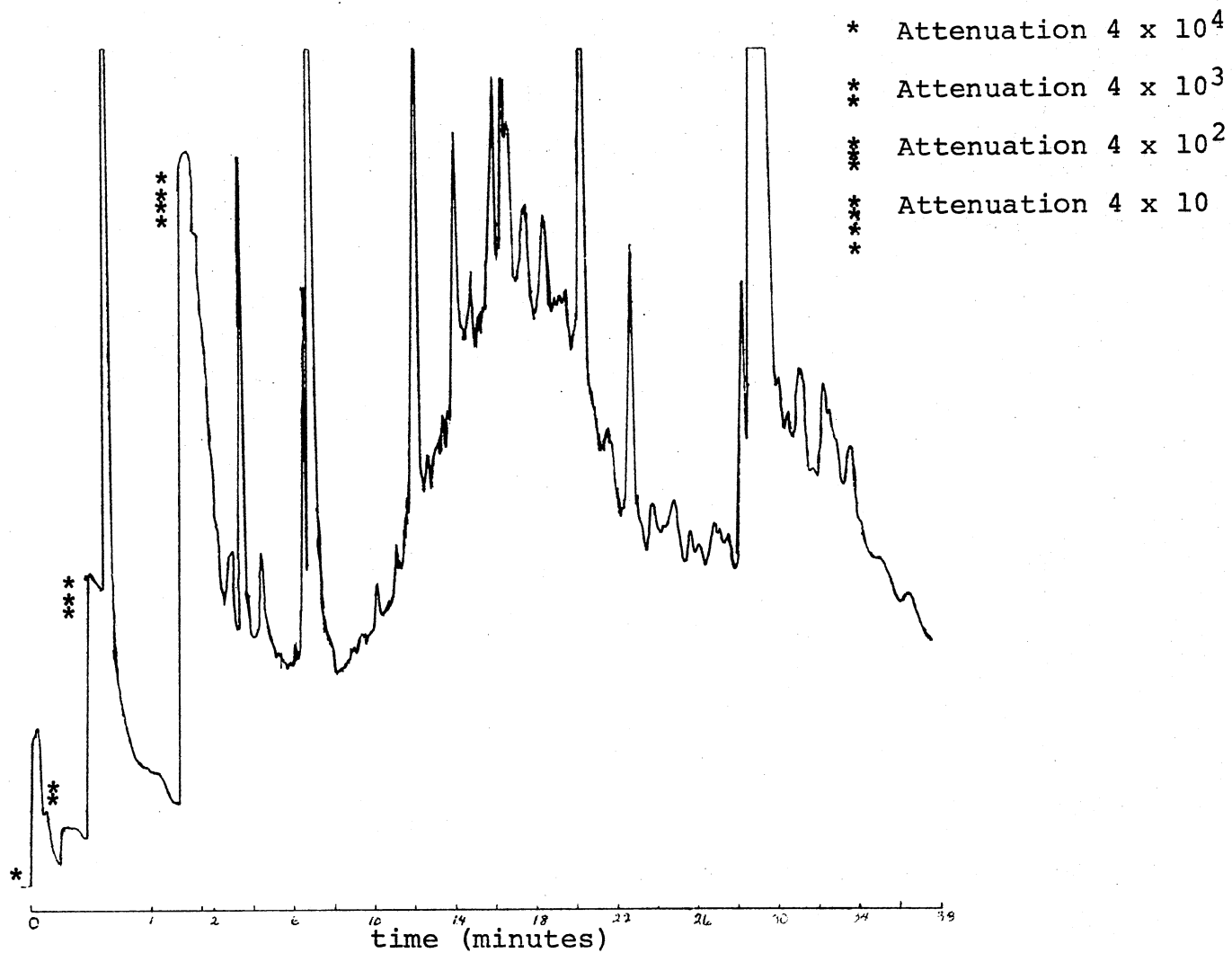


Figure 11. Chromatogram of Volatile Organics in Drinking Water Concentrate - Organics Fraction From Condenser A, Air Stripping System.

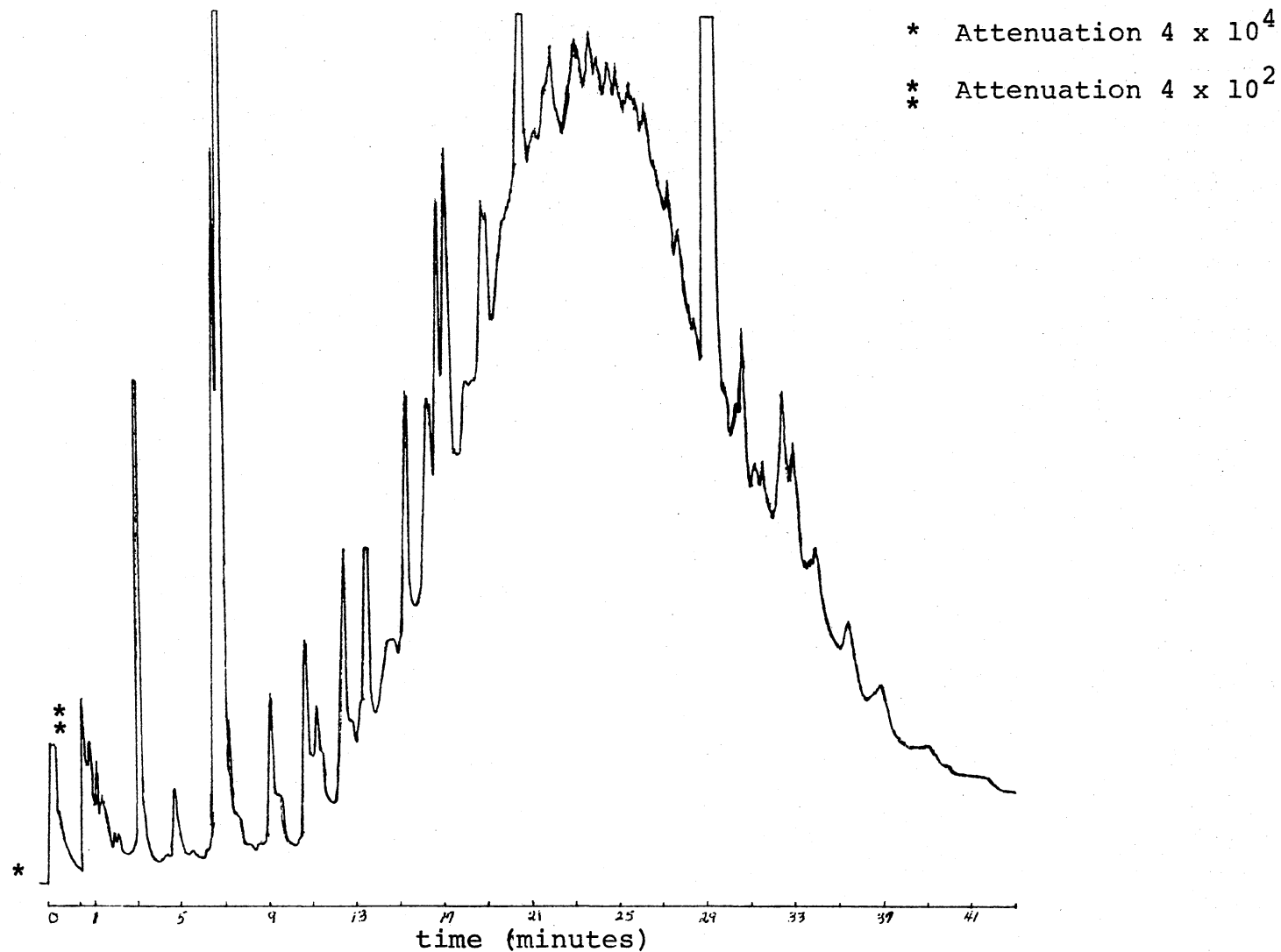


Figure 12. Chromatogram of Volatile Organics in Drinking Water Concentrate - Organic Fraction from Condenser C (Freeze Trap), Air Stripping System.

