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Characteristics of microtrap-based injection systems for continuous monitoring of volatile organic compounds by gas chromatography

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Abstract

A sample valve is a common GC injection device for continuous monitoring of organic compounds in air. We have reported the use of a microtrap in on-line analysis applications. These devices not only make automatic injections, but also serve as a sample preconcentrator. In this paper, the characteristics of microtrap-based injection systems in continuous on-line monitoring is presented. Air emissions from a pilot plant scale catalytic incinerator were monitored to demonstrate the applicability of the microtrap.

Keywords: Injection methods; Microtraps; Air analysis; Sample introduction; Volatile organic compounds

1. Introduction

As regulatory requirements for pollution monitoring become more stringent, continuous monitoring methods that can track emission sources such as industrial stacks and vents on a continuous basis are becoming more important. Continuous monitoring is also useful for keeping an emission inventory and for process control. Continuous monitors can almost immediately detect an upset in a chemical process, so that corrective actions may be taken. Not only does this reduce environmental problems, but it can also save industry money in terms of resource conservation and recovery.

In general, spectroscopic techniques are ideal for process monitoring because of their analysis speed. For example, infrared (IR) methods are used in real-time monitoring of compounds such as ammonia, hydrochloric acid, ozone, CO_2 and NO_x, as well as some organic compounds [1]. However, water vapor which commonly exists in emission streams can interfere seriously with IR analysis. Another problem is that it is difficult to identify individual organic compounds in complex mixture owing to the overlapping of absorbance bands from the different compounds [2]. Mass spectrometers have also been used for monitoring organic pollutants in air emissions [3]. They face similar challenges, such as deconvolution of individual spectra in a complex matrix and interference from H_2O and CO_2. Moreover, both these technique are quite expensive.

Gas chromatography is an excellent techniques for separating individual compounds in a complex mixture. It has been used in process monitoring since 1956 [4,5] even though GC separation is much slower than spectroscopic measurements. However, recent developments in GC have significantly re-

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duced the separation time which makes GC a viable continuous-monitoring technique.

A critical component of on-line GC monitoring is the sample introduction device, which has to make automatic injection at certain intervals of time. Multi-port sample valves are the most common injectors for a GC process. However, this method has certain limitations in trace analysis. To obtain a large signal from a low concentration sample a large injection volume is necessary, but a large injection requires long injection time which causes band breading especially in capillary columns. Normally, the injection volume is limited to several microliters to a milliliter which in turns raises the detection limit. Consequently, the sample valve is not enough to face the challenges of trace analysis at the ppb level. Furthermore, a sample valve intermittently injects an aliquot of sample from the process stream and no information is available in the period between two injections. This can be a serious limitation for monitoring processes that change rapidly with time. A cryogenic trap has been used to concentrate the trace organic compounds in air analysis and may also be used on-line in GC. Cryogenic traps have also been used in combination with gas sampling valves to make injections in fast gas chromatographic separation [6,7]. However, the cryogenic traps are not suitable for samples with high humidity as moisture freezes in a cryogenic trap. Cryogenic cooling prolongs the analysis time because alternate heating and cooling takes time.

Recently we have reported the use of a microtrap for continuous on-line GC monitoring [8–10]. It is a short length of narrow-bore tubing which is packed with an adsorbent. It can be used to concentrate analytes and then rapidly heated to desorb the organics as a concentration pulse which acts as a GC injection. It can be used as a stand-alone device or in conjunction with a gas sampling valve. It can be attached directly in front of a GC column in place of a sampling valve. It is called the on-line microtrap (OLMT) in this mode of operation. The gaseous sample stream is passed through the OLMT and the organic analytes of interest are trapped in the microtrap. The adsorbed analytes can then be thermally desorbed by electrical heating. Because the microtrap has low heat capacity, rapid heating is possible to desorb the organics as a narrow injection band. Continuous monitoring is done by heating the microtrap at regular intervals, and corresponding to each injection a chromatogram is obtained. The microtrap accumulates the analytes during the interval between injections (pulse interval), so it serves as an injector as well as a preconcentrator.

We have also reported the use of a microtrap in conjunction with a gas sampling valve [9]. In this technique, a microtrap is connected in series with a gas sampling valve and is referred to as the sequential valve microtrap (SVM). A large volume injection (several milliliters) or several small volume (e.g. multiple 100-μl injections) are made by the sample valve. The analytes are trapped by the microtrap. Then the microtrap is heated to inject the analytes into the GC. The SVM configuration has the advantage that the microtrap can be isolated from the process stream when not in use.

