

AD-A124 404

DRSAR-LEP-L

AD A-124404

TECHNICAL  
LIBRARY

**CHEMICAL SYSTEMS LABORATORY TECHNICAL REPORT**

**ARCSL-TR-82034**

**IDENTIFICATION OF VOLATILE ORGANIC COMPOUNDS IN WATER BY GAS  
CHROMATOGRAPHY/MASS SPECTROMETRY USING PURGE-AND-TRAP  
SAMPLE CONCENTRATION AND INTRODUCTION**

by

Bruce T. Heitke, Ph.D.

Research Division

January 1983



**US ARMY ARMAMENT RESEARCH AND DEVELOPMENT COMMAND**

**Chemical Systems Laboratory  
Aberdeen Proving Ground, Maryland 21010**



Approved for public release; distribution unlimited.

Disclaimer

The findings in this report are not to be construed as an official Department of the Army position unless so designated by other authorized documents.

Disposition

Destroy this document when it is no longer needed. Do not return it to the originator.

UNCLASSIFIED

SECURITY CLASSIFICATION OF THIS PAGE (When Data Entered)

REPORT DOCUMENTATION PAGE		READ INSTRUCTIONS BEFORE COMPLETING FORM
1. REPORT NUMBER ARCSL-TR-82034	2. GOVT ACCESSION NO.	3. RECIPIENT'S CATALOG NUMBER
4. TITLE (and Subtitle) IDENTIFICATION OF VOLATILE ORGANIC COMPOUNDS IN WATER BY GAS CHROMATOGRAPHY/ MASS SPECTROMETRY USING PURGE-AND-TRAP SAMPLE CONCENTRATION AND INTRODUCTION	5. TYPE OF REPORT & PERIOD COVERED Technical Report April 1980-November 1980	
	6. PERFORMING ORG. REPORT NUMBER	
7. AUTHOR(s)  Bruce T. Heitke, Ph.D.	8. CONTRACT OR GRANT NUMBER(s)	
9. PERFORMING ORGANIZATION NAME AND ADDRESS Commander, Chemical Systems Laboratory ATTN: DRDAR-CLB-R Aberdeen Proving Ground, Maryland 21010	10. PROGRAM ELEMENT, PROJECT, TASK AREA & WORK UNIT NUMBERS USATHAMA Analytical Systems Technology Program	
11. CONTROLLING OFFICE NAME AND ADDRESS Commander, US Army Toxic and Hazardous Materials Agency, ATTN: DRXTH-TS Aberdeen Proving Ground, Maryland 21010	12. REPORT DATE January 1983	
	13. NUMBER OF PAGES 27	
14. MONITORING AGENCY NAME & ADDRESS (if different from Controlling Office)	15. SECURITY CLASS. (of this report) UNCLASSIFIED	
	15a. DECLASSIFICATION/DOWNGRADING SCHEDULE NA	
16. DISTRIBUTION STATEMENT (of this Report)  Approved for public release; distribution unlimited.		
17. DISTRIBUTION STATEMENT (of the abstract entered in Block 20, if different from Report)		
18. SUPPLEMENTARY NOTES		
19. KEY WORDS (Continue on reverse side if necessary and identify by block number)		
Dynamic headspace analysis	Water analysis	Operating parameters
Hewlett-Packard model 7675A	Purge and trap	Thermal desorption
Volatile organic compounds	Sparging	Priority pollutants
Gas chromatography/mass spectrometry	Capillary columns	Rocky Mountain Arsenal
20. ABSTRACT (Continue on reverse side if necessary and identify by block number)		
<p>The objective of this investigation was to evaluate the purge and trap method and the Hewlett-Packard model 7675A purge-and-trap sampler for the identification of volatile compounds in water by gas chromatography/mass spectrometry. The manner in which this instrument accomplishes the transfer of volatile components in water to the chromatographic column is thoroughly described. Guidance is given to the analyst in the specification of operating parameters for the optimization of this transfer. The instrument was evaluated with both packed and capillary columns by using: (1) the</p> <p>(Continued on reverse side)</p>		

## 20. ABSTRACT (Continued)

volatile organics among Environmental Protection Agency's (EPA's) priority pollutants and (2) ground water samples from Rocky Mountain Arsenal. The Hewlett-Packard model 7675A purge-and-trap sampler proved to be adequate for identifying removable organic compounds in water at concentrations of 4 ng/ml (4 ppb) provided that packed-column chromatography is sufficient to resolve the components. This instrument is not suitable for capillary column applications.

## PREFACE

The work described in this report was authorized under the United States Army Toxic and Hazardous Material Agency's Analytical Systems Technology Program. This work was started in April 1980 and completed in November 1980. The experimental data are recorded in notebook 10024.

The use of trade names in this report does not constitute an official endorsement or approval of the use of such commercial hardware or software. This report may not be cited for purposes of advertisement.

Reproduction of this document in whole or in part is prohibited except with permission of the Commander, USA Army Toxic and Hazardous Material Agency, ATTN: DRXTH-TS, Aberdeen Proving Ground, Maryland 21010. However, the Defense Technical Information Center is authorized to reproduce the document for United States Government purposes.

### Acknowledgments

Suggestions regarding the format and careful reading of this report by C. Parker Ferguson are appreciated.

## CONTENTS

	Page
1. INTRODUCTION .....	7
2. THE PURGE-AND-TRAP TECHNIQUE .....	8
2.1 Operation of the Hewlett-Packard Model 7675A Purge-and-Trap Sampler .....	8
2.2 Discussion and Specification of Purge-and-Trap Parameters .....	9
3. EXPERIMENTAL RESULTS AND DISCUSSION .....	10
3.1 Volatile Components of EPA's Priority Pollutants. ....	10
3.2 Rocky Mountain Arsenal Groundwater Samples. ....	12
3.3 Use of Capillary Columns With Hewlett-Packard Model 7675A Concentrator .....	13
4. CONCLUSIONS AND RECOMMENDATIONS .....	14
LITERATURE CITED .....	17
APPENDIXES	
A. Figures .....	19
B. Tables .....	23
DISTRIBUTION LIST .....	25

# IDENTIFICATION OF VOLATILE ORGANIC COMPOUNDS IN WATER BY GAS CHROMATOGRAPHY/MASS SPECTROMETRY USING PURGE-AND-TRAP SAMPLE CONCENTRATION AND INTRODUCTION

## 1. INTRODUCTION

The traditional method of analyzing organic compounds in water by gas chromatography (GC) involves extraction of the water with solvent, concentration of the extract by partial evaporation of the solvent, and syringe injection into the gas chromatography. When this traditional method is applied to the analysis of volatile organic compounds (bp < 150°C), some of the compounds may escape detection. There are three principal reasons for this. First, the most volatile compounds, particularly gases, may equilibrate more rapidly with the atmosphere than the solvent during extraction, and thus be lost. Second, some of the compounds may be evaporated with the solvent during concentration. Third, there may be interference of the large solvent peak with some of the volatile compounds during chromatography.

Other methodologies have been developed with the objective of avoiding some of the sources of sample loss inherent in the traditional method. Direct injection of the water avoids loss of volatile compounds during extraction, but the detection limit is higher since there is no concentration of components.

