



**HAL**  
open science

## **A micro gas preconcentrator with improved performance for pollution monitoring and explosives detection**

El Hadji Malick Camara, Philippe Breuil, Danick Briand, Nicolaas F de Rooij, Christophe Pijolat

### ► **To cite this version:**

El Hadji Malick Camara, Philippe Breuil, Danick Briand, Nicolaas F de Rooij, Christophe Pijolat. A micro gas preconcentrator with improved performance for pollution monitoring and explosives detection. *Analytica Chimica Acta*, 2011, 688 (2), pp.175-188. 10.1016/j.aca.2010.12.039 . hal-00567201

**HAL Id: hal-00567201**

**<https://hal.science/hal-00567201>**

Submitted on 18 Feb 2011

**HAL** is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.

# A MICRO GAS PRECONCENTRATOR WITH IMPROVED PERFORMANCE FOR POLLUTION MONITORING AND EXPLOSIVES DETECTION

E. H. M. Camara<sup>(1, 3)</sup>, P. Breuil\*<sup>(1)</sup>, D. Briand<sup>(2)</sup>, N. F. de Rooij<sup>(2)</sup>, C. Pijolat<sup>(1)</sup>

<sup>(1)</sup> Ecole Nationale Supérieure des Mines, Centre SPIN, LPMG-UMR CNRS 5148, 158  
Cours Fauriel, 42023 Saint-Etienne, France

<sup>(2)</sup> Ecole Polytechnique Fédérale de Lausanne, Institute of Micro-Engineering,  
Rue Jaquet-Droz 1, P.O. Box 526, CH-2002 Neuchâtel, Switzerland

<sup>(3)</sup> Faculté des sciences, Université de Neuchâtel,  
Avenue du 1<sup>er</sup> mars, 26, CH-2002 Neuchâtel, Switzerland

\*Corresponding author : P. Breuil, Phone 33 4 77 42 01 51, Fax 33 4 77 49 36 20, [pbreuil@emse.fr](mailto:pbreuil@emse.fr)

**Abstract:** This paper presents the optimization of a micro gas preconcentrator based on a micro-channel in porous and non-porous silicon filled with an adequate adsorbent. This micro gas preconcentrator is both applicable in the fields of atmospheric pollution monitoring (Volatil Organic Compounds-VOCs) and explosives detection (nitroaromatic compounds). Different designs of micro-devices and adsorbent materials have been investigated since these two parameters are of importance in the performances of the micro-device. The optimization of the device and its operation were driven by its future application in outdoor environments. Parameters such as the preconcentration factor, cycle time and the influence of the humidity were considered along the optimization process. As a result of this study, a preconcentrator with a total cycle time of 10 minutes and the use of single wall carbon nanotubes (SWCNTs) as adsorbent exhibits a good preconcentration factor for VOCs with a limited influence of the humidity. The benefits of using porous silicon

24 to modify the gas desorption kinetics are also investigated.

25

## 26 **KEYWORDS**

27 Gas preconcentrator, Micro-channel, Porous silicon, Carbon nanotubes, Adsorbent

## 28 **1. INTRODUCTION**

29 In miniaturization of physical analysis methods, preconcentration appears as the essential element for  
30 improving both the sensitivity and the selectivity of these devices <sup>[1, 2, 3, 4, 5]</sup>. Thus, micro-preconcentrators find  
31 their applications in various systems for gas analysis such as solid phase micro gas chromatography ( $\mu$ -GC)  
32 <sup>[6, 7, 8, 9, 10]</sup>, ion mobility spectrometry (IMS) <sup>[11, 12, 13]</sup> and electronic nose (E-nose) <sup>[14, 15, 16, 17]</sup>.

33 The use of detection systems based on the preconcentration is growing since the need to quantify very  
34 low concentration is growing up as well as in the field of civil security as in agribusiness and healthcare. For  
35 example, in the later, there is a demand of preconcentrators for medical diagnostics as addressed by Mr.  
36 Cho Seong et al <sup>[17]</sup> and William A. Groves et al <sup>[18]</sup>. They have analyzed through a preconcentration system,  
37 the air exhaled by a patient while knowing that the appearance of some gas molecules in exhaled air is  
38 characteristic of the metabolism, thus the state of patient's health. The presence of some of these VOCs is  
39 attributed to a definite disease; for example, alkanes, benzene derivatives o-toluidine and aniline are referred  
40 to lung cancer, while acetone is linked to diabetes...

41 In the environmental field, it should be noted that the increasing of industrialization around some major  
42 cities causes great vigilance in the monitoring environmental pollution and the prevention of disasters. Each  
43 country, through an environmental quality agency, sets tolerance limits for some VOCs. For example, in  
44 United States, the threshold for benzene is determined by the U.S. EPA (U.S. Environmental Protection  
45 Agency) to 500ppb in ambient air and 5ppb in drinking water <sup>[19]</sup>. While in France, the limit is set by IFEN  
46 (French Institute of Environment) to  $10\mu\text{g}/\text{m}^3$  <sup>[20]</sup>. These limits continuously being reviewed to lower levers  
47 require the implementation of more performing detection equipments with a low detection limit and very short  
48 sampling time.

