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HEATED PURGE AND TRAP METHOD DEVELOPMENT AND TESTING

by

Samuel V. Lucas and Hazel M. Burkholder
BATTELLE
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Technical Project Monitors: James Longbottom
Thomas Pressley

Project Officer: Robert O'Herron

Environmental Monitoring and Support Laboratory
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16. ABSTRACT

The goal of this research was to develop a heated purge and trap method that could be used in conjunction with SW-846 method 8240 for the analysis of volatile, water soluble Appendix VIII analytes. The developed method was validated according to a partial single laboratory method validation test to determine its performance characteristics using mass spectrometric detection. A group of 33 polar analytes comprising selected aldehydes, ketones, alcohols, ethers, nitriles, a thiol and 9 nitrogen bases were examined. All but eight of the compounds were eliminated from the method due to:

1. Poor chromatographic performance,
2. Hydrolytic instability,
3. Purge and trap/desorb unsuitability, and
4. Compounds not commercially available.

The eight compounds found suitable for analysis for heated purge and trap were: acrolein, methacrylonitrile, acrylonitrile, acetonitrile, 2-butanone, 1,4-dioxane, isobutanol and propionitrile.

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FOREWORD

Environmental measurements are required to determine the quality of ambient waters and the character of waste effluents. The Environmental Monitoring and Support Laboratory - Cincinnati, Ohio conducts research to:

- Develop and evaluate methods to measure the presence and concentration of physical, chemical, and radiological pollutants in water, wastewater, bottom sediments, and solid waste.
- Investigate methods for the concentration, recovery, and identification of viruses, bacteria and other microbiological organisms in water; and, to determine the responses of aquatic organisms to water quality.
- Develop and operate an Agency-wide quality assurance program to assure standardization and quality control of systems for monitoring water and wastewater.
- Develop and operate a computerized system for instrument automation leading to improved data collection, analysis, and quality control.

This report is concerned with one of the steps in an on-going program to develop and evaluate analysis methods addressing organic analytes for inclusion in EPA SW-846. In the present case, a method for the analysis of polar, water soluble organic analytes has been developed and tested. The developed method involves sample processing using a heated purge-trap-desorb approach. The developed method was tested using gas chromatograph-mass spectrometry techniques.

Robert L. Booth, Director
Environmental Monitoring and Support
Laboratory - Cincinnati

Abstract

A heated purge-trap-desorb (H-PTD) analysis method for polar, water soluble volatile organic analytes was developed and tested. The research goal was to obtain analysis sensitivities for the target analytes comparable to those achieved presently for nonpolar analytes using the room temperature PTD approach of EPA SW-846 Method 5030 while at the same time not deviating significantly from the type of apparatus currently in use for Method 5030. Thirty-three polar, water soluble analytes from Appendix VIII and the Michigan list were included in the scope of work. Eight of those analytes proved to be amenable to the developed method: acrolein, methyl ethyl ketone, methylacrylonitrile, acrylonitrile, acetonitrile, propionitrile, 1,4-dioxane and isobutanol. The GC-MS method detection limits for the analytes ranged from 2 to 9 ug/L and were about 5-fold higher than would be obtainable with more optimized chromatography. Three alcohols, propargyl alcohol, 2-chloroethanol and 1,3-dichloro-2-propanol could not be recovered to any degree by H-PTD even using 80 percent saturation of the sample with salts and dramatically increased purge gas volumes. One analyte, 3-chloropropionitrile, could not be recovered from the trap desorption step, even though it was shown to be only slightly hydrolytically unstable. The other 21 analytes had plausible chemical reasons for the absence of any H-PTD recovery for them: nine were nitrogen bases, six were hydrolytically unstable, two were mercaptans and four had very low volatility and/or very high water solubility. The absolute H-PTD recoveries obtained ranged from about 80 percent for analytes such as acrylonitrile and methylacrylonitrile to about 30 percent for 1,4-dioxane. The developed method employs a standard 5-mL purge vessel with an integral, very small volume water-cooled condenser and the same all-Tenax trap as specified in Method 5030 for use in Method 8030. Commercially available PTD apparatus can be used without modification except to accommodate the 90 ^{o}C water bath used to heat the purged sample.

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The U.S. EPA Project Officer, James E. Longbottom, Environmental Monitoring and Support Laboratory, Cincinnati, is acknowledged for his conception and direction of this research program.

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SECTION 1

INTRODUCTION

The Resource Conservation and Recovery Act, RCRA, requires predisposal monitoring of about 370 organic species listed in Appendix VIII to 40 CFR Part 261. In response to a petition by the State of Michigan, the U.S. EPA has proposed the amendment of RCRA Appendix VIII by the addition of over 100 other organic compounds. Using the hierarchical approach shown in Figure 1, these analytes were evaluated for suitability for gas chromatography-mass spectrometry (GC-MS) determination and classified as volatile or semivolatile for eventual inclusion in the analyte sets of available standard methods. GC-MS suitability studies were performed in Work Assignment 4 of the current contract. Purge-trap-desorb (PTD) methods such as EPA SW-846 Method 5030 work well for the nonpolar, relatively water-insoluble volatile analytes, while methods based on liquid-liquid extraction followed by extract volume reduction, as described in EPA SW-846 Method 3510, typically are effective for the nonpolar semivolatile analytes. Work Assignments 10 and 8 of the current contract yielded results on the suitability of Methods 5030 or 3510, respectively, for selected analytes.

Some of the Appendix VIII or Michigan List organic compounds are not amenable to either of these approaches because they are so highly volatile that they are partially or totally lost on solvent reduction of organic extracts and are too water soluble to be effectively recovered by liquid-liquid extraction or effectively purged by the typical room temperature purge-trap-desorp (RT-PTD) approach such as that of Method 5030. Typically, such analytes can only be analyzed by direct aqueous injection which is inherently about 1000-fold less sensitive than PTD analysis using a 5-mL sample. Reasonable recoveries of a few highly water-soluble analytes have been obtained with a heated PTD (H-PTD) approach analogous to Method 8030, which has been validated for acetonitrile, acrylonitrile, and acrolein.

The goal of this research effort is to develop an H-PTD method to be used in conjunction with Method 5030 for the analysis of a wide range of volatile, water-soluble Appendix VIII and Michigan petition analytes. The target characteristics for the desired method are:

- Provide analysis capability for analytes currently

restricted to direct aqueous injection methods.

- o Incorporate the advantages of fused silica capillary chromatography.
- o Be readily adaptable to the RT-PTD apparatus and detection systems currently in use.
- o Obtain sensitivity comparable to existing RT-PTD methods for the determination of less water-soluble analytes.
- o Avoid, if possible, analysis steps involving two-stage, trap to trap desorptions or special cryofocusing apparatus.

In the work reported here, all of the organic Michigan petition and Appendix VIII analytes which (1) had not proved amenable or had displayed poor analysis characteristics in Methods 8240 and/or 3510 and (2) were thought to be potentially amenable to an H-PTD approach, were included in the study. Initially, the following 13 analytes of seven functional group types were specified by the EPA Project Officer for inclusion in this research program:

Nitriles
- Acetonitrile
- Acrylonitrile
- Propionitrile
- Malononitrile
- 3-Chloropropionitrile

Aldehyde
- Acrolein

Nitrogen Base
- Pyridine

Ketones
- Methyl ethyl ketone
- Bromoacetone

Alcohols
- Isobutyl alcohol
- Propargyl alcohol

Ether
- 1,4-Dioxane

Thiol
- Trichloromethanethiol

Subsequently, based on the results of other heirarchical scheme-structured Work Assignments which had, at that time, just been completed, the EPA Project Officer added another 20 analytes which had not qualified for inclusion in those methods. These 20 analytes could be classified in two groups:

(1) Analytes eliminated from Methods 8010, 8015, and 8020 validation due to poor RT-PTD recovery:

Method 8010	Method 8015	Method 8020
Chloral hydrate	Acrylamide	2-Picoline
2-Chloroethanol	Beta-Propiolactone	Thiophenol
1,3-Dichloro-2-propanol	Methacrylonitrile	

(2) Analytes not detected or very poorly detected using GC-MS and the packed column specified in Method 8240 with the performance deficit attributable to the use of an inappropriate GC column:

Nitrogen Bases

Hydrazines:

Methylhydrazine
1,1-Dimethylhydrazine
1,2-Dimethylhydrazine

Amines:

1^{o}: n-Propylamine
2^{o}: Aziridine
Methylaziridine
3^{o}: N-2-Hydroxyethylaziridine

Nitriles

2-Hydroxypropionitrile
2-hydroxy-2-methylpropionitrile

Miscellaneous

Tetranitromethane
Methyl mercaptan
2-Butanone Peroxide

The experimental design employed for this study directed attention to:

- o use of chromatographic systems optimized for polar analytes
- o novel trapping materials and approaches
- o effective control of water vapor exiting the heated purge vessel
- o the effect of temperature on recovery of the purge step
- o the effect of dissolved salts on recovery of the purge step.

The H-PTD experimental conditions which evolved from previous investigations (See Bibliograhy) were tested using fused silica capillary column GC-MS analysis for the determination of all of the originally included analytes which proved recoverable to some degree with the H-PTD conditions developed.

SECTION 2

CONCLUSIONS

Some of the conclusions regarding the potential analytical performance of an H-PTD-based analysis method for polar, volatile organic analytes are the following:

- Eight of the 33 analytes included in the study were determined to be amenable to H-PTD. Those eight analytes are: acrolein, methyl ethyl ketone, methacrylonitrile, acrylonitrile, acetonitrile, propionitrile, 1,4-dioxane and isobutanol.

- Twenty-one of these 33 analytes tested were not amenable to H-PTD because they are nitrogen bases (9 analytes), hydrolytically unstable (6 analytes), mercaptans (2 analytes), or had both very low volatility and very high water solubility (4 analytes).

- A small volume condenser was effective for controlling the amount of water vapor exiting the heated purge vessel and subsequently condensing in the PTD device plumbing. The use of this condenser enabled a reliable achievement of adequate analysis precision, i.e., less than 15 percent relative standard deviation.

- The use of salt enhanced purge recovery of all analytes that were not quantitatively recovered without salt. Salting out at the levels used, 80 percent saturation at 85 C, is difficult using conventional purge vessels and probably promotes poorer reproducibility. Since highly soluble salts with both mono- and di-valent cations and anions were used, other salts are not expected to prove more effective than those used in this study.

- H-PTD GC-MS method detection limits (MDLs) for the eight analytes tested were 5- to 10-fold higher than could have been expected for an optimal case based on Method 8240 performance for nonpolar analytes. The higher than desired MDLs result from a combination of three factors: (1) variable and incomplete purge recovery, (2) water-broadened chromatographic peaks and (3) MS fragmentation characteristics resulting in lower detection response factors.

- As expected, H-PTD recovery was predictably related to the purge temperature: the higher the purge temperature, the higher the recovery.

- The use of zeolite dessicants such as molecular sieve to remove water from the purge stream was shown to have no possibility for further development.

- None of the novel trapping materials tested showed promise for overcoming the technical problems of H-PTD. While Tenax adsorbent traps have almost no reserve capacity for the most polar and volatile analytes, they nevertheless are expected to remain the trapping material of choice for H-PTD.

- The five hydrazines and aziridines studied displayed poor chromatographic characteristics or were not amenable to GC on either of the GC columns tested, even when injected in non-aqueous or solvent-free media, i.e., gaseous or neat. These analytes were: 1,1-dimethylhydrazine, 1,2-dimethylhydrazine, ethyleneimine, 2-methylaziridine and N-2-hydroxyethylaziridine.

- Chloral hydrate, 2-butanone peroxide, 2-hydroxypropionitrile, and 2-methyl-propionitrile are thermally labile and were found to be not amenable to GC analysis. Beta-Propiolactone was apparently solvolyzed by both methanol and water used as injection solvent, and could be eluted from the GC only when injected neat.

- Bromoacetone was unacceptably hydrolytically unstable with 60 to 90 percent loss over a 15-minute exposure to pH 7 and 85°C. Tetranitromethane and thiophenol were quantitatively lost under these conditions.

- 1,3-Dichloro-2-propanol, which was apparently stable toward the heated purge conditions, could not be recovered when injected directly on the trap and then desorbed after a normal purge sequence. Propargyl alcohol and 2-chloroethanol could be adequately recovered from the trap but could not be purged from an aqueous sample.

- Other compounds which failed to qualify for inclusion in the method due to nonpurgeability were: acrylamide, malononitrile, pyridine, and 2-picoline.

SECTION 3

RECOMMENDATIONS

Based on the results obtained in this study, the following recommendations can be made:

- Further evaluation of less polar columns should be conducted to improve the chromatographic performance of the H-PTD method developed in this study. The choice of the polar, Carbowax-type column was driven principally by extremely polar analytes which later had to be excluded from the method due to nonpurgeability. It is very likely that other stationary GC phases, e.g. DB-624, might reduce the peak broadening caused by the reverse solvent effect attributed to desorbed water.

- Further work on the eight analytes which qualified for the developed H-PTD method and similar analytes should be directed toward modifying Method 8240, using the standard Tenax/coconut charcoal trap, to enable the inclusion of these analytes in that method. A separate method for the eight analytes may not be cost-effective. The use of the combination heated purge vessel-condenser unit developed in this work should dramatically improve Method 5030 performance for partially recovered analytes such as naphthalene, tri- and tetrachlorobenzene and hexachloropropene without any detrimental effect on the more volatile Method 8240 analytes.

- Salt addition and/or purge temperatures higher than 90 ^{o}C should not be used for H-PTD analyses.

- Non-PTD method development work should be conducted for the determination of most of the alcohols of interest. Some of the approaches that might be successful for these types of analytes include fractional distillation, fractional crystallization, solid phase extraction, and development of large volume, i.e., 50 to 250 µL, direct aqueous injection methods

- Further method development activity for the volatile nitrogen bases of interest (hydrazines, alkyl amines, aziridines and pyridines) should involve solid phase extraction using ion exchange resins, ion chromatography, fractional crystallization, and/or large volume direct aqueous injection.

SECTION 4

EXPERIMENTAL

Materials

Sources

Commercial sources and purities of the 33 analytes originally included in this study are shown in Table 1. Reagent water was prepared by boiling for 15 minutes 1-L quantities of commercial distilled water which was first processed through a Milli-Q water purification system modified by placing activated carbon modules in the last two cartridge positions. The boiled, cooled water was stored until use at which time it was passed through a 2.5 cm I.D. by 45 cm long column of activated carbon (Barneby and Cheney, type PC, Lot 2547).

Preparation and Use of Stock and Standard Solutions

For the method development phase of this study, stock solutions and analyte mixture spiking standards were prepared in aqueous solution to avoid possible interference in FID chromatograms from any H-PTD-recovered methanol that is usually used as a spiking solvent. In the early stages, individual aqueous analyte stocks were prepared at 100 mg/mL and then used to prepare spiking and septum injection calibration standards. Initially, these stock solutions were prepared gravimetrically using 2.0 or 10.0 mL volumetric glassware with analyte dispensed from an appropriately sized microliter syringe according to its known or determined density. In later work, volumetric dispensing of neat analytes to prepare stock solutions was used without checking weights because that approach had been shown to result in gravimetric errors of less than 2 to 3 percent. Finally, the intermediate step of preparing individual stock solutions was omitted and analyte spiking stock mixtures were prepared directly from neat analytes. Dilutions to working standards were performed in 10.0-, 5.0-, or 2.0-mL volumetric glassware using appropriately sized syringes. Final concentration working standards were prepared in 10.0-mL quantity and immediately bottled in five

seals. These working standards were stored at - 4 °C when not in actual use, and a previously unused vial of spiking and calibration standard was used for each day of experimental trials. Typically, these standards were prepared at about one-week intervals, and analyte degradation during storage over that time period was never found to be a problem.

Since all of the method development work was evaluated on the basis of absolute H-PID recovery, the preparation of a working standard always involved two concentration levels: (1) purged sample spiking standard of which 5.0 uL was dispensed from a 5-uL syringe into the 5.0 mL aqueous sample and (2) septum injection calibration standard at 2.5-fold higher concentration than (1), above, of which 2.0 uL was injected directly onto the GC column, again, using a 5.0-uL syringe. Thus, the 2.0 uL septum injection corresponded to a 100 percent H-PID recovery standard. To insure reproducibility of the septum-injected 100 percent recovery standard, the clean, dry 5.0-uL syringe was primed with reagent water and indexed to 0.0 uL. The 2.0 uL sample was then drawn into the syringe so that the needle full of reagent water would act to flush all of the calibration standard from the syringe needle.

Method Development Activities

GC Testing

Analytes were tested individually for chromatographic performance on both a polar and nonpolar megabore capillary GC column. The GC conditions and columns used were:

Gas Chromatograph	Carlo Erba Model 4160
Detector	Flame Ionization
Columns	1. 30 m x 0.53 mm ID fused silica with 1 uM SupelcoWax-10 film (Supelco)
	2. 60 m x 0.75 mm ID borosilicate glass with 1.5 uM proprietary film, VOCOL (Supelco)
Oven Program	40°C (2 min), 8°C/min, 225°C (10 min)
Injector Temperature	230°C

Detector Temperature	250°C
Carrier Gas	Helium at 10 mL/min, flow controlled
Injection Volume	1.0 uL by autosampler using 1.0 or 10 ug/uL solutions

Initially, analytes were tested in aqueous solution since trap-desorbed samples and calibration standards in later work were expected to be equivalent to an aqueous injection. Analytes that were not detected satisfactorily were retested first in methanol injection solvent. If the analytes were still not detected, pentane injection solvent was used or analytes were injected as neat liquids or headspace vapors above neat reagent. Except in the subsections that follow, the GC conditions shown above and the Supelcowax-10 column were used in all subsequent testing.

