



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

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► To cite this version:

Huian Liu, Jérôme Randon. Behavior of micro pillar array column in high pressure gas chromatography.. Journal of Chromatography A, 2021, 1656, pp.462551. 10.1016/j.chroma.2021.462551 . hal-03356055

HAL Id: hal-03356055

<https://hal.science/hal-03356055>

Submitted on 16 Oct 2023

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

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

26 High pressure gas chromatography

27 Micro pillar array column

28 Intrinsic column efficiency

29 Gases, VOC, gasoline samples

1. Introduction

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

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

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

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

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

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

2. Experimental

2.1 High pressure gas chromatography system for gas and liquid injection

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

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

For liquid injection (fig.2-b), the sample was injected with an autosampler 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 Autosystem XL instrument. However, because of the limited carrier gas pressure regulation systems of such conventional GC instrument, the carrier gas line and the split line of the injector have been disassembled. A high pressure carrier gas line with pressure regulation was installed and a fused silica capillary was connected directly to the split line of injector. Due to commercial fittings of μPAC column, capillaries have been added at both ends to connect the column to the split injector and to the FID (20 μm I.D.

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

2,2 Materials and reagents

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

3. Results and Discussion

3,1 Gas separation μ PAC

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

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

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

3.2 Evaluation of μ PAC efficiency in HPGC

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

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

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

(1)

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

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

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

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

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

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

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

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

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

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

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

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

3,2 Liquid injection on μ PAC

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

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

3.2.2 Separation of gasoline on μ PAC

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

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

Conclusion

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

Figure caption

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

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

Fig 3:(a) separation of ME mixture (methane ethane), room temperature, inlet pressure at 40 bar, sample pressure at 6 bar. CO_2 as carrier gas (b) separation of 8lh mixture (methane, ethane, ethylene, acetylene, propane, cyclopropane, n-butane, 1-butene), room temperature, inlet pressure at 40 bar, sample pressure at 11 bar. CO_2 as carrier gas.

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

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

Fig.6: Chromatogram of a separation of a mixture of alkanes from C_6 to C_{14} in CH_2Cl_2 , temperature at 130 $^\circ\text{C}$, inlet pressure 30 bar, argon as carrier gas.

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

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

Table

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

Figure 1

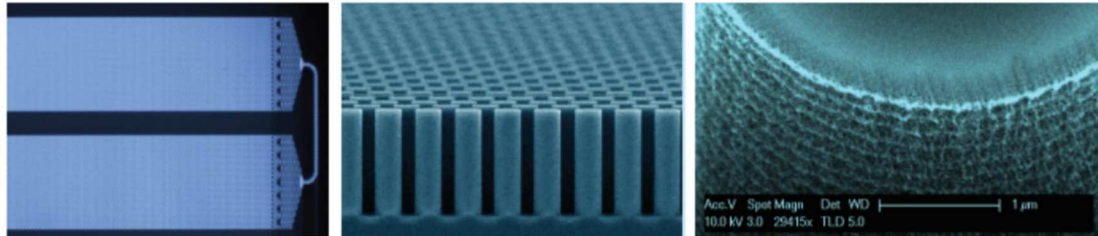
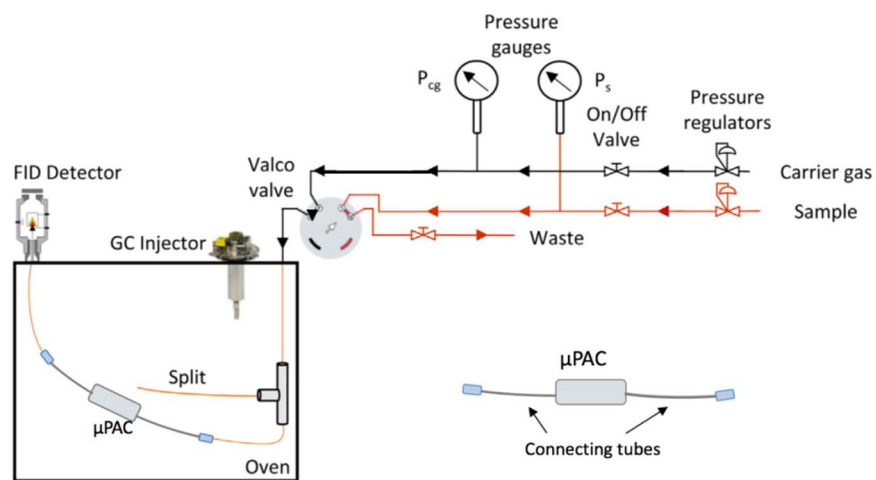
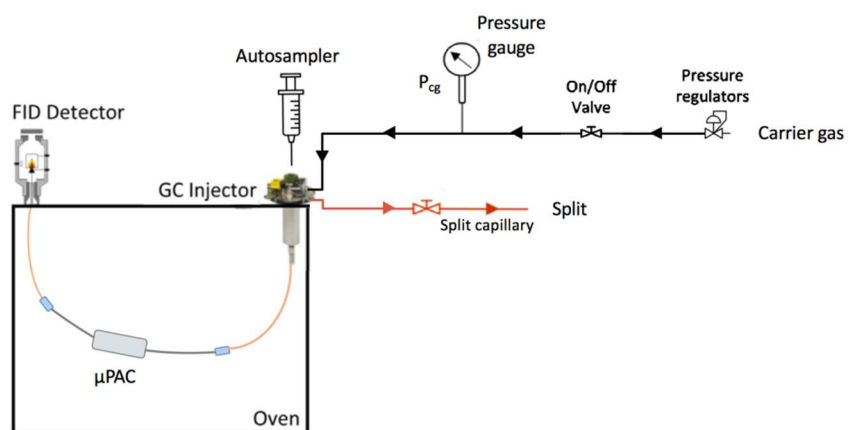