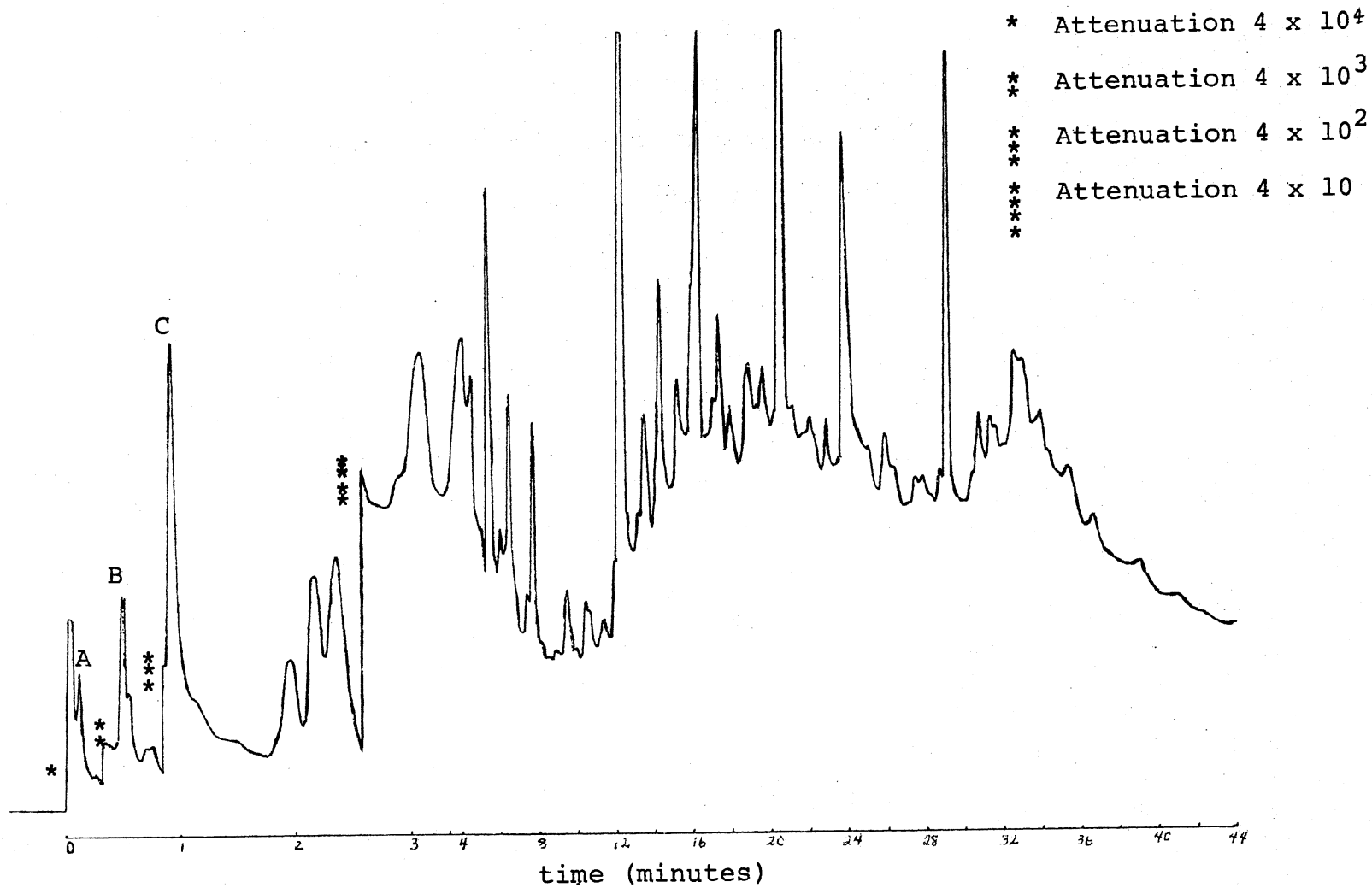


Figure 13. Chromatogram of Volatile Organics in Drinking Water Concentrate - Condenser A (Ice Water Bath), Flash Evaporated Carbon. Peaks A, B, and C - Subsequently Identified as Haloforms.

