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A microfluidic device for digital manipulation of gaseous samples

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Abstract

Digital microfluidics is known for fine manipulation of sub-millimeter samples, with applications from biological sample preparation to diagnostic testing. Unfortunately, until now, it is only limited to liquid phases. In this paper, we present a new system based on a digital microfluidic platform (DMFP), which is able to digitally manipulate gaseous samples, such as alkanes from n-hexane to n-nonane. The DMFP relies mostly on interconnected micropreconcentrators (μ PC) to trap and release the samples depending on their controlled temperature. We show that the DMFP is capable to perform all basic operations of digital microfluidics: trapping/releasing and moving samples, adding samples and separating samples, i.e. making a substraction. As a first example of more complex programmable use of our DMFP, we measured the breakthrough volume of alkanes on Tenax TA adsorbent. The results were consistent with tabulated values obtained with standard laboratory instruments. Such DMFP promises great possibilities for more complex programmable gas microfluidics digital devices and the development of new digital gas sample preparation and analysis methods.

Keywords

Digital microfluidics; gas samples preparation and analysis; silicon microfabrication; miniaturization; preconcentrator

Introduction

Over the past decade, microfluidics, defined as the manipulation of fluids at small scale, mainly sub-millimeter scale, have steadfastly progressed^{1–12}. It is also compounded by the understanding of the fluid mechanics at this scale, the chemical interactions and the microfabrication techniques mandatory to craft these devices. The development of microfluidics has yielded several techniques of small-scale fluid control, for example efficient and reproducible droplet generation by making two immiscible liquids flow through specific shapes. This technique is very useful: droplets are almost a closed medium, as diffusion to the surrounding fluid is very low, and allows for encapsulation of useful substances, such as enzymes for enzymatic assays¹³. Another technique emerged, among lots of others: electrowetting, more specifically electrowetting on a dielectric (EWOD). In this mode, two electrodes are used to create an electric field on a dielectric, which changes the wettability of the dielectric and so the contact angle of the droplet. This change allows for movement or immobilization of the droplet. It is then possible to make a grid with these electrodes, and move droplets at will on this grid. These two techniques paved the way for digital microfluidics: microfluidics programmable by analogy to a digital computer. This means that the droplets are commanded by a set of simple instructions, from known state to known state while a clock is used to synchronize the system. This leads to several operations such as moving, trapping, mixing or merging, storing, and extraction of samples. Most of these devices use liquid phases samples, mostly droplets in an immiscible

44 surrounding fluid. Several devices also use bubbles surrounded by liquid^{14,15}. To our knowledge, no
45 digital microfluidic device has been made to manipulate gas samples within a carrier gas.

46 In the meantime, developments in miniaturization of air analysis devices have yielded
47 micropreconcentrators¹⁶⁻¹⁸ (μ PC). These devices consist of a chamber containing an adsorbent, a
48 heating element and a temperature probe. It is then possible to trap a gas on the adsorbent, or release
49 it at will by changing the μ PC temperature. When the compound of interest is trapped on the μ PC, it
50 does not diffuse within the surrounding gas. These characteristics make μ PC a suitable building block
51 for digital microfluidics. Digital microfluidics for gases could help to design programmable, automatic
52 and versatile gas sample preparation and analysis systems. These systems could be free from diffusion
53 related issues that are met in conventional instruments¹⁹. They could also allow sample manipulation
54 without losses. As applications, such devices could be combined with conventional analytical
55 techniques or open new approaches for portable miniaturized instruments.

56 In this work, a digital microfluidic platform (DMFP) using pumps, μ PC and a detector was assembled.
57 We showed that the digital manipulation of gas samples was possible with the DMFP, and
58 demonstrated all elementary operations: trapping/releasing and moving a compound, merging two
59 compounds and separating two compounds. Several alkanes, ranging from n-hexane (C6) to n-nonane
60 (C9) were used to demonstrate these operations. These elementary operations were carried-out by
61 controlling precisely, step by step, the state of the pumps and the temperature of the μ PCs. These
62 elementary operations were also the first step towards a more complex device, which could be used
63 to perform high-level functions, such as separation of mixed samples.

64 As a first proof of concept of a more complex programmable application, the DMFP was used to
65 measure the breakthrough volume of these alkanes on a classical adsorbent (Tenax TA). Breakthrough
66 volume measurements with standard laboratory instruments, such as a gas chromatograph, are labor
67 intensive, as they need several injections, one for each temperature studied. As an illustration of
68 potential applications, it was possible to measure automatically with the DMFP the breakthrough
69 volume on a wide range of temperatures using only one injection, by manipulating without loss the
70 same initial gas sample.

71 Experimental

72

73 Components fabrication

74 The micropreconcentrator chip fabrication has been already described elsewhere^{20,21}. The size of the
75 μ PC chip was 21 mm x 7.6mm. On the front side of the silicon chip, 400 μ m deep inlet/outlet and a
76 central cavity were etched in silicon, and sealed with a Pyrex glass. The 6.6 μ L cavity was filled with
77 Tenax-TA adsorbent powder, a polymer of 2,6-diphenylphenol. Tenax TA is widely used for trapping
78 volatile organic compounds from air samples. Inlet/outlet of the chip were glued to nickel capillaries.
79 On the back side of the chip Ti/Pt thin film heaters and thermoresistive probes were deposited. Several
80 other similar designs have been reported in the literature²²⁻²⁴.

