Transactions on Ecology and the Environment vol 21, © 1998 WIT Press, www.witpress.com, ISSN 1743-3541

Development of a thermoelectric cold trap system for use in the analysis of trace atmospheric compounds

Anna Scrugli
Consorzio Ricerche Associate, C.P. 234, Trav. 2 °Strada Est, I-09032 Assemini (Cagliari) Italy
Email: scrugli.softec@interbusiness.it
Michael Holdren, Scott Danhof, Michael Grassi, Joseph Stets, William Keigley & Victor Woodruff
Battelle, 505 King Avenue, Columbus, OH 43201 U.S.A.
Email: holdren@battelle.org

Abstract

A prototype of a thermoelectric cold trap system has been designed, built and evaluated. The unit is used to preconcentrate trace atmospheric compounds prior to analysis. The thermoelectric cold trap unit provides an alternative to the liquid nitrogen cooled traps normally used as a means to preconcentrate sampled components. The thermoelectric system is especially applicable in field monitoring programs, where logistical burdens are often encountered when supplying large amounts of liquid cryogens. Likewise, one does not have to be concerned with the expense and downtime associated with the use of liquid cryogens. The thermoelectric cold trap assembly can be easily interfaced with any chromatographic system using a two position six-port valve. The operating principle is based upon the normal sample adsorption/desorption cycle and GC analysis. In this study we report on the trapping and release efficiency using low ppb levels of targeted volatile organic compounds (VOCs).

Introduction

Many of the volatile organic compounds (VOCs) found in ambient air are present at very low parts per billion (ppb) and parts per trillion (ppt) levels. To identify and quantify these species, researchers must employ collection techniques that preconcentrate sufficient amounts of these materials for analytical detection.

The use of cryogenic trapping to concentrate VOCs prior to analysis has been established as a proven technique for VOC monitoring (1-5). This method involves collecting the sample on an inert material (e.g. glass beads) at subambient temperatures. The temperature of the trap is below the condensation temperatures for trace VOCs but above the condensation temperature for major constituents of ambient air (e.g. nitrogen, oxygen). After collection, the trap is rapidly heated, the VOCs are desorbed, and typically the compounds are analyzed using a gas chromatographic (GC) system.

An alternative trapping method involves the use of adsorbent materials to collect VOCs at ambient temperatures. Popular adsorbents include Tenax-TA, silica gel, carbon molecular sieves, and activated charcoal. Desorption again is accomplished by elevating the trap temperature prior to GC analysis. Deficiencies reported with monoadsorbent traps are their inability to completely collect and/or desorb samples possessing a wide range of molecular weights, and the presence of artifact materials (6,7). By using selected adsorbents in a multi-bed trap configuration, collection devices can be tuned to capture a wide range of compounds with minimal artifact interferences.[8-10]

Following sample collection and desorption, chromatographic peak resolution is further enhanced by refocusing the desorbed material onto the head of the analytical column. To accomplish this task, cryogenic refocusing devices are required. Commercial units employing cryogens are available and connect directly to the inlet of the analytical column (11-13). Novel approaches that make use of closed cycle coolers and/or thermoelectric devices have also been developed (14,15). Alternatively, some operators make use of gas chromatographs that are equipped with sub-ambient oven accessories and cool the entire column.

Typically, liquid cryogens such as nitrogen or carbon dioxide are used to cool the sample collection trap and to refocus desorbed material onto the head of the column. However, large amounts of cryogen are consumed during normal operations and result in added expenses and inconveniences of changing out cylinders. Likewise, logistical burdens are often encountered in moving the cryogens from the point of delivery to their final destination. Safety is also a major concern when carrying out handling operations.

Several commercial gas chromatographic systems have been recently designed to automatically preconcentrate volatile organic compounds and analyze the enriched samples (11-13). All units, except one, make use of a liquid cryogen to facilitate operations (15). The non-liquid cryogenic GC system utilizes a thermoelectric means to cool the collection trap. However, this device is an integral part of the GC system, and can not be transferred to a different GC.

Thermoelectric modules are small solid-state heat pumps, ranging in size from that of a fingernail to over 5 cm square. They move heat from one area to another, thus creating a temperature differential. The thermoelectric module is made up of an array of semiconductor couples connected electrically in series and thermally in parallel. When a DC potential is applied, heat is absorbed on one side of the module, thus cooling it, while heat is rejected on the other side, where the temperature rises. This phenomenon is known as the Peltier effect. With careful attention paid to the thermal isolation of cold side surfaces, minimization of thermal losses, and promotion of heat transfer away from the hot side of the thermoelectric module, we designed a stand-alone cold trap assembly.

