Journal of Chromatography, 329 (1985) 399–405
Elsevier Science Publishers B.V., Amsterdam — Printed in The Netherlands

CHROM. 17 848

Note

Precolumn sample enrichment device for analysis of ambient volatile organics by gas chromatography–mass spectrometry

ROBERT R. ARNTS
Atmospheric Sciences Research Laboratory, U.S. Environmental Protection Agency, Research Triangle Park, NC 27711 (U.S.A.)
(Received April 22nd, 1985)

Gas chromatographic–mass spectrometric (GC–MS) identification of air pollutants generally requires a preconcentration step to provide sufficient sample for analysis. Cryogenic trapping is often used to enrich the sample since nitrogen and oxygen are not condensed[1,2]. It does, however, concentrate enormous quantities of water and carbon dioxide, sufficient to plug high-resolution, narrow-bore capillary columns necessary for separation of complex environmental samples.

A current technique popular for the collection of air pollutants is to adsorb organics in the field by drawing air through a cartridge packed with a solid sorbent, such as Tenax GC or XAD-2[3–9]; the cartridge is then returned to the laboratory for GC–MS analysis. In our laboratory we often collect whole air samples in stainless-steel containers or Tedlar bags for analysis by GC with flame ionization detection (GC–FID). In order to provide identification of unknown peaks and confirmation of tentatively named peaks (based on retention times) the system described herein was designed and built to enrich samples for GC–MS analysis of volatile organics. The preconcentration system consists of a solid sorbent trap and a cryogenic trap used in sequence to collect organic vapors and focus them for analysis by GC–MS.

EXPERIMENTAL

Apparatus

The first-stage trap (see Sorbent trap, Fig. 1) is a nickel 200 tube (5 in. × 5/8 in. O.D. × 1/16 in. wall thickness) packed with 2.1 g of Tenax-GC, 60/80 mesh (Alltech Assoc., Deerfield, IL, U.S.A.). The adsorbent is held in place by plugs of silanized acid washed glass wool (Analabs., North Haven, CT, U.S.A.). Connections to the Tenax cartridge are made via Swagelok fittings. The cartridge and its fittings are encased in an aluminium block, which can be rapidly heated. One end of the cartridge is connected to the common port of a three-way PTFE electric solenoid valve, V_1 (1/8-inc. orifice, Model DV3 122A1, Fluorocarbon Co., Anaheim, CA, U.S.A.). The normally closed (NC) port is connected to a female Quick connect (SS-QC4-B1-400, Swagelok, Cleveland, OH, U.S.A.) to facilitate rapid, clean sample introduction. The normally open (NO) port is connected to port 5 of a 6-port gas sampling valve (Seiscor Model VIII HT, Seismograph Co., Tulsa, OK, U.S.A.). The

