

## A High Efficiency All Glass Sampling and Concentration Device for Adsorptive Semivolatile Organics

Mark Gehrke<sup>a,c</sup>, Shubhen Kapila<sup>a,c</sup>, Paul Nam<sup>c</sup> and Virgil Flanigan<sup>b,c</sup>

<sup>a</sup>Department of Chemistry, <sup>b</sup>Department of Mechanical Engineering,  
<sup>c</sup>Center for Environmental Science and Technology  
University of Missouri-Rolla, Rolla, MO 65409 USA

### Abstract

A low-volume, and inert sampling and enrichment device for semivolatile organic vapors is described. The device consists of two concentric fused silica capillaries. A small portion of the inter-capillary volume, cooled with a burst of compressed carbon dioxide, serves as a trap for the semivolatile organics. The low mass of the trap permits rapid sampling and desorption cycles suitable for applications requiring fast monitoring of semivolatile chemicals. The device is devoid of switching valves in the sampling train and consequently does not suffer from analyte loss due to irreversible adsorption or interference resulting from cross contamination. The device was successfully used for sampling low concentrations of highly adsorptive nitroaromatic compounds and is applicable for polychlorinated dibenzo-p-dioxins (PCDDs), polyaromatic hydrocarbons (PAHs).

### Introduction

Determination of volatile and semivolatile compounds at trace levels and ultra trace levels in the gas phase can be carried out with cryogenic trapping and thermal desorption devices. A number of such devices have been reported in literature.<sup>1-3</sup> The early applications of cryogenically cooled devices were primarily directed at solute transfer in two dimensional gas chromatography systems. In the most common vapor-sampling configuration, a cryogenically cooled sampling loop is connected to a switching valve. An aliquot of the gas is drawn through the cooled loop and analytes of interest are then condensed in the loop. After set sampling time periods, the switching valve is rotated and the temperature of the loop is increased through resistive or inductive heating and condensed analytes are transferred into the analyzer gas stream for quantitative determination.<sup>4</sup> Switching valves with polyimide-carbon rotors have been used extensively in such devices. However, these switching valves have been found to be unsatisfactory for sampling of reactive and/or adsorptive chemicals. For example, vapors of explosives such as 2,4- dinitrobenzene (2,4-DNB), 2,6-dinitrotoluene (2,6-DNT), 2,4,6- trinitrotoluene (2,4,6-TNT) and PCDDs are invariably lost through irreversible adsorption in the switching valves. Similar adsorption problems have been encountered with adsorbent-based sample collection / enrichment devices.<sup>5</sup> To minimize the problem of irreversible adsorption a variety of modified adsorbents have been investigated.<sup>5-7</sup> However, a comprehensive evaluations of the adsorbent based sampling devices and their overall efficacy for nitroaromatic compounds are not available in the literature. Based on available literature one can conclude that sampling and enrichment devices should be constructed without carbon-containing rotor switching valves to minimize the adsorption effects.

The present study was initiated to design a rapid sampling and enrichment device for nitroaromatic and other adsorptive semivolatile compounds. The specific objectives of the study were:

- examine adsorption problems encountered in sampling and analyzing adsorptive solutes such as nitroaromatic explosive, PCDDs and PAHs
- design a low volume, inert device for rapid sampling and enrichment of organic vapors,
- evaluate the applicability of the device for rapid and efficient detection of nitroaromatic explosives PCDDs and PAHs in air at ultra trace levels.

### Experimental

The stated objectives were met through a comprehensive set of experiments. The experiments involved the assembly of a tandem gas chromatographic system, a vapor generator design, and the fabrication and evaluation of a sampling device.

**Adsorption Experiments:** The adsorption characteristics of chlorinated dioxins and nitroaromatic explosive compounds were examined with the aid of tandem gas chromatographs (GCs). The system consisted of the two bench top gas chromatographs (a Model 8410 and a Model 8500, Perkin-Elmer Corp. Norwalk, CN). The GCs were interfaced to each other through a heated transfer line maintained at 210°C. Introducing known amounts of analytes into a fused silica capillary column (15-m x 0.25mm (I.D.) with 95% methyl - 5% phenylsiloxane stationary phase) in the first GC monitored the adsorption characteristics of selected analytes. The column was extended through a heated transfer line into the second GC where it was connected to an 80mm x 3mm (I.D.) tube. The tubes made from four test materials: borosilicate glass, Teflon, stainless steel, and aluminum were used during the study. The extent of analyte losses through adsorption on each material was determined at different temperatures.