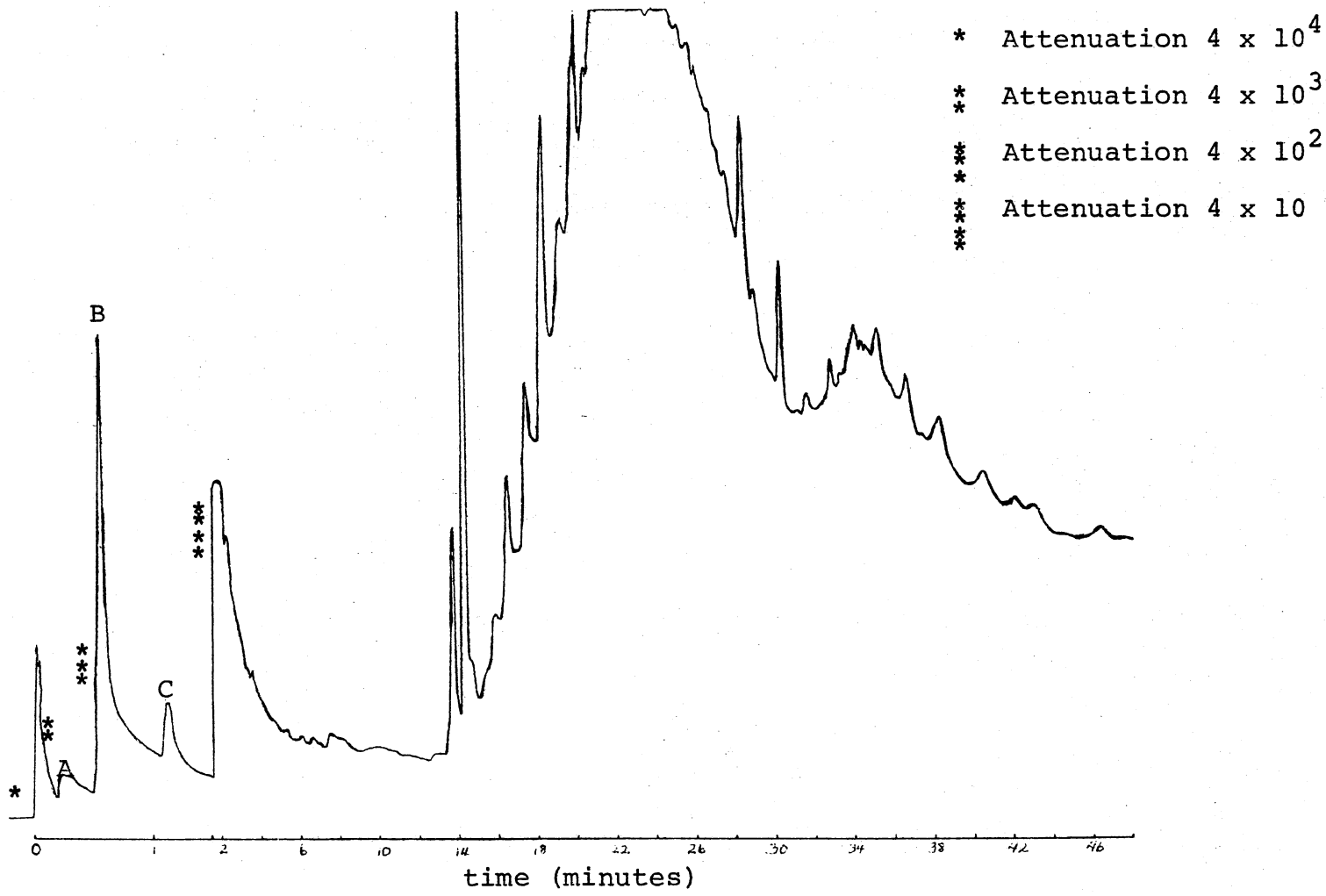


Figure 14. Chromatogram of Volatile Organics in Drinking Water Concentrate - Condenser B (Freeze Trap), Flash Evaporated Carbon. Peaks A, B, and C - Subsequently Identified as Haloforms.

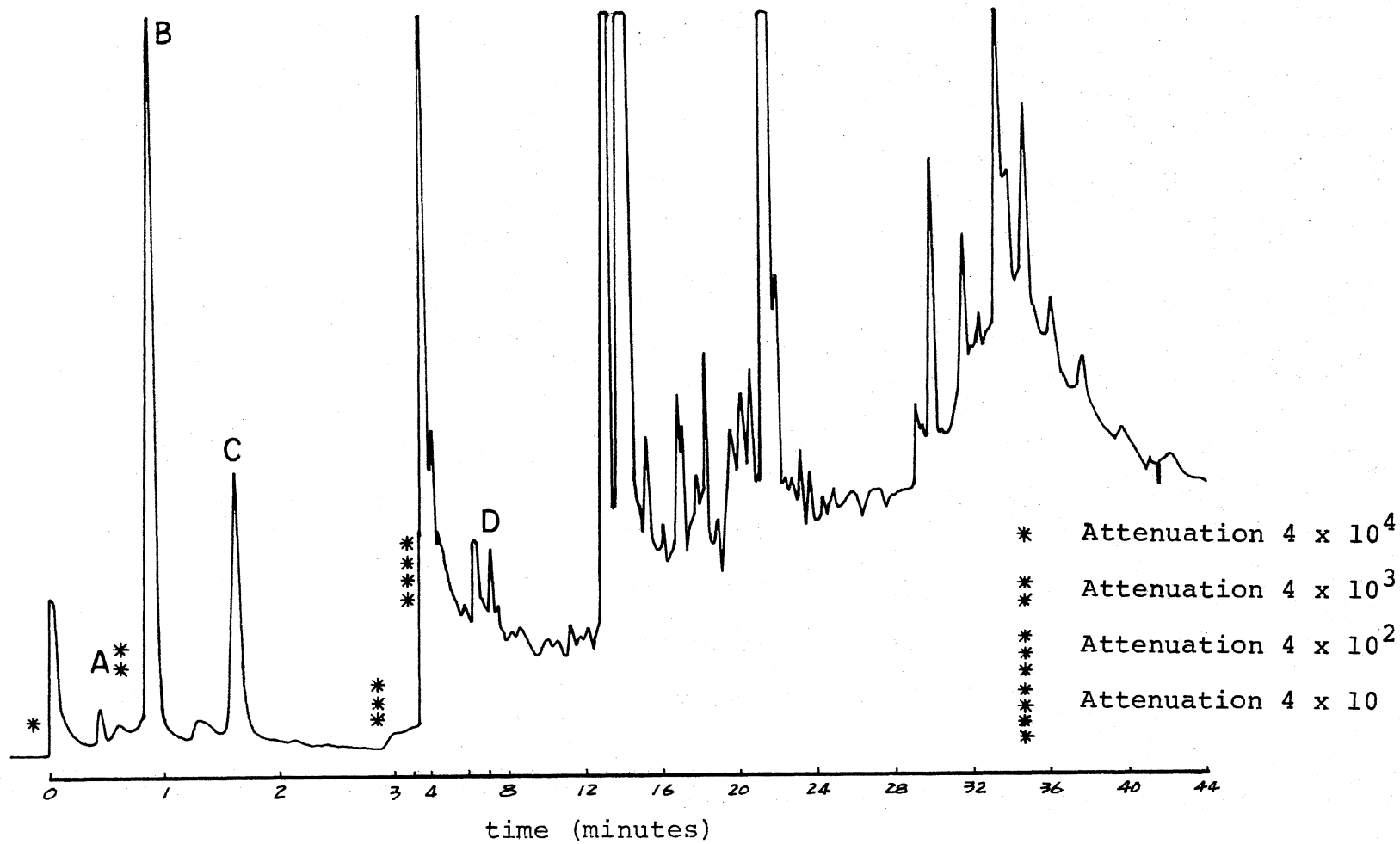


Figure 15. Chromatogram of Water Concentrate (Ice Water Condenser, Flash Evaporation). Peaks A, B, and C - Subsequently Identified as Halofoms. Peak D, Retention Time - 7 min, is the Earthy, Musty Compound.

