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Development of a MEMS preconcentrator for micro-chromatography analyses

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Abstract

This paper presents the development of MEMS gas preconcentrator (GP) for the detection of trace level Volatile Organic Compounds (VOCs). Besides the development of the MEMS gas preconcentrator, we have also worked on the coupling of this preconcentration device with a micro gas chromatograph (μ -GC) for achieving an accurate detection system for gas trace monitoring. Preliminary results have highlighted a significant contribution of the MEMS GP on the μ -GC efficiency and a detection limit below 35ppbv for different vapors like toluene, vinyl acetate monomer, chloroform and methylisobutylketone was reported.

Keywords

Gas Preconcentration; Adsorption; Desorption; Detection; Micro Gas Chromatograph

1. Introduction

Process control presents a major challenge for the chemical industry to ensure product quality, cost control, maintaining productivity and risk control. The direct analysis within the heart of the process is the most effective way, but most of the gas analysis processes are hampered by the limit of detection. So in the field of analytical techniques, the preprocessing of the gases is generally a very important step, especially to get a preconcentration effect in order to increase the limit of detection. Moreover, one major trend is to miniaturize analytical techniques for *in situ* analysis.

The development of μ -GC system has driven an important research effort. Portable gas chromatographs or micro-gas chromatographs (μ -GCs) provide an analytical tool that permits a quick analysis of volatile organic compounds (VOC) for *online* monitoring. Adding a preconcentration step should allow increasing the sensitivity of miniaturized analyzer [1].

Therefore we have worked on the integration of our MEMS gas preconcentrator into a μ -GC module already developed and commercialized by SRA Instruments Company. The design of the MEMS gas preconcentrator and the experimental parameters were optimized in regards to the future application. Experiments conducted with preconcentrator filled carbon nanopowder and associated to a micro chromatograph have shown an accurate separation and identification of various VOCs in trace within a gas mixture.

2. Preconcentrator's design and adsorbent material

The main part of the device used in this study is a silicon microchannel (20x85 mm², thickness 500 μ m) obtained by deep reactive ion etching (DRIE) and designed with fluidic micro-structures at the inlet/outlet leading to a preconcentration chamber with a volume of 14 μ l. The microchannels were produced on a 5 Ω -cm, n-type, (100)-oriented 1mm μ m-thick silicon wafers. The first step of the fabrication was the DRIE with a thick photoresist used as an etch mask. Then the micro-channels were bonded with a Pyrex[®] glass wafer by anodic bonding. Finally capillaries were sealed at the inlet/outlet with ceramic cement and a glass paste. The inlet/outlet has a depth of 500 μ m, corresponding to the diameter of the capillaries used as fluidics interconnections [2].

The preconcentrator allows desorbing at relatively high temperature (230°C) all the molecules collected after an adsorption step made at ambient temperature thanks to an adsorbent which is described below. On the backside of the silicon device, a platinum resistance was screen printed to act as a heater with a heating rate of 40°C/s (Figure 1).

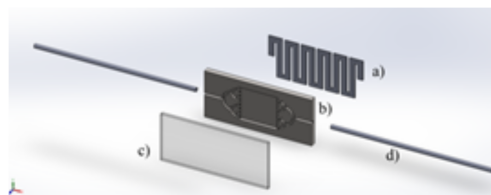
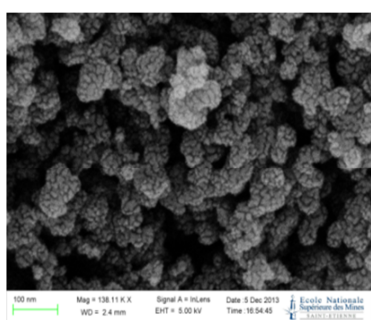
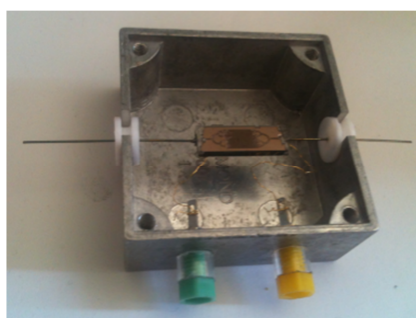


Figure 1: Design and schematic device composition; a) platinum heater, b) MEMS, c) glass cover, d) capillaries

In this study, the device was designed [3] to ease the introduction of a carbon nanopowder (activated charcoal from Aldrich $95\text{m}^2/\text{g}$) used as adsorbent (Figure 2). The carbon-based adsorbent has shown a good adsorption capacity and a low desorption temperature for a large range of COVs, according to Thermal Programmed Desorption (TPD) characterizations. This adsorbent material was introduced into the micro-channel in the form of powder by fluidic solution.



a)



b)

Figure 2: a) SEM Image of carbon nanopowder b) Filled preconcentration device in a box

3. Tests on laboratory bench

First of all, the preconcentrator was tested with a laboratory setup. A micro-PID was used as a gas analyzer. Toluene has been chosen as a representative of Volatiles Organic Compound. The carrier gas was air. Calibrated concentrations of this vapor were generated by using a permeation tube and a gas generator. Results reported (Figure 3) show the response of the PID analyzer after an adsorption of 1 ppm toluene during 5 min at 10L/h. When the temperature is increased up to 230°C a desorption peak of toluene is clearly observable. The results have shown a preconcentration factor of 35 (ratio of outlet to inlet concentration). The preconditioning effect of the device filled with carbon powder is therefore demonstrated since no desorption peak has been observed when this device has no carbon powder inside under the same conditions.