In this research, we studied the characteristics of the microtrap used as an OLMT as well SVM. Furthermore, the performance of the OLMT, SVM and a conventional gas sampling valve are compared. We also present some data from continuous monitoring of a catalytic incinerator used as a VOC control device.

2. Experimental

A schematic diagram of the continuous monitoring system used in this study is presented in Fig. 1. The gas sample valve was a six-port air actuated valve with a digital interface (Valco Instruments, College Station, TX, USA). The operation of the valve was controlled by a computer. The microtrap was made by packing a 0.53 mm I.D., 10–14 cm long silica lined stainless steel tubing with an adsorbent such as Carbotrap. The microtrap was connected to a variable power supply (20–50 V a.c.). A computer controlled electronic switch was used to control the interval between pulses and also the duration for which the heating was carried out. Further details of the microtrap and its operation are presented elsewhere [8–10].

A Hewlett-Packard 5890 Series II GC equipped with a conventional flame ionization detector (FID) was used for this study. A 30 m long DB-624 fused-silica open tubular column from J&W Sci-

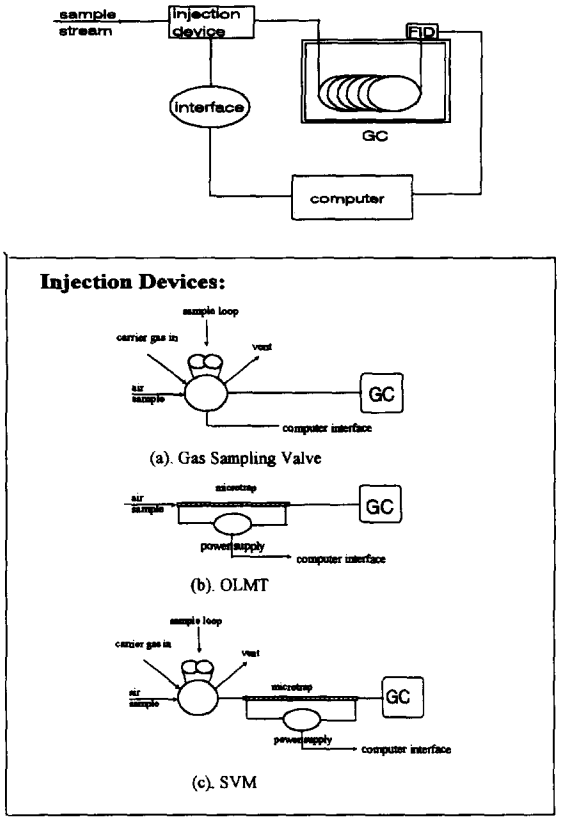

Fig. 1. Continuous-monitoring system showing the different injection systems.

entific (Folsom, CA, USA) was used. The column inner diameter was 0.53 mm and the stationary phase thickness was 3.0 μm. Nitrogen was used as the carrier gas and flow-rates were between 5 and 7 ml/min.

The organic compounds used to make standards were obtained from Fisher Scientific. Absorbents such as Carbotrap were purchased from Supelco (Bellefonte, PA, USA). Gas samples were prepared in 6-l evacuated canisters by injecting pure liquid and filling with dry zero air to 40 lb/inch^2. The gas samples were verified using certified gas standards from ALPHAGAZ (Morrisville, PA, USA).

3. Results and discussion

The three injection devices (valve, SVM and OLMT) were tested using simulated stack gas standard. The gas contained 1 ppm each of benzene, toluene, ethylbenzene and trichloroethane along with combustion products such as CO_2 (9.27%), CO (75 ppm), SO_2 (164 ppm) and O_2 (10.9%). In each case the gas stream continuously flowed through the injection device and an injection were made every 2 min. A chromatogram containing the four peaks was obtained for each injection.