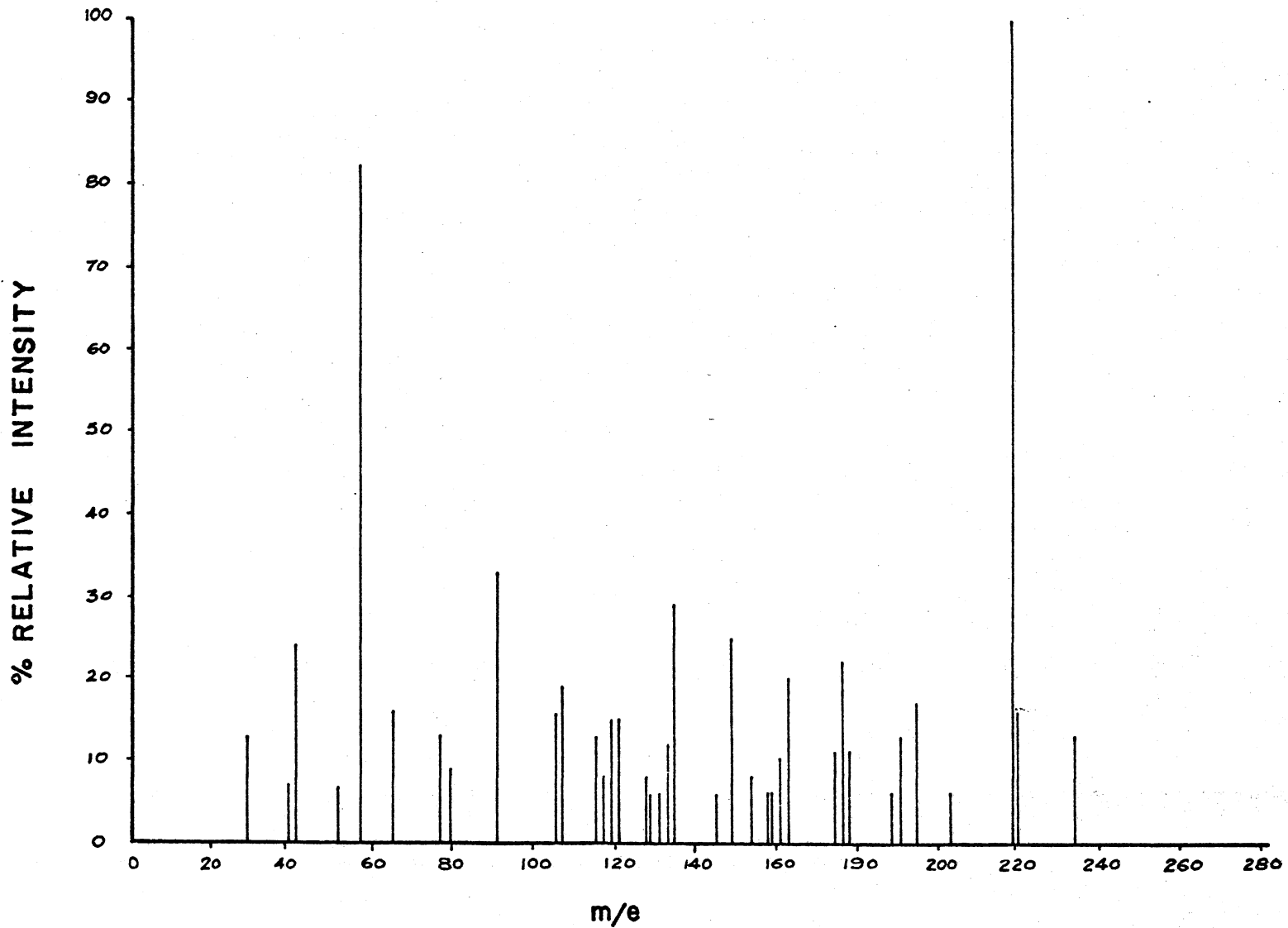


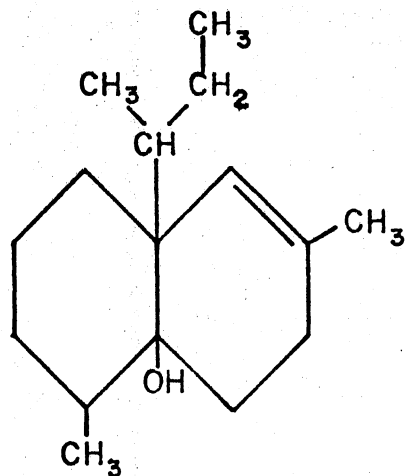
Figure 16. Mass Spectrum of GLC Peak D, Tap Water Contaminate.

17 along with taste and odor compounds identified by other investigators. The molecular weight (M^+) of the compound is 236; the base peak (mass number 219) appears to be the dehydration product. Figure 18 shows a possible fragmentation pattern. Further mass spectrometric, infrared, and nuclear magnetic resonance studies would be needed for complete identification.

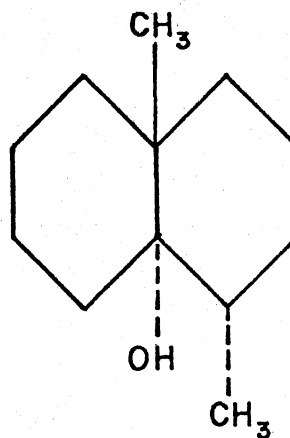
In most sample chromatograms, three large peaks (A, B, and C, Figures 10 and 13) occurred immediately after the solvent. Observers noted very pungent odors, dizziness, and nausea in relationship to each of them.

Mass spectral analysis was accomplished for all three peaks. Peak A had a molecular weight (M^+) of 164 (Fig. 19a). The base peak was 83, and the fragmentation pattern was similar to that of bromodichloromethane. Empirical isotopic ratios were identical to published data for chlorobromo organics (Beynon 1960). The fragmentation pattern (Fig. 19b) of a sample of bromodichloromethane was identical to the unknown. It was thus concluded that the unknown compound (peak A) was bromodichloromethane (CHBrCl_2).

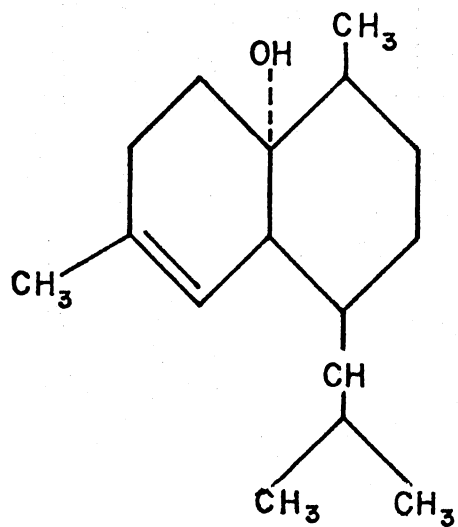
Peak B had a molecular weight (M^+) of 208 (Fig. 21a). The base peak was 129, and the fragmentation pattern was similar to that of dibromochloromethane. Empirical isotopic ratios were identical to published data for chlorobromo organics (Beynon 1960). The fragmentation pattern (Fig. 20b) of a sample of dibromochloromethane was identical to the unknown. It was thus concluded that the unknown



1-secbutyl-3,7-dimethyl-6-
hydroxy-bicyclodec-2-ene
(proposed)



1,10-dimethyl-trans-
9-decalol



cadin-4-ene-1-ol

Figure 17. Structural Formulas of Earthy Musty Metabolites.

