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Continuous gas chromatographic monitoring of low concentration sample streams using an on-line microtrap

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ABSTRACT

An on-line microtrap was made by packing a few centimeter long narrow bore capillary tubing with an adsorbent. The sample stream containing the analytes is introduced into the GC column through the microtrap. The analytes are trapped in the microtrap as they **flow** through it, and can be desorbed by heating the microtrap using a pulse of electric current. The heating is done very rapidly, so that the "desorption pulse" is sharp enough to be an injection for the GC separation. Thus, the microtrap serves as a sample pre-concentrator as well as an injector. Continuous monitoring is done by making these injections at fixed intervals of time (every few seconds to every few minutes) and for each injection a chromatogram is obtained. In this investigation, microtrap characteristics have been studied and particular attention has been given to its sample trapping characteristics.

INTRODUCTION

Continuous, on-line analysis of chemical processes and environmental emissions at trace levels is an interesting and challenging problem. Many analytical techniques such as Fourier transform infrared spectrophotometry **(FT-IR)** and mass spectrometry have been used in such applications. Recently some chemical **microsen-**sors have also been developed to carry out this type of analysis. Gas chromatography is particularly important as an on-line analysis technique because of its ability to separate and detect the different components of a mixture.

The important feature of any continuous, on-line GC instrumentation is the sample introduction device, which is required to make automatic, reproducible injections. In chemical industries, process gas chromatography is done using multi-port sample valves as injectors. Valves can automatically make injections from a sample stream intermittently into a GC column. However, sample valves have certain limitations. Being mechanical devices, they tend to wear during extended operations. Another problem with sample valves is that they withdraw a small fraction of the sample stream for injection into the GC. The sample size that is injected into the GC is between a few microliters to a couple of milliliters. Injecting a larger sample quantity causes excessive band broadening and degrades chromatographic resolution. A small injection volume results in a small sample quantity and this limits sensitivity. For example, a sub parts per million (v/v) gaseous sample stream can not be effectively analyzed using valves. In many applications, especially in environmental monitoring, low concentrations are encountered and sample valves are found to be inadequate.

Analysis of dilute gaseous streams containing organic analytes such as stack emissions and

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ambient air is carried out by concentrating the analytes from a large sample volume (several milliliters to a few liters). The concentration is done either cryogenically (as in whole air samples such as Tedlar bags and Canisters) or using an adsorbent. These procedures usually require separate sampling and analysis steps. So the measurements can not be done on-line in a continuous fashion.

To do real-time GC monitoring of trace level analytes, not only is it necessary to have an automated injection device but also a sample preconcentrator. In this paper we report the use of an on-line microtrap for the dual purpose of sample concentration and injection.

On-line microtrap

An on-line microtrap is made by packing a small diameter tubing with an adsorbent. The sample containing the analyte is introduced into the analytical column through the microtrap. The analytes are trapped in the microtrap and can be thermally desorbed by electrical heating. When the heating is rapid enough, the "desorption pulse" serves as an injection for the GC column. The different components separate and are analyzed by the detector. The mode of operation for continuous monitoring is that electrical/thermal pulses or injections are made at fixed intervals of time and corresponding to each injection, a chromatogram is obtained. Due to its small size and thermal mass, it heats and cools rapidly, and frequent injections can be made as long as the GC separation is completed. Since the amount of sample trapped in the microtrap is proportional to the concentration of the stream flowing in, the microtrap response is proportional to sample concentration.

The principle of the microtrap is similar to that of thermal desorption modulators reported in previous papers [1–5]. In these applications, the temperature of a small segment of a capillary column was thermally modulated to generate a modulation signal from the sample being eluted by the mobile phase. The modulations have been done at the head of the GC column [1–4], as well as, in the middle of two columns used in multi-dimensional chromatography [5]. The microtrap is more like a small sorbent trap, which is put on-line with the sample stream, and is operated at a fixed intervals of time. In short, the microtrap traps the sample for a period of time and then releases it as a desorption pulse.