49 The need to improve both the sensitivity and the selectivity of some detection systems has prompted  
50 many laboratories to review the implementation of their gas pre-conditioning system. Thus, systems with

51 multiple stages of preconcentration were developed to reduce both the influence of water vapor and other  
52 interfering gases such as alcohol derivatives <sup>[17, 21]</sup>. S. M. Cho et al <sup>[17]</sup> have implemented two-stage  
53 preconcentrators filled with a hydrophobic adsorbent (carbotrap) allowing to reduce the influence of water  
54 vapor in the analysis of human exhaled breath. There are also other multiple stages preconcentration  
55 techniques based on the difference of desorption temperature between the two preconcentration units to  
56 overcome the influence of other interfering gases upon detection as demonstrated by B. Alfeeli et al <sup>[21]</sup> in  
57 their concept of cascaded micro-preconcentrator.

58 A new innovative process in the field of micro-preconcentration is the use of porous silicon. Indeed, the  
59 use of porous silicon as a binding surface for filling adsorbent appears as a very attractive approach in the  
60 development of miniaturized preconcentration because it offers the possibility to deposit by fluidic solution  
61 various types of adsorbent while avoiding the problems of overpressure during the experiences.

62 In our previous study <sup>[22, 23, 24]</sup>, a gas pre-concentrator based on porous silicon micro-channels filled with  
63 carbon nanopowders from a fluidic solution has been developed. The present work aims to improve the  
64 performance of this device, with new approaches in the design as well as in the choice of adsorbent  
65 materials and modes of operation. We have further investigated the contribution of porous silicon in the  
66 adsorption and desorption phases since besides the increase of its specific surface area as reported in <sup>[26]</sup>,  
67 porous silicon when coupled with the adequate adsorbent can also modify the desorption kinetics of the  
68 target gas.

69 Alternative adsorbent materials such as carbon nanotubes and polymers, whose surface areas, pores-  
70 size distributions, and structures can be varied to serve as conformal adsorbents, were evaluated for the  
71 improvement of the performance of the preconcentrator <sup>[5]</sup>.

72 The devices in this study have been developed targeting the preconcentration of benzene and  
73 nitrobenzene which are representative gases for several types of applications relevant from atmospheric  
74 pollution control to explosives detection.

## 75 2. EXPERIMENTAL

### 76 2.1. Adsorbent Materials

77 The choice of the adsorbent material is an important factor in the performance of a micro gas  
78 preconcentrator. The suitable adsorbent must have a strong affinity with the target gas, a low activation  
79 energy of desorption, a large adsorption capacity vis-à-vis of the target gas and finally a good binding of its  
80 particles on the preconcentrator substrate in order to avoid an evacuation of the deposited adsorbent under  
81 high gas flow which is harmful for the performance of the devices. The activation energy of the adsorbent is  
82 symbolized by its desorption temperature; while the adsorption capacity is linked to the specific area.

83 Therefore, four different adsorbents such as activated carbon, carbon nanotubes (Single Walled Carbon  
84 NanoTubes-SWCNTs, Multi Walled Carbon NanoTubes-MWCNTs) and Tenax polymer have been tested for  
85 the preconcentration of benzene and nitrobenzene in presence of humidity by using various techniques: BET  
86 (Brunauer, Teller and Emmett) method, Thermal Programmed Desorption (TPD) and applying them to micro-  
87 preconcentrator devices.

88 The BET method is a volumetric adsorption of gas point by point, which allows obtaining the complete  
89 isotherms (adsorption and desorption). These gas adsorption/desorption isotherms (Nitrogen, Argon,  
90 Krypton...) will permit the determination of the specific area and the adsorbent texture. The value of the  
91 specific area is obtained from the absorption isotherms of a gas at the liquid nitrogen temperature (77K).  
92 TPD technique is often used to discern the different desorption products of a given adsorbent after an  
93 adsorption phase. This technique consists in programming the desorption heating rate and selectively  
94 measuring the desorption products with a mass spectrometer. In some cases, the adsorption phase can be  
95 done in situ and the desorption heating rate is set to 100°C/min in order to make easier the discrimination of  
96 the various desorption products.

97 The carbon adsorbent used in this test has been activated by thermal process. The activation of carbon  
98 is an oxidizing reaction in order to release internal porosity created during the carbonization, to expand the  
99 pores, to create new micropores and to increase its specific area. This step must be controlled to avoid the  
100 total elimination of the carbon structure as the activation at high temperature (up to 900°C) under oxygen can  
101 cause the total disappearance of carbon structure. That is why we have done the activation of carbon

102 nanopowder at 500°C during 3 hours in presence of oxygen. All the others adsorbents materials were not  
103 activated because this process was not needed due to of their specific area already higher.

