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1 **Behavior of micro pillar array column in high pressure gas**
2 **chromatography.**

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9 **Abstract:**

10 Micro pillar array column with interpillar distance of 2.5 μm for pillars diameter
11 of 5 μm has been introduced in high pressure gas chromatographic systems
12 for online industrial analysis. Separation of gas mixtures have been performed
13 under carrier gas pressure as high as 60 bar using rotating valve for gas
14 injection without sample decompression stage prior to injection. A very low
15 intrinsic height equivalent to a theoretical plate value of 14 μm has been
16 obtained in few seconds. Instead of conventional gas chromatography, carrier
17 gas nature such as helium, argon and carbon dioxide and pressure can be
18 used to tune the selectivity. Liquid hydrocarbon samples have been
19 successfully introduced in the column using a septum based split/splitless
20 injector modified to work up to 40 bar. Separations of VOCs and gasoline
21 samples have been successfully performed.

22

23

24

25 **Keywords:**

26 High pressure gas chromatography

27 Micro pillar array column

28 Intrinsic column efficiency

29 Gases, VOC, gasoline samples

30

31 **1. Introduction**

32 Since 1960's, gas chromatography (GC) plays a significant role in industry
33 owing to its exceptional separation capabilities, and more specifically, online
34 GC has become a very popular option due to several advantages such as
35 automatic sampling, fast response, minimized contamination and security of
36 the staff. However, several industrial processes are performed under very high
37 pressure conditions and require a sample depressurization stage in order to
38 later introduce the sample into the analyzer. Unfortunately, a pressure
39 reduction stage can modify the composition of the sample and then the
40 analytical method trueness is not anymore guaranteed. To avoid the pressure
41 reduction stage, a GC system operated under high carrier gas pressure
42 conditions could be a powerful tool because the sample can then be
43 transferred directly from the process to the analytical column. Such high
44 pressure gas chromatography (HPGC) approach involves two conditions to be
45 fulfilled: the GC instrument must be able to control the carrier gas pressure
46 above 7 bar (conventional gas chromatography instruments usually operate
47 under an inlet pressure lower than 7 bar), and the GC column must have a flow
48 resistance leading to a mobile phase velocity in agreement with the
49 chromatographic requirements. If pressure regulation can be managed with
50 home-made design, column choice is still a challenging task.

51 The concept of HPGC showed up in 1960s, when Myers and Giddings carried
52 out the separation of light hydrocarbons on packed columns as long as 4000
53 feet (1200 m) at an inlet pressure up to 2500 psi (172 bar) [1]. Later, several
54 research groups have performed GC on packed capillary columns [2-9] with
55 two distinct goals: decrease analysis time or increase efficiency. In 1970's,
56 monolithic columns appeared in the field of the GC [10-11] but did not attract
57 too much attention because open capillary columns have emerged at the
58 same time leading to highly efficient separations which can be performed with
59 low carrier gas pressure. However, for HPGC, monolithic columns still have
60 specific advantages over packed columns: simplicity of preparation, good
61 mechanical integrity, and higher permeability [12]. Column length can then be

62 increased and so, for the same Height Equivalent to a Theoretical Plate value,
63 monolithic column was able to produce higher efficiency. A.A. Kurganov and
64 his team has deeply investigated silica monolithic column in gas
65 chromatography [13-16]. They studied the effects of several parameters like
66 the carrier gas nature and the nature of stationary phase, but only few reviews
67 have been dedicated later to monolithic columns in GC [17-19]. Only recently,
68 Maniquet et al. have investigated the behavior of short silica and vinyl silica
69 monolithic column in HPGC for light hydrocarbon separations [20-21].

70 Since the early work of Terry et al. in 1979 [22], silicon based technology
71 leading to microfabricated open tubular columns have been applied to GC, and
72 microchip gas chromatography review has been recently published [23]. In
73 2009, a new type of chromatographic design based on micropillar array has
74 been proposed by Nakai et al. [24] and Ali et al. [25]. These columns, also
75 called semi-packed columns, have been used with conventional injection
76 systems (for gas and liquid) and with such strategy the interpillar distance was
77 in the range of 50 μm in order to be able to use electronic pressure controller
78 working below 7 bar. Recently, a commercial silicon pillar array column grafted
79 with C_{18} groups, μPAC column [26-27], has been introduced for nanoscale
80 liquid chromatography and used for separation of peptides in complex samples
81 [28-30]. μPAC separation columns are formed by etching away the interstitial
82 volumes out of a solid silicon wafer, leaving an array of pillars. The resulting
83 channels are folded onto a small footprint by concatenating bed segments with
84 optimized flow distributors that limit peak dispersion (fig.1).

85

86

87 The pillar bed is of a width of 315 μm and a height of 18 μm , where pillars
88 diameter of 5 μm are successively arrayed with an inter-pillar distance of
89 2.5 μm . Such an organization creates an internal column volume of 4 μL and
90 the column was designed to be able to bear an inlet pressure up to 360 bar
91 [31]. If this type of column has been developed for nanoLC, up to now no

92 attempt has been done to use them in GC probably because, with an interpillar
93 distance of 2.5 μm , the inlet carrier gas pressure to be used has to be higher
94 than 10 bar. This paper describes a first study of μPAC in HPGC system with
95 two high pressure injection adaptations for both gas and liquid analysis.