In a previous paper the effect of capacity factor in thermal desorption modulators was described [1]. Some of the same concepts can be used in the case of the microtrap. Both adsorption and desorption processes play important roles in the on-line trapping/desorption involved in the continuous monitoring. The microtrap does not necessarily trap a hundred percent of the analytes, as some tend to breakthrough. The sample desorption from the stationary phase generates a positive concentration profile, and the immediate sample readsorption generates a negative concentration profile. Thus, a microtrap peak contains a positive and a negative part and an example is shown in Fig. 1. The time interval AD in Fig. 1 is the time taken by the sample to migrate through the microtrap. This is denoted as

$$t_b = (k + 1)\, L/u \qquad (1)$$

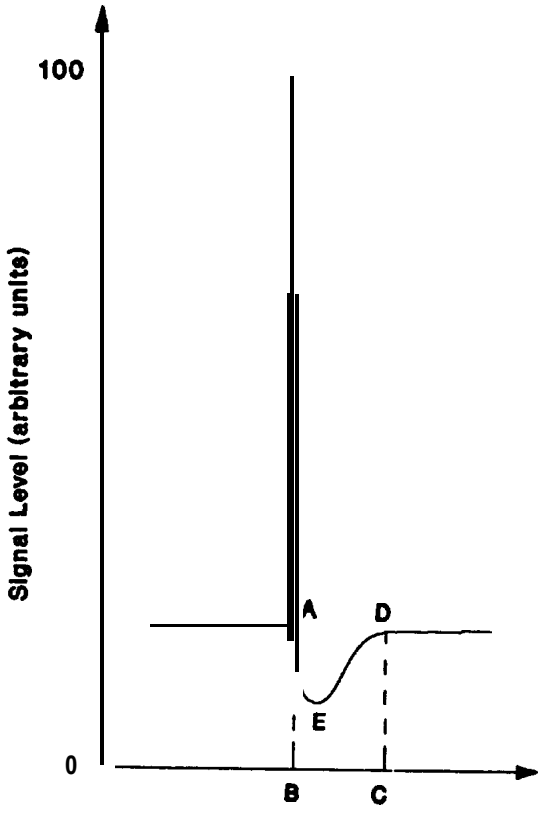

Fig. 1. Characteristic peak from a microtrap.

where L is the length of the microtrap, u is the flow-rate and k is the capacity factor of sample in the microtrap. As k increases, t_b increases, the negative peak becomes shallow and appears to merge with the baseline so that the chromatogram resembles a conventional chromatogram without a negative peak. The peak in Fig. 1 was obtained at a lower capacity factor so that the negative peak was exaggerated.

In this investigation, a microtrap has been developed for continuous, on-line analysis of somewhat volatile organic compounds. The microtrap characteristics have been studied and particular attention has been given to its sample trapping abilities.

EXPERIMENTAL

The experimental system is as shown in the Fig. 2. The sample stream was generated by entraining the analytes from a diffusion cell into a flow of nitrogen. The analyte concentrations was controlled by changing the capillary diameter and the height of the liquid level in the diffusion capillary [6]. The concentration of the stream was predicted using diffusion equations published by Savitsky and Siggia [6]. The concentration of the analytes was maintained between a few ppm to ppb level (on a volumetric basis). Although a variety of compounds have been used in the laboratory, data using benzene, toluene, xylene and hexane have been presented in this paper. The choice of these compounds was arbitrary.

