

NEAR REAL-TIME GC ANALYSIS OF VOLATILE ORGANIC COMPOUNDS USING AN ON-LINE MICRO-TRAP

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ABSTRACT

Micro-traps act as sample pre-concentrators for gas chromatography (GC) that can be used to make repetitive injections every few seconds. A thermal desorption micro-trap is made from a short segment of thin tubing containing an adsorbent or a chromatographic stationary phase. A carrier gas containing the analyte of interest can be introduced into the GC analytical column through the micro-trap which acts as a sample trap. Rapid heating of the micro-trap releases a "concentration pulse" of the analyte that serves as a GC injection similar to that from an injection valve. Micro-traps can be used in various applications such as process stream analysis, fast and multi-input chromatography.

INTRODUCTION

In recent days, the volatile organic compounds (VOCs) have received much attention as air pollutants and several are listed in the Clean Air Act Amendment of 1990, Title III. The analysis of VOCs is particularly challenging because they are usually present in very low concentration (ppmv to ppbv level). VOCs in gaseous matrices such as stationary stack emissions are analyzed using whole air samples collected either with the Volatile Organic Sampling Train (VOST)¹ or with Tedlar bags using EPA Method 18². Both these approaches attempt to analyze dilute gaseous matrices by concentrating a small amount of analyte from a large volume of gas. While these methods are quite effective in VOC measurements, they can not be used for continuous or near real-time monitoring.

The important feature of any continuous, on-line GC instrumentation is the sample introduction system, that is required to make automatic, reproducible injections. In many chemical industries, process GC is accomplished by the use of sample valves as injectors. Valves can automatically make injections from a sample stream onto a GC column. However, sample valves have certain limitations. Being mechanical devices, they tend to deteriorate during extended operation. Also, sample valves can only handle small volumes of gas, generally between a few μL and two mL. Injecting a large sample volume causes excessive band broadening and degrades chromatographic resolution. A small sample volume results in reduced sensitivity. As a result, sample streams that are at sub part per million concentration levels can not be effectively analyzed using sampling valves. In many applications, especially in environmental monitoring, low VOC concentrations are encountered and sample valves are found to be inadequate.

Real-time VOC monitoring (at trace levels) using a GC, requires an automated injection device and a sample preconcentrator. The research reported here used an on-line micro-trap to serve the dual purpose of

sample concentration and injection.

On-line Micro-trap

An on-line micro-trap was made by packing a short (few cm long) piece of metallic or fused silica tubing with an adsorbent. The sample containing the analyte is introduced into the analytical column through the micro-trap. The analytes are retained in the micro-trap and can be thermally desorbed by electrically heating the micro-trap. When the heating is rapid enough, the desorption generates a concentration pulse that serves as an injection. The different compounds are separated by the column and analyzed by the detector. The mode of operation for continuous monitoring is that injections (or pulses) are made at fixed intervals of time and corresponding to each pulse, a chromatogram is obtained. The advantage of the micro-trap is that it has low thermal mass and can be heated/cooled very rapidly. So, repetitive injection can be made as long as GC separation is completed. The amount of sample trapped in the micro-trap is proportional to the concentration of the stream sampled. Consequently the micro-trap response is proportional to sample stream concentration.

EXPERIMENTAL SYSTEM

The experimental system is shown in the Figure 1. The VOC sample stream was generated by entraining the analytes from a diffusion tube onto a flow of nitrogen. The analyte concentration was controlled by changing the diameter and the height of the liquid level in the diffusion capillary. The concentration of the stream was calculated using diffusion equations.

A Hewlett Packard GC (model 5890) equipped with a flame ionization detector (FID) was used in this study. The micro-trap was made by packing 0.5 mm ID stainless steel tubing with different adsorbents. The micro-trap was heated by passing a pulse of electric current (duration 100 to 700 msec) directly through its metal wall. The injections were controlled by an IBM compatible personal computer using the digital output of the analog to digital converter (DAS8-PGA, Metrabyte Corp.) and an electronic switch (OAC5P, Opto 22, Huntington Beach, CA). The micro-trap was heated at fixed intervals of time. The interval between injections varied between 5 and 300 sec. A computer program written in Quick Basic was used for making injections as well as for data acquisition.

