ELSEVIER

Journal of Chromatography A, 805 (1998) 169–176

JOURNAL OF CHROMATOGRAPHY A

Two-stage microtrap as an injection device for continuous on-line gas chromatographic monitoring

Chaohua Feng, Somenath Mitra*

Department of Chemical Engineering, Chemistry and Environmental Science, New Jersey Institute of Technology, Newark, NJ 07102, USA

Received 11 January 1997; received in revised form 13 January 1998; accepted 14 January 1998

Abstract

A microtrap is a small diameter sorbent trap packed with adsorbent. In previous studies it has been used as a concentration cum injection device for on-line GC monitoring of trace level organics. The microtrap is prone to breakthrough as it contains a small quantity of adsorbent. A larger diameter trap with more adsorbent reduces breakthrough, but generates broad injection bands that reduce chromatographic resolution. In this paper, we present a two-stage microtrap system. The first, a large diameter retention trap is packed with more sorbent material to increase the breakthrough volume or time. The retention trap is desorbed and the analytes are refocused onto the smaller diameter microtrap referred to as the injection trap. A few seconds delay is provided and then the injection microtrap is desorbed to generate a sharp band injection for GC separation. © 1998 Elsevier Science B.V.

Keywords: Sample preparation; Air analysis; Microtraps; Monitoring, continuous; Volatile organic compounds

1. Introduction

The conventional approach to measurement of volatile organic compounds requires sampling of organics using a sorbent trap or into a whole air sampler (for example canisters) [1–4]. This is followed by laboratory analysis using GC or GC–MS. Recently, there has been much effort in the development of analytical techniques for continuous, on-line measurement of these species in air emission and in ambient air. The on-site (or on-line) analysis not only provides instantaneous results but also provides higher accuracy by eliminating the errors associated with the delay between sampling and laboratory analysis. During transport and storage of sample, the sample can degrade and contamination can occur. For example, many organic compounds, especially the polar compounds, are known to be unstable in electropolished canisters. Extensive quality control steps are also necessary for these measurements to ensure that there was no error introduced at each step of the process. Consequently these methods are more expensive in terms of time and effort required for analysis.

To develop GC systems that can perform continuous measurements, it is important to have a device that can perform on-line sampling and sample introduction from the stream. The most common sample introduction device in process GC is a gas-sampling valve. It withdraws a small aliquot from the sample stream and injects into the GC system. The typical injection volumes for injection valves vary anywhere

*Corresponding author.

0021-9673/98/$19.00 © 1998 Elsevier Science B.V. All rights reserved.
PII S0021-9673(98)00041-7

from a few microliters to 1 or 2 ml. A gaseous sample stream with low concentrations of organic compounds cannot be effectively analyzed using valves because a small injection volume contains a small quantity of analyte which results in high detection limits. The injection volume cannot be increased by using a larger sample loop because the injection band becomes wide and reduces chromatographic resolution.

A microtrap has been developed as an automatic sampling and injection device for continuous, on-line GC analysis of volatile organic compounds (VOCs) from air [5–8]. The microtrap is a small I.D. (typically 0.5 mm) capillary tubing packed with an adsorbent. The sorbent traps the organics as air is sampled through it. The retained organics can be rapidly desorbed by resistive heating using a pulse of electric current to make an injection for GC separation. The major advantage of using microtrap as an injection device over sample valves is that it is also a sample preconcentrator, which allows larger volume to be analyzed for trace measurements. The microtrap has been used in different configurations. Microtrap can replace the injection port and be attached directly in front of the GC column and is referred to as the on-line microtrap (OLMT). Here the gaseous sample stream is passed continuously through the microtrap. Heating the microtrap at regular intervals does continuous monitoring, and corresponding to each pulse a chromatogram is obtained. In the sequential valve microtrap (SVM) mode, the microtrap is connected in series with a gas-sampling valve. Here a large volume (1–10 ml) injection is made with a gas-sampling valve onto the microtrap. The organics are retained while other components pass through. Then the microtrap is heated to inject the organics. The SVM configuration has an advantage that the microtrap can be isolated from the process stream when not in use. However, the SVM may have lower sensitivity as compared to the OLMT for a given cycle time. Water vapor present in the sample has no influence on the performance of the microtrap because hydrophobic sorbents are used as microtrap packing.

