

**Triple Sorbent Thermal Desorption/Gas Chromatography/Mass Spectrometry  
Determination of Vapor Phase Organic Contaminants**

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# **Triple Sorbent Thermal Desorption/Gas Chromatography/Mass Spectrometry Determination of Vapor Phase Organic Contaminants**

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## **ABSTRACT**

A thermal desorption/gas chromatography/mass spectrometry (TD/GC/MS) method has been evaluated for the determination of volatile organic compounds (VOCs) in vapor phase samples using Carbosieve S-III/Carbotrap/Carbotrap C triple sorbent traps (TST), similar to those available from a commercial source. The analysis was carried out with a Hewlett-Packard 5985A or 5995 GC/MS system with a modified injector to adapt an in-house manufactured short-path desorber for transferring desorbate directly onto a cryofocusing loop for subsequent GC/MS analysis. Vapor phase standards generated from twenty six compounds were used for method validation, including alkanes, alkyl alcohols, alkyl ketones, and alkyl nitriles, a group of representative compounds that have previously been identified in a target airborne matrix. The method was validated based on the satisfactory results in terms of reproducibility, recovery rate, stability, and linearity. A relative standard deviation of 0.55 to 24.3% was obtained for the entire TD process (generation of gas phase standards, spiking the standards on and desorbing from TST) over a concentration range of 20 to 500 ng/trap. Linear correlation coefficients for the calibration curves as determined ranged from 0.81 to 0.99 and limits of detection ranged from 3 to 76 ng. For a majority of standards, recoveries of greater than 90% were observed. For three selected standards spiked on TSTs, minimal loss (10 to 22%) was observed after storing the spiked traps in a 4°C refrigerator for 29 days. The only chromatographable artifact observed was a 5% conversion of isopropanol to acetone. The validated method has been successfully applied to the determination of VOCs collected from various emission sources in a diversified concentration range.

## **INTRODUCTION**

Recently, our laboratory has been involved in sampling and analyzing VOCs collected from various target airborne matrices. In order to evaluate the sampling adequacy and to assess any health-related impact based on the analysis results, a validated method must be employed. Therefore, the main objective of this study was to develop a methodology for TD/GC/MS determination of VOCs in the vapor phase samples collected on Carbotrap/Carbotrap C/Carbosieve S III triple sorbent traps. The validated method will eventually be used to monitor VOCs present in the headspace of potential emission sources. Techniques used for method validation included VOC standard generation, thermal desorption efficiency, reproducibility of spiking on and recovery from TST, internal standard selection, determination of detection limits, construction of calibration curves, and examination of possible artifact formation. As an example of applying the validated

methodology to a problem directed task, analytical results of VOCs present in the headspace in an underground waste storage tank at the Hanford site will be discussed.

In the recent years, various TD/GC/MS methodologies have been reported in the literature (1-10). A majority of the thermal desorption interfaces used in the prototype or the commercially available thermal desorption devices employ one of the following pre-concentration techniques: (a) A short-path desorber uses solid sorbent traps of defined dimensions (1-5). The desorbed material is concentrated on an intermediate narrow sorbent trap, followed by transferring to the GC column via a second thermal desorption step. However, the existence of the second trap affords the opportunity for both sample loss and artifact formation. (b) A thermal desorption interface transfers VOCs directly onto a GC column (6-10), a packed or a cryogenically maintained capillary column. With this technique, unless a jet separator is installed on the transfer line (between GC outlet and MS source), the desorption flow will be limited by the carrier gas flow. Thus, the long desorption time will eventually cause band broadening of the analytes at the column inlet (7). However, with a jet separator, the instrument detection limit will be increased. In this study, a simple TD/GC/MS interface was constructed which enables us to change the injector port (HP 5985, or HP 5995) readily from injection mode to thermal desorption mode while maintaining the carrier gas at the optimal flow rate (less than 2 ml/min) and without installing a jet separator. The column was disconnected from the cryofocusing loop via a low dead volume union during the TD process, allowing the desorption gas purging through the TSTs at a flow rate of 40 ml/min. An in-house manufactured short-path desorber, capable of heating TSTs from ambient to 400°C in 2 min, was installed on a modified injector port to transfer the desorbed material directly through the glass liner in the injector port into the cryofocusing loop. This minimized any band-broadening of the analyte.