RESULTS AND DISCUSSIONS

The operation of the continuous analysis system was demonstrated by continuously monitoring a stream containing ppb_m levels of hexane, dichloromethane, toluene and ethylbenzene. The injection from the micro trap (referred to as a pulse) was similar to that from an injection port or valve. A series of pulses were generated at one minute intervals. Each pulse produced a four peak chromatogram as shown in Fig. 2. The high sensitivity of the micro-trap is quite obvious, chromatographic separation may be reduced by shorting the pulse interval to 45 seconds or installing microbore columns.

Reproducibility of retention time as well as peak height was very good for the micro-trap and was comparable to that of an injection port. Since the flow through the micro-trap is very compatible to the flow through the column and there is practically no dead volume, the micro-trap produces sharp peaks. Linearity of the calibration curve is also an important consideration for on-line measurements. The amount of sample trapped by the micro-trap is theoretically proportional to the concentration of sample flowing through it. Here we found the calibration curve to be linear in the ppb to ppmv range.

REFERENCES

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2. U.S. Government Printing Office, Code of Federal Regulations, 40CFR, Part 60, Appendix A, 1993.

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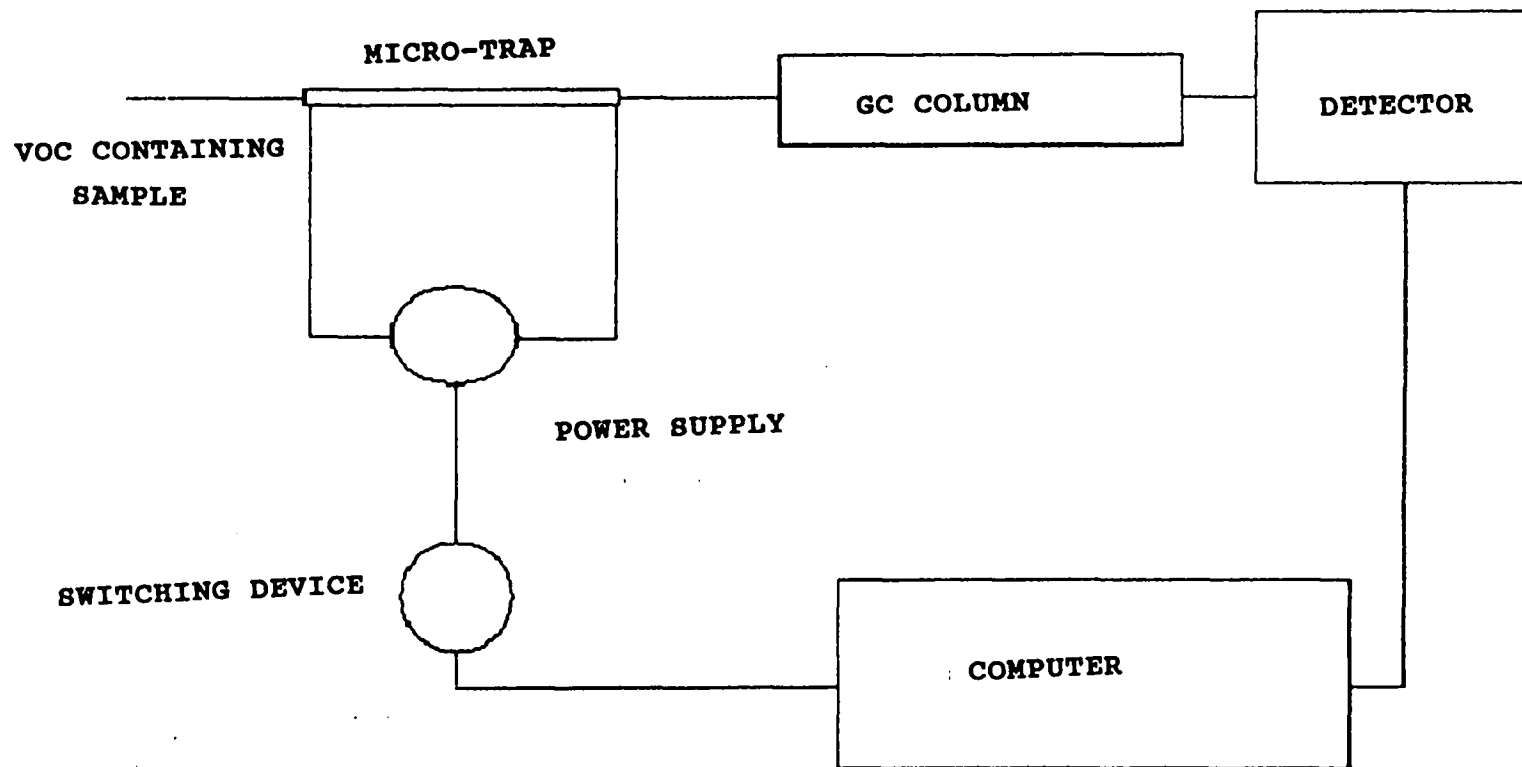