96

97 **2. Experimental**

98 2.1 High pressure gas chromatography system for gas and liquid injection

99 Because conventional electronic pressure controllers for gas chromatography
100 only allow 7 bar of carrier gas pressure, GC chromatographs from
101 Perkin-Elmer (Autosystem XL and Clarus 590) have been modified to high
102 pressure configuration for gas and liquid injection.

103 For gas injection (fig.2-a), the injection system has been fully described in [20].
104 The gas sample was brought from a sample bottle using a four port Vici valve
105 with a maximum carrier gas pressure at 69 bar (1000 psi) equipped with an
106 internal sample loop of 5 μL . The carrier gas pressure was set by a pressure
107 reducing regulator (single or double stage) linked to a manometer to monitor
108 the applied pressure. A T-connection with a split capillary ($\phi = 75 \mu\text{m}$, $L = 15$
109 cm) was introduced to control the injected sample amount and so to avoid
110 column overload.

111 For liquid injection (fig.2-b), the sample was injected with an autosampler
112 using a syringe ($V_{\text{syr}}=0.5 \mu\text{L}$; $V_{\text{inj}}=0.1 \mu\text{L}$) to a split/splitless GC injector on an
113 Autosystem XL instrument. However, because of the limited carrier gas
114 pressure regulation systems of such conventional GC instrument, the carrier
115 gas line and the split line of the injector have been disassembled. A high
116 pressure carrier gas line with pressure regulation was installed and a fused
117 silica capillary was connected directly to the split line of injector. Due to
118 commercial fittings of μPAC column, capillaries have been added at both
119 ends to connect the column to the split injector and to the FID (20 μm I.D.

120 and 20 cm length). With such configuration, a carrier gas pressure up to 40 bar
121 can be used with a commercial septum based split/splitless injector.

122 2,2 Materials and reagents

123 The μ PAC column was from PharmaFluidics (Gent, Belgium). An ODS-4
124 packed column was purchased from Shimadzu. Fused silica capillaries with 10
125 μ m, 20 μ m, and 75 μ m I.D., 375 μ m O.D. were purchased from Cluzeau
126 (France). CO₂, He and Ar cylinders were from Air Liquide (Paris, France). The
127 sample bottle coded ME was from Air Liquide (Paris, France) and contained
128 two alkanes at high concentration: methane (15 mol%) and ethane (15 mol%)
129 with nitrogen as balance gas. Sample bottle 8lh was from Air Liquide (Paris,
130 France) and contained 8 hydrocarbon compounds with low concentration:
131 methane (0.1 mol%), ethane (0.1 mol%), ethylene (0.1 mol%), acetylene (0.1
132 mol%), propane (0.1 mol%), cyclopropane (0.1 mol%), n-butane (0.1 mol%),
133 1-butene (0.1 mol%), with nitrogen as balance gas. Sample bottle MEP7lh
134 from Air Liquide (Paris, France) contains 10 compounds: methane (77.6 mol%),
135 ethane (4 mol%), ethylene (0.05%), propane (15 mol%), propylene (0.1 mol%),
136 n-butane (0.5 mol%), isobutene (0.5 mol%), pentane (0.1 mol%), isopentane
137 (0.1 mol%) and hexane (0.05 mol%). The pressure for the three sample
138 cylinders was in the range from 1 to 11 bar. The organic volatile compounds
139 including hexane, heptane, octane, nonane, decane, undecane, dodecane,
140 tridecane and tetradecane were from Sigma-Aldrich (St Quentin Falvier,
141 France). A real gasoline #98 sample was collected at a local petrol station
142 (Villeurbanne, France).

143

144 3. Results and Discussion

145 3,1 Gas separation μ PAC

146 High Pressure Gas Chromatography (carrier gas pressure 40 bar) has been
147 performed on micro-pillar (5 μ m diameter, 2,5 μ m interpillar distance) array
148 column (500 mm long, 315 μ m width, 18 μ m height) from Pharmafluidics

149 connected to a gas injection valve. Two light hydrocarbon mixtures from
150 sample cylinders (sample ME 6 bar, sample 8lh 11 bar) were directly injected
151 into the μ PAC column without any sample decompression stage, using carbon
152 dioxide as carrier gas.

153

154

155 The mixture of methane (15 mol%) and ethane (15 mol%) (ME sample) was
156 separated in 10 seconds (fig.3-a) and the C1-C4 sample (fig.3-b) was
157 analyzed within 20 seconds at a mean carrier gas linear velocity of 5.2 cm.s^{-1} .
158 The column permeability was in the range of 10^{-13} m^2 and require such high
159 carrier gas pressure to work in the carrier gas velocity range for gas
160 chromatography applications. Quantitatively, in terms of peak intensity, the
161 methane (C1) peak for ME was expected to be around 82 times higher than
162 methane peak for 8lh considering the injected amount in both conditions (ME:
163 15 mol%, 6 bar, 8lh: 0.1 mol% ,11 bar). The observed peak area ratio was
164 equal to 83 for methane (ME 16.2 mV.s , 8lh 0.195 mV.s) in agreement with
165 the previous assumption. Regarding the separation, μ PAC C18 stationary
166 phase was able to separate C3 isomers as well as saturated and unsaturated
167 C4 alkanes at room temperature (on other silica based columns, cyclopropane
168 was eluted after propane, and butene was eluted after butane [21]). C2
169 isomers are still coeluted at 25 °C and a lower temperature should be required
170 to separate them. All these first results demonstrated the μ PAC ability for light
171 organic compounds separation with a modified gas injection HPGC system.

