Concentration of Air Toxics from SUMMA® Canisters on a Solid Sorbent Trap

Application Note

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Introduction

Volatile organic air toxics analyses are routinely performed using gas chromatography/mass spectrometry (GC/MS.) With this technique the sample, taken from a SUMMA passivated canister must be concentrated in order to achieve the required detection limits. Historically, the analytes have concentrated on a glass bead packed, cryogenic cooled trap due to inertness and retentive characteristics.

Two major issues limit these traps. While glass beads are an effective mechanism for trapping volatile organic compounds (VOCs), they also concentrate interferences such as carbon dioxide, water, and inorganic gases. Without a means for removal, these interferences can affect data quality, especially for the early eluting VOCs. Additionally, cryogenic fluids are required to cool the trap. These cryogens, commonly liquid nitrogen, are expensive and can be cumbersome.

The focus of this work is to show an alternative to a glass bead packed, cryogenic trap. The experimentation is tailored to mimic Compendium Method TO-14. Representative calibration and chromatographic data will be shown to illustrate the effectiveness of this trap for air toxics analyses.

Experimental

The trapping of VOCs on solid sorbent materials has long been a mainstay of purge and trap gas chromatography. This technique purges an aqueous sample with an inert gas to strip the VOCs from the sample matrix. Once stripped from the matrix, the VOCs are collected on an ambient temperature trap. The VOCs are then desorbed to a GC or GC/MS with carrier gas for separation and detection.

Analogies can be drawn between purge & trap GC and the concentration of VOCs from SUMMA canisters. In air concentration and analysis, a volume of the gas sample is metered to a trap. Once on the trap, the trap is desorbed to the GC, as in the purge & trap analysis. With this in mind, sorbent materials commonly used in purge and trap systems make a logical starting point for evaluating their applicability to air concentration systems.

A survey was taken of commercially available sorbent materials currently in use for purge and trap systems. Initially, these traps were used to determine their feasibility in an air concentrator. After some initial testing, a trap was developed to concentrate the 41 VOCs from the TO-14 compound listing. The trap was tested initially on GC/FID and then for final analysis, a GC/MS was used. The selection of the trap material was based upon its ability to trap and desorb analytes, while eliminating the use of cryogens and minimizing the adsorption of carbon dioxide and water. Less emphasis was place upon using these traps as a mechanism of water removal, as successful operation of this instrumentation with its inherent moisture control system has been displayed for polar and non-polar analytes.[2]

Standards

The standards were diluted from a 2 ppmv TO-14 standard from Alphagasz (Morrisville, PA) with ultra-zero air. The resulting concentration of the standard was 20 ppbv for the FID work, and 40 ppbv for the GC/MS.

The 40 ppbv standard was prepared by adding 150 µL of water into an evacuated canister through a septum and nut screwed onto the top of the canister. This was allowed to equilibrate for 2 hours and the resulting relative humidity in the canister becomes 35% after 300 ml of the stock standard and dilution gas, to a pressure of 22 psig, is added. Once the standard has been prepared, it is allowed to equilibrate overnight.

As an additional part of the GC/MS study, the air matrix in the standard was modified to simulate a landfill gas sample, and also a highly humidified sample. Since landfills often have percent levels of carbon dioxide, a 40 ppbv canister was prepared 5.0% CO_2. This standard was prepared as the calibration standard, except that 300 mL of CO_2 was added. The wet sample was prepared by taking 150 µL of water and injecting it into a 6 liter canister, and pressurizing it to ambient pressure. The concentration was held at 40 ppbv, and thus required 120 mL of the stock TO-14 standard.

An internal standard was used for the GC/MS portion of the testing. This standard was prepared from a liquid mixture of equimolar amounts of four compounds.

The liquid mixture was made by adding:

      265 µL bromochloromethane
      420 µL 1,4-difluorobenzene
      420 µL d5-chlorobenzene
      450 µL 4-bromoflurobenzene

into a 2 mL amber, septum-topped vial. A secondary standard of this internal standard was made in a static dilution bottle (SDB.)

A 16.4 µL aliquot of the liquid soup was injected into a 2 liter SDB to make the secondary standard. The concentration of this standard was 500 ppmv. The SDB contained glass beads to assist vaporization of the liquid VOCs. The SDB was allowed to equilibrate for two hours before making a final dilution into a 6 liter canister.

The final dilution of the internal standard mixture was made by humidifying a canister to 35%, adding 1.5 mL of the SDB standard, and pressurizing the canister with ultra-zero air to a final pressure of 22 psig. The concentration of this internal standard is 50 ppbv. The spreadsheet used to determine the amounts of liquid in the soup, the concentrations of the SDB/canister, and the amount of dilution gas/water required is listed in Table 1.