A Hewlett-Packard GC (Model 5890) equipped with a flame ionization detector was used in this study. A megabore, DB-624 column (J&W Scientific, Folsom, CA, USA) with a 3-pm stationary phase was used for separation. The microtrap was made by packing a 23 gauge (0.33 mm I.D.) stainless-steel tubing (Hamilton, Reno, NV, USA) with Carbotrap C (Supelco, Supelco Park, PA, USA). The microtrap was heated by passing current directly through the walls of the metal tubing. Modulators were also made by packing 0.53 mm I.D. deactivated fused-silica tubing with Carbo Trap C. The fused-silica microtrap was externally coated with electrically conductive paint and could be heated by passing current through it. The current through the cool microtrap can be between 5 and 10 A, but as it heats up its resistance increases and the current is reduced. More details about the resistive heating process can be found elsewhere [3,4]. Power resistors were put in series with the microtrap to control the current through it. The injections were controlled by the personal computer (IBM compatible) using the digital output of the analog-to-digital converter (DAS8-PGA, Metrabyte, Elmwood Park, NJ, USA) and electronic switch (OAC5P, Opto 22, Huntington Beach, CA, USA). The microtrap was heated by turning on the current for a prespecified duration and at fixed intervals of time. The interval between injections were anywhere between 5 and 300 s. The duration for which the current was turned on was between 100 and 1000 ms. Since the microtrap heats up and cools down in 1 or 2 s, it is difficult to accurately measure the exact heating rate and the final temperature. A measurement using a thermocouple showed that temperature as high as 300°C can be obtained in fraction of a second.

The data acquisition was also done using the analog-to-digital converter and the personal computer. A computer program was written in Quick Basic for making injections as well as data acquisition.

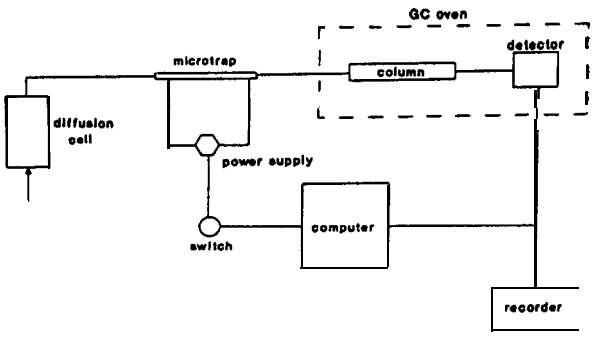

Fig. 2. Schematic diagram of the experimental system.

RESULTS AND DISCUSSION

On-line analysis

The operation of the continuous analysis system is demonstrated by continuously monitoring a stream containing benzene, toluene and

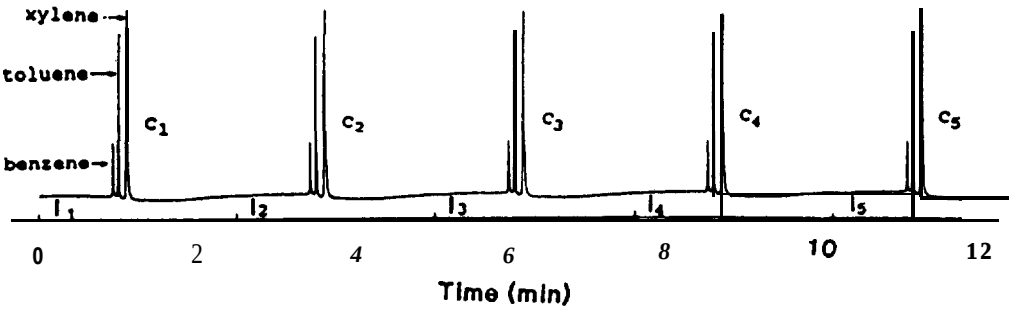

Fig. 3. Continuous monitoring of a stream containing ppb (v/v) levels of benzene, toluene and xylene using a 6.5 cm long fused-silica microtrap at 22°C. Corresponding to each injection I_1, I_2,I_3. a chromatogram C_1,C_2,C_3... was obtained. The microtrap current was turned on for 500 ms. The column flow-rate was 7.9 ml/min and temperature was 180°C.

xylene. The injection from a microtrap was similar to that from an injection port or an injection valve. A series of injections were made and corresponding to each injection a chromatogram containing the three peaks were obtained. A section of the recorder output is shown in Fig. 3. In Fig. 3, the capacity factor was such that negative peak disappeared. Some of the characteristics of the chromatograms are presented in Table I. An injection of the same compounds was also made using the split/splitless capillary injection port of the GC and comparative results at similar retention time are presented in Table I. Each quantity in Table I is based on five separate measurements.