## 104 **2.2. Preconcentrator**

105 Micro-devices with different designs have been fabricated (figure 1) by deep reactive ion etching (DRIE)  
106 of silicon wafers using a thick photoresist mask. In the case of porous silicon channels, prior to the DRIE, a  
107 silicon nitride film is deposited to act as a masking layer during the porous silicon formation. Then, for both  
108 types, a 50 nm thick thermal oxide of is grown prior to their sealing with a glass cover by anodic bonding.  
109 The different channels are designed with the necessity of having some pillars or walls within the channels in  
110 order to control the powders deposition by fluidic solutions <sup>[23, 24]</sup>. The neutral microchannel is designed  
111 without structures in the internal chamber while the zigzag design with channel system at inlet/outlet, mostly  
112 used in this work, is made with "V" shaped structures in order to improve the flow distribution not only during  
113 the adsorbent deposition but also during experiments.

114 The first micro-devices realized at the beginning of this study were made following two depths of etching.  
115 The internal chamber etched at 120µm into the silicon contains parallel channels, either smooth or with the  
116 "scales". In order to receive the metallic micro-capillaries of 350µm used as fluidic connectors, the inlet and  
117 outlet of the device were etched to a depth of 325µm. But we faced a non-uniform distribution of flow (Figure  
118 1) and overpressure during the experiments, which have been confirmed by some fluidic simulations done  
119 under three hypotheses such as:

- 120 - The pressure is applied only in the entrance of the microdevice while the outlet is under atmospheric  
121 pressure;
- 122 - No interaction between the substrate and the fluid except the friction forces;
- 123 - And the turbulence effect was not considered in this simulation model.

124 New micro-components were designed with a uniform depth of 325µm for both the inlet/outlet and the  
125 internal chamber in order to compensate the overpressure observed on previous devices during tests. In  
126 addition, inlet and outlet were fabricated with a channel system to promote a uniform distribution of fluid  
127 unlike the old micro-components. Indeed, the latter did not have this channel system and we observed for  
128 them a non-uniform distribution of flow when performing the fluidic simulation developed below.

129 This improvement in the design of the micro-channels was confirmed by series of simulation devoted to  
130 new micro-devices which have pointed, on one hand, an improvement in the distribution of the gas flow with  
131 the presence of channel system at the inlet/outlet of the micro-devices (Figure 1) and on other hand, a  
132 reduction of pressure losses thanks to the uniform depth of 325 $\mu\text{m}$  through all the microchannel in this new  
133 design.

134

### 135 **2.3. Adsorbent deposition**

136 The adsorbent insertion in micro-channels has been realized by two methods. The first one is a  
137 deposition using a fluidic solution <sup>[24]</sup>, and the second one consists to deposit the adsorbent in a paste form  
138 before the sealing of the glass cover. The choice of the deposition method is closely related to the adsorbent  
139 nature. According to dimension of the metallic capillary used as fluidic connection (220 $\mu\text{m}$  of internal  
140 diameter), the first deposition method is more suitable for adsorbent materials with a particle size less than  
141 5 $\mu\text{m}$  of external diameter. Thus, the activated carbon (100nm of particle size) and carbon nanotubes (CNTs)  
142 were inserted in the microchannels by fluidic solution while Tenax TA was deposited in a paste form before  
143 the sealing of the microdevices because of its large particle size close to 250 $\mu\text{m}$ .

144 These experiments on the fluidic deposition of the adsorbent have shown that the presence of pillars in  
145 the preconcentration chamber, particularly in the “zigzag” design, is a key factor to homogenize the  
146 distribution of the liquid flow through the entire device and to enhance the carbon deposition. It was observed  
147 that the use of porous silicon has increased the quantity of deposited carbon in the micro-channels. In fact,  
148 the presence of pores on the surface of the walls constitutes an important asset to get a good binding layer  
149 and thus to increase the quantity of adsorbent filled in the micro-channel compared to non-porous silicon <sup>[23]</sup>.

150 Once the devices filled with adequate adsorbent material, the fluidic connections are made with metallic  
151 capillaries (steel) having 220 $\mu\text{m}$  of internal diameter. The capillary is filed, partially introduced in the device  
152 and then fixed with a ceramic cement in order to not block the connectors during the sealing.

### 153 **2.4. Heating element**

154 In order to have an autonomous component, for either the thermal treatments of the adsorbent materials  
155 and the desorption of the trapped gases, a platinum heater is integrated on the backside of the device by

156 screen printing and the electrical connections are made with gold wires pasted on a platinum lacquer. This  
157 heating element is used to heat the device at temperatures up to 500°C with a very homogeneous  
158 distribution of the temperature considering the good thermal conductivity of the silicon, as it was reported in  
159 our previous works <sup>[23, 24]</sup>. To have a good regulation of temperature, the micro-preconcentrator is suspended  
160 in a metallic box (Figure 2).