Hydrolytic Stability Testing

The following 13 analytes were tested for hydrolytic stability:

Acrolein	3-chloropropionitrile	Methyl mercaptan
Acrylamide	1,1-dimethyl hydrazine	Propargyl alcohol
Acrylonitrile	Methylaziridine	Tetranitromethane
Bromoacetone	Methylhydrazine	Thiophenol
N-2-Hydroxyethylaziridine		

Each analyte was tested individually in duplicate by direct septum injection of an aqueous standard held at 85°C. The aqueous media was 10 mM phosphate buffer at pH 6.8. For each test, sufficient neat analyte, except for acrylamide in 100 mg/mL methanol, was injected into a 42-mL septum sealed serum vial filled nearly headspace free with room temperature buffer for a final concentration of 100 ug/mL. The sample was quickly mixed by multiple inversion aided by glass beads, and then a 2-uL aliquot was injected into the GC. This zero time sample functioned as the 100 percent recovery sample. The sample was then submerged in an 85°C water bath and sampled a second time after 15 min to determine the amount of analyte remaining intact. The GC conditions used were isothermal at 10°C below the elution temperature of the analyte in question. If necessary to eliminate

ambiguity in GC peak identity assignment, the same isothermal conditions were used for analyte injections as a neat liquid, using a syringe needle wet with analyte, or as gas, using headspace above the neat analyte.

H-PTD Recovery Pre-Screening

The compounds that performed adequately or marginally during the GC testing and hydrolytic stability testing were divided into three analyte sets:

Set 1	Set 2	Set 3
Methyl mercaptan	Methyl ethyl ketone	n-Propylamine
Methacrylonitrile	Acrolein	Acrylonitrile
Propionitrile	Acetonitrile	2-Methylaziridine
Propargyl alcohol	1,4-Dioxane	Pyridine
Thiophenol	Isobutanol	2-Picoline
Acrylamide	Bromoacetone	N-2-hydoxy-ethylaziridine
Malononitrile	2-Chloroethanol	
	3-Chloropropionitrile	
	1,3-Dichloro-2-propanol	

Analytes were assigned to sets on the basis of GC retention time and functional group types. Preliminary testing of H-PTD was done using the GC conditions given above in the GC Testing subsection except that a Varian 3700 GC was used. The H-PTD conditions were:

Purge-Trap-Desorb System	Tekmar LSC-2
Purge Line and Valve Temp.	130°C
Purge Temperature	85°C
Desorb Temperature	180°C
Trap Bake Temperature	210°C
Purge Time	15 min
Desorb Time	4 min
Trap Bake Time	10 min
Purge Gas	Helium at 35 mL/min
Post Condenser Make-up Gas	Helium at 10 mL/min
Condenser Cooling Water Temperature	4°C

Recoveries were determined by comparing peak areas from the 250 ng

septum injection corresponding to 100 percent PID recovery to the corresponding peak areas from the 5 mL H-PID samples which also contained 250 ng of each analyte (50 ug/L). Peak areas of two replicates of septum-injected 100 percent recovery standards were averaged and used to quantify the recoveries obtained for the three replicates of H-PID analysis. The septum-injected recovery standards were always the first and last runs of a given set. The condenser used in this work was the first design (c.f. Section 5, Results and Discussion, "Refinement of the Condenser Design") which was a commercially available condenser with 1/4 inch OD by 8 cm long cold zone modified to attach to the purge vessel outlet with a 1/4 inch Swagelok union. The condenser cold zone was packed with 3 mm glass helices.

Purge Recovery Enhancement Through Salting-Out

The four anhydrous salts used, sodium chloride, sodium sulfate, magnesium chloride, and magnesium sulfate, were heated in a muffle furnace at 450°C overnight to remove any trace organic impurities. Using Chemical Handbook data (CRC, 65th Edition), the amount of each salt required to produce 80 percent saturation at 85°C was computed, assuming a linear relationship for solubility versus temperature, using the two solubility data points closest to (above and below) 85°C. For 5 mL aqueous samples, those salt amounts were: NaCl, 1.5 gm; Na_2SO_4 1.5 gm; $MgCl_2$, 2.8 gm; $MgSO_4$, 2.7 gm. Samples were prepared for analysis by: (1) the premeasured amount of the tested salt was added to a clean, dry purge vessel, (2) the purge vessel/condenser unit was attached to the PID and condenser water flow lines, (3) the 5-mL aqueous sample, which had immediately before been spiked with the analyte mixture, was added to the purge vessel, (4) the salt was dissolved by repeated inversions of the purge vessel/condenser unit, and (5) the purge vessel/condenser unit was installed in the 85°C water bath and the purge flow initiated. The analytes used in this study were: acrolein, methyl ethyl ketone, acrylonitrile, acetonitrile, propionitrile, 1,4-dioxane, isobutanol, 2-chloroethanol, 1,3-dichloro-2-propanol, 3-chloropropionitrile, and cyclohexanone. These analytes were spiked at the 50 ug/L level (250 ng in a 5-mL water sample). The condenser used in this work was the second design (c.f. Section 5, Results and Discussion, "Refinement of the Condenser Design") which was an open, Vigreux-type, with

a 6-mm ID by 3 cm long cold zone operated with 20°C condenser water. The purge flow was 30 mL/min for 15 min. A desorb preheat temperature of 150°C was used in initial experiments but changed to 50°C in later experiments due to apparent partial decomposition on desorption of acrolein and acrylonitrile. Otherwise the GC and H-PID conditions were identical with those given or referenced above in the "H-PID Recovery Pre-Screening" subsections.

Effect of Purge Temperature on Analyte Recovery

The following nine analytes were used to examine H-PID recovery variation as a function of the purge temperature: acrolein, methyl ethyl ketone, methylacrylonitrile, acrylonitrile, acetonitrile, propionitrile, 1,4-dioxane, isobutanol and cyclohexanone. The purge temperatures tested were room temperature (22°C), 40, 60, 85 and 99°C. All experiments were performed in duplicate except for the 60°C trial which was in triplicate. Septum injection 100 percent recovery calibration standards were analyzed in triplicate. Except for the 22°C trial, 500 ng of each analyte, i.e. 100 ug/L in the 5.0 mL purged sample, was the spiking level. The 22°C data set was part of the salting out study, and, thus, the spiking level was 250 ng (50 ug/uL) and methacrylonitrile was omitted from the analyte set. The analysis conditions for the 22°C data set were identical to those given in the preceding subsection on salting-out. The analysis conditions for the other temperatures tested were different from those for 22°C as follows: an OI Model 4460 PID unit was used and the third condenser design was employed (c.f., Section 5, Results and Discussion, "Refinement of the Condenser Design"). This condenser was of a Vigreux design with 9 mm OD by 18 cm long cold zone and 9 mm purge vessel outlet and condenser inlet which was connected with a 3/8 inch Swagelok union. The trap was maintained at 25°C during the purge step for which the flow was 40 mL/min for 15 min. No post-condenser make-up flow was used. The PID unit maintained the valve and transfer lines at 90°C and employed a 50°C desorption pre-heat. The experimental design called for a highest purge temperature trial at 100°C, but, due to the barometric pressure on the day the experiment was performed, the boiling temperature of the water bath used to heat the purge vessel was 99°C.

Purged Water Removal Using a Desiccant

Linde type 3A molecular sieve in 1/16 inch spherical pellets were obtained from MCB Chemicals. The pellets were ground with a mortar and pestal and size selected using 14 and 30 mesh standard sieves (1.41 and 0.59 mm, respectively). A 30 cm length of 1/4 inch stainless steel tubing was cleaned, acid washed, packed with 3 gm of the prepared molecular sieve and installed in the oven compartment of a Varian 1400 GC. The dryer unit was conditioned overnight at 200°C with 40 mL/min helium. The amount, 3 gm, of molecular sieve used was ten percent in excess of that estimated to be necessary based on the computed quantity of water expected to exit the purge vessel and isotherms provided in Union Carbide specification sheets on 3A molecular sieve. The molecular sieve drying unit was then attached to the H-PTD system between the purge vessel and trap by means of an external 6-port valve and heated transfer lines, both of which were maintained at 103°C. Water breakthrough was determined by observing condensate formation in a Pasteur pipette attached to the dryer outlet which was maintained at room temperature. Using a 15 minute, 40 mL/min purge with the sieve at 100°C, water breakthrough was observed at 12 minutes, i.e., 480 mL of purge flow. By determining the weight of water collected in the Pasteur pipette, the following dryer operating conditions were adopted: the dryer module was held at 90°C during the 15 minute purge followed by a 20 minute bake cycle at 230°C and 150 mL/min helium in the same flow direction as that for the purge cycle. The analyte throughput of the dryer module was tested by spiking 2 uL of an aqueous standard containing 500 ng/uL of each analyte into the inlet of the drying module and then executing a normal 85°C H-PTD cycle. This experiment corresponded to 100 percent purge recovery with all analytes exposed to the dryer module. The 100 percent dryer throughput standard was similarly produced by identically spiking the outlet of the dryer module, i.e., the transfer line leading to the trap. These experiments, including a septum injection of the spiking standard, were performed in duplicate. In a second experiment, the spike was applied to the dryer module inlet at the tenth minute of the 15 min purge cycle to pre-load the dryer module with water. The analytes used in this study were acrolein, methyl ethyl ketone, methyacrylonitrile, acrylonitrile,

acetonitrile, propionitrile, 1,4-dioxane, isobutanol, cyclohexanone, propargyl alcohol, 2-chloroethanol, 1,3-dichloro-2-propanol and acrylamide. Except where noted otherwise, the H-PTD and GC instrumentation and conditions for these experiments were identical to those cited in the preceding subsection.

High Retention Trapping Materials

High retention trapping materials which might be able to retain analytes at temperatures above the dew point of the heated purge vessel effluent were tested. The rationale for this approach was the complete elimination of the formation of condensate which could recapture analytes purged from the sample.

Two trapping materials with relatively strong retention characteristics were obtained from Supelco. (1) Carbotrap, a carbonaceous adsorbent in common use for air sampling, for example, workspace sampling, of volatile materials such as benzene, and (2) Carboseive, a new proprietary adsorbent with uncommonly high retention characteristics (i.e. a specific breakthrough volume for methyl chloride of - 12 L/gm). A standard configuration Tekmar trap was packed with 24 cm of Carbotrap and installed in the GC oven as a substitute for the column. A splitter valve ahead of the detector was used to reduce the flow into the detector to a reasonable amount. Trap breakthrough for methyl ethyl ketone was tested using carrier which was a 30 mL/min purge flow through a purge vessel containing reagent water and held at 85°C. This carrier was diluted upstream of the trap with 150 mL/min of helium make-up flow giving a dew point of 48.7°C. The breakthrough volume of 10 ug of methyl ethyl ketone with the trap at 50°C was approximately 900 mL for the peak top and about 600 mL for the one set corresponding to only 150 and 100 mL, respectively, of purge vessel flow. A similar experiment was performed with Carbosieve, and the breakthrough volume for methyl ethyl ketone was greater than 6300 mL at 200°C, about 1900 mL at 250°C and about 800 mL at 285°C. Based on these results, a mixed bed trap containing 4:1, w/w, of Carbotrap and Carbosieve, respectively, was prepared with the Carbotrap at the inlet end. This trap was conditioned overnight at 300°C with 30 mL/min of dry helium. The ability of this trap to adsorb and desorb analytes under H-PTD conditions and enable adequate GC analysis of the

desorbed analytes was tested using the same 13 analytes cited in the preceding subsection. An Oceanographics International (OI) Model 4460 PTD unit was used and the transfer line between the purge vessel and OI 4460 was heated to 87°C. In duplicate experiments the analytes were spiked into the transfer line between the purge vessel and trap using 2.0 uL of an aqueous standard containing each analyte at 500 ng/uL. The GC conditions were identical to those described in preceding subsections. The H-PTD conditions were:

Condenser -- none used
Purge bath -- 85 °C
Trap during purge step -- 90 °C
OI 4460 valve and transfer line -- 90 °C
Purge flow -- 30 mL/min, helium, 15 min
Post-purge vessel make-up -- none
Trap desorption preheat -- variable, see text
Trap desorption -- 300 oC for 4 min
Trap bake -- 300 oC, 20 min, dry helium

These trials produced chromatograms with split analyte peaks (see Section 5), and desorption preheat temperatures of 90, 100, 120, 250 and 300°C were tried to alleviate this problem. Since this attempt was not successful, samples with analytes spiked into the 5-mL of reagent water were not analyzed.

Breakthrough Volume Testing for
Tenax and Novel Trapping Materials

Tenax trap analyte breakthrough testing employed commercially available all-Tenax traps (Supelco, No. 2-0295). Identical empty traps were packed with two types of novel trapping materials which are chemically described in the corresponding subsection of Section 5, Results and Discussion. For breakthrough testing, these traps were installed as a GC column in a Varian 3700 GC with an FID. The GC oven control was used to thermostat the trap for above-ambient or carefully temperature controlled breakthrough volume testing. The GC injector carrier supply was 40 mL/min consisting of 30 mL/min of purge flow from a standard 5-mL purge vessel containing reagent

water which was held at 85°C plus 10 mL/min of dry helium added at the condenser outlet. A condenser was used at the purge vessel outlet exactly as for the analysis of H-PTD samples during the various method development phases. Trap breakthrough experiments were conducted twice: preliminary testing early in the study and a second time late in the study using precise trap temperature control. In early work, the condenser used was the first design, and in later work the third condenser design was employed. These condensers are discussed in the subsection, "Refinement of the Condenser Design" in Section 5. The temperature of the condenser cooling water used with the earlier work was 4°C and that used for the later work was 20°C.

In the earlier work, which involved only Tenax traps, seven analytes were tested that were thought, on the basis of boiling point and polarity, to be potential breakthrough candidates: acetonitrile, acrylonitrile, acrolein, methyl ethyl ketone, isobutanol, methyl mercaptan and n-propylamine. Analytes were injected individually in the transfer line connecting the purge vessel to PTD unit just after the point where the 10 mL/min make-up flow was added. The trap temperature for these trials was the ambient temperature, estimated to be between 19 and 24°C. The injected sample was 5 uL of a 0.2 ug/mL aqueous standard (1.0 ug total) and the breakthrough trials were performed in triplicate for analytes that broke through in less than 1200 mL (30 min of purge flow) or two replicates for analytes with breakthrough volumes exceeding 1200 mL. Between each run, the trap was heated to 220°C until a stable baseline was once again achieved. The breakthrough point was taken as the intercept of the extrapolated recorder baseline and the up-slope of the triangulated breakthrough peak. This intercept typically represented 0.1 to 1.0 percent of analyte breakthrough.

In the later experiments, the temperature was much more carefully controlled, and only two analytes were investigated, acrolein and acetonitrile, which were known to be the only analytes of the set for which trap breakthrough might be an issue. Tenax and the two novel trapping materials described above were investigated, and the experimental approach used was very similar to the one described above for the earlier work. The only differences were the following:

- o trap temperatures below 30°C (Tenax only) were measured to the nearest 0.1°C using a calibrated mercury thermometer

- o the samples were gaseous injection of headspace diluted to achieve 10 ± 2 ug of injected analyte
- o samples were injected through the septum of the GC injector
- o the H-PTD carrier gas flow was 40 mL/min and no post-condenser make-up dilution was used.

The tested trapping temperatures are given in Table 2.

H-PTD GC-MS Method Testing

Instrumentation and Equipment

The GC-MS system used was a Finnigan 3200 quadrupole unit interfaced to a Carlo Erba Model 4160 GC. A Finnigan INCOS MS data system with version 5.5 software was used for data acquisition and processing. The GC column was interfaced to the mass spectrometer through a glass jet separator for which 50 mL/min helium make-up gas was required for maximum analyte throughput across the jet. The GC column used was a 30m by 0.53 mm I.D. fused silica capillary coated with 1.0 um Supelcowax-10 (Supelco Co.). A Tekmar LSC-2 PTD unit equipped with an all-Tenax trap (Supelco No. 2-2095) was used in its normal configuration with the sample transfer line connected to the GC injector carrier inlet line. This configuration permitted septum injection of samples directly onto the GC column. The purge vessel-condenser unit is described in detail in a pertinent part of Section 5. The purge vessel was heated with a magnetically-stirred 1.5-L water bath using an ordinary stirring hot plate. Condenser cooling water was circulated from a Haake Model FK2N refrigerator bath with Model FN circulating heater control unit.

Analysis Conditions

The H-PTD conditions used were the following:

Purge:	40 mL/min for 11 min at 90 °C
Trapping Temp:	Less than 25 °C
Trap Desorption:	180 °C for 4 min with 50 °C preheat

Trap Bake:	210 °C for 10 min, dry helium
Heated Zones:	Valve and transfer lines at 100 to 120 °C
Post-Condenser Makeup:	None

The chromatographic conditions were:

Carrier:	Helium at 10 mL/min, flow controlled giving a head pressure of 5.6 psi at 40 °C
Helium make-up gas:	50 mL/min, between column and jet separator, to maintain maximum analyte throughput across the jet.
Oven Program	40 °C for 4 min (during trap desorption) then program to 130 °C at 8 °C/min. and hold for 2 min.
Temp. Zones:	Injector, 200 °C Separator oven, 210 °C Separator to MS transfer line, 150 °C

The MS operating conditions were:

Ionization:	70 eV, electron impact
Beam current:	200 uA, total
Ion source tuning:	Adjusted to meet EPA criteria for bromofluorobenzene mass spectrum
Scan:	35 to 250 amu, 1 sec per scan
Preamplifier:	10^{-7} amp/volt
Electron multiplier:	Gain sufficient for 180K to 220K area for m/e 84 of the quantification internal standard, benzene-D_6, 250 ng

Spiking and Calibration Standards

The eight analytes included in the study were: acrolein, methyl ethyl ketone, methylacrylonitrile, acrylonitrile, acetonitrile, propionitrile, 1,4-dioxane and isobutanol. Four surrogate standards were also used: methyl ethyl ketone-D_5, acetonitrile-D_3, 1,4-dioxane-D_8, and

bromofluorobenzene (BFB). The quantification internal standard was benzene-D_6. Stocks and spiking standards of analytes were prepared in reagent water. Acrolein and acrylonitrile aqueous stocks were always prepared from reagent on the same day as calibration or sample spiking were performed to avoid any loss of these analytes to decomposition. The other six analytes were prepared as a mixture as long as one week prior to use and stored at 4 °C without headspace in 1.8-mL screw cap GC autosampler vials with Teflon-faced silicone septa seals. A new vial was used each time calibration or spiking standards were prepared. Stock and spiking standards of the surrogate and internal standards were prepared in methanol and stored at -10 °C when not in use.