Reproducibility of retention time as well as peak height was very good for the microtrap and was comparable to that of the injection port. The microtrap also produces sharp peaks and at the same retention time, the terminal band length (measured as the length of the solute zone emerging from the end of the column [7]; equivalent to four times the standard deviation) is somewhat smaller for the microtrap than for the injection port. This is to be expected, because there is practically no dead volume in the microtrap. In continuous GC monitoring, the goal is to make injections as frequently as possible. Since the microtrap has short heating/cooling cycle, the time needed for separation in the column becomes the limiting factor. As a result, the column conditions may be optimized for speed rather than efficiency.

The GC analysis in Fig. 3 was done isothermally. The heating/cooling of the column in a conventional GC oven is relatively slow and can not keep up with the injection frequency used in this study. Conceptually, temperature-programmed separation is feasible if the column temperature control system is designed for this application.

Trapping efficiency. The microtrap operation

TABLE I

COMPARISON OF MICROTRAP WITH INJECTION PORT

	Microtrap			Injection port		
	Benzene	Toluene	p-Xylene	Benzene	Toluene	p-Xylene
Retention time (s)	57.38	61.85	68.41	56.27	62.22	70.97
% R.S.D. of retention time	0.22	0.23	0.20	0.13	0.17	0.16
% R.S.D. of peak height	1.14	0.97	1.46	1.60	1.50	2.90
Band duration' (s)	0.76	0.78	1.12	0.80	1.00	1.20
Terminal band length" (mm)	385.09	365.74	475.62	411.30	467.02	490.38

[a] Measured at half height.

is somewhat different from conventional sorbent traps, which are normally much larger in size and are seldom used in a continuous operation. A microtrap has low capacity and may trap only a fraction of the sample flowing through it. However, it is desirable that the microtrap accumulate as much sample as possible before making an injection so that a large signal can be obtained at the detector. Moreover, the untrapped sample breaks through the microtrap and contributes to the detector background. Trapping efficiency of the microtrap is defined as the fraction of the incoming sample retained by the microtrap before a injection is made:

$$\text{Trapping efficiency (T)} = \frac{\text{sample retained}}{\text{sample entering microtrap}} \quad (2)$$

The retention mechanism in a microtrap is similar to that of a GC column. There is an equilibrium between the concentration of the sample in the stationary and the mobile phase. The injections are normally made at fixed intervals of time (referred to as injection interval). So trapping efficiency,

$$T = \frac{t_b M_s}{t_i M_t} \quad (3)$$

$$T = \frac{t_b M_s}{t_i (M_s + M_m)} \quad (4)$$

where, M_s is the amount of sample trapped per unit time in the stationary phase, M_t is the sample amount per unit time flowing into the microtrap, M_m is the amount of sample per unit time that remains in mobile phase and t_i is the injection interval. Thus the above equation reduces to:

$$T = (t_b/t_i)k/(k + 1) \quad (5)$$

If the injections are made very frequently such that $t_i < t_b$ then the microtrap accumulates sample only for t_i and eqn. 5 becomes:

$$T = k/(k + 1) \quad (6)$$

Thus in this case T depends only upon k and does not change with the injection interval t_i. If injection interval is large and $t_i > t_b$ then trapping efficiency is given by eqn. 5 and T is inversely proportional to t_i.

The trapping efficiency can be computed from the microtrap response such as in Fig. 1. The sample retained by the microtrap is proportional to the area under curve **AED**. The total sample flowing into the microtrap is equal to the area ABCD. The experimentally determined trapping efficiency as a function of injection interval (t_i) is presented in Fig. 4. When injection interval is less than t_b, as predicted by eqn. 6, the trapping efficiency is constant. When the interval is increased higher than t_b the trapping efficiency begins to decrease.