161

## 162 **2.5. Optimization of the experimental parameters**

163 Five main parameters are of importance for the optimum operation of a preconcentrator device with a  
164 given geometry and filled with a fixed quantity of specific absorbent material: the gas flow rate during the gas  
165 adsorption, the gas flow rate during the desorption phases, the heating rate during the gas desorption phase,  
166 the duration of the gas adsorption and desorption phases, and the gas volume of the detector.

167 The miniaturization of such device imposes us a limitation on the gas flow rate, but for preconcentration,  
168 high flow rates are preferred during the adsorption in order to increase the desorption peak amplitude for a  
169 given time of adsorption. The adsorption phase flow was set at 167mL/min, which allowed us to inject a  
170 significant quantity of pollutant in a short time, while the desorption phase flow was maintained at 33mL/min  
171 to avoid an important dilution of the desorbed quantity. Likewise, to avoid a considerable detection volume,  
172 the metallic capillary at the outlet of our micro-preconcentrator was directly connected to the inside of the  
173 detector through its packaging (Sensor from FIGARO ref. 2620), and the latter was then calibrated in order  
174 to correct the influence of the gas flow on the characteristics of its response <sup>[23]</sup>. Otherwise, some  
175 experiments were initially made with a miniaturized sub ppm PID (Photo Ionization Detector, RAE ppb).

176 Since the maximum of the desorption peak is an increasing function of the heating rate <sup>[23]</sup>, the  
177 preconcentration tests were performed with a heating rate of 160°C/min, which corresponds to the maximum  
178 rate that can reach the heating resistance deposited on the backside of the micro-channels. the maximal  
179 temperature is 350°C.

180 Finally, the increase of the adsorption time can lead to an enhancement of the desorption peak  
181 amplitude, but in the same time causes a longer preconcentration cycle which for some applications might  
182 not be desirable. Therefore, the adsorption and desorption times were maintained constant all through the

183 experiments and lasted for 5 minutes since for these targeted applications as the pollution monitoring, a  
184 short preconcentration cycle is more appropriate.

185 So, it is very difficult to define a preconcentration factor since, for a given preconcentrator, the  
186 “amplification” of the concentration is closely related to the duration of the gas adsorption phase, the  
187 flowrates during adsorption and desorption phases, and the heating rate. However, we will measure a  
188 “practical” preconcentration factor which we defined as the ratio between the maximum of the measured  
189 concentration during the desorption phase and the concentration of the injected gas.

### 190 **3. RESULTS AND DISCUSSIONS**

#### 191 **3.1. Specific area measurement**

192 The first tests were especially dedicated to the measurement of the specific area of the selected  
193 adsorbent materials namely carbon nanopowder, carbon nanotubes (SWCNTs, MWCNTs) and a polymer  
194 (Tenax TA) by nitrogen adsorption using the BET method. These results show that the specific area of the  
195 activated carbon nanopowder and the SWCNTs nanotubes are higher than the one of the three other  
196 adsorbents (Table 1).

197 However, a large specific surface does not mean necessarily a large adsorption capacity because the  
198 latter is closely related to the degree of affinity between the adsorbent and adsorbed gas. So the best  
199 solution is to evaluate the adsorption capacity of these adsorbents towards to benzene and nitrobenzene.

200

#### 201 **3.2. Benzene adsorption**

##### 202 *3.2.1. Thermal Programmed Desorption (TPD)*

203 The second series of experiments concerned the evaluation of the adsorption capacity of the adsorbents by  
204 TPD technique coupled with a mass spectrometer.

205 The adsorption capacity for benzene of the four adsorbents has been evaluated in similar conditions and  
206 in the presence of humidity obtained by bubbling the gas in a bottle of water at ambient temperature. On the  
207 one hand, there is a significant desorption peak of water with the activated carbon nanopowder unlike the

208 three other adsorbents which have a low affinity with water vapor (Figure 3). This result reflects a higher  
209 decrease of the adsorption capacity of the activated carbon nanopowder in a presence of water, which is  
210 very harmful for the experimentation in ambient air. On the other hand, the benzene desorption peak  
211 obtained with the activated carbon nanopowder and SWCNTs is about 5 times higher than the one obtained  
212 with MWCNTs and Tenax TA. This demonstrates a strong affinity of these two compounds with benzene  
213 since the same adsorbent mass has been used for these TPD experiments (Figure 4, 5 and 6).

214 However, it should be noted that the temperature of the maximum of the desorption peak amplitude  
215 varies with the adsorbent material. It is estimated at about 120, 180, 280 and 490°C respectively for Tenax  
216 TA, activated carbon nanopowder, SWCNTs and MWCNTs, respectively. The high desorption temperatures  
217 of the MWCNTs manifest an important activation energy of the desorption synonym with a strong link  
218 between the adsorbent and adsorbed gas which is bad for the reduction of the power budget and also for the  
219 reliability of the device. Therefore, we decided to not use MWCNTs for the following experiments. It should  
220 be noted too secondary benzene peaks between 400 and 600°C, probably due to other sites and  
221 mechanisms of adsorption-desorption.