Headspace analysis is also utilized to improve upon the traditional extraction method. In this method an aqueous sample is sealed in a partially filled container. After an equilibrium is established between the aqueous and gaseous phases for each volatile component, an aliquot of the gaseous phase is injected into the gas chromatograph. In the analysis of the most volatile and water insoluble components, this technique results in concentration of the compound as well as avoidance of solvent interference. In order to apply this method more broadly to volatile organic compounds, the equilibrium between the liquid and gas phases must be shifted toward the gas. One way of shifting the equilibrium is to utilize the technique known as dynamic headspace analysis.

Dynamic headspace analysis involves removing volatile compounds from the equilibrium system by passing a gas through the water, called sparging or purging, and subsequently through a solid sorbent. This process results in the transferral of volatile compounds to and entrapment in a sorbent, for example, activated charcoal or a porous polymer. Following desorption from the solid sorbent with a small quantity of solvent, the volatile compounds can be injected into a gas chromatograph. This analytical method results in concentration of a broad range of volatile compounds but does not avoid the possibility of solvent interference during chromatography.

Bellar and Lichtenberg<sup>1</sup> have utilized the dynamic headspace technique, while avoiding solvent interference, by thermal desorption of the trapping sorbent into a relatively small volume of gas which is then introduced directly into the chromatographic column.

The Environmental Protection Agency (EPA) has "popularized" this technique, as the purge-and-trap method, by implementing it in the regulation of trihalomethanes<sup>2</sup> and volatile compounds on the priority pollutant list.<sup>3</sup> The regulation stimulus of EPA has resulted in the development of at least seven different GC concentrators capable of performing purge-and-trap sample concentration and introduction.

The Army is engaged in environmental analytical programs at its facilities in an effort to identify the presence of chemicals resulting from previous and current operations.

(USATHAMA) requested the Analytical Branch of Research Division, Chemical Systems Laboratory to evaluate the purge-and-trap method and the Hewlett-Packard model 7675A purge-and-trap sampler for the identification of volatile components in water by gas chromatography/mass spectrometry (GC/MS). This report describes the work performed in fulfillment of this task.

## 2. THE PURGE-AND-TRAP TECHNIQUE

### 2.1 Operation of the Hewlett-Packard Model 7675A Purge-and-Trap Sampler.

The operation of the Hewlett-Packard model 7675A concentrator is schematically diagrammed in figure A-1. The diagrams display a purging vessel, a trap, an eight port valve, and a six port valve. The Hewlett-Packard concentrator requires three gas flows for its operation: house air at 70 psi to actuate valves and to cool the sorption trap prior to purging the water sample; zero-grade helium at 10 psi for purging volatile compounds from the water sample onto the trap; and zero-grade helium at 60 psi for backflushing the volatile compounds from the trap into the chromatographic column and for use as the carrier during gas chromatography. The paths of these gases for the various operation conditions of the concentrator are indicated in figure A-1. The concentrator is supplied with a number of controls which the operator may vary to tailor the concentrator operation to a specific analysis.

Following is the sequence of events in the analysis of a water sample using the concentrator. While the concentrator is in the pre-purge condition (see figure A-1), a sample of water is placed in the purge vessel. In this condition compressed air is passed over the outside of the trap for an operator-selected period of time. This brings the trap to room temperature and helps to ensure that volatile compounds are trapped, since the higher the temperature, the more likely volatile compounds will pass through the trap.

At the expiration of the cooling condition, the eight port valve rotates and the purge condition begins. This purge condition continues for an operator-selected period of time. As can be seen in figure A-1, during the purge condition an operator selected helium flow is passed through the water sample which transfers the volatile compounds from the water to the trap.

At the end of the purge condition, both valves rotate, the cooling flow of air is stopped, and the trap is heated to an operator-selected temperature. As can be seen in figure A-1, rotation of the two valves stops the purging flow of helium through the water and initiates the operator-selected carrier flow through the trap. The trap (0.25 inch O.D., 5 inches long) acts as a short chromatographic column such that, as volatile compounds are transferred to it from the water, some are retained strongly and remain at the bottom of the trap (as oriented in figure A-1) while others migrate further into the trap. As figure A-1 illustrates, the direction of carrier flow through the trap in the desorb condition is opposite the purge flow in the purge condition. The relative retention times of volatile compounds are the same regardless of flow direction so that backflushing of the trap in the desorb condition helps to effect the transfer of all volatile compounds to the column at approximately the same time. Heating the trap speeds desorption which contributes further to minimizing the volume of gas in which all of the volatile compounds are transferred.

At the end of the desorb condition, the six port valve rotates and the temperature of the trap is increased 50°C for an operator-selected period of time. This vent condition simply cleans the trap to ensure that nothing remains on the trap to be desorbed during the analysis of the next sample. The possibility of sample cross contamination is also diminished because the two valves are enclosed in an oven equipped with a variable temperature control.

The Hewlett-Packard model 7675A purge-and-trap sampler provides for operator specification of the following parameters: length of cooling condition; length of purge condition; purge gas flow rate; trapping material; length of desorb condition; desorption temperature; carrier gas flow rate; length of vent condition; and temperature of valve oven. Factors considered in the specification of the most important of these parameters as well as interdependence of these parameters are discussed in the next section.

## 2.2 Discussion and Specification of Purge-and-Trap Parameters.

As described in the previous section, the Hewlett-Packard model 7675A concentrator allows the analyst to specify a rather large number of parameters. If the analyst thoroughly explored the ranges and combinations of these parameters, it would be a formidable task. Fortunately, EPA methodology<sup>2,3</sup> and the Hewlett-Packard manual<sup>4</sup> give guidance with regard to specifying parameters. The analyst is left with the task of optimizing a reduced number and range of parameters for a particular group of compounds.

Analytical results of the purge-and-trap method depend on how effectively volatile compounds are transferred from the water sample to the chromatographic column. This transfer can be divided into three steps: first, transfer from the water to the purge gas; second, transfer from the purge gas to the trap; and third, transfer from the trap to the column. Ideally, the efficiencies of these steps would be 100% for all volatile compounds. In practice, the volatile organics present have different vapor pressures and solubilities in water, and therefore it is often impossible to achieve 100% efficiencies for each of these steps for all of the compounds present.

The first two steps are interrelated. The degree to which a volatile organic is purged from the water sample depends on the volume of gas that is passed through the sample. A given volume of gas can be produced in an infinite number of ways by changing the purge time and purge flow rate. If the purge volume were the only important operating parameter, one would select a volume great enough so that the least volatile, most water soluble component would be completely removed from the water. However, this approach would assume that the trap is able to retain volatiles regardless of the purging volume. In fact, the degree to which a volatile organic is removed from the purging gas by the trap depends on both the trapping sorbent and the purging volume.

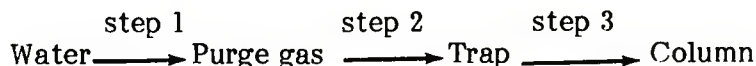
The trap is essentially a short chromatographic column. As with any column, volatile organics introduced into the trap will have a retention time which depends on the packing, temperature, and purge flow rate. If this retention time is less than the purge time for a particular volatile organic, then at least part of that component breaks through the trap. To ensure the identification of a given group of volatile organics, a purge volume must be selected that will remove a detectable quantity of the least volatile component from the water without causing excessive trap breakthrough of the most volatile component.

