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Project Summary

Heated Purge and Trap Method Development and Testing

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A heated purge-trap-desorb (HPTD) analytical method for eight polar, water soluble, volatile organic analytes was developed and tested. This method uses a standard 5-mL purge vessel with an integral, low volume, water-cooled condenser, and a Tenax trap. A commercially available PTD apparatus can be used, but a water bath (90°C) is required to heat the sample as it is being purged. A 5-mL sample aliquot heated to 90°C was purged with helium gas (flow of 40 mL/min); purged analytes were trapped on a Tenax trap and desorbed through a small volume condenser into a gas chromatograph (GC) equipped with a wide bore (0.53 mm), fused silica capillary column coated with a polar stationary phase (Supelcowax-10). As analytes eluted from the GC, they were detected and measured with a flame ionization detector during method development and with a mass spectrometer during method testing.

Of 33 compounds tested, 8 were amenable to determination with HPTD procedures. Those 8 compounds were acetonitrile, acrolein, acrylonitrile, 2-butanone, 1,4-dioxane, isobutanol, methylacrylonitrile, and propionitrile. Analyte recoveries ranged from about 80% for acrylonitrile and methylacrylonitrile to about 30% for 1,4-dioxane. With the chromatographic conditions used, calculated method detection limits were 2-9 μg/L. Of 25 compounds for which the method was not appropriate, 9 were nitrogen bases, 6 were hydrolytically unstable, 2 were mercaptans, and 8 were too involatile or too water soluble to be purged from water. One compound was not available for testing.

This Project Summary was developed by EPA's Environmental Monitoring and Support Laboratory, Cincinnati, OH, to announce key findings of the research project that is fully documented in a separate report of the same title (see Project Report ordering information at back).

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. Environmental Protection Agency (USEPA) has proposed amendment of RCRA Appendix VIII by addition of over 100 other organic compounds. Some Appendix VIII and Michigan list compounds are not amenable to standardized USEPA methods involving either liquid/liquid solvent extraction or room temperature purge, trap, desorb (PTD) procedures.

The PTD procedures described in several methods in "Test Methods for Evaluating Solid Waste" (SW-846) were developed for relatively water insoluble, volatile compounds. Method 5030 describes a general PTD extraction/concentration procedure to introduce sample components into a gas chromatograph (GC) for detection and measurement with procedures described in other methods, such as 8010, 8020, 8030, and 8240. Methods 8010, 8020, and 8030 are designed for specific classes of compounds; 8010 for purgeable halogenated compounds (electrolytic conductivity detector), 8020 for purgeable aromatic compounds (photoionization detector), and 8030 for acrolein, acrylonitrile, and acetonitrile (flame ionization detector). Method 8240 uses a electron ionization mass spectrometer (MS) detector, which is applicable to many classes of compounds.

Some Appendix VIII and Michigan list compounds are so volatile that they are lost during sample preparation procedures in methods using liquid/liquid extraction followed by extract concentration or are too water soluble to be removed efficiently by ambient temperature PTD procedures. Although some of these coumpounds have been successfully determined by injection of a water sample aliquot directly into a GC, this procedure provides much higher detection limits (DLs) than are achievable with PTD procedures for compounds that are effectively purged at room temperature.

The goal of this project was to test the feasibility of determining some or all of the 33 selected compounds by purging samples at temeratures higher than ambient laboratory temperature and, for those amenable to PTD, to develop standardized procedures for their determinations. Because determination of as many compounds as possible in one sample aliquot was desired, a fused silical capillary column was used instead of the packed columns currently used in SW-846 methods, because the former provide increased analyte separation.

The 33 compounds included in this study were:

Nitriles

Acetonitrile
Acrylonitrile
Propionitrile
Malononitrile
3-Chloropropionitrile
Methacrylonitrile
2-Hydroxypropionitrile
2-Hydroxy-2-methylpropionitrile

Alcohols

Isobutanol
Propargyl alcohol
Chloral hydrate
2-Chloroethanol
1,3-Dichloro-2-propanol

Aldehyde and Ketones

Acrolein
2-Butanone
Bromoacetone

Thiol

Trichloromethanethiol
Thiophenol
Methyl mercaptan

Nirtogen Bases

Pyridine
2-Picoline
Methylhydrazine
1,1-Dimethylhydrazine
1,2-Dimethylhydrazine
n-Propylamine
Aziridine
Methylaziridine
N-(2-Hydroxyethyl)aziridine