172

173 3.2 Evaluation of μ PAC efficiency in HPGC

174 In any chromatographic system, when the column size is reduced, the relative
175 contribution of extra-column band broadening is consequently enlarged, and
176 the observed efficiency will no longer display the true performance of the
177 column. For an estimation of true column efficiency of μ PAC, intrinsic column

178 efficiency and instrumental band broadening contributions were evaluated
 179 according to Gritti et al. [32] after adaptation to GC. The theoretical basis for
 180 calculation of intrinsic HETP is based on observed HETP values for several
 181 compounds with retention factors in the range from 1 to 10. For each
 182 compound:

$$183 \quad H_{obs} = L \cdot \frac{\sigma_{v,obs}^2}{V_R^2}$$

184 (1)

185 where L is the column length. $\sigma_{v,obs}^2$ is the observed total volume variance
 186 which includes the extra-column volume variance $\sigma_{v,ext}^2$ and the contribution
 187 of the column $\sigma_{v,col}^2$ to the recorded band width according to:

$$188 \quad \sigma_{v,obs}^2 = \sigma_{v,ext}^2 + \sigma_{v,col}^2 = \sigma_{v,ext}^2 + \frac{V_R^2}{N_{intrinsic}} \quad (2)$$

189 where V_R is the retention volume and $N_{intrinsic}$ is the intrinsic column efficiency.

190 In equation (1), the retention volume V_R is given by:

$$191 \quad V_R = V_{ext} + V_0 \cdot (1 + k) \quad (3)$$

192 where V_0 is the column void volume, V_{ext} is the extra-column volume (0.4 μ L)
 193 which is negligible compared to the parameter $V_0 \cdot (1 + k)$ for retention
 194 factors higher than 1 with μ PAC column volume V_0 equal to 4 μ L.

195 From Eq. (2) and Eq. (1), a relationship between observed H_{obs} value and
 196 $H_{intrinsic}$ can be obtained.

$$197 \quad H_{(k),obs} = L \cdot \frac{\sigma_{v,ex}^2}{V_R^2} + \frac{L}{N_{intrinsic}} = L \cdot \frac{\sigma_{v,ex}^2}{V_0^2} \cdot \frac{1}{(1+k)^2} + H_{intrinsic} \quad (4)$$

198 So, as long as σ_{ext}^2 is significant compared to σ_{column}^2 , the observed HETP
 199 values for a set of several injected compounds in a single run depend on
 200 retention factor k. The plot of observed HETP (H_{obs}) values versus $1/(1+k)^2$ is

201 expected to be linear. The intercept of the linear line is then an estimation of
202 the intrinsic HETP value of the column for the applied inlet pressure.

203 As an illustration (fig.4), the sample mixture MEP7lh has been used to
204 estimate $H_{intrinsic}$ at two different mobile phase velocities corresponding to inlet
205 pressure of 28 bar and 60 bar.

206

207

208 The slope of each curve is related to the external band broadening σ_{ext}^2 at the
209 corresponding velocity and so a higher mobile phase velocity brings a higher
210 σ_{ext}^2 . Moreover, $H_{intrinsic}$ can be determined for different carrier gas velocities
211 and the corresponding Van Deemter curve of the intrinsic efficiency of μ PAC
212 has been plotted (fig 5). The $H_{intrinsic}$ value reached a minimum of 14 μ m
213 within the pressure limit (60 bar) applied in the HPGC system and this value
214 was obtained for mobile phase velocity higher than 5 cm.s^{-1} . Extra column
215 band broadening is still a significant issue which decreases observed
216 efficiency. Detector was setup to avoid band broadening, connection
217 contribution could probably be reduced but not with the commercialized design
218 used in these experiments.

219

220

221

222 3,2 Liquid injection on μ PAC

223 A septum based split/splitless injector has been modified in order to perform
224 liquid injection using the autosampler syringe with inlet pressure as high as 40
225 bar. A mixture of alkanes (C_6 to C_{14}) in solution in CH_2Cl_2 was injected under
226 isothermal condition with oven temperature from 100 to 160 $^\circ\text{C}$ using argon as
227 carrier gas and as an illustration the chromatogram obtained at 130 $^\circ\text{C}$ is
228 shown in figure 6.

229

230 For compounds from C₈ to C₁₄, the logarithm of retention factor k has been
231 plotted as function of 1/T. For each compound, a linear trend was observed
232 which is in agreement with ideal thermodynamic equilibrium relationships
233 (temperature independence of enthalpy and entropy changes). As expected,
234 the effect of temperature on the retention of heavier compounds was more
235 significant than on lighter compounds as observed by the slope of the linear
236 relations $\log(k)=f(1/T)$ reported on table 1.

237

238 The enthalpy change depends on the number of carbon atoms in the carbon
239 chain and every $-CH_2-$ group contributes to the enthalpy (the slope
240 increased by 200 for each $-CH_2-$ group added in the molecule). Such model
241 can be used to predict the retention factor of different alkanes at different
242 temperature on μ PAC.

243 3,2,1, Effect of carrier gas nature on retention of μ PAC column

244 The effect of carrier gas nature (helium, argon and carbon dioxide) was
245 studied at temperature of 100 °C and 150 °C. Using helium as carrier gas, the
246 inlet pressure did not have any influence on compound retention factors, so
247 helium was considered as a reference gas and relative retention factors were
248 used for argon and carbon dioxide in figure 7.

