

Application of carbon nano-powders for a gas micro-preconcentrator

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Abstract

This paper presents a feasibility study on the development of a gas preconcentrator based on micro-reactor technology on silicon. The objectives are to select a gas adsorbent material, to produce a silicon micro-reactor with an integrated heater, and finally to introduce the most suitable adsorbent into the micro-channels of the device. Preliminary results related to the characterization of a carbon adsorbent for the development of a device for the preconcentration of benzene are reported. Carbon nano-powders have been tested as adsorbent material by the determination of the breakthrough time on a dedicated test bench consisting of gas sensors and a non-selective photoionization detector (micro-PID) analyzer. A fluidic deposition process allows filling up the silicon micro-channels with the carbon nano-powder. The interest in using porous silicon to enhance the binding of the carbon nano-particles in the micro-channels was also investigated. A silicon micromachined preconcentrator filled with 0.30 mg of commercial activated charcoal powder (Aldrich, 30–100 nm) was designed and built up. The total capacity of adsorption was determined by using the breakthrough time, which is of 2.2 min under a gas flow of 100 ppm of benzene at 1 l/h. Preliminary tests of preconcentration with 100 and 1.3 ppm benzene in dry air were performed.

Keywords: Benzene; Carbon powder; Gas sensor; Silicon micro-channels; Micro-reactor; Preconcentrator

1. Introduction

In the field of gas detection, one major trend is to miniaturize analytical techniques (gas chromatograph, IR-UV analyzers, mass spectrometers, ion mobility spectrometers . . .). These technological developments are part of the field of Micro Total Analysis Systems, referred to as “ μ TAS”. In such devices, the pre-processing of gases is generally of high interest during the sampling step. There are two main relevant for the pre-processing of the sample of gases to be analyzed: first a modification of the gas mixture to increase the selectivity of the detection (especially in the case of direct detection with gas sensors with poor selectivity), and second, a preconcentration effect to increase the sensitivity of the detection (especially in the case of trace detection as in atmospheric pollution control or explosive detection) [1–4]. For several types of applications, there is currently a high request for preconcentration systems, as for example in the fields of health monitoring and security. Indeed, there is a growing interest in coupling preconcentrators linked with gas sensing systems to identify analytes linked to specific

diseases [5]. The same observation is valid with the detection of trace levels of gases generated by explosives [6]. Finally, preconcentration might also be applied for odor detection in waste applications [7], for indoor air quality monitoring [8], as well as for the detection of very low concentration of gases in food samples [9].

The aim of this work is to realize an autonomous microsystem based on micro-reactor technology dedicated to gas preconcentration. In a previous study, such a device has been developed for catalytic conversion either for hydrogen production [10] or for gas transformation to improve the selective detection by a sensor placed at the exit of the micro-fluidic reactor [11]. In order to achieve these objectives, a silicon micro-reactor with micro-channels fabricated by deep reactive ion etching (DRIE) has been developed. The catalyst was deposited within the channels by a fluidic process. These types of components have been successfully used for hydrogen production from methylcyclohexane, or to realize a gas filter before a gas sensor for selective detection of CO and CH₄.

In the present publication, we suggest to use a similar technology to realize gas preconcentrators on silicon based on micro-fluidics. The main difference with our previous work is that the catalyst is replaced by an adsorbent which is introduced in the form of a powder, such as for micro-gas chromatograph

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systems [12]. The issues related to the deposition of functional materials in micro-channels have been previously exposed, for example with the deposition of a catalyst in micro-reactors for chemical reactions [13]. The preconcentration of benzene has been chosen in this study since the detection of trace levels of benzene is very representative of the two types of applications which we target, the atmospheric pollution control (BTEX detections) and explosive detection (such as nitro-benzene). It is also recognized that carbon materials have a good adsorption capacity for benzene and this material was investigated as adsorbent in this work [14]. The best solution could be to realize the synthesis of nano-carbon materials directly in the channels, however, this type of preparation of nanoporous carbon raises a certain amount of issues [15–17]. Hence, it has been decided to use only a commercial carbon nano-powder and to insert it within the micro-channels using a process based on micro-fluidics. Micro-channels made of silicon and porous silicon were investigated [18,19]. The high specific area offered by porous silicon can be used as interesting support for the adsorbent materials, for example to increase the quantity of carbon powder which could be deposited in the channels. Besides, porous silicon presents also itself a high capacity of molecules adsorption which in combination with the carbon powder could provide an interesting preconcentration effect [20].