## **INSTRUMENTATION AND ANALYSIS**

### **Triple Sorbent Traps Preparation**

Triple sorbent traps (TST, 6 mm OD, 76 mm x 4 mm ID stainless steel tubing) were prepared in batches of 15 as the following: the traps were plugged at the upstream end of the sampling flow with approximate 15 mm of silanized glass wool and filled with a 14 mm length each of three carbonaceous adsorbents from Supelco (Bellefonte, PA). The least adsorptive one (20-40 mesh Carbotrap C) was packed first, tapping the side of the tube after adding the adsorbent to settle it in the tube. Carbotrap (20-40 mesh), was added next, again settling the adsorbent by tapping the tube. The most adsorptive material, Carbotrap S-III (60-80 mesh), was added last with similar treatment. Another 15 mm plug of silanized glass wool was then inserted in the downstream end. Swagelok stainless steel caps and nuts and Vespel/Graphite ferrules (1/4" OD) were used to seal the traps. These traps are similar to Supelco Carbotrap 300, which was packed with a less proportion of Carbotrap S-III and with glass wool partitions between sorbents. Each batch of TSTs was conditioned by thermal desorption on a manifold, which was placed in a gas chromatograph oven. The traps were heated at 400°C for 3 hours with helium (high purity, passed through an oxygen and molecular sieve trap) flowing opposite to the sampling direction at a flow rate of 60 ml/min. Two blank traps randomly selected from each batch were analyzed by TD/GC/MS prior to spiking and/or sample collection to ensure the cleanliness of the traps.

### **Gas Phase Standard Preparation and Spiking of TST's**

The gas generation methodology used in this study is similar to those described in the static dilution method and the EPA Methods TO-1 and TO-2 (9-11), except for the differences in analytes. The gas standard mixture of the neat liquid standards as listed in Table 1 and 2, was generated in a concentration range of 0.2 to 1.0 ug/ml. Briefly, 2 to 10 ul of neat liquid standard mixture was injected through a Mininert® valve into a 250 ml preheated (70°C) glass bottle. The mixture was stirred with a magnetic stirring bar and glass beads for 30 min to ensure complete vaporization of the liquid. Aliquots of this gas standard mixture were spiked onto TSTs via a preheated (70°C) injector to obtain a concentration of 20 to 1000 ng/trap. The injector was constructed with a 1/4" stainless steel Swagelok Tee with the trap attached to one end of the Tee, and helium gas pushed from the opposite end of the Tee at a rate of 200 ml/min. Gas standard was slowly injected into the stream of helium through a septum attached to the third end (90° to the trap) of the Tee. A total of 400 ml of helium was pushed through the trap after the injection to ensure even distribution of the standards on the trap.

### **TD/GC/MS Analysis of VOCs Collected on TSTs**

Mass spectral analysis was performed either on a Hewlett-Packard 5985 GC/MS (equipped with an EI/CI dual ionization source), or on a Hewlett-Packard 5995 GC/MSD system. A modification was made on the capillary split/splitless inlet system (Figure) to introduce the desorbed gas sample onto the column. A male Swagelok 1/4" nut was welded on the septum retainer nut for direct connection of TST traps. A section of aluminum clad fused silica capillary tubing (0.53 mm ID, 5 cm in length) was inserted through the septum to serve as a transfer line to the glass liner in the injector port. A capillary inlet adaptor fitting (Restek, Port Matilda, PA, Cat. No. 20633) with a 1/16" Swagelok was installed at the base of the injector port. A cryogenic loop, constructed with 15 cm of stainless steel tubing (0.04" ID, 1/16" OD) was connected to the inlet adaptor with a 1/16" Vespel/graphite ferrule. A fused silica capillary column (Restek, Bellefonte, Rtx-5, 60 m, 0.32 mm ID, 1 um film thickness) was connected to the cryogenic loop via a 1/16" Valco zero-dead volume union. A flash heating tube furnace, capable of heating TSTs up to 400°C in 2 min, was constructed from a coiled resistor cable heater (Watlow Cable Heater Co., St. Louis, MO, 50 mm x 7 mm ID, 120 V, 240 W, 2 A). The heater was encased in a ceramic tube using high temperature cement.