Although the standard has a concentration of 50 ppbv, the calibration of the system is based upon a 500 ml sample. Since only 100 mL of the internal standard is injected with each sample, one has effectively performed a 5 to 1 dilution. This results in a concentration of 10 ppbv, as seen by the analytical system.

Concentrator

For this work a Tekmar 6000 concentrator was modified to accept a packed trap. Modification included removal of the glass bead packed cryogenic trap, and replacement of the heated line between the bottom of the trap/6 port rotary valve. The trap was not actively cooled in this prototype situation. With forced air cooling, the trap cooling rate would be greatly increased.

GC/FID

A Varian 3700 FID was used to initially verify trap performance. This system was equipped with 75 m, 0.53 mm ID column. The initial temperature for the GC acquisition was 35°C, and no cryofocusing was used. The purpose of this work was to verify performance of the trap/system relative to standard EPA protocol. Since most GC methods for drinking and waste water require greater than .995 correlation coefficient for the calibration curve, this was set as the target for this step in the analysis. While quantitation was based upon external standards, typical GC/MS internal standards were analyzed, but were not used for quantitation purposes.

The calibration curve for the FID analyses contained eight points: 25, 50, 75, 125, 250, 375, 500, 600 ml of the 20 ppbv standard. This corresponds to concentrations ranging from 1 to 2 to 24 ppbv over the calibration curve.

GC/MS

Once performance was verified by GC/FID, the system was moved the HP 5890/5972 GC/MS. Since a 320 micron column was used, the system was equipped with a cryofocusing module.

A calibration curve was prepared using 100 ml aliquots of the internal standard and the following volumes of 40 ppbv calibration standard: 25, 50, 75, 125, 250, 375, 500 mL. This is representative of concentrations from 2 to 40 ppbv. The calibration curve was compared to the criteria stated in Method TO-14 to determine the system's applicability to the method. For the purpose of this testing, a 30% relative standard deviation was established as the cutoff criteria for the relative response factor for each component.

Conditions

Tekmar 6000/AEROCan		
Line/Valve Temp	150°C	
Standby Flow	10 mL/min	
Trap Standby Temp	100°C	
Sweep Gas	Nitrogen	
	Flow Rate	75 mL/min
	Sweep/Flush time	1 min
Sorbent Trap Temperatures	Cooldown	35°C
	Desorb Time	5 min
	Bake	10 min
	Bake Flow	50 mL/min
Moisture Control System	Standby Temp	150°C
	Desorb Temp	50°C
	Bake Temp	320°C
Cryofocusing Module (GC/MS only)	Standby	100°C
	Cooldown	-175°C
	Inject	100°C

Varian 3700 FID		
Column	DB-624	
	ID	0.53 mm ID
	Film Thickness	3 µm
	Length	75 m
Injection port	Bypassed	
	Transfer Line	0.32 mm ID
Carrier Gas	Helium, flow controlled	
	Flow Rate	10.0 mL/min @35°C
Oven Profile	Initial Temp	35°C for 5 min
	Ramp	6°C/min
	Final Hold	210°C for 1 min
Detector	FID	
	Temp	250°C
	Air Flow	300 ml/min
	Hydrogen Flow	30 ml/min

Hewlett Packard 5890		
Column	DB-5	
	ID	0.32 mm ID
	Film Thickness	1 µm
	Length	60 m
Injection port	Bypassed	
	Transfer Line	0.32 mm ID
Carrier Gas	Helium, constant flow EPC	
Flow Rate	1.0 mL/min @35°C	
Head Pressure	2.8 psig @ 35°C	
Oven Profile	Initial Temp	35°C for 6 min
	Ramp 1	15°C/min to 120°C
	Ramp 2	4°C/min to 160°C
	Ramp 3	25°C/min to 220°C
	Final Temp	220°C

Hewlett Packard 5972	
MS I/O Temperature	280°C
MS Source Temp	175°C
EM Voltage	1900
Scan Rate	4 scans/ 0.1 amu
Scan Range	29-260 amu