Thermoelectric Cold Trap System

The thermoelectric cold trap system includes three key components: (1) a cold trap module, (2) an adsorbent tube heater that is inserted into the cold trap module, and (3) an electronics package to control operations. Design goals for our work, based on standard VOC field measurement procedures, were as follows:

- Achieve a target cold set point temperature of –30 ± 5 C
- Achieve a target hot set point temperature of 300 ± 5 C
- Heat the adsorbent tube from –30 to 300 C in less than 20 seconds
- Cool the adsorbent tube from 300 to –30 C in less than 10 minutes
- Minimize the size of the cold trap module (i.e. ~ 15 x 15 x 15 cm) so that it could easily interface to a two position six-port valve on any gas chromatographic system.

These goals were easily achieved, and the design aspects of the thermoelectric cold trap system are discussed elsewhere (16). The purpose of this paper is to report on chemical testing of the cold trap system.

Chemical Testing

Chemical testing was carried out to evaluate the performance of the thermoelectric cold trap system as a preconcentration device. Two series of chemical tests have been conducted to date. In the first series of tests, a target set of seven volatile organic compounds was chosen that included the common C_2 through C_4 hydrocarbons. These compounds were targeted because they are very volatile and therefore difficult to capture with a preconcentration cold trap system (17). These compounds are also ubiquitous in urban atmospheres at concentrations of a few ppb. Furthermore, these compounds are among the most volatile of the ozone precursor compounds that are currently being measured in the United States by State agencies at Photochemical Assessment Monitoring Stations (PAMS).

Preliminary results are also reported for a second series of chemical tests, which included the 41 compounds listed in the U.S. EPA TO-14 Methodology. This list primarily includes halogenated organics ranging in volatility from dichlorodifluoromethane through hexachlorobutadiene.

Methodology

The gas chromatographic systems that were assembled for chemical testing were equipped with flame ionization detectors (FID). The detector output signal was connected to a personal computer running state-of-the-art GC software. For the C_2 through C_4 chemical tests, the following operating conditions were used:

- Separation was accomplished using an aluminum oxide (Al_2O_3) PLOT capillary column (Chrompack), 50 m long by 0.32 mm i.d. Analytical separation for the compounds of interest was obtained using a temperature program of –30°C to 120°C with an initial hold of two minutes and a ramp of 15°C/minute. Zero grade nitrogen with a flow rate of 4 cm^3/min constituted the carrier gas. The FID gases were ultra zero air (300 cm^3/min) and ultra zero hydrogen (30 cm^3/min).
- The adsorbent trap was a fused silica lined stainless steel tube (25 cm by 0.2 cm i.d.) that is packed sequentially with two adsorbents. The first adsorbent was ~0.02 grams (2 cm long) of Carbopack B (60/80 mesh) and the second material was ~0.02 gm (1 cm long) of Carbosieve S-III (60-80 mesh). The temperature of the adsorbent

trap during sample collection was -30°C. The temperature during thermal desorption was 250°C.

For the preliminary test runs of the TO-14 mixture, the following conditions were used:

- Separation was carried out using a CP-Sil 5 capillary column (Chrompack), 60 m long by 0.53 mm i.d. A temperature program of -50°C to 200°C, with an initial hold of 2 minutes and a ramp of 8°C/minute. Zero grade helium served as the carrier gas (7 cc/min).
- The adsorbent trap was a stainless steel tube (25 cm by 0.16 cm i.d.) that was packed with 0.04 grams of 60/80 mesh Carboxen 569 (~3 cm long). The temperature of the adsorbent trap during sample collection was -30°C. The temperature during thermal desorption of the trap was 300°C.

Sample flow through each trap was controlled using: (1) a mass flow controller/readout unit and (2) a vacuum source (e.g. diaphragm pump). The sample flow rate was controlled at 20 cc/minute with a collection time (load time) of five minutes, thereby resulting in a sample volume of 100 cm^3.

Each trap was installed so that during thermal desorption, the trapped VOCs were backflushed off the trap. Each trap was connected to a two-position VICI six-port valve, which in turn was interfaced to the GC.