Factors effecting microtrap response

The value of t_b is an important microtrap characteristic and is given by eqn. 1. For a given analyte and microtrap packing, the temperature determines the capacity factor and in turn t_b. Variation of maximum trapping efficiency (corresponding to the flat portion of Fig. 4) and t_b with temperature is presented in Fig. 5. The trapping efficiency decreases with increase in microtrap temperature and its decrease closely parallels

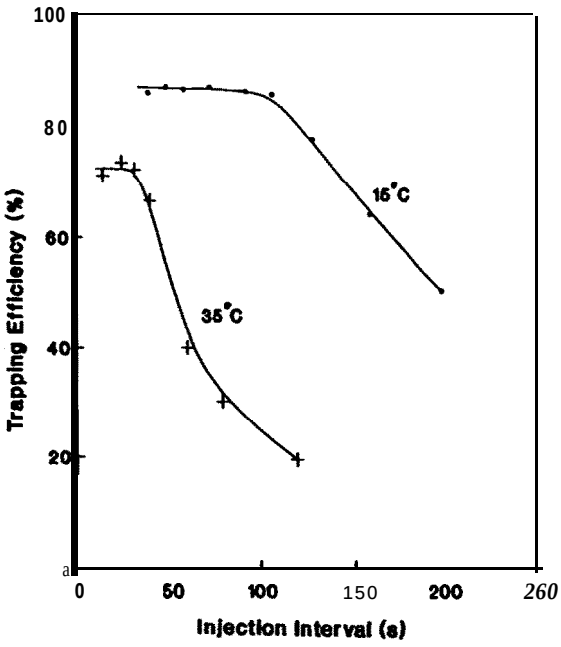

Fig. 4. Trapping efficiency as a function of injection interval. A 6 cm long fused-silica microtrap was used with hexane as the sample. The microtrap current was turned on for 500 ms.

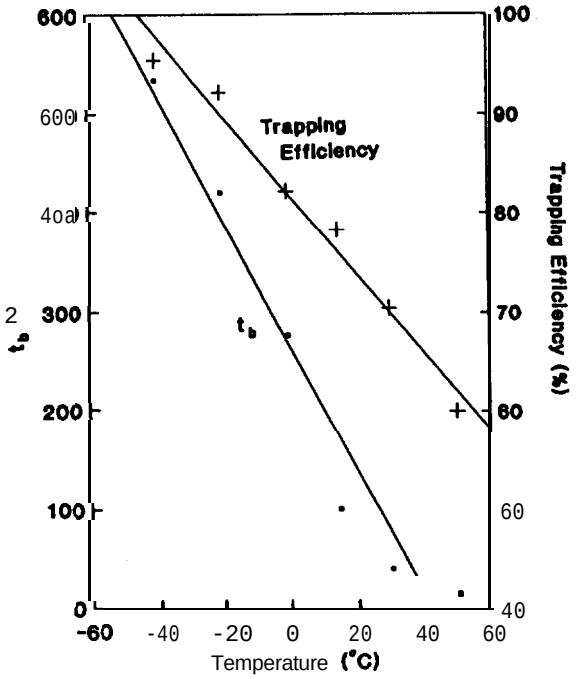

Fig. 5. Dependence of trapping efficiency and t_b of hexane on microtrap temperature. A 6 cm long fused-silica microtrap at a flow-rate of 8.1 ml/min was used. The microtrap current was turned on for 500 ms.