In a typical analysis, the cryogenic loop was first immersed in a liquid nitrogen bath and the column was disconnected from the zero-dead volume union. A TST trap was then placed in the tube furnace and heated to 400°C. The trap was purged with helium at a flow rate of 40 ml/min for 7 min in the opposite direction of sampling flow. The column was connected back to the union to transfer the desorbed material from the cryogenic loop to the head of the column. The GC oven temperature program was initiated when the liquid nitrogen bath was removed from the cryogenic loop. The GC oven was held at 10°C for 10 min, then increased to 230°C at a rate of 3°C/min. The flow rate of carrier gas (helium) was held at 1.33 ml/min (16 psig head pressure). Both injector temperature and GC/MS transfer line temperature were held at 280°C. EI spectra were obtained with an electron energy of 70 eV, emission current of 300 uA, and a source temperature of 200°C. Mass spectral data were acquired at a scan rate of 266 amu/sec over a mass range of 35 to 300 amu. The integrated area of the total ions or of a selected ion was obtained for each

component for data manipulation.

## RESULTS AND DISCUSSION

### Thermal Desorption Efficiency

The gas standard was generated by evaporating a neat mixture of liquid standards in a heated gas bottle as described in the static dilution method (11). Aliquots of the gas standard were spiked onto triplicate TSTs at a concentration of 200 ng/trap for subsequent TD/GC/MS analysis. The air-based standard has several advantages over the standard method of spiking a liquid standard onto the trap. It represents more accurately the air sample matrix than liquid standards. By eliminating a large deposition of solvent (such as methanol) on the sorbent bed, not only all the active sites are available to trap small molecules, but also the capillary column performance improves, because evaporation of a large volume of solvent can cause flooding of the column. For each standard, the desorption efficiency was calculated based on the ratio of the integrated area for a selected ion generated from TD/GC/MS to that generated from direct injection of the same standard followed by GC/MS analysis. As indicated in Table 1, TD/GC/MS efficiency is greater than 91% for all the standards studied.

Recently, a number of investigations (12,13) have examined the issues of artifact formation from the VOCs that have been collected on TSTs. Because under the thermal desorption conditions, the large surface of TST carbonaceous media may act as a catalytic surface to facilitate thermal decomposition reaction for VOCs. In order to address this issue, we have compared the total ion chromatograms obtained from direct injection of a gas standard mixture with those obtained from TST that have been spiked with the same standard mixture. Results indicated that the two sets of total ion chromatograms were virtually identical, suggesting there is no chromatographable artifact formation produced from thermal desorption. The only indication that may suggest an artifact formation is a small frontal peak observed when isopropanol was in the standard mixture. Systematic further examination of the desorption of isopropanol from TST revealed that approximately 5% of isopropanol is converted to acetone during thermal desorption, probably through an oxidation process.

### Internal Standards Selection

In order to monitor shipping, handling, sampling and recoveries, three surrogate standards were spiked on TSTs prior to sampling. A calibration internal standard was spiked on TSTs just prior to TD/GC/MS analysis to quantitate the analytes. The selection criteria included: (a) the selected compounds are thermally stable, and not likely to be present in the samples (deuterated analogs of the analyte are ideal), (b) their chemical structures and volatilities are similar to those of the analytes. Six compounds were initially selected and spiked on TSTs for TD/GC/MS analysis over a period of five days. They are  $d_6$ -acetone,  $d$ -chloroform, hexafluorobenzene,  $d_8$ -toluene,  $d_5$ -bromobenzene, and  $d_6$ -benzene. TD/GC/MS analysis results indicated that, with the exception of the first two compounds, the short term reproducibility was within 23% relative standard deviation (%RSD). Because of their high volatilities, the %RSD for  $d_6$ -acetone and  $d$ -chloroform was greater than 33%. In order to minimize possible exposure to a potential carcinogen during shipping and sampling,  $d_6$ -benzene was selected as a calibration internal standard, and hexafluorobenzene,  $d_8$ -toluene, and  $d_5$ -bromobenzene were selected as surrogate standards. A long term stability study was

carried out by spiking the three surrogate standards on TSTs and storing the traps in vials at 4°C. Duplicate or triplicate TSTs were analyzed on the 13th, 20th, 23rd, and 29th days of storage. The range of variation (10 to 24%) for the 29-day holding time experiments compares well with those obtained from the 5-day experiments (12 to 23%).