For the C_2 to C_4 mixture, we prepared a calibration cylinder with each compound at a nominal concentration of 1 ppm (± 5%), in high purity nitrogen. A dynamic dilution system was then used to dilute the calibration standard using ultra zero air as the diluent. For the TO-14 mixture, a cylinder from Liquid Air was purchased with each component at 1 ppm (± 10%). Dilute calibration standard was statically prepared using 6-liter glass-lined stainless steel canisters. Humidified (~90% RH) zero grade air was used as the diluent.

Test Results

C_2-C_4 Hydrocarbons

Multipoint calibration curves were generated using a calibrated 1.18 cm^3 sample loop as well as with the preconcentration cold trap. Very good linearity was obtained for all seven compounds as indicated by correlation coefficients of 0.99 or better. The instrument noise level corresponded to 600 ± 200 area units. Using a signal-to-noise ratio of 3 as the minimum detection level (MDL), the MDL was 100 ± 30 ppbC for all seven compounds when sampling with a 1.18 cm^3 loop. The calibration curve with the loop samples ranged from 100 ppbC to 1000 ppbC. The cold trap calibration levels ranged from 20 ppbC to 100 ppbC. Using a MDL of three times the noise level (1800 area units), a MDL of 1 ± 0.3 ppbC was observed when sampling with the cold trap and preconcentrating 100 cm^3 of air.

Comparison chromatograms at a nominal challenge concentration of 100 ppbC are shown in Figure 1. The chromatogram on the left was obtained with a 1.18 cm^3 sample loop. The chromatogram on the right was obtained with a preconcentrated volume of 104 cm^3.

Collection/recovery efficiencies were determined using experimentally measured sample loop (1.18 cm^3) and cold trap (104 cm^3) volumes, and the corresponding signal responses from the challenge concentrations. These results are shown in Table 1. The loop area response is that amount measured when the sample loop is challenged with the undiluted cylinder mixture of the seven targeted compounds (nominally 1 ppm ± 10%). The trap area response results when the cold trap is challenged with three diluted levels of the cylinder mixture. The percent recovered is determined by the measured trap/loop ratio divided by the product of the dilution factor and the enrichment factor. As the data indicate, for the three preconcentration runs the amounts recovered with the cold trap were essentially 100 percent (100 ± 3%).

Table 1. Collection/recovery efficiencies for target compounds (average of 3 runs)

Compound	Amount Recovered (%)
ethane	98 ± 3
ethylene	102 ± 3
propane	101 ± 1
proypylene	105 ± 2
isobutane	101 ± 1
n-butane	100 ± 1
acetylene	95 ± 6

TO-14 Compounds

Collection/recovery efficiencies were also determined for the TO-14 compounds. Preconcentrated samples of the TO-14 standard prepared