81 The micro thermal conductivity detectors (μ TCD) were also batch processed on 200 mm silicon wafers.
82 The size of the μ TCD chip was 9.6 mm x 5.4 mm. Two 100 μ m deep 200 μ m wide microchannels were
83 etched in the silicon chip by anisotropic deep reactive ion etching (DRIE) following by isotropic plasma
84 etching. Each channel contained two suspended membranes. Each membrane was made of 200 nm
85 thin silicon nitride membrane on which a platinum thermoresistive conductor had been deposited by
86 sputtering. The other half of microchannels was etched by wet etching on a Pyrex glass that was finally
87 sealed on top of the silicon wafer. The μ TCD was then glued and wire-bonded to a printed circuit board

88 holder. 80 μm inner diameter and 150 μm outer diameter fused silica capillaries were then glued in
89 the inlets/outlets of the silicon chip microchannels. The membranes were then connected electrically
90 in a Wheatstone bridge structure. Several similar other designs have been reported in the
91 literature^{25,26}.

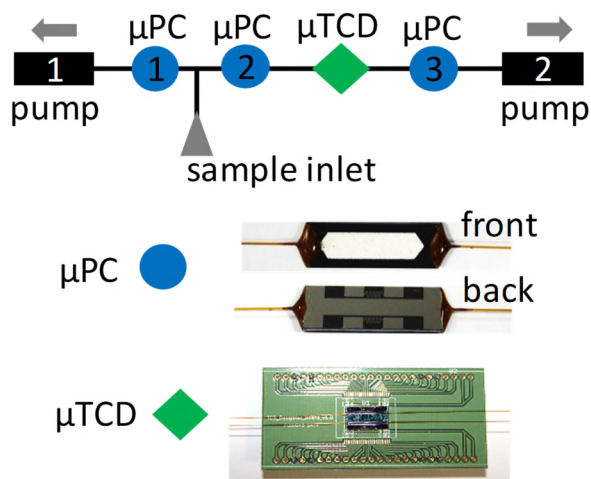
92 When the μTCD is functioning, the membranes are heated and thermal exchanges with the
93 surrounding gas reach a stationary state. If the surrounding gas changes its thermal conductivity, for
94 example by changing its chemical composition, the thermal exchanges are disrupted. This causes the
95 membranes to change their temperatures, and their resistance. This changes the output of the
96 Wheatstone bridge, which is monitored. The μTCD output is then related to the concentration of the
97 sample inside the carrier gas. When samples go through the μTCD , the resulting signal has the shape
98 of a peak. The peak's height is related to the concentration of the sample, and its area to the amount
99 of sample.

100 The μTCD was checked for linearity: as expected, the area of the peaks scaled linearly with the amount
101 of sample within the studied range. The results are available in the supplementary data.

102

103 Experimental setup

104 The schematics of the DMFP are presented in Figure 1.



105

106

Figure 1 : DMFP schematics and pictures of the elementary bricks. The arrows indicate flow direction.

108 As shown on Figure 1, the DMFP contained three μPC and one μTCD , with two pumps linked to them.
109 The pumps were not miniaturized, but the main building bricks of the system were. The pumps may
110 be miniaturized in the future, as such pumps have already been reported²⁷. No valves were used here,
111 however miniaturized valves have been reported²⁸. Pumps were Xavitech models (V200-O2C12V) and
112 connected to the DMFP with Tygon[®] tubes (1/6'' outer diameter, 1/10'' inner diameter). The carrier
113 gas used to move samples inside the DMFP was ambient air. 1/16'' unions were used to connect the
114 components together, with 1/16'' ferrules and nuts. The μTCD was connected between the $\mu\text{PC}2$ and
115 $\mu\text{PC}3$ using one of its two gas channels (as analytical channel); the second μTCD gas channel was
116 connected between $\mu\text{PC}3$ and pump 2 (as reference channel) to lower the baseline drift. The second
117 reference connection is not shown in the Figure 1 for simplification. A fused silica capillary, 1.50m x
118 250 μm inner diameter, was used to connect the $\mu\text{PC}2$ to the μTCD . This capillary was found to reduce

119 artefacts on the μ TCD signal. The artefacts were caused by transitory states during the heating of a
 120 μ PC or the pumps starting. They appeared close to the sample peak, disturbing the baseline. The
 121 pumps and μ PC were powered by a 12 V supply device, and the μ TCD by a 9 V battery. An electronic
 122 setup connected to a computer through USB allowed to control the pumps, the μ PC heaters as well as
 123 to acquire signal from the μ TCD and the μ PC temperature probes. Labview 2012 was used to program
 124 and control the sequence of states of the DMFP, as well as acquire and register the data.

125 Samples could be injected on either μ PC1 or μ PC2 by pumping with pump 1 or pump 2 respectively.
 126 Samples were prepared by injecting a few microliters of liquid sample inside a Tedlar[®] bag of 1 L
 127 (Supelco, 24633) filled with 5.0 nitrogen (Air Liquide). The samples used were n-hexane (C6) (Carlo
 128 Erba, 99% HPLC grade), n-heptane (C7) (99 % anhydrous, Sigma Aldrich), n-octane (C8) (\geq 99%
 129 anhydrous, Sigma Aldrich) and n-nonane (C9) (\geq 99 % anhydrous, Sigma Aldrich). Prior to injection, the
 130 bag was cleaned by filling it 3 times with 5.0 nitrogen and emptying with a vacuum pump. After
 131 injection of the sample in the bag, the bag was let at room temperature for 15 minutes to equilibrate.
 132 For the injection of samples, the Tedlar[®] bag was connected to the inlet of the T-junction. The
 133 connection was made with a 1/16'' stainless steel capillary. Several samples were prepared: C6 5 ppm,
 134 C7 10 ppm, C7 5 ppm, C9 5 ppm, C7-C9 5 ppm, C6 1 ppm, C7 1 ppm, C8 1 ppm, C9 1 ppm. Mass flow
 135 rates inside the DMFP were around 0.30 mL/min.