The microtrap is made small in dimension such that it has low heat capacity and can be heated/cooled very rapidly. The trap is heated resistively, so heat has to migrate from the external tube wall into the sorbent. The heat transfer in larger diameter traps takes a longer time and desorption of organics is slower. Fast desorption is essential for generating a narrow injection band so that high resolution separation can be achieved. However, due to its microdimensions it can only be packed with a small quantity (fraction of mg) of sorbent. The ideal sorbent for microtrap would be one that has a large sampling capacity or breakthrough volume for the very volatile species, and at the same time providing rapid, quantitative desorption of the large-molecular-mass compounds. Several studies have been performed to determine the breakthrough characteristics of different compounds on different sorbents [5,6,9–11]. There is still no single commercial sorbent that can satisfy the above mentioned criteria of efficient trapping of the light molecules and high desorption efficiency of heavier ones. Conventional sorbent traps used for air sampling usually use layers of different sorbents to trap a wide range of compounds. These traps are also designed to sample a large volume of air and a breakthrough volume of the order of several liters is required. On the contrary, the microtrap is required to retain the sample for a few seconds to a few minutes. It is desirable to accumulate as much sample as possible in the microtrap prior to making an injection in order to maximize sensitivity. If a component breaks through, only a fraction of the sample is desorbed during injection generating a small signal at the detector. As the microtrap contains only a small quantity of sorbent, it is prone to breakthrough problems. The breakthrough volume (specific breakthrough volume defined as l/g of sorbent) for the microtrap is a function of the amount of the adsorbent. Increasing the mass of sorbent in the microtrap is a way to increasing the breakthrough time of the microtrap at a given flow rate. A larger diameter trap can hold more adsorbent, but requires longer desorption time. In addition, the heat transfer is slow in a larger tube. All these factors add up to a wide injection band and poor chromatographic separation. Thus, on one hand we have the problem of sample breakthrough in small diameter traps, and on the other hand we have the problem of a broad desorption band in larger diameter traps.

Using two traps in series and operating sequentially can solve this problem. The first, a larger diameter

trap referred to as the retention trap, is packed with more material to increase the time (or volume) required for breakthrough to occur. The retention trap is desorbed and the analytes are refocused onto the smaller diameter microtrap referred to as the injection trap. A few seconds delay is provided and then the injection microtrap is desorbed to generate a sharp band injection for GC separation. The objective of this study is to demonstrate the effectiveness of using two microtraps in series to enhance the breakthrough time as well as perform on-line analysis by making a series of injections from a flowing sample stream.

2. Experimental

The experimental system is as shown in the Fig. 1. A Varian GC system (Model 3700) equipped with a flame ionization detector was used in the study. A DB-624 column (J&W Scientific, Folsom, CA, USA) was used for separation. Data collection was using Minichrom Chromatography data system (Cheshire, UK). The microtraps were made by packing Carbopack C (Supelco, Supelco Park, PA, USA) in 10 cm×0.53 mm, 10 cm×1.1 mm and 10 cm×1.3 mm I.D. stainless-steel tubings. The microtrap was resistively heated by passing current directly through the wall of the metal tubing. Typical temperatures of the trap are about 350–400°C. The interval between injection and the duration of microtrap pulse were controlled using a microprocessor. This has been described in our previous publications and is not repeated here for brevity [5–7]. The sample stream consisted of gas standards prepared in the laboratory. The gas standards were made by evacuating and cleaning a gas cylinder by repeated flushing with N_2. Then, a calculated quantity of the analyte was injected into the cylinder as it was refilled with zero grade N_2.

