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Application of Multisorbent Traps to Characterization and Quantification of Workplace Exposure Source Terms ¹

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ABSTRACT

Multisorbent traps have been used for several years to characterize complex atmospheres. Only more recently have multisorbent traps been used for quantitative analysis. The traps provide an effective method for retaining a wide range of airborne organic contaminants, since these carbonaceous sorbents are relatively hydrophobic, have large surface areas, do not have active functional groups, and have fewer chemical artifacts than other sorbents. Multisorbent traps, which are 76 mm in length and have a 6 mm outside diameter, contain sequentially loaded beds of Carbotrap C, Carbotrap, and Carbosieve SIII, similar to a commercially available trap. The injection port of a gas chromatograph is configured for thermal desorption analysis of the traps via an in-house modification. Currently, multisorbent traps are being used to sample the headspace of underground storage tanks at the Department of Energy's Hanford site, in Richland, Washington. The analyses are performed by flame ionization or mass spectrometric detection. Target organic analytes include C₆ to C₁₃ alkanes, alkyl nitriles, alkyl ketones, dibutyl butyl phosphonate and tributyl phosphate. Pre-analytical holding times or practical reporting times for many target analytes are at least 84 days under either refrigerated or ambient conditions. Traps are fabricated, conditioned, and spiked with three surrogate standards in the vapor phase prior to shipment to the site. Recovery of the surrogates from the multisorbent traps serve as a statistical process control. Source concentrations of Hanford underground storage tank headspaces range from 0.96 mg/m³ to 1200 mg/m³.

INTRODUCTION

Classically, sorbent traps have been used to characterize ambient air since they provide a way of concentrating species that are present in low concentrations. It was later determined that combining multiple sorbents in a single trap could extend the range of species that could be retained (1). Only more recently have multisorbent traps been used for quantitative analysis. Multisorbent or triple sorbent traps (TSTs) contain sequentially loaded beds of Carbotrap C, Carbotrap, and Carbosieve SIII, similar to Carbotrap 300 traps, which are commercially available from Supelco, Inc. Carbotrap 300 traps and TSTs differ in the following ways: (1) TSTs have a larger proportion of Carbosieve SIII; (2) TSTs do not have glass wool partitions between sorbent beds. These stainless steel traps, which are 76 mm in length and have a 6 mm outside diameter, can be valuable in numerous applications since the carbonaceous sorbents are relatively hydrophobic, have no surface ions or active functional groups, and have fewer chemical artifacts than other sorbents (2).

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Multisorbent traps are currently being used to sample the headspace of underground storage tanks at the Department of Energy's Hanford site, in Richland, Washington. The Hanford reservation, which is 560 square-miles, is located about 120 miles south of Spokane, Washington. After approximately 40 years of nuclear weapons production at the site, 60 million gallons of mixed radioactive waste have accumulated in 177 underground storage tanks (3). The tank capacities vary from 0.5 to 1 million gallons, although most are not filled to capacity. The general methodology for analyzing tank headspace samples by thermal desorption/gas chromatography/mass spectrometry (TD/GC/MS) was presented at 1994 EPA/AWMA Measurement of Toxic and Related Air Pollutants Symposium. The purpose of this discussion is to describe some of the results that have been obtained and the quality assurance controls that have been implemented to improve the methodology.

DISCUSSION

Westinghouse Hanford Company (WHC) is characterizing the waste tank headspace vapors for primarily three reasons (4). First, there are worker health and safety issues. The tanks are workplace source terms. Thus, WHC needs to adequately characterize the tanks since there exists a potential hazard to tank farm workers. A second significant issue is headspace flammability. Although combustible gas meters are used to monitor tank headspace flammability, some headspace composition issues may not be addressed by these meters. Lastly, WHC would like to identify, based on headspace organic concentrations, those tanks which could potentially have pools of organic liquids.