249

250 For both carrier gases, Ar and CO₂, regardless of the temperature, higher
251 pressure always led to a lower retention factor. Such behavior could be linked
252 to adsorption of carrier gas molecules on stationary phase, or condensation in
253 its porous structure, which was more significant under higher pressure
254 conditions leading to a decrease of the number of accessible sites for the
255 analytes. Similarly, for a selected carrier gas, carrier gas molecules were more
256 adsorbed onto the stationary phase at lower temperature, thus a lower

257 retention factor was observed at lower temperature for both argon and carbon
258 dioxide.

259 3.2.2 Separation of gasoline on μ PAC

260 Gasoline 98 is a light petroleum mixture which contains a large set of light
261 hydrocarbons including paraffins, iso-paraffins, cycloalkanes, and aromatics
262 from C₄ to C₁₂. Such real sample from a gas station has been injected under
263 temperature programming conditions: 50 °C – 175 °C, 25 °C/min at inlet
264 pressure of 40 bar for two different carrier gas argon and carbon dioxide
265 (fig.8).

266

267

268 The separation was performed faster with CO₂ (3.75 min) compared to Ar
269 (around 5 min) and a selectivity effect related to carrier gas nature was
270 observed. The three main compounds between octane and nonane which
271 were co-eluted with Ar as carrier gas, are fully separated when CO₂ was used.
272 Conversely, co-elutions happened less seriously for lighter compounds (peaks
273 around hexane) with Ar than CO₂. Such behavior could be linked to the carrier
274 gas absorption onto the stationary phase, different for both argon and carbon
275 dioxide, reducing the accessible sites on stationary phase for analytes but to
276 different extent.

277

278 **Conclusion**

279 μ PAC column has been used in high pressure gas chromatographic systems.
280 Compared to other silica based columns investigated on HPGC, μ PAC column
281 showed very good performance in terms of column efficiency and very fast
282 separation can be carried out: HETP value as low as 14 μ m has been
283 observed with argon as carrier gas, with a hold-up time of only 5 second. Not
284 only for gas injection, liquid injection on modified HPGC system with μ PAC

285 column has also been performed. Analysis of complex real samples has
286 demonstrated that such approach using μ PAC column is a promising tool for
287 industrial gas chromatography. In addition, μ PAC column is based on 50 cm
288 separation bed arranged into several parallel channels on a micro-chip in a 3
289 mm thin pad, which gives the column an excellent compatibility to a future
290 miniaturized on-line HPGC system.

291

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409

410 **Figure caption**

411

412 Fig 1. The structure of the micro-pillar array column. Left: top view of two parallel separation
413 channels (315 μm wide) interconnected with flow distributor structures. Middle: transverse
414 section with 5 μm diameter cylindrical pillars. Right: 300 nm porous shell layer into a 5 μm
415 pillar. Reprinted from Koen Sandra's paper
416 [http://www.chromatographyonline.com/evaluation-micro-pillar-array-columns-pac-combined-high-res](http://www.chromatographyonline.com/evaluation-micro-pillar-array-columns-pac-combined-high-resolution-mass-spectrometry-lipidomics?pageID=3)
417 [olution-mass-spectrometry-lipidomics?pageID=3](http://www.chromatographyonline.com/evaluation-micro-pillar-array-columns-pac-combined-high-resolution-mass-spectrometry-lipidomics?pageID=3) Authorization necessary

418

419 Fig.2 Configuration of Injection and pressure regulation for High Pressure Gas
420 Chromatography.

421

422 Fig 3:(a) separation of ME mixture (methane ethane), room temperature, inlet pressure at 40
423 bar, sample pressure at 6 bar. CO₂ as carrier gas (b) separation of 8lh mixture (methane,
424 ethane, ethylene, acetylene, propane, cyclopropane, n-butane, 1-butene), room temperature,
425 inlet pressure at 40 bar, sample pressure at 11 bar. CO₂ as carrier gas.

426

427 Fig.4: Apparent HETPs vs $1/(1+k_2)^2$ of μPAC column for light hydrocarbon compounds at 28
428 bar (orange) and 60 bar (blue) using argon as carrier gas, room temperature.

429

430 Fig.5 Van Deemter curve of intrinsic column efficiency for μPAC column for light hydrocarbons
431 separation carried out at room temperature with argon as carrier gas.

432

433 Fig.6: Chromatogram of a separation of a mixture of alkanes from C₆ to C₁₄ in CH₂Cl₂,
434 temperature at 130 °C, inlet pressure 30 bar, argon as carrier gas.

435

436 Fig 7. Relative retention factor of decane with argon and carbon dioxide as carrier gases as a
437 function of carrier gas pressure, oven temperature of 100 °C and 150 °C. Helium was used as
438 a reference (retention factor did not change with helium pressure)

439

440 Figure 8: Separation of gasoline #98 sample on HPGC system with μ PAC. Inlet pressure at
441 40 bar. Oven temperature program: 50 – 175 °C, 25 °C/min. Carrier gas (a): Ar (b) CO₂.