4. Coupling between a preconcentrator and a micro-chromatograph

Experiments were conducted with a preconcentrator associated to a micro gas chromatograph (μGC) in collaboration with SRA Instruments Company (Figure 5). The capillary column used was an OV1 type, 12 m long and has allowed the mixture separation of compounds in less than 5 minutes. Considering the removal and purging steps, the complete analysis cycle does not exceed 20 minutes for this application. First, we have studied a mixture of toluene, vinyl acetate monomer, chloroform and méthylisobutylketone (MIBK) with initial concentrations range of 10 ppmv, and have obtained preconcentration factor (ratio of peak areas with and without preconcentration step at the same experimental conditions) of 600 to 800 (Figure 4).

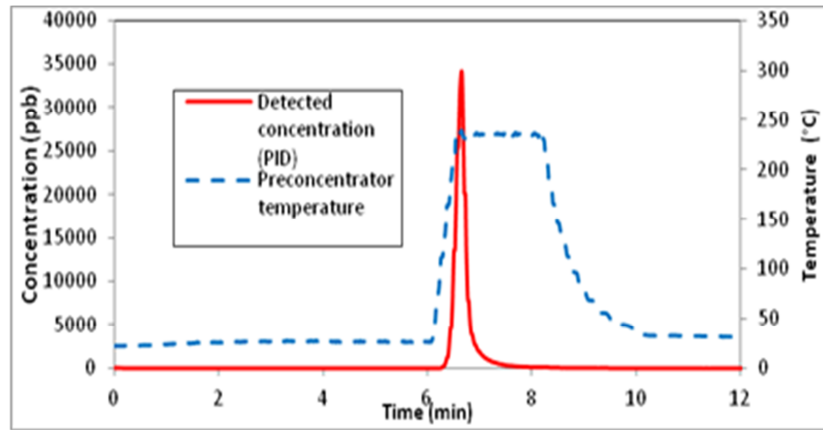


Figure 3: Sensor response for a preconcentrator filled with 1 mg of activated carbon nanopowder when exposed to 1 ppm of toluene during 5 minutes and desorbed at 230°C at 10L/h

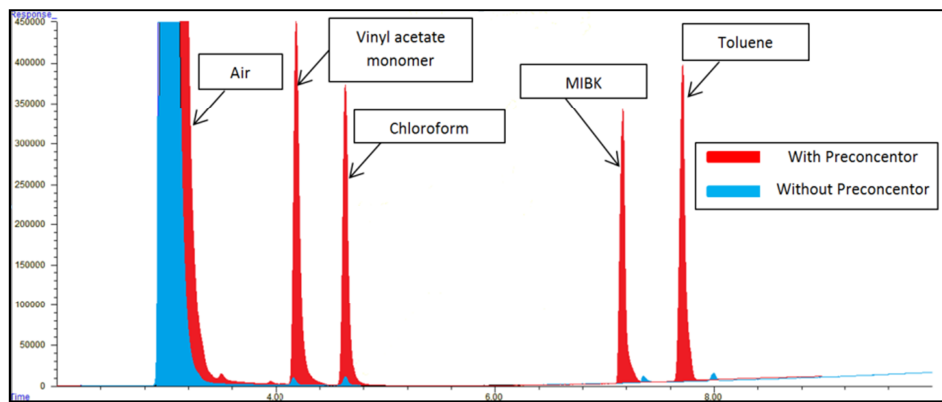


Figure 4: ppm range analysis of a VOCs mixture by gas micro-chromatography

Then we tested the same mixture in range of concentrations about 35 ppbv in presence of interference like natural gas and using an OV1 column type, 6 m long. These parameters are very representative for gas chromatograph analysis in field test (Figure 5).

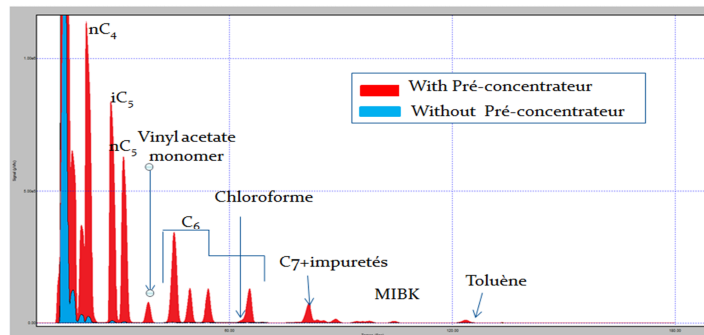


Figure 5: ppb range analysis of VOCs mixture with interference by micro-chromatography

Table 1. Preconcentration factors for different VOCs.

Target Gas	Concentration (ppb)	Preconcentration factors
Toluene	37	200
Vinyl acetate monomer	39	800
Chloroform	46	600
Méthylisobutylketone	35	200

This concept of miniaturized preconcentrator has allowed the detection of VOCs in concentration range of 35 ppbv while maintaining the speed of the μ -GC analysis. This experiment has also demonstrated significant preconcentration factors (up to 200) with a maximum about 800) (Table 1).

5. Conclusion

These results have shown that with the micro-preconcentration device we can increase the detection limits of the coupling micro gas chromatograph for different vapors. The capacity of the carbon nanopowder to adsorb a mixture of different VOCs has been proved. This study has allowed developing a preconcentration step for better VOC analysis with these experimental conditions. However studies of the adsorption temperature influence and of the humidity should be performed to determine the effectiveness of this process for outdoor air or a specific atmosphere.

Moreover, another challenge is to realize the same approach for explosive analysis which required more technology. Indeed explosive compounds are mainly characterized by a low vapor pressure and a strong bond on solid matters which makes their detection very difficult.

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