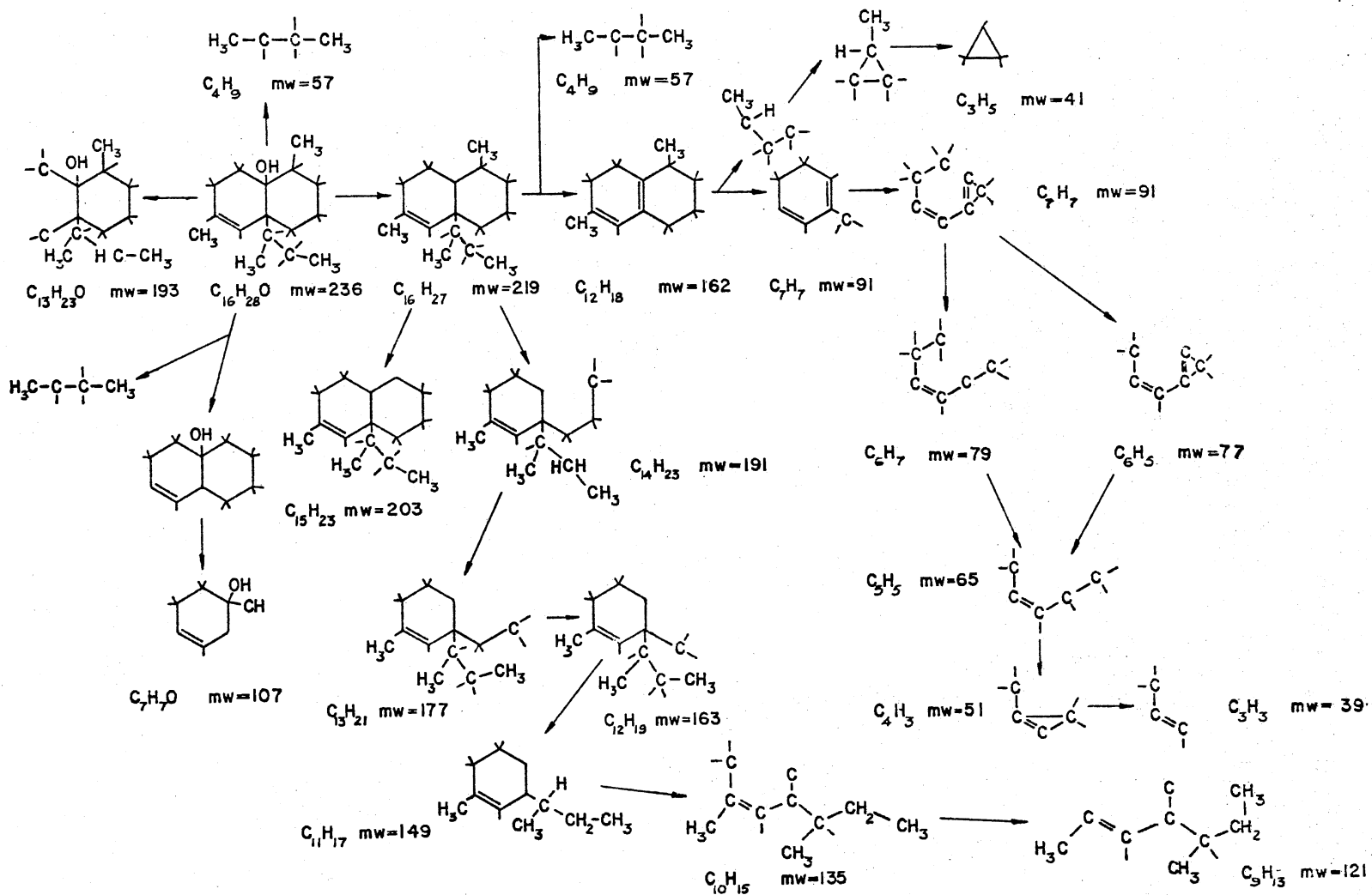


Figure 18. Fragmentation Pattern for Earthy, Musty Compound.

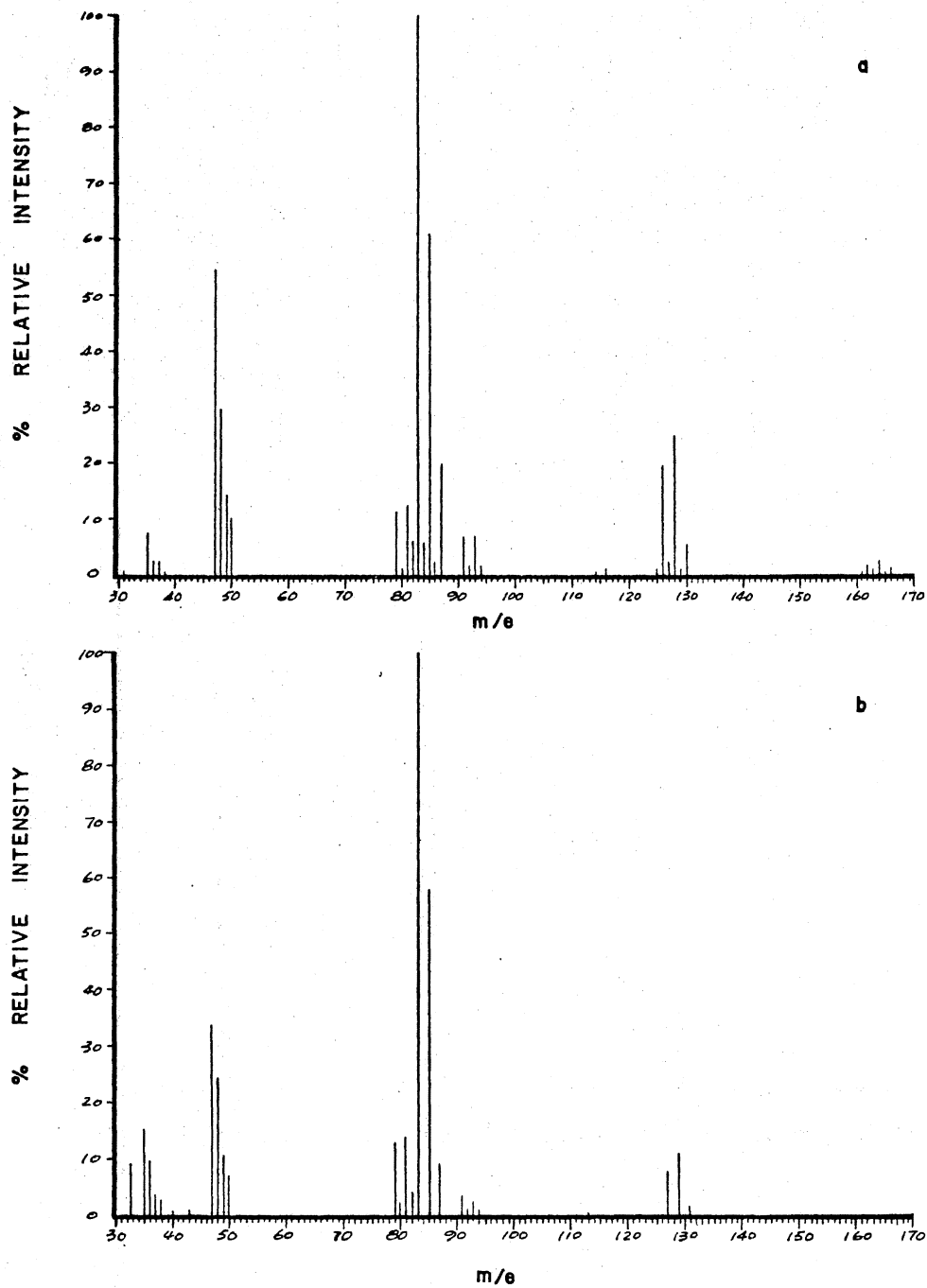


Figure 19. Comparison of Bromodichloromethane Standard with Water Compound.
a. Mass spectrum of GLC peak A, collected from drinking water.
b. Mass spectrum of standard CHBrCl_2 introduced directly into MS vacuum chamber.