A variety of compounds were used in this study. Particular attention was given to oxygenated volatile organics, which typically have low breakthrough times. A combination of different microtraps in series was tried. The 1.1 and 1.3 mm I.D. microtraps were packed with 0.4 and 0.8 g adsorbent, respectively. These served as the retention traps. The injection microtrap was the smaller diameter 0.53 mm I.D. microtrap, packed with only 0.02 g of sorbent. While the sample stream flowed through, first the retention trap was heated, then after a 5 s delay the injection microtrap was desorbed.

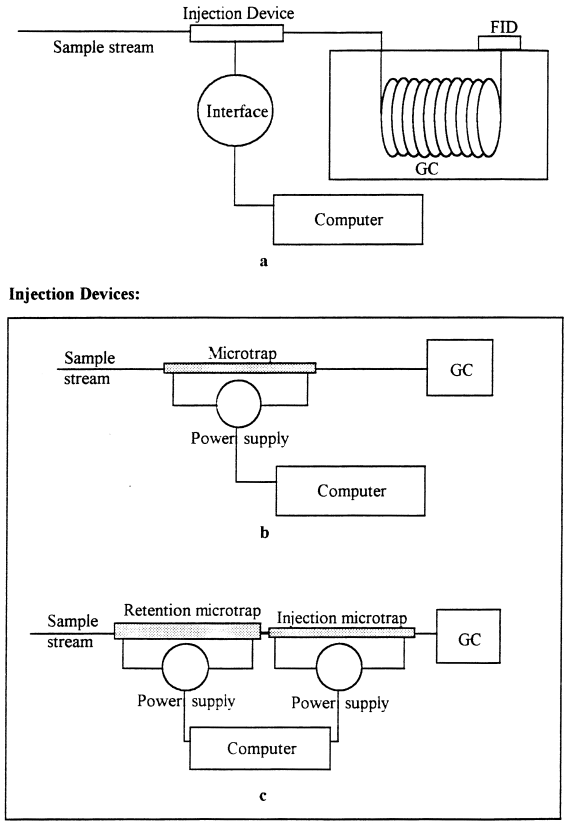

Fig. 1. Schematic diagram of the experimental system. (a) Instrument system. (b) Single stage microtrap. (c) Two-stage microtrap injection system.

3. Results and discussion

3.1. Breakthrough characteristics of the microtrap

As the air stream continuously flows through the microtrap, the organics already trapped in the microtrap begin to migrate because the air acts as a mobile phase. The (specific) breakthrough volume is defined as the volume of carrier gas per unit mass of adsorbent necessary to cause a mass of adsorbate molecules introduced at the front of the adsorbent

trap to migrate to the back [12]. The volume of sample that may be quantitatively sampled (greater than 99% collection efficiency) is always less than the breakthrough volume of the least retained component. As mentioned before, breakthrough is a serious issue with the microtrap. Although in some studies the breakthrough volume has been approximated to be equal to the retention volume, there is significant difference between them. Usually breakthrough volume is calculated using a frontal chromatography experiment. A flowing stream containing the analytes of importance is introduced into the column and the breakthrough time corresponds to time at which the concentration front emerges. Detection of the concentration front is often difficult with a low concentration sample. In this study, breakthrough of the microtrap was measured by three different methods. The first was to measure response from a microtrap pulse as a function of injection interval [13]. Increasing interval time increases the response as more sample is accumulated by the microtrap. Once the sample begins to breakthrough, the response does not increase when injection interval is increased. The breakthrough corresponds to the time required to reach the maximum response.

The second method uses the peak shape of the microtrap injections as the sample continuously flows through [14]. When the microtrap is heated, a desorption peak occurs. The analytes are readsorbed in the microtrap from the flowing stream. This lowers the base line into the negative territory appearing as a negative peak. As sample begins to breakthrough, the detector response increases to the baseline level. Basically, the negative readsorption peak is followed to determine the breakthrough time. The width of the negative peak at the baseline equals the breakthrough time.