Ten cases of worker exposure to vapors from tank 241-C-103 prompted the establishment of the Tank Vapor Issue Resolution Program (4). Consequently, tank 241-C-103 was the first tank to be comprehensively studied by the program. Based on the results from initial scoping experiments with 241-C-103, a list of target analytes was generated by a panel of Pacific Northwest Laboratory experts in various areas of toxicology. The target organic analytes listed in Table 1 include C₆ to C₁₃ alkanes, alkyl nitriles, alkyl ketones, dibutyl butyl phosphonate and tributyl phosphate. Target analyte concentrations are quantified against calibration standards for each tank. Therefore, these analytes serve as way of integrating the data for tank to tank comparisons. TD/GC/MS methodology validation studies were performed using these target analytes, including measurements of pre-analytical holding times.

A holding time study was performed on a representative subset of the target analytes using a method developed at ORNL(5). The Practical Reporting Time, or PRT, is defined as the time (in days) when there is a 15% risk that the concentration will be below the critical (initial) value. The method depends on approximating models to represent the degradation of analyte concentrations with time. For this study, either zero-order (linear) kinetic model, log-term model, or inverse-term model was applied to the data. The majority (84%) of the data was fitted to the linear model. One attribute of this method is that it allows for judgement beyond the last experimental data points. Therefore, a prediction can be made to assess the probability of being below the critical value during any time period. A total of 56 triple sorbent traps were spiked with vapor phase organic analytes (nominal 400 ng/trap) for the PRT study. The experiments were divided into two disciplines according to how the traps were stored: refrigerated (2°C) and ambient (22°C). Each day's analyses consisted of three standards and four PRT "samples", which were analyzed by thermal desorption/gas chromatography/flame ionization detection (TD/GC/FID). Just prior to analysis, each TST was spiked with three vapor phase internal standards, namely hexafluorobenzene, d₁₀-ethylbenzene, and d₂₆-dodecane. PRT samples were analyzed on 0, 7, 14, 21, 28, 63, and 84 days of storage at both ambient and refrigerated temperatures. Data from only one analyses was discarded due to experimental error. Therefore, the conclusions are based on 55 data points. The PRT results are presented in Table 2 (6). Eleven of the sixteen analytes (i.e, acetone, butanal, 1-butanol, pentanenitrile, and 2-pentanone were the exceptions) stored at refrigerated temperatures showed no significant decreases during 84 days. The PRTs for these eleven analytes under refrigerated conditions are at least 84 days. Also, nine of the sixteen analytes (i.e, acetone, 1-butanol, butanal, 2-octanone, pentanenitrile, propanenitrile, and 2-pentanone were the exceptions) stored at ambient temperatures showed no significant decreases during 84 days. The ketones that were stable under

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refrigerated conditions were not stable under ambient conditions for the entire 84 days. The PRTs for these nine analytes under ambient conditions are at least 84 days. Note that these experiments were performed under controlled conditions, and did not address the possibility of the tank matrix stabilizing or destabilizing the analytes on the sorbent beds.