222  
223  
224 TPD experiments performed with carbon nanopowder deposited on porous and nonporous silicon have  
225 shown that the benzene kinetics of desorption on carbon is closely linked to the substrate nature on which  
226 the carbon is deposited. Indeed, the desorption temperature of benzene adsorbed on carbon deposited on  
227 porous silicon substrate (200°C) is about 60°C lower than the one obtained with a non-porous silicon  
228 substrate (260°C) (Figure 7).

229

### 230 ***3.2.2. Experiments with the micro-preconcentrator***

231 Following the conclusions drawn from the previous TPD experiments presented in the sections above,  
232 the preconcentration tests have been performed on silicon and porous silicon micro-channels with a “zigzag”  
233 design. In order to study in similar conditions the effect of optimized parameters, the quantity of deposited  
234 adsorbent on all micro-channels will be equal to about 1mg.

235 On one hand, the tests of these porous silicon micro-channels with carbon deposition have shown that  
236 the porous silicon, besides increasing the quantity of deposited carbon, contributes to the effectiveness of  
237 the gas preconcentration by making the desorption easier and thereby reducing the desorption temperature  
238 and at last the duration of the preconcentration cycle (Figure 8).

239 This complete desorption of the couple porous silicon-carbon is, maybe, due to its activation energy of  
240 desorption lower than the one for the pair non-porous silicon-carbon. The maximum of concentration  
241 obtained during desorption is about 15 ppm corresponding to a “practical” factor of preconcentration (as  
242 defined above) of about 60.

243  
244 On other hand, the preconcentration tests of the non porous silicon micro-channels filled with SWCNTs  
245 have shown that the influence of water vapor in the performance of the micro-preconcentrator is lower than  
246 the one filled with activated carbon nanopowder, for which the sensor response during the desorption is  
247 intensely reduced in presence humidity (Figure 9, 10).

248  
249 However, it should be noted that the desorption parameters of the non porous silicon micro-channels  
250 filled with SWCNTs are not optimum since we have observed a low factor of preconcentration and a spread  
251 of its desorption peak, which is synonym of a insufficient both heating rate (160°C/min) and desorption  
252 temperature (240°C). Some experiments are underway to optimize the preconcentration characteristics of  
253 the device when using SWCNTs.

254 The other experiments under benzene with SWCNTs and Tenax TA are summarized in the table 2 have  
255 shown firstly, the interest of using SWCNTs for reducing of the influence of water vapor during the adsorption  
256 phase and secondly, the low desorption temperature when Tenax is used as adsorbent material in  
257 opposition of the activated carbon.

258 Others VOCs with high saturation vapor pressure such as xylene have been tested with our micro-  
259 preconcentrator and the results are shown in the table 2. They confirm the interest of using Tenax for these  
260 typical VOCs.

### 261 3.3. Nitrobenzene adsorption

#### 262 3.3.1 *Thermal Programmed Desorption*

263 These TPD experiments with nitrobenzene adsorption have shown a strong link between the  
264 nitrobenzene molecules and carbon nanopowder particles making thereby the desorption more difficult.  
265 Indeed, there is a low desorption of nitrobenzene at 200°C and a high desorption of benzene is observed  
266 meaning thus the decomposition of nitrobenzene molecules in benzene at above 300°C (Figure 11). Unlike  
267 carbon, the polymer Tenax TA released easily nitrobenzene molecules during the desorption at a  
268 temperature below 150°C and no decomposition of the latter is observed since the benzene desorption peak  
269 is very small compared to nitrobenzene peak (Figure 12).

270

#### 271 3.3.2. *Experiments with the micro-preconcentrator*

272 Tests under nitrobenzene realized with a micro-preconcentrator have confirmed that the nitrobenzene  
273 molecules are strongly adsorbed on the carbon adsorbent making thus the desorption quasi impossible. As  
274 shown in the Figure 13, after a cleaning step at 200°C followed by an injection of 1ppm of nitrobenzene  
275 during 120min, no nitrobenzene is desorbed even with a temperature of about 200°C.

276

277 In addition, when this experiment has been performed again by heating the micro-preconcentrator until  
278 350°C during one hour, only a small amount of nitrobenzene is desorbed. While the Tenax, after a cleaning  
279 step at 150°C followed by an injection of 1ppm of nitrobenzene, a total desorption of the target gas is  
280 observed only at 120°C before the end of the heating confirming therefore the TPD observations (Figure 14).

281

### 282 3.4. Summary and perspectives

283 All these tests experimented with our micro-preconcentrator have shown that the efficiency of the latter is  
284 closely related not only to the adsorbent material but also to the nature of the micro-preconcentrator  
285 substrate on which the test has been done. Therefore, the table 2 summarizes the results obtained with our

286 micro-preconcentrator with respect to the adsorbent, the nature of the substrate and the target gas. The  
287 preconcentration of nitrobenzene with macroporous silicon microchannel filled with carbon adsorbent  
288 (symbolized by the question mark) has not been done yet. It will be an interesting test in order to confirm the  
289 reduction of the desorption temperature of the nitrobenzene easing thus the use of carbon material for the  
290 preconcentration of nitroaromatic gases deriving from explosive compounds.