### **Reproducibility, Linearity, and Limit of Detection of TD/GC/MS**

Triplicate TSTs were spiked with the gas standard at five concentrations, ranging from 20 to 500 ng/trap. Spiked TSTs were analyzed by GC/MS in random order over period of five days. The integrated area of a selected ion within an appropriate GC retention time window for each of the standards was used to calculate %RSD and the correlation coefficient ( $R^2$ ). The ratio of the area for each standard to the area for the calibration internal standard ( $d_6$ -benzene) was also used in this calculation. Table 2 summarizes %RSD for 26 standards, calculated based on the area ratios. As indicated, once the instrument was tuned according to the manufacturer's specification, variation of the entire procedure (including gas standard generation, spiking onto and desorbing from TST) is less than 25%. As expected, reproducibility increases as the concentration of standard on TST increases. Linear regressions were performed using the same set of area ratios, and the results are summarized in Table 3. The correlation coefficients for all 24 standards ranged from 0.81 to 0.99, indicating the calibration curves remained linear over a concentration range of 20 to 500 ng/trap. This is a practical concentration for sampling, because 20 ng is generally near the instrument detection limit for most of the analytes, and 500 ng is within the breakthrough mass for TSTs. The instrument detection limits were estimated based on a signal to noise ratio of 3 (14,15). As shown in Table 3, except for 1-butanol, the detection limits for the remaining 23 standards are below 30 ng (or approximately 7 ppbv for a compound with a molecular weight of 100). The 1-butanol exhibits very poor chromatographic characteristics on the Rtx-5 (5%-diphenyl-95%-dimethylpolysiloxane) column because it is a polar compound. This may contribute to the high detection limit.

### **Application of the Validated Methodology**

DOE's Hanford nuclear site is a 560 square miles installation in southeastern Washington State, at which are 177 large (0.5-1.1 million gallon) underground waste storage tanks (16). In order to determine the headspace components of these tanks, a number of TST were fabricated and shipped to the site for sampling. Prior to shipping the TSTs to the Hanford site, three surrogate standards were spiked on 50 TSTs at a concentration of 500 ng/trap from three batches of gas standard preparation. Every fifth spiked TST was retained for quality control usage. Five spiked TSTs were analyzed by TD/GC/MS to ensure the spiking reproducibility, and the remaining five were analyzed with the sample TSTs to evaluate the recovery rate. As indicated in Tables 4 and 5, the %RSD fell within 9% for the three surrogate standards, and the recovery rate from TST samples ranged from 45% to 117%, with hexafluorobenzene exhibiting the lowest recovery. VOCs identified in the headspace sample collected from a Hanford underground storage tank represent a wide range of chemical class and volatility (details of these findings will be reported elsewhere). Briefly, the VOCs found were alkanes and alkenes (C3-C16), alkanones (C3-C10), alkyl nitriles (C3-C9), aromatic hydrocarbons (one and two rings), and alkyl substituted (C1-C4) aromatic hydrocarbons, tributylphosphate, and dibutyl butylphosphonate. The concentrations for these compounds ranged from 0.15 to 60 mg/m<sup>3</sup>, with long chain hydrocarbons (C10 to

C15) being the most abundant components.

## CONCLUSION

A thermal desorption/gas chromatography/mass spectrometry methodology has been developed for the determination of volatile organic compounds collected on the carbonaceous-based triple sorbent traps. An in-house manufactured short-path desorber was adapted to a modified GC/MS injector for easy conversion of the injection port into a thermal desorption interface. A cryofocusing loop was installed at the injector base and can be disconnected from the GC column via a low dead volume union in order to accommodate the high flow during the thermal desorption process. The method was validated in terms of reproducibility, desorption efficiency, linearity, and detection limit. The validated method has been successfully applied to the characterization of VOCs collected from various emission sources including an underground storage tank at the Hanford site.