**Sampling and Enrichment Device:** A schematic of the sampling and analyte enrichment device is shown in Figure 1. The two concentric capillary tubes placed in a heated block formed the core of the device. The inner capillary was a 0.4mm O.D. (0.25mm I.D.) deactivated fused silica tubing. The outer capillary was a 0.8 mm O.D. (0.53mm I.D.) deactivated fused silica capillary. The capillary tubes were obtained from Supelco, Inc. (Supelco Park, PA). Air sample

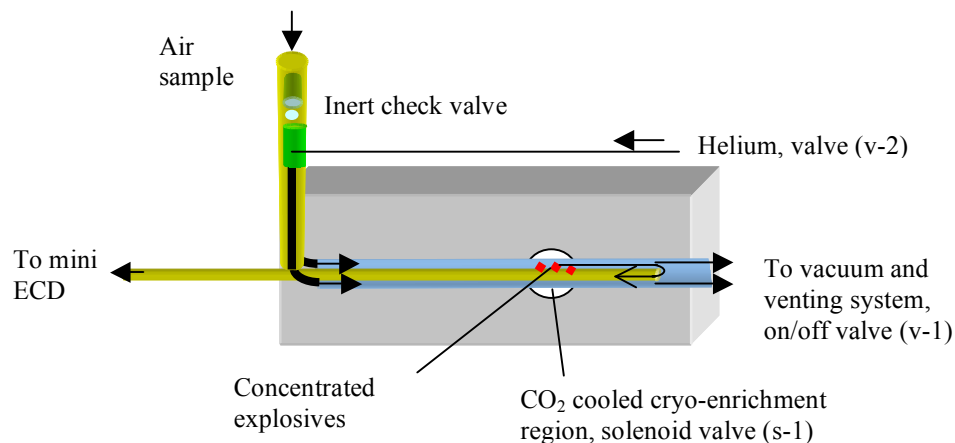


Figure 1. A schematic of the low mass, low-volume enrichment device.

was drawn through the outer capillary via the borosilicate glass one-way valve fabricated in our

laboratory. The exit end of the outer capillary was connected to a shut-off valve, which, in turn, was connected to a vacuum pump. The input end of the inner capillary was recessed from the exit end of the outer capillary. The other end of the inner capillary was connected to a low volume (250 $\mu$ L) electron capture detector (m-ECD) designed in our laboratory or a quadrupole mass spectrometer. A short length of the concentric capillaries was exposed to compressed CO<sub>2</sub> through a 2.2-mm port. The port was connected to a 2mm ID stainless tube, which served as the conduit for compressed CO<sub>2</sub> during the analyte trapping cycle. Analytes were trapped in a small part of the inner capillary volume. The active trap volume was estimated to be ~210nL. At the end of the trapping and purge periods, the vacuum and CO<sub>2</sub> flow were shut off and the trapped analytes were volatilized and carried to a detector with helium. The entire trap assembly was enclosed in a thermostatic aluminum block. The block was wrapped in a ceramic-insulating blanket.

Vapor Generator: Evaluations of the sampling and analyte enrichment device were carried out with a vapor generator capable of providing a gas stream with a known concentration of analyte. The evaluation experiments were carried out with 2,6- DNT, TNT and selected PCDDs. The analyte enriched gas stream was produced by equilibrating the generator chamber's air with vapors emanating from analyte coated 2mm borosilicate glass beads. Two generators a 150mL stainless steel cylinder or a 4L gas-tight glass bottle were utilized.

### Results and Discussion

Characterization of Hazardous Chemical Adsorption: Adsorption of analyte molecules in the sampling train can cause anomalies during the quantitative determination of adsorptive semi-volatile organics in air through analyte loss and cross contamination. During the present study, it was observed that whenever an adsorptive analyte come in contact with a polyimide-carbon rotor the signal for compounds was dramatically reduced. The results of one such experiment showed that nearly all of TNT and approximately 80 percent of DNT were lost due to the irreversible adsorption on the switching rotor. An extended evaluation of OCDD and DNT adsorption on several different materials was carried out with the tandem GC system. The results showed that the adsorption losses were dependent on the material. For example, even at temperatures as low as 60°C only a minor amount of DNT was lost to irreversible adsorption in the borosilicate glass. By contrast, nearly 60% of DNT remained adsorbed on aluminum even at temperatures as high as 230°C. The adsorption losses in the stainless steel tube was significantly lower, at elevated temperatures, e.g., only about 40% of the analyte remained adsorbed at temperatures above 180°C. The superior transmission of DNT molecules through borosilicate glass is clearly evident. These results clearly indicate that selection of materials for construction of sampling and enrichment devices is very important for the detection of adsorptive semivolatiles in air.