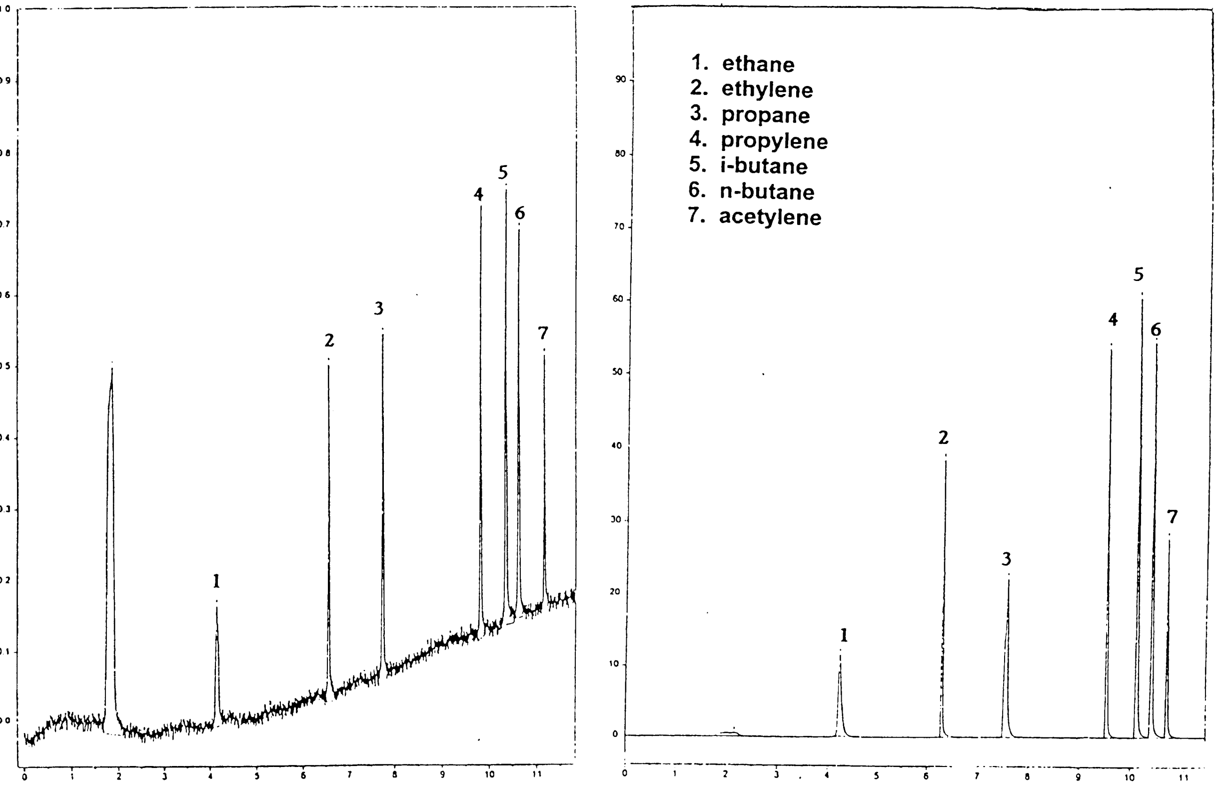

Figure 1. Chromatograms at a nominal challenge concentration of (loop on the left versus trap on the right)

at two dilution levels (8 ppb and 16 ppb) were analyzed and those peak responses were compared with values obtained from the analysis of the 1 ppm standard directly (e.g. 1 cc loop sample). Preliminary results indicate reasonably good collection/recovery efficiencies for most of the TO-14 compounds. Figure 2 shows a chromatogram from the analysis of the diluted TO-14 mixture (16 ppb). Recoveries generally ranged from 90 to 100%. There were several exceptions. Abnormally high recoveries were obtained for dichloromethane (170 and 600%). We also use dichloromethane as a solvent in our laboratory facility and suspect that contamination of our dilution mixtures may have occurred. Low recoveries were also observed for 1,2,4-trichlorobenzene and hexa-chlorobutadiene (~50%). These compounds are the least volatile of the TO-14 mixture. We believe that because these two compounds are more strongly retained by the Carboxen 569 adsorbent during sample collection, the 300°C desorption temperature may not have been sufficient to allow for complete thermal desorption.

We are continuing work efforts to optimize the system for TO-14 compounds. In the near future we plan to conduct air sampling in urban and rural environments on the island of Sardegna.

Summary

A thermoelectric cold trap system has been designed and has been shown to successfully preconcentrate air samples containing volatile organic compounds. The thermoelectric cold trap system included a cold trap module, an adsorbent tube heater that is inserted into the cold trap module and an electronics package to control operations. The system easily met the following criteria:

- A target cold set point temperature of –30 ± 5 C
- A target hot set point temperature of 300 ± 5 C
- Transition from –30 to 300 C in less than 20 seconds
- Transition from 300 to –30 C in less than ten minutes
- Small size of the cold trap module (i.e. ~ 15 x 15 x 15 cm).

The prototype system was also shown to be easily interfaced to any gas chromatographic system that is equipped with a two-position six-port sampling valve and electronic actuator.

Chemical testing was carried out with a target set of seven C_2 to C_4 hydrocarbons as well as with the TO-14 calibration standard. Experimental results showed good recoveries for most of the VOCs, (≥ 90%). The two least volatile compounds (1,2,4-trichlorobenzene and hexa-chlorobutadiene) showed recoveries of ~50%. We suspect