Fig 1. The structure of the micro-pillar array column. Left: top view of two parallel separation channels (315 μm wide) interconnected with flow distributor structures. Middle: transverse section with 5 μm diameter cylindrical pillars. Right: 300 nm porous shell layer into a 5 μm pillar. Reprinted from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

Figure 2



(a) Gas sample

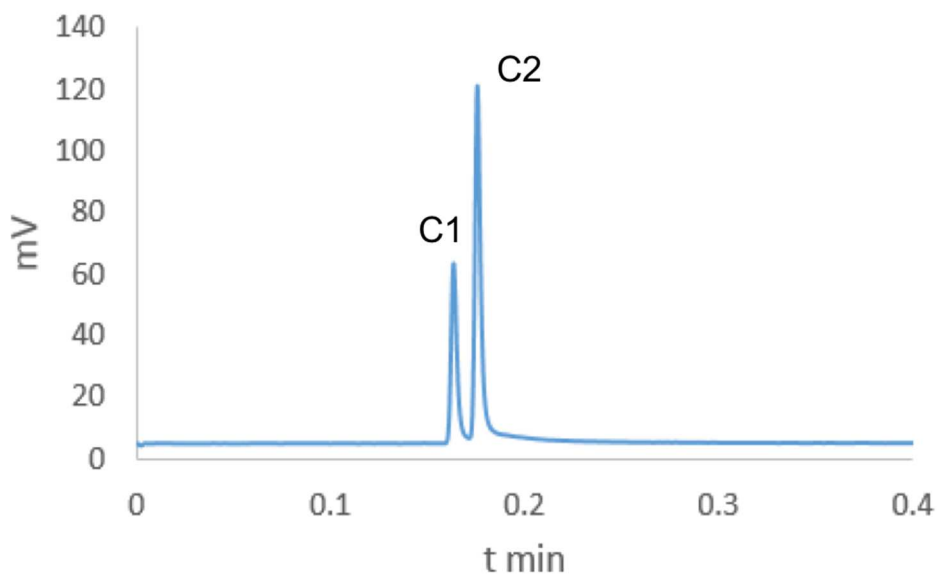


(b) Liquid sample