The third step in the transfer of volatile organics from the water sample to the chromatographic column is the transfer from trap to column. This transfer is accomplished by heating the trap while column carrier gas is flowing through it. The efficiency of this step depends on the flow rate and the maximum temperature that the sorbent material allows. In practice, the flow rate is determined by analytical column considerations. The maximum temperature must be chosen so that detectable quantities of all components are desorbed while excessive sorbent bleed is avoided.

The characteristics of a good solid sorbent are that it has a high affinity for organics, a low affinity for water vapor, and good thermal stability.

As discussed above, analytical results of the purge-and-trap method depend on how effectively volatile compounds are transferred from the water sample to the chromatographic column. Thus, the ultimate test of a particular set of purge-and-trap parameters is the degree to which detector responses to the components of the test mixture compare to the detector responses when the test mixture is introduced directly onto the column by syringe injection. If the response obtained for any component introduced by purge and trap is less than that obtained by syringe introduction, the possibility must be considered that some of the sample was lost in one of the three steps involved in the purge-and-trap technique. Determination of the step in which sample is lost allows one to change the correct parameters so that loss is avoided or diminished.

The step during which the sample is lost can be determined by the following tests:



Analyze a standard water sample by the purge-and-trap method, then recycle the concentrator without changing the water in the purging vessel. If a response is obtained from the second analysis, then sample could have been originally lost in steps 1 and 3.

Inject sample directly on the bottom of the trap (as oriented in figure A-1) and cycle the concentrator with pure water in the purging vessel. If the response is less than that obtained by syringe injection, then sample was lost in steps 2 or 3.

Inject sample directly on the top of the trap (as oriented in figure A-1) and immediately desorb the trap thermally. If the response is less than that obtained by syringe injection, then sample was lost in step 3. Sample loss in this step can also be demonstrated by redesorbing the trap. If a response is obtained, then less than 100% of the sample was transferred during the first desorption.

### 3. EXPERIMENTAL RESULTS AND DISCUSSION

#### 3.1 Volatile Components of EPA's Priority Pollutants.

The conditions used to carry out a purge-and-trap analysis depend on the concentrator and the compounds to be analyzed. The volatile organics among EPA's priority pollutants consist of thirty compounds whose boiling points range from below 0° and as high as 150° C and whose solubilities in water range from miscible to immiscible. Since these thirty compounds vary so widely in their physical properties and are so readily available from GC supply companies, it was decided to use them to evaluate the purge-and-trap method and the Hewlett-Packard model 7675A concentrator. The priority pollutant volatiles were purchased from Supelco Inc. as dilute solutions in four different vials (table B-1).

The Hewlett-Packard concentrator is supplied with Tenax GC as the trapping material. Tenax was used exclusively in this evaluation. Although other sorbents may be superior for certain components of the volatile priority pollutants, Tenax is a good sorbent for a wide range of organic compounds.

Techniques described in the last section were used to optimize the analysis of 200 ng of each of the thirty volatiles in 10 ml of water (20 ppb). Regardless of the purge-and-trap parameters utilized, the following six compounds were never detected: chloromethane; vinyl chloride; dichlorofluoromethane; bromomethane; chloroethane; and acrolein. On the basis of their physical properties, the compounds undetected can be divided into two groups. Acrolein is

very soluble in water and has a boiling point of 53°C. The possibility that acrolein was being transferred inefficiently from the water to the column was checked by introducing 1 µg each of the acrolein and acrylonitrile solution into the gas chromatograph/mass spectrometer with a syringe. Still, acrolein was not detected. This leads to the suspicion that the standard was formulated incorrectly by Supelco.

The remaining five undetected compounds are gases at room temperature and are only slightly soluble in water. An injection containing 200 ng of each of the gases in 1 µl of methanol was made into the gas chromatograph/mass spectrometer. Still, the gases were not detected. This result leads to the conclusion that either the standards were not formulated correctly or that between the time of formulation and analysis, these volatile compounds diffused out of the methanol solvent.

Also while optimizing the operating parameters, it was discovered that the concentrator displayed memory of tetrachloroethene. After analysis of the purgeable priority pollutants, the concentrator was recycled with the purge time set at zero. In essence, this simply results in the analysis of anything that remains on the trap. When this was done, tetrachloroethene was detected. Tetrachloroethene was detected upon repeated thermal desorption even when the Tenax trap was replaced with an unused Tenax trap. Since tetrachloroethene is not a component of Tenax bleed, its source must be within the concentrator plumbing. The transfer line from the trap to the column is suspect since it is heated only by conduction from the heated valve compartment.

Optimization of the purge-and-trap parameters having been completed, the thirty volatile priority pollutants (quantities listed in table B-1) were transferred by syringe from the four original vials directly into 10 ml of previously purged distilled water contained within the purge vessel. The vessel was immediately screwed onto the concentrator and the sample was analyzed utilizing the following instrumental parameters:

Hewlett-Packard model 7675A concentrator parameters

Valve oven temperature: 200°C  
Cooling condition: 5 min  
Purge condition: 12 min  
Purge gas helium @ 50 ml/min  
Trap sorbent: Tenax  
Desorption condition: 3 min  
Desorption temperature: 200°C  
Vent condition: 3 min  
Carrier flow rate: 40 ml/min helium

Column parameters

Column: stainless steel, 8 ft long, 2 mm ID, 1% SP-1000 on 60/80 Carbopack B  
Column temperature: 45°C for 3 min, 45 to 220°C with an increase of 8° each min, 220° for 15 min.

Hewlett-Packard model 5985A gas chromatograph/mass spectrometer parameters

Jet separator temperature: 250°C  
Source temperature: 200°C  
Source pressure:  $6 \times 10^{-6}$  mm Hg  
Ionizing potential: 70 ev  
Electron multiplier gain:  $1.5 \times 10^4$  at mass 69

A/D conversions per 0.125 amu: 6  
Scan range: 33 to 320 amu.

Figure A-2 displays the total ion chromatogram obtained from this analysis. The compounds represented by the peaks can be identified by finding in table B-1 the retention time of any peak displayed in figure A-2. As described above, during optimization of the analysis, six compounds were not detected. There are no retention times listed in table B-1 for these compounds.

The amplitude of the acrylonitrile peak obtained from 1  $\mu\text{g}$  is similar to the amplitudes of peaks representing 40 ng of other components. Difficulty in analyzing acrolein and acrylonitrile by the purge-and-trap technique is noted in the EPA method.<sup>3</sup> Because of their polarity, they are lost both by inefficient purging and Tenax trap breakthrough.

The broad peak starting near a retention time of 24 min is due to column bleed. Column bleed was much less obvious during optimization of the parameters when 200 rather than 40 ng of the components was analyzed.

It should be noted that three components elute together at a retention time of 18.5 min and that two components coelute after 23.6 min. This result is not unexpected, since the column utilized in this evaluation is specified in the EPA method<sup>3</sup> for the analysis of purgeable priority pollutants and retention data in the method indicates that these same components coelute. Initially, one might consider such coincidental retention times reason enough to declare invalid the analysis of the purgeable priority pollutants with this column. The reason such analyses are not necessarily invalid is based on the fact that the purgeable priority pollutants are known and, as a consequence, their retention times and mass spectra are known.