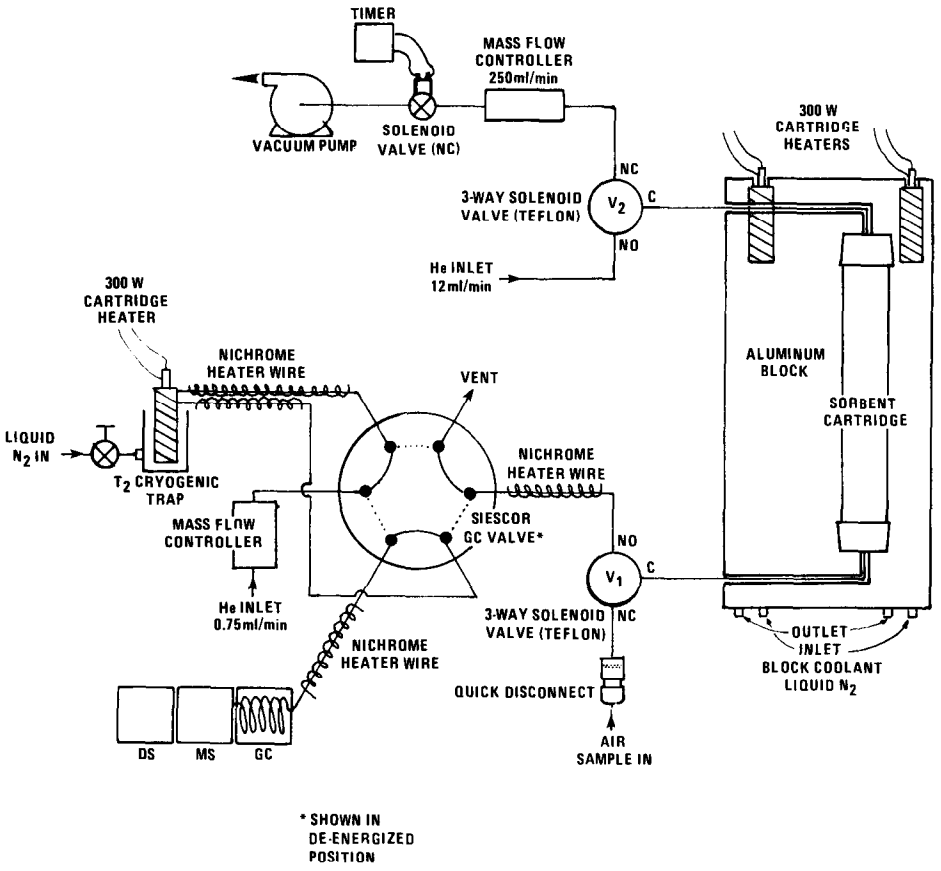

Fig. 1. Diagram of enrichment device.

other end of the adsorbent cartridge is connected to the common port of another three-way PTFE solenoid valve, V_2. The NC port of V_2 is connected to a vacuum pump via a mass flow controller (0–500 ml/min, Model 5850, Brooks Instruments, Hatfield, PA, U.S.A.) and a two-way NC solenoid valve. The NO port of V_2 supplies helium to backflush the cartridge.

The second-stage cryogenic trap is connected across ports 1 and 4 of the gas sampling valve. The trap consists of 20 in. of 0.05 in. I.D. × 1/16 in. O.D. type 316 stainless-steel tubing packed with 60/70 mesh glass beads held in place with glass wool plugs. In order to facilitate rapid heating and cooling, the trap is wrapped in a spiral groove around a 1.25 × 0.5 in. O.D. aluminum cylinder, the center of which contains a cartridge heater (250 W); the base of the cylinder is anchored inside a small metal cup, which can be supplied with liquid nitrogen. The trap assembly is wrapped with woven fiberglass to provide thermal insulation.

Port 2 of the gas sampling valve is connected to the helium carrier supply via a mass flow controller (0–10 ml/min, Model 5850, Brooks Instruments, Hatfield, PA, U.S.A.). Port 3 is connected to the GC capillary column using a capillary butt con-

nector with Vespel ferrule (Cat. No. 2-3796, Supelco, Bellefonte, PA, U.S.A.). Port 6 is a vent open to the atmosphere.

Temperature control of the system is accomplished through a modified Nutech 320 thermal desorption system control module (Nutech, Durham, NC, U.S.A.). The unit monitors temperatures of the adsorption cartridge block, GC sampling valve, and cryogenic trap via type K chromel-alumel thermocouples and compares their temperatures with those set on the controller; power is supplied to the cartridge heaters to achieve the desired temperature. The adsorbent cartridge block is heated by eight 300-W, 5 × 1/4 in. O.D. cartridge heaters. Post-desorption block cooling is achieved by flowing liquid nitrogen through a series of passages in the block. The GC valve is heated by a 215-W, band-type heater (500-2D-P-215 W-240V, Thermal Co., Huntsville, AL, U.S.A.). Modifications to the Nutech controller included replacement of solid state relays with heavy duty relays to handle the cartridge and band heater power requirements. Also, the original internal solenoid valve used for controlling nitrogen to the trap was replaced with an external cryogenic type solenoid valve (Cat. No. 826 320 511, Automatic Switch Co., Florham Park, NJ, U.S.A.) for metering liquid nitrogen to T_2. Lastly, all sample transfer lines from introduction to the column connection inside the GC oven are wrapped with insulated heating wire, and power is supplied by a variac.