Surrogate and internal standards were spiked as 10-uL aliquots into each 5.0-mL calibration sample just prior to analysis using a 10-uL syringe. The levels used were: benzene-D_6 and BFB, 50 ug/L; methyl ethyl ketone-D_5, 60 ug/L; acetonitrile-D_3, 400 ug/L; and 1,4-dioxane-D_3, 300 ug/L. For the high and low level spiked samples, the deuterated analytes were spiked into the reagent water before bottling the individual analysis replicates and only benzene-D_6 and BFB were spiked into the 5.0 mL sample just prior to analysis.

Sample Preparation

The reagent water used for calibration samples and spiked replicate samples was prepared as specified for the method development activities. To prepare the high and low level spiked sample replicates, reagent water in a 500 mL volumetric flask was spiked with an aqueous, freshly prepared analyte mixture and a methanolic mixture containing the three deuterated analyte surrogate standards. After diluting to the calibration mark and thoroughly mixing, standard screw-cap 40-mL VOA vials were filled and sealed headspace free with Teflon-faced silicone septa. Typically, eleven such replicate samples could be produced from the 500-mL spiked sample. Three 40-mL blank reagent water samples were similarly bottled for use as GC-MS analysis blanks. The samples were stored inverted on ice for analysis on the following day. The analyte spiking levels for the low and high spiking level replicates are given in the pertinent results tables in Section 5.

Data Processing

All GC-MS data processing was performed using standard Finnigan INCOS version 5.5 software. Search libraries used the three most intense ions in the scan range that were above 20 percent relative abundance. Calibration response factors were generated by the data system using the best linear fit of the data over the five calibration levels used. Verificiation of proper integration of the quantification ion peaks was performed by examining each integrated peak on the CRT screen during final data processing. All of the calibration and replicate analysis data was archived on 9-track magnetic tape.

SECTION 5

RESULTS AND DISCUSSION

OVERVIEW

Based on the results of the information gathering activities, described below, the central difficulty for H-PTD analysis concerns the problems created by the large amount of water vapor which exit the heated purge zone with the purge gas. For a typical 11 minute purge at 40 mL/min, standard temperature and pressure, and a 90°C purge temperature, the amount of water vapor exiting the purge vessel is about 0.75 g. Condensation of this relatively large amount of water in the PTD device, especially the trap, has been observed by other investigations to cause extremely poor reproducibility and even prevent quantitative analysis. Three main effects were cited: (1) promotion of unacceptable memory effects due to analytes sequestering in water droplets in the connecting lines and 6-port valve, (2) degradation of chromatography through the introduction of very large amounts of water onto the GC column, and (3) loss of analyte dissolved in liquid water exiting the outlet of the trap during the purge step. Thus, one of the main focuses of the work reported here was concerned with minimizing the effect from this water during the trap and desorb cycles. Three main approaches were investigated:

- The use of a condenser at the purge vessel outlet to return most of the evaporated water to the purge vessel
- The use of traps having substantially greater retention of organic analytes than Tenax so that these traps could operate at an elevated temperature during the purge and trap step. Post-purge make-up gas was used to reduce the purge carrier dew point and the trap temperature was maintained above the resulting dew point, thereby eliminating any possibility of condensation of water vapor from the purge carrier
- The use of a Zeolite-type dessicant held at a temperature above the dew point between the purge vessel and the trap to adsorb water vapor from the heated purge carrier, while permitting purged analytes to pass through without retention.

The experimental design for the key elements of the method development phase addressed the parameters that were expected to affect H-PTD

performance, and those parameters were examined in a hierarchial scheme as follows:

- Polar and nonpolar fused silica capillary GC columns were tested using direct injection of all candidate analytes. The column providing the best GC performance was used in all subsequent work
- Analytes were screened for hydrolytic instability; those which could not be detected by direct injection of a pH 7.0 buffered standard solution held at 85°C for 15 minutes were not included in subsequent work
- Analytes which were hydrolytically stable were tested using preliminary purging conditions similar to H-PID Method 8030 for acetonitrile, acrolein, and acrylonitrile. In most cases, analytes for which no recovery could be detected at levels above 1000 µg/L were eliminated from further testing
- The enhancement of purge recovery by 80 percent saturation salting-out was examined
- The effect of variation of the temperature during purging was examined
- Alternatives not involving condensation for control of the water evaporated from the purge vessel were examined.

The method performance parameters used to evaluate the progress of the method development activities were the percent recoveries and analysis precisions for the analytes. Each day that experimental trials were performed, two or more replicates of calibration standards which represented 100 percent PID recovery were analyzed by direct septum injection of 2.0 µL of the same analyte mixture used, to fortify the 5-mL purged samples. In the later case, use of a 2.5-fold dilution was made to enable a 5.0 uL volume for spiking 5-mL samples. Typically, these 100 percent calibration analyses contained 250 ng of each analyte which corresponded to a 50 µg/L concentration in the 5.0 mL purged sample. Experimental trials were always performed in at least duplicate and usually in triplicate or higher replication with all experimental trials and calibration standards analyzed on the same day. These method development experiments all employed flame ionization detection (FID), so all stock and spiking standards had to be prepared in water to avoid methanol which interfered chromatographically

with some of the analytes.

Based on the results obtained in these method development activities, H-PID conditions were adopted and tested using MS detection. The H-PID GC/MS testing was designed to define accuracy, precision, and MDL values for all of the analytes for which any level of PID recovery had been obtained during the method development phase.

PRELIMINARY ACTIVITIES

Information Gathering

Two information gathering activities were completed before the experimental plan for H-PID method development was completed: (1) computer-assisted search of recent scientific literature and (2) direct telephone inquiry of scientists known or thought to have conducted related research activities.

Scientific Literature--

The Chemical Abstracts Service (CAS) on-line data base was searched for the period 1967 to the present. The Registry file was searched using CAS numbers and compounds names linked with a logical "and" to key words and word stems and an initial 811 references were selectively reduced by further search criteria limitations to 369 references for which keyword listings and/or abstracts were used to select nine pertinent publications. Photocopies of these nine references, listed in the Bibliography, were obtained and reviewed.

Direct contact of Other Researchers--

The scientists who were contacted directly by phone and queried about their experience and expectations regarding the H-PID analysis approach were:

Tom Bellar, EPA Cincinnati
Bob Westendorf, Tekmar
Eric Johnson, Finnigan
Dennis Gere, Hewlett Packard
Phil Wylie, Hewlett Packard Avondale Applications Lab

Bernie Barnard, OI

Neil Mosesman, Supelco

Robert Freeman, J & W Scientific

Some of the findings from these telephone discussions that were of interest to this H-PTD method development program were:

- Purge temperatures above 60 C are reported to coat the Tenax trap with liquid water which can move as a bulk liquid phase and apparently substantially reduce trapping efficiency of polar analytes dissolved in the liquid water exiting the trap outlet.
- Desorbed water causes chromatographic peak broadening, tailing, and retention time shift.
- Condensers at the outlet of the purge vessel, used to reduce the amount of water reaching the trap, result in significant reduction in PTD recovery of the more water soluble analytes.
- A glass lined open split GC/MS interface had been substituted for a jet separator and was effective with flow rates greater than 7 mL/min.
- Major carry-over problems had been attributed to unheated areas in post purge vessel plumbing which provide liquid water sites for analyte reabsorption.
- Recovery problems attributed to metal tubing in PTD units was alleviated by acid washing which appears to deactivate the surface similar to silylation of glass surfaces.
- Needle sparge was found to be effective for H-PTD foam control with recoveries of moderately polar analytes within 1 to 2 percent of recoveries obtained with a frit purge.
- A permeation dryer was being developed to strip moisture from the purge flow before entering the trap.
- Nafion permeation dryers had been observed to be totally ineffective for polar analytes such as acetone and alcohols since these highly water soluble analytes are removed along with the water.

Analyte Screening

One analyte on the lists originally included by the EPA Project

not commercially available, based on the 1985 edition of Chem Sources. In addition, the CAS No., 594-42-3, was found to correspond to the industrial chemical perchloromethylmercaptan, Cl_3CSCl, which is highly reactive with water, rather than the listed analyte. Therefore, trichloromethylmercaptan was dropped from the study. A second analyte, ethyleneimine, was obtained from two commercial suppliers and, in both cases, the material received was completely polymerized. Therefore, ethyleneimine was also dropped from the study. During the method development phase, GC data quantification by the internal standard method was attempted, and one of the internal standards tried was cyclohexanone. This compound was not 100 percent purged, so it was ruled out as an appropriate internal standard. However, it's H-PTD behavior and elution position in the chromatogram made it desirable to add to the set of tested analytes even though the use of internal standard quantification was not incorporated in the remaining method development activities. Thus, for the studies in which data were generated for cyclohexanone, it has been included in the corresponding results tables even though it was not one of the originally included analytes.

METHOD DEVELOPMENT ACTIVITIES

Selection of GC Conditions

Only megabore fused silica columns were tested in the selection of the GC system to be used for this work. There were two reasons for this limitation:

- The greater resolving power and greater elution temperature range of capillary, open tubular columns were thought to be of substantial value to the future usefulness and flexibility of the method for solid/hazardous waste matrices.
- The desire to use existing trap technology without additional prefocusing absorptive or cryogenic traps required a very wide bore capillary to accommodate the minimum 10 mL/min desorption flow rate for these traps as the flow rate for the GC column.

GC column testing was limited to only two types of stationary phases:

(1) a highly polar phase essentially equivalent to Carbowax (30 meter by 0.53 mm I.D. fused silica with 1.0-μm Supelcowax-10 coating) and (2) a relatively nonpolar phase which is often used for Method 8240 analysis (60 meter by 0.75 mm I.D. glass with 1.5-μm proprietary siloxane coating, VOCOL). Both of these columns were obtained from Supelco. The GC retention characteristics for the analytes on these two columns are presented in Table 3. The significantly greater selectivity of the polar GC column for these polar analytes is obvious from the distribution of the analytes in k' ranges shown in Table 4. As a more convincing demonstration of the superiority of the polar GC column for these analytes, the Figure 2 chromatograms were generated using 17 analytes from Table 3 for which reasonable GC characteristics were obtained with aqueous injection solvent. Figure 2 compares the chromatographic performance obtained on these two columns and clearly demonstrates the superior separating power of the polar Carbowax column over the nonpolar siloxane column. The Figure 2 chromatograms were obtained using identical conditions for both columns which are shown below:

(1) same gas chromatograph,
(2) 10 mL/min helium carrier,
(3) identical injected samples,
(4) identical injector cavity conditions,
(5) identical vertical scale factors for the FID signal, and
(6) identical GC oven programs (40°C for 4 minutes, then 8°C/min until final analyte elutes).

Because the polar GC column was, as predicted, superior for these highly polar analytes, all subsequent work was performed using the Supelcowax-10 column.

Hydrolytic Stability Testing

Analytes which were thought potentially labile were tested for hydrolytic stability toward neutral pH (0.01 M phosphate in reagent water, pH 6.8) at 85°C. Although some of the analytes tested had relatively poor chromatographic characteristics, as indicated in Table 3, the chromatographic characteristics were good enough for the assessment of

analyte stability. The results for the 13 analytes selected for hydrolytic stability testing are given in Table 5. Based on these results, six analytes were dropped from all subsequent work: bromoacetone, N-2-hydroxyethylaziridine, methylaziridine, methylhydrazine, tetranitromethane, and thiophenol. Although acrolein and 3-chloropropionitrile displayed a significant degree of hydrolytic instability, they were clearly candidates for inclusion in subsequent method development activity. The greater than 100 percent recovery indicated for 1,1-dimethylhydrazine probably indicates that the GC peak assigned for it is actually a decomposition product of it. Nevertheless, it was also included in subsequent work.

H-PTD Recovery Prescreening

Twenty-two analytes were screened for their potential to be recovered by H-PTD. Nine analytes not tested were ones for which chromatographic testing results, reasonable chemical expectation, and/or hydrolytic instability testing results indicated essentially no possibility of ultimate inclusion in the method: 2-methyl-2-hydroxypropionitrile, 2-hydroxypropionitrile, 2-butanone peroxide, chloral hydrate, 1,2-dimethylhydrazine, 1,1-dimethylhydrazine, methylhydrazine, Beta-propiolactone, tetranitromethane. The 22 analytes were tested in three groups of six to nine analytes per set with all of the nitrogen bases tested in the same group to avoid potential chemical reactivity problems. The H-PTD conditions used were ones thought *a priori* to be reasonable but not optimized. To control the water vapor exiting the purge vessel, a small, water-cooled condenser (4 mm ID by 10 cm long) was packed with glass helices and attached to the purge vessel outlet using 1/4-inch Swagelok fittings. The condenser water temperature ranged from 20 C to 5 C.

The H-PTD recovery results for the prescreening tests are tabulated in Table 6. The recoveries obtained for some of the analytes tested were significantly lower than those previously obtained in other research programs. For example, on Work Assignments 3 and 5 of US EPA Contract 68-03-1760, absolute H-PTD recoveries of 40, 60 and 85 percent were obtained for acetonitrile, acrolein and acrylonitrile, respectively. In more recent work on Work Assignment 1 of US EPA Contract 68-03-3224, recoveries of 37 $\pm$ 3, 56 $\pm$ 2 and 78.7 $\pm$ 0.3 percent were obtained for these three analytes

respectively. Methyl ethyl ketone was recovered at 81 ± 2 percent in that same Work Assignment and at 92 ± 6 percent in Work Assignment 9 of Contract 68-03-1760. Also found in the Work Assignment 9 study were absolute H-PTD recoveries for 1,4-dioxane and allyl alcohol of 15 ± 8 and 12 ± 6, respectively. Although allyl alcohol is not an analyte in the present work, its H-PTD recovery might be expected to be similar to propargyl alcohol which is one of the Table 6 analytes.

In the earlier work, the purge vessel was immersed in the heated bath only to the point of the liquid-headspace interface during purging so that the upper part of the purge vessel and outlet tube functioned as an air-cooled condenser. In the present work, the helix-packed water-cooled condenser (first condenser design) held up so much condensate that the purge gas bubbled through it and, apparently, a significant amount of the purged analyte was lost to this low temperature aqueous phase. Because of these results, the condenser design was changed to an open, Vigreux design of 6-mm OD glass which was attached to the purge vessel outlet with a 1/4-inch Swagelok union for subsequent tests. This and other aspects of the evolution of the purge vessel condenser design are more fully discussed in a later section. Based on the prescreening results, 8 of the 22 Table 3 analytes were omitted from any further method development testing: thiophenol, malononitrile, bromoacetone and all five of the nitrogen bases of analyte Set 3. Although both acrylamide and malononitrile seemed to behave similarly, only malononitrile was eliminated since there was additional experimental data indicating malononitrile is highly reactive to one or more of the other analytes that qualified for continued inclusion in the study.

Purge Recovery Enhancement Through Salting-out

In theory, H-PTD recovery enhancement should be possible through a shift in the aqueous phase-vapor phase equilibrium constant toward the vapor phase by using high salt levels to lower the activity coefficient of the aqueous solvent. Salts were selected to examine this salting-out effect on the basis of solubility, commercial availability, and mono- and divalent options to achieve high ionic strength. A salt concentration of 80 percent saturation at 85°C was chosen to achieve maximum ionic displacement without

the inevitable dissolution problems expected when attempting to work near 100 percent saturation. The salts chosen were NaCl, Na_2SO_4, $MgCl_2$ and $MgSO_4$. The quantity of salt needed for an 80 percent saturation level was approximated assuming linearity of the solubility versus temperature relationship for the two literature solubility values for temperatures closest to the 85°C purge temperature. The amounts of anhydrous salt used in each of the four cases are shown in Table 7.

Initial salt dissolution testing showed that the chlorides of sodium and magnesium for 80 percent saturation at 85°C dissolved fairly rapidly and completely with good possibility of reasonable reproducibility in an analytical protocol. The sulfate salts were highly exothermic on dissolution, were subject to caking in the purge vessel, and did not always fully dissolve. Magnesium sulfate resulted in a highly viscous liquid that apparently facilitated the formation of a liquid plug at the purge vessel outlet/condenser inlet through which the purge flow would percolate. This phenomenon apparently resulted in the highest variability in recovery of all four salts. Thus, in spite of magnesium sulfate having the highest ionic strength of the four salts tested, it was clearly the least desirable from the aspect of practical use.

Typical recoveries for the four salts at 80 percent saturation are shown in Table 8. The recovery enhancement was, as predicted, the greatest for the two most polar, water soluble analytes. The recovery of dioxane increased from 21 percent without salt to 56 percent with sodium sulfate, and acetonitrile increased from 59 percent without salt to 88 percent with magnesium chloride. Perhaps the most noteworthy result was that 2-chloroethanol, which had been shown to be well recovered from traps when spiked directly onto them, was still not detected in any of the salting-out experiments. The use of salt increased the recovery of all analytes which were not quantitatively recovered without salt. Based on the increased difficulty of sample handling with salt, this recovery enhancement, which appeared to bring with it a considerable deterioration in reproducibility, was judged not to be an advantage for the method, and no further near-saturation salting-out experiments were performed.