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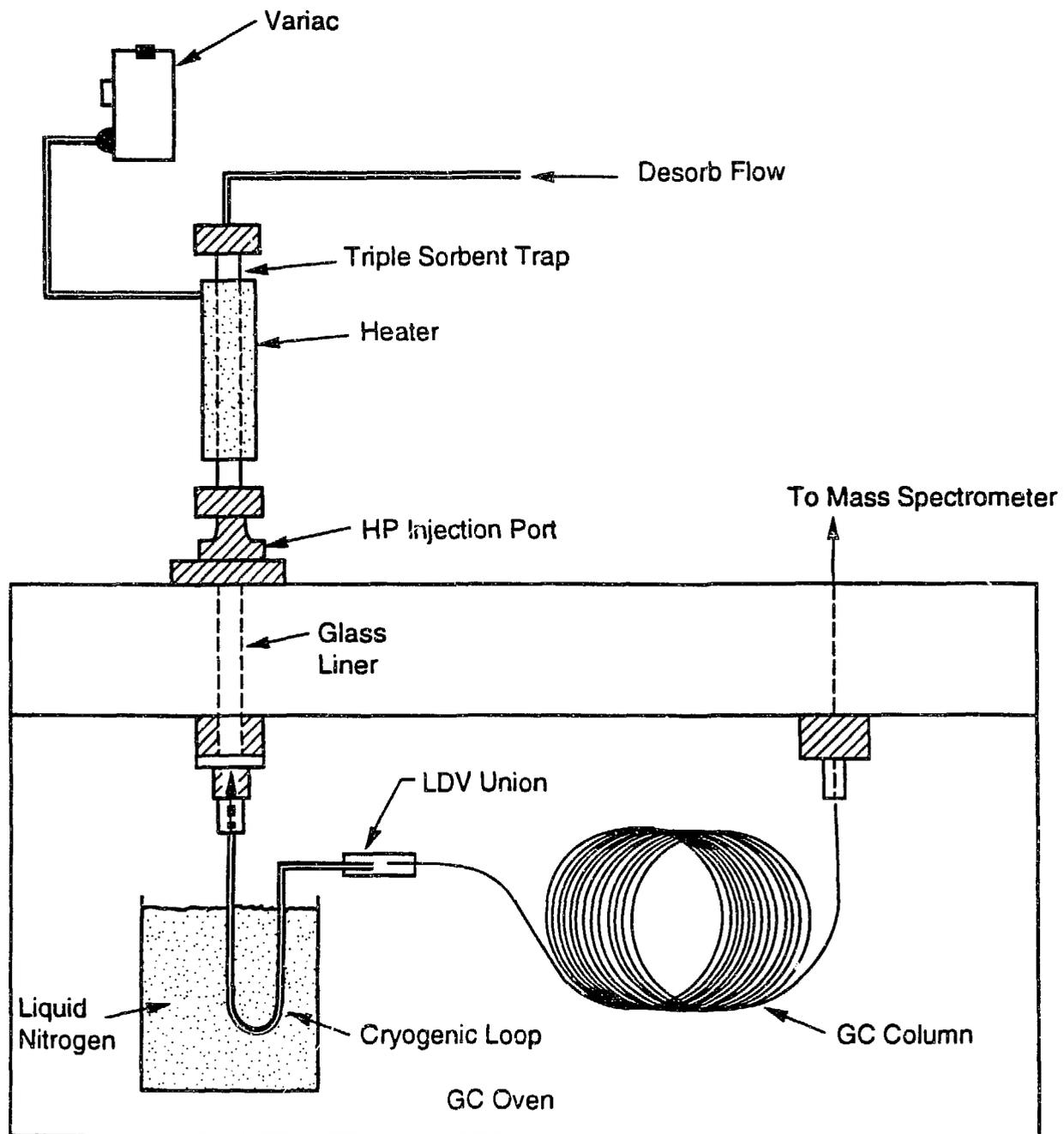
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## Thermal Desorption/Gas Chromatography/Mass Spectrometry System



**Table 1. Triple Sorbent Trap Desorption Efficiencies by Thermal Desorption/Gas Chromatography/Mass Spectrometry.**

COMPOUNDS	% RECOVERY (HP 5985)	% RECOVERY (HP 5995)
Acetonitrile		111
Acetone	132	102
Hexane	96	98
1-Butanol	115	91
Benzene	102	97
Butane Nitrile	96	101
2-Pentanone	111	91
Heptane	99	104
Pentane Nitrile	102	106
Octane	99	110
Hexane Nitrile	102	104
2-Heptanone	97	109
Nonane	107	111
2-Octanone	119	112
Octane Nitrile	92	104