136

137 Results and discussion

138

139 The manipulation of gaseous samples relies mostly on the adsorption/desorption of compounds using
 140 adsorbent packed in the μ PCs. The compounds are trapped on the adsorbent and released when the
 141 μ PC is heated. Using pumps, it is possible to control the gas flow and thus the samples displacement.

142 Trapping and preconcentration

143 The ability of our μ PC to trap compounds was checked using n-hexane (5 ppm). C6 was first loaded on
 144 μ PC2 before starting the experiment. Table 1 presents the DMFP program used for this experiment.

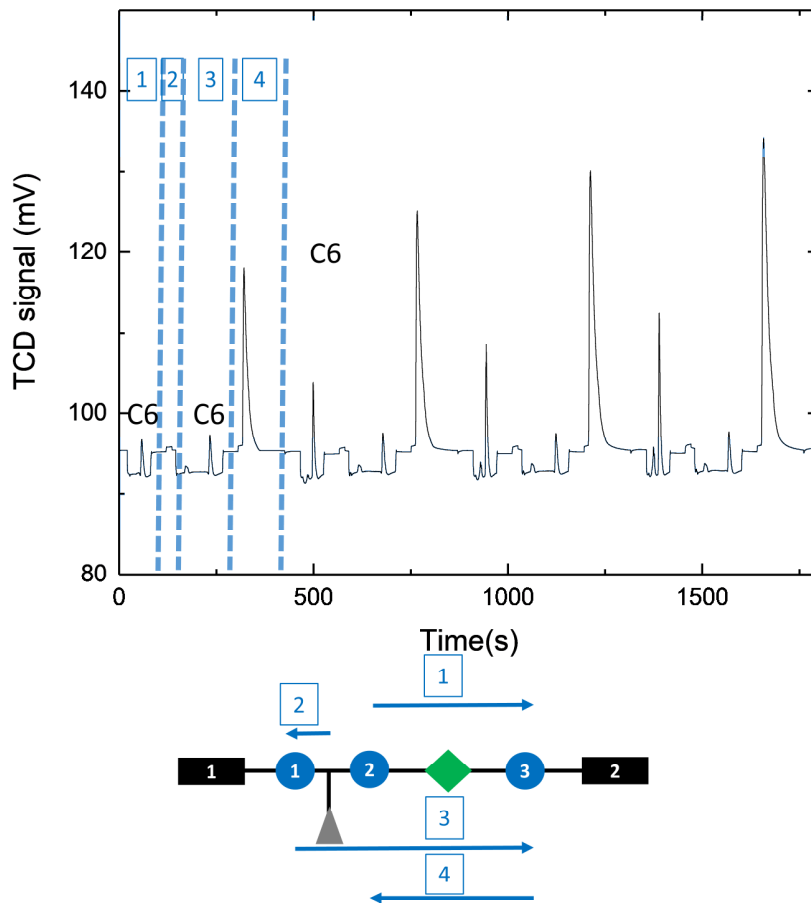
	μ PC1 temperature (°C)	μ PC2 temperature (°C)	μ PC3 temperature (°C)	Pump 1 state	Pump 2 state	Duration (s)
Step 1	Ambient	150	Ambient	OFF	ON	60
Step 2	Ambient	Ambient	Ambient	ON	OFF	15
Step 3	150	150	Ambient	OFF	ON	120
Step 4	Ambient	Ambient	150	ON	OFF	120

145

146 *Table 1 : Program of the DMFP used for the preconcentration experiment. On every step 2 a Tedlar bag containing C6 in*
 147 *nitrogen was connected to the injector to load C6 on μ PC1.*

148 On step 1, the sample moved from μ PC2 to μ PC3. On step 2, the Tedlar bag containing C6 5 ppm was
 149 plugged to the injector: supplementary C6 was loaded on μ PC1. The bag was then plugged out and the
 150 injector closed. On step 3, the supplementary C6 moved from μ PC1 to μ PC3. On step 4, the sample
 151 moved to μ PC2.

152 Results are shown on Figure 2.



153

154 *Figure 2 : Concentration of 5 ppm n-hexane in nitrogen on μPC2. The 4 steps are indicated by the numbers on the figure: Step*
 155 *1 was the movement of the sample from μPC2 to μPC3. Step 2 was the loading of the sample on μPC1. Step 3 was the*
 156 *movement of the sample from μPC1 to μPC3. Step 4 was the movement of the sample from μPC3 to μPC2. Step 1,2,3,4 were*
 157 *repeated 4 times in total. Each time the compound went through the μTCD a signal (peak) is produced. The height of the C6*
 158 *peak increased on every cycle, meaning C6 was effectively being concentrated.*

159 As shown in Figure 2, μPCs are very effective at concentrating compounds, trapping them and releasing
 160 them on demand. During each step 3, the height and area of the C6 peak was the same, indicating the
 161 amount of C6 loaded during step 2 was constant. During each step 1 and step 4, the height and area
 162 of the n-hexane peak rose, meaning the amount of C6 trapped on μPC3 was increasing. This is
 163 consistent with the fact that C6 was trapped on the μPC3 and could be released on demand, and that
 164 more C6 was added to the DMFP at each step 2.