Effect of Purge Temperature on Analyte Recovery

A fundamental assumption underlying the experimental design of the method development plan was that the distribution ratio for polar, water soluble analytes between the aqueous and gas phases would be uniformly shifted toward the gas phase as the purge temperature was increased. Thus, initially no experiments were planned to demonstrate this thermodynamic assumption. At the EPA Project Officer's request, a purge temperature variation study was performed near the end of the method development work since there were reports of many labs already using 40 to 60°C purge temperatures to achieve more reproducible results in Method 8240. H-PID recovery results for five purge temperatures 22, 40, 60, 85, and 100°C, are summarized in Table 9. In these experiments, a 15-minute purge at 40 mL/min (total volume 0.6 L) was used (third condenser design) with the condenser water maintained at 20°C and the trap at 23-25°C during the purge step. Three replicates were obtained at 60°C and 2 replicates were obtained for the other three temperatures. Because of a slightly below standard atomospheric pressure on the day these experiments were performed, the 100°C trials were actually at 99°C which was the boiling temperature of the water bath. The most noteworthy conclusions that can be made from Table 9 are the following:

- So far as H-PID recovery is concerned, there is no optimal temperature between room temperature and 100°C since the recoveries of all analytes increase with temperature.
- The most volatile/least water soluble analytes, i.e., those with the highest recoveries at 22 and 40°C, were recovered essentially quantitatively at or above 85°C: methyl ethyl ketone, methacrylonitrile, and acrylonitrile.
- The least volatile/most water soluble analytes, 1,4-dioxane, acetonitrile, and cyclohexanone, cannot be expected to approach quantitative recovery at any temperature using a 5-mL sample and a purge gas volume of 600 mL.
- Although more replicates at each temperature are required to make a final conclusion, the precision

obtainable is in the 1 to 5 percent RSD range and is apparently not a function of the purge bath temperature.

- Since methyl ethyl ketone, acrylonitrile, and methacylonitrile are known from prior experiments to be essentially quantitatively recovered by H-PTD at 85°C, the Table 9 results indicate the presence of a leak in the system between the purge vessel and trap during purging, between the trap and head of the column during desorption, or both. Because of the precision obtained and rational recovery change with temperature, the leak was apparently constant throughout the series of experiments, and has no impact on the conclusions made from the H-PTD recovery results.

On the basis of these results, 90°C was adopted as the purge temperature for the GC-MS method performance evaluation study. Since a water bath is the most likely means for purge vessel thermostating, adoption of a 90°C purge temperature should accommodate the use of a water bath in all but the most extreme conditions.

Refinement of the Condenser Design

As noted above, the first condenser design used a small commercially available condenser with 1/4-inch O.D. by 8-cm length cold zone which was packed with 3-mm glass helices. The condenser was attached to the purge vessel outlet using a 1/4-inch Swagelok union with Teflon ferrules. For this and all other variants of purge vessel/condenser design, the unit was immersed in the heated bath up to the beginning of the condenser cold zone. The packed condenser retained essentially all of the condensate causing the purge flow to percolate through the liquid and become well equilibrated with such a large volume of cold aqueous phase that purged analytes were effectively recaptured and overall H-PTD recoveries were significantly reduced.

The second condenser design was fabricated in the Battelle glass-blowing shop and retained the 1/4-inch O.D. tubulations and Swagelok attachment to the purge vessel outlet, but substituted a 6-mm I.D. by 3-cm

long Vigreaux type cold zone. Improved analyte H-PTD recoveries were obtained with this second design, but the 1/4-inch tubulation and/or Swagelok union allowed the formation a plug of water in the connecting tubing after about 3 to 5 minutes of purge flow. Thus, the purge flow percolated through this liquid water at the hot-cold zone transition point, i.e., the inlet of the condenser, creating good conditions for recapture of purged analytes. Poor analysis precision was correlated with the severity of this condensate plug problem. Careful acid washing of both the condenser and purge vessel to promote clean draining of the condensate and prevention of water plug formation was not reliably effective.

The third design involved (1) modification of the purge vessel outlet and condenser inlet to 9-mm O.D. glass, (2) the use of a 3/8-inch Swagelok union connector, and (3) lengthening of the Vigreux cold zone to 18 cm. Except for some condensate hold-up in the Swagelok union, this design eliminated the problem of condensate plugs at the condenser inlet, and, as a result, analysis precision for all analytes and recoveries for some of the analytes were improved.

The final purge vessel-condenser design, used only for the GC-MS testing described below, is shown in Figure 3. The only changes from the previous design were the reduction in length of the condenser cold zone to 10 cm and the elimination of the 3/8-inch Swagelok union by changing to a one-piece, glass-blown design.

A clean, dry purge vessel-condenser unit was required for each analysis to avoid carryover problems. Since thorough rinsing of the purge vessel in place did not eliminate carryover, the problem was probably due to analyte left in the small volume of cold water on the surfaces of the condenser. If the condenser were also rinsed, the relatively large amount of water left behind wetting its entire length apparently recaptured purged analytes in the next run thereby reducing their recovery from that obtainable with a dry purge vessel-condenser unit. Thus, in all of the trials at each stage of the condenser design, multiple units were cycled through cleaning and drying steps so that each analysis was done with a clean, dry purge vessel and condenser. Although typically only the bottom 2 to 3 cm of the condenser cold zone appeared wet with water droplets at the end of the purge step, no experiments were performed to establish the effect of the length of the cold zone on the analysis result. The 10-cm length used for the final

experiments is thought to be somewhat longer than actually necessary. One aspect of condenser operation that definitely had an effect on H-PTD recovery was the temperature of the water circulated through the condenser cooling jacket. Temperatures between 0°C and room temperature were used and the results from a number of trials all indicated that lower cold zone temperatures gave lower analyte recoveries, as would be expected.

Purged Water Control Options Not Involving a Condenser

Two noncondenser approaches to the control of the water vapor exiting the heated purge vessel were investigated. These activities were pursued due to the total lack of recovery in the prior experiments for three analytes that were thought to be at least partially recoverable by H-PTD: propargyl alcohol, 2-chloroethanol, acrylamide. All three of these analytes had been shown to be well-recovered when spiked directly onto traps prior to a blank heated purge cycle followed by desorption in the normal sequence. Their nonrecovery was thought to be due to the recapture of purged analyte by the small amount of cold condensate present in the condenser. The two noncondenser approaches involved (1) the use of a desicant to remove water and (2) the use of highly retentive trapping materials which could be operated at temperatures above the dew point of the purge stream.

Water Removal Using Zeolite Desicant--

Removal of water vapor from the purge flow was accomplished using a zeolite-type molecular sieve dessicant between the purge vessel and the trap. No post-purge purge carrier dilution was used, so the molecular sieve (Linde 3A) was maintained at 100°C to preclude condensation of water anywhere in the system. Type 3-A molecular sieve was chosen since the other types would definitely be expected to retain the analytes in the set with smallest molecular size. Zeolite-based molecular sieve was chosen since an easily recyclable system would be required for routine operation. Additionally, if most of the water adsorptive capacity was inside the nominally 3-Å cavities, the loss of analyte to adsorption on surface sites would be minimized. Isotherms for water adsorption provided by Linde were used to predict the quantity of molecular sieve necessary to just adsorb all of the purged water at a sieve temperature of 100°C. Spherical 1/16-inch 3A

sieve was ground and sized to 14-30 mesh and 3 g were packed into a 1/4-inch stainless tube. Using a 450-mL purge at 85°C, water breakthrough was found to occur at sieve temperatures higher than 95°C, so the trials were performed at 90°C to ensure essentially complete water removal. The use of a near-stoichiometric quantity of dessicant was expected to minimize the loss of analytes by adsorption onto the molecular sieve surface.

The ability of the molecular sieve trap to remove water but not analytes was tested by spiking the analyte mixture into the line between the purge vessel and the molecular sieve module (i.e., recovery) and proceeding through the usual H-PTD sequence. This experimental design examined the efficiency of analyte throughput for the 100 percent purge recovery situation. A 100 percent molecular sieve throughput standard was generated by spiking the same mixture onto the head of the trap followed by the usual H-PTD sequence. Between runs, the molecular sieve dryer was cycled through a 230°C, 20 minute bake step using dry helium at 150 mL/min. Under these conditions, the dryer throughput performance was totally unacceptable with less than 1.0 percent throughput of methyl ethyl ketone, methacrylonitrile and acrylonitrile and no throughput of the other analytes which were acrolein, acetonitrile, propionitrile, 1,4-dioxane, isobutanol, proparagyl alcohol, 2-chloroethanol, 1,3-dichloro-2-propanol, acrylamide, and cyclohexanone. The experiment was repeated by spiking the analytes upstream of the dryer at the 12th minute of the 15 minute purge to preload the dryer with water in an attempt to deactivate its analyte adsorptive capacity, but the throughput results were only slightly improved; less than a factor of 20 increase in the three analytes detected in the first experiment with none of the other analytes detected.

Highly Retentive Trapping Materials--

The strategy of this approach was to operate the trap at a high enough temperature to prevent water condensation. By partially diluting the purge flow at its exit from the heated purge zone, the trap can be maintained at a temperature that is possibly low enough to prevent thermal degradation of analytes but that is slightly above the dew point of the resulting purge flow carrier. Thus, the trapping effectiveness boundary conditions were to prevent breakthrough or chemical decomposition at a 90°C trapping temperature with 450 mL of total flow (no dilution) or to exhibit larger

room temperature breakthrough volumes of less than 13,000 mL for the most volatile analytes (purge carrier diluted 28-fold to achieve a dew point of 18°C). Since the very high flow required for room temperature operation would far exceed acceptable velocities for analyte trapping, only a 90°C and 70°C trapping temperature with no dilution and 1:1 dilution make-up flow, respectively, were tested.

The two high-retention trapping materials tried were Carbosieve and Carbotrap, both supplied by Supelco. Carbotrap was not retentive enough for the most volatile analytes at the elevated trapping temperature. While Carbosieve was apparently effective at preventing breakthrough at the elevated trapping temperature, poor desorption characteristics resulted in essentially no separation of the early eluting analytes. This result may have been partially due to adsorption and desorption of excessive amounts of water since excellent chromatograms could be produced with analytes spiked onto these traps at room temperature followed by a 4-min dry purge flow and then identically desorbed. A combination trap consisting of 4:1 Carbopack: Carbosieve with the Carbotrap at the inlet was used with the 90°C trapping temperature and no purge carrier dilution. Good chromatograms were obtained from this trap when analytes were spiked directly onto it followed by the normal H-PTD sequence using reagent water. However, the GC peaks for the early eluting analytes, especially acrolein and methyl ethyl ketone, were severely split and the mid elution range analytes were broadened due to the significantly different desorption characteristics of these two trapping materials. An example chromatogram is shown in Figure 4. Chromatographic performance of the mixed trap could possibly have been improved using a two-step desorption sequence, i.e., desorbing the Carbosieve onto the Carbotrap followed by Carbotrap desorption onto the GC column. However, this type of instrumentation and modification was judged outside the scope of work and the high temperature trapping investigations were terminated without proceeding to recovery experiments in which analytes were spiked into a 5.0-mL aqueous purge sample.

Breakthrough Volume Testing for Tenax and Novel Trapping Materials

Traps containing activated carbon and silica gel were not considered in this work since both of those materials are known to result in the

adsorption and desorption of significantly greater amounts of water than Tenax. In agreement with earlier work, initial tests for Tenax breakthrough problems for the most poorly retained analytes indicated that, with only one exception, breakthrough would not occur for traps held at room temperature and total purge flow volumes of less than 450 mL. The one exception was methyl mercaptan which broke through Tenax in only 200 mL of purge gas volume. Minor to significant degrees of trap breakthrough was observed to occur for acrolein and acetonitrile in a series of experiments which tested the effect on H-PTD recovery of varying the temperature of the condenser cooling water. In those experiments, the trap was held at the same temperature as the condenser cooling water and breakthrough of acetonitrile and acrolein was clearly indicated by the recovery results for 40°C and possibly indicated as near onset at 30 to 33°C. Because of these results, it was decided to (1) test some novel trapping materials prepared at Battelle under an earlier research program for the US EPA and (2) more carefully determine the temperature dependency of acetonitrile and acrolein trap breakthrough for Tenax.

Testing of Novel Trapping Materials--

Two traps were packed with Battelle-synthesized trapping materials. Standard traps as supplied by Supelco for the Tekmar PTD apparatus were packed in the usual 24-cm bed length. These materials were copolymer polyamides of pyromellitic dianhydride (PMDA) with 4,4'-diaminodiphenylsulfone (DADS), and 4,4'-diaminodiphenylmethane (DADM). The resulting polyamides are thus designated DADS/PMDA and DADM/PMDA. A third copolymer with 2,6-dichloro-p-phenylenediamine (DCPDA), designated DCPDA/PMDA, had been shown in Work Assignment 1-05 of the present contract to be equal to DADM/PMDA in retention of vinyl chloride, so it was not tested.

Breakthrough volumes for the two analytes of highest interest, acrolein and acetonitrile, were determined over a temperature range high enough to give reasonable elution, i.e., breakthrough, times. The resultant data were then reduced using linear plots of log retention vs. 1/T(°K) which enabled extrapolation to 25°C for the predicted elution volume. This experimentation was essentially equivalent to using the trap as a GC column. Because of the asymmetry of the eluted peak, the elution volume at the peak

top corresponded to approximately a 25 percent breakthrough fraction. These "peak height" elution volumes were then corrected to give a breakthrough onset volume. The results are given in Table 10.

Since DADS/PMDA and DADM/PMDA were clearly retentive of these analytes, further testing was performed to check the desorption efficiency of 11 analytes which had been shown to desorb effectively from Tenax: acrolein, methyl ethyl ketone, methacrylonitrile, acrylonitrile, acetonitrile, propionitrile, 1,4-dioxane, isobutanol, cyclohexane, proparagyl alcohol, and 2-chloroethanol. A mixture containing 500 ng of each analyte in 2 μL of water was applied in duplicate experiments directly onto the inlet of each trap and then the usual H-PTD sequence was initiated to create a trap-desorb experiment corresponding to 100 percent purging efficiency. Each trap was evaluated in duplicate. The resulting chromatograms showed very poor separation due apparently to poor desorption characteristics of these strongly polar trapping materials. The use of a 120°C preheat rather than 50°C, which should have provided narrower bands of desorbed analyte, afforded no improvement in chromatographic quality. The chromatograms illustrating these results are given in Figure 5, which is a septum-injected reference chromatogram obtained from a septum injection; Figure 6, obtained from desorption from DADS/PMDA with 50°C preheat; Figure 7, obtained from desorption from DADS/PMDA desorption with 120°C preheat; and Figure 8, obtained from desorption from DADM/PMDA with 50°C preheat. For the desorbed samples, chromatographic separation was so poor that quantification versus the septum-injected 100 percent recovery standards was judged not to be a worthwhile activity. Furthermore, the results found for the two-component trap of Carbosive and Carbopack, described in the preceding section, indicated that using Tenax and one of these polar trapping materials would probably result in split GC peaks for the early eluting components, as illustrated in Figure 4, which is caused by the time lag for desorbing the more retentive back-up section of the trap. Therefore, it was decided to continue to use the all-Tenax trap and to choose purge flow and purge time conditions that would accommodate the less than optimal retention characteristics of Tenax.

Acrolein and Acetonitrile Breakthrough Characteristics for Tenax—

In similar fashion to the breakthrough experiments described above for

novel trapping materials, breakthrough volumes for acrolein and acetonitrile from Tenax were determined, and the results are shown in Table 11. At the trap temperature proposed for the GC-MS method testing, 25°C, the average breakthrough onset for acetonitrile and acrolein was about 510 and 525 mL, respectively, providing a 13 and 17 percent margin, respectively, against breakthrough for a 450 mL purge volume. This margin against breakthrough is considered adequate because the elution volume corresponding to the top of the peak for acetonitrile and acrolein at 25°C are essentially equal at 590 and 600 mL, respectively. This latter purge volume corresponds to accidental overpurging by 4.5 min (i.e., 30 percent) at 30 mL/min. Alternatively, the linear plot of log (retention) vs. 1/T(°K) can be used to predict the same breakthrough situation at 450 mL of purge flow if the trap temperature were accidently at 29°C instead of 25°C. Using these hypothetical analysis procedure errors and the observed breakthrough profile asymmetries, 35 percent and 15 percent of the acetonitrile and acrolein, respectively, that exited the purge vessel at a purge time of 0.0 min would be lost to breakthrough. Since breakthrough onset precedes the peak top by 3 min or less, an average of 18 and 8 percent of the acetonitrile and acrolein, respectively, exiting the purge vessel during the first 3 min of purging would potentially be lost to breakthrough under these conditions. Assuming that 40 percent of the total analyte purged is recovered in the first 20 percent, i.e., 3 min, of the purge time, the amount of analyte lost in each case can be estimated to be:

Acetonitrile: 18 percent of 40 percent = 7 percent
Acrolein: 8 percent of 40 percent = 3 percent

Thus, a reasonable margin of error of 5 percent on purge flow rate/purge time (the example above is a 33 percent error) which would require purge flow to be no higher than 31.5 mL/min or the purge time to be no greater than 15 min and 45 sec, would not result in any breakthrough loss of these two analytes. With regard to trap temperature, a 2°C error, i.e., the trap at 27°C during the first 3 min of purging, can be expected to result in breakthrough losses for these two analytes of less than 1 and 2 percent for acrolein and acetonitrile, respectively. Thus, specification in the H-PTD method for use of the standard all-Tenax trap at a temperature less than or

equal to 25.0°C (77°F). A purge flow of 30.0 ± 0.5 mL/min and a purge time of 15 min ± 10 sec is adequate for ensuring good trapping of the two analytes with greatest potential for breakthrough.