Consider the example of tetrachloroethene and 1,1,2,2-tetrachloroethane; both elute after 23.5 minutes, and because of the similarity of their structures, their mass spectra have many peaks in common. However, masses 164 and 129, found in the spectrum of tetrachloroethene, are not found in the spectrum of 1,1,2,2-tetrachloroethane, while the 83 and 168 peaks found in the spectrum of 1,1,2,2-tetrachloroethane are not found in the spectrum of tetrachloroethene. The knowledge that they coelute and that they have the above mentioned differences in their mass spectra allow these two compounds to be identified in the presence of each other. This is an example of identifying compounds on a "hit list" when the following question is posed: "Are any compounds on this list present?" Of course, one can encounter a mixture more complex where one or more additional components coelute with the two considered above. In such a case, there is a possibility that none of the compounds coeluting could be identified.

With the exception of the coeluting components, the 24 volatiles detected were identified using the Hewlett-Packard computerized library search. The five volatiles which coelute were easily identified because their retention times and mass spectra were known. For acrylonitrile, this represents a satisfactory analysis at a concentration of 1  $\mu\text{g}/10\text{ ml}$  (100 ppb); for the remaining 23 volatiles detected, this represents a satisfactory analysis at a concentration of 40 ng/10 ml (4 ppb).

### 3.2 Rocky Mountain Arsenal Groundwater Samples.

A Calgon Corporation charcoal treatment process is used at Rocky Mountain Arsenal (RMA) to clean groundwater before it migrates off post. Samples of water taken before (influent) and after (effluent) the charcoal treatment were sampled on 13 December 1979 and sent to Chemical Systems Laboratory for analysis under a project unrelated to this report.

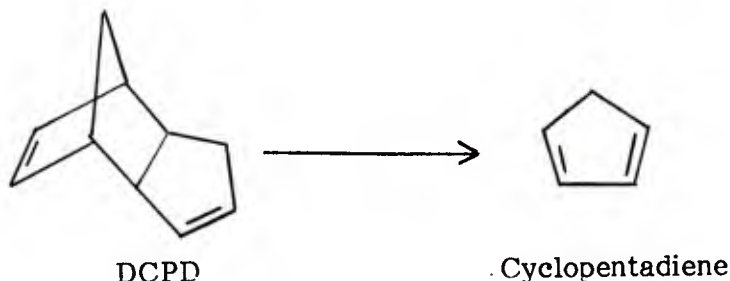
Since the analysis of actual environmental samples as well as standard solutions is recommended during the evaluation of an analytical technique, and since RMA groundwater is familiar to USATHAMA personnel, the Calgon plant influent and effluent waters were analyzed using almost the identical conditions arrived at while optimizing the analysis of the volatile priority pollutants. The only parameter which differed was the electron multiplier gain which was lowered for the more concentrated influent water sample.

Figures A-3 and A-4 display the total ion chromatogram obtained in the analyses of Calgon plant influent and effluent water, respectively. The compounds represented by the peaks can be identified by finding the retention times corresponding to peaks shown in figures A-3 and A-4 within tables B-2 and B-3, respectively.

Quantification of these compounds was beyond the scope of this work and, in any case, might well be meaningless because of the length of time between sampling and analysis. However, some idea of the relative responses can be obtained by comparing the column bleed at a retention time of 27 min in figures A-2, A-3 and A-4.

The peak at 23.6 min, identified as tetrachloroethene, in both figures A-3 and A-4 is probably due to sample carryover from the volatile priority pollutants as described previously.

The broad peak between 21 and 26 minutes is due to cyclopentadiene. Based on the breadth and retention time of this peak relative to its Diels-Alder adduct, dicyclopentadiene (DCPD), at 26 minutes, it is likely that cyclopentadiene is formed by a retro Diels-Alder reaction within the gas chromatograph.



A reaction of this type may not be reproducible from run to run and might explain low precision in the analysis of DCPD.

The presence of carbon disulfide and benzene in the effluent water and their absence in the influent water is difficult to explain, but it is possible that they are introduced during treatment of the water.

### 3.3 Use of Capillary Columns With the Hewlett-Packard Model 7675A Concentrator.

As discussed in a previous section, knowledge of the retention times and mass spectra of each component greatly facilitates identifications. In fact, identifications are possible even when two or more compounds interfere chromatographically, provided that there is a list of all the compounds of interest. In regulating the priority pollutants, EPA has the analytical luxury of such a "hit list" since it regulates only the compounds on the list. When the objective of an organization or analyst is to identify all the chemical compounds present in an environmental sample, the luxury inherent in such a "hit list" is nonexistent.

As an example, assume that an unknown mixture is composed of chlorobenzene and DCPD in approximately equal concentrations. From the retention times listed in tables B-1

and B-2, it is clear that these two compounds would interfere severely with each other under these chromatographic conditions. Unless an analyst knew that these two compounds coeluted and what their mass spectra were, there is a good chance that neither would be identified.

The point to be made here is that, even though a mass spectrometer is a very powerful instrument for identifying components of a mixture, in most cases the components must be separated. Capillary columns generally separate the components of complex mixtures better than packed columns. Accordingly, a wall-coated open tubular (WCOT) capillary column was interfaced with the Hewlett-Packard concentrator and 10 ml of water containing 200 ng each of the compounds received in vial A (see table B-1) was analyzed under identical conditions listed previously with the following exceptions:

Hewlett-Packard model 7675A concentrator parameters  
carrier helium at 1.2 ml/min

Column parameters  
Column glass: 30m, 0.25 mm ID, WCOT, Carbowax 20 M.  
Column temperature: 70°C for 2 min, 20-220°C @ 4°/min

Hewlett-Packard model 5985A GC/MS parameters  
No separator, direct flow into source  
A/D conversions per 0.125 amu: 3.

The peaks on the resulting chromatogram were about one minute wide and, as a consequence, peak separation was much worse than displayed on the chromatogram obtained using a packed column (figure A-2). The reason for these broad peaks relates to plug injection, dead volume, and the length of time required to desorb the Tenax trap. The best chromatography is obtained when the sample is introduced into the smallest possible volume of carrier gas, i.e. plug injection, since the period of time during which the detector will respond to a component will be brief. Plug injection is desirable regardless of whether the sample is in liquid form and introduced by syringe or in gas form and introduced by thermal desorption of a Tenax trap. When using packed columns, the dead volume of the Tenax trap is insignificant compared to the 40-ml/min carrier flow and adequate plug injection is achieved. However, using a capillary column, the dead volume of the Tenax trap is large compared to the 1.2-ml/min carrier flow and the injection plug is too large for a capillary column. In addition, the length of time required to heat the Tenax trap to 200°C will be a contributing factor in determining the volume of carrier gas into which the sample is desorbed. It takes the Hewlett-Packard concentrator over a minute to heat the tube to 200°C.

In summary, the highest probability of identifying unknown purgeable organics in water requires the greatest possible chromatographic separation of the compounds. In general, capillary columns afford greater separation than packed columns, but the concentrator must be compatible with capillary columns. The dead volume of the trap and the length of time required to heat the trap make the Hewlett-Packard model 7675A concentrator unsuitable for capillary column applications.