165

166 Controlled movements of samples

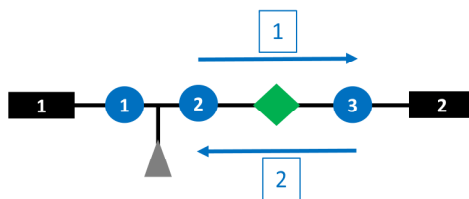
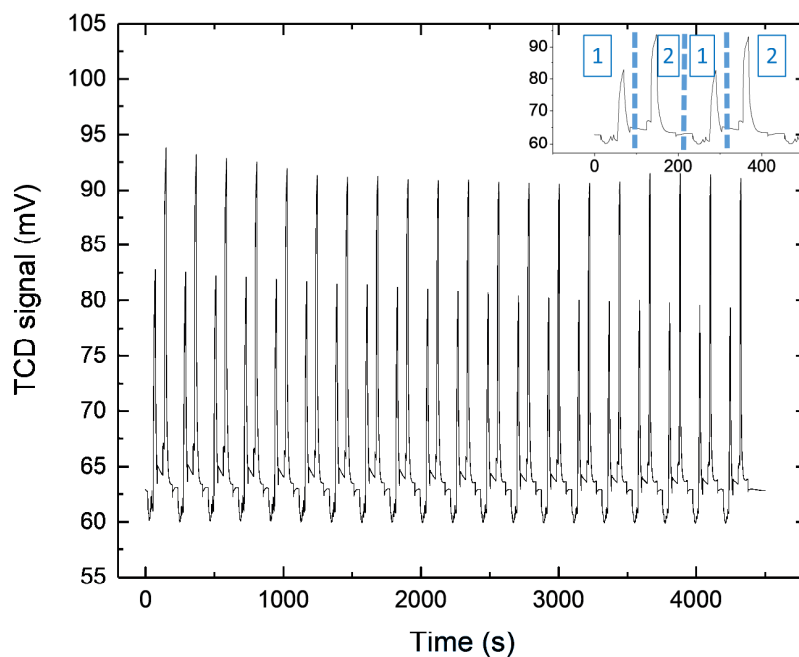
167 The sample, C7 (10 ppm), was loaded on μPC2, and then moved back and forth 20 times between μPC2
 168 and μPC3. Table 2 shows the DMFP program used for this experiment. It consisted of two steps: step
 169 1 consisted in heating μPC2 with pump 2 on: the sample was carried to μPC3. Step 2 consisted in
 170 heating μPC3 with pump 1 on: the sample was carried to μPC2.

	μ PC1 temperature (°C)	μ PC2 temperature (°C)	μ PC3 temperature (°C)	Pump 1 state	Pump 2 state	Duration (s)
Step 1	Ambient	150	Ambient	OFF	ON	30
Step 2	Ambient	Ambient	150	ON	OFF	30

171

172 *Table 2 : Program of the DMFP used for the controlled movements experiment.*

173 Figure 3 shows the TCD signal collected during a sequence of 20 movements of the sample.



174

175 *Figure 3 : Controlled movement of n-heptane 10 ppm between μ PC2 and μ PC3. Two steps were done: on step 1, μ PC2 was*
 176 *heated to 150°C for 30 s and n-heptane went to μ PC3. μ PC2 cooled down for 40 s. On step 2, μ PC3 was heated to 150°C and*
 177 *n-heptane went to μ PC2. μ PC3 cooled down for 40s. See the inset for a more detailed view of the steps. Steps 1 and 2 were*
 178 *then repeated 20 times. A signal peak was observed every time n-heptane went through the μ TCD.*

179 Figure 3 shows that the sample could be moved 20 times without significant losses over time due to
 180 diffusion, or non-efficient trapping. Indeed, the peaks obtained during the 20 steps 1 looked similar,
 181 with an area distribution of 4583 ± 683 mV*s. The peaks obtained during the 20 steps 2 also looked
 182 similar: their area distribution was 7063 ± 1226 mV*s. This means the μ PC was effective at trapping
 183 compounds, and managed to release them efficiently when heated. However, one can notice a slight
 184 variation in the height of the peaks obtained during step 1 and the height of the peaks obtained during
 185 step 2 was observed, certified by a statistical test. This variation could be attributed to the fused silica
 186 capillary between PC2 and the μ TCD: its volume was 75 μ L, compared to the 1.5 μ L capillary volume
 187 between PC3 and the μ TCD. The sample diffused more when traveling through the 75 μ L, causing a

188 decrease in local concentration and thus a decrease in the μ TCD peak signal. The amplitude of this
 189 variation was low and did not hinder the conclusions. This could be investigated and solved in a future
 190 setup if needed.