H-PID GC-MS METHOD TESTING

Overview

Using the H-PID conditions resulting from the method development activities, only the following eight analytes of the original set could be recovered to some extent: acrolein, methyl ethyl ketone, methacrylonitrile, acrylonitrile, acetonitrile, propionitrile, 1,4-dioxane and isobutanol. The final H-PID conditions are presented in detail in the corresponding portion of Section 4, Experimental. The experimental design for the H-PID GC-MS testing involved the following elements and features:

- Preliminary testing to approximate H-PID GC-MS detection limits and, thereby, plan spiking levels
- Establishment of GC-MS calibration curves for each analyte from a level 3- to 5-fold above the estimated MDL to a 100-fold higher level in half orders of magnitude increments, i.e., 1X, 3X, 10X, 30X and 100X calibration levels
- Analysis of 10 replicates of a reagent water sample spiked at a level approximately 5-fold above the estimated MDL (low spiking level)
- Analysis of 10 replicates of a reagent water sample spiked 10-fold higher than the low level spike
- Computation of recoveries and analysis precision from the quantified replicate analyses, and computation of an estimated MDL value for each analyte from the low spiking level analysis precision

H-PID GC-MS Analysis Results

Calibration Results--

Calibration standards were analyzed in duplicate at the 3X, 10X, 30X and

100X levels and in quadruplicate at the 1X level. The lowest calibration level used for each analyte (the 1X level) is given in Table 12 along with quantification response factors and the percent deviation of the calibration curve from the best straight line fit. The response factors and linear model fit results are given for the case of inclusion of all five calibration levels as well as that for which the lowest level (1X level), which had the poorest reproducibility, was omitted.

The lowest response factors found were for acrolein and 1,4-dioxane. The base peak and major fragment ions for both of these analytes are in the m/e 27 to 30 range, partially explaining their low response factors. MS detection sensitivity in the best case, for acrylonitrile, was still only 28 percent of the MS sensitivity for the quantification internal standard, benzene-D_6. This unfortunately low inherent MS sensitivity is a combination of relatively poor MS ionization and detection characteristics as well as incomplete H-PTD recovery.

Analysis Results for Spiked Reagent Water

The spiked reagent water analysis results for individual replicates plus the average percent recoveries and precisions are shown in Table 13 for the low spiking level and in Table 14 for the high spiking level. Table 13 also shows MDL values computed from the precisions found for the low spiking level. Without exception, the analysis precisions are very good, typically about 5 percent relative standard deviation for the high spiking level and about 7 percent relative standard deviation for the low spiking level. Average recoveries at both spiking levels are typically between 85 and 100 percent for all analytes at both spiking levels, the only exception being acrylonitrile with an average recovery of 66 percent at the high spiking level. Since the three high spiking level calibration check standards also gave an average recovery of 67 percent for acrylonitrile and since the low spiking level gave an 83 $\pm$ 4 percent recovery for acrylonitrile, the low recovery for the high spiking level is probably due to an improperly made acrylonitrile stock solution for either the calibration data set or the spiked reagent water/calibration check standard data set.

The MDL values shown in Table 13 are 10- to 30-fold higher than those reported for the most well-behaved nonpolar analytes of Method 8240.

Certainly, part of this sensitivity difference is attributable to less than quantitative H-PTD recovery for these polar analytes as well as inherently less sensitive MS detection due to lower ionization cross sections and unfavorable fragmentation pathways. The major cause of the high MDLs, however, is the excessive width of the GC peaks for the analytes. A GC-MS chromatogram for the highest level H-PTD calibration standard is shown in Figure 9. The most significant feature of this chromatogram is the substantial difference in peak widths for the group of analytes as compared with that for BFB. Water was found to elute in the range of 5.8 to 8.8 minutes as a very heavily fronted peak under the chromatographic conditions used. Thus, all of the method analytes elute ahead of the desorbed water which is, in effect, the injection solvent, and the BFB elutes significantly after the water "solvent". Clearly, what Figure 9 indicates is a reverse solvent effect chromatographic band broadening of these pre-solvent analytes eluting ahead of the "solvent": the peak widths at half height in Figure 9 are about 15 sec for isobutanol and about 4 sec for BFB. For comparison to the GC-MS data, Figure 10 shows a typical FID chromatogram obtained during the method development phase. The isobutanol peak width at half height for this FID chromatogram is about 10 sec. Thus, reverse solvent effect band broadening was occuring in both cases. The more severe band broadening of Figure 9 for GC-MS may be due to a higher amount of desorbed water in that case. The FID chromatogram was from H-PTD conditions which employed a lower temperature condenser and a 20 percent past-condenser dilution of the purge carrier, and these conditions may have resulted in less adsorption and desorption of purged water.

To further ellucidate this band broadening phenomenon, septum injections were made on the GC-MS system using a 10:1 injector split ratio. The peak widths obtained for the analytes with H-PTD sample processing and the split septum injection are shown in Table 15. The injector cavity of the GC-MS was about 1.0 mL. Assuming a 10 mL/min column flow, and a 2-uL sample vaporizing to 2.0 mL volume, the time-width of the sample band entering the column would be about 1.2 sec. Adjusting for injector cavity dilution and non instantaneous evaporation kinetics but neglecting the column head pressure sample compression factor, a maximum sample band width of about 1.5 sec can be assumed. Table 15 shows for acrolein and methyl ethyl ketone the band broadening expected for the normal chromatographic

performance on the type of column used. Progressively later eluting analytes are progressively broadened until, for isobutanol, which elutes during the water elution, the band widths are equal to the H-PID case. This behavior clearly indicates that only 0.1 uL of injected water can have a serious band-broadening effect using this chromatographis system. The conclusion is that a nonpolar chromatographic system such as DB-624 that is less vulnerable to polar solvent band broadening might provide better chromatographic performance and, consequently, lower MDLs for these analytes.

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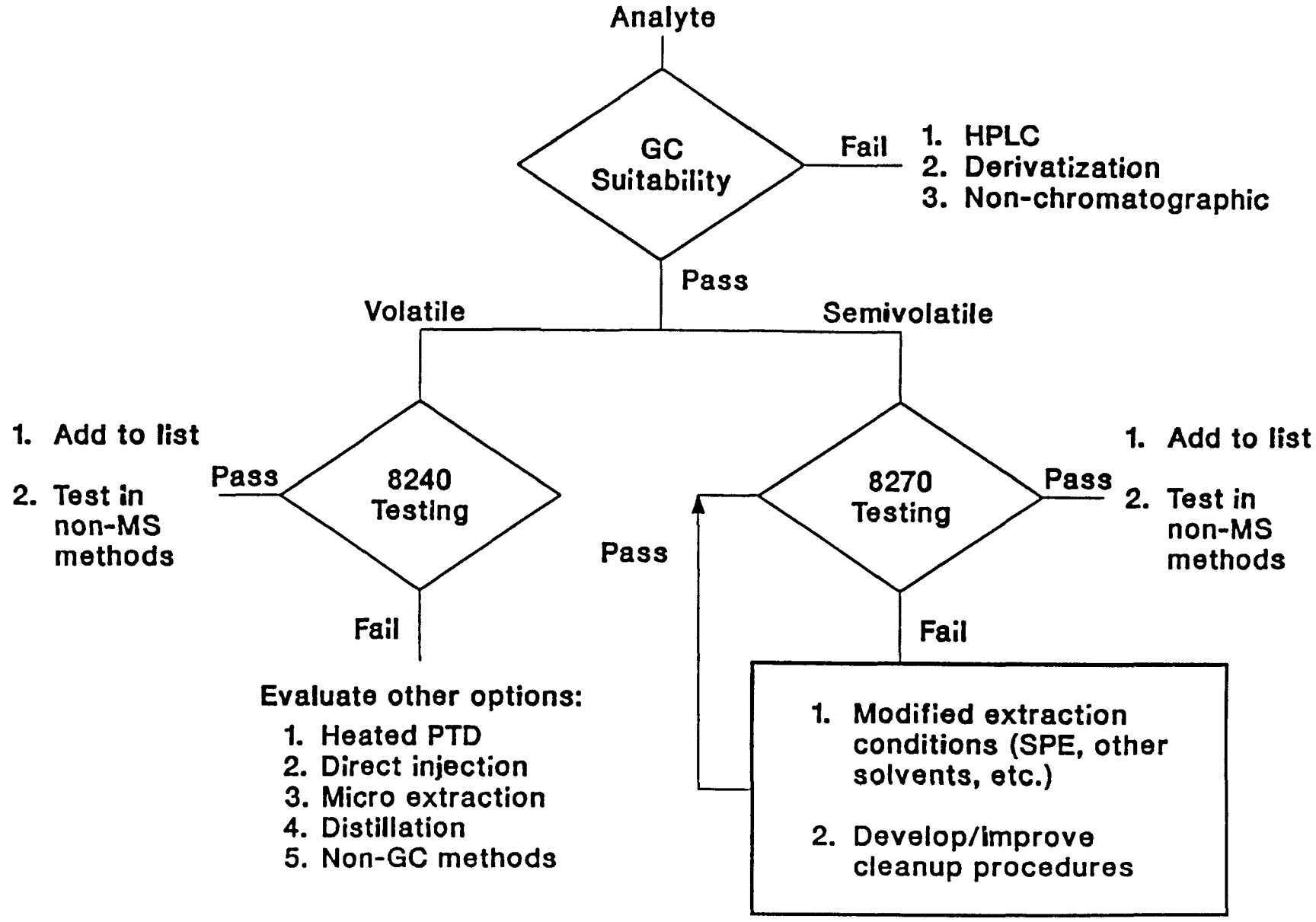

Figure 1. Hierarchical Approach for Analytical Method Development For Organic RCRA Analytes.

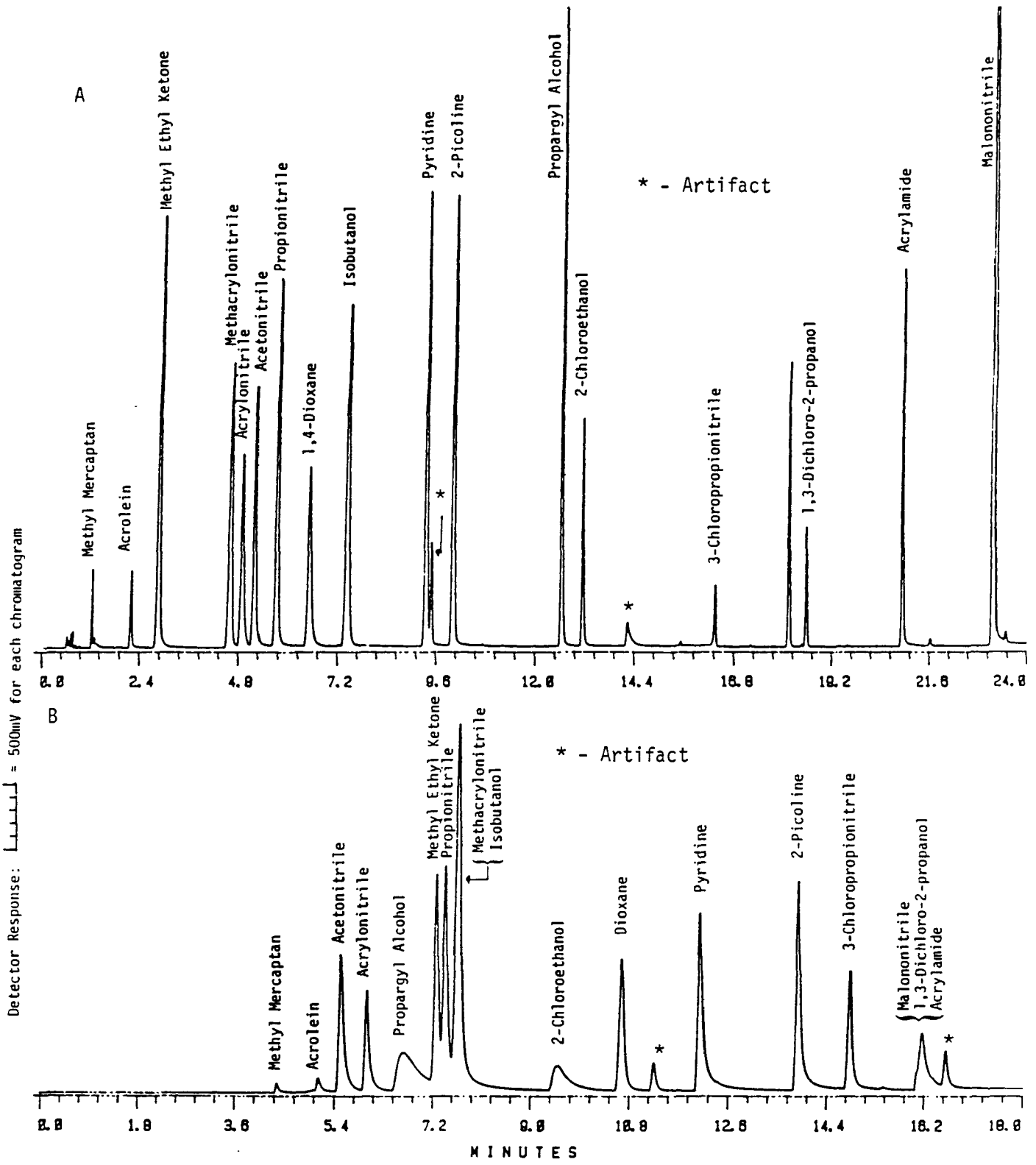

Figure 2. Gas Chromatograms of H-PTD Analytes on (A) 0.53 mm ID Supelcowax-10 Fused Silica Column and (B) 0.75 mm ID Borosilicate Glass VOCOL column. See text for GC conditions.

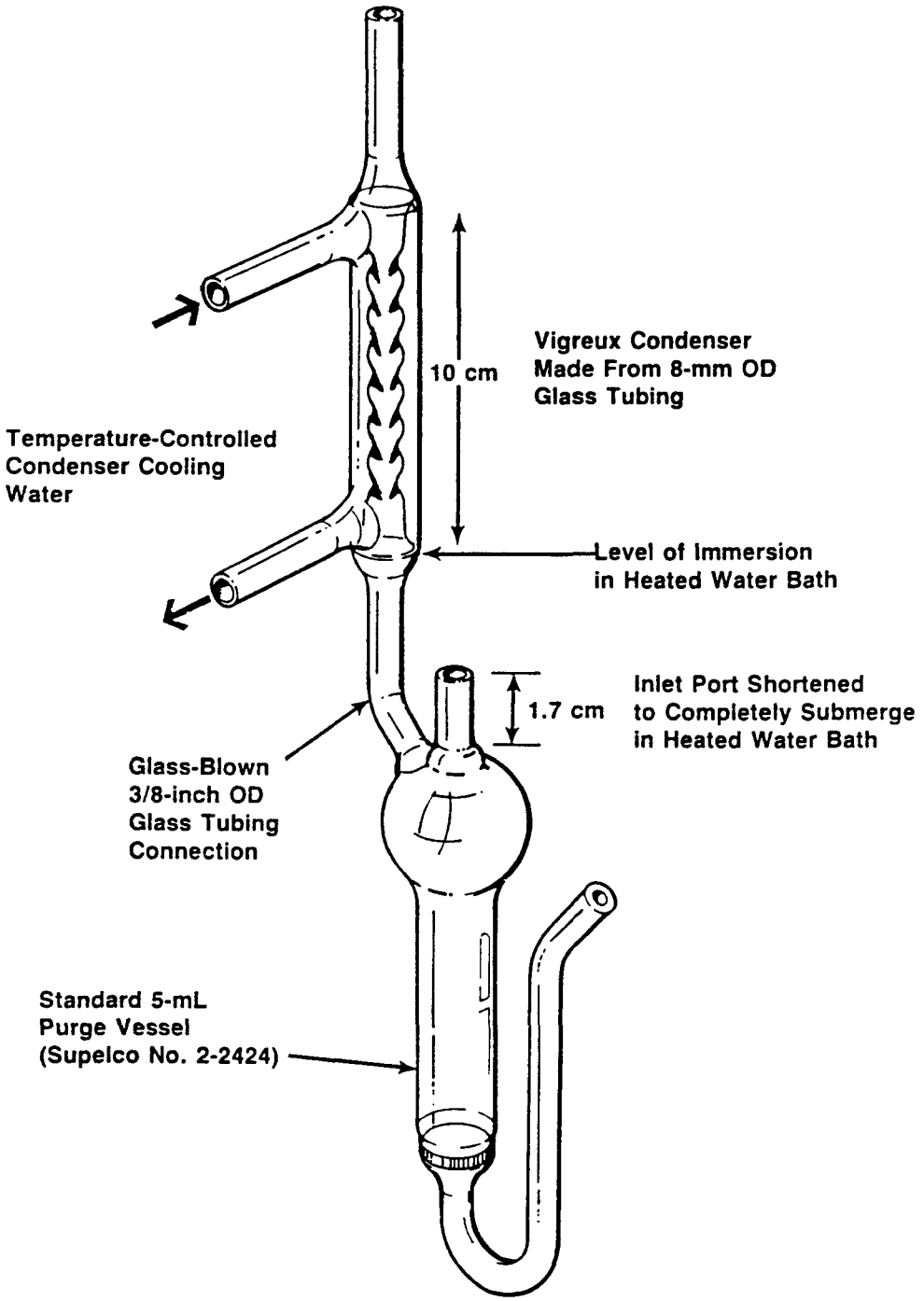

Figure 3. Purge vessel - Condenser Unit Used for H-PTD GC/MS Method Performance Testing.

