Short communication

Novel calibration technique for headspace analysis of semivolatile compounds

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Abstract

Vapor phase trap spiking methods have been developed and used for the analysis of volatile organic compounds. Because of their lower vapor pressures, this approach is not suitable for some semivolatile analytes, such as tributyl phosphate (TBP) and dibutyl butyl phosphonate (DBBP). A method was developed to independently quantify TBP and DBBP using a unique trap loading technique, and subsequent thermal desorption/gas chromatographic analysis. Modification of a gas chromatograph injection port allowed methanolic standards to be loaded onto sorbent traps quantitatively. The loaded calibration traps were then thermally desorbed and analyzed. Linearity, reproducibility, accuracy and method detection limits were established and will be reported for TBP and DBBP standards. © 1998 Elsevier Science B.V.

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1. Introduction

In recent years, tributyl phosphate (TBP) has been used as an extractant for the separation of radioactive elements from waste tank sludge [1–8] in nuclear weapon production facilities such as the US Department of Energy's Hanford site in Richland, Washington. Consequently, TBP and dibutyl butyl phosphonate (DBBP), which is frequently observed as an impurity component of TBP, are present at fairly high concentrations in the headspace of Hanford underground waste storage tanks, despite their low volatility.

Since conventional vapor phase standards of TBP and DBBP cannot be prepared by the static dilution method [9] that is used to quantify volatile organic

compounds collected on solid sorbent traps, liquid phase standard solutions must be used. Spiking liquid standards is often done by loading the liquid on the glass wool plug with a syringe, and then passing helium through the trap to introduce the analytes to the sorbent bed. When a liquid solution is transferred using a syringe, it leaves the syringe needle as a jet. This could lead to a non-uniform distribution of the standard on the sorbent bed [10] and variability in calibration measurements. Therefore, a systematic approach for vaporizing and quantitatively loading semivolatile compounds, like TBP and DBBP, onto solid sorbent traps was developed. The liquid standard is vaporized in a preheated injection port prior to reaching the calibration trap. The vaporized standard is then evenly distributed onto the sorbent bed at a controlled flow-rate, which simulates how an actual field sample is

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collected on the trap. The methanol passes through the trap, while the TBP and DBBP are retained. This note describes a novel standard loading technique developed specifically for TBP and DBBP quantification by thermal desorption using solid sorbent traps.

2. Experimental

2.1. Chemicals

Tributyl phosphate (CAS 126-73-8) was obtained from Kodak (Rochester, NY, USA), dibutyl butyl phosphonate (CAS 78-46-6) was obtained from Pfaltz and Bauer (Waterbury, CT, USA), and methanol (Ultra-Resi Analyzed grade) was obtained from J.T. Baker (Phillipsburg, NJ, USA). Stock methanolic standards of TBP and DBBP were prepared gravimetrically. Working standards (5 ng/μl, 10 ng/μl, 25 ng/μl, 50 ng/μl, 100 ng/μl) were prepared by diluting the stock standards using variable-volume pipettes (Rainin Instrument Company, Woburn, MA, USA).

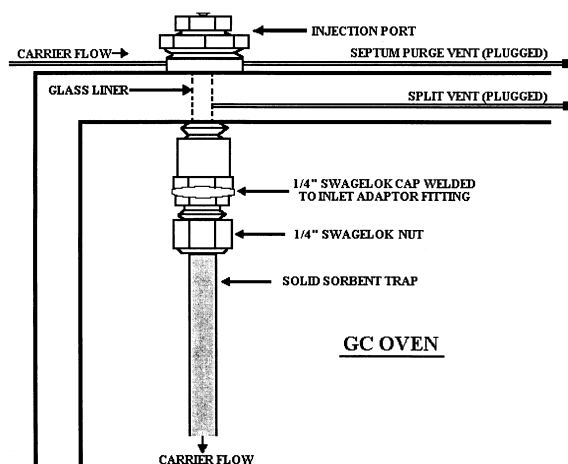**CAPILLARY INLET SYSTEM CONFIGURED FOR VAPOR SAMPLE LOADING ONTO SOLID SORBENT TRAP**

Fig. 1. Schematic of modified injection port of Hewlett-Packard GC oven, configured for vapor phase loading onto solid sorbent trap.