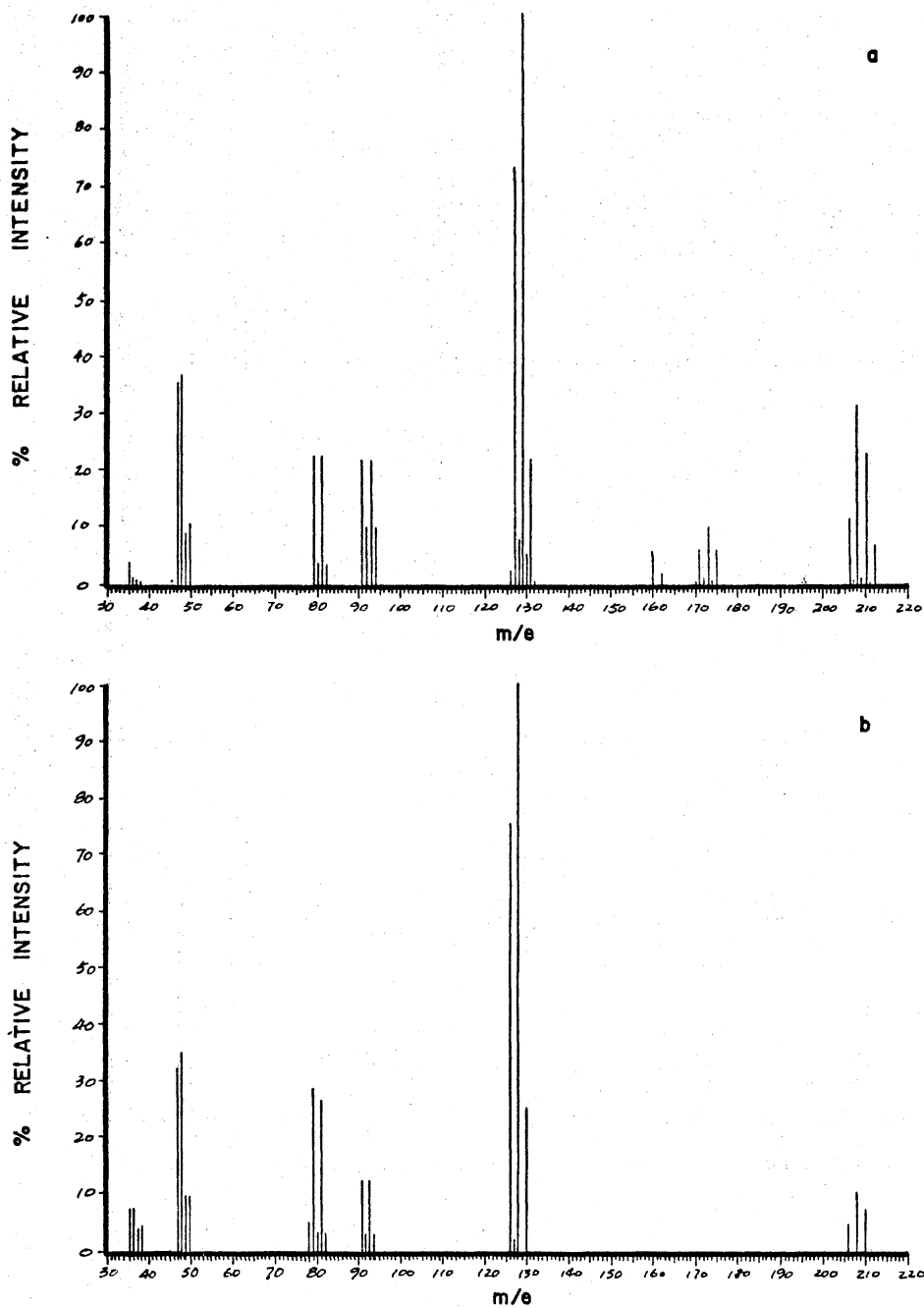


Figure 20. Comparison of Dibromochloromethane Standard with Water Compound.
a. Mass spectrum of GLC peak B, collected from drinking water.
b. Mass spectrum of standard CHBr_2Cl , introduced directly into MS vacuum chamber.

compound (peak B) was dibromochloromethane (CHBr_2Cl).

Peak C had a molecular weight (M^+) of 253 (Fig. 21a). The base peak was 173, and the fragmentation pattern was similar to that of bromoform. Empirical isotopic ratios were identical to published data for chlorobromo organics (Beynon 1960). The fragmentation pattern (Fig. 21b) of a sample of bromoform was identical to the unknown. It was concluded that the unknown compound (peak C) was bromoform (CHBr_3).

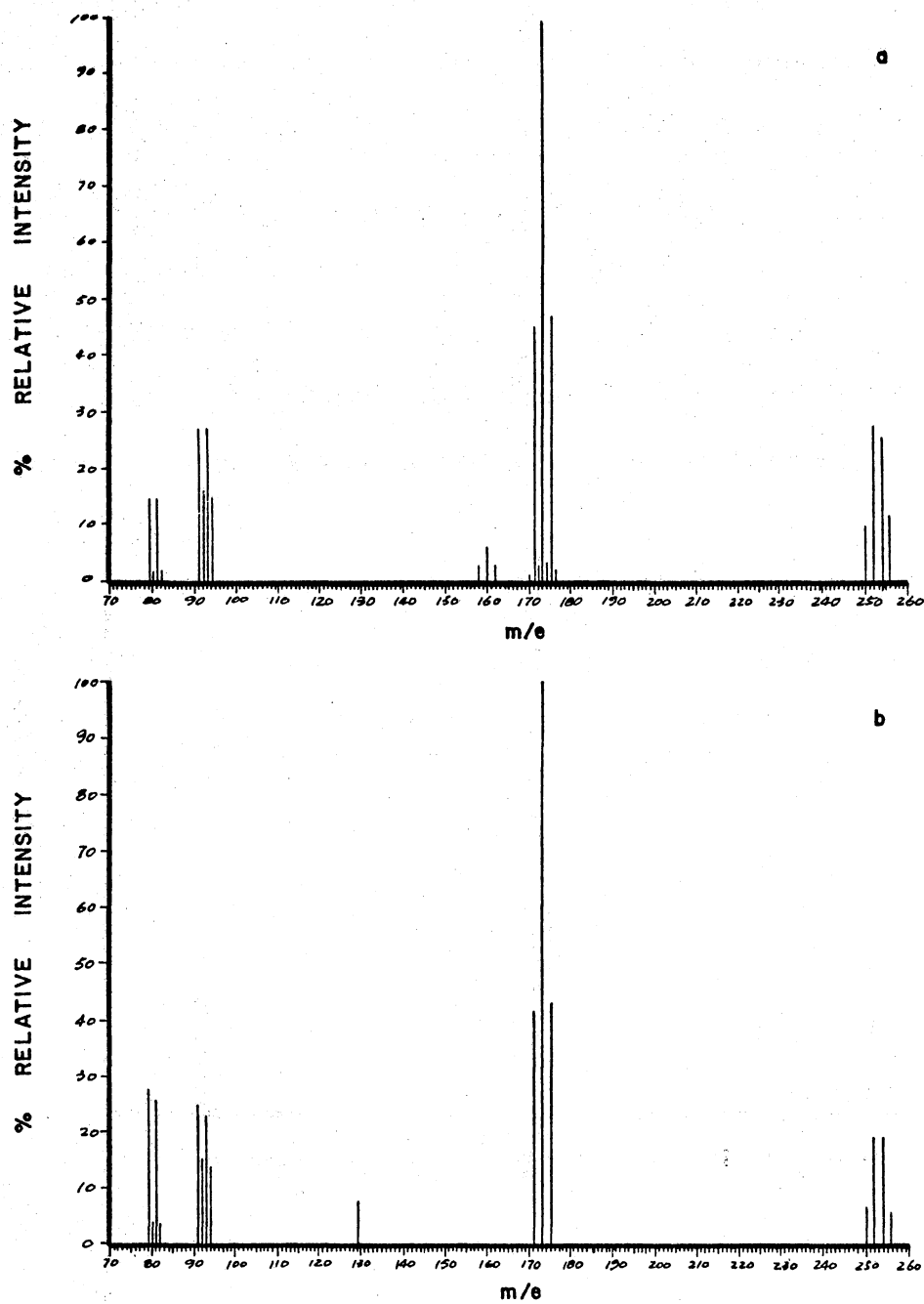


Figure 21. Comparison of Bromoform Standard with Water Compound. a. Mass spectrum of GLC peak C, collected from drinking water. b. Mass spectrum of standard CHBr_3 , introduced directly into MS vacuum chamber.

CHAPTER V

DISCUSSION

Taste and Odor Compounds

During the taste and odor identification efforts several subjective observations were made. First, the odor intensity was not evenly evidenced throughout the Stillwater water distribution system. While the odor was intense to the point of being intolerable at some locations, it was barely discernable at others. Interaction between the responsible compound and the water distribution system is implied. Biological growth in the water distribution system is a probable factor.