The third method, which is the conventional method, is using frontal chromatography. When a sample stream containing organics is introduced, initially the response stays constant and then as the sample front breaks through, the response increases to a steady state value. Here the breakthrough volume is calculated based on the time required for the concentration front to appear. In our experiments, a three-way valve was used to switch between N_2 and a sample containing the analyte of interest.

The results from the three methods are shown in Fig. 2. The breakthrough time of acetone on a 1.1 mm I.D. microtrap was measured to be approximately 1.5 min by all three methods. Thus, all the methods provided equivalent results, and anyone of them could be chosen for the determination of breakthrough time. For the rest of the study, the first method was chosen because it was operationally the simplest, and the breakthrough measurements did not require any instrumental modification.

Breakthrough is a function of the amount of adsorbent. As the packed amounts of the adsorbent vary with the sizes of the microtrap, the larger traps will retain organics longer in comparison to the smaller one. The breakthrough times for methanol, acetone, 1-propanol and 2-butanone on the different size microtraps are list in Table 1. For all these four components, the breakthrough times on the microtrap with 1.3 mm I.D. are significantly increased com-

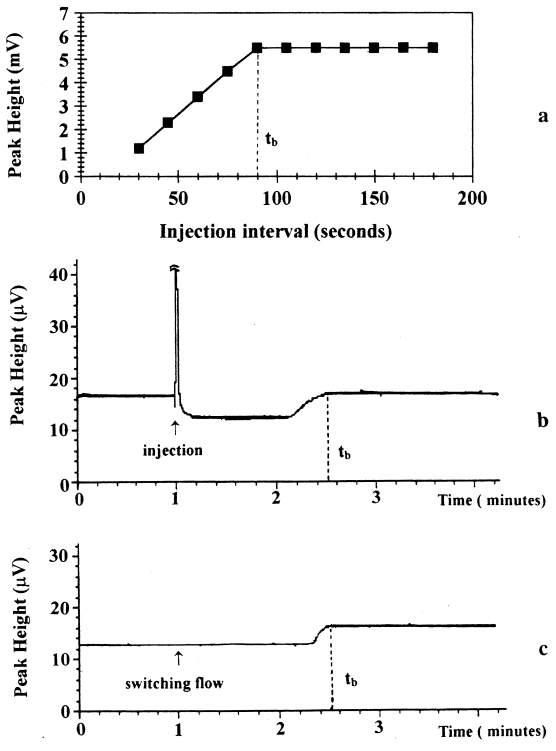

Fig. 2. Breakthrough of acetone on a 1.1 mm I.D. microtrap measured by three different methods at a sample flow rate of 6.0 ml/min. (a) Response of the analytical system as a function of interval between microtrap pulses. (b) Characteristic peak from a microtrap. (c) Chromatogram generated by frontal chromatography.

Table 1
Breakthrough times in different size microtraps at a flow-rate of 6 ml/min

Breakthrough time (min)	Trap 1 (0.53 mm I.D.)	Trap 2 (1.1 mm I.D.)	Trap 3 (1.3 mm I.D.)
Methanol	0.5	1.2	1.9
Acetone	0.8	1.5	2.1
1-Propanol	1.4	1.8	2.5
2-Butanone	2.3	3.7	6.3

pared to those on the microtrap with 0.53 mm I.D. It is clear that increasing the mass of the sorbent in the microtrap increases breakthrough time. It should be noted that other factors such as the number of theoretical plates, which is a function of the I.D. of the microtrap, also effect the breakthrough time. With the limited data available here it was not possible to develop quantitative relationship between the amount of sorbent and the breakthrough time.

3.2. Quantitative desorption from the microtrap

The desorption of adsorbate from the microtrap is achieved by passing a pulse of electric current directly through the wall of the microtrap. If enough energy is not supplied to the microtrap, quantitative desorption does not occur and a small peak results. Here the duration of the electrical pulse was increased till the peak area reached the maximum value indicating quantitative desorption. Fig. 3 is the plot of peak height as a function of pulse time for microtraps of different diameters. The pulse time required for complete desorption of the 0.53 mm I.D. microtrap was 1.5 s as compared to 4 s for the 1.1 mm I.D., and 5 s for the 1.3 mm I.D. microtrap. The larger I.D. traps have higher thermal mass and their thicker walls slow down the transfer of heat to the center of the trap.