2.2. Trap preparation

Sorbent traps were prepared in-laboratory according to a previously used procedure [11]. Briefly this procedure involves volumetrically filling stainless-steel tubes (76 mm$\times$6 mm O.D.) with solid sorbent material. Glass wool plugs are placed at both ends of the tube to keep the material in place. The trap is sealed using stainless-steel Swagelok fittings. Dual sorbent traps, containing Carbotrap C and Carbotrap (Supelco, Bellefonte, PA, USA), were used in this study.

2.3. Modified inlet system for trap loading

TBP and DBBP were loaded onto dual sorbent traps using a modified injector port of a Hewlett-Packard, Model 5840A gas chromatograph (Hewlett-Packard, Palo Alto, CA, USA). A schematic of the configuration is presented in Fig. 1. A welded 1/4 in. (1 in.=2.54 cm) nut was fabricated in-laboratory so that a sorbent trap could be directly connected to the base of the injector port. The injector port housed a 2 mm I.D. splitless sleeve (Restek, Bellefonte, PA, USA). The septum purge and split vents were plugged, so that the split/splitless modes were bypassed. The gas chromatography (GC) instrument and injection port, once modified, were dedicated to trap loading applications.

2.4. Trap spiking

To spike a trap with calibration analytes, a dual sorbent trap was attached to the base of the injector port. The rate of carrier gas (helium, 99.996% purity) through the sorbent trap was 100$\pm$5 ml/min. The GC oven door was closed so that the oven could be cryogenically cooled to 30$\pm$1°C. An aliquot (1 μl) of standard was loaded into a 10 μl syringe (Hamilton, Reno, NV, USA) with air gaps above and below the liquid plug, allowing visual inspection of the volume. The standard was injected through the injection port (maintained at 250°C) and swept onto the sorbent trap with the carrier gas for 1 min. The loaded sorbent trap was then analyzed immediately or capped and stored at 4$\pm$2°C until analysis.

2.5. Thermal desorption-gas chromatography–flame ionization detection setup

The thermal desorption (TD) configuration was very similar to that which has been described elsewhere [11]. The analytical instrument was a Hewlett-Packard 5890 gas chromatograph equipped with flame ionization detection (GC–FID). Hydrogen (purity: 99.996%) flow-rate into the FID system was ~40 ml/min and certified grade D air flow-rate was ~270 ml/min. The short-path thermal desorption unit was fabricated in-laboratory by coating a 1/4 in. I.D. coiled heater (Tennessee Heater and Control, Nashville, TN, USA) with Omega CC high temperature cement (Omega Engineering, Stanford, CT, USA). The 45 mm long heater was thermally regulated using a Variac W5MT3 autotransformer (General Radio USA, Concord, MA, USA). The heater was calibrated using a thermocouple and digital thermometer to establish and maintain the desorption temperature (400°C). A Swagelok 1/4 in. nut was welded on the septum retainer nut for direct connection of the trap to the injector port. A section of aluminum-clad fused-silica capillary tubing (5 cm× 0.53 mm I.D.) was inserted through the septum to serve as a transfer line to a 2 mm splitless sleeve glass liner in the injector port. A capillary inlet adaptor fitting (Restek) with a 1/16 in. Swagelok nut was installed at the base of the injector port, and was connected to the cryogenic loop. The cryogenic loop was constructed from SilcoSteel tubing (Restek) that was ca. 23 cm×0.030 in I.D., 1/16 in. O.D. A low dead volume (LDV) union (1/16 in.) joined the cryogenic loop with the fused-silica DB-5 capillary column (60 m×0.53 mm I.D., 1.0 μm film thickness, J&W Scientific, Folsom, CA, USA). Carrier gas (helium) flow-rate was ca. 7 ml/min. The injector

port and detector temperatures were both maintained at 250°C. The GC instrument was interfaced with a Hewlett-Packard 3396a integrator for data acquisition.