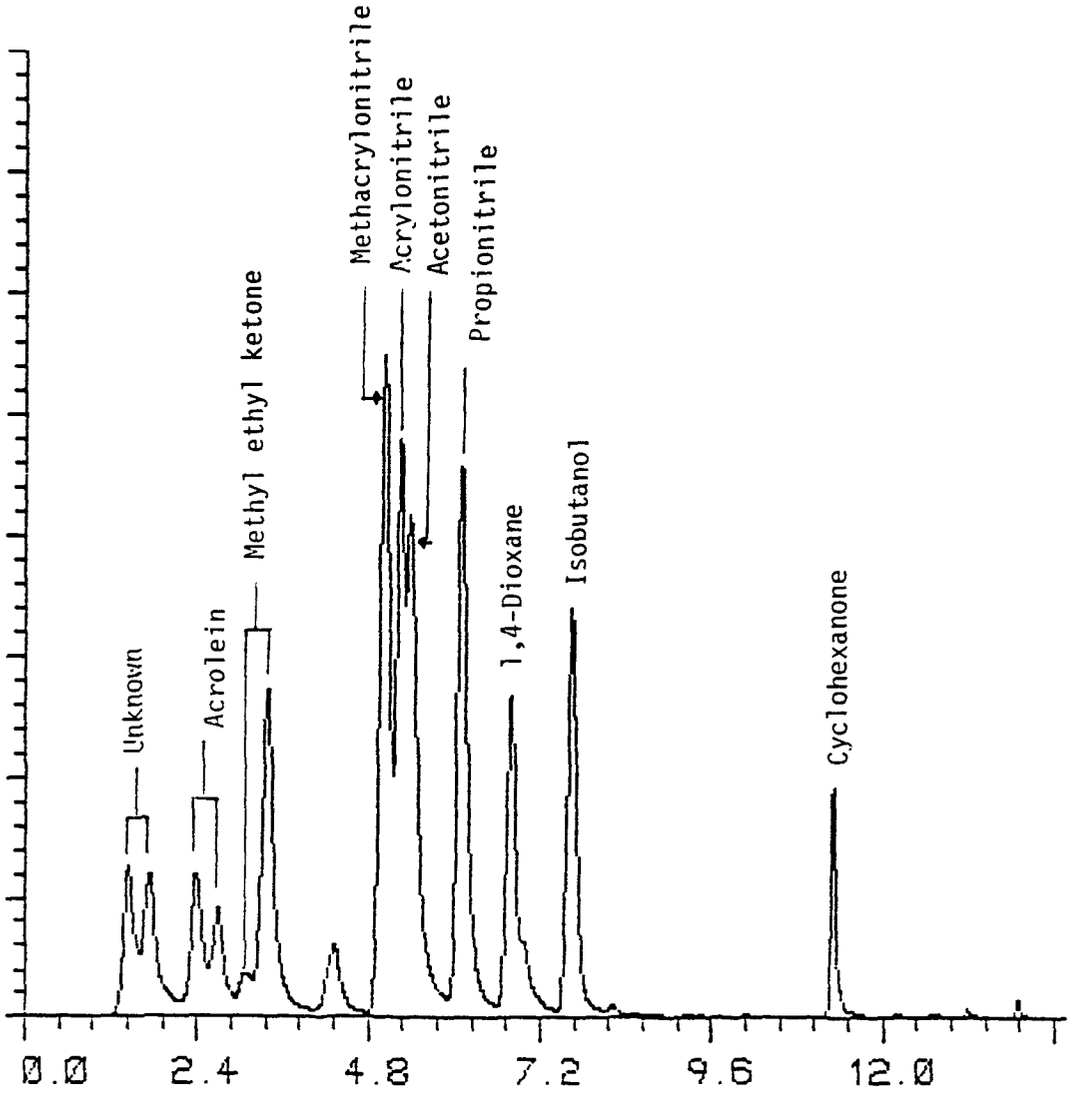

Figure 4. GC-FID Chromatogram Demonstrating Band Splitting of Analytes With a Carbotrap: Carbosieve, 4:1, Trap.

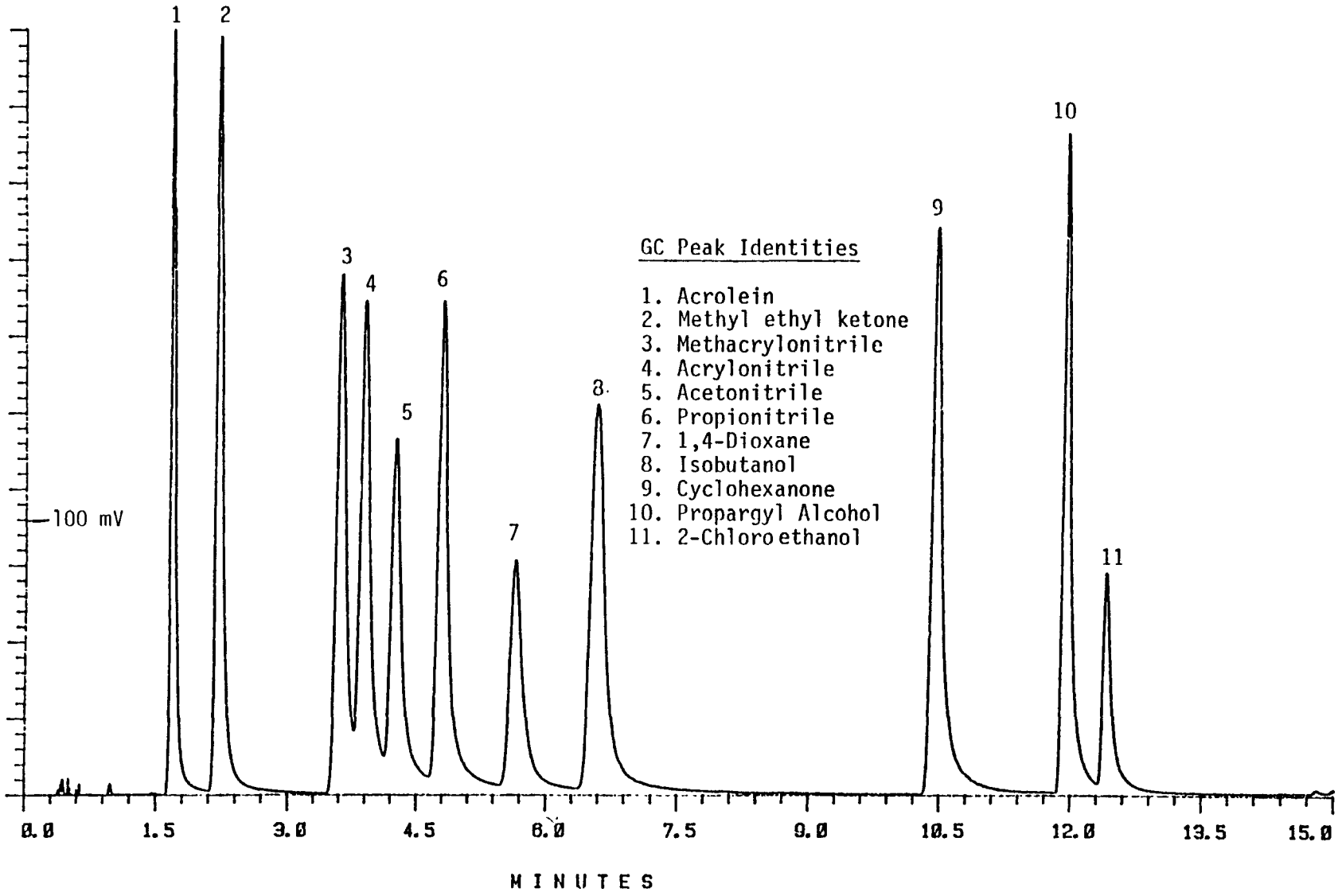

Figure 5. GC-FID Chromatogram for Septum Injection of 11 H-PTD Analytes (500 ng, each analyte).

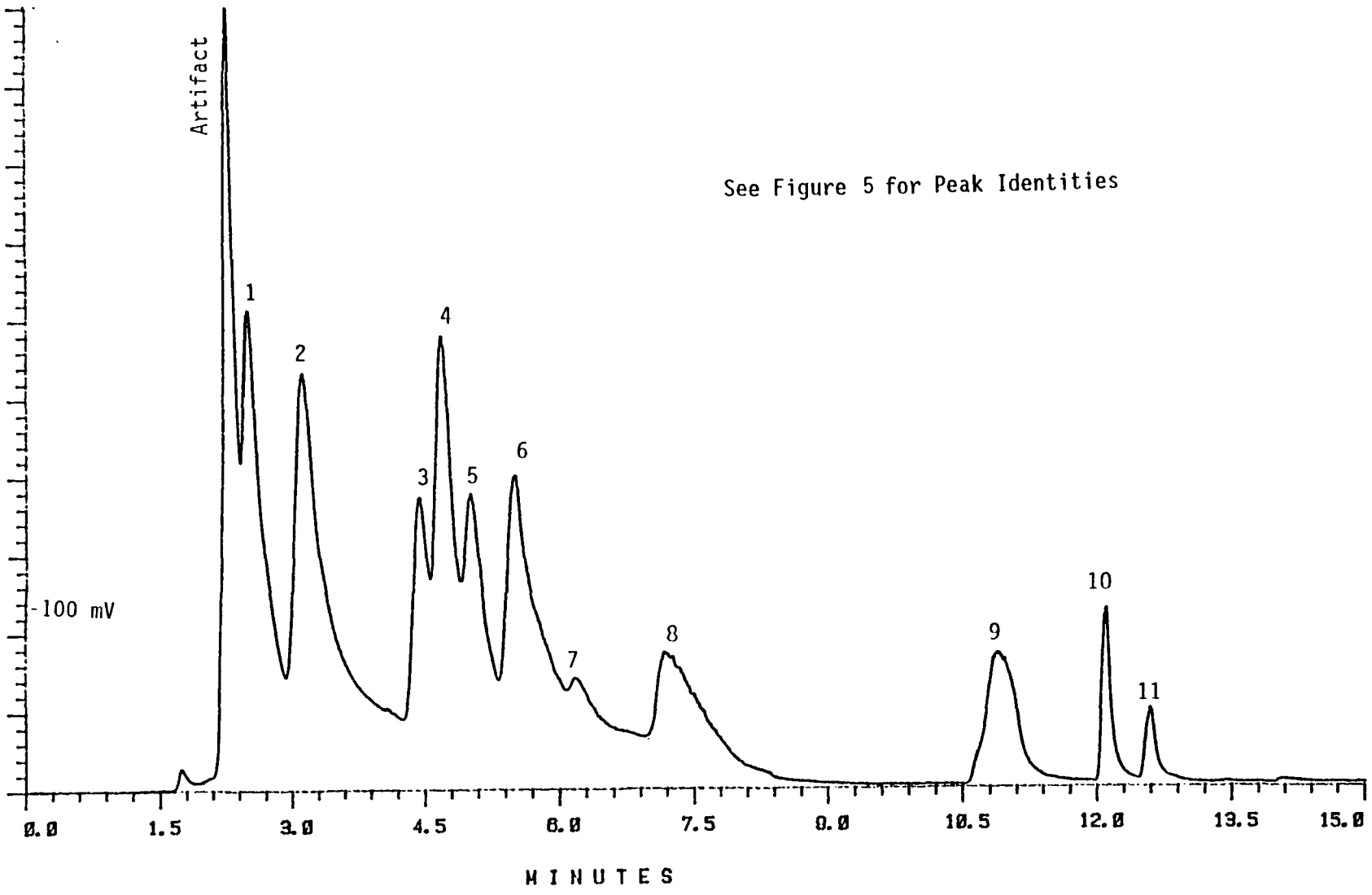

Figure 6. GC-FID Chromatogram for H-PTD Analytes Spiked Directly Onto the DADS/PMDA Trap and Then Desorbed with 50°C Preheat (500 ng, each analyte).

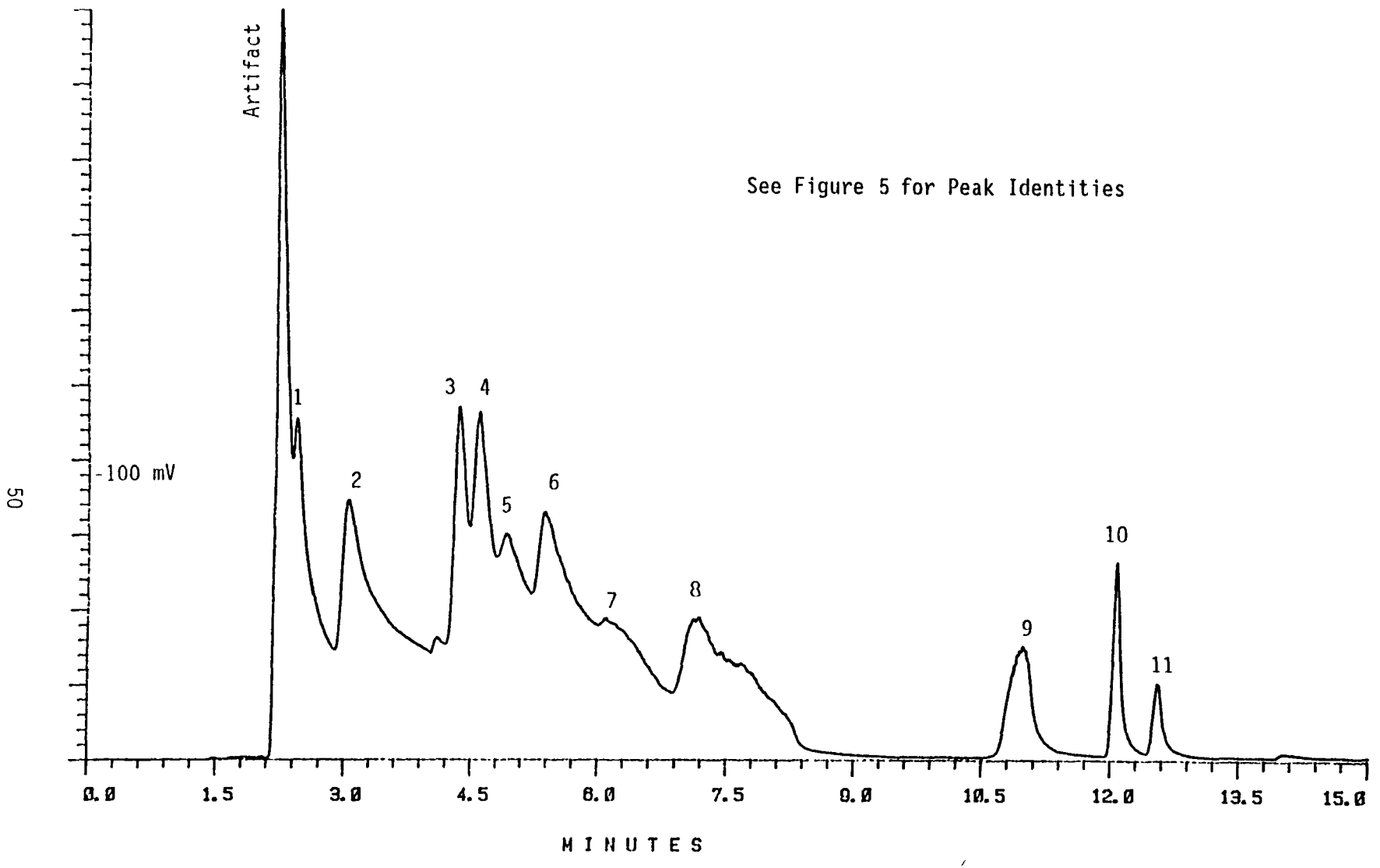

Figure 7. GC-FID Chromatogram for H-PTD Analytes Spiked Directly Onto the DADS/PMDA Trap and Then Desorbed with 120°C Preheat (500 ng, each analyte).

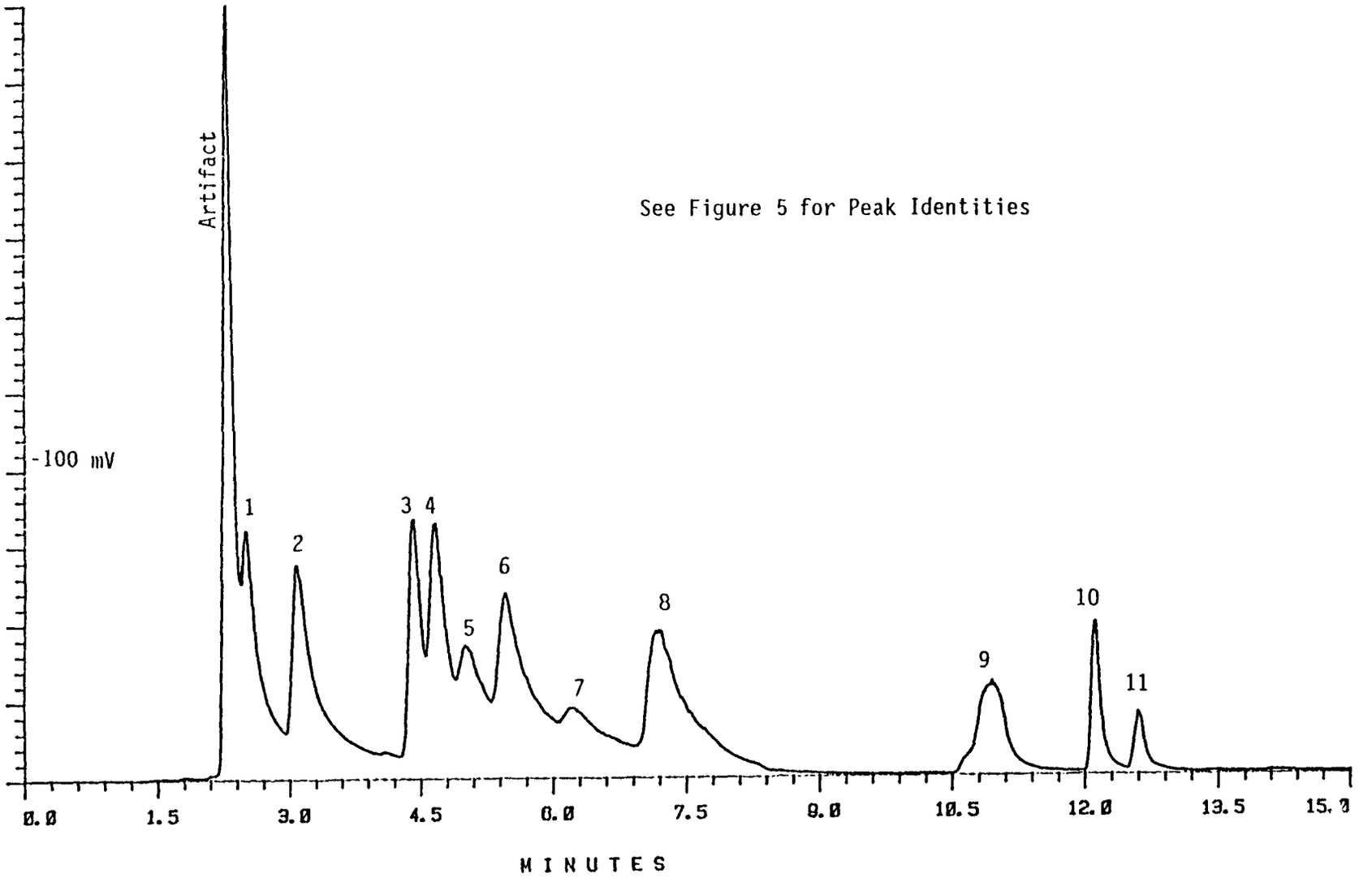

Figure 8. GC-FID Chromatogram for H-PTD Analytes Spiked Directly Onto the DADM/PMDA Trap and Then Desorbed with 50°C Preheat (500 ng, each analyte).