**Table 2. Reproducibility of Thermal Desorption/Gas Chromatography/Mass Spectrometry.**

COMPOUNDS	QUANTITIES SPIKED ON TST				
	20 ng	50 ng	90 ng	180 ng	500 ng
Acetonitrile	7.29*	5.76	7.34	6.32	8.34
Acetone	15.0	4.58	6.82	11.2	2.71
Methylene chloride	3.71	2.53	0.85	1.97	1.25
trans-1,2-Dichloroethylene	5.51	12.5	5.85	4.74	2.06
Propane Nitrile	1.49	4.13	8.80	19.7	3.71
Hexane	15.5	19.5	3.63	7.50	7.14
Hexafluorobenzene (SS)**	10.1	8.82	6.78	21.0	8.94
Benzene	2.95	2.30	4.22	0.57	1.65
1-Butanol	13.8	10.5	9.24	14.4	4.45
Butane Nitrile	5.57	5.28	4.49	10.2	5.19
2-Pentanone	8.32	4.91	9.75	7.57	3.11
d <sub>8</sub> -Toluene (SS)**	1.73	4.67	1.02	1.71	1.36
Toluene	5.85	7.53	1.22	2.58	0.79
Pentane Nitrile	11.5	13.8	5.96	9.17	2.79
2-Hexanone	14.7	11.0	12.4	12.2	1.13
Octane	19.8	7.04	13.1	14.1	0.91
Hexane Nitrile	17.7	10.8	6.07	10.6	2.75
2-Heptanone	17.2	9.56	6.96	8.50	1.57
Nonane	24.3	7.44	9.23	9.06	1.30
d <sub>5</sub> -Bromobenzene (SS)**	2.96	3.51	2.46	3.16	2.55
Heptane Nitrile	0.50	5.87	4.74	6.93	2.60
2-Octanone	20.7	5.54	6.14	9.27	1.50
Octane Nitrile	17.5	2.86	2.56	3.81	3.97
Nonane Nitrile	20.1	5.05	1.96	3.62	6.91
Dodecane	0.55	11.2	5.55	3.61	10.0
Tridecane	11.1	8.86	1.06	6.55	14.0

\* Relative standard deviation

\*\* Surrogate standards were spiked at a concentration of 500 ng/trap

**Table 3. Linearity of Calibration Curves and Limit of Detection for Thermal Desorption/Gas Chromatography/Mass Spectrometry.**

COMPOUNDS	HP 5995		HP 5985	
	Linearity (R <sup>2</sup> )	Limit of Detection (ng)	Linearity (R <sup>2</sup> )	Limit of Detection (ng)
Acetonitrile	0.9919	5		
Acetone	0.9991	4	0.9511	19
Methylene Chloride	0.9985	8		
trans-1,2-Dichloroethylene	0.9925	10	0.9181	27
Propane Nitrile	0.9940	8	0.9536	18
Hexane	0.9883	10		
Benzene	0.9931	6	0.9934	7
1-Butanol	0.9627	10	0.8122	76
Butane Nitrile	0.9984	4	0.9329	30
2-Pentanone	0.9821	3	0.9044	20
Heptane	0.9998	6		
Toluene	0.9899	5	0.9827	4
Pentane Nitrile	0.9911	11	0.9515	16
2-Hexanone	0.9919	3	0.9906	10
Octane	0.9915	5	0.9946	11
Hexane Nitrile	0.9992	8	0.9856	7
2-Heptanone	0.9996	10	0.9756	7
Nonane	0.9999	13	0.9869	7
Heptane Nitrile	0.9999	18	0.9672	7
2-Octanone	0.9999	9	0.9614	7
Octane Nitrile	0.9947	26		
Nonane Nitrile	0.8126	27		
Dodecane	0.8471	31	0.9756	5
Tridecane	0.8414	30	0.8756	7

**Table 4. Results of Thermal Desorption/Gas Chromatography/Mass Spectrometry Analysis of Quality Control Triple Sorbent Traps for Sampling of Hanford Underground Storage Tank.**

TST Spiked with Gas Standard	Hexafluorobenzene*	d <sub>5</sub> -Toluene*	d <sub>5</sub> -Bromobenzene*
Standard A	5778**	14387	5246
Standard B	5873	12815	4842
Standard B	6158	14991	4900
Standard C	6501	16424	5263
Standard C	6269	15281	5193
Average Response	6078	14780	5089
Standard Deviation	239	1324	202
% Relative Standard Deviation	3.93	8.96	3.96

\* Surrogate standard spiked on TST's

\*\* Selected ion response to approximate 500 ng surrogate IS

**Table 5. Recovery of Surrogate Standards from Triple Sorbent Traps Sampled from a Hanford Underground Storage Tank\*.**

Hexafluorobenzene	d <sub>5</sub> -Toluene	d <sub>5</sub> -Bromobenzene
63	108	86
45	96	103
70	89	113
117	83	107
81	94	106
49	86	105
106**	117	103

\* % Recovery analyzed with HP 5995 GC/MS

\*\* % Recovery analyzed with HP 5985 GC/MS