Preliminary results obtained with a carbon nano-powder for benzene adsorption are presented. They aim at optimizing some parameters to increase the preconcentration ability of the microsystem. Therefore, the micro-channel designs as well as their surface treatments used to improve the binding and the accumulation of carbon powders are presented and discussed. The breakthrough time is evaluated with the help of a dedicated test bench that is fully described in this communication. Preliminary tests of preconcentration with 100 and 1.3 ppm benzene in dry air were performed.

2. Experiments and results

2.1. Adsorption of benzene on carbon powder

A commercial nano-powder of activated charcoal (Aldrich) has been selected for the first experiments. The particle sizes are in the range 30–100 nm and the specific area determined by nitrogen adsorption according to the BET method is close to 100 m²/g. The morphology of these carbon particles is presented in Fig. 1.

Benzene adsorption capacity has been measured first by thermogravimetric analysis (TGA). The sample is submitted to a flow of 1 l/h of 100 ppm of benzene in nitrogen. Adsorption is measured at room temperature, and desorption is observed during the increase in temperature. A typical TGA curve obtained with the carbon powder pre-treated under nitrogen at 100 °C is shown in Fig. 2. Under these conditions, the adsorption capacity is equal to 5.3 mg of benzene per gram of carbon. In comparison with the values found in the literature, the obtained value seems very low. This might be due to our experimental conditions that are not optimal, especially at low concentration (100 ppm) and perhaps to the presence of water vapor in the analyzer. New

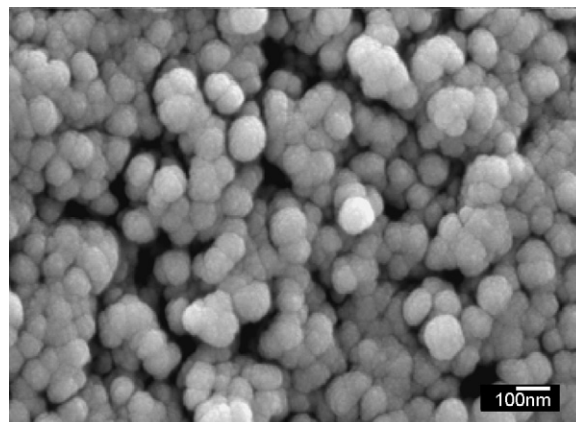


Fig. 1. SEM picture of the activated charcoal nano-powder (commercial powder from Aldrich).

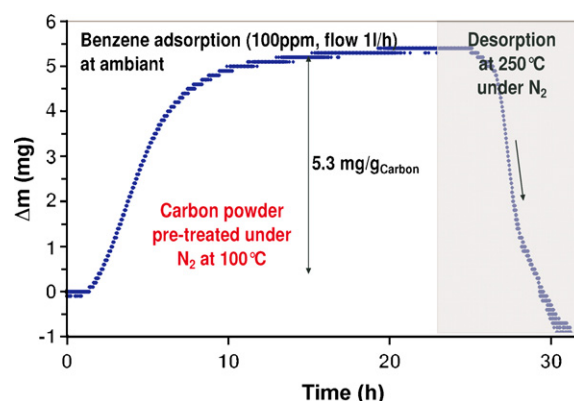


Fig. 2. TGA curves during benzene adsorption on carbon powders at room temperature and desorption at 250 °C.

TGA experiments are ongoing to clarify the aforementioned issues.