#### 4. CONCLUSIONS AND RECOMMENDATIONS

Utilizing the instrumental parameters listed in this report, the Hewlett-Packard model 7675A purge-and-trap sampler proved to be an adequate concentrator for identifying purgeable organic compounds in water at the 4 ng/ml (4 ppb) level when the compounds are on a "hit list." If the analysis required is more general than determining whether or not compounds on a "hit list" are present, then the use of capillary columns together with a concentrator

compatible with capillary columns will lead to more identifications of the components of a complex mixture. This investigator is aware of one concentrator that is compatible with capillary columns: it is the UNACON concentrator manufactured by Envirochem.

Regardless of the concentrator used, the 23 volatile compounds received in vials A and B (table B-1) afford a good test mixture. If they can be identified together at a given concentration, then the analytical parameters used will probably be suitable for analyzing actual environmental samples at the same concentration. The probability of successfully identifying the components in this test mixture can be increased by tuning the mass spectrometer such that published performance criteria<sup>3</sup> are met. Note that EPA<sup>3</sup> now specifies the introduction of 50 ng of decafluorotriphenylphosphine (DFTPP) into the chromatographic column rather than 20 ng, as was suggested in the original publication.<sup>5</sup> In addition, EPA now recommends p-bromofluorobenzene (BFB) as a secondary spectrum validation compound, which is used with GC columns that do not elute DFTPP.<sup>3</sup> BFB is the standard of choice with the column used in this evaluation.

It is not possible to ensure the identification of all components at a certain concentration in a mixture even by specifying the instrumentation, operating parameters, and procedures since the most important factor is unknown. The degree of interference between the components is the most important and unpredictable factor. It can be controlled to an appreciable extent by the chromatographic parameters the analyst selects. Thus, the care and experience of the analyst himself are important factors and the analyst is ultimately responsible for the correct identification of an unknown.

Of course, proper instrumentation, operating parameters, and procedures are important also. Procedures not within the scope of this evaluation include sample collection and preservation until analysis. There is a thorough discussion of this analytical technique in the published EPA method.<sup>3</sup>

## LITERATURE CITED

1. Bellar, T. A. and Lichtenberg, J. J. Determining Volatile Organics at Microgram-Per-Liter Levels by Gas Chromatography. *J. Am. Water Works Assoc.* 66 739 to 744 (1974).
2. Federal Register. Analyses of Trihalonophemes in Drinking Water by the Purge-and-Trap Method. 44, 231, 68672-82 (1979).
3. Federal Register. Gas Chromatography/Mass Spectrometric Method for Purgeables-Method 624. 44, 233, pp 69532 to 69539 (1979).
4. Hewlett-Packard, Operating and Service Manual for Purge-and-Trap Sampler 7675A, part no. 07675-90109. May 1979.
5. Eichelberger, J. W., Harris, L. E., and Budde, W. L. Reference Compound to Calibrate Iron Abundance Measurement in Gas Chromatography-Mass Spectrometry Systems. *Anal. Chem.* 47, pp 995 to 1000 (1975).