The preconcentration system was tested using a bench-top Hewlett-Packard 5992a gas chromatograph–mass spectrometer. Separations were performed using a 30 m × 0.25 mm I.D., DB-1 fused-silica capillary column with a 1-μm bonded film (J&W Scientific, Rancho Cordova, CA, U.S.A.). The column effluent was introduced to the ion source without splitting or separation. All analyses were performed using a GC temperature program of −50°C isothermal for 10 min followed by heating at 8°C/min to 200°C and a hold.

Procedure

The procedure required to preconcentrate a given analyte or analytes is dictated by the properties and concentration of the analyte(s) and the solid sorbent chosen to retain them. For ambient air samples the major criteria for selecting a sorbent are (i) the ability to quantitatively retain and thermally release the analyte(s) and (ii) low water and carbon dioxide retention. In addition, the sorbent should have low bleed, good thermal stability, and inertness to the sample matrix. The sorbent chosen for this study was the porous polymer Tenax-GC. The minimum quantity of sorbent required is governed by the breakthrough volume of the analyte, the concentration of the analyte in the sample, and the minimum quantity of anlyte required by the mass spectrometer for a clean spectrum (approximately 10 ng in these experiments).

To calculate the minimum quantity of sorbent required, the volume of air to be sampled (V_s) is calculated. This is obtained by dividing the minimum quantity of analyte required by MS by the estimated concentration of the analyte in the sample. Sufficient sorbent must be used to retain most of the analyte without breakthrough. This can be estimated from gas chromatographic retention volume (V_g) data. Published sources of these data for numerous sorbents are available[6,7,10–13]. To calculate the amount of sorbent required (S_{50}), the sample size (V_s) is divided by the retention volume (V_g). However, use of S_{50} will result in 50% breakthrough of the analyte.

For our device we chose to use at least 2 × S_{50} to ensure efficient analyte retention for the most volatile of the analytes.

In preparation for preconcentrating a sample the sorbent is heated to its temperature limit with helium backflush (V_1 and V_2 in unenergized NO position). For Tenax in this system, 275°C for about 30 min at 12 ml/min of helium is sufficient to desorb and flush most contaminants. The sorbent block is then cooled to 25°C for sampling. The bag or can to be analyzed is connected to the sample-in of V_1. To draw the sample through the sorbent, V_1 and V_2 are energized. In our system the maximum controlled sampling rate is about 250 ml/min. The total volume sampled as noted above is dictated by the quantity required to collect about 10 ng of analyte. If the objective is to characterize the sample in general, rather than target a specific analyte, then roughly 10–20 l of samples will provide identification of components seen in a similar capillary column GC–FID analysis of a 500-ml sample.

Upon completion of sample collection, V_1 and V_2 are de-energized, allowing helium to backflush the sorbent. This is necessary to purge water from the sorbent. Tenax, which has a low affinity for water, retains quantities of water large enough to plug a cold capillary column. Based on retention volume data[13] water should take about 7 min to elute. However, experience has shown that approximately 30 min are required to thoroughly purge the sorbent and its associated plumbing of water.

At 26 min into the water-purge cycle, cooling of the cryogenic trap is initiated. Within 4 min the trap is cooled to −196°C by liquid nitrogen. The Seiscor valve is then activated to route the Tenax effluent to the cryogenic trap. Simultaneously, the sorbent heater block is rapidly heated to the chosen set point (up to 350°C). The desorption temperature selection is based on the retention volume of the least volatile analytes. Lower temperatures are preferable to minimize analyte reactions and also to minimize sorbent degradation. In our system desorption was typically performed at 250°C for 30 min. This resulted in a helium purge of 360 ml.