A second type of experiments has been realized using a dedicated test bench as shown in Fig. 3. It is composed of a small furnace, consisting in a quartz tube filled in with the carbon powder, and a micro-PID gas analyzer. It is also possible to control the gases with a semi-conductor gas sensor (TGS 2602). Benzene is generated with a diffusion tube closed with a diffusion membrane. The mass flow controllers allow varying the ben-

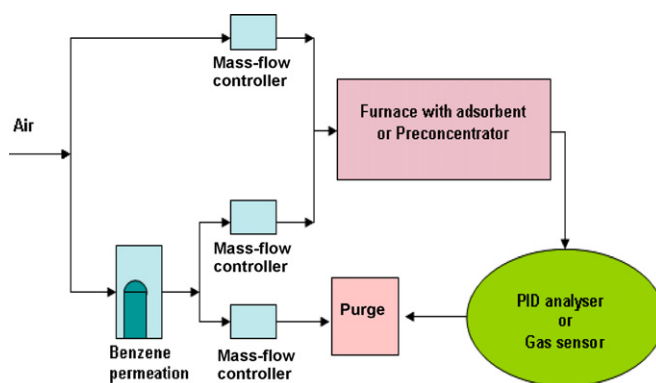


Fig. 3. Gas test bench to evaluate the carbon powder adsorption and to test the preconcentrators.

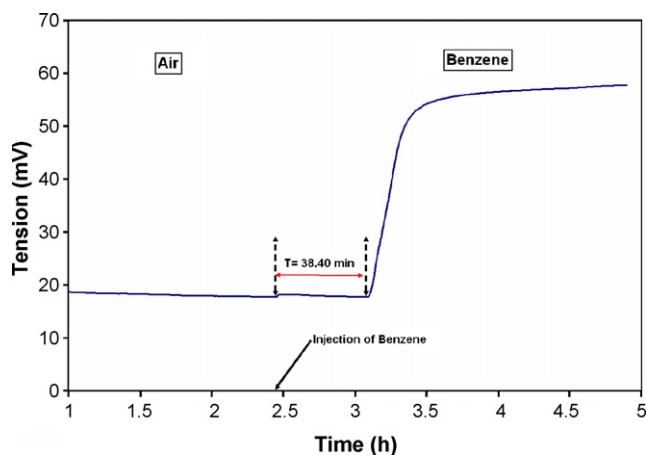


Fig. 4. Determination of the breakthrough time using a TGS sensor placed after the carbon powder.

zene concentration from a few ppm to several thousands of ppm. This bench can be also used to directly test the silicon micro-components that will be developed afterwards. The following experiments described in this section have been performed under the following conditions: 3550 ppm of benzene under a synthetic air flow of 1 l/h. On the basis of calibration curves determined in previous experiments, we have also checked that the response of the TGS gas sensor after the drilling is the same response as the one obtained when flowing air with 3550 ppm of benzene.

The adsorption capacity of the carbon load is evaluated with the determination of the time of breakthrough (“drilling”) corresponding its saturation. The mass of carbon powder placed in the tube is 157.5 mg. The gas sensor’s response after injection of benzene on the load of carbon at room temperature versus time is reported in Fig. 4. The exact period between the benzene injection to the beginning of the TGS response, which corresponds to the saturation time, is of 38.4 min. According to our experimental conditions this period matches an adsorption of 6.65 mg of benzene in the carbon load. Consequently, the mass of benzene adsorbed is 42.2 mg per gram of carbon powder. This adsorption capacity is near 5% (mass).

The benzene desorption from the carbon powder has also been studied. We can observe in Fig. 5 two desorption maximums (at 5 and 7 h on x -axis) when the temperature is increased first from room temperature to 100 °C and then up to 280 °C. It can be also observed that the desorption is completed at room temperature (at 30 h on x -axis) when the flow of benzene is shut