2.6. TD-GC–FID analysis

In a typical analysis, the cryogenic loop was disconnected from the capillary column via the LDV union and immersed in a liquid nitrogen bath. A sorbent trap was then placed in the desorption unit and flash-heated to 400°C in 1.5 min. The trap was purged with helium at a flow-rate of 50±5 ml/min for 7 min, in the opposite direction of sampling flow. After the desorption was completed, the desorption flow valve was closed, the LDV was reconnected, and the carrier gas valve was opened to transfer the desorbed material from the cryogenic loop to the head of the column. The GC oven temperature program (35°C, hold 5 min, ramp at 2°C/min to 230°C, hold 7.5 min) was initiated when the liquid nitrogen bath was removed from the cryogenic loop. The analyses were performed in splitless mode for the entire chromatographic run. For the liquid injection analysis, split mode was performed for 2 min, then splitless mode for the rest of the chromatographic run.

3. Results and discussion

3.1. Method performance

Triplicate analyses at each of four concentration levels were performed to investigate the precision of the trap loading technique. The precision is defined as the relative standard deviation (R.S.D.) of repli-

Table 1
Summary of method performance characteristics

Analyte	R.S.D.[a]				% Recovery[b]		R[b,c]	MDL[d]
	5 ng/μl	10 ng/μl	25 ng/μl	50 ng/μl	10 ng/μl	50 ng/μl		
DBBP	13	18	6	4	95	104	0.990	9.5
TBP	6	22	8	2	94	92	0.983	10.5

[a] Relative standard deviation determined from triplicate analyses at each level.
[b] Calculated from the mean response of three desorptions versus the mean response of three injections at each level.
[c] Correlation coefficient of a calibration curve constructed from triplicate analysis at four concentrations (5, 10, 25 and 50 ng/μl).
[d] Method detection limit in ng/trap, determined from triplicate analysis at four concentrations (5, 10, 25 and 50 ng/μl).

Flame Ionization Detection Profile of Sorbent Trap Sample of Hanford UST Headspace
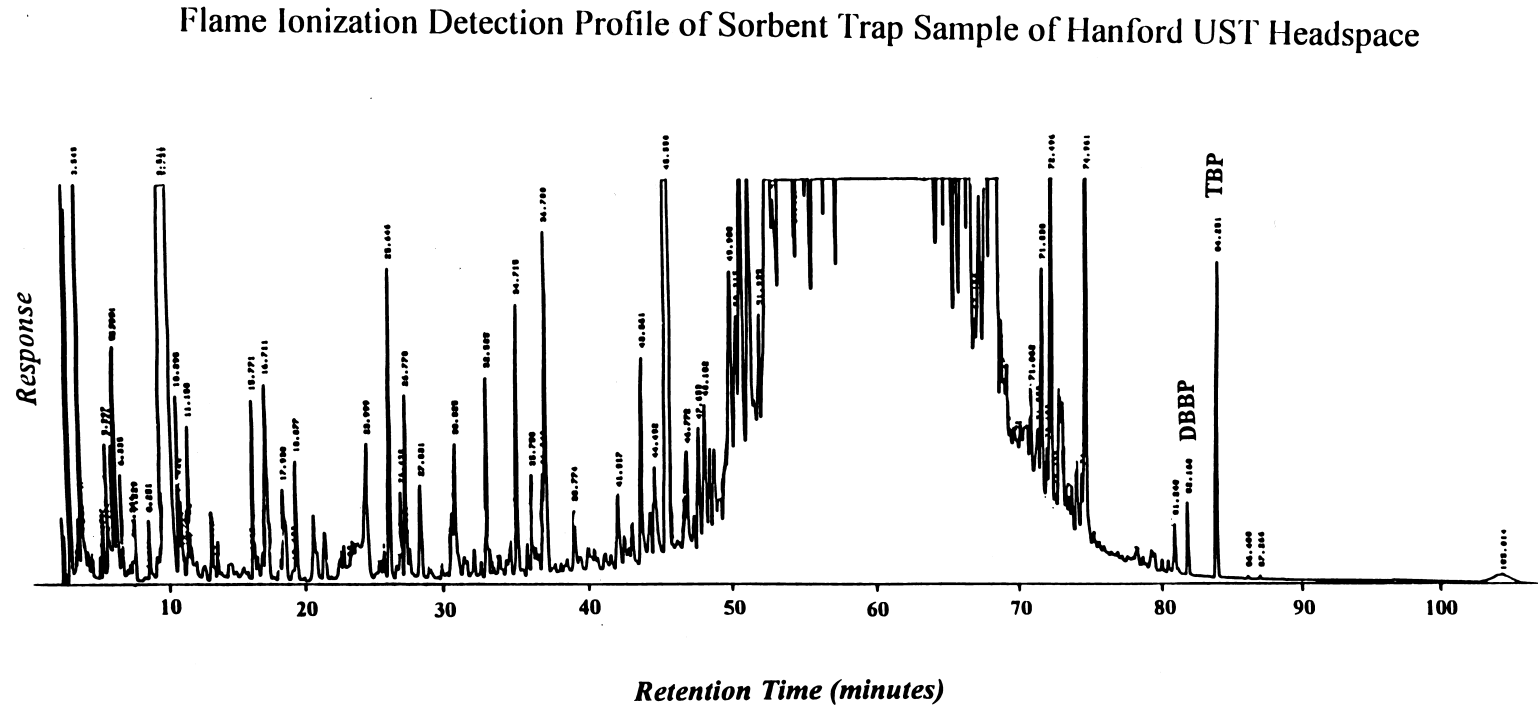