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

1 **Figure 3**

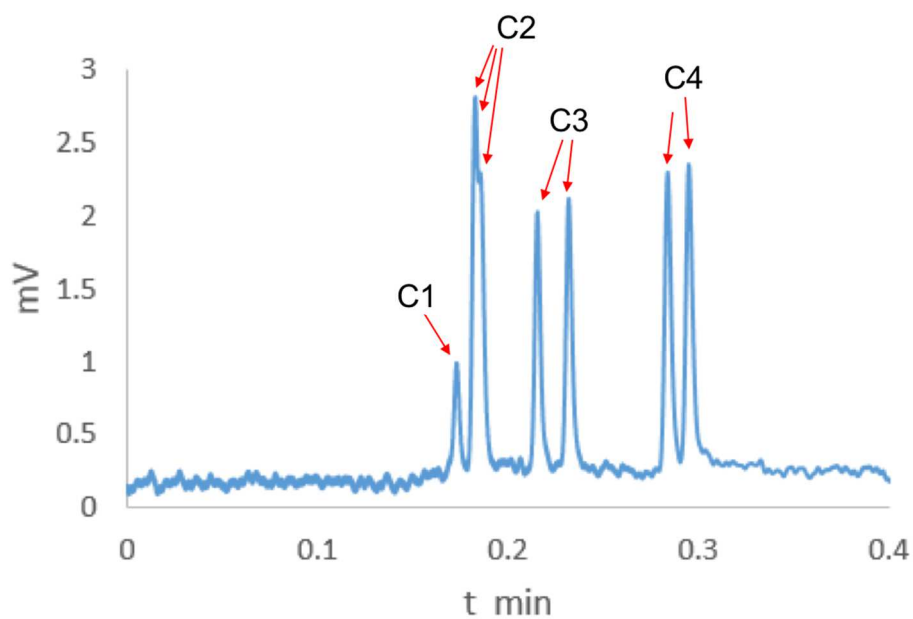
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(a)



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(b)

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

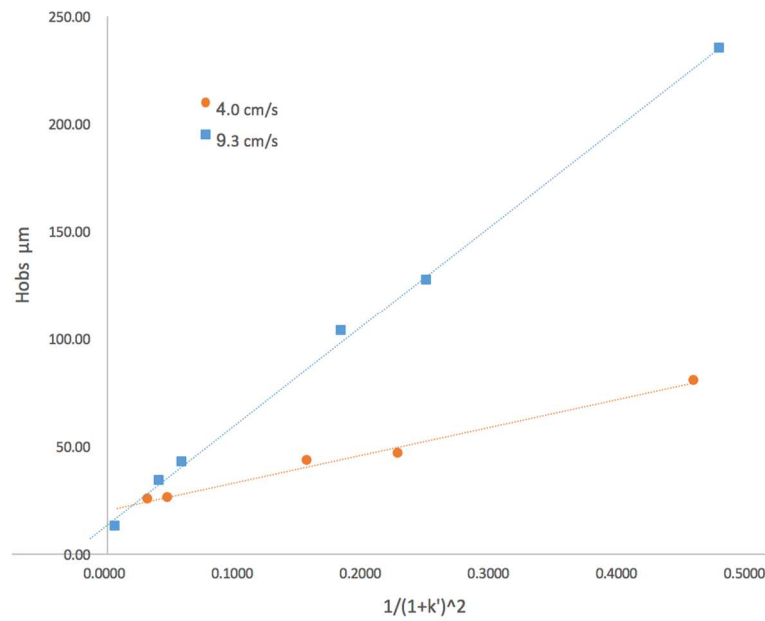
8 6 bar. CO₂ as carrier gas (b) separation of 8lh mixture (methane, ethane, ethylene, acetylene, propane,