At 26 min into the desorption cycle the chromatographic oven is cooled to −50°C. After the full 30 min have elapsed and the GC oven has stabilized at −50°C the Seiscor valve is switched to put the cryogenic trap in-line with the capillary column. Simultaneously, the temperature program of the GC–MS system is activated, and the cryogenic trap is flash heated to 300°C. The capillary column is held at −50°C for 10 min, concentrating analytes on the head of the column. This completes the preconcentration operation of the system. The procedure can be modified to suit use of different sorbents, more or less volatile analytes, and reactive analytes.

RESULTS AND DISCUSSION

Fig. 2a and b shows the analysis of a typical rural air sample collected outside our laboratory at Research Triangle Park using, respectively, GC–FID and GC–MS with the total ion current monitor. The GC–FID analysis is the result of single stage cryogenic trapping of 500 ml of sample. Details of the analytical procedure are described elsewhere[14]. The GC–MS analysis is the result of trapping 11 l of the same air sample using the two-stage trapping system.

Both methods of analysis cover roughly the same range of volatility. The two-stage technique, however, loses some of the more volatile compounds when the sorbent is backflushed to elute the water. Also, compounds in this region are poorly

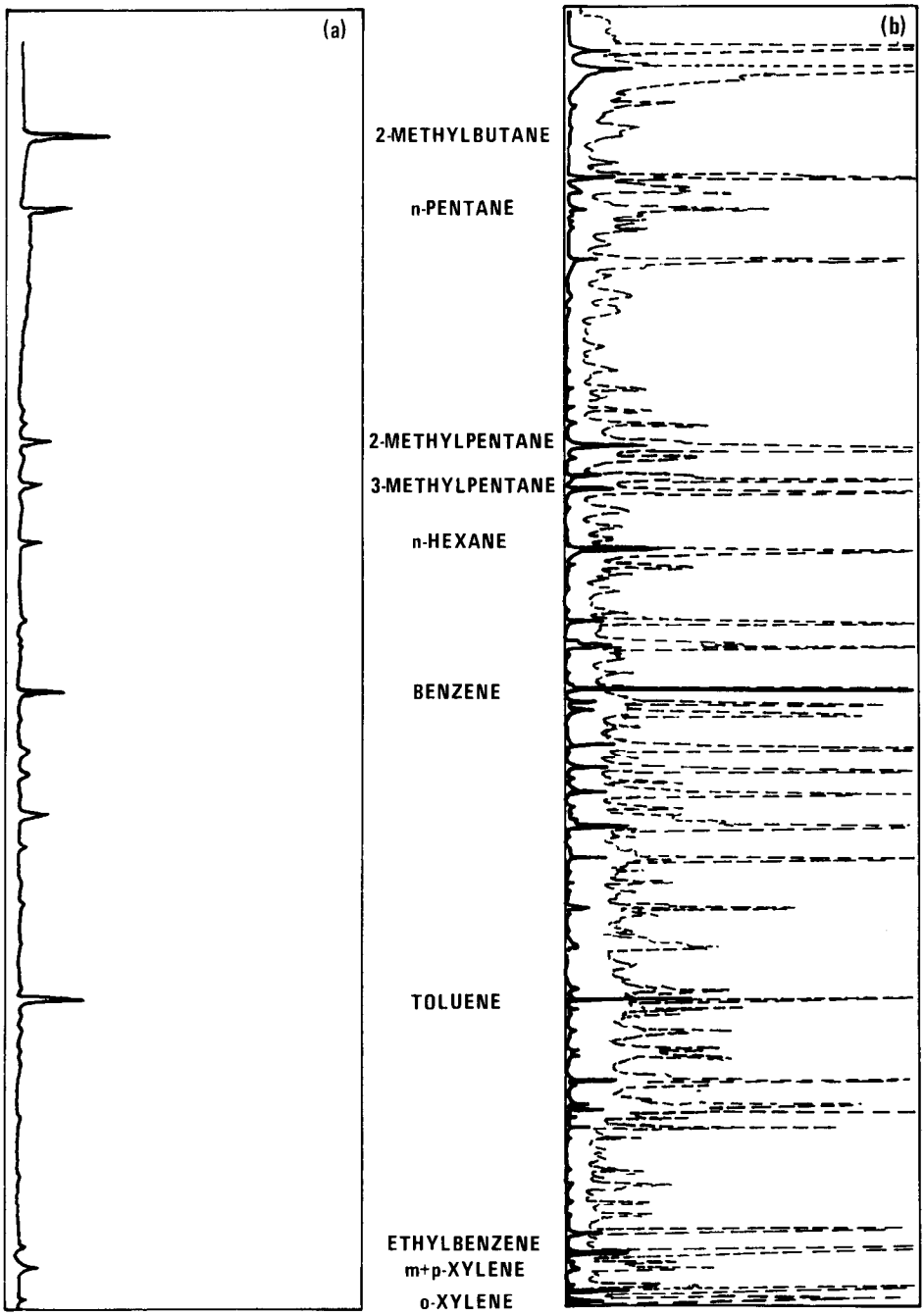

Fig. 2. (a) GC-FID chromatogram of 500 ml of ambient air; 9–23 min. (b) GC–MS total ion chromatogram (33–300 m/z) of 11 l of same air sample using precolumn enrichment device; 13–27 min.

retained by the Tenax-GC. Thus in the GC–MS run the most volatile compound seen is 2-methylbutane (b.p., 28°C). In the GC–FID analysis the earliest well-resolved analyte observed is propene (b.p., −47°C). This "blind spot" created by the water backflush is not a serious problem, since experience has shown that most of the unknown analytes occur at later retention times (in the less