Miscellaneous

Acreylamide
1,4-Dioxane
-Propiolactone
Tetranitromethane
2-Butanone peroxide

Procedures

Method Development

Experimental parameters expected to affect analyte performance were sequentially examined. Two fused silica capillary columns were used. One was a 30 m X 0.53 mm i.d. column coated with a 1.0-μm film of polar stationary phase, Supelcowax-10, and the other was a 60 m X 0.75 mm i.d. column coated with a 1.5-μm film of relatively nonpolar siloxane stationary phase, Vocol. Both columns (obtained from Supelco, Bellefonte, Pennsylvania) were tested by directly injecting an aliquot of a water solution containing all candidate analytes, and the column judged to provide better overall performance was used in all subsequent work. Analytes were detected and measured with a flame ionization detector (FID).

Each day that aliquots of analyte fortified reagent water were analyzed, two or more aliquots of a calibration solution were also directly injected into the GC. The injected quantity of each analyte was the same as the quantity used to fortify 5-mL samples that were purged. Typically, 250 ng of each analyte was injected: this corresponded to an analyte concentration of 50 μg/L in a 5-mL sample. Results of duplicate or triplicate analyses of 5-mL aliquots of reagent water containing analytes were used to calculate absolute recovery of each analyte. (Recovery was 100 times the GC peak area for a purged analyte divided by the GC peak area measured when an equal quantity of that analyte was injected directly into the GC.) The effect of purging temperature on analyte recovery was tested at five temperatures (22, 40, 60, 85, and 99°C).

Analytes were screened for hydrolytic stability; those not detected by direct injection of an aliquot of a pH 6.8 buffered (0.01 M phosphate in reagent water) standard solution held at 85°C for 15 minutes were not included in subsequent work. Analytes that were hydrolytically stable were further tested using purging conditions similar to those described in Method 8030 for acetonitrile, acrolein, and acrylonitrile. In most cases, analytes not recovered at concentrations >1000 μg/L were eliminated from further testing.

Also tested was the possible enhancement of analyte recovery by shifting the aqueous/vapor phase equilibrium constant toward the vapor phase by adding salt to the aqueous solvent. Salts were selected on the basis of their solubility, commercial availability, and high ionic strength. Chloride and sulfate salts of sodium and magnesium were used at concentrations that provided 80% saturation at 85°C.

Three alternatives were tested to control water vapor that exits the heated aqueous sample along with analytes. A condenser was attached to the purge vessel outlet via a 0.25-in. Swagelok union with Teflon ferrules. One condenser had a 0.25 in. o.d. X 8 cm cold zone that was packed with 3-mm glass helices. Another condenser had an 8 mm o.d. X 10 cm cold zone with the temperature of the condenser cooling water controlled at 20°C. The condenser was immersed in a heated water bath up to the beginning of the condenser cold zone. Each sample was purged for 15 min at 40 mL/min (total volume 0.6 L) was used with the condenser water maintained at 20°C and the trap at 23-25°C during the purge step. Two non-condenser alternatives for control of the water evaporated from the purge vessel were examined. One approach used a molecular sieve (Linde zeolite type 3A) between the purge vessel and the trap. In the other approach, two high-retention trapping materials, Carbosieve and Carbotrap (Supelco), were used when the trap temperature was held above the dew point of the purge gas. This temperature was 90°C when purge gas was not diluted with a post-purge make-up gas and 70°C with 1:1 purge gas/make-up gas. A combination trap consisting of 4:1 Carbopack: Carbosieve (with the Carbotrap at the trap inlet) was also tested at 90°C trapping temperature with no purge carrier dilution.

Method Performance

The final chromatographic and HPTD experimental conditions (90°C sample purge temperature) resulting from the method development activities were tested using an MS detector. Samples were purged in a 5-mL purge vessel contained in a commercially available apparatus (LSC-2, Teckmar Co., Cincinnati, Ohio). After passing through a 10-cm X 8-mm o.d. glass Vigreux condenser, purged analytes were collected in a Tenax trap. Sample temperature was maintained at 90°C while helium purge gas flowed at 40 mL/min and the trap

temperature was maintained below 25°C. Sorbed analytes were desorbed from the trap at 180°C for 4 min after a 50°C preheat. After desorption, the trap was baked at 210° for 10 min to prepare it for the next sample. Desorbed analytes were introduced into a GC equipped with a 30-m × 0.53-mm i.d. fused silica capillary column coated with a 1.0-μm film of Supelcowax-10 (Supelco) with helium carrier gas flow of 10 mL/min. The oven temperature program was 40°C for 4 min (during trap desorption), then 8°C/min to 130°C. The GC was interfaced to an MS through a glass-jet separator. The quadrupole MS was scanned from m/z 35 to 250 at 1 scan/sec, and the MS was calibrated according to the standard USEPA criteria for bromofluorobenzene. The MS detector response to each analyte was determined relative to 50 μg/L of an internal standard, benzene-d_6, which was added to each sample just before purging.