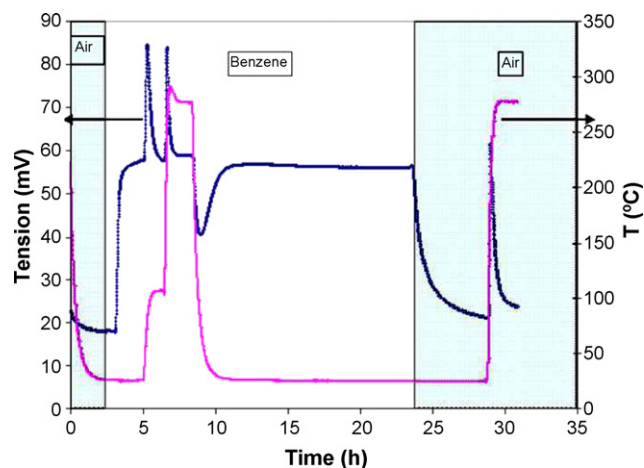


Fig. 5. Adsorption–desorption of benzene measured by gas sensors located after the carbon powder with an indication of the temperature of the device.

down and replaced by pure air. The influence of the temperature during the adsorption step has also been investigated with a cooling bath. Our calculations demonstrate the adsorption of benzene is increased by a factor 50 when the temperature is reduced from 20 to 15 °C. This observation is in good agreement with literature data and it is highly relevant for the future operation of the final micro-component.

Finally another observation confirming the good adsorption efficiency of the carbon nano-powder has been realized by replacing it by a load of Carbotrap™. The latter is a carbon black powder similar to the previous one used, but its specific area is only of 3.4 m²/g. With such an adsorbent we have almost no delay time for the response of the TGS sensor after benzene injection (3.6 min corresponding the volume of the cell), and no desorption with increasing temperature.

2.2. Formation of porous silicon

We have investigated the possibility to use porous silicon to enhance the binding of the carbon powders on the silicon walls. Porous silicon was formed from various types of silicon wafers and etching conditions to obtain different morphologies and densities of the pores (Table 1). The specific areas were determined by BET measurements. A typical microstructure obtained with n -type substrates and with a current density of 40 mA/cm² for an etching time of 20 min is shown in Fig. 6. The diameters of the pores are in the range of 870–1920 nm with a penetration

Table 1
Porous silicon morphology as a function of the parameters used for its formation

Wafer type	Wafer resistivity [Ω cm]	Current density [mA/cm ²]	Etching time [min]	Pore diameter [nm]	PS thickness [μm]	Etch rate [μm/min]	Specific area [m ² /g]
p	0.015	75	6	8–13	6.3	1.05	0.77
p	0.015	150	6	8–13	20.4	3.40	3.07
p	5	300	30	11–25	NA	NA	0.10
n	5	2	40	73–515	28.1	0.70	0.45
n	5	30	20	122–305	22.5	1.13	0.36
n	5	40	20	348–1060	136	6.80	2.33
n	5	40	20 + RIE	871–1920	130	6.80	2.58

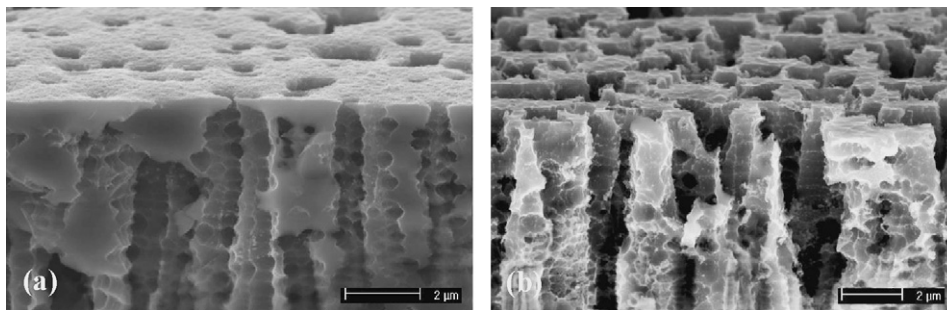


Fig. 6. SEM picture of the cross-section of a porous silicon substrate (n-type, 20 min, 40 mA/cm²). (a) Before dry plasma etching and (b) after dry plasma etching.