291

292

293 Another idea now is to reduce the dimension of the microchannel because at the beginning of this project,  
294 we opted for a large deposit of adsorbent in the micro-device but over time we realized that for the detection of  
295 trace VOCs (concentrations of hundreds of ppb), few milligrams of carbon are efficient to perform these  
296 experiences. Therefore, reducing the size of micro-component seems necessary, firstly, to obtain a more  
297 compact deposit of the adsorbent promoting interstitial porosity, more uniform distribution of the flow and  
298 secondly, to improve the thermal inertia because of its small size (Figure 15).

299

#### 300 **4. CONCLUSIONS**

301 The effect of gas preconcentration in micro-channels has been demonstrated following a preliminary  
302 optimization of both the microchannel designs and the operating parameters. The use of four different  
303 adsorbent materials has been evaluated in a presence or not of relative humidity. To this end, SWCNT  
304 appears as adequate adsorbent for preconcentration of benzene in presence of humidity because of its high  
305 specific area and adsorption capacity and its low affinity with water vapor. While Tenax TA polymer seems  
306 the ideal candidate for the preconcentration of nitrobenzene since the latter is completely desorbed below  
307 150°C.

308 Another important result of this study is the development of micro-preconcentrator on porous silicon. In  
309 fact, the porous aspect of the micro-preconcentrator substrate contributes to increasing the quantity of  
310 adsorbent filled by fluid through the micro-device. Besides this, it facilitates the desorption of gas molecules  
311 adsorbed on the adsorbent deposited on it by reducing the temperature of desorption of adsorbent-

312 adsorbate couple. This advantage can also make easy the detection of VOCs with very low vapor pressure  
313 of saturation that are very difficult to be desorbed.

314 In addition, the adsorption capacity of the microporous silicon itself is not uninteresting since, due to its  
315 low desorption temperature, it could probably be directly used as adsorbent material for certain vapors such  
316 as nitrobenzene.

317 Moreover, we are currently studying the preconcentration of VOCs mixture by exploiting the difference of  
318 desorption between gases in order to separate their desorption peaks. In this case, the combining of porous  
319 silicon and other alternative materials seems an interesting way to improve the performance of our micro-  
320 preconcentrator.

## 5. REFERENCES

- [1] P. R. Lewis, R. P. Manginell, D. R. Adkins, R. J. Kottenstette, D. R. Wheeler, Recent Advancements in the Gas-Phase MicroChemLab. *IEEE Sensors Journal*, Vol. 6, N<sup>o</sup>. 3, June 2006 pp 784-795.
- [2] I. Gràcia, P. Ivanov, F. Blanco, N. Sabaté, X. Vilanova, X. Correig, L. Fonseca, E. Figueras, J. Santander, C. Cané, Sub-ppm gas sensor detection via spiral micro-preconcentrator. *Sensors and actuators B* 132 (2008) pp 149-154.
- [3] A.M. Ruiz, I. Gracia, N. Sabate, P. Ivanov, A. Sanchez, M. Duch, M. Gerboles, A. Moreno, C. Cane, Membrane-suspended microgrid as a gas preconcentrator for chromatographic applications. *Sensors and Actuators A* 135 (2007) pp 192–196.
- [4] I. Voiculescu, R. A. McGrill, M. E. Zaghoul, Micropreconcentrator for enhanced trace detection of explosives and chemical agents. *IEEE Sensors Journal*, Vol. 6, N<sup>o</sup>. 5, October 2006 pp 1094-1104.
- [5] F. Zheng, D. L. Baldwin, L. S. Fifield, N. C. Anheier Jr., C. L. Aardahl, and J. W. Grate, Single-walled carbon nanotube paper as a sorbent for organic vapour preconcentration. *Anal. Chem.* 2006, 78 pp 2442-2446.
- [6] W.-C. Tian, H. K. L. Chan, C.-J. Lu, S. W. Pang and E. T. Zellers, Multiple-Stage Microfabricated Preconcentrator-Focuser for Micro Gas Chromatography System. *Journal of Microelectronical system* vol. 14, N<sup>o</sup> 3, June 2005 pp 264-272.
- [7] G. Serrano, H. Chang, E. T. Zellers, A micro gas chromatograph for high-speed determinations of explosive vapors. *Proceeding of Transducers 2009 conference*, Denver, CO, USA, June 21-25, 2009 pp 1654-1657.
- [8] C. Lu, W. H. Steinecker, W.-C. Tian, M. C. Oborny, J. M. Nichols, M. Agah, J. A. Potkay, H. K. L. Chan, J. Driscoll, R. D. Sacks, K. D. Wise, S. W. Pang, E. T. Zellers, First-generation hybrid MEMS gas chromatograph. *The Royal Society of Chemistry, lab Chip* 5 (2005) pp 1123-1131.
- [9] S.-I. Ohira, K. Toda, Micro gas analyzers for environmental and medical applications. *Analytica Chimica Acta* 619 (2008) pp 143–156.
- [10] E. T. Zellers, K. D. Wise, K. Najafi, R. B. Brown, Q. J. Cai, J. Driscoll, Determination of complex vapor mixtures in ambient air with a wireless microanalytical system : vision, progress, and homeland