The GC/MS system was calibrated with solutions containing the eight analytes over a 100-fold concentration range beginning near the estimated detection limit (DL) of each compound. Data were obtained for ten replicates of a water sample fortified with each analyte at a concentration thought to be low enough to allow computation of its method detection limit (MDL) according to a standard Agency procedure (Appendix B to Part 136, 49 FR 26189). An MDL is defined as the lowest concentration at which an analyte can be measured and reported with 99% confidence that the analyte concentration is greater than zero. The MDL is the product of Student's *t* factor and the standard deviation of seven or more replicate measurements at a concentration near but greater than the estimated analyte DL. Method performance data were also obtained for ten additional replicates of a water sample fortified with each analyte at a concentration 10 times greater than that used to calculate MDLs.

Results and Discussion

GC Testing

Only megabore (≥0.53 mm o.d.) fused silica columns were used in this study, because a wide bore column is required to accommodate the 10 mL/min desorption flow rate, unless prefocusing sorptive or cryogenic traps are used. Two types of GC column stationary phases were tested; one was a highly polar phase (Supelcowax-10) and the other was a relatively nonpolar siloxane phase (Vocol) that is often used for Method 8240 determinations. Because the polar phase (Supelcowax-10) provided significantly greater analyte selectivity and substantially reduced GC peak tailing of polar analytes, it was used for all subsequent work. Unfortunately, many polar analytes (especially alcohols) for which the Supelcowax-10 provided the most dramatic chromatographic improvement compared to the Vocol column, were not sufficiently recovered by HPTD. Therefore, the choice of GC column was principally driven by candidate analytes that were later shown to be inappropriate for HPTD determinations. Furthermore, all candidate analytes that were appropriate for HPTD eluted before water on the Supelcowax-10 column, but the effect of this desorbed water was not apparent during method development activities.

Hydrolytic Instability Testing

Six candidate analytes were eliminated from further study because they were not sufficiently stable in reagent water buffered to pH 6.8 and held at 85°C. Those compounds were N-(2-hydroxyethyl)aziridine, methylaziridine, methylhydrazine, 1,1-dimethylhydrazine, tetranitromethane, and thiophenol. Although acrolein and 3-chloropropionitrile displayed some hydrolytic instability, they were retained for subsequent method development studies.

Effect of Salt on Analyte Recoveries

Analyte recovery with HPTD procedures should be enhanced through a shift in the aqueous phase-vapor phase equilibrium constant toward the vapor phase. This shift is produced by using high salt concentrations to lower the activity coefficient of the aqueous solvent. Initial testing showed that sodium and magnesium chlorides dissolved fairly rapidly with good reproducibility. The sulfate salts, however, were highly exothermic on dissolution, produced salt cakes in the purge vessel, and did not always completely dissolve. The high concentration of magnesium sulfate required to achieve 80% saturation produced a viscous liquid that apparently formed a liquid plug at the purge vessel outlet/condenser inlet.

The greatest enhancement of analyte recovery with salt addition was observed for the two most polar, water soluble analytes, 1,4-dioxane and acetonitrile. Dioxane recovery increased from 21% without salt to 56% with sodium sulfate, and acetonitrile recovery increased from 59% without salt to 88% with magnesium chloride. Although 2-chloroethanol was well recovered from traps when spiked directly onto them, it was not detected in any HPTD experiments.

Although the use of salt increased recoveries of all analytes that were not quantitatively recovered without salt, the advantages of using salt were judged to be less important than the disadvantages of using salt. Salt particles transported as an aerosol from the purge vessel can be deposited in the PTD apparatus and sorb or chemically degrade some analytes. Deposited salt can also block the transfer line; this results in a plugged and ruined column. Because of these difficulties, the use of salt with HPTD procedures was discontinued.