APPENDIX A

FIGURES

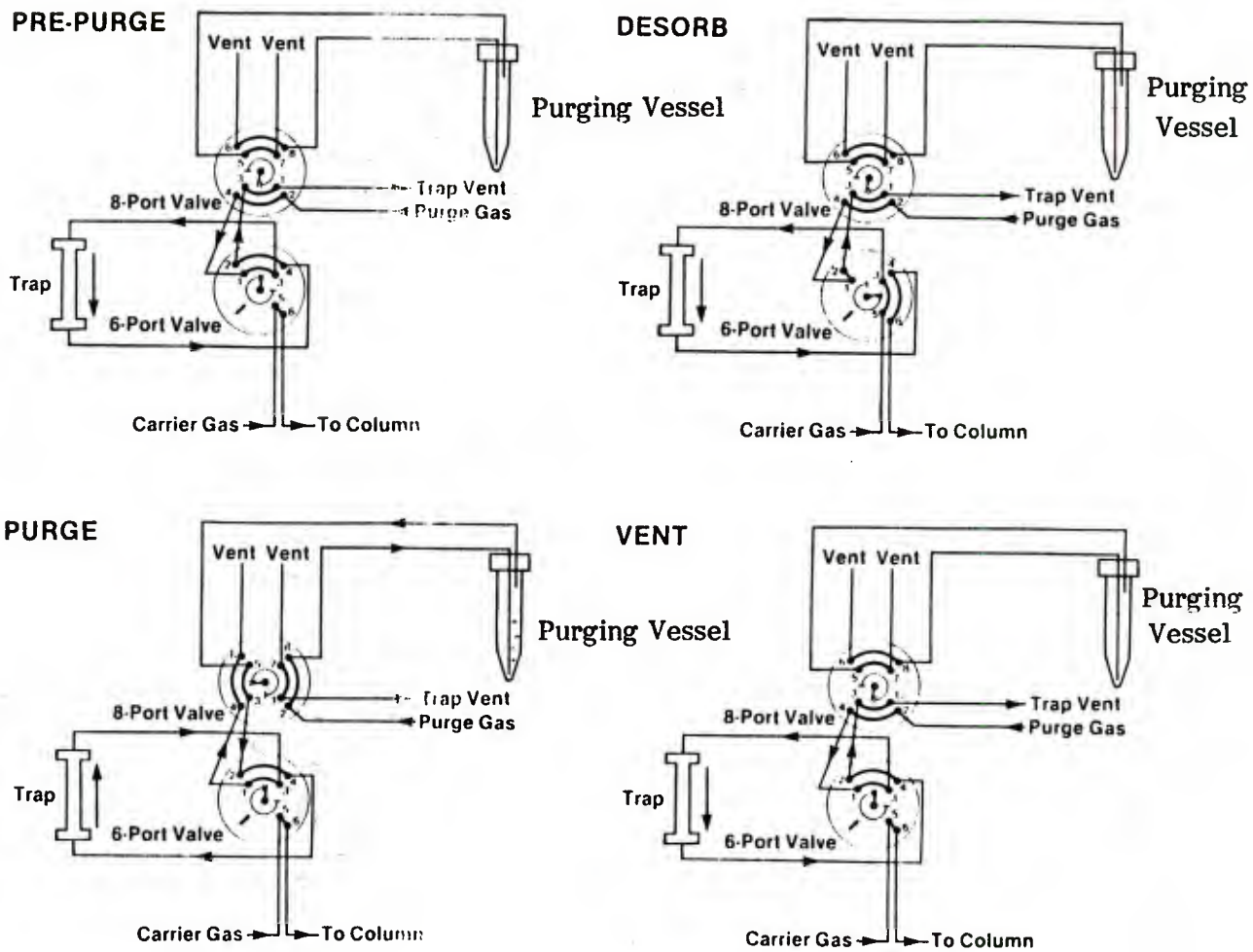


Figure A-1. Operation of the Hewlett-Packard Model 7675A Purge-and-Trap Sampler

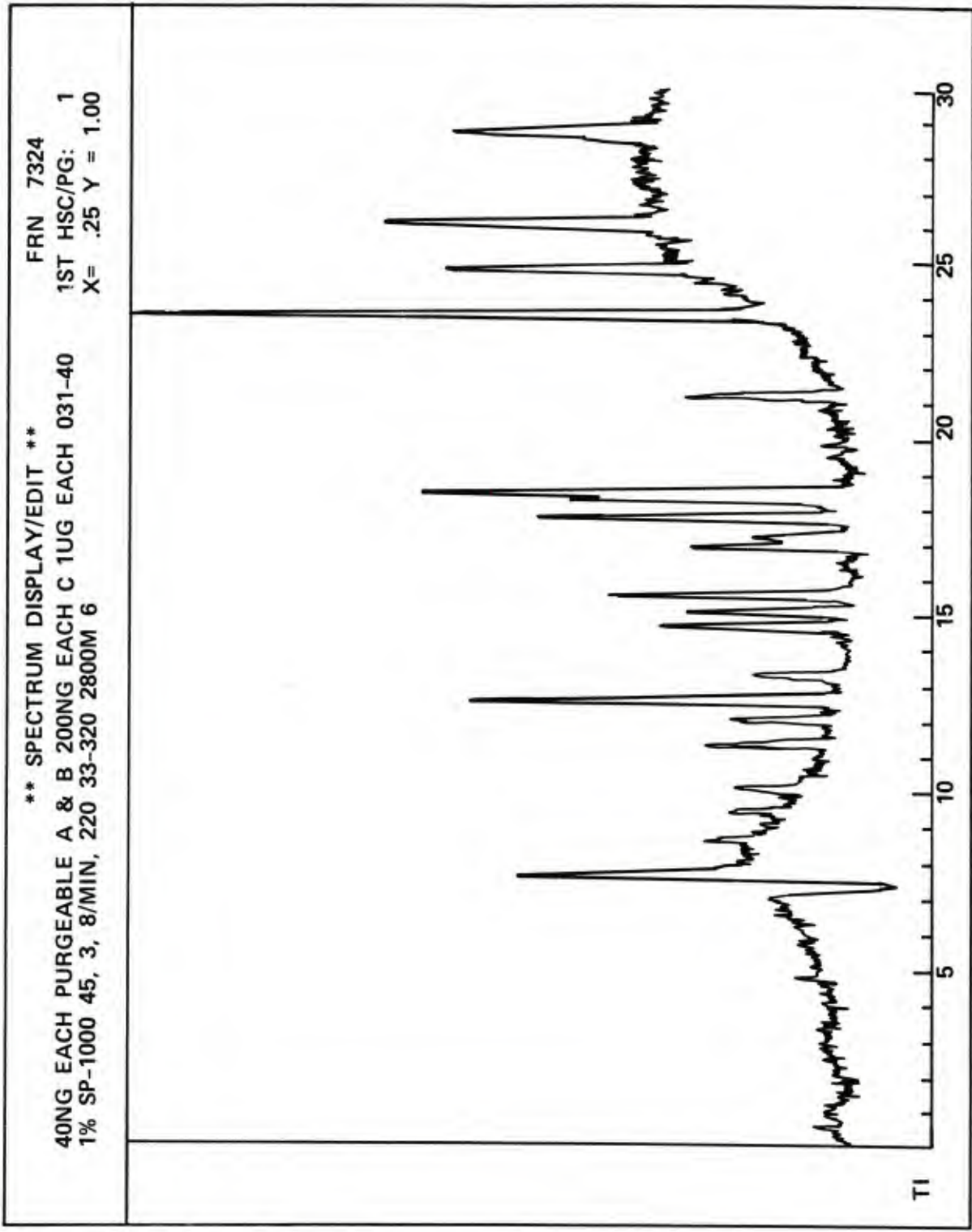


Figure A-2. Total Ion Chromatogram of Volatile Priority Pollutants

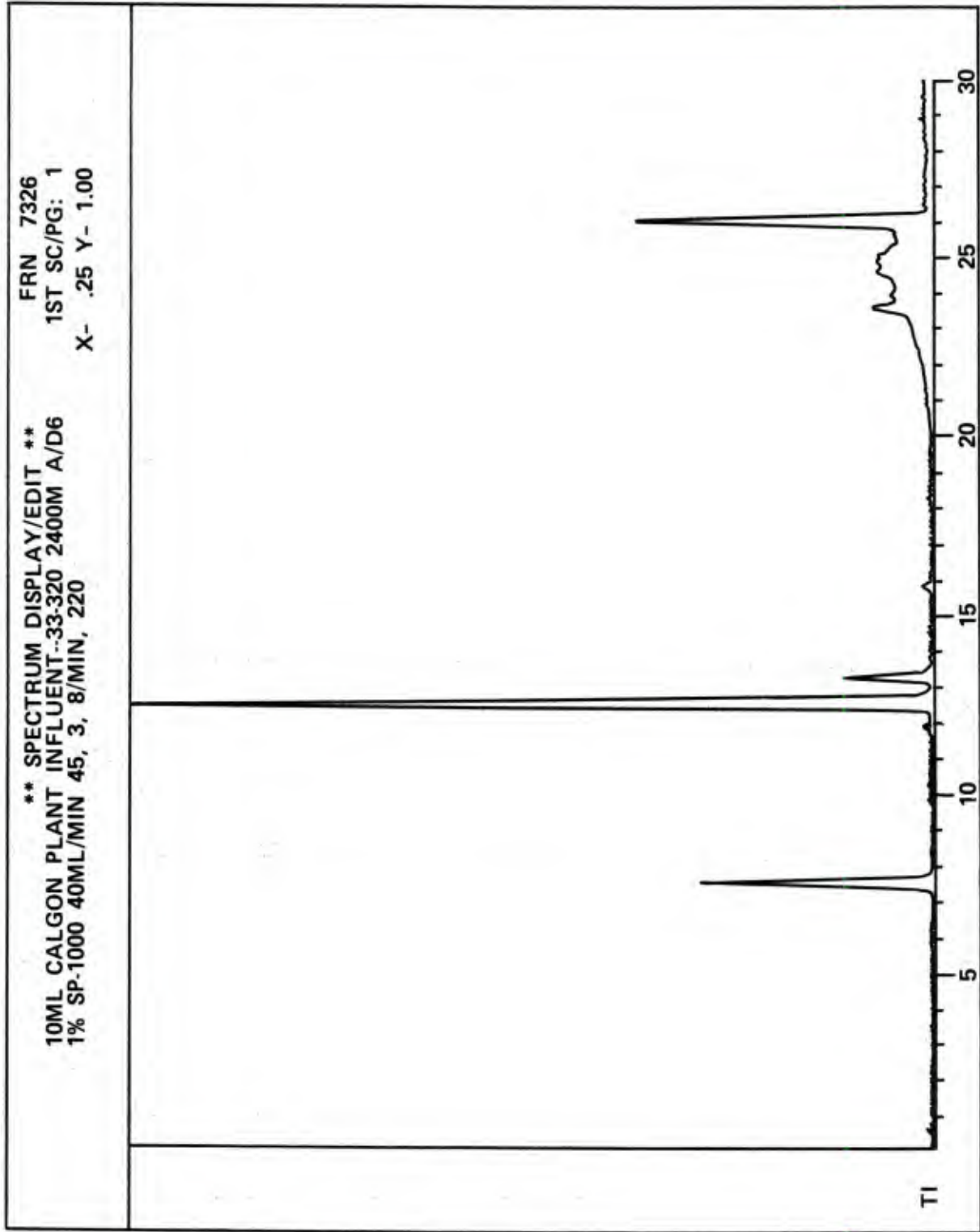


Figure A-3. Total Ion Chromatogram of RMA Calgon Process Influent Water

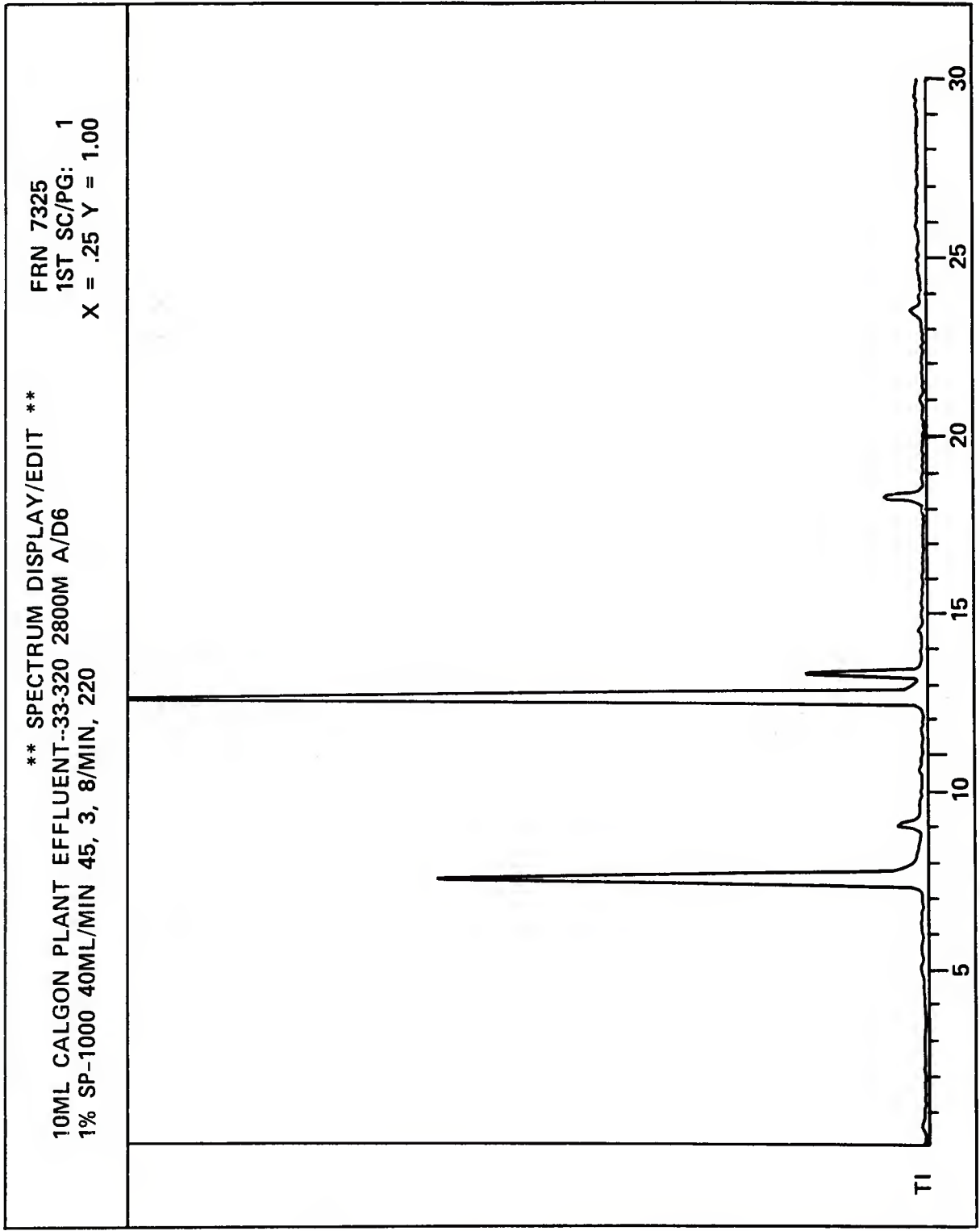


Figure A-4. Total Ion Chromatogram of RMA Calgon Process Effluent Water

## APPENDIX B

## TABLES

Table B-1. Volatile Priority Pollutants

Vial <sup>a,b</sup>	Compound	Quantity	Retention time <sup>c</sup>
		ng	min
C	Chloromethane	200	
C	Vinyl chloride	200	
C	Dichlorofluoromethane	200	
C	Bromomethane	200	
C	Chloroethane	200	
A	Dichloromethane	40	7.7
D	Acrylonitrile	1000	8.7
D	Acrolein	1000	
B	Trichlorofluoromethane	40	9.5
A	1,1-Dichloroethene	40	10.1
A	1,1-Dichloroethane	40	11.4
B	Trans-1,2-dichloroethene	40	12.1
A	Trichloromethane	40	12.7
B	1,2-Dichloroethane	40	13.4
B	1,1,1-Trichloroethane	40	14.7
A	Tetrachloromethane	40	15.1
B	Bromodichloromethane	40	15.6
A	1,2-Dichloropropane	40	17.0
B	Trans-1,3-dichloropropene	40	17.3
A	Trichloroethene	40	17.8
B	Benzene	40	18.8
B	Cis-1,3-dichloropropene	40	18.5
A	1,1,2-Trichloroethane	40	18.5
A	Chlorodibromomethane	40	18.5
B	Tribromomethane	40	21.3