191 **Mixing two different compounds**

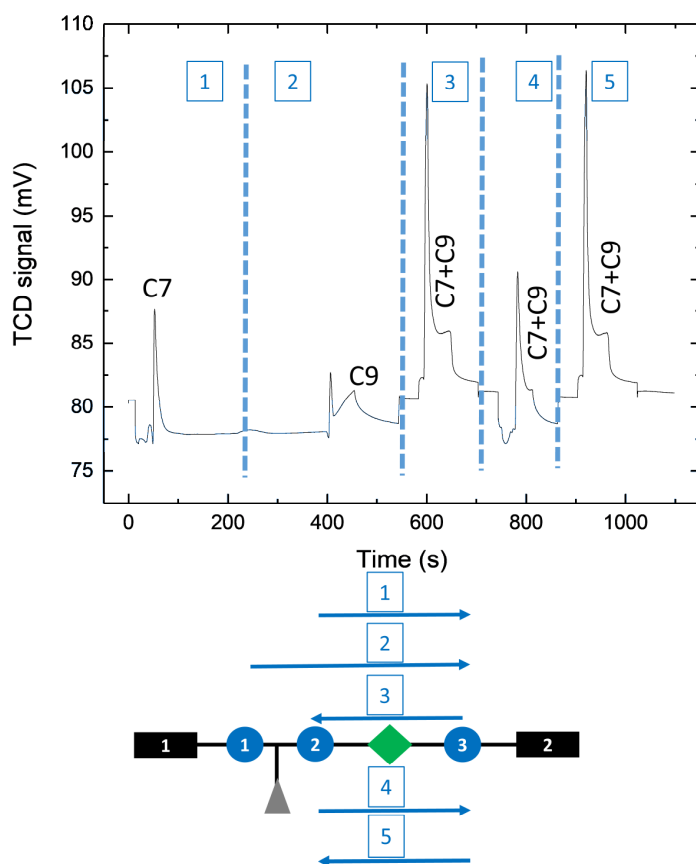
192 It was also possible to use this device to mix two compounds. To demonstrate this, μ PC1 and μ PC2
 193 were loaded with C9 (5 ppm) with C7 (5 ppm), respectively. The compounds were added on μ PC3 and
 194 then moved back and forth between μ PC2 and μ PC3. The Table 3 shows the DMFP program used for
 195 this experiment.

	μ PC1 temperature (°C)	μ PC2 temperature (°C)	μ PC3 temperature (°C)	Pump 1 state	Pump 2 state	Duration (s)
Step 1	Ambient	150	Ambient	OFF	ON	180
Step 2	150	150	Ambient	OFF	ON	360
Step 3	Ambient	Ambient	150	ON	OFF	120
Step 4	Ambient	150	Ambient	OFF	ON	120
Step 5	Ambient	Ambient	150	ON	OFF	120

196

197 *Table 3 : Program used for the C7-C9 addition experiment.*

198 The results are shown on Figure 4.



199

200 *Figure 4* : Addition of n-heptane 5 ppm with n-nonane 5 ppm. The peaks are labelled on the figure. Each time a compound
 201 went through the μ TCD a signal peak was observed. The peaks observed at 600 s, 800 s and 900 s were a combination of the
 202 peaks observed at 80 s (C7), and the peak observed at 480 s (C9). To move compounds, the μ PCs were heated to 150°C.

203 Figure 4 shows that the two compounds, C7 and C9, produced, visually, different peaks when they
 204 went through the μ TCD. C7 went through the μ TCD on step 1; C9 went through on step 2. On step 3
 205 both of them were added on μ PC3, the resulting peak being the sum of the two individual peaks. This
 206 meant that the addition was successful, and the two compounds could move together during steps 4
 207 and 5: they did not separate on their own.

208

209 **Separating different compounds**

210 Using the DMFP it was also possible to separate two different compounds. To show this, C7-C9 5 ppm
 211 was loaded on μ PC1, and then moved on μ PC3 during a preliminary step, which is not shown.

212 A three-step procedure was then performed: on step 1, μ PC2 and μ PC3 were heated to 180°C: the
 213 sample moved from μ PC3 to μ PC1. On step 2, μ PC2 was set to 115°C and the mix C7-C9 moved from
 214 μ PC1 to μ PC3. As the mix went through μ PC2, the separation was performed: 115°C was hot enough
 215 for C7 to move through, but too cold for C9, which was not volatile enough to be displaced. C9 was
 216 trapped on μ PC2. On step 3, μ PC2 was then heated to 180°C to release C9. The DMFP program used
 217 for this experiment is shown in Table 4.

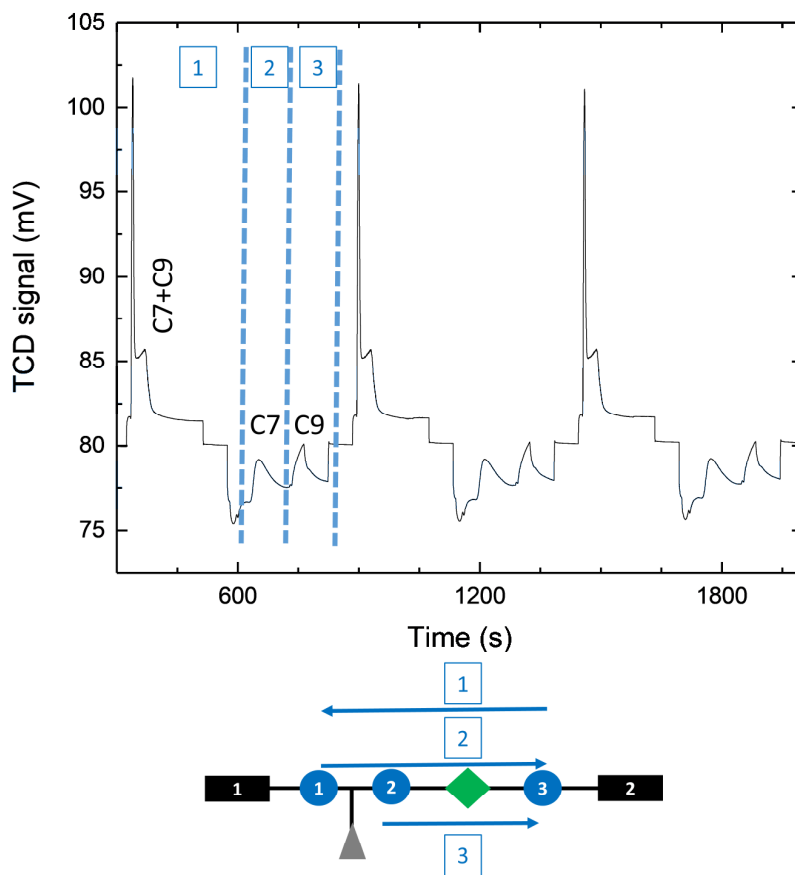
	μ PC1 temperature (°C)	μ PC2 temperature (°C)	μ PC3 temperature (°C)	Pump 1 state	Pump 2 state	Duration (s)
Step 1	Ambient	180	180	ON	OFF	180
Step 2	180	115	Ambient	OFF	ON	120
Step 3	Ambient	180	Ambient	OFF	ON	120