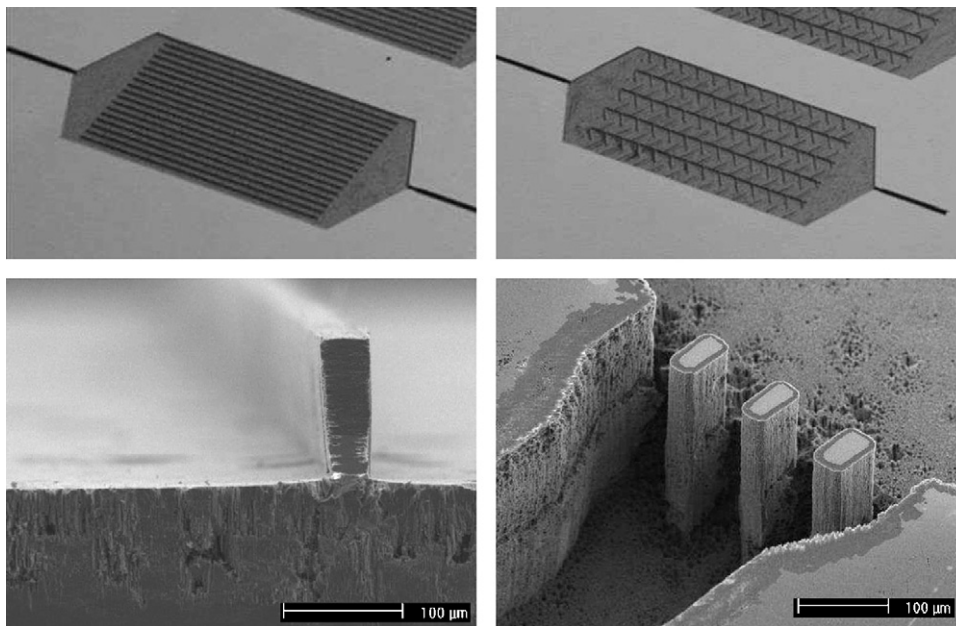


Fig. 7. Silicon micro-channels obtained by DRIE. Top pictures: the two designs "straight" (left) and "ear" (right). Bottom picture: detail of an inner wall (left) and pillars at the outlet (right).

of 130 μm deep in the silicon substrate. The specific area is of 2.5 m²/g. For several samples, the access to the pores has been widened by removing silicon at the surface of the substrate using dry plasma etching (Fig. 6b).

2.3. Micro-channels fabrication and integration of heater and fluidic interconnects

As our objective is to develop a micro-preconcentrator, silicon micro-channels have been realized with standard etching processes. Low-stress LPCVD silicon nitride and silicon oxide are used as etch masks for the porous silicon formation and for the patterning of the micro-channels by DRIE, respectively. Preconcentrators with two different types of design have been fabricated ("Straight" and "Ear" types). The different channels are designed with the necessity of having some pillars or walls within the channels in order to control the powders deposition by fluidic solutions. The area of the chamber of the preconcentrator is 20 mm × 10 mm. The depth of the inlets and the outlets is of 325 μm, while the channels are 120 μm deep. The width of the silicon walls inside the chamber is of 50 μm (Fig. 7). The silicon micro-channels are closed with a glass cap by anodic bonding.

The integration of the heating element and of the fluidic interconnects are realized with similar processes as the ones used in our previous development of a catalytic micro-reactor. A platinum thick film resistance is screen-printed onto the backside of the silicon chip (Fig. 8a). Gold wires are used for the electrical connections. The heating element allows the component to

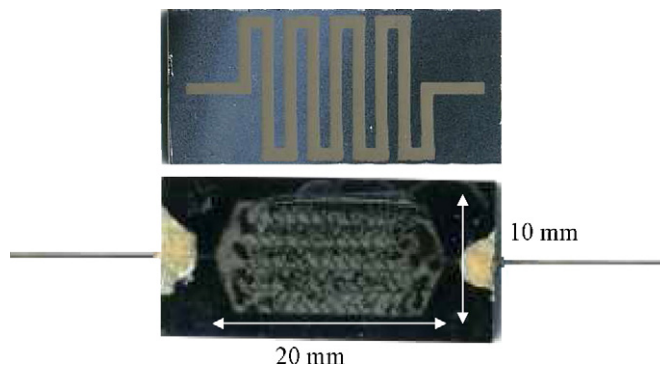


Fig. 8. Pictures of the preconcentrating components: (a) from the backside with the platinum thick film used as heating element (deposited by screen printing), (b) final component with metallic capillary tubes glued using a ceramic cement.