With the increase of the microtrap diameter, the amount of packed adsorbent also increased. The pulse time required for complete desorption of adsorbate became longer. As expected, the larger microtraps due to their slower heating rate generated broader chromatographic bands. The chromatograms generated by each microtrap are presented in Fig. 4a–c. The 0.53 mm I.D. microtrap generated a high resolution chromatogram where all components were well separated. For the larger microtraps the resolution was significantly lower. For example, 1-propanol and 2-butanone were not well separated

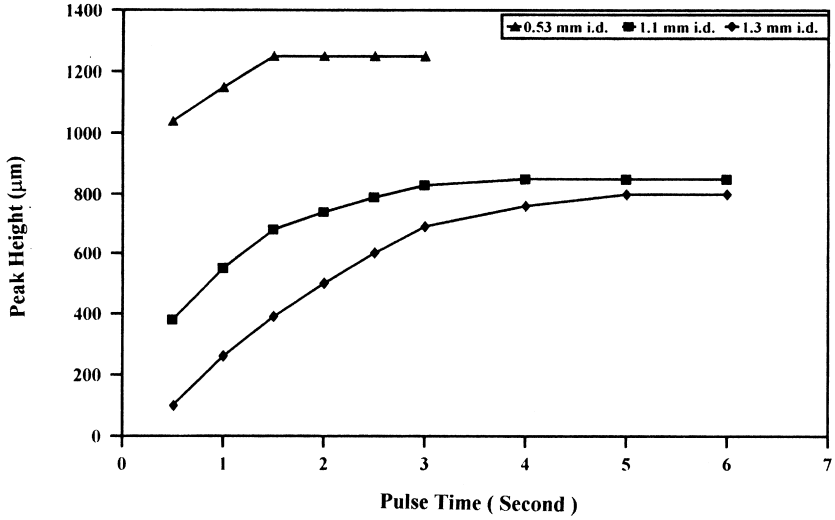

Fig. 3. The plot of peak area as a function of pulse time for different size microtraps.

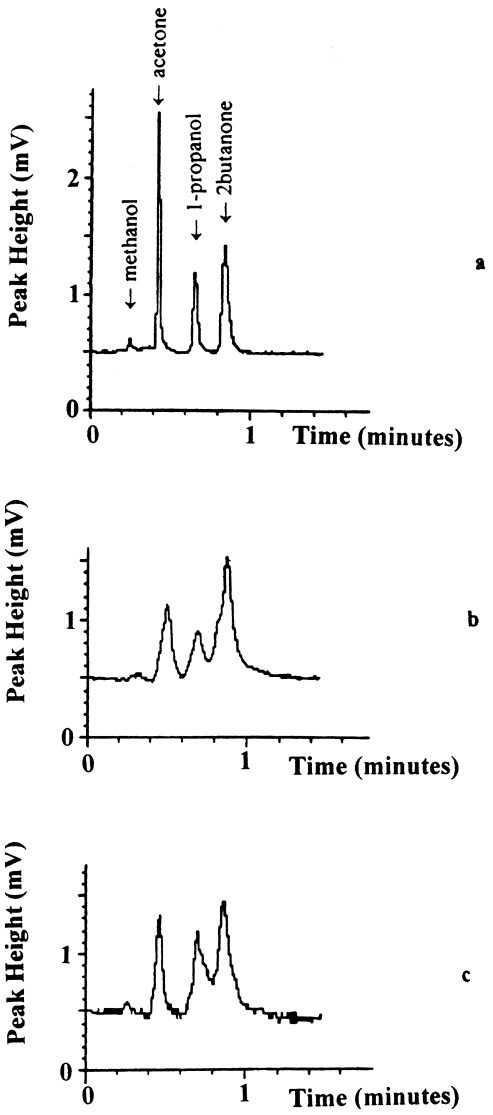

Fig. 4. Chromatograms generated by using different size microtraps. (a) 0.053 mm I.D. microtrap. (b) 1.1 mm I.D. microtrap. (c) 1.3 mm I.D. microtrap. The sample stream contained 20 ppm acetone, 20 ppm propanol, 16 ppm 2-butanone and 9 ppm methanol.