volatile range). The upper limit of compounds (high boilers) which are seen by the two stage trapping system is defined by the desorption temperature of the sorbent, the volume of helium used to desorb the Tenax, and the temperature of the valves, fittings, and transfer lines in the sample path. In the example shown in Fig. 2b the highest boilers observed are in the range of 234–245°C (*n*-tridecane and 2-methylnaphthalene). The minimum volume of helium required for desorption can be calculated or estimated from published retention volumes[12,13]. Equally important, the temperature of the sample path from the sorbent to the column head must be sufficient to prevent condensation and adsorption of the analyte. Thus the operating conditions of the preconcentration procedure can be tailored to allow quantitative collection and transfer of a desired analyte (consistent with the thermal stability of the analyte).

The system is relatively easy to maintain free of contamination, since it is designed to purge with carrier when not in use. Typically the sorbent can be baked out at or below its upper temperature limit to remove the most tenacious contaminants or residual analytes. To avoid thermal decomposition of the sorbent the temperature is then lowered to a lesser level (*i.e.*, 250°C for Tenax) or returned to ambient temperature. Note that helium carrier should be passed through a oxygen scrubber to prevent oxidation of the sorbent. A blank check of the system by collecting zero air in the prescribed manner reveals several significant peaks. The largest peaks are benzaldehyde at 27.94 min, an unknown at 29.76 min, and acetophenone at 30.32 min. Benzaldehyde and acetophenone have been seen by other investigators[15–16] and are attributed to oxidation of the Tenax. To a lesser degree, there are four C_8 alkenes eluting in the region after toluene, 24.32–24.56 min. The source of these is unknown. The appearance of these peaks in an actual sample is discounted.