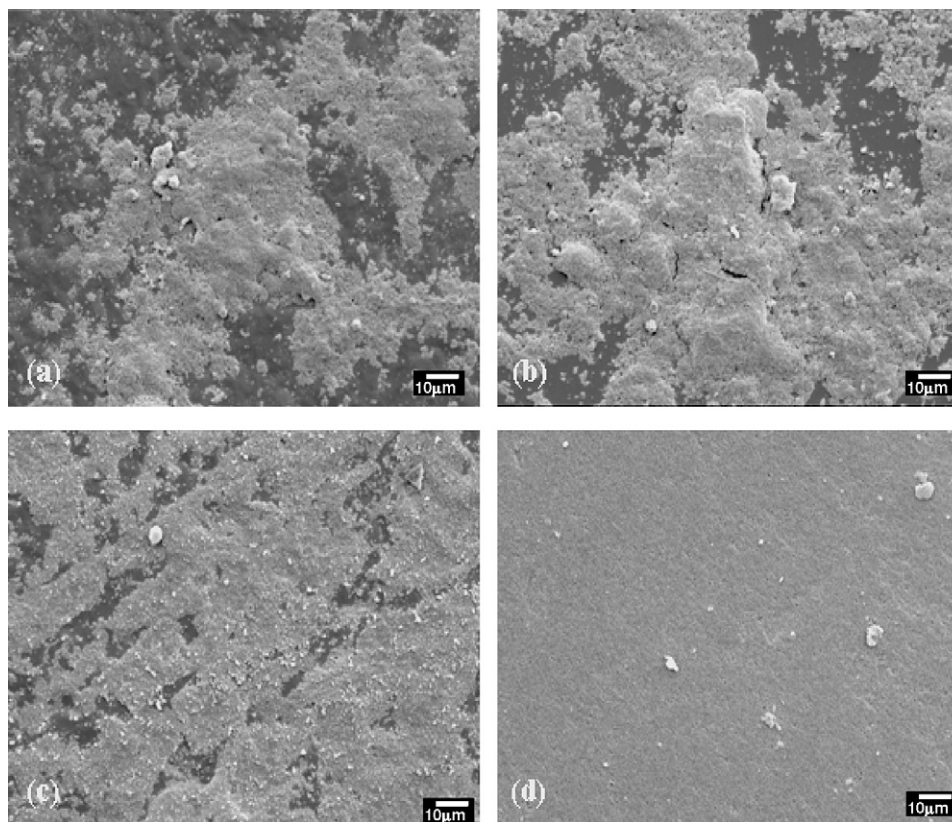


Fig. 9. SEM picture of carbon deposited by dip-coating: (a) silicon wafer dipped in a carbon suspension without dispersant, (b) silicon wafer dipped in carbon suspension with dispersant, (c) oxidized silicon wafer dipped in a carbon suspension without dispersant, (d) oxidized silicon wafer dipped in a carbon suspension with dispersant.

reach temperatures up to 500°C . The fluidic interconnects are realized with metallic capillary tubes ($325\ \mu\text{m}$ in diameter) that are glued to the silicon chip with a ceramic cement. The tightness is maintained at temperatures as high as 500°C (Fig. 8b).

2.4. Deposition of carbon in the micro-channels

The first experiments on filling the micro-channels with the carbon nano-powder have been performed with a suspension of the powder in an adequate dispersant. Then, this suspension is injected with a micro-syringe through the fluidic interconnects. The dispersant is removed by evaporation a temperature of 400°C using the integrated heater. In order to characterize the carbon deposition, which depends both on the nature of the dispersant and on the surface of the wafer, prior tests were performed by dip-coating various pieces of silicon wafers in the two different carbon suspension, with and without a dispersant. As shown in Fig. 9, some homogenous carbon layers have been obtained on oxidized silicon surfaces when dipped in a solution containing a dispersant.