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445

446 **Table**

447 Table 1: Slope and intercept of linear relationships for alkanes from C₈ to C₁₄..

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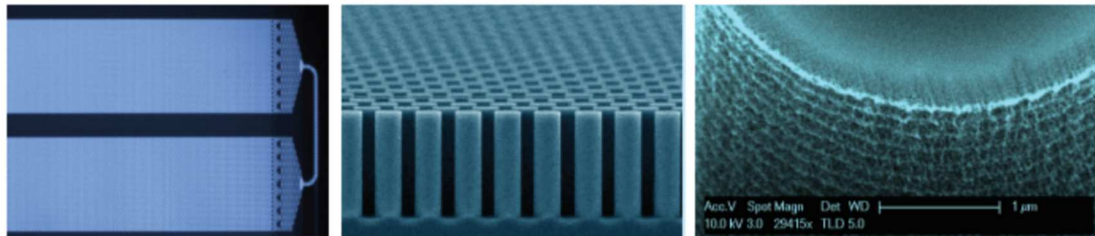
450

1 **Figure 1**

2

3

4



5 Fig 1. The structure of the micro-pillar array column. Left: top view of two parallel separation channels (315 μm wide)
6 interconnected with flow distributor structures. Middle: transverse section with 5 μm diameter cylindrical pillars. Right:
7 300 nm porous shell layer into a 5 μm pillar. Reprinted from Koen Sandra's paper
8 <http://www.chromatographyonline.com/evaluation-micro-pillar-array-columns-pac-combined-high-resolution-mass-spectrometry>
9 -lipidomics?pageID=3 Authorization necessary

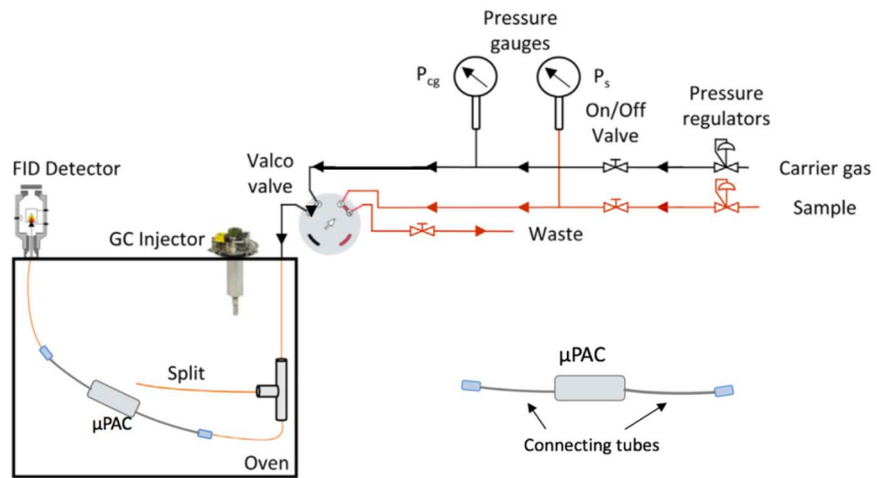
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1 **Figure 2**

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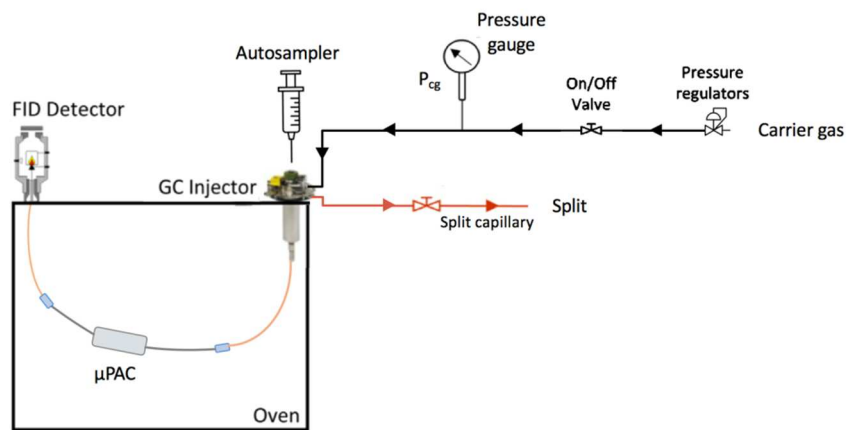


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(a) Gas sample



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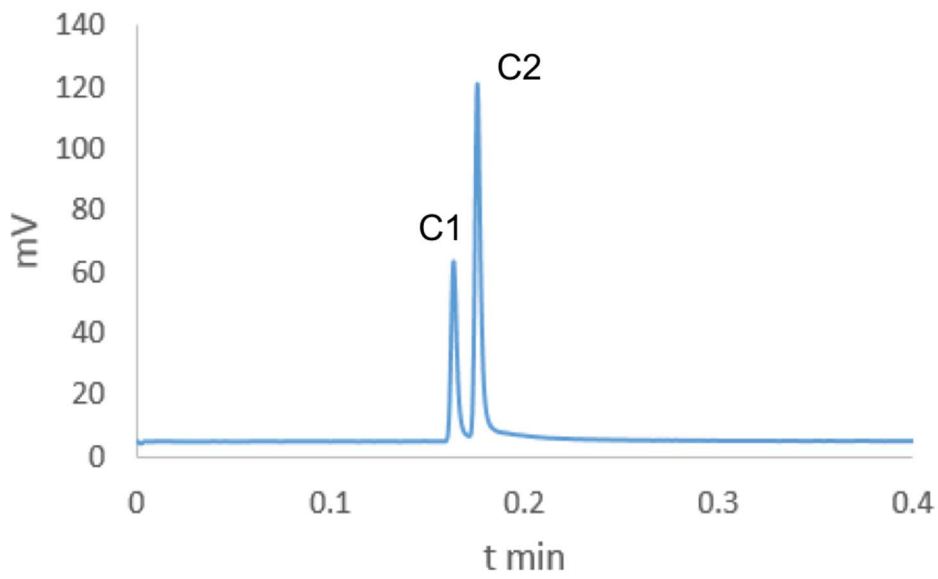
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Fig.2 Configuration of Injection and pressure regulation for High Pressure Gas Chromatography.