218

219 *Table 4 : DMFP program used for the C7-C9 separation experiment.*

220

221 The results are shown on Figure 5.

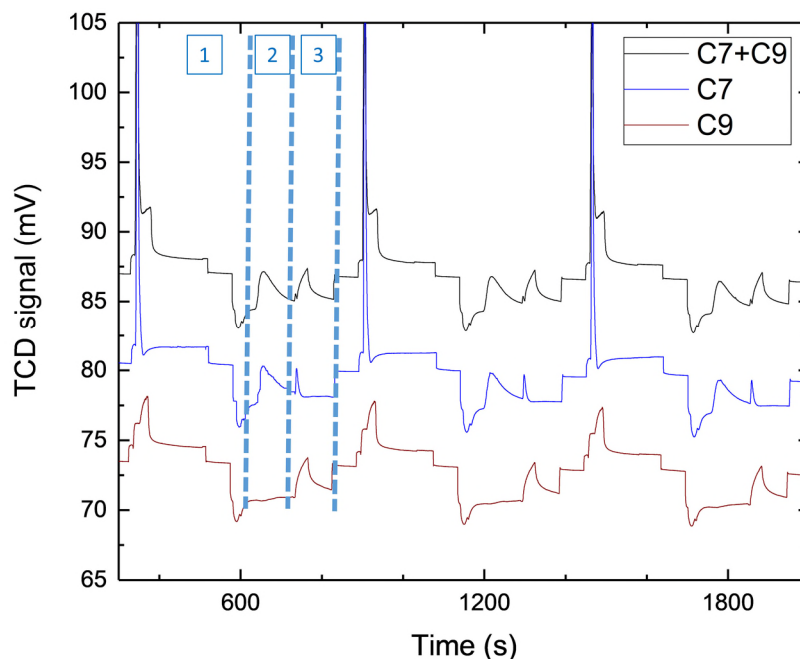


222

223 *Figure 5 : Separation of C7 and C9. C7 and C9 were first loaded on μ PC1. A preliminary step was done to move the sample*
224 *from μ PC1 to μ PC3. This step is not shown. Three steps were done: on step 1, the C7-C9 mix was pumped to μ PC1, μ PC2 and*
225 *μ PC3 were heated to 180°C. On step 2, μ PC2 was set to 115°C and the mix went to μ PC2. 115°C was hot enough for C7 to go*
226 *through μ PC2 and not be trapped: it went through the μ TCD to μ PC3. C9 is not volatile enough and was trapped on μ PC2. On*
227 *step 3, μ PC2 was heated to 180°C: C9 was released and went to μ PC3 through the μ TCD. Steps 1, 2 and 3 were then repeated*
228 *twice.*

229 Figure 5 shows that the separation was effective: by keeping μ PC2 at 115°C C7 was able to go through
230 but C9 was trapped. C9 was only released by heating μ PC2 at 180°C. Three successive successful
231 separations showed the process was repeatable. As co-elutions between C7 and C9 might be possible,

232 control experiments were done by analysing C7 5 ppm and C9 5 ppm with the same program shown in
233 Table 4. Results are shown on Figure 6.



234
235 *Figure 6: Separation of C7 5 ppm and C9 5 ppm. The program is the same as shown on Table 4. For the black trace, both C7 5*
236 *ppm and C9 5 ppm were loaded on μ PC1. For the blue trace, only C7 5 ppm was loaded. For the red trace, only C9 5 ppm was*
237 *loaded.*

238 Figure 6 shows that the separation was quite effective, as C9 was totally trapped on μ PC2 during step
239 2. However, the separation was not complete: a small amount of C7 went through the μ TCD during
240 step 3, meaning it was trapped on μ PC2 during step 2. By measuring the peak area, around 11% of the
241 total C7 amount was trapped on μ PC2 during step 2 and 89% of the amount went through. The DMFP
242 could not perform a perfect single-step separation, but it is still capable of separating different
243 compounds, which is one of the basics operations of digital microfluidics. The performances could be
244 enhanced by repeating the separation step.

245 Measuring breakthrough volumes

246 The DMFP was used to measure breakthrough volumes (BV) on n-alkanes ranging from n-hexane to n-
247 nonane (C9). With standard laboratory instruments, BV studies requires multiple samplings, injections
248 and analyses, as the sample is lost after each analysis. The DMFP used the same sample that was
249 digitally manipulated to gather in about 10 minutes the data needed for one BV measurement at a
250 specific temperature. As the BV was assessed automatically for one compound with the DMFP on a
251 wide range of temperatures in one experiment, the experiment duration was about 3 hours. The BV is
252 the volume of carrier gas needed to elute 50% of the analyte through the adsorbent, at a specific
253 temperature. It is expressed in liters/ grams of adsorbent. The BV is an intrinsic value, which can be
254 tabulated. It characterizes the strength of the interaction between one compound and one adsorbent.
255 At constant flow rate of carrier gas, the BV only changes with temperature for a couple
256 analyte/adsorbent: as temperature increases, the BV decreases due to the adsorption equilibrium
257 shifting towards the desorption of the analyte. The BV tables are useful to assess which adsorbent to
258 use for a specific target, and the range of temperatures in which the target is trapped or released.