using the larger microtraps. The methanol peak was broadened to the point that it could not be distinguished from the baseline noise. The peak width at half height for different components are listed in Table 2. It is evident that the size of the trap had a significant effect on band broadening. As seen here, the narrow injection band is particularly important for components that are present in small quantities. In the case of methanol injection using the larger traps, the broad peaks could not be detected even though the breakthrough was less when compared to the small trap.

Table 2
Peak width (min) at half height in chromatograms generated using different size microtraps

	Methanol	Acetone	1-Propanol	2-Butanone
Trap 1	0.02	0.025	0.035	0.045
Trap 2	0.07	0.05	0.075	0.075
Trap 3	0.12	0.07	0.085	0.09

Trap 1: stainless steep trap 0.53 mm I.D.×0.79 mm O.D..
Trap 2: stainless steep trap 1.1 mm I.D.×1.5 mm O.D..
Trap 3: stainless steep trap 1.3 mm I.D.×1.8 mm O.D..

3.3. Performance of two-stage microtrap

The objective of using two microtraps in series was to enhance the breakthrough time by using a larger diameter trap while maintaining high resolution. The first microtrap, namely retention trap, prevents breakthrough while the second microtrap serves as an injector. For example, from Table 1, the breakthrough times for trap 1 and trap 3 for methanol were 0.5 and 1.9 min, respectively. When the two microtraps are used in sequence, the time required to breakthrough the two-trap system increases to approximately 2.4 min (sum of individual retentions) at constant volumetric flow rate. An important consideration is that the analytes desorbed from the retention trap should not breakthrough the injection trap. Since breakthrough depends only upon the total volume of gas flowing through the trap, at a constant flow rate it is prevented by having a short (or an optimum) time delay between the first and second trap desorption.

The same sample stream presented in Fig. 4 was analyzed using two-stage microtrap injection and the chromatogram is shown in Fig. 5. In both cases, trap 1 was used as the injector. A 5 s delay between the desorption of the first and second microtrap was found to be adequate for readsorption of the trapped

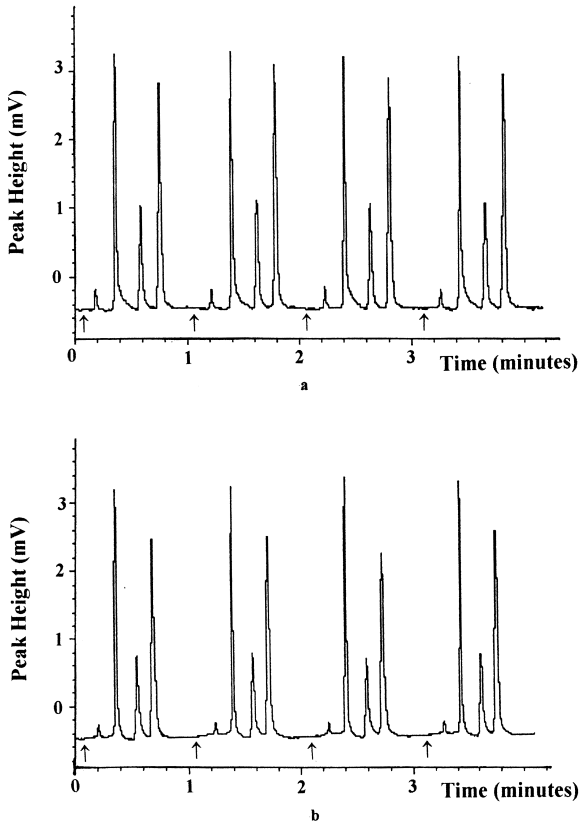

Fig. 5. Chromatograms generated using two-stage microtraps as the injection device. (a) 1.1 mm I.D. retention trap and 0.53 mm I.D. for injection microtrap. (b) 1.3 mm I.D. retention trap and 0.53 I.D. for injection trap. The sample stream contained 20 ppm acetone, 20 ppm propanol, 16 ppm 2-butanone and 9 ppm methanol. The injections are indicated by the arrows.