Prior to shipping traps to Hanford for tank sampling, each TST is spiked with three surrogate vapor phase standards (hexafluorobenzene, d_8 -toluene, and d_5 -bromobenzene). At least 10% of the spiked traps are analyzed to check spiking consistency. Additional traps are spiked with each tank set and reserved for later analysis with the samples. Surrogate recovery is determined by comparing the amount of surrogate on the samples with the amount on the reserved trap. From January 1994 to September 1994, surrogate recoveries were determined for eleven sampling jobs (69 samples). (Note that tank samples analyzed between January and May 1994 were acquired during the developmental stages of sampling methodology. Therefore, surrogate recovery data from this time period has been included in this discussion, while tank headspace analyses have not.) This initial surrogate recovery data set was evaluated to establish a reference point for future surrogate recovery determinations. Quality control decision limits using 95% confidence intervals were established for surrogate recoveries and associated variance. Once these quality control decision limits were established, each set of tank samples was evaluated against the limits, based on the number of samples analyzed. Individual samples were then independently examined for anomalies. Data was flagged if the mean recovery values were outside the quality control limits, since this may be an indication that biases have been introduced into the measurement. In general, for at least one surrogate, 75-80% of the samples fell within, 5-20% fell above, and 5-15% fell below the quality control limits for recovery. Approximately 83% of the samples had all surrogate recovery values within the established variance level. High surrogate recoveries tend to indicate that the source matrix had little or no effect of the efficient retention of analytes on the sorbent beds. Additionally, it indicates that sample handling activities were executed properly. No adjustments have been made for low surrogate recoveries since it is difficult to assess exactly when, where, or how the losses occurred. A new data set including 149 samples analyzed from January 1994 to March 1995 was statistically examined (7). The data was segregated into three categories, according to when the data was generated: (1) January to September 1994; (2) September to December 1994; and (3) January to March 1995, using a new GC/MS system. Statistical analysis of the data revealed improvement in the accuracy and precision of the surrogate recovery measurements with the third data set. In Figure 1 is presented a comparison of 95% confidence intervals (N=6 samples) for both the entire data set and data set 3 only. The confidence intervals determined for the entire data set are quite comparable to the limits established from data set 1. The quality control limits are tighter and more centered around 100% for the data set 3 intervals. Since the data acquired between January 1995 and March 1995 is most representative of the recoveries that are currently being generated, the data set 3 confidence intervals will be used to judge future surrogate recovery determinations.

From May 1994 to March 1995, we completed analyses on 24 tanks, encompassing six different tank farms. For the majority of the tanks that are analyzed, little or nothing is known prior to sampling with regard to headspace concentration. Therefore, multiple levels of samples are acquired in an attempt to obtain the appropriate loading level. Although many have similar properties, each tank headspace is unique. For example, acetonitrile, acetone, or 1-butanol is usually the predominant target analyte in a headspace, but the total organic headspace values from tank to tank span a wide dynamic range. Periodically, WHC has supplied ORNL with total organic concentration values ranging from 0.20 mg/m³ for Tank 241-C-111 to 2000 mg/m³ for tank 241-C-103. We have estimated headspace organic concentration for each tank by summing the mean concentrations of all target analytes and tentatively identified compounds detected by GC/MS analyses. Our estimates range from 0.96 mg/m³ for 241-C-108 to 1200 mg/m³ for tank 241-C-103. Each of the 24 tanks is presented with its corresponding estimated headspace concentrations in Figure 2. The log of the concentration (in mg/m³) was taken so the values could be normalized.

CONCLUSIONS

Multisorbent traps are being successfully deployed at the Hanford site for underground storage tank headspace characterization and quantitative analyses. A significant driver for this activity is worker health and safety. Practical reporting time experiments verify that many of the target analytes are stable on the trap at refrigerated and ambient temperatures for at least 84 days. Surrogate standards loaded on the traps prior to shipment to Hanford serve as a statistical process control for the methodology. In general, surrogate recovery results indicate that sample handling activities are being executed properly and that the source matrices have had a minimal effect on the retention of the analytes on the sorbent beds. Although many have similar properties, each tank headspace has an unique organic signature.

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TABLE 1
List of Target Analytes

1-Butanol	Butanenitrile	Nonane
2-Heptanone	Decane	Octane
2-Hexanone	Dibutyl butyl Phosphonate	Pentanenitrile
2-Octanone	Dodecane	Propanenitrile
2-Pentanone	Heptane	Toluene
Acetone	Heptanenitrile	Tributyl Phosphate
Acetonitrile	Hexane	Tridecane
Benzene	Hexanenitrile	Undecane
Butanal	Methylene Chloride	Vinylidene Chloride

TABLE 2
Practical Reporting Times (PRTs)
Selected Organic Analytes on Triple Sorbent Traps