- security applications.. Technical Digest of the IEEE Conference on Technologies for Homeland Security, Waltham MA, USA, November 13-14, 2002 pp 92-95.
- [11] V. Gabelica, Intérêt de la spectrométrie de mobilité ionique pour l'étude de la conformation et des assemblages non-covalents de biomolécules. *Spectra Analyse* N<sup>o</sup>. 251, Septembre - Octobre (2006) pp 21-27.
- [12] H. Borsdorf, G. A. Eiceman, Ion Mobility Spectrometry: Principles and Applications. *Applied Spectroscopy Reviews*, vol. 41, N<sup>o</sup>. 4 (2006) pp 323 -375.
- [13] M. Martin, M. Crain, K. Walsh, R. E. McGill, E. Houser, J. Stepnowski, S. Stepnowski, H.-D. Wu, S. Ross, Microfabricated vapor preconcentrator for portable ion mobility spectroscopy. *Sensors and actuators B* 126 (2007) pp 447-454.
- [14] K. Persaud and G. H. Dodd, Analysis of discrimination mechanisms in the mammalian olfactory system using a model nose. *Nature* 299 (1982) pp 352–355.
- [15] X. Xu, F. Tian, S. X. Yang, Q. Li, J. Yan, J. Ma, A solid trap and thermal desorption system with application to a medical Electronic Nose. *Sensors*, 8 (2008) pp 6885-6898.
- [16] F. Bender, N. Barié, G. Romoudis, A. Voigt, M. Rapp, Development of a preconcentration unit for a SAW sensor micro array and its use for indoor air quality monitoring. *Sensors and Actuators B* 93 (2003) pp 135–141.
- [17] S. M. Cho, Y. Jun Kim, G. S. Heo, S-M. Shin, Two-step preconcentration for analysis of exhaled gas of human breath with electronic nose. *Sensors and actuators B* 117 (2006) pp 50-57.
- [18] W. A. Groves, E. T. Zellers, G. C. Frye, Analyzing organic vapors in exhaled breath using a surface acoustic wave sensor array with preconcentration: Selection and characterization of preconcentrator adsorbent. *Analytica chimica Acta* 371 (1998) pp 131-143.
- [19] United States Environmental Protection Agency: <http://www.epa.gov/>.
- [20] Institut Français de l'Environnement : <http://www.ifen.fr/>.
- [21] B. Alfeeli, M. Agah, Selective preconcentration by temperature manipulation of cascaded Micro preconcentrators. *Proceeding of Transducers 2009 conference*, Denver, CO, USA, June 21-25, 2009 pp 1662-1665.
- [22] E.H.M. Camara, P. Breuil, D. Briand, C. Pijolat, N.F. de Rooij, A Micro Gas Preconcentrator with

improved performances for environmental monitoring. Proceeding of Transducers 2009 conference, Denver, CO, USA, June 21-25, 2009 pp 983-986.

- [23] E.H.M. Camara, P. Breuil, D. Briand, L. Guillot, C. Pijolat, N.F. de Rooij, "Micro gas preconcentrator in porous silicon filled with a carbon absorbent" *Sensors and Actuators B* 148 (2010) pp 610–619.
- [24] C. Pijolat, M. Camara, J. Courbat, J-P. Viricelle, D. Briand, N.F. de Rooij, "Application of carbon nanopowders for gas micro-preconcentrator" *Sensors and Actuators B*, 127 (2007) pp 179-185.

## FIGURES

Figure 1: Velocity cartographies obtained after a CFD simulation with microchannels in neural design without channel system at the inlet/outlet for a flow rate of 20L/h (a) and 40L/h (b) and in neutral (c) and zigzag (d) designs with channel system at the inlet/outlet for a flow rate of 20L/h.

Figure 2: Micro-channel in porous silicon filled with carbon with metallic gas capillaries and suspended in metallic box.

Figure 3: TPD spectrum of Carbon nanopowder after benzene adsorption.

Figure 4: TPD spectrum of Tenax polymer after benzene adsorption.

Figure 5: TPD spectrum of SWCNTs after benzene adsorption.

Figure 6: TPD spectrum of MWCNTs after benzene adsorption.

Figure 7: TPD spectrum of carbon nanopowder deposited on porous and non-porous silicon after benzene adsorption.

Figure 8: Comparison of gas sensor response between porous silicon and non porous silicon micro-channels filled with carbon nanopowder after an adsorption step of 250ppb and desorption step at 200°C with a heating rate of 160°C/min.