It is difficult to precisely compare the response of the flame ionization detector to that of the mass spectrometer. The flame ionization detector responds to the total amount of carbon present in a given peak. However, the amount of analyte required to procedure a useable spectrum is more complicated. In general about 5 ng is adequate to produce a clean spectrum. As little as 0.1 ng may be sufficient for aromatics and halocarbons owing to their distinctive fragmentation pattern. In the example shown in Fig. 2 alkanes could be identified at amounts ranging from 0.6–3 ng while aromatics could be distinguished in the 0.1–0.6 ng range. This is equivalent to 0.1–0.9 ppbC* for alkanes and 0.02–0.1 ppbC for aromatics for an 11-l air sample. Since the FID limit of detection is on the order of 0.1 ppbC for a 500-ml sample, this is more than adequate for peak confirmation or identification. The primary method for spectrum identification in this system is a user-generated library. Compounds entered in this library were generated from samples of the pure compound run on the same capillary column. Retention times are also entered. The compounds selected are developed from lists of common industrial solvents, auto exhaust components, and

* Throughout the article, the American billion is meant.

gasoline hydrocarbons. This user-generated library proved to be more useful than HP-supplied libraries of the EPA/NIH mass spectral data base.

REFERENCES

1 B. J. Tyson and G. C. Carle, *Anal. Chem.*, 46 (1974) 610.
2 R. A. Rasmussen, H. H. Westberg and M. Holdren, *J. Chromatogr. Sci.*, 12 (1974) 80.
3 E. D. Pellizzari, J. E. Bunch, B. H. Carpenter and E. Sawicki, *Environ. Sci. Technol.*, 9 (1975) 552.
4 E. D. Pellizzari, J. E. Bunch, B. H. Carpenter and E. Sawicki, *Environ. Sci. Technol.*, 9 (1975) 556.
5 A. I. Clark, A. E. McIntyre, J. N. Lester and R. Perry, *J. Chromatogr.*, 252 (1982) 147.
6 R. H. Brown and C. J. Purnell, *J. Chromatogr.*, 178 (1979) 79.
7 J. Namiesnik, L.Torres, E. Kozlowski and J. Mathieu, *J. Chromatogr.*, 208 (1981) 239.
8 B. V. Ioffe, V. A. Isidorov and I. G. Zenkevich, *J. Chromatogr.*, 142 (1977) 787.
9 G. M. Russwurm, J. A. Stikeleather, P. M. Killough and J. G. Windsor, Jr., *Atmos. Environ.*, 15 (1981) 929.
10 J. Namiesnik and E. Kozlowski, *Chem. Anal. (Warsaw)*, 25 (1980) 999.
11 C. Vidal-Madjar, M. F. Gonnord, F. Benchah and G. Guiochon, *J. Chromatogr. Sci.*, 16 (1978) 190.
12 R. F. Gallant, J. W. King, P. L. Levins and J. F. Piecewicz, *Characterization of Sorbent Resins for use in Environmental Sampling, U.S. Environmental Protection Agency Report, EPA-600/7-78-054*, U.S. Environmental Protection Agency, Research Triangle Park, NC, 1978.
13 E. D. Pellizzari and J. E. Bunch, *Ambient Air Carcinogenic Vapors: Improved Sampling and Analytical Techniques and Field studies, U.S. Environmental Protection Agency Report, EPA-600/2-79-081*, U.S. Environmental Protection Agency, Research Triangle Park, NC, 1979.
14 F. F. McElroy, V. L. Thompson, D. M. Holland, W. A. Lonneman and R. L. Seila, *J. Air Pollut. Control Assoc.*, submitted for publication.
15 H. Knoeppel, B. Version, H. Schlitt, A. Peil, H. Schauenburg and H. Vissers, in B. Versino and H. Ott (Editors), *Organics in Air: Sampling and Identification, Proceedings of the First European Symposium on Physiochemical Behavior of Atmospheric Pollutants, Ispra, 16–18 October 1979*, Commission of the European Communities, Luxembourg, 1980, p. 25.
16 E. Pellizzari, R. Demian and K. Krost, *Anal. Chem.*, 56 (1984) 793.