Although taste and odor episodes occur regularly in Lake Carl Blackwell in late summer and early fall, odor intensity, duration, and the odor itself vary each year. In 1971 intense odor was present from mid-July through mid-November; in 1972 the episode lasted the month of August only, and was barely discernable much of the month. Since these taste and odor compounds are probably actinomycete and algae metabolites, varying climatic conditions may have influenced the production of earthy, musty metabolites. In 1971 the summer was unusually cool and wet until the middle of August when it was hot for

two weeks. In 1972 the summer and fall was hot and dry.

The stability of the earthy, musty compounds encountered is evidenced by the ineffectiveness of the conventional water purification procedures utilized in odor reduction; however the compounds did not appear to be totally resistant to biological attack. An activated carbon filter installed on a raw water line at the Stillwater Municipal Water Treatment Plant was odor free after a one week sampling period during the height of odor production. Investigation of filtering conditions (flow rate of 500 ml/min; temperature range 80-85° F; diffuse light, high bacterial levels in the water) revealed that filtration had taken place under what appeared to be optimal conditions for bacterial decomposition. The taste and odor compounds were apparently decomposed during filtration and adsorption.

Haloforms

In view of the presence of CHBr_3 , CHBr_2Cl and CHBrCl_2 , chloroform (CHCl_3) is notably absent. Conditions which would produce the identified haloforms would be expected to produce CHCl_3 as well (Abrams et al. 1975, Environmental Protection Agency 1975). GC-MS peaks with retention times near to the haloform peaks were examined; none were identified as chloroform. However it was noted that for each compound, as the degree of chlorination increased, retention time decreased, and since the haloform retention times were very short it is possible that chloroform was present

but was not adequately separated from the solvent peak under gas chromatographic conditions used.

CHBr_3 , CHBr_2Cl , CHBrCl_2 and CHCl_3 are resistant to biological decomposition. Since they are environmentally persistent, injection of low levels for long periods of time could result in the accumulation of toxic concentrations in the body (Gleason 1969). All four halogens are potential carcinogens, (Gleason 1969, Toxic Substances 1974), but their acute toxicity is relatively low. Chronic effects include decrease in blood catatase, decrease in phagocytic capacity of leucocytes, structural lesions, lipid degeneration and proliferation of interstitial cells in the myocardium, and reduced capacity of conditioned reflexes (Water Quality Criteria Data Book 1970, The Toxic Substances List 1974, Hawley 1971). The presence of these compounds in tap waters where ingestion over long periods of time can occur raises serious questions concerning the appropriateness of current water treatment technologies.

Identification of haloforms in tap water samples was unexpected. The source of these compounds was not immediately obvious. Because Lake Carl Blackwell, the raw water source, receives no industrial effluent, the presence of haloforms could not be attributed to an industrial source. Other possibilities were that the compounds originated from agricultural pesticide runoff, or may have originated during water purification. At the Stillwater Municipal Water Treatment Plant, chlorination is the final

step in the water treatment process. Haloforms may result from the chlorine disinfection step by the reaction of chlorine and residual bromine with organic compounds not removed by conventional water treatment.

Rook (1972, 1974) has shown that under chlorination conditions, chlorine and bromine residuals, occurring naturally in concentrations of 0.1 to 1.0 mg/l (Houghton 1946), react with organic substances of natural and industrial origin to form haloforms. Virtually all bromide residuals are very rapidly oxidized to hypobromous acid (HOBr) by aqueous chlorine. The resulting HOBr reacts more extensively and rapidly with ammonia and organic matter than does HOCl. Bromide, regenerated in the reduction of HOBr by organic compounds, is readily reoxidized by excess HOCl, thereby serving as a catalyst in the oxidation reactions. Bromine also acts to a significant extent in electrophilic substitution reactions with aromatics forming compounds such as 2,4,6-tribromophenol. Rook suggests that virtually all aqueous bromide is converted to the reactive HOBr specie which in turn reacts completely with organic constituents in the water. In the HOCl-HOBr organic reaction mechanism (Fig. 22) the initial enolisation stage is rate determining. In the subsequent substitution stage chlorine and bromine compete equally at the reaction site.

HOCl and HOBr have been shown to react readily with acetone, various substituted quinones, hydroquinones,

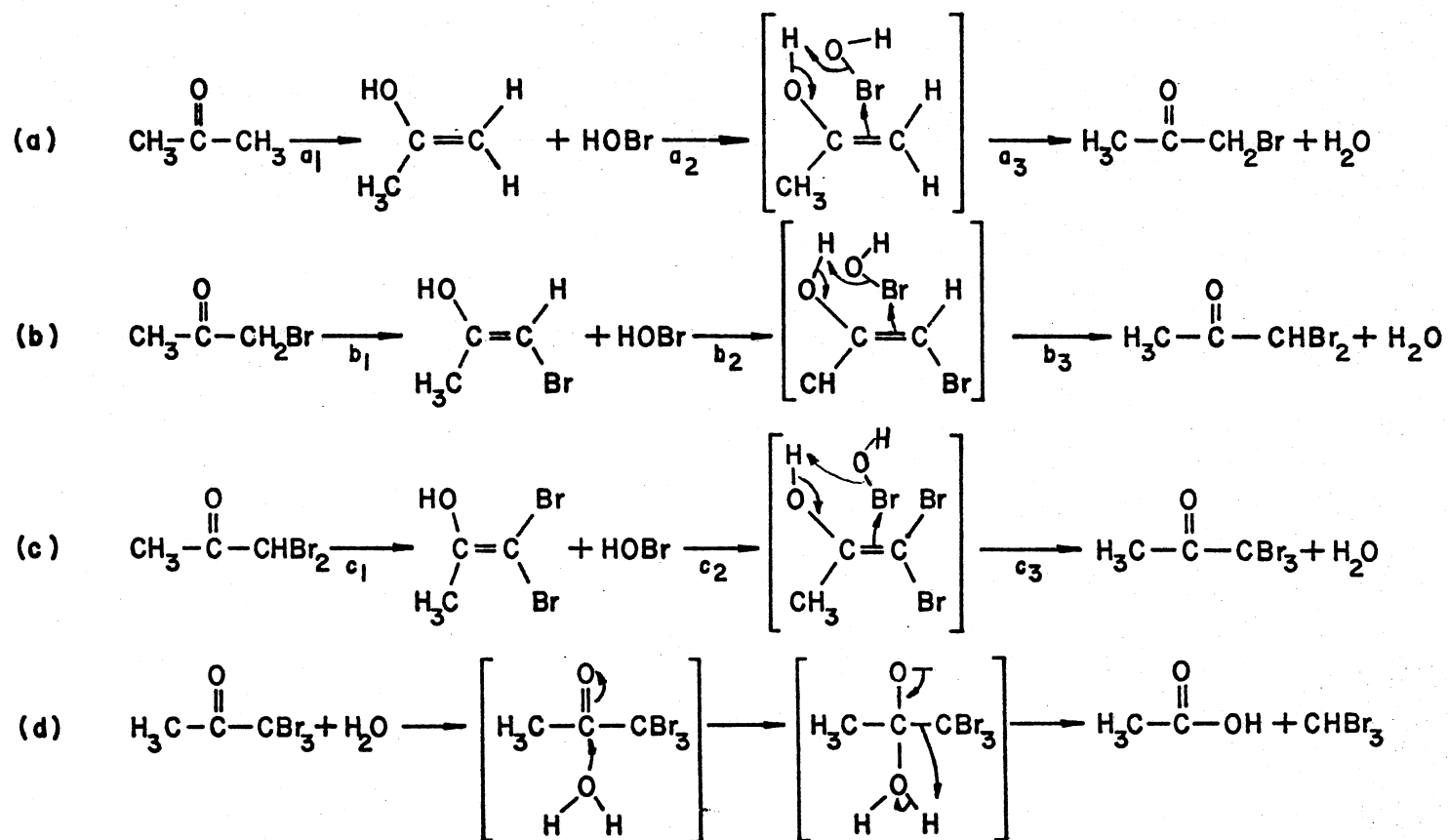


Figure 22. Mechanism for Bromination of Acetone to Produce CHBr_3 ;
 Enolisation Step (a_1, b_1, c_1), Substitution Step (a_2, b_2, c_2).

catechol, resorcinol, pyrogallol, phloroglucinol, di- and trimethyl amine, polyhydroxybenzenes, and naturally occurring humic substances to form haloforms (Rook 1974, Morris 1975, Barnhart and Campbell 1972). Functional group affinities are for carbonyl, carboxyl, amine and hydroxyl groups; all of which are present in humic substances stable to biological decay.