If the deposition is realized onto a silicon wafer without a layer of silicon oxide, it is more difficult to obtain a homogeneous film of carbon powder (with or without the use of the dispersant). On oxidized silicon and using a solution without dispersant, we can observe that the deposited film is also less homogeneous, but SEM observations have shown that the carbon film is thicker. As a result, the dispersant solu-

tion has not been used for the carbon deposition in the micro-channels.

The final process to introduce the carbon suspension in water in the micro-channels was to alternate several time between the flow of the suspension within the channels and its drying using a hotplate. A special attention had to be paid to avoid the connection tubes to clog and the tightness to deteriorate, which resulted in a pressure increase. The amount of deposited carbon in the channels depends on their design with an efficiency that seems higher for the straight design. Another important result concerns the use micro-channels made of porous silicon. The comparisons with normal silicon micro-channels show that the quantity of carbon deposited within the channels is larger (by near a factor 2) with porous silicon having pores with diameters between 1 and $2\ \mu\text{m}$ (Table 1). Therefore, the most suitable substrate type for the actual application is an n-doped silicon wafer with a resistivity of $5\ \Omega\ \text{cm}$.

At the moment, the amount of carbon deposited is typically of $0.30\ \text{mg}$. If the pressure loss is very low without carbon, it increases with the carbon deposition to a final value typically of about 2 bars with an air flow of $1\ \text{l/h}$ (straight design with $0.30\ \text{mg}$ carbon).

2.5. Tests of micro-preconcentrators

After filling with the carbon powder, the performances of the micro-channels filled with $0.30\ \text{mg}$ of carbon powder have been

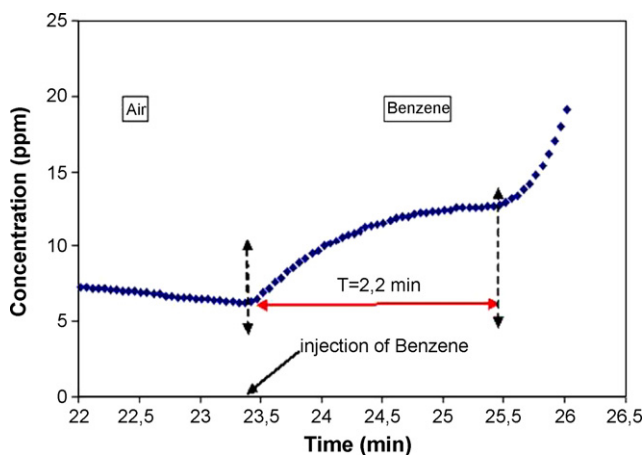


Fig. 10. Breakthrough time determined by the response to benzene of the PID analyzer located at the exit of the micro-channels filled with 0.30 mg carbon.

evaluated by performing benzene adsorption/desorption steps. The same procedure as previously described was used to test the absorption capacity of the filled micro-channel by determining the breakthrough time when exposed to a concentration of 100 ppm of benzene with a flow of 1 l/h. For these experiments the concentration of benzene is still as high as beforehand (100 ppm). The micro-channel is placed on the test bench and the monitoring of the benzene concentration is achieved by the PID analyzer placed at the outlet. A typical response of the PID analyzer to benzene in a straight micro-channel is presented in Fig. 10. The breakthrough time is 132 s. From this result, the quantity of benzene adsorbed in the channel can be estimated to be 0.012 mg according to the experimental conditions (0.3 mg of carbon, gas flow of 1 l/h, benzene concentration of 100 ppm). This corresponds to a capacity of adsorption of 4%, which is in good agreement with the one obtained with the carbon powder tested in the furnace, as reported in Section 2.1.

Final experiments in which the benzene concentration has been reduced to 1.3 ppm by multi-dilutions have been carried out. Results reported in Fig. 11 show the response of the PID analyzer after an adsorption of 1.3 ppm benzene during 2.40 min.