As expected, the valve with a 100-μl sample loop showed a small response compared with the SVM and the OLMT (Fig. 2A). When the volume of the sample in the valve was increased to 8 ml, broad overlapping peaks were obtained as in Fig. 2B. In the SVM mode, when the microtrap is connected in series with the 8-ml sample loop, then the analytes are re-focused and injected onto the GC system, generating sharp peaks as shown in Fig. 2C. The

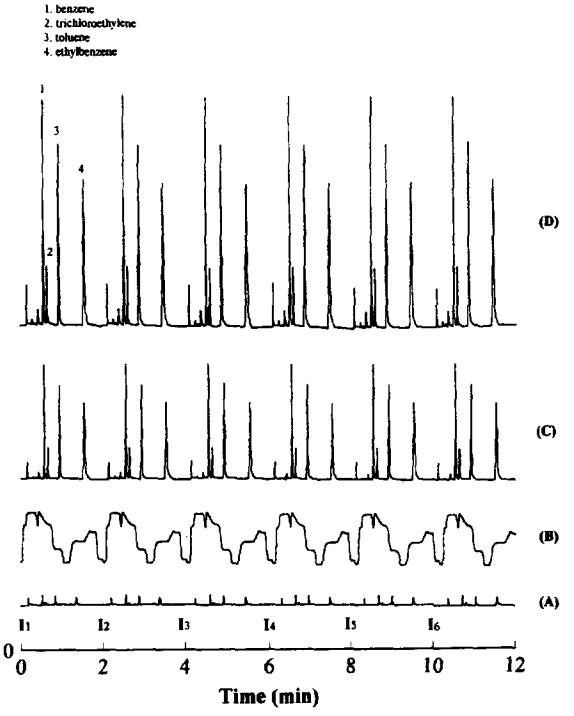

Fig. 2. Continuous monitoring of a simulated stack gas containing combustion products along with some volatile organic compounds. In each case injections were made every 2 min at points I_1, I_2...: (A) response using a 100-μl gas sampling valve; (B) response from an 8-ml sample loop; (C) response using the SVM mode (D) response from the OLMT mode.

OLMT generates even larger signals than the SVM (Fig. 2D). In this case the sample flows continuously through the microtrap and effectively concentrates all the analytes. The effective sample volumes analyzed by the SVM and OLMT in Fig. 3 were 8 ml and 20 ml, respectively. In Fig. 2, all the chromatograms were measured at same attenuation. For the same sample concentration OLMT generated the largest signal followed by SVM and then the conventional sample valve.

3.1. Response characteristics of SVM and OLMT

Most process/emission streams change with time and the goal of on-line measurement is to monitor these changes. Sometimes the variation can be very fast and, the changes may occur for a few minutes or even a few seconds. In chromatography, the separation time may be of the order of several minutes. Conventional gas sampling valves inject the sample every a few minutes from the process stream. No information about the process stream can be obtained during the period between two injections. On the other hand in the OLMT, the sample continuously flows through the microtrap and it acts as a sample accumulator. Eventually when the trap is heated, a signal proportional to the amount of accumulated sample is obtained. So indirectly, we do get information about the time period between the pulses. Here we tested the response of the three injection devices to impulses of various frequency.

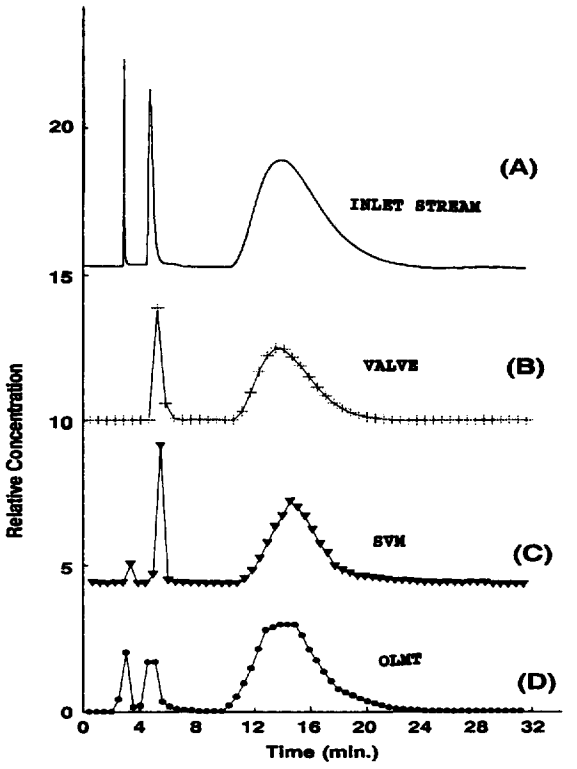

Fig. 3. Response of the different injection systems to a changing concentration stream: (A) concentration profile of the inlet stream; (B) monitoring using a gas sampling valve; (C) monitoring in the SVM mode (three valve injections followed by a microtrap pulse); (D) monitoring in the OLMT mode. In each case injections were made every 30 s.