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



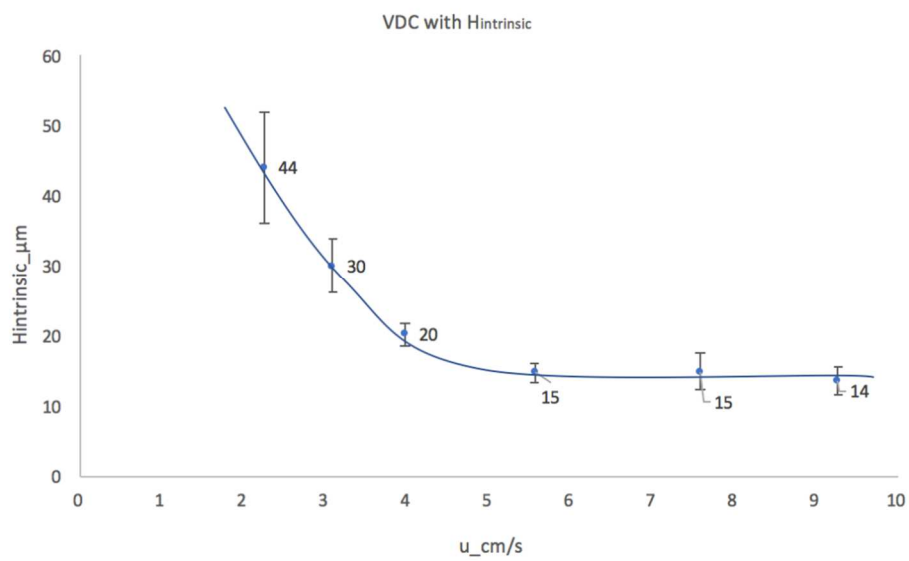
3

4 Fig.4: Apparent HETPs vs $1/(1+k')^2$ of μPAC 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

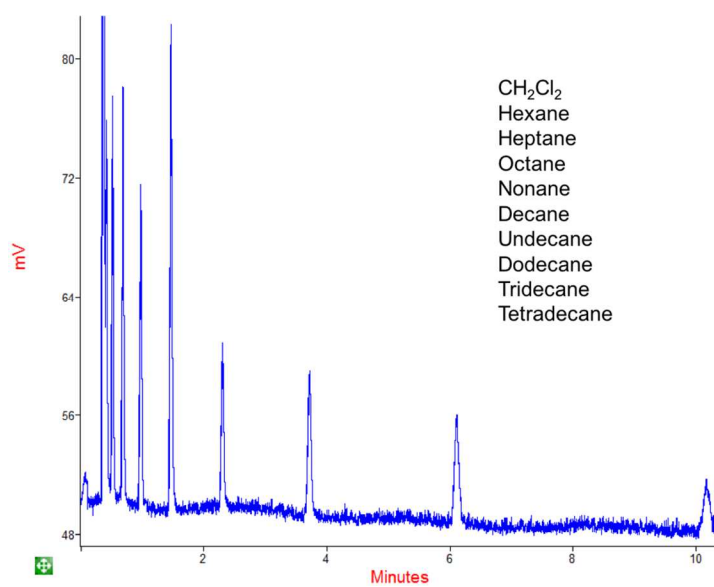
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1 **Figure 6**

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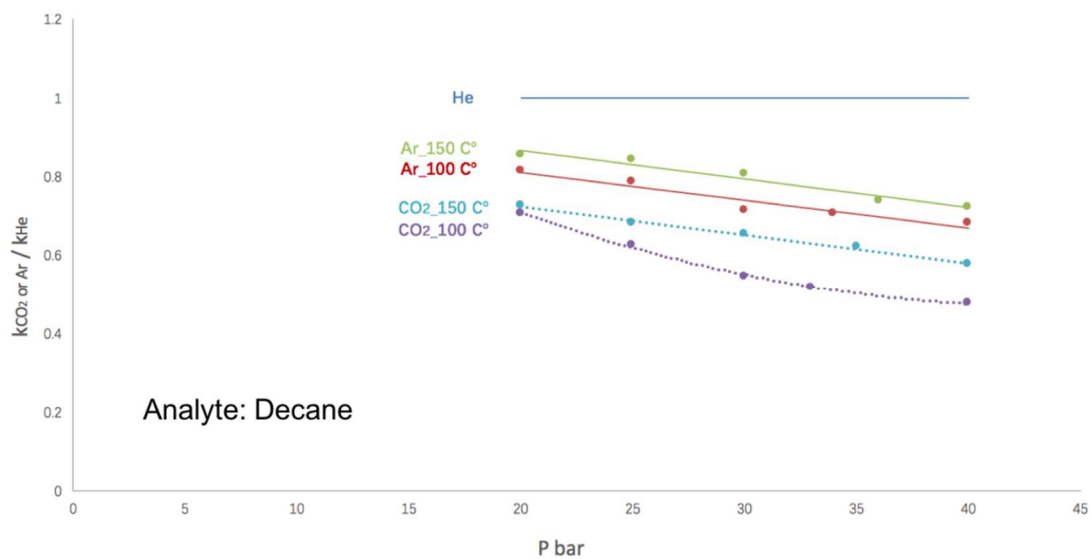
4 Fig.6: Chromatogram of a separation of a mixture of alkanes from C₆ to C₁₄ in CH₂Cl₂, temperature at 130 °C, inlet
5 pressure 30 bar, argon as carrier gas.