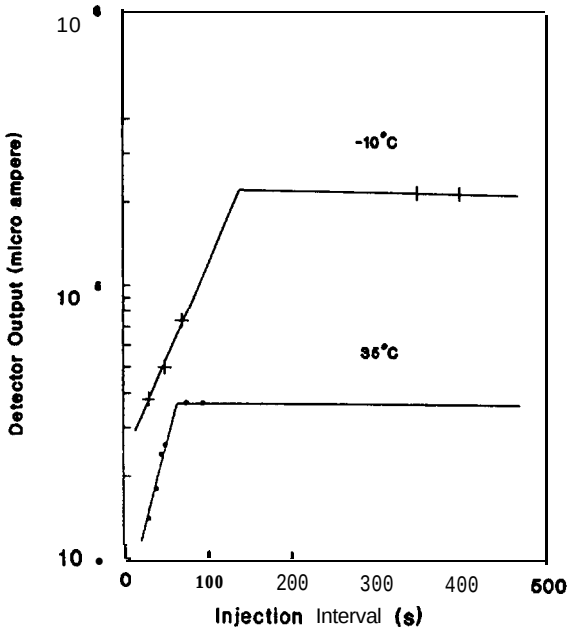

Fig. 6. Microtrap response as a function of injection interval at − 10°C and 35°C. Hexane was used as the analyte and a 5.5 cm long fused-silica microtrap at a flow-rate of 4.7 ml/min was used. The microtrap current was turned on for 500 ms.

that of t_r. This is to be expected because at a certain capacity factor, the trapping efficiency is directly proportional to t_b (eqn. 5). In fact, if T and t_b are plotted against one another, a linear relationship is obtained. The decrease in trapping efficiency and t_b with temperature may be approximated by linear relationships.

One of the factors that need to be taken into consideration during continuous operations is at what frequency the microtrap is to be operated. Making injections very often offers the advantages of obtaining information more often, but may have other disadvantages such as lower sensitivity and not enough time for chromatographic separation. It should be realized that the microtrap can not hold the sample very long. The sample trapping characteristics of a microtrap can be studied by operating the microtrap at different injection intervals. In Fig. 6 as we increase the injection interval, the sample accumulated by the microtrap increases and thus a larger peak is obtained. However, once the interval equals t_b, the sample begins to break through and the response cannot be increased further by increasing the injection interval. So the response profile involves a linear increase in microtrap response upto t_b followed by a constant response beyond t_b.

The microtrap temperature strongly effects the microtrap response. Due to higher trapping efficiency at a lower temperature, a larger desorption peak is generated from the microtrap, *i.e.*, sensitivity is increased. For example, at injection interval of 50 s (Fig. 6), the microtrap response at − 10°C is more than twice that at 35°C. The longer t_b at lower temperature also allows the microtrap to trap sample for a longer period of time. For a continuously flowing sample, this translates to larger sample accumulation in the microtrap and consequently higher sensitivity. Due to the dual effect of higher trapping efficiency and longer t_b, the maximum attainable response at − 10°C is nearly six times higher than that at 35°C. In short, the increase in sensitivity at lower microtrap temperature is observed

whether the injection interval is longer or shorter than t_b.

There may be certain limitations to lowering the temperature to very low values because some components may adsorb so strongly that they can not be desorbed from the microtrap. In practice one has to optimize the temperature for the analytes of interest. For example in Fig. 3, 22°C was appropriate for the sample studied and no sub-ambient cooling was necessary. However, sub-ambient cooling could be used to increase the sensitivity and to lower the detection limit. Moreover, since the microtrap response varies with temperature, it needs to be controlled carefully during extended periods of continuous operation. A change in temperature would require recalibration of the system as the sensitivity would change.

Linearity of the calibration curve is also an important consideration for on-line measurements. In this system, the linearity of the microtrap has to be taken into account. Conceptually, the retention characteristics of microtraps has been explained using theories of partition chromatography. The amount of sample trapped by the microtrap is theoretically proportional to concentration of sample flowing through it. The microtrap generated linear response in the ppm (v/v) to ppb (v/v) concentration range.

An important feature of the on-line microtrap is that the sample continuously flows through the system, *i.e*, sampling is done continuously and the microtrap produces a time-averaged response over the injection interval. So, if a large concentration spike was to occur between two injections, a microtrap would still be able to identify it. This is an advantage over monitoring devices that sample intermittently.

CONCLUSIONS

Due to the preconcentration effect, the on-line microtraps are able to continuously monitor low concentration sample streams. Their-small size and thermal mass make them very fast and responsive devices, and the analysis can be done every few seconds as long as GC separation can be achieved within that time. The microtrap response is stable during long periods of operation and precision is comparable to other injection devices.

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