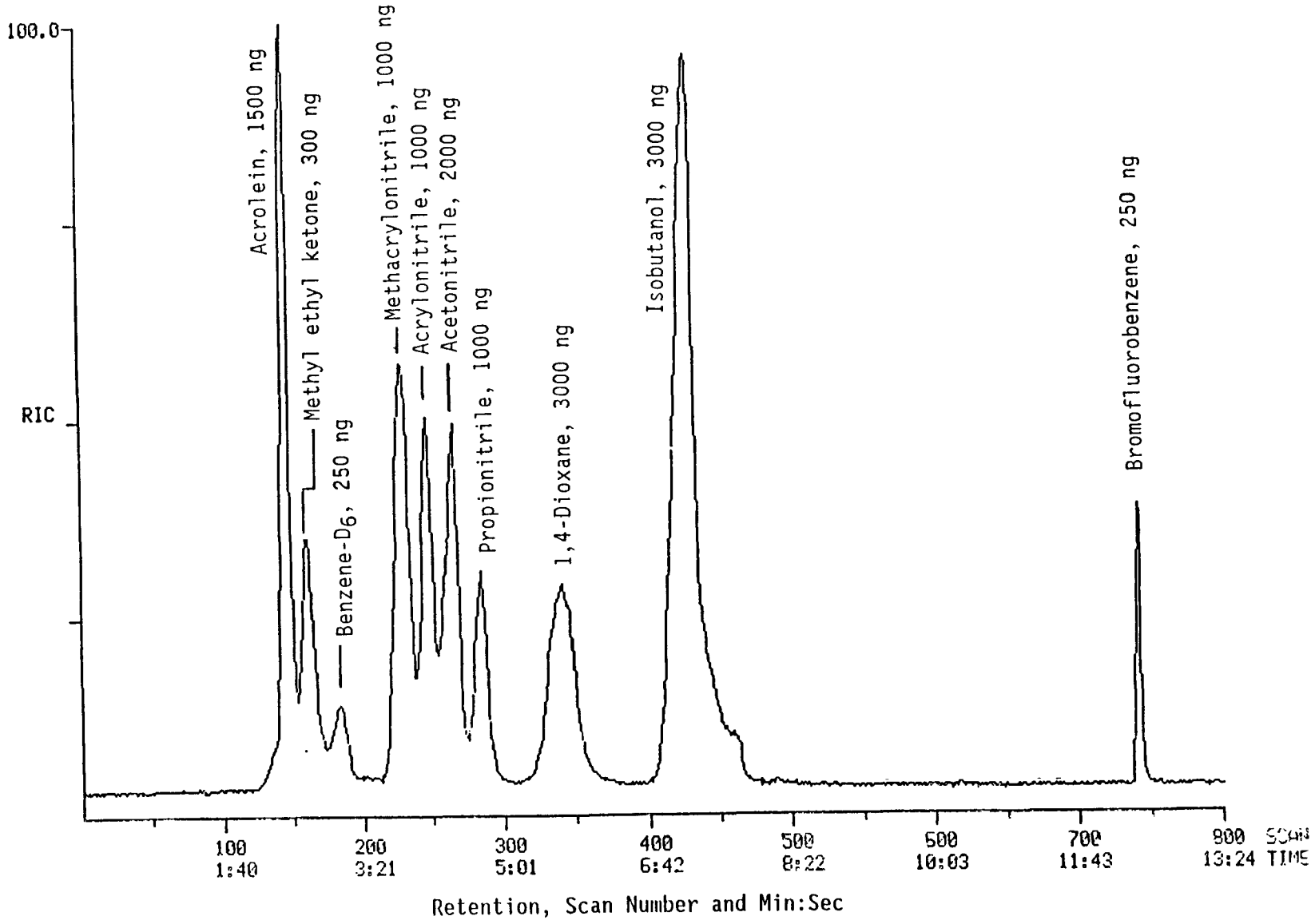

Figure 9. GC/MS Chromatogram for H-PTD Analysis of the Highest Calibration Level.

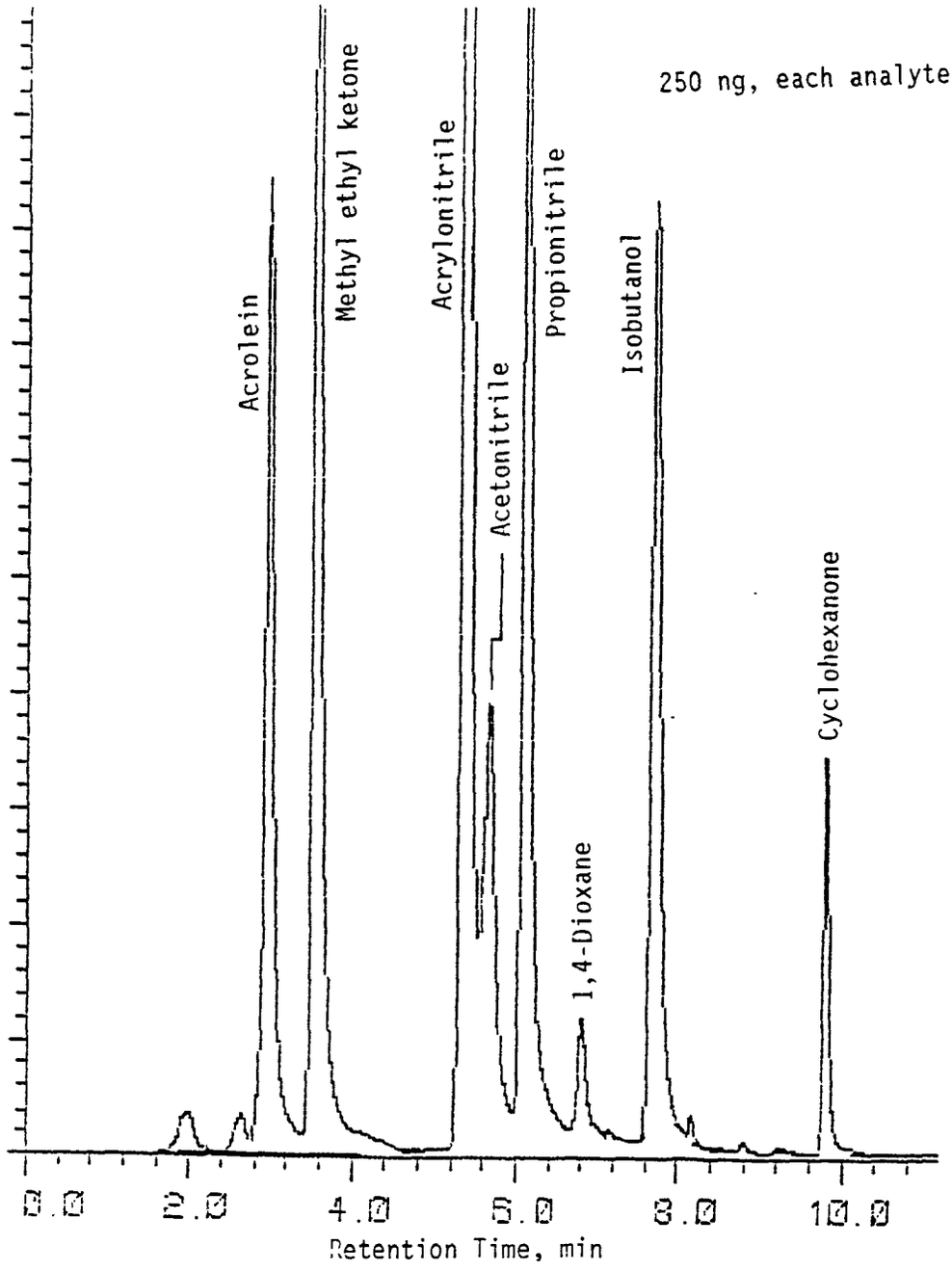

Figure 10. FID Chromatogram Showing Typical Analyte Resolution For H-PTD Analysis Obtained During the Method development Phase.

TABLE 1. COMMERCIAL SOURCES AND PURITIES OF ANALYTES INCLUDED IN THE STUDY

Compound	CAS No.	Source	Purity	Lot No.
2-Hydroxy-2-methylpropionitrile	75-86-5	Aldrich	0.99	01321BP
Acetonitrile	75-05-8	B & J	-	AK526
Acrolein	107-02-8	Aldrich	0.99	4811BL
Acrylamide	79-06-1	Rebottled	-	
Acrylonitrile	107-13-1	Aldrich	-	2020HK
N-2-Hydroxethylaziridine	1072-52-2	Aldrich	0.97	01021PL
Bromoacetone	598-31-2	Chem Service		2297B
2-Butanone peroxide	1338-23-4	Aldrich	50 wt %	0209CL
Chloral hydrate	302-17-0	Fisher	-	792836
2-Chloroethanol	107-07-3	Eastman	-	131
3-Chloropopionitrile	542-76-7	Fluka	0.97	226860
1,3-Dichloro-2-propanol	96-23-1	Aldrich	0.98	0819CM
1,1-Dimethyl hydrazine	540-73-8	Chem Serv	-	
1,2-Dimethyl hydrazine hydrochloride	57-14-7	Chemserv	-	4155J
1,4-Dioxane	123-91-1	B&J 087	-	AK688
Ethyleneimmine	151-56-4	Chemserv	(a)	
2-Hydroxypropionitrile	78-97-7	Fluka	0.90	
Isobutanol	78-82-1	Aldrich	0.99	2108BK
Malononitrile	109-77-3	Aldrich	0.99	1204AL
Methacrylonitrile	126-98-7	Aldrich	-	
2-Methylaziridine	75-55-8	Fluka	0.98	226923
Methyl ethyl ketone	78-93-3	B&J 247	-	AJ635
Methyl hydrazine	60-34-4	Aldrich	0.98	JL092597
Methyl mercaptan	74-93-1	Matheson		
2-Picoline	109-06-8	Fluka	0.98	20043882
Propargyl alcohol	107-19-7	Aldrich	0.97	2821PL
β-Propiolactone	57-57-8	Aldrich	0.99	0347AM
Propionitrile	107-12-0	Aldrich	0.99	KE032097
n-Propylamine	107-10-8	Aldrich	0.98	MK4428
Pyridine	7291-22-7	Baker	0.99	644354
Tetranitromethane	509-14-8	Chem Serv	-	7968B
Thiophenol	108-98-5	Aldrich	0.97	120907
Trichloromethanethiol	594-42-3	(b)		

(a) Ethyleneimine was polymerized when recieved and was therefore not used.
(b) The CAS number given by EPA is for perchloromethylmercaptan CCl_3SCl which is the precursor for trichloromethanethiol.

TABLE 2. TEMPERATURES USED FOR TRAP TESTING

Analyte	Trap Temperatures, °C, Used for Testing Given Trap Material		
	Tenax	Novel Material No.1 DADM/PMDA	Novel Material No. 2 DADS/PMDA
Acrolein	20.6	44	70
	25.1	66	72
	24.9	92	91
	30.1		121
	30.0		
Acetonitrile	20.8	44	91
	24.8	66	100
	25.0	92	123
	29.9	120	150
	30.0		

TABLE 3. GC RETENTION DATA AND CHROMATOGRAPHY CHARACTERISTICS FOR ANALYTES USING THE SUPELCOWAX AND VOCOL COLUMNS

Compound	Retention Time, min, Using Given Column(a)		Comments on Chromatography Characteristics of Given Column(b)	
	Supelcowax-10	VOCOL	Supelcowax-10	VOCOL
Methyl mercaptan	1.17	4.29	Good	Good
n-Propylamine	1.60	5.51	Substantial tailing	Substantial tailing
Methyl ethyl ketone	1.81	6.93	Good	Good
1,1-Dimethylhydrazine	1.68	5.84*	Acceptable only from injection of headspace above neat analyte; aqueous standards give RT 5.33 min; RT variable using methanol	Unacceptable from injection of headspace above neat analyte; probable decomposition in aqueous standard.
Acrolein	2.03	4.99	Good	Good
Methylacrylonitrile	3.34	7.28	Good	Good
Acetonitrile	3.36	5.38	Good	Good
Acrylonitrile	3.50	5.80	Good	Good; slight tailing.
Propionitrile	4.20	7.11	Good	Good
1,4-Dioxane	4.58	9.77	Good	Good; slight fronting at 1000 ng injection.
2-Methylaziridine	4.23	6.37	Good	Probably unacceptable; nice peak on top of broad, pre- and post-eluting foot.
Isobutanol	5.31	7.30	Good	Acceptable; slight fronting; unusual tailing, possibly due to water injection solvent.

TABLE 3. (Continued)

Compound	Retention Time, min(a)		Comments on Chromatography Characteristics of Given Column(b)	
	Supelcowax-10	VOCOL	Supelcowax-10	VOCOL
Pyridine	6.70	10.99	Good	Good
Methylhydrazine	4.22	ND(c)	Possibly acceptable only in methanol and pentane for which there is substantial tailing; decomposition in water	No peaks attributable to to analyte from headspace or aqueous injection.
2-Picoline	7.38	12.65	Good	Good
2-Butanone peroxide	ND	ND	No peak attributable to analyte for any injection method.	No peak attributable to analyte for any injection method.
Bromoacetone	7.50	11.86	Acceptable with headspace injection, but required injector temperature reduction to 100 C; not detected with aqueous standards.	Acceptable; slight tailing.
Propargyl alcohol	9.96	6.36	Good	Unacceptable, severe fronting at 1000 ng injection (aqueous).
2-Chloroethanol	10.36	8.71	Good	Unacceptable, very badly fronting peak for aqueous injection.

TABLE 3. (Continued)

Compound	Retention Time, min(a)		Comments on Chromatography Characteristics of Given Column(b)	
	Supelcowax-10	VOCOL	Supelcowax-10	VOCOL
Chloral hydrate	10.35	9.78	Probably unacceptable; very broad peak with all injection solvents; possible on-column decomposition.	Acceptable with pentane only; peak may be due to anhydride with hydrate at 10.9 min; aqueous injection extremely broad, misshapen peak at 10.8 min; data are indicative of hydrate/ anhydride equilibrium present during chromatography.
N-2-Hydroxethylaziridine	11.01	12.53	Probably unacceptable, substantial tailing for aqueous injection.	Acceptable; slight fronting; 7% impurity at 11.12 min.
β-Propiolactone	11.50	11.92	Unacceptable, solvolyzed in both H_2O and methanol injection solvent.	Nice peak for headspace above neat analyte; obvious decomposition in aqueous sample.
Thiophenol	12.95	16.40	Acceptable; may be sensitive to injection decomposition	Good
3-Chloropropionitrile	13.65	13.60	Good; slight amount of on-column decomposition	Good
2-Hydroxy-2-methyl-propionitrile	ND	12.3	Substantial injection and on-column decomposition in water, methanol, and pentane.	Can be seen by injection of neat material only; 100% decomposition using aqueous injection.

TABLE 3. (Continued)

Compound	Retention Time, min(a)		Comments on Chromatography Characteristics of Given Column(b)	
	Supelcowax-10	VOCOL	Supelcowax-10	VOCOL
1,3-Dichloro-2-propanol	15.79	14.90	Good	Acceptable; somewhat fronted using 1000 ng aqueous injection
2-Hydroxypropionitrile	17.50	12.3	Unacceptable; clear evidence of on-column degradation	Unacceptable; significant decomposition to two early eluting materials at 3.7 and 3.9 min
Acrylamide	1840	14.98	Good	Unacceptable; distinctly fronted using 1000 ng aqueous injection; fronting impurity at 5.2 min
Malononitrile	20.07	14.49	Good	Unacceptable; nice peak on top of a broad pre- and post-eluting foot
Tetranitromethane	20.79	11.11	Peak found for neat injection only	No peak for aqueous injection; RT obtained from neat analyte injection (500 ug) and fresh pentane standard only

(a) Using the following GC conditions for both columns: carrier, helium at 10 mL/min flow controlled; oven program, 40 C for 2 min, then 8 C/min to 225 C.
(b) Good: GC peak was narrow and symmetrically shaped. Acceptable: GC peak shape was less than perfect with regard to width and degree of tailing but was definitely considered adequate for the generation of good data. Unacceptable: excessive peak width, tailing, fronting, apparent decomposition or other evidence of inadequate GC performance indicates the analyte could not be determined using that GC system.
(c) Not detected.

TABLE 4. SUMMARY OF GC SEPARATION EFFECTIVENESS IN TERMS OF k' VALUES

k' Range(a)	Number of Analytes in Given k' Range Using Given Column(a) Supelcowax-10	VOCOL
0-1	1	1
1-2	2	9
2-3	2	3
3-4	0	7
4-5	3	4
5-6	0	4
6-7	4	0
7-10	1	0
10-15	3	0
15-20	5	0
20-25	2	0
25-30	3	0
30-35	2	0
ND(b)	3	3
TOTAL	31	31

(a) The column void times, i.e., RT for k'= 0.0, were 0.60 and 2.40 min for Supelcowax-10 and VOCOL, respectively.
(b) Not Detected.