259 During these experiments, the sample was loaded on μ PC1. The experiments then consisted in two
 260 steps: at step 1, μ PC1 was heated to 150°C and μ PC2 to a selected temperature, ranging from 150°C
 261 to 70°C. Pump 2 was switched on for 300 s. At step 2, μ PC3 and μ PC2 were heated to 150°C. Pump 1
 262 was switched on for 60 s. Every time step 1 was repeated, μ PC2 temperature was lowered by 5°C.
 263 Table 5 shows the DMFP program used for this experiment.

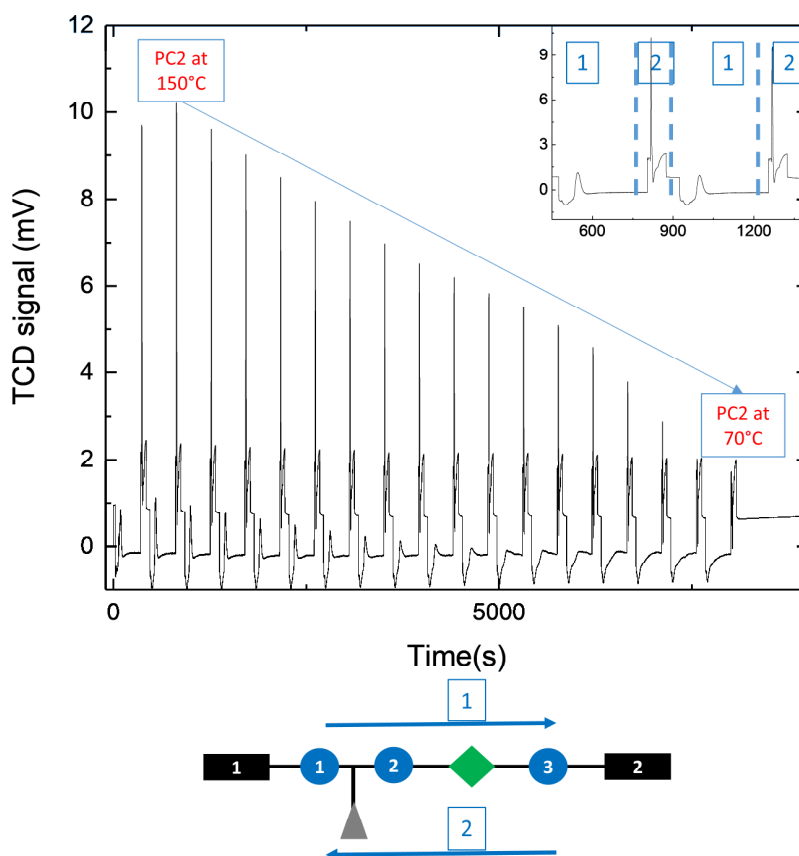
	μ PC1 temperature (°C)	μ PC2 temperature (°C)	μ PC3 temperature (°C)	Pump 1 state	Pump 2 state	Duration (s)
Step 1	150	150-70	Ambient	OFF	ON	300
Step 2	Ambient	150	150	ON	OFF	60

264

265 *Table 5 : DMFP program used for the C6 breakthrough experiment.*

266

267 Figure 7 shows a typical breakthrough experiment.



268

269 *Figure 7: Breakthrough curve of 1 ppm n-hexane in nitrogen. The baseline drift and its offset were corrected. Every intense*
 270 *peak observed at step 2 showed the movement of C6 to μ PC1 from μ PC3, meaning breakthrough occurred. See the inset: the*
 271 *peak observed at 545 s was the breakthrough of C6 through μ PC2 at 150°C during step 1. The peak observed at 817 s was the*
 272 *return of C6 from μ PC3 to μ PC1 during step 2. Every time step 1 was repeated, μ PC2 temperature was lowered by 5°C.*