Results

GC/FID

The system was optimized for flow rate through the trap, desorption temperature, and desorption time. A graphical representation of this optimization is shown in Figure 1. Once all data points for the calibration curve were acquired, the chromatograms were integrated and a first-order calibration curve was developed. While all attempts were made to eliminate coeluting analytes, there were still
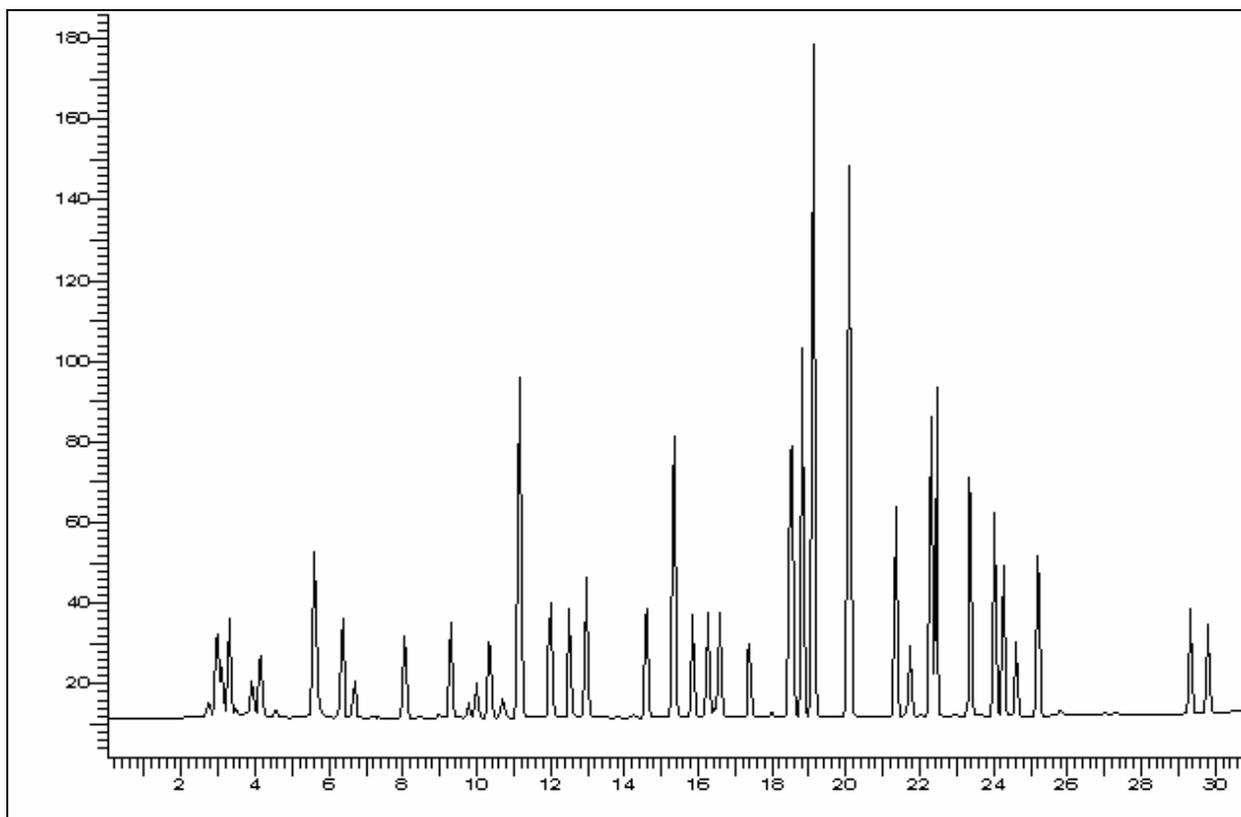
Figure 1. Chromatogram of 125 mL of a 20 ppbv calibration standard on GC/FID

# of cmpounds in standard	4
Barometric Pressure (mm Hg)	**760**
SDB Volume (liters)	**2**
Canister Volume (liters)	**6**
Desired Soup Volume(µl)	**1500**
Desired SDB conc.(ppm)	**122**
Desired Can conc(ppbv)	**200**
Desired % RH (in canister)	**50%**
Final Can Pressure(psig)	**22**
Final Can Pressure(psia)	36.7
µmoles of each analyte in soup	4093

SDB Preparation

µl of soup needed in SDB	**4**

Canister Preparation

mL SDB needed in Can	**25**
µl of H2O needed	**50**

Shading Indicates Input Required from User

Compound Name	CAS #	MW g/mol	Boiling Pt, °C	density (g/mL)	Soup Vol (µL) needed to SDB	SDB Conc (ppm)	Canister Conc (ppbv)
Bromochloromethane		129.39	68	1.991	266.00	118.08	197.06
Difluorobenzene, 1,4-		114.09	88	1.11	421.00	118.16	197.20
Chlorobenzene, d5		117.6	130	1.157	416.00	118.07	197.05
Bromofluorobenzene, 4-		175.01	150	1.593	450.00	118.16	197.20
				Total Soup Volume (µL)	1553.00	118.12	
Approximated numbers were generated assuming a molecular weight of					134.02	1.46	g/ml