Fig. 2. Flame ionization detection profile of dual sorbent trap sample of Hanford underground storage tank headspace.

cate measurements. These data were also evaluated to determine the sensitivity (method detection limit) of the method. Accuracy of the method was ascertained by comparing the response determined from the thermal desorption of the sorbent trap with the response determined from the direct injection of the standard into the GC. Direct injection versus desorption analyses were performed in triplicate at two different concentration levels. The percent recovery (accuracy) was calculated from the mean of the triplicate analyses. The results are discussed below.

Table 1 summarizes the method performance characteristics. The precision of the loading method was evaluated using triplicate analyses at 5, 10, 25 and 50 ng of each analyte/μl of standard. The R.S.D.s for DBBP ranged from 4% (at 50 ng/μl) to 18% (at 10 ng/μl). The R.S.D. for TBP was below 10% for all test concentrations except 10 ng/μl (22%). The correlation coefficient (R^2) of the calibration curve was 0.990 for DBBP and 0.983 for TBP. The accuracy of the method, represented by the overall recovery of TBP and DBBP, was evaluated using three desorptions at 10 ng/μl and 50 ng/μl of both analytes. The recovery exceeded 92% for both analytes at the two test concentrations. The method detection limit (MDL) is defined by the US Environmental Protection Agency (EPA) as the minimum concentration of a substance that can be measured and reported with 99% confidence that the analyte concentration is greater than zero [12]. MDLs were determined to be 9.5 ng/trap for DBBP and 10.5 ng/trap for TBP by the TD-GC–FID method. Assuming a nominal sampling volume of 1 l for headspace analysis applications, the MDLs would be less than 1 parts per billion by volume (ppbv) under STP conditions.

3.2. Application of the method

Validation of the method and optimization of analytical conditions has been described elsewhere [11]. Non-selective detection (FID) and extended GC conditions were used in this study, since TBP and DBBP were not the only analytes of interest. If TBP and DBBP were the only analytes of interest, a trap containing only Carbotrap C would have been used. A second sorbent, Carbotrap, was employed so that additional analytes could be collected from the

underground storage tank headspace. Fig. 2 shows a chromatogram of a dual sorbent trap Hanford tank headspace sample analyzed by TD-GC–FID. A slow column oven temperature ramp rate (2°C/min) was employed to afford the separation of DBBP and TBP from the normal petroleum hydrocarbon envelope, which is critical for GC–FID analyses. Calibration curves to quantify TBP and DBBP were constructed by analyzing calibration traps prepared using the newly developed method. Measured amounts of TBP and DBBP in this tank headspace sample were 4.6 mg/m^3 (387 ppbv) and 1.0 mg/m^3 (89.6 ppbv), respectively.

4. Conclusions

Although TBP and DBBP are not very volatile, they can be detected in underground storage tank headspace at considerable levels. The modified calibration trap loading technique allows the TBP and DBBP content to be quantified. The method has proven to be accurate and precise and has been utilized in actual field sample quantification. It is expected that this solid sorbent trap loading method can be applied to almost any thermally stable semivolatile material. The modification outlined in this note is applicable to any commercially available GC.

Acknowledgements

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