Sampling and Enrichment Device: The results of the adsorption study lead to the design of a sampler and cryogenic concentrator shown in Figure 1. The salient features of the design are a small void volume (210nL), low mass, and absence of switching valves and other highly adsorptive surfaces. The device was evaluated with low concentrations of PCDDs, PAHs and nitroaromatics air. The contaminated air samples were obtained from the vapor generator. The analyte vapors in the air were trapped for preselected sampling periods. The duration of the sampling period was based on the concentration of the analyte in air, detection limit of the monitoring device, and the desired duty cycle. A compact quadrupole mass spectrometer and an electron attachment detector were used as the monitoring devices. Signal of these devices is adversely affected by air and successful detection of nitroaromatics in air is feasible only when air (oxygen) is essentially absent from the gas stream entering the detector. In the present design the

oxygen is purged out of the system with an inert gas such as nitrogen or helium before the trapped analytes were desorbed.

The borosilicate check valve offers two advantages over switching and solenoid valves. First, the glass valve is less prone to analyte adsorption. The second, the check valve permits rapid purging of the trap volume with inert gas and thus minimizes cross-contamination between samples. Very high cross contamination was observed when the borosilicate check valve was replaced with a three-way switching valve. The low volume and low mass of the cryo-concentrator when coupled with the high sensitivity of the mini-ECD detector and MS operating in the selected ion-monitoring mode yielded reproducible and quantitative output for very low concentrations of semi volatile analytes. Reproducible results for 500 femtograms of DNT in air were readily obtained. The cryogenic cooling in the small inter-capillary volume permits nitroaromatic vapor enrichment and focusing.

The sample enrichment obtained with the device is a function of four parameters shown in equation 1.

$$E_f = \frac{\text{concentration of DNT in detector gas stream}}{\text{concentration of DNT in sampled air}} = \frac{S_r \times S_t}{V_t \times T_v \times D_r} \quad \text{Eq. 1}$$

where  $S_r$  is the air sampling flow rate,  $S_t$  is the sampling time,  $V_t$  is the trap volume,  $T_v$  is the volatilization time, and  $D_r$  is the gas flow rate through the detector. The signal obtained with the device is a function of the concentration of the analyte-entering detector and is inversely related to the trap volume. Furthermore, the cryogenic focusing with the low inter-capillary volume lead to sharp peaks and improved the detection limits. The low volume of the present trap gave a high enrichment factor ( $1.4 \times 10^5$ ) and ensured good signal to noise ratio for analyte amounts at sub picogram levels. The device can be used in combination with micro ECD or MS for on-line determination of variety of semivolatiles including PCDDs and nitroaromatic explosives.

#### Acknowledgments

This material is based upon work supported in part by the U.S. Army Research Office under contract DAAG55-97-1-0014.

#### References

1. M. J. Cohen and R.W. Crave, US Patent 3,742,213, 1973.
2. D. E. Willis, *Adv. Chromatography*, 28, pp 65-125, 1989.
3. M. A. Klemp and R. D. Sacks, *Journal of Chromatographic Science*, 29, pp 114-121, 1991.
4. D. W. Grant, "Capillary gas chromatography", Chishester, N.Y., 1996
5. D. P. Raunbehler, et al., US Patent 5,551,278, 1996.
6. A. Dravnieks and M.J. Salkowski, U.S. Patent 3430482 690304.
7. R. F. D. Bradshaw, *Platinum Met. Rev.*, pp 129-132, 1977.
8. F. J Conrad, T. A Burrows, and W. D Williams, *Journal of Chromatography*, pp 37-41, 1979.
9. M.A. Klemp, M. L. Akord, and R.D. Sacks, *Analytical Chemistry*, pp 2516-2521, 1993.
10. S. Jacobsson, *J. of High Resolution Chromatography & Chromatography Communications*, pp 185-190, 1984.
11. D. R. Deans, *Chromatographia*, pp 18-22, 1968.
12. R., Annino and J. Leone, *Journal of Chromatographic Science*, 20, pp 19-26, 1982.
13. R. L Wade, and S. P. Cram, *Analytical Chemistry*, 44, pp 131-139, 1972.
14. N. S. Arnold, W. H. McClennen, and H. L. C. Meuzelaar, *Analytical Chemistry*, 63, pp 299-304, 1991.