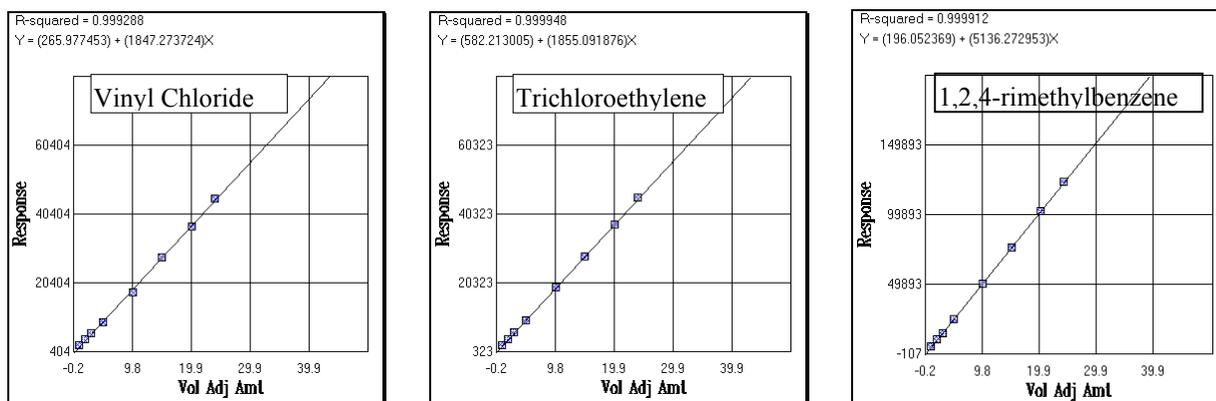Table 1. Internal standard spreadsheet

R-squared = 0.999288
Y = (265.977453) + (1847.273724)X

Vinyl Chloride

Response

60404
40404
20404
404

-0.2   9.8   19.9   29.9   39.9
Vol Adj Amt

R-squared = 0.999948
Y = (582.213005) + (1855.091876)X

Trichloroethylene

Response

60323
40323
20323
323

-0.2   9.8   19.9   29.9   39.9
Vol Adj Amt

R-squared = 0.999912
Y = (196.052369) + (5136.272953)X

1,2,4-rimethylbenzene

Response

149893
99893
49893
-107

-0.2   9.8   19.9   29.9   39.9
Vol Adj Amt

Figure 2. Calibration plots for vinyl chloride, trichloroethylene, and 1,2,4-trimethylbenzene

Method Detection Limits

The method detection limits are displayed from seven, 20 mL aliquots of the calibration standard. The MDLs are listed below in Table 2 and show the concentration values calculated from these samples, the standard deviation, and the method detection limits.

Table 2. Method Detection Limits for Seven Replicate Analyses

NIST-traceable Audit Samples

Once the sensitivity and the linearity of the system were determined, the NIST audit sample, cylinder No. AAL-21390, was analyzed. The resulting concentrations from the three aliquots each at 500 and 1000 mL are listed. These values were averaged and compared to the true concentration in Table 3.

Figure 2. 500 mL of a NIST-traceable reference mixture

Table 3. System Accuracy as compared to NIST-traceable audit mixture

Discussion

The results from the calibration show excellent linearity and precision for the 6 sample volumes taken during calibration. This also illustrates the wide sample volume which can be loaded onto the glass bead-packed, cryogenic trap (50 mL to 1000 mL.) This system was also stable over the one month period as evidenced by the similarities of the precision and response factors from the two calibration curves. This also gives a good indication of the precision at which the standards were diluted over this same period. The data from July exhibits a slightly higher than expected value for the precision of the dichlorodifluoromethane and is probably due to interfering hydrocarbons from the dilution gas.

The method detection limits are similar to those expected from a TO-14 analysis by GC/MS. Some holes in the data appear in the permanent gases, peaks one through 6, and are attributed to the sensitivity of the FID to these halogenated C1 and C2 compounds.

The NIST standard was evaluated on the system to determine accuracy of the system to a reference. The determined concentration agreed well with this standard. Of the fifteen analytes in the mixture, 11 analytes were well within the true concentration range provided with this standard, dated July 1991.

Conclusion

The system is a reliable and rugged mechanism for screening air toxics samples prior to analysis. This can also be used as a final analysis tool in well characterized sampling sites. This technique shows impressive sensitivity for the TO-14 compounds, the additional three brominated trihalomethanes, and the five polar analytes.

There are two drawbacks with this system. The three sets of coeluting peaks could limit final analysis on this system unless a conformational column is used. In addition, the sensitivity to C1 and C2 hydrocarbons to FID can also be prohibitive. The addition of an electron capture detector to the system could partially resolve this issue. Overall, the system exceeded expectations for sensitivity and linearity for the analytes tested.

References

1. Winberry, J.T.; Carhart, B.S.; Randall, A.J., Decker, D.L.,"Method TO-14,"Compendium of Methods for the Determination of Toxic Organic Compounds in Ambient Air, EPA-600/4-89-017, U.S. Environmental Protection Agency, Research Triangle Park, NC, 1988.