Fig. 3A is a profile of the hexane concentration in a simulated process stream. Within this 30 min there were three concentration spikes of hexane: the first spike occurred after 2.5 min and finished within 10 s; the second spike occurred at 4.5 min and lasted for 1.2 min; the third spike occurred at 10 min and lasted for about 12 min. The results of monitoring the simulated gas stream are presented in Fig. 3B, Fig. 3C, Fig. 3D. In each case injections were made every 30 s. It can be seen that the first spike was missed by the valve. The only way the valve could detect this spike is if an injection was made right at the moment the concentration spike occurred. The probability of such an occurrence is quite low. We repeated this experiment 20 times and the results were positive only twice. In the SVM operation here, three 100-μl valve injections were followed by a microtrap pulse. This mode of operation was chosen because it injects sample more frequently from the process stream and is more suitable for monitoring process transients. The valves required 5 s each for loading and injection. The SVM also missed the first spike occasionally, in this case the probability of positive results were 75%. The OLMT was able to identify the first spike 100% of the time because the sample continuously flows through it. This clearly demonstrates the effectiveness of the OLMT and the SVM injection systems in on-line monitoring of streams that change rapidly with time.

Linearity of the calibration curve is an important consideration for quantitative analysis. The amount of analytes trapped by the microtrap is theoretically proportional to the concentration of sample through

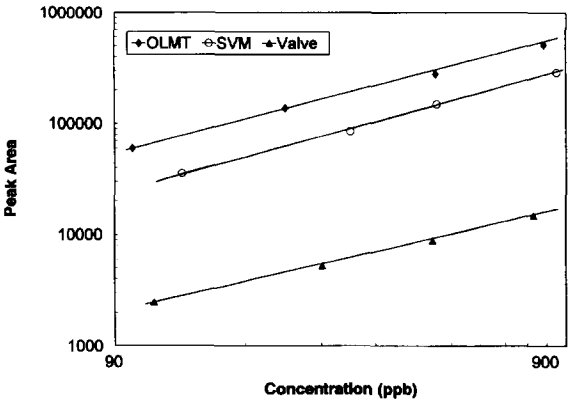

Fig. 4. Calibration curve using the three injection devices.

it. The calibration curves for these three techniques are presented in Fig. 4. All the techniques exhibited linear response and it can be seen that the response of OLMT was larger than that of the SVM. The SVM signal was an order of magnitude larger than that of a conventional gas sampling valve. Again the higher response of the OLMT system is because it effectively measures a larger volume. Consequently the OLMT exhibits lower detection limits than SVM, the valve being a distant third. The detection limits for some volatile organic compounds (VOCs) are presented in Table 1. The advantage of the OLMT and the SVM is clearly demonstrated by the sub-parts per billion detection limits attainable using these devices.

Table 1
Detection limits for benzene, toluene and xylene using a gas sampling valve, OLMT and SVM

Compounds	Detection limits (ppb_v)[a]		
	Valve[b]	SVM[c]	OLMT[d]
Benzene	23.6	0.28	0.15
Toluene	8.35	0.092	0.045
m-Xylene	7.55	0.048	0.026

[a]The detection limits were calculated at a signal-to-noise ratio of 3.
[b]The volume of sample loop is 100 μl.
[c]The volume of sample loop is 8.0 ml and the sequential valve microtrap was operated by one valve injection following one microtrap pulse. The temperature of microtrap was 28°C.
[d]Flow-rate of the sample stream was 5.6 ml/min and the interval between two microtrap pulses is 3 min. The temperature of the microtrap was 28°C.

3.2. Retention mechanism in the microtrap

The microtrap is made from capillary tubing so that it has low heat capacity and can be heated very quickly to generate a sharp injection band. Consequently it contains a small quantity of adsorbent which can retain the analytes for a limited amount of time before breakthrough occurs. The microtrap is equivalent to a short GC column. When a pulse of sample is introduced at the head of the column, the retention time (t_R) depends upon its capacity factor [8]:

$$t_R = (K + 1)b/u \quad (1)$$

where K is the capacity factor of analyte in the microtrap, b is the length of the microtrap and u is the linear velocity of the carrier gas. This scenario is appropriate for the SVM mode of operation, where a pulse injection is made by the valve at the head of the microtrap. In the OLMT mode the sample continuously passes through the microtrap, a frontal analysis is more appropriate. Here, the breakthrough volume/time (defined as the time or volume corresponding to 1% elution loss of the analyte) can be significantly different from the retention volume/time. However, for a sorbent trap the breakthrough volume is known to be close to the retention volume if the trap exhibits large number of theoretical plates [11]. In case of the microtrap the number of theoretical plates was calculated to be between 300 and 350. Thus the breakthrough volume is assumed to be close to retention volume, and t_R can be assumed to be a reasonable estimate of the breakthrough time.