A	Tetrachloroethene	40	23.6
B	1,1,2,2-Tetrachloroethane	40	23.6
B	Toluene	40	24.9
A	Chlorobenzene	40	26.2
B	Ethylbenzene	40	28.8

a Compounds in vials A, B and C were received as solutions in methanol at concentrations of 200 ug/ml.

b Compounds in vial D were received as a solution in water at concentrations of 1 mg/ml.

c Retention times were obtained under the following GC conditions:

Column: stainless steel, 8 ft long, 2 mm ID, 1% SP-1000 on 60/80 Carbopack B

Carrier: helium at 40 ml/min

Column temperature: 45° for 3 min., 45 to 220° with an increase of 8°/min, 220° for 15 min.

Table B-2. Compounds Identified in  
Calgon Plant Influent Water

Compound	Retention time*
	min
Dichloromethane	7.6
Trichloromethane	12.6
1,2-Dichloroethane	13.3
Tetrachloroethene	23.5
Cyclopentadiene	25.0
Dicyclopentadiene	26.1

Table B-3. Compounds Identified in  
Calgon Plant Effluent Water

Compound	Retention time*
	min
Dichloromethane	7.6
Carbon disulfide	9.0
Trichloromethane	12.7
1,2-Dichloroethane	13.4
Benzene	18.3
Tetrachloroethene	23.5

\* Retention times were obtained under the following GC conditions:  
 Column: stainless steel, 8 ft. long,  
 2mm ID, 17° SP-1000 on 60/80  
 Carbopack B  
 Carrier: helium at 40 ml/min  
 Column temperature: 45° for 3 min,  
 45-220 with an increase of 8°/min,  
 220° for 15 min.