12

1 **Figure 3**

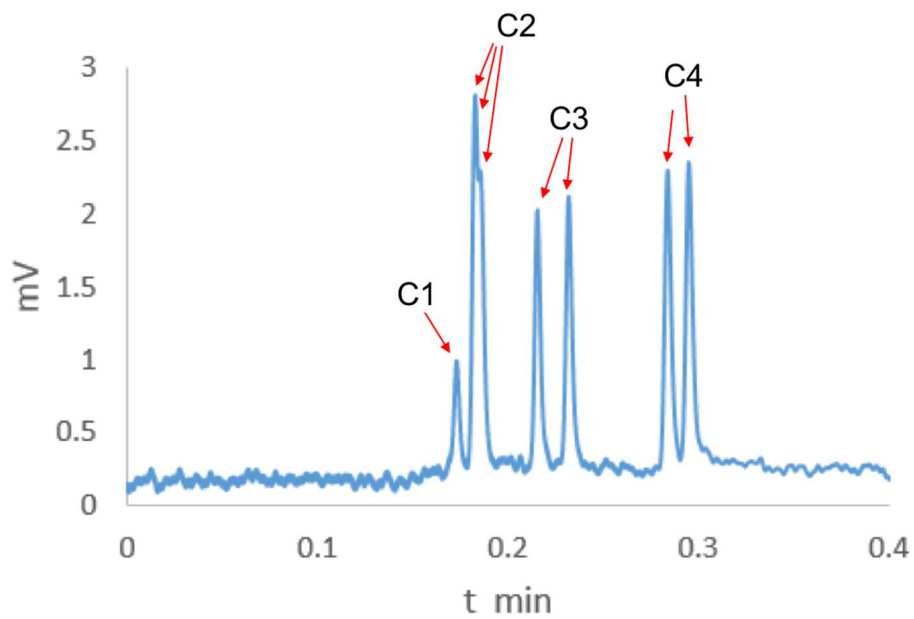
2



3

4

(a)



5

6

(b)

7 Fig 3:(a) separation of ME mixture (methane ethane), room temperature, inlet pressure at 40 bar, sample pressure at

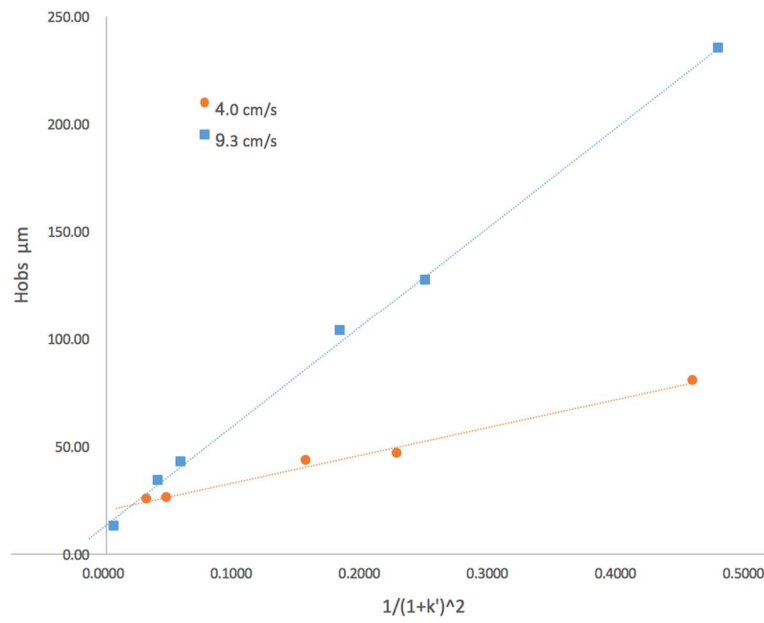
8 6 bar. CO₂ as carrier gas (b) separation of 8lh mixture (methane, ethane, ethylene, acetylene, propane,

9 cyclopropane, n-butane, 1-butene), room temperature, inlet pressure at 40 bar, sample pressure at 11 bar. CO₂ as

10 carrier gas.