According to Eq. 1, for a microtrap of certain length, the breakthrough time increases with the capacity factor if the linear velocity through the microtrap is held constant. The capacity factor, of course, depends upon analyte–adsorbent interactions. Fig. 5 presents an elution profile of several typical analytes in the microtrap. For example, toluene was retained by the microtrap for 23 min while ethanol was retained for 15 s. This is because polar molecules are not strongly retained in the non-polar adsorbent used here [12]. Trapping efficiency as a function of time is presented in Fig. 6. The trapping efficiency of acetone decreases rapidly since acetone has a short breakthrough time. For toluene, which

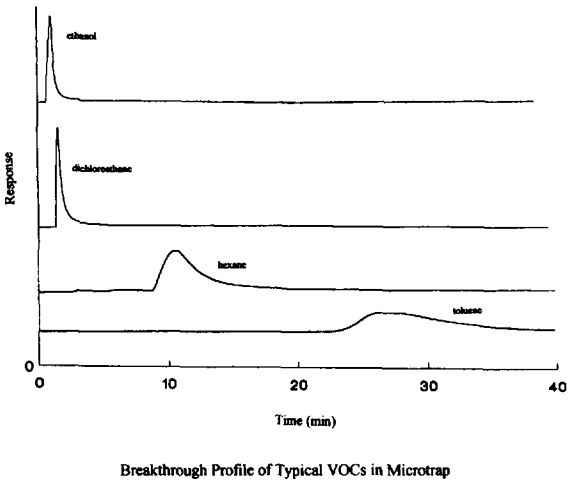

Fig. 5. Elution profiles of different organic compounds in a 9-inch long microtrap. Microtrap temperature was 30°C and flow-rate of the carrier gas was 6 ml/min.

has high capacity factor and long breakthrough time, the trapping efficiency stays at 100% for about 23 min before dropping slowly. The advantage of high capacity factor is two-fold. First the sample is retained for a long time and second the emerging band is broad so that even if the trap is heated during the elution of the analyte band, at least part of the sample can be desorbed for analysis. For example, in case of toluene it takes almost 10 min for trapping efficiency to decrease from 100% to 0%.

The breakthrough time also decreases with linear velocity of the carrier gas. A linear relationship exists between t_R and $1/u$. For a given analyte–adsorbent the capacity factor depends upon the microtrap temperature. An empirical equation of the following form has been suggested [13]:

$$K = K_0 \exp(\Delta H/RT) \quad (2)$$

here K_0 is the capacity factor at reference temperature, H is the enthalpy of adsorption, R is the universal gas constant and T is the temperature of the microtrap. When temperature increases the capacity factor decreases so that breakthrough occurs more quickly. Replacing K in Eq. 1 with Eq. 2:

$$t_R = (1 + K_0 \exp[\Delta H/RT])b/u \quad (3)$$

The adsorbents are chosen so that the capacity factor is relatively high and significantly higher than 1, thus Eq. 3 is approximated as:

$$\ln t_R = C/T \quad (4)$$

where C is a constant and T is the temperature. As expected from Eq. 4, a straight line was obtained when $\ln t_R$ was plotted against $1/T$ (Fig. 7) at different flow-rates. A linear relationship also exists between retention volume V_r and $1/T$ (Fig. 7). The retention volume, of course, is independent of the flow-rate. It is obvious that the breakthrough time and breakthrough volume decrease rapidly with

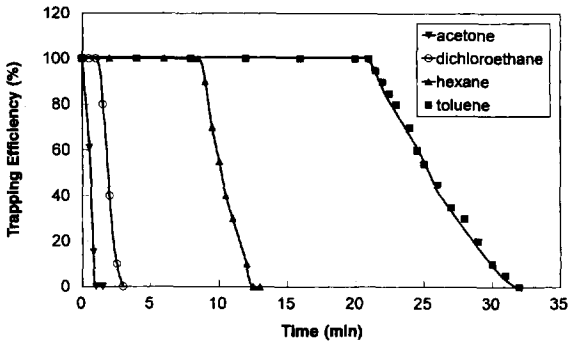

Fig. 6. Trapping efficiency of a microtrap as a function of time. Conditions were the same as for Fig. 5.