DISTRIBUTION LIST 6

Names	Copies	Names	Copies
<b>CHEMICAL SYSTEMS LABORATORY</b>		<b>DEPARTMENT OF THE ARMY</b>	
ATTN: DRDAR-CLB	1	HQDA	
ATTN: DRDAR-CLB-C	1	ATTN: DAMO-NCC	1
ATTN: DRDAR-CLB-R	1	ATTN: DAMO-NC/COL Robinson	1
ATTN: DRDAR-CLB-R(M)	1	WASH DC 20310	
ATTN: DRDAR-CLB-T	1	Federal Emergency Management Agency	
ATTN: DRDAR-CLC-B	1	Office of Research/NPP	
ATTN: DRDAR-CLC-C	1	ATTN: David W. Bensen	1
ATTN: DRDAR-CLF	1	Washington, DC 20472	
ATTN: DRDAR-CLJ-R	2	HQ Sixth US Army	
ATTN: DRDAR-CLJ-L	2	ATTN: AFKC-OP-NBC	1
ATTN: DRDAR-CLN-S	1	Presidio of San Francisco, CA 94129	
ATTN: DRDAR-CLN-TE	1	Commander	
ATTN: DRDAR-CLT	1	USASTCFEO	
ATTN: DRDAR-CLW-C	1	ATTN: MAJ Mikeworth	1
ATTN: DRDAR-CLW-P	1	APO San Francisco 96328	
ATTN: DRDAR-CLW-E	1	Army Research Office	
COPIES FOR AUTHOR(S)		ATTN: DRXRO-CB (Dr. R. Ghirardelli)	1
Research Division	1	P.O. Box 12211	
RECORD COPY: DRDAR-CLB-A	1	Research Triangle Park, NC 27709	
<b>DEPARTMENT OF DEFENSE</b>		<b>OFFICE OF THE SURGEON GENERAL</b>	
Defense Technical Information Center		Commander	
ATTN: DTIC-DDA-2	12	US Army Medical Bioengineering Research	
Cameron Station, Building 5		and Development Laboratory	
Alexandria, VA 22314		ATTN: SGRD-UBD-AL, Bldg 568	1
Director		Fort Detrick, Frederick, MD 21701	
Defense Intelligence Agency		Commander	
ATTN: DB-4G1	1	USA Medical Research Institute of	
Washington, DC 20301		Chemical Defense	
Commander		ATTN: SGRD-UV-L	1
USASED, USAINSCOM		Aberdeen Proving Ground, MD 21010	
ATTN: IAFM-SED-III	1		
Fort Meade, MD 20755			

Commandant  
Academy of Health Sciences, US Army  
ATTN: HSHA-CDH 1  
ATTN: HSHA-IPM 1  
Fort Sam Houston, TX 78234

US ARMY MATERIEL DEVELOPMENT AND  
READINESS COMMAND

Commander  
US Army Materiel Development and  
Readiness Command  
ATTN: DRCLDC 1  
ATTN: DRCSF-P 1  
5001 Eisenhower Ave  
Alexandria, VA 22333

PM Smoke/Obscurants  
ATTN: DRCPM-SMK-S 3  
Aberdeen Proving Ground, MD 21005

Commander  
US Army Toxic & Hazardous Materials Agency  
ATTN: DRXTH-AS 1  
ATTN: DRXTH-ES 1  
ATTN: DRXTH-TE 1  
Aberdeen Proving Ground, MD 21010

Commander  
US Army Foreign Science & Technology Center  
ATTN: DRXST-MT3 1  
220 Seventh St., NE  
Charlottesville, VA 22901

Director  
US Army Materiel Systems Analysis Activity  
ATTN: DRXSY-MP 1  
ATTN: DRXSY-CA (Mr. Metz) 1  
Aberdeen Proving Ground, MD 21005

Commander  
US Army Missile Command  
Redstone Scientific Information Center  
ATTN: DRSMI-RPR (Documents) 1  
Redstone Arsenal, AL 35809

Director  
DARCOM Field Safety Activity  
ATTN: DRXOS-SE (Mr. Yutmeyer) 1  
Charlestown, IN 47111

US ARMY ARMAMENT RESEARCH AND  
DEVELOPMENT COMMAND

Commander  
US Army Armament Research and  
Development Command  
ATTN: DRDAR-LCE-C 1  
ATTN: DRDAR-LCM-SA 1  
ATTN: DRDAR-LCU-CE 1  
ATTN: DRDAR-NC (COL Fields) 3  
ATTN: DRDAR-SCS 1  
ATTN: DRDAR-TDC (Dr. D. Gyroog) 1  
ATTN: DRDAR-TSS 2  
Dover, NJ 07801

Commander  
ARRADCOM  
ATTN: DRDAR-QAC-E 1  
Aberdeen Proving Ground, MD 21010

US ARMY ARMAMENT MATERIEL READINESS  
COMMAND

Commander  
US Army Armament Materiel Readiness Command  
ATTN: DR SAR-ASN 1  
ATTN: DR SAR-IRI-A 1  
ATTN: DR SAR-ISE 1  
ATTN: DR SAR-LEP-L 1  
Rock Island, IL 61299

Commander  
US Army Dugway Proving Ground  
ATTN: Technical Library (Docu Sect) 1  
Dugway, UT 84022

US ARMY TRAINING & DOCTRINE COMMAND

Commandant  
US Army Missile & Munitions Center  
and School  
ATTN: ATSK-TME 1  
Redstone Arsenal, AL 35809

Commandant  
 US Army Chemical School  
 ATTN: ATZN-CM-C 1  
 ATTN: ATZN-CM-AD 2  
 ATTN: ATZN-CM-TPC 2  
 Fort McClellan, AL 36205

Commander  
 US Army Infantry Center  
 ATTN: ATSH-CD-MS-C 1  
 Fort Benning, GA 31905

Commander  
 USA Training and Doctrine Command  
 ATTN: ATCD-N 1  
 Fort Monroe, VA 23651

Commander  
 US Army Armor Center  
 ATTN: ATZK-PPT-PO-C 1  
 Fort Knox, KY 40121

DEPARTMENT OF THE NAVY

Project Manager  
 Theatre Nuclear Warfare Project Office  
 ATTN: TN-09C 1  
 Navy Department  
 Washington, DC 20360

Chief of Naval Research  
 ATTN: Code 441 1  
 800 N. Quincy Street  
 Arlington, VA 22217

Commanding Officer  
 Naval Weapons Support Center  
 Applied Sciences Department  
 ATTN: Code 50C, Bldg 190 1  
 Crane, IN 47522

Commander  
 Naval Air Development Center  
 ATTN: Code 2012 (Dr. Robert Helmbold) 1  
 Warminster, PA 18974

DEPARTMENT OF THE AIR FORCE

ASD/AESD 1  
 Wright-Patterson AFB, OH 45433

HQ AFTEC/TEL 1  
 Kirtland AFB, NM 87117

USAF TAWC/THL 1  
 Eglin AFB, FL 32542

AFATL/DLV 1  
 Eglin AFB, FL 32542

USAF SC  
 ATTN: AD/YQO (MAJ Owens) 1  
 Eglin AFB, FL 32542

AFAMRL/TS  
 ATTN: COL Johnson 1  
 Wright-Patterson AFB, OH 45433

OUTSIDE AGENCIES

Battelle, Columbus Laboratories  
 ATTN: TACTEC 1  
 505 King Avenue  
 Columbus, OH 43201

Toxicology Information Center, JH 652  
 National Research Council 1  
 2101 Constitution Ave., NW  
 Washington, DC 20418

US Public Health Service  
 Center for Disease Control  
 ATTN: Lewis Webb, Jr. 1  
 Building 4, Room 232  
 Atlanta, GA 30333

Director  
 Central Intelligence Agency  
 ATTN: AMR/ORD/DD/S&T 1  
 Washington, DC 20505