1 **Figure 4**

2



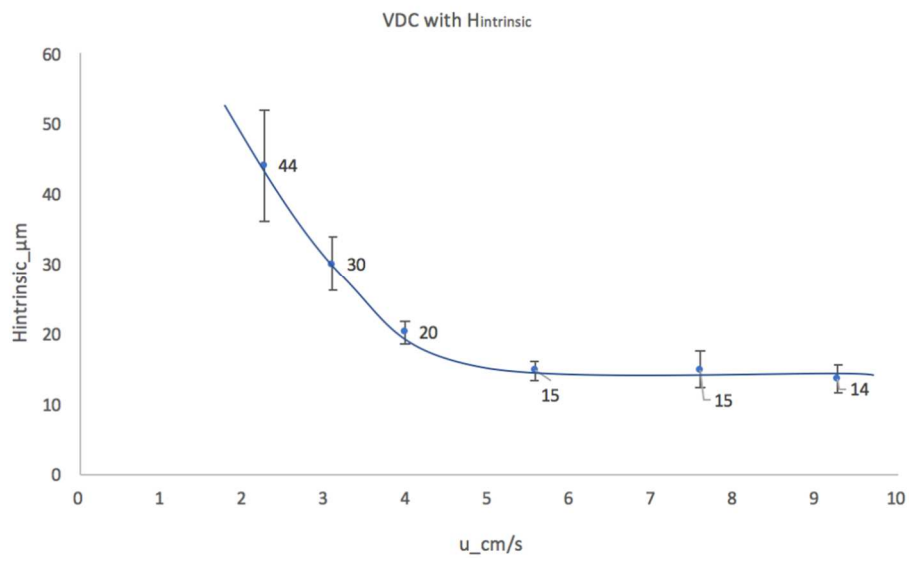
3

4 Fig.4: Apparent HETPs vs $1/(1+k)^2$ of μ PAC column for light hydrocarbon compounds at 28 bar (orange) and 60 bar

5 (blue) using argon as carrier gas, room temperature.

1 **Figure 5**

2



3

4 Fig.5 Van Deemter curve of intrinsic column efficiency for μ PAC column for light hydrocarbons separation carried out
5 at room temperature with argon as carrier gas.

6

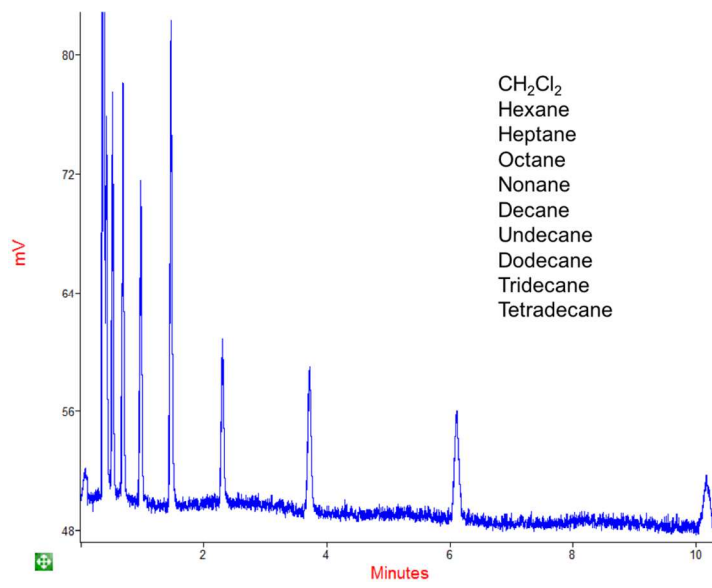
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1 **Figure 6**

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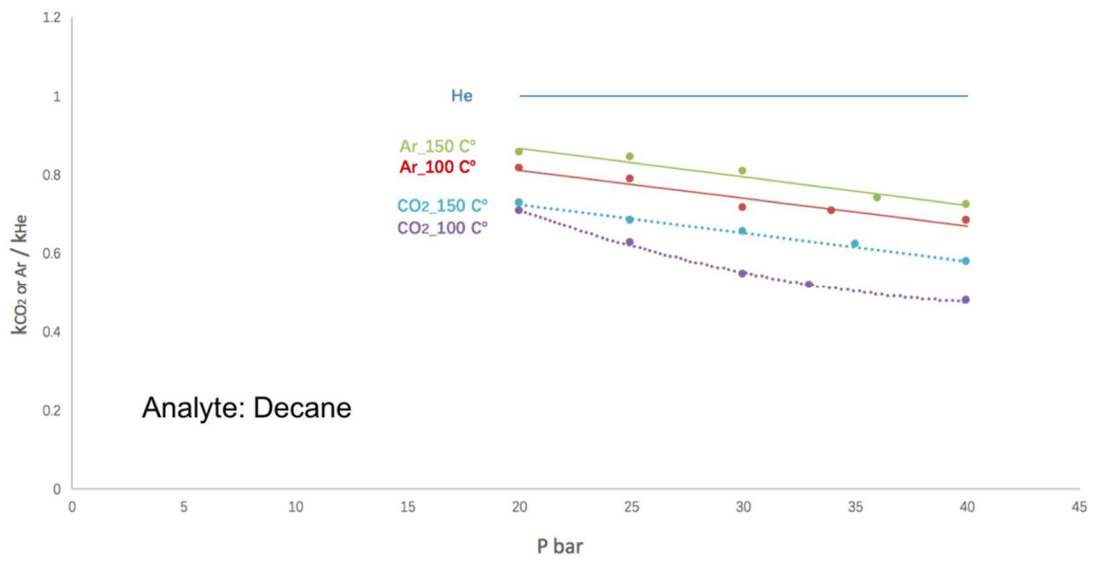
4 Fig.6: Chromatogram of a separation of a mixture of alkanes from C₆ to C₁₄ in CH₂Cl₂, temperature at 130 °C, inlet
5 pressure 30 bar, argon as carrier gas.