Figure 1. Schematic diagram of the experimental system

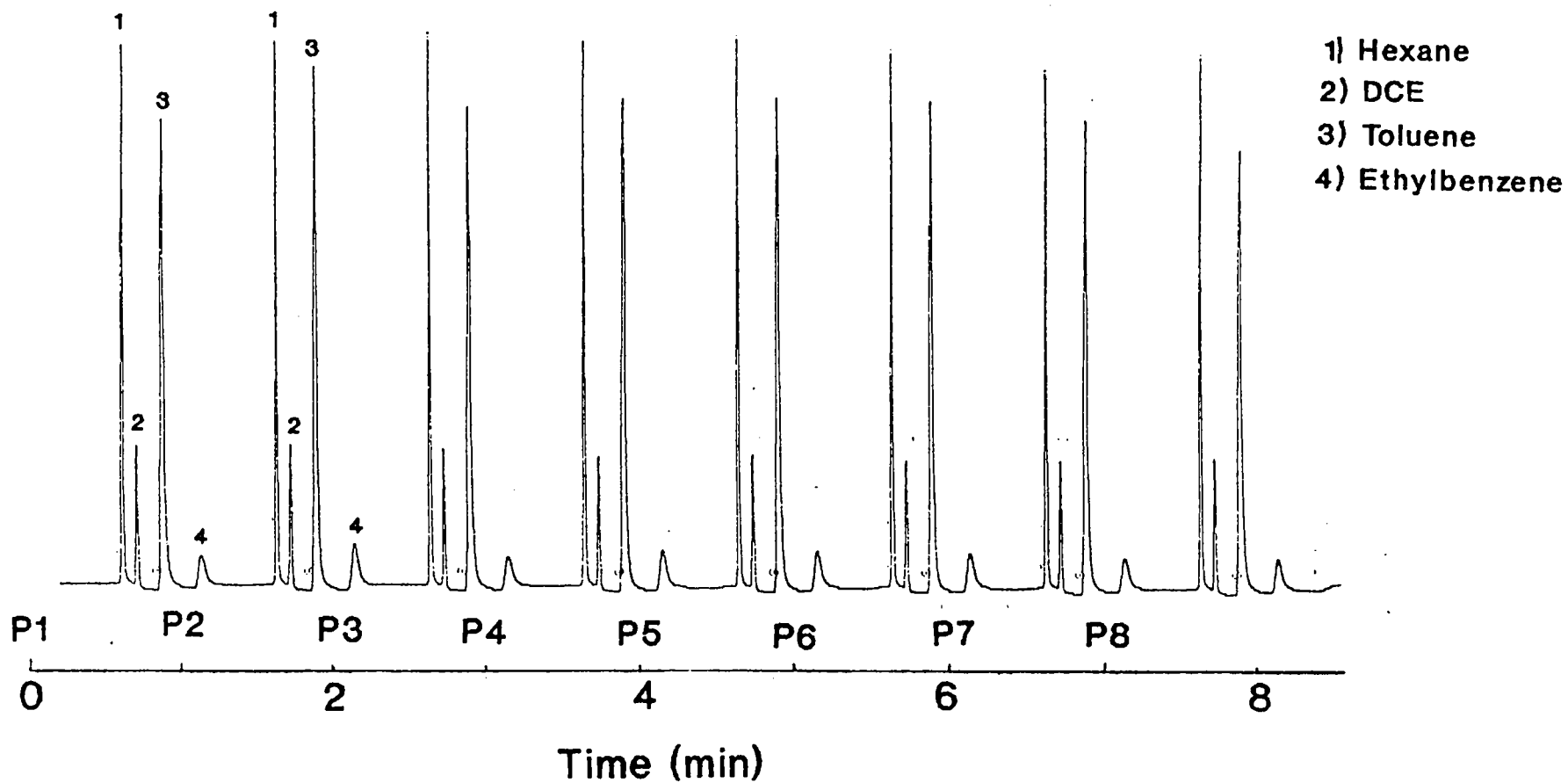


Figure 2. Continuous monitoring of VOCs using the on-line micro-trap. P₁, P₂ ... are the different injections corresponding to which chromatograms were obtained.

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