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# Microtrap modulated flame ionization detector for on-line monitoring of methane

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## Abstract

A microtrap for on-line analysis of trace methane was developed. Silicosteel tubing, 15 cm long, 1.02 mm i.d. and 1.59 mm o.d. was packed with Carbosphere 80/100 mesh and placed between the standard gas source and the flame ionization detector (FID) to be used as a preconcentrator and an injector. The sample stream was passed continuously through the microtrap that was heated at a fixed interval by an electric pulse. To achieve the highest adsorption and desorption efficiency, parameters affecting the response of the system were optimized, and adsorption temperature in the range of 25 to −50 °C was studied. The response from the microtrap as compared to that from direct-flame ionization detector was enhanced by as much as 260 times. The on-line microtrap system showed good linearity ($r^2 > 0.99$), low detection limit (28.3 ppbv) and good long term stability (relative standard deviation, RSD of less than 5.0%). Therefore, this simple device is suitable for on-line analysis of trace methane and similar small molecules in the environment as in high purity gases.

*Keywords:* Methane; Microtrap; Carbosphere; High purity gases

## 1. Introduction

Methane, due to its abundance, can occur even in high purity gases which are crucial for research and development applications and this contamination can have a negative impact on the process [1]. Therefore, measurements and control of the impurities play an important role in high purity gases research applications.

To determine methane concentration, samples are generally collected before injected into a gas chromatograph [2]. A small injection volume is preferred but this will limit the sensitivity of the detector and a preconcentration step is generally needed. Even when the sensitivity is increased by a preconcentration step, there is always the delay between sampling and analysis [3–5]. This is clearly not acceptable for continuous, on-line monitoring, but also adds error to the measurement process. One approach is using an on-line cryogenic trap to focus the sample in a narrow band at the head of the column. The trap rapid cooling and re-heating, ensuring the reproducibility and optimum peak shape. However, if the source has a lot of water, it freezes and plugs the sorbent trap [6]. It is also quite complicated to apply, therefore, a microtrap was introduced as an alternative.

A microtrap is a small capillary tubing packed with a small amount of adsorbent. Sample containing the analytes continuously flow into the microtrap, and the organics are trapped by the sorbent while the gas flows through. The retained organics are rapidly desorbed by resistive heating with pulse of electric current which make an injection for GC separation.

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The main advantage of microtrap as an injection device over a sample valve is, it also serves as a sample preconcentrator, which allows the larger sample volume to be analyzed for trace components [7–10].

In this paper, the development of an on-line microtrap that is interfaced directly to the flame ionization detector (FID) for the determination of methane is reported.

## 2. Experiment

### 2.1. Instrumentation

Fig. 1a shows the schematic diagram of the on-line system used for methane monitoring. All experiments were carried out by a gas chromatograph equipped with a conventional FID and the results were integrated by CR-4A Integrator (GC-14A and CR-4A Integrator, Shimadzu, Japan). Methane standard concentration of 11.6 part per million by volume (ppmv) (TIG, Thailand) was used to study the characteristics of the microtrap packed with a suitable adsorbent.

### 2.2. Microtrap

By considering the suitability of pore size and surface area, Carbosphere 80/100 mesh (Alltech, IL, USA) was selected as the adsorbent. It was packed in a 15 cm long, 1.02 mm i.d., and 1.59 mm o.d., silicosteel welded/drawn 304 grade stainless steel tubing (Restek Co., Bellefonte, PA, USA). The microtrap was placed in-line of the stream of the standard gas and in front of the detector to act as a trap/concentrator as well as an injector (Fig. 1a). The microtrap was rapidly heated by applying a current pulse from a lab-built heating system and a temperature as high as 250–300 °C was reached within a few milliseconds. This was to desorb and to inject the analyte into the FID. The effect of heating was similar to using an injection port in term of retention time, peak height, band duration and terminal band length [7]. A microprocessor-based timer was used to control the interval between the adsorption and desorption times and the duration for which the current was applied.

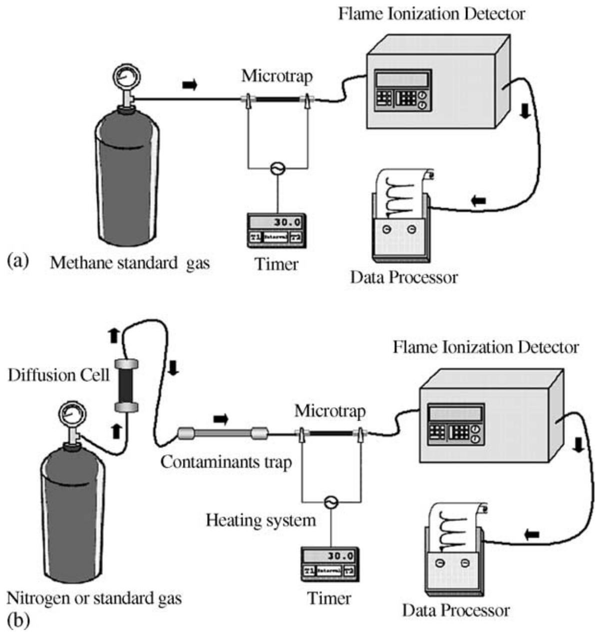

Fig. 1. Schematic diagram showing the analysis system. (a) microtrap interfaced to flame ionization detector for on-line determination of methane. (b) Diffusion cell was used to introduce organic in the $N_2$ stream to test the ability of the contaminants trap to remove the organic.

### 2.3. Breakthrough characteristics

To determine breakthrough in a microtrap, the method using the variation in microtrap response as a function of injection interval [4] was implemented. The capacity, in term of breakthrough, was studied by passing a stream of standard methane gas (11.6 ppmv) through the microtrap. Methane molecules were adsorbed while the background stream served as a carrier gas. The system was first investigated at room temperature (25 °C). Desorption voltage and time were varied in the range of 10–50 V and 1–4 s. The optimum desorption voltage and time were then used to determine the breakthrough by varying the adsorption time until stable response peaks were obtained.

### 2.4. Enhancement of microtrap capacity

The most important factor for trace quantity analysis is enhancement. A higher enhancement (or enrichment) factor can be obtained by decreasing the microtrap temperature. The microtrap was placed inside an insulating foam box, surrounded by dry ice. The temperatures were varied from 25 °C (room temperature) to −50 °C by varying the amount of dry ice. At each adsorption temperature, the optimized desorption voltage and time were investigated to obtain the maximum desorbed analyte from the microtrap. The adsorption time at each temperature was then varied to determine the breakthrough time. The responses were used to calculate enhancement.

### 2.5. Performance of the microtrap

To study the linear response of the on-line microtrap system, a series of standard gas concentrations, 11.6, 5.8, 3.9, 1.1 and 0.2 ppmv, was prepared by dynamic dilution method [11] using nitrogen gas (99.99% TIG, Thailand) as the dilutor. Each concentrations of methane were continuously passed through the microtrap. The injections were made at 6 min interval using a pulse time of 3.5 s at 40 V for five replications at −50 °C. The signals were used to plot the standard curve.

High purity nitrogen gas (99.99%) was used as blank. It was continuously applied through the microtrap. The desorptions, i.e., injections were done every 6 min and the obtained data were used to calculate the limit of detection based on IUPAC method [12].