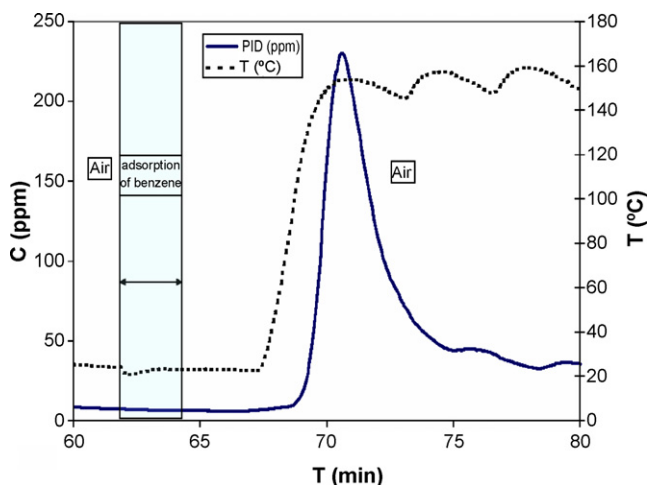


Fig. 11. Response of the PID to a desorption step occurring at 160 °C after an adsorption of 1.3 ppm of benzene for 2.40 min.

When the temperature is increased up to 160 °C a desorption peak of benzene is clearly observable. In addition, since no desorption peak has been observed when using micro-channels with no carbon powder inside under the same conditions; the pre-conditioning effect of the device filled with carbon powder is demonstrated.

3. Discussions and conclusion

We have demonstrated the feasibility to fill a micro-channel with a carbon nano-powder using a deposition process based on micro-fluidics. The capacity of this powder to adsorb benzene has been proven on the basis of the breakthrough time determination with a dedicated test bench equipped with a gas analyzer. Preliminary experiments realized with micro-channels filled with 0.30 mg of carbon powder have shown that such components can be used in the future for the development of micro-preconcentrators. Obviously, some more validations are needed. Reproducibility and repeatability tests must be performed with different micro-channels. As an example, a small desorption peak is observable with blank adsorption–desorption cycles under pure air without benzene. This peak is clearly smaller than the one with benzene adsorption, but it shows a non-selective adsorption of the carbon powder. New experiments are definitely required to explain and control such phenomena. Our current experiments concern the influence of interfering gases, especially water vapor. It is essential to determine the best temperature cycles with the carbon powder in order to improve the efficiency of the preconcentrator. Moreover, as the adsorption is higher when the chip is cooled (for example down to 10 °C), its efficiency will be improved in the future by using a small Peltier element.

The development of a complete preconcentration device can be now investigated. Nevertheless, the choice of the adsorbent material will depend on the targeted applications. In the present study, we have decided to deposit a commercial carbon nano-powder from a fluidic solution. In the future however, it could be relevant to replace this deposition process by a synthesis of carbon materials directly within the channels. There are now some methods to produce mesoporous materials [21], and especially mesoporous carbon [22] using for example silica template that could be used perhaps with our silicon micro-channels. In addition, regarding to carbon materials there are currently many studies to produce carbon nano-tubes (CNTs) that appear to be well suitable for gas adsorption [23] and especially preconcentration devices [24]. The second type of interesting materials with high adsorption efficiencies are the organic materials, such as polymers. Silicones have been used successfully for nitroaromatic detection in the case of explosive application [25]. Such organic adsorbing materials have been deposited within micro-channels for preconcentration [26–28]. We will also pay a special attention to these materials according to their ability of both selective adsorption and in situ synthesis. Another important direction of future actions is related to the comparison of micro-channels and micro-hotplates for preconcentration. Several recent publications are focused on the use of micro-hotplates for the developments of preconcentrators [29,30]. According to

the wide range of applications, and therefore to the wide range of possible gases to be detected and adsorbent materials to be used, it will certainly be interesting to have a parallel development of two types of preconcentrating devices based respectively on the micro-channel and micro-hotplate technologies. Both can offer adequate solutions to specific applications. Micro-hotplates are simpler and they can be used to evaluate quickly performances of materials as adsorbents. They can offer a short term solution when large volumes of gases are required. The micro-channels are more sophisticated, for instance regarding the deposition of the adsorbent material, and their complete development will take a little bit more time, but they will constitute a good solution to the development of integrated devices with a high degree of miniaturization.

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