TABLE 5. RECOVERY RESULTS FOR HYDROLYTIC STABILITY TESTING

Analyte	Replicate 1 Peak Area Found for The Given Reaction Time, min. 0.0	15	Percent Recovery[a]	Replicate 2 Peak Area Found for The Given Reaction Time, min. 0.0	15	Percent Recovery[a]	Mean ± DM[b]
Acrolein	420	310	72	340	240	70	71 ± 1.4
Acrylamide	270	270	100	290	270	96	98 ± 2.0
Acrylonitrile	490	420	865	305	009	49	0 ± 4
N-2-Hydroxethylaziridine	ND[c]	ND	--	ND	ND	--	
Bromoacetone	140	58	42	150	12	8	25 ± 17[d]
3-Chloropropionitrile	200	130	66	200	120	61	63 ± 3
1,1-Dimethylhydrazine	41	67	170	46	31	67	120 ± 50[e]
Methylaziridine	ND	ND	--	ND	ND	--	(f)
Methylhydrazine	ND	ND	--	ND	ND	--	
Methyl mercaptan	150	150	100	210	180	87	94 ± 7
Propargyl alcohol	670	450	68	570	350	62	65 ± 4
Tetranitromethane	ND	ND	--	ND	ND	--	
Thiophenol	ND	ND	--	ND	ND	--	(f)

(a) Using the 0.0 min. result as a 100 percent recovery standard.
(b) DM = deviation from the mean for the two replicates.
(c) ND = Not detected.
(d) Chromatograms show evidence for decomposition product(s) produced during and possibly before injection as well as decomposition on the GC column.
(e) The quantified peak is probably an artifact or a decomposition product; see discussion in text.
(f) Chromatograms indicate only decomposition products, formed prior to and/or during injection, were eluted.

TABLE 6. RECOVERY RESULTS FOR H-PTD ANALYTE SCREENING

Analyte	Septum Injection[a] 100% Recovery Standard Peak Area			Purged Sample[a] Peak Area			Purged Sample[a] Percent Recovery[b]			
	Rep 1	Rep 2	Mean	Rep 1	Rep 2	Rep 3	Rep 1	Rep 2	Rep 3	Mean
Set 1										
1. Methyl mercaptan	1270	1048	1109	55	--[d]	--	5	0	0	<5
2. Methacrylonitrile	5492	5747	5619	2371	2314	2033	42	41	36	40
3. Propionitrile	5889	6026	5957	1834	1740	1534	31	29	26	29
4. Propargyl alcohol	7569	7542	7556	--	--	--	0	0	0	0
5. Thiophenol	--	--	--	--	--	--	0	0	0	0
6. Acrylamide	3131	1080	(c)	487	144	62	(c)	(c)	(c)	5 to 15
7. Malononitrile	17029	6225	(c)	4394	1048	405	(c)	(c)	(c)	5 to 25
Set 2										
8. Methyl ethyl ketone	4957	4707	4832	1500	1611	1641	31	33	34	33
9. Acrolein	6558	6330	6444	2045	2157	2468	32	33	38	34
10. Acetonitrile	4089	4074	4082	377	486	742	9	12	18	13
11. 1,4-Dioxane	3869	3910	3890	42	37	161	1	1	4	2
12. Isobutanol	7345	7218	7282	296	336	1178	4	5	16	8
13. Bromoacetone	3288	305	(c)	--	--	--	0	0	0	0
14. 2-Chloroethanol	2506	2550	2528	--	--	--	0	0	0	0
15. 3-Chloropropionitrile	4350	1033	(c)	--	--	--	0	0	0	0
16. 1,3-Dichloro-2-propanol	1888	1751	1820	11	6	3	0.6	0.4	0.2	0.4[e]
Set 3										
17. n-Propylamine	22	21	22	--	--	--	0	0	0	0
18. Acrylonitrile	3251	3604	3428	1108	1109	1473	32	32	43	36
19. 2-Methylaziridine	58	62	60	--	--	1	0	0	3	1[d]
20. Pyridine	7881	9188	8536	--	--	--	0	0	0	0
21. 2-Picoline	8803	9191	8997	--	--	--	0	0	0	0
22. N-2-Hydroxethyl-aziridine	358	495	426	9	8	5	2	2	1	2[e]

(a)250 ng each analyte injected or spiked into 5.0 mL of purged water.
(b)Versus the average response for the septum injected 100% recovery standards.
(c)Apparent decomposition in aqueous calibration standard over time and in the heated purge vessel.
(d)A dash indicates the analyte was not detected.
(e)PTD recovery is so low that peak identities are not confidently known.

TABLE 7. CONCENTRATIONS AND IONIC STRENGTHS OF SALTS USED FOR H-PTD RECOVERY ENHANCEMENT

Salt	Amount Used, g[a]	Weight Percent[a]	Approximate Molarity	Ionic Strength[b]
NaCl	1.5	23	4.7	5.1
Na_2SO_4	1.5	23	2.0	6.3
$MgCl_2$	2.8	36	5.5	17.6
$MgSO_4$	2.7	35	4.2	18.0

(a) Amount used per 5-mL aqueous sample

(b) Ionic strength = 1/2 $CiZi^2$ where Ci is the concentration, in molality, of the ith ion of the salt and Zi is the charge on that ion.

TABLE 8. SUMMARY OF H-PTD RECOVERY ENHANCEMENT BY SALT ADDITION

	Percent Recovery and Precisions(a) for the Given Experimental Conditions														
	No Salt											NaCl(b)			
	Trial 1	Trial 2		Trial 3		MgSO4(b)		MgCl2(b)		Na2SO4(b)		Trial 1		Trial 2	
Analyte	% Rec(d)	Mean % Rec	% RDM(c)	Mean % Rec	% RSD(e)	Mean % Rec	% RSD(b)	Mean % Rec	% RSD(f)	Mean % Rec	% RDM(c)	Mean % Rec	% RDM(c)	Mean % Rec	% RDM(c)
Acrolein	78	99	2	75	5	-		103	3	74	11	77	6	96	0.2
Methyl ethyl ketone	65	46	7	39	34	-		108	4	96	3	117	39	110	4
Acrylonitrile	79	151(g)	1	124(g)	4	101	41	100	2	100	24	115(g)	6	103	0.3
Acetonitrile	53	69	8	55	7	81	32	88	5	79	3	63	9	75	0.6
Propionitrile	76	98	2	74	4	89	48	107	1	90	2	86	9	102	0.2
1,4-Dioxane	21	21	12	22	10	46	38	47	12	56	11	32	27	38	5
Isobutanol	87	96	1	67	5	73	51	97	1	85	13	83	14	102	5
2-Chloroethanol	-(h)	-		-		-		-		-		-		-	
3-Chloropropionitrile	-	-		-		-		(i)		-		-		(i)	
1,3-Dichloro-2-propanol		-	-		-		-		3.5	55	-		-		-
Cyclohexanone, IS		37	11	29	32	(i)		54	17	(i)		70		48	

(a)Versus septum injection of the spiking standard as a 100% recovery standard performed in 2 or 3 replicates as per H-PTD replication.
(b)See Table 7 for salt concentrations used.
(c)Percent RDM, percent relative deviation from the mean (2 replicates).
(d)Only one replicate.
(e)Percent RSD, percent relative standard deviation, 4 replicates.
(f)Percent RSD, percent relative standard deviation, 3 replicates.
(g)Interference due to co-elution of a decomposition product of 3-chloropropionitrile.
(h)A dash indicates the analyte was not detected.
(i)Analyte was omitted from the analyte set.

TABLE 9. DEPENDENCE OF H-PTD RECOVERY ON PURGE TEMPERATURE

Analyte	Percent Recovery(a) at the Given Temperature								
	22 C(b)		40 C		60 C		85 C		99 C
	Mean ± DM(c)	Versus 99 C	Mean ± DM(c)	Versus 99 C	Mean ± SD(d)	Versus 99 C	Mean ± DM(c)	Versus 99 C	Mean ± DM(c)
Acrolein	22 ± 7	24	40.9 ± 1.1	45	53 ± 4	58	73.1 ± 0.8	80	91.3 ± 0.2
Methyl ethyl ketone	11 ± 2	15	23.3 ± 0.8	32	50 ± 6	68	70.3 ± 0.6	97	72.5 ± 0.3
Methacrylonitrile	(b)		48.3 ± 0.2	70	60 ± 6	86	68.4 ± 0.9	99	69.2 ± 0.5
Acrylonitrile	18 ± 3	22	40.5 ± 0.8	50	62 ± 6	76	81.0 ± 0.1	99	81.8 ± 0.4
Acetonitrile	6.8 ± 1.2	9	14.6 ± 0.9	19	28 ± 2	36	58.4 ± 1.2	75	78.4 ± 1.4
Propionitrile	7.2 ± 1.5	9	16.6 ± 1.1	22	35 ± 3	45	68.2 ± 0.9	89	76.6 ± 0.6
1,4-Dioxane	0.0	0.0	2.7 ± 1.2	8	8.2 ± 0.8	25	21.1 ± 0.5	64	33 ± 8
Isobutanol	2.9 ± 0.4	3	6.0 ± 0.7	9	21.2 ± 1.4	31	57.7 ± 1.0	84	68.5 ± 2.3
Cyclohexanone	1.7 ± 0.9	4	2.6 ± 0.2	6	9.1 ± 0.8	20	31.9 ± 0.8	69	46 ± 7

(a) Versus injections of an identical spiking aliquot through the GC injector septum.
(b) The room temperature data were generated in an experimental trial different from that of the other four temperatures, and the analyte methacrylonitrile was not included in that work.
(c) DM = Deviation from the mean for two replicates.
(d) SD = Standard deviation for three replicates.

TABLE 10. BREAKTHROUGH CHARACTERISTICS OF ACROLEIN AND ACETONITRILE ON NOVEL TRAPPING MATERIALS

Trap Type(a) Analyte	Temperatures Tested, °C	25°C Breakthrough Volume(b), L	Specific Breakthrough Volume, L/gm at 25°C
DADS/PMDA(a)			
Acrolein	70, 72, 91, 121	27	76
Acetonitrile	91, 100, 123, 150	36	99
DADM/PMDA(a)			
Acrolein	46, 66, 92	3.3	14
Acetonitrile	46, 66, 92, 120	10	44

(a) See text for chemical description of trapping material. The amounts of trapping materials used were: DADS/PMDA, 0.36 gm; DADM/PMDA, 0.23 gm.
(b) From extrapolation of the plot of log (retention time) versus 1/T(°K) to 25°C

TABLE 11. BREAKTHROUGH CHARACTERISTICS OF ACROLEIN AND ACETONITRILE ON TENAX

Analyte	Temp, °C		Elution Volume, mL	
	Tested	Extrapolated[a]	Onset[b]	Peak Top[c]
Acetonitrile	29.9		360	412
	30.0		348	400
	25.0		504	592
	24.8		512	584
	20.8		720	852
		18.0	860[a]	996[a]
		15.0	1,070[a]	1,240[a]
Acrolein	30.0		352	400
	30.1		352	396
	24.9		552	648
	25.1		504	584
	20.6		808	912
		18.0	988(a)	1,130(a)
		15.0	1,250(a)	1,430(a)

(a) Computed from an extrapolation of the other data for which a plot of log elution volume vs. 1/T(°K) is a straight line.
(b) Less than 0.1% of the analyte had eluted at the onset volume.
(c) Peak asymmetry factors at 10% peak height (front:back):acetonitrile, 1:3.7 and acrolein, 1:7.2.

TABLE 12. ANALYTE CALIBRATION RESPONSE FACTORS FOR GC-MS QUANTIFICATION

Analyte	Quantification ion,(a) m/e	Analyte Level (e) of Lowest Calibration Standard mg/L	Response Factor and Percent Fit(b) for the Given Calibration Range: 100- Fold Range Average Response Factor(c)	100- Fold Range Percent Fit(b)	30-Fold Range Average Response Factor(c)	30-Fold Range Percent Fit(b)
Acrolein	56	20	0.098	8	0.102	4
Methyl ethyl ketone	43	1.5	(d)	(d)	(d)	(d)
Methacrylonitrile	41	5	0.24	11	0.22	7
Acrylonitrile	53	5	0.28	23	0.25	22
Acetonitrile	41	10	0.18	14	0.17	9
Propionitrile	54	5	0.20	13	0.19	8
1,4-Dioxane	88	15	0.09	16	0.09	16
Isobutanol	43	15	0.24	15	0.22	7

(a) In all cases, the quantification ion was the base peak over the mass range scanned.
(b) The percent fit value is provided by the data system software as an average measure of how near the calibration points fall to the best straight line calibration model.
(c) Relative to the molecular ion, m/e 84, of the quantification internal standard, benzene-D_6
(d) Due to the background level of methyl ethyl ketone in the reagent water used, only the three highest level standards were useable, i.e., a 10-fold range, for which the response factor was 0.73 and the percent fit 17.
(e) The other four calibration levels were 3-, 10-, 30-, and 100- fold higher than that for the lowest calibration standards.

TABLE 13. H-PTD GC/MS ANALYSIS METHOD PERFORMANCE FOR THE LOW SPIKING LEVEL: METHOD DETECTION LIMITS FOR ANALYTES

	Spiking Level ug/L	Level Found, ug/L										Percent Recovery		Method Detection Limit(b), MDL, ug/L
		Rep 1	Rep 2	Rep 3	Rep 4	Rep 5	Rep 6	Rep 7	Rep 8	Rep 9	Rep 10	Mean	% RSD(a)	
Analytes														
Acrolein	30	26.8	26.1	28.5	27.9	22.7	28.8	23.8	28.3	23.7	25.9	88	8	6
Methyl ethyl ketone	6	14.9	13.3	15.7	14.0	15.2	14.3	13.1	13.6	13.2	12.8	233(c)	7	-
Methacrylonitrile	20	23.0	16.7	20.8	19.1	19.2	22.9	20.6	28.5	18.0	19.2	99	10	6
Acrylonitrile	20	16.5	16.0	16.9	17.4	15.2	17.5	16.1	17.1	17.6	16.5	83	5	2.3(d)
Acetonitrile	40	34.2	28.2	36.0	32.8	28.8	37.3	35.8	36.0	36.4	35.3	85	9	9
Propionitrile	20	19.2	17.0	17.3	19.8	18.4	18.5	17.4	18.5	18.7	20.0	92	5	3(d)
1,4-Dioxane	60	53.6	53.5	60.8	56.6	50.0	52.3	59.1	51.2	60.4	51.8	92	7	4(d)
Isobutanol	60	48.8	48.3	51.3	53.2	45.7	52.8	47.0	49.9	50.1	47.6	82	5	7(d)
Surrogate Standards														
Methyl ethyl ketone-D_5	60	61.8	57.5	63.3	63.5	61.3	62.2	63.2	65.3	60.1	65.1	104	4	-
Acetonitrile-D_3	400	380	349	395	396	372	389	394	385	378	399	95	5	-
1,4-Dioxane-D_8	300	300	280	316	318	292	306	304	304	306	304	101	4	-
p-Bromofluorobenzene	50	46.8	46.0	47.1	48.9	46.9	48.2	49.1	49.3	48.2	49.0	95.9	2.4	-

(a) % RSD = Percent Relative Standard Deviation.
(b) Where MDL = SD x $t_{(n-1,0.001)}$. In this case where n = 10, $t_{(9,0.01)}$ = 2.821.
(c) Uncorrected for a relatively high background level of this analyte in the reagent water used as the sample matrix.
(d) Spiking level too high for computed MDL to be considered the true MDL

TABLE 14. H-PTD GC/MS ANALYSIS METHOD PERFORMANCE FOR THE HIGH SPIKING LEVEL

	Spiking Level ug/L	Level Found, ug/L										Percent Recovery	
		Rep 1	Rep 2	Rep 3	Rep 4	Rep 5	Rep 6	Rep 7	Rep 8	Rep 9	Rep 10	Mean	% RSD(a)
Analytes													
Acrolein	300	283	319	303	324	304	292	297	311	280	284	100	5
Methyl ethyl ketone	60	48.1	50.9	51.6	53.3	52.3	50.9	54.8	50.5	49.7	51.9	86(b)	4
Methacrylonitrile	200	172	189	175	188	190	177	190	185	168	166	90	5
Acrylonitrile	200	124	142	130	136	133	127	142	138	125	126	66	5
Acetonitrile	400	334	350	336	363	330	328	355	369	322	323	85	5
Propionitrile	200	170	182	168	181	176	165	187	182	162	161	87	5
1,4-Dioxane	600	496	552	616	609	520	543	565	621	505	483	92	9
Isobutanol	600	458	519	518	525	522	493	541	557	478	488	85	6
Surrogate Standards													
Methyl ethyl ketone-D_5	60	61.9	65.7	62.7	67.8	62.3	62.6	68.6	66.7	60.8	60.8	107	5
Acetonitrile-D_3	400	390	419	412	429	389	405	422	434	379	383	102	5
1,4-Dioxane-D_8	300	298	330	321	340	298	311	330	341	300	291	105	6
p-Bromofluorobenzene	50	51.0	51.3	47.9	50.2	49.2	49.6	52.6	51.8	48.6	49.1	100	3

(a) % RSD = Percent Relative Stadnard Deviation.
(b) Uncorrect for the background level of this analyte which may be as high as 6 to 10 ug/L.

TABLE 15. COMPARISON OF CHROMATOGRAPHIC PEAK WIDTHS FOR H-PTD PROCESSED AND SPLIT SEPTUM INJECTED SAMPLES

Analyte	Peak Width[a] at Half Height, sec, for the Given Sampling Condition			
	H-PTD(b)		Split Septum Injection(c)	
	Rep 1	Rep 2	Rep 1	Rep 2
Acrolein	6	7	3	2
Methyl ethyl ketone	10	9	4	4
Methacrylonitrile	12	12	6	6
Acrylonitrile	9	9	5	6
Acetonitrile	8	8	5	5
Propionitrile	10	9	5	6
1,4-Dioxane	20	20	7	7
Isobutanol	13	14	15	16

(a) For the extracted ion current profile of the quantification ion.
(b) The sample was the next to highest level H-PTD calibration standard.
(c) The injector split ratio was 10:1 and the 2.0 uL injected sample contained 10 ug/uL of all analytes in water. The internal and surrogate standards were excluded.

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