Organic Analyte	PRTs, days	
	Refrigerated (2°C)	Ambient (22°C)
Acetone	51	32
Benzene	≥84	≥84
Butanal	1	5
1-Butanol	17	2
Dodecane	≥84	≥84
Heptanenitrile	≥84	≥84
Hexane	≥84	≥84
Methylene Chloride	≥84	≥84
Nonane	≥84	≥84
2-Octanone	≥84	1
Pentanenitrile	56	30
2-Pentanone	34	2
Propanenitrile	≥84	30
Toluene	≥84	≥84
Tridecane	≥84	≥84
Undecane	≥84	≥84

Figure 2
Estimated Organic Concentration
Hanford Underground Storage Tanks

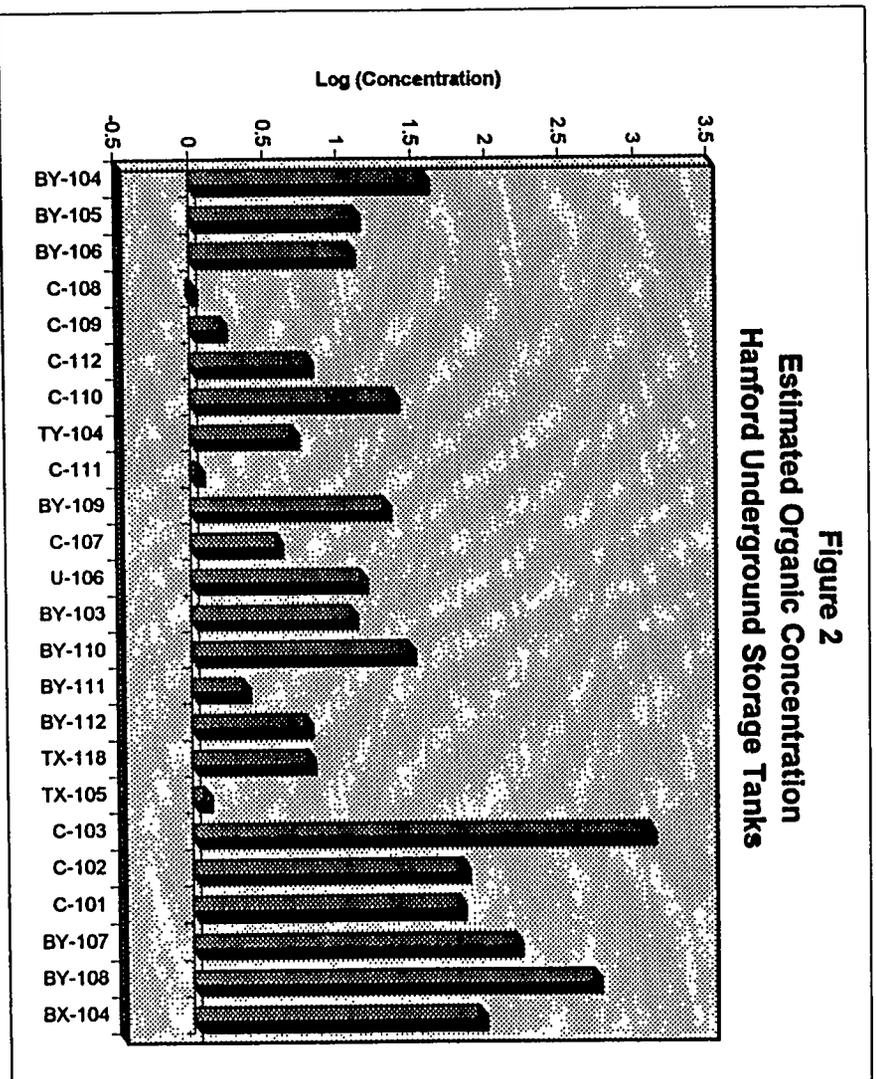
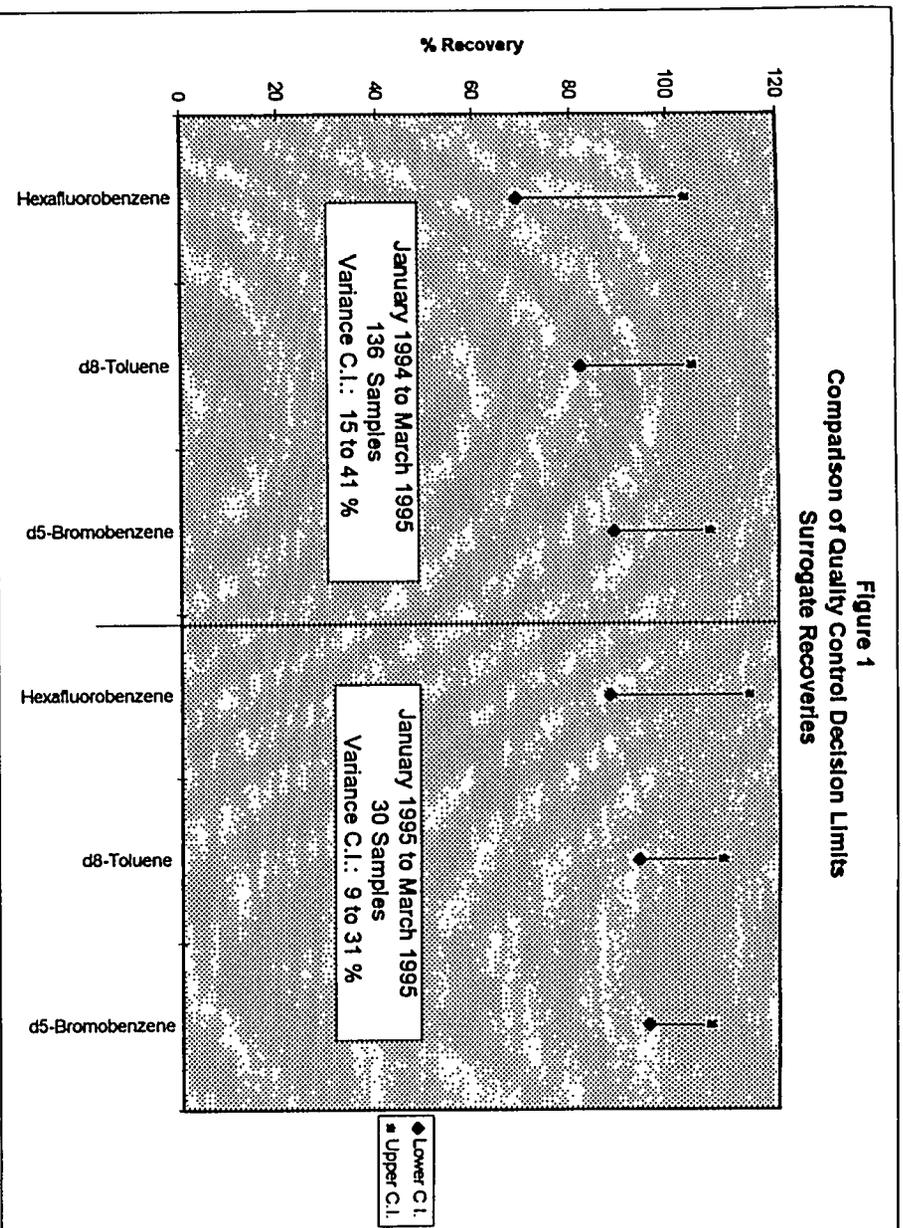


Figure 1
Comparison of Quality Control Decision Limits
Surrogate Recoveries



Key Words

Carbotrap™

Carbosieve™

Sorbent

Trap

Air

Sampling