Figure 9: Sensor response for a silicon micro-channel filled with activated carbon nanopowder with and without humidity, when exposed to 5min to 250ppb of benzene and desorbed during 5min at a temperature of 200°C.

Figure 10: PID response of silicon micro-channel filled with SWCNTs with and without humidity when exposed to 5min to 250ppb of benzene and desorbed at 240°C.

Figure 11: TPD spectrum of Carbon nanopowder after nitrobenzene adsorption

Figure 12: TPD spectrum of Carbon Tenax polymer after nitrobenzene adsorption.

Figure 13: PID response of a silicon micro-channel filled with activated carbon nanopowder when exposed to 120min to 1ppm of nitrobenzene and desorbed at a temperature of 200°C.

Figure 14: PID response of a silicon micro-channel filled with Tenax TA when exposed to 45min to 1ppm of nitrobenzene and desorbed a temperature of 140°C.

Figure 15: Pressure and velocity cartographies obtained after a CFD simulation at 20 L/h with a new microchannel in neutral design.

## TABLES

Table 1: Specific area and particle size of different adsorbents.

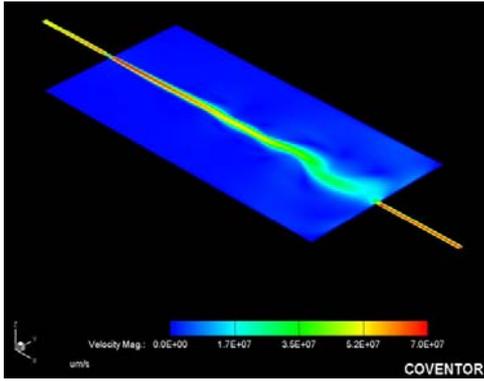
Table 2: Summary of results obtained with our micro gas preconcentrator according the adsorbent material, the preconcentrator substrate and the target gas. Symbols +++, ++, + and – mean respectively very good, good, medium and bad results

<b>Adsorbent</b>	<b>Specific area (m<sup>2</sup>/g)</b>	<b>Particle size (μm)</b>
Carbon nanopowder	99 +/-1	0.1
Activated carbon nanopowder	490 +/- 8	0.1
SWCNTs	399 +/- 5	2
MWCNTs	21 +/- 1	5
Tenax TA	35 +/- 2	250

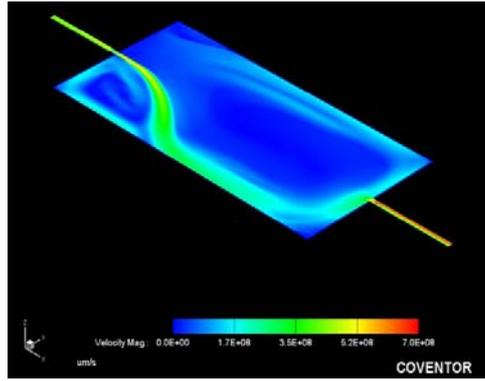
*Table 1: Specific area and particle size of different adsorbents.*

<b>Gas</b> →			
<b>Adsorbent/Substrate</b> ↓	Benzene	Xylene	Nitrobenzene
Carbon / Silicon	+++	++	–
Carbon / Macroporous silicon	+++	+++	NA
SWCNTs / Silicon	++	+	–
SWCNTs / Macroporous silicon	+++	+++	
Tenax TA / Silicon	++	++	++

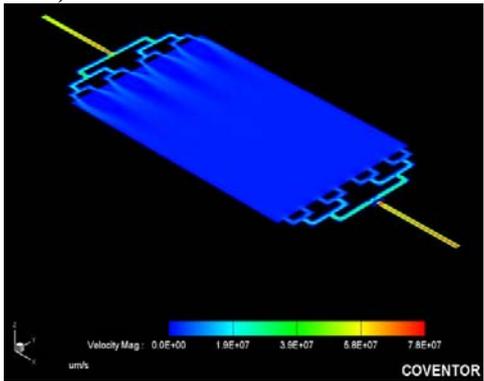
*Table 2: Summary of results obtained with our micro gas preconcentrator according the adsorbent material, the preconcentrator substrate and the target gas, +++, ++, + and – mean respectively very good, good, medium and bad results, .*



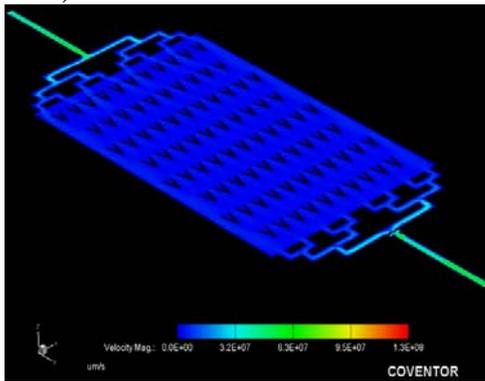
a)



b)



c)



d)