organics from retention trap onto the injection trap. Fig. 5 demonstrates the application of the two-stage microtrap for continuous monitoring of a sample stream by making a series of injections. The same sample used in Fig. 4 was used here. The chromatograms have excellent resolution and the methanol peak is clearly distinguishable. Peaks of 1-propanol and 2-butanone were also well resolved.

Precision in terms of retention time and peak height for the two-stage microtrap was excellent. Relative standard deviation in peak height of five repeat measurements was 1.7%. The preconcentration effect due to reduced breakthrough of the two-stage microtrap is evident from comparing Fig. 4a and Fig. 5a. In Fig. 5a, peak heights for methanol, acetone, 1-propanol and 2-butanone were 0.24, 3.65, 1.41 and 3.36 mV, respectively. The peak heights of the same components in Fig. 4a were 0.1, 1.96, 0.71 and 0.95 mV, respectively. The reason for the smaller response at the same concentration is sample breakthrough in the smaller I.D. microtrap. Thus by using the two traps in series, the response for methanol, acetone, 1-propanol and 2-butanone increased 2.4, 1.9, 2.0 and 3.5 times, respectively. This represents a significant enhancement in sensitivity. Fig. 5a,b also showed that the diameter of the retention trap did not have significant influence on resolution because the same trap in both cases made the GC injection.

4. Conclusion

The results demonstrated that the two-stage microtrap system was effective in reducing (if not eliminating) the breakthrough problem in the microtrap. The two-stage microtrap produced a high resolution chromatogram and increased sensitivity by accumulating sample for a longer period of time.

Acknowledgements

This project was funded by a grant from the US Environmental Protection Agency at Research Triangle Park, NC, USA. Dr. John B. Phillips is acknowledged for valuable suggestions.

References

[1] C. Vidal-Madjar, M. Gonnord, F. Benchah, G. Guiochon, J. Chromatogr. Sci. 16 (1978) 190.
[2] H. Frank, D. Renschen, A. Klein, H. Scholl, J. High Resolut. Chromatogr. 18 (1995) 83.
[3] V. Burger, Z. Munro, J. Chromatogr. 370 (1986) 449.
[4] B.V. Bertoni, F. Bruner, A. Liberti, C. Perrino, J. Chromatogr. 203 (1981) 263.
[5] S. Mitra, Y. Xu, W. Chen, A. Lai, J. Chromatogr. A 727 (1996) 111–118.
[6] S. Mitra, C. Yun, J. Chromatogr. 648 (1993) 415.
[7] S. Mitra, A. Lai, J. Chromatogr. Sci. 33 (1995) 285.

[8] S. Mitra, Continuous Monitoring of Organic Pollutants, US Pat., 5 169 435 (1995).
[9] Supelco GC Bulletin 849C, Division of Rohm and Haas, Supelco, Bellefonte, PA, 1988.
[10] P. Lovkvist, J. Jonsson, Anal. Chem. 59 (1987) 818.
[11] L.D. Butler, M.F. Burke, J. Chromatogr. Sci. 14 (1976) 117.
[12] W.R. Betz, K.S. Ho, S.A. Hazard, S.J. Lambiase, Sampling and Analysis of Airborne Pollutants, Lewis Publishers, New York, 1993.
[13] Y.H. Xu, S. Mitra, J. Chromatogr. A 688 (1994) 171.
[14] S. Mitra, J.B. Phillips, J. Chromatogr. Sci. 26 (1988) 620.