Effect of Purge Temperature on Analyte Recoveries

No optimal temperature between room temperature and 100°C was observed, because recoveries of all analytes increased uniformly with temperature. The three most volatile and least water soluble analytes (i.e., those with the highest recoveries at 22 and 40°C), 2-butanone, methacrylonitrile, and acrylonitrile, were recovered essentially quantitatively at ≥85°C. The least volatile and most water soluble analytes, 1,4-dioxane and acetonitrile, were not expected to be recovered quantitatively at any temperature using a 5-mL sample and a purge gas volume of 600 mL. On the basis of these results, 90°C was adopted as the purge temperature for the GC-MS method performance evaluation study. A 90°C purge temperature should allow use of a water bath in all but the most extreme altitudes and hypobaric climatic conditions.

Trap Breakthrough

Because methyl mercaptan was not retained in the trap when only 200 mL of purge gas was used, this compound was not appropriate for determination with HPTD procedures. At the trap temperature (25°C) proposed for GC-MS determinations, acetonitrile and acrolein began to breakthrough at about 510 and 525 mL, respectively. This was considered to be adequate for a 450-mL purge volume. With reasonable control of HPTD conditions, these two analytes should be trapped.

Control of Purged Water Vapor

The major difficulty for HPTD determinations is created by the large amount of water vapor that exits in the purge gas along with analytes from the heated sample purge vessel. For a typical 11-min purge at 90°C and purge gas flow of 40 mL/min, about 0.75 g of water vapor exit the purge vessel. Condensation of this relatively large amount of water in the PTD apparatus,

especially the trap, can cause extremely poor reproducibility, and can even prevent, measurement of analyte concentrations. Three main effects are observed: (1) analytes are sequestered in water droplets in the connecting lines and valve; (2) GC separation is degraded when water is introduced into the GC column; and (3) analytes are lost when dissolved in water exiting the trap during sample purging. Therefore, a major concern was to minimize the effect of water.

Three main approaches were investigated:

- A condenser was attached to the purge vessel outlet to return most water vapor to the purge vessel.
- A trap that could be used at an elevated temperature during purging was used with a post-purge make-up gas to reduce the purge carrier dew point and with the trap temperature maintained above the dew point to eliminate any possibility of condensation of water vapor from the purge carrier.
- A dessicant was placed between the purge vessel and the trap to adsorb water vapor from the heated purge carrier while allowing purged analytes to pass through.

Effect of Condenser Design

The packed condenser that was used for initial method development work retained essentially all of the water condensate. The purge gas percolated through the liquid water and equilibrated with a large volume of cold aqueous phase. Recovery of purged analytes was significantly reduced. Subsequent modifications in condenser design focused on minimizing the volume of cold condensate to reduce purged analyte recapture and determining the effect of the condenser cooling water temperature on analyte recovery. As expected, analyte recoveries increased with increasing temperature of the condenser cooling water and decreasing volume of cold condensate. In the improved condenser, which was used during later GC-MS testing, condenser cooling water temperature was maintained at 20°C to ensure that condensate would not form in the PTD apparatus.

A clean, dry condenser was required for each analysis, but thorough rinsing of the purge vessel in place did not eliminate analyte carryover, probably because some analytes remained in the small volume of cold water on the condenser surfaces. When the condenser was also rinsed, a relatively large amount of water was left behind and apparently recaptured analytes purged during the next sample analysis. The result was reduced analyte recovery, compared to that obtained with a dry condenser. The 10-cm long condenser used for the GC/MS experiments is probably somewhat longer than actually necessary, but no experiments have been performed to determine the optimum length.

Purged Water Control Options Not Involving A Condenser

Because three candidate analytes thought to be recoverable by HPTD were not recovered using a condenser, two other approaches to control the water vapor were investigated. All three of those compounds, propargyl alcohol, 2-chloroethanol, and acrylamide, had been recovered when placed directly onto traps before a normal PTD procedure. The lack of recovery of these compounds with a condenser was thought possibly to be caused by recapture of purged analyte in the small amount of cold condensate present in the condenser.

The two noncondenser approaches were using a molecular sieve to remove water and using trapping materials that could withstand temperatures above the dew point of the purge stream. With a molecular sieve, water vapor was removed between the purge vessel and the trap. Isotherms for water adsorption provided by the manufacturer were used to predict that 3.0 g of molecular sieve would adsorb all of the purged water at a sieve temperature of 100°C. The use of a near.stoichiometric quantity of molecular sieve was expected to minimize analyte adsorption onto the molecular sieve surface. With standard HPTD conditions, however, analyte throughput was totally unacceptable, with <1.0% throughput of 2-butanone, methacrylonitrile and acrylonitrile, and no throughput of the other 11 analytes tested.