6

7

1 **Figure 7**

2



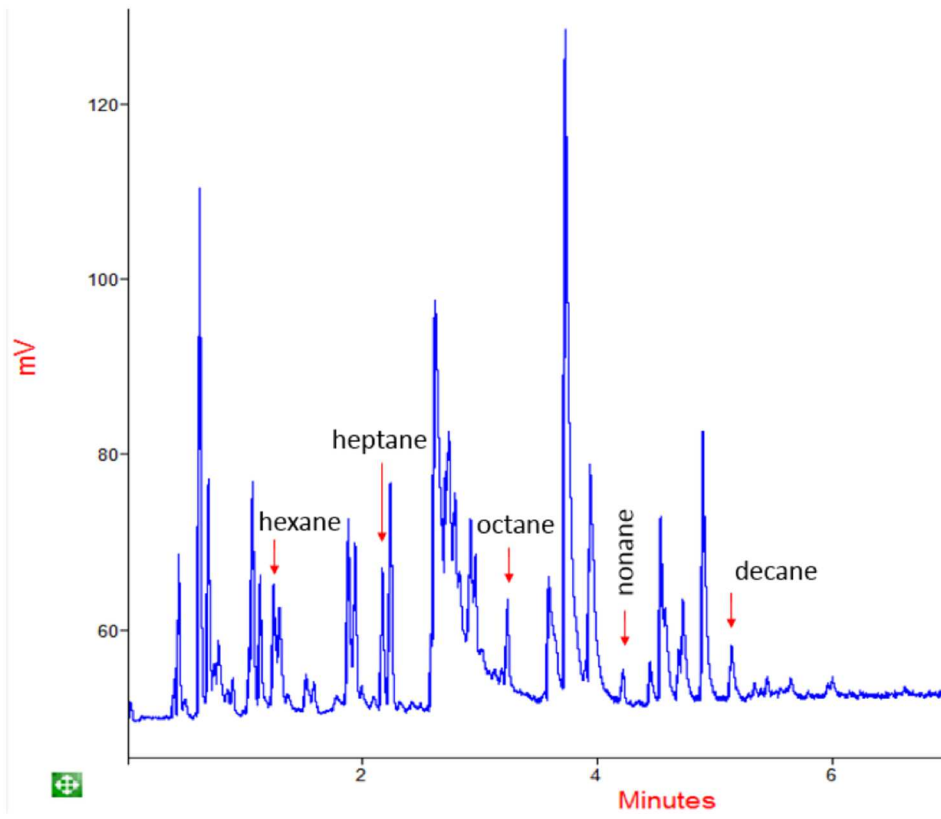
3

4 Fig 7. Relative retention factor of decane with argon and carbon dioxide as carrier gases as a function of carrier gas
5 pressure, oven temperature of 100 °C and 150 °C. Helium was used as a reference (retention factor did not change
6 with helium pressure)

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8

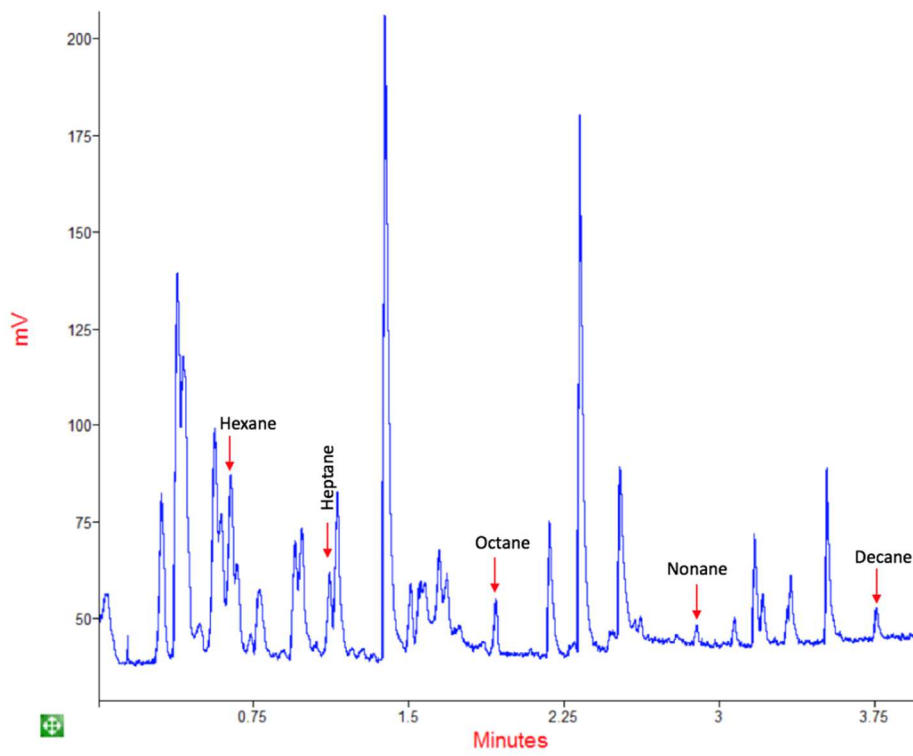
1 **Figure 8**



2

3

(a)



4

5

(b)

6 Figure 8: Separation of gasoline #98 sample on HPGC system with μ PAC. Inlet pressure at 40 bar. Oven
7 temperature program: 50 – 175 °C, 25 °C/min. Carrier gas (a): Ar (b) CO₂.
8
9

1 **Table 1**

2

N*	8	9	10	11	12	13	14	Linear regression
slope	1451	1665	1854	2045	2257	2465	2682	$y = 203.43x - 177.86$
intercept	-3.6437	-3.9027	-4.1202	-4.3299	-4.6327	-4.9121	-5.2179	$y = -0.2591x - 1.5444$

3

N*: the number of carbon.

4

Table 1: Slope and intercept of linear relationships for alkanes from C₈ to C₁₄..

5