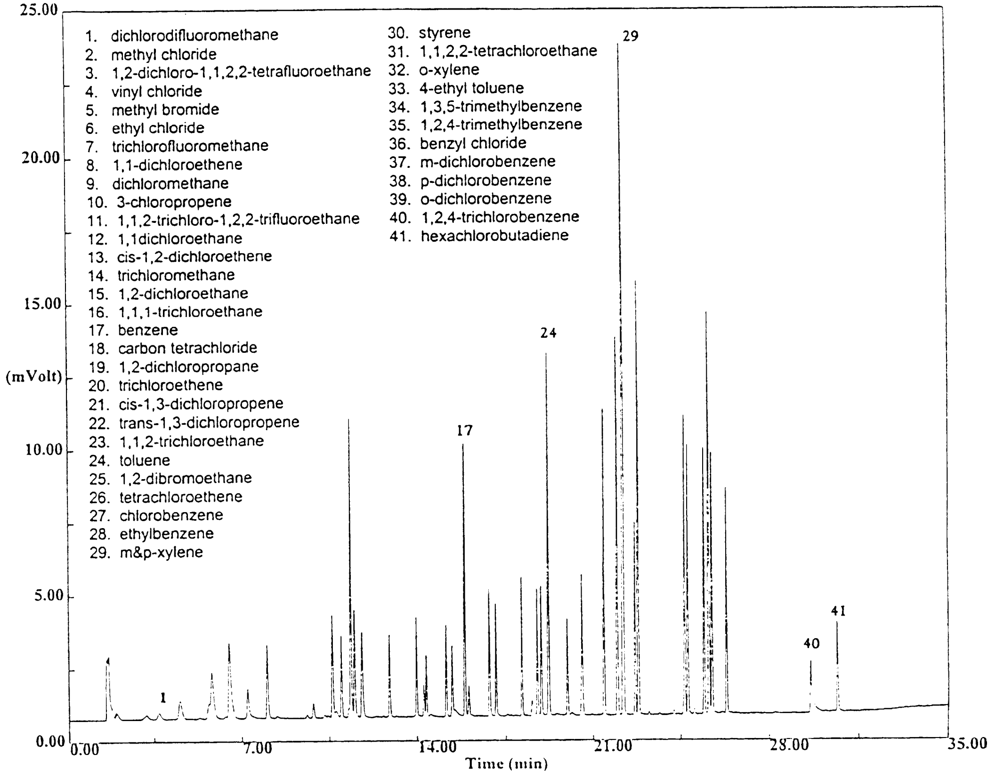

Figure 2. Chromatogram of TO-14 mixture at 16 ppb

that increased desorption temperatures and time are needed to improve these results.

References

[1] Rasmussen, R. A.; Harsch, D. E.; Sweany, P. H., *JAPCA*, **27**, 579, 1977.

[2] Farwell, S. O.; Gluck, S. J.; Bamesberger, W. L.; Schuttle, T. M.; Adams, D. F., *Anal. Chem.*, **51**, 609, 1979.

[3] Westberg, H; Lonneman, W.; Holdren, M., *Identification and Analysis of Organic Pollutants in Air*; L. H. Keith, Ed., Butterworth Pblishers; 1984.

[4] McClenny, W. A.; Pleil, J. D.; Holdren, M. W.; Smith, R.N., *Anal. Chem.*, **56**, 2947, 1984.

[5] Holdren, M.; Rust, S.; Smith, R.; Koetz, J., *EPA-600/4-85-002*, a final report on Contract 68-02-3487 from Battelle to U.S. Environmental Protection Agency, Research Triangle Park, NC, 1985.

[6] Brown, R. H.; Purnell, C. J., *J. Chrom.*, **178**, 79, 1979.

[7] Pellizzari, E.; Demian, B.; Krost, K., *Anal. Chem.*, **56**, 793, 1984.

[8] Pollack, A., J.; Holdren, M. W.; McClenny, W. A., *J. Air & Waste Manage. Assoc.*, **41**, 1213, 1991.

[9] McClenny, W. A.; Oliver, K. D.; Daughtrey, H. E., *J. Air & Waste Manage. Assoc.*, **45**, 792, 1995.

[10] Kelly, T. J.; Callahan, P. J.; Pleil, J. D.; Evans, G. F., *Environ. Sci. Technol.*, **27**, 1146, 1993.

[11] Entech Instruments Inc. (www.entechinst.com).

[12] Tekmar-Dohrmann Company (www.tekmar.com).

[13] Graseby-Nutech Company (www.graseby.com).

[14] Bertman, S. G.; Buhr, M. P.; Roberts, J. M., *Anal. Chem.*, **65**, 2944, 1993.

[15] Perkin-Elmer Corporation (www.perkin-elmer.com).

[16] Submitted to Anal. Chem., 1998.

[17] Tang, Y., Tran, Q, Fellin, P., Cheng., W., Drummond, I., *Anal. Chem.*, **65**, 1932, 1993.