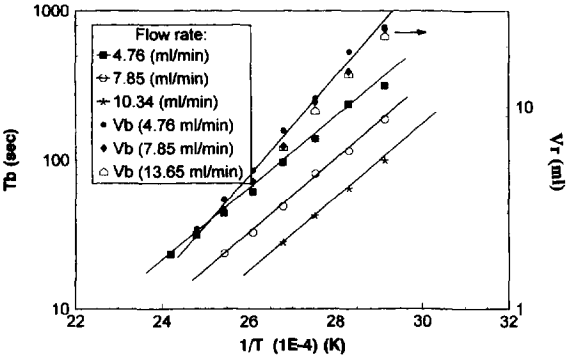

Fig. 7. Effect of microtrap temperature on retention time and retention volume.

increasing temperature. For practical reasons it may be advantageous to design the microtrap operation near the room temperature. Sub-ambient operation requires cryogenic or other elaborate cooling devices, while higher temperature reduces the system response.

3.3. Continuous monitoring of catalytic incinerator

Catalytic incineration is used in industry to catalytically oxidize organics in air emissions [14]. Typical destruction efficiencies in catalytic incinerators can be anywhere from 75% to 99.99%. Continuous monitoring at the incinerator outlet can be quite challenging because for an inlet concentration at ppm levels, the outlet concentrations can drop to ppb levels. It is important to monitor the outlet concentrations to ensure that destruction efficiency has not dropped due to catalyst poisoning or other process factors.

Microtrap was used in the SVM mode to monitor VOCs at the outlet of a pilot plant scale catalytic incinerator as shown in Fig. 8. The catalytic incinerator has been described elsewhere [14] and is not described here. Organics were oxidized using a 1.5% Pt/Y-Al_2O_3 catalyst at 350°C and at a space velocity of 3000 v/v/h. A split flow from the reactor outlet was passed through the microtrap injection system and the outlet stream was monitored using GC. Experiments were performed using a variety of organic compounds and their mixtures. Data for toluene and trichloroethylene are presented here. In Fig. 9, outlet concentrations and conversion (or destruction efficiency) as a function of inlet concentration are presented. An important finding here was that conversion decreased when the inlet concentration dropped below 1 ppm. The details of this study are beyond the scope of this paper. At this point it is sufficient to say that the microtrap in the SVM or the OLMT mode was able to monitor VOCs at ppb levels to provide useful information such as that shown in Fig. 9.

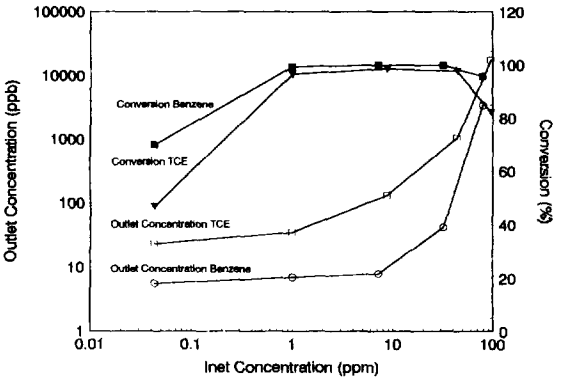

Fig. 9. Outlet concentration and conversion (destruction efficiency) as a function of inlet concentration.

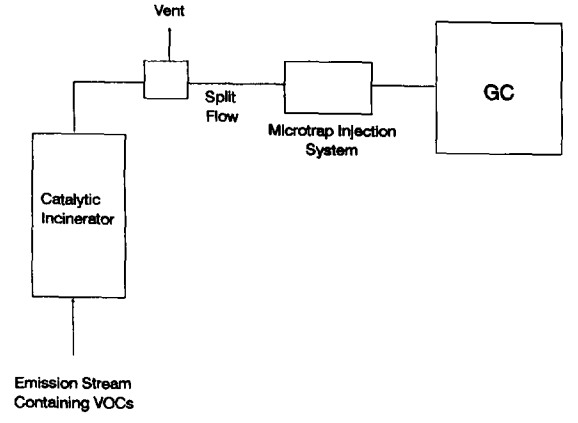

Fig. 8. Schematic diagram of the system used to monitor the catalytic incinerator.

4. Conclusions

The microtrap-based injection devices clearly show some advantages as injection devices in continuous GC monitoring of organic analytes. The OLMT has a higher sensitivity and a lower detection limit than the SVM. The OLMT and the SVM can track the concentrations of a sample stream almost continuously. Real tests carried out by monitoring the outlet of a catalytic incinerator demonstrated that the microtrap-based injection systems are reliable for monitoring at ppb levels.

Acknowledgments

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