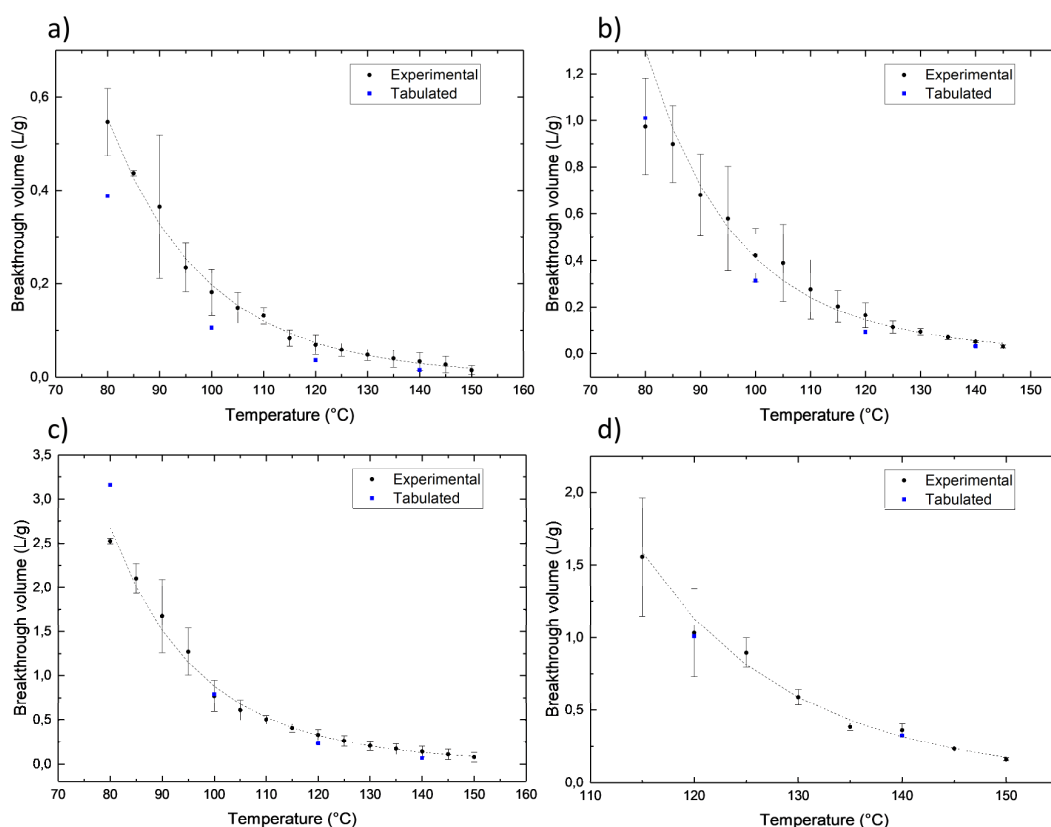
273 Figure 7 shows that breakthrough happened over a wide range of temperatures, as evidenced by a
 274 peak observed during step 1. The peak observed during step 2 was a second proof of a breakthrough:

275 if it appeared, it meant C6 came back to μ PC1 from μ PC3. It was only possible if C6 managed to reach
276 μ PC3 during step 1 and went through μ PC2.

277 As temperature of μ PC2 was decreased during the experiment, breakthrough became less
278 pronounced. This breakthrough efficiency loss is shown in step 2: the peak observed during step 2
279 became less and less intense. For low temperatures, breakthrough did not occur and there was no
280 peak observed during step 2, such as, in the C6 case shown on Figure 7, the steps done below 75°C.
281 During this experiment, the setup was not opened, meaning only a single sample was loaded and then
282 travelled during the duration of the whole experiment.

283 For several alkanes the experiment did not yield values for every temperature in the range, as the BV
284 was too high compared to the volume pumped through the μ PC. BV values were normalized by
285 subtracting the dead volume, measured at the start of every experiment by doing a breakthrough at
286 180°C with the sample. At this temperature, analytes were not retained on the adsorbent. Data were
287 then fitted according to Kroupa et al.²⁹. They proposed a two or three parameters model for the
288 dependence of the BV with the temperature. One of the parameters is directly related to the
289 adsorption enthalpy of the compound on the adsorbent, which is an intrinsic characteristic of the
290 compound/adsorbent interaction.

291 Figure 8 shows the measured breakthrough volume for C6, C7, C8 and C9.



292

293 *Figure 8: Breakthrough volume measured for a) C6, b) C7, c) C8 and d) C9. Experiments were made in duplicate.*

294 Figure 8 shows that the fit, according to the model proposed by Kroupa et al.²⁹, of the BV as a function
295 of the temperature was in good agreement with the measured data for all of the analysed samples. It
296 was also possible to measure the adsorption enthalpy of C6 on Tenax at 25°C : the measured value of

297 -46.8 ± 15.0 kJ/mol was in the same order of magnitude as the value of -23.8 kJ/mol obtained by
298 Kroupa et al²⁹.

299 Data were also compared with tabulated values found on SIS website³⁰ : a slight deviation was
300 observed from tabulated values. This deviation was consistent with Kroupa et al. findings²⁹ : they
301 attributed the deviation to a fitting error in SIS interpolations.

302 Conclusion

303 The digital microfluidic platform presented in this study allows step by step programmable digital
304 manipulations of gas samples without losses. All elementary operations (trapping/releasing, moving,
305 mixing, and separating samples) have been demonstrated using n-hexane to n-nonane alkanes.
306 Moreover, by programming a succession of elementary operations, it is possible to perform more
307 complex operations and applications. This could be a first step towards digital chromatography, since
308 the elementary operations performed by the DMFP presented here can be related to a single
309 theoretical plate as in Martin and Synge theory³¹. As a first illustration, the measurements of
310 breakthrough volumes of gases have been performed. The results were in agreement with the
311 tabulated values obtained with standard laboratory instruments, and showed good agreement with
312 fundamental values, such as the adsorption enthalpy of the gases on the adsorbent.

313 Beyond this first DMFP made of three μPC, other DMFP with more complex network of μPC could be
314 developed in the future. With the development of a more complex DMFP and gas manipulation
315 algorithm, this work could lead to new miniaturized digital systems and methods for gas sample
316 preparation and analysis. These new methods of sample handling would be suitable for portable gas
317 analysis systems, but also conventional gas analysis systems. For example, a digital sample handler
318 could be used to extract compounds within a certain volatility range from a gas sample prior to
319 injection in a conventional gas chromatograph. As another example, a system similar to the DMFP
320 presented here could be used as an online miniaturized trap for chromatographic applications in a
321 similar fashion to thermal modulators for comprehensive bi-dimensional gas chromatography.

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