6

7

1 **Figure 7**

2



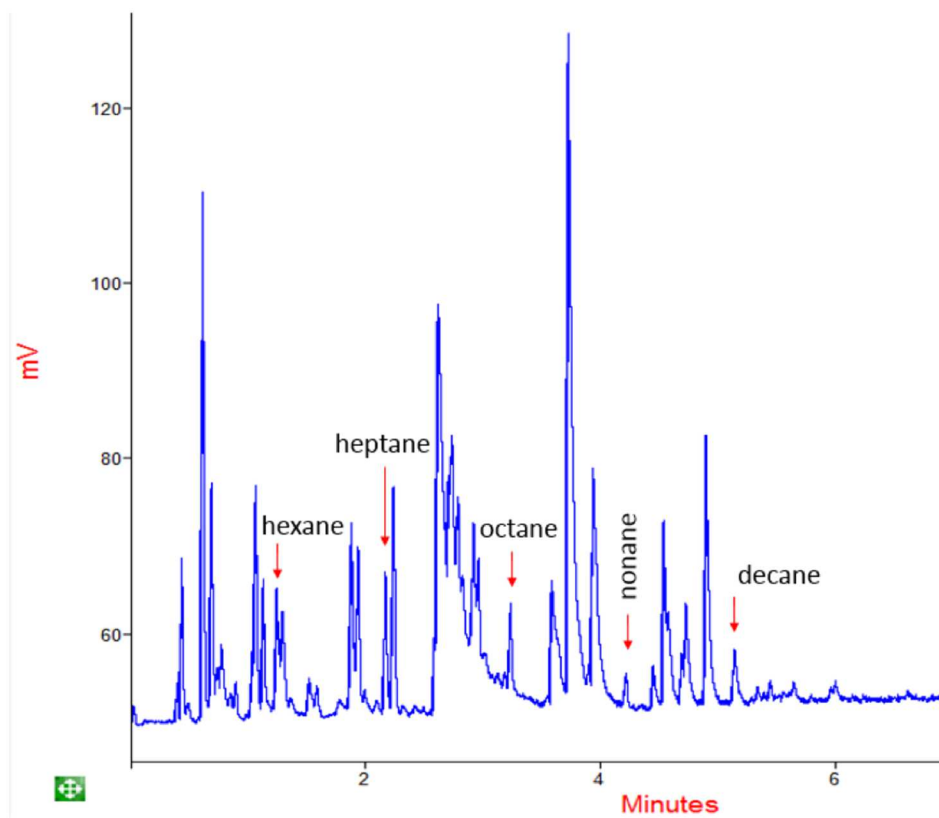
3

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)

7

8

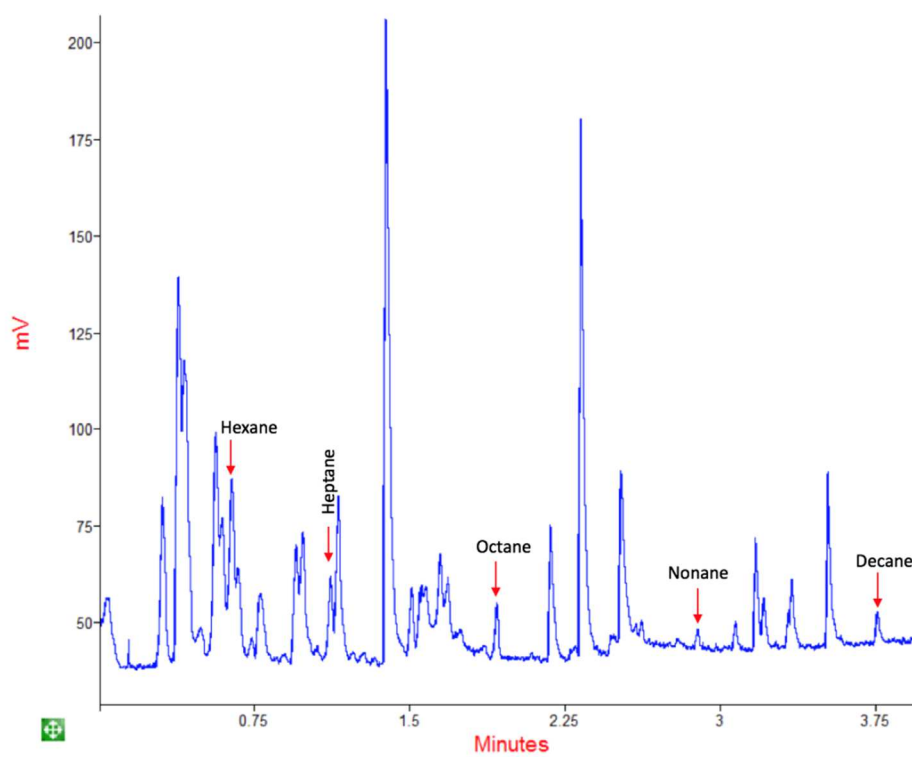
1 **Figure 8**



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

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