Techniques of Volatile Compound

Removal from Water

Both methods utilized in this study are quicker and less complicated than the CAM technique. In the carbon adsorption-flash evaporation procedure the drying step (where volatile compounds may be lost) is eliminated. The CAM procedures require a minimum of 2.5 days for extraction of saturated carbon; the evaporation modification requires about one hour.

Air stripping appears to be superior to both the CAM and the CA/E techniques. Water extraction and sample concentration can be completed within 24 hours. Because there is no adsorption onto an active surface or use of elevated temperatures, the risk of compound modification during concentration is eliminated. The apparent advantages of these techniques warrant further investigation of their appropriateness to volatile organic compound removal from water.

Laboratory results indicate that both carbon adsorption and air stripping remove organics from water and may be

suited for large scale use. Activated carbon technology has been available for many years and is useful for removing taste and odor compounds and volatile organics from water. Air stripping may prove to be a feasible water purification procedure since extensive aeration is a form of air stripping.

CHAPTER VI

SUMMARY AND CONCLUSION

Air stripping and a flash evaporation modification of the carbon adsorption method were used to concentrate trace volatile organic compounds from tap water in Stillwater, Oklahoma. Compound separation and identification were performed on a combination gas chromatograph-mass spectrometer.

Many compounds were evidenced but remain unidentified. A taste and odor compound was resolved and tentatively identified as 1-secbutyl-3,7-dimethyl-6-hydroxy-bicyclo-dec-2-ene. Bromoform, dibromochloromethane and bromodichloromethane were identified from tap water extracts. This constituted one of the first identifications of haloforms in tap water. Their presence may result from the application of chlorine during water treatment. Further research on identification, quantitation, and effects of these and other tap water constituents is strongly recommended.

Flash evaporation of activated carbon extracts and air stripping were found to be more effective in volatile organic analysis than the traditional carbon adsorption method. However, the selectivity and removal efficiency of these methods remains to be determined.

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APPENDIX

TABLE III

SAMPLING DATA - CARBON ADSORPTION/EVAPORATION TECHNIQUE

Sample Number	Sampling Period		Flow Rate (liters/min)	Total Volume Filtered (liters)
	Begin. date	End (1971)date		
1-1	8/11	8/19	2.0	31,352
1-2	8/12	8/20	2.1	17,221
1-3	8/13	8/23	.51	7,191
1-4	8/14	8/24	2.0	34,204
2-1	8/19	8/26	varied	4,038
2-2	8/20	8/27	varied	7,453
2-3	8/23	8/30	.51	5,224
2-4	8/24	8/31	2.3	22,191
3-1	8/26	9/2	varied	14,477
3-2	8/27	9/6	1.8	20,131
3-3	8/30	9/6	.51	5,393
3-4	8/31	9/7	varied	19,457
4-1	9/2	9/9	varied	22,434
4-2	9/6	9/14	varied	20,199
4-3	9/7	9/13	.51	4,774
4-4	9/9	9/14	2.2	17,942
4-5	9/7	9/8	2.1	2,341
5-1	9/9	9/16	varied	22,246
5-2	9/14	9/17	varied	6,743
5-3	9/14	9/20	.51	4,452
5-4	9/14	9/21	varied	23,752
6-1	9/16	9/23	1.9	16,936
6-2	9/19	9/24	varied	12,463
6-3	9/22	9/27	.51	3,764
6-4	9/22	9/28	varied	17,952
7-1	9/24	9/30	2.3	17,100
7-2	9/25	10/2	varied	18,480
7-3	9/28	10/4	.51	4,317
7-4	9/28	10/5	varied	28,780
8-1	10/2	10/7	varied	14,399
8-2	10/4	10/9	varied	13,671
8-3	10/6	10/11	.51	3,699
8-4	10/6	10/13	3.35	69,087
9-1	10/7	10/14	2.6	31,493
9-2	10/9	10/15	varied	24,090
9-3	10/11	10/19	.51	5,980
9-4	10/13	10/21	2.4	32,091
10-1	10/14	10/21	2.5	36,239
10-2	10/15	10/23	1.5	16,983
11-1	11/17	11/26	varied	25,508
11-2	11/19	11/26	2.3	24,596
11-3	11/19	11/26	2.5	27,422
11-4	11/26	12/3	.51	5,064
1 (1972)	8/1	8/11	4.8	68,428
2 (1972)	8/24	8/30	varied	15,290

TABLE IV
SAMPLING DATA - AIR STRIPPING TECHNIQUE

Sample No.	Sampling Period		Flow Rate (liters/min)	Total Volume Air Stripped (liters)
	Beginning (1971)	End (1971)		
W-1				
W-2	9/10	9/14	5.7	33,439
W-3	9/14	9/15	5.7	8,156
W-4	9/15	9/20	5.7	44,270
W-5	9/20	9/21	5.0	5,977
W-6	9/21	9/22	5.0	7,142
W-7	9/22	9/23	5.0	7,142
W-8	9/24	9/24	6.0	7,912
W-9	9/24	9/25	6.0	6,638
W-10	9/25	9/26	6.0	9,966
W-11	9/26	9/27	6.0	9,006
W-12	9/27	9/28	6.0	8,221
W-13	9/28	9/29	6.0	8,813
W-14	9/29	9/30	6.0	8,710
W-15	9/30	10/2	6.0	17,039
W-16	10/2	10/3	6.0	8,534
W-17	10/3	10/4	6.0	9,084
W-18	10/4	10/5	6.0	8,335
W-19	10/5	10/6	6.0	8,009
W-20	10/6	10/7	6.0	8,631
W-21	10/7	10/9	6.0	9,942
W-22	10/9	10/10	6.0	10,304
W-23	10/10	10/11	6.0	10,510
W-24	10/11	10/13	6.0	14,031
W-25	10/13	10/13	6.0	3,976
W-26	10/13	10/14	6.0	8,849
W-27	10/14	10/15	5.44	7,834
W-28				
W-30	10/16	10/17	4.56	8,518
W-31	11/17	11/19	4.56	9,996
W-32	11/19	11/19	4.56	2,754
W-33	11/19	11/20	5.36	7,906
W-34	11/20	11/21	5.36	7,636
W-35	11/21	11/23	5.36	14,906
W-1 (1972)	7/17	7/18	--	--
*T-1	9/10	9/17		
T-2	9/17	9/21		

* These samples are extraction of water deposited in the water trap installed between the air stripping column and the condensers. They are not directly related to the flow rates or to the number of liters of water passed through the air stripper.

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