The use of trap packing material that could be operated at higher temperatures was not successful. Carbotrap did not retain the most volatile analytes at the elevated trapping temperature. While Carbosieve apparently retained analytes at the elevated temperature, GC separation of early eluting analytes was unacceptable. When analytes were placed directly onto the combination (4:1 Carbopack/Carbosieve) trap, a normal HPTD sequence using reagent water produced severely split GC peaks for early eluting analytes (especially acrolein and 2-butanone) and broadened peaks for mid-elution range analytes.

Method Performance

Method performance was determined by GC/MS analysis of 10 replicate aliquots of reagent water fortified with each analyte at a concentration estimated to be near its DL and 10 replicates fortified at a concentration 10 times the estimated DL (Table 1). Relative standard deviation (RSD) was about 5% for the higher concentration and about 7% for the lower concentration. In the low concentration samples, mean measured concentration bias ranged from -18% to -1% for seven of the eight analytes. For 2-butanone, background concentrations of 6-10 μg/L prevented measurement of the fortified concentration of 6 μg/L. In the high concentration samples, mean analyte bias ranged from -34% to 0%. Without the acrylonitrile bias of -34%, mean analyte bias ranged from -15% to 0%.

Results from analyses of reagent water fortified with low concentrations of the eight compounds produced calculated MDLs of 2-9 μg/L for seven compounds. With low concentration data, an MDL could not be calculated for the eighth compound 2-butanone, because a high background concentration prevented accurate measurement of a fortified concentration of 6 μg/L. When data obtained from analyses of reagent water containing 2-butanone at a concentration of 60 μg/L were used, an MDL of 8.5 μg/L was calculated. Four of the seven MDLs calculated from low concentration data may not, however, be realistic because four compounds were fortified at concentrations that were >5 times the calculated MDLs. Additional data are required to assess MDLs for those compounds. Such data should be acquired with different GC conditions that produce sharper GC peaks. All method analytes eluted before desorbed water, which was in effect, the injection solvent. This water caused a reverse solvent effect for analytes eluting before the solvent, and peak shape and resolution were impaired.

Conclusions

Acceptable method performance was observed for the eight compounds that were amenable to removal from aqueous samples with HPTD procedures. Future efforts should be directed toward modifying Method 8240 to incorporate these eight additional analytes, because a separate method for only eight analytes is probably not cost effective. In addition, using a heated sample purge vessel and a condenser to trap purged water vapor may improve recovery of some Method 824

Table 1. *Method Performance Data*

Analytes/ Surrogate Stds.	High Concentration Fort. Conc. µg/L	High Concentration Mean Meas. Conc.[a] µg/L	High Concentration Std. Dev. µg/L	Low Concentration Fort. Conc. µg/L	Low Concentration Mean Meas. Conc.[a] µg/L	Low Concentration Std. Dev. µg/L	MDL µg/L
Acrolein	300	300	5	30	26	7	6
2-Butanone	60	52[c]	3	6	14[c]	16	-
Methacrylonitrile	200	180	5	20	20	10	6
Acrylonitrile	200	132	3	20	17	5	2[d]
Acetonitrile	400	340	4	40	34	8	9
Propionitrile	200	174	5	20	18	5	3[d]
1,4-Dioxane	600	552	9	60	55	7	4[d]
Isobutanol	600	510	5	60	49	4	7[d]
2-Butanone-d_5	60	64	5	60	62	4	-
Acetonitrile-d_3	400	408	5	400	380	4	-
1,4-Dioxane-d_8	300	315	6	300	303	4	-
p-Bromofluorobenzene	50	50	3	50	48	2	-

[a] Mean of 10 determiniations.

[b] Method detection limit, where MDL = Std. Dev. X t, where t = 2.821 for 10 measurements

[c] Uncorrected for the background concentration, which was 6-10 µg/L

[d] Fortified concentration was <5 time calculated MDL.

analytes (such as naphthalene, trichlorobenzenes, tetrachlorobenzenes, and hexachloropropene) while not adversely affecting recovery of more volatile sample components. Capillary columns other than the two used in this study should be evaluated to select a column providing better chromatographic characteristics.

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The complete report, entitled "Heated Purge and Trap Method Development and Testing," (Order No. PB 88-242 607/AS; Cost: $14.95, subject to change) will be available only from:
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