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► **To cite this version:**

Huian Liu, Guy Raffin, Guillaume Trutt, Vincent Dugas, Claire Demesmay, et al.. Hyphenation of short monolithic silica capillary column with vacuum ultraviolet spectroscopy detector for light hydrocarbons separation. *Journal of Chromatography A*, 2019, 1595, pp.174-179. 10.1016/j.chroma.2019.02.033 . hal-02109278

HAL Id: hal-02109278

<https://hal.science/hal-02109278v1>

Submitted on 22 Oct 2021

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1 **Hyphenation of short monolithic silica capillary column with**
2 **vacuum ultraviolet spectroscopy detector for light**
3 **hydrocarbons separation**

4
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14
15 **Keywords**

- 16 • monolithic silica capillary column
- 17 • vacuum ultraviolet detector
- 18 • hyphenation for ultra-fast GC separation
- 19 • light hydrocarbons

20

21 **Abstract**

22 Compared to conventional bench top instruments, on-line GC analyzers
23 require specific characteristics. On one hand, for some applications operating
24 with a reactor pressure as high as several tens of bars, sample pressure has to
25 be reduced before GC separation, or specific valves and columns have to be
26 designed to perform separation with high carrier gas inlet pressure. On the
27 other hand, informative detectors such as mass spectrometer are valuable but
28 low maintenance detectors are preferred. To fit these two requirements
29 (sampling at high pressure without decompression stage, and informative
30 detector with low maintenance), short monolithic silica capillary column
31 operated with inlet pressure as high as 60 bar has been hyphenated to VUV
32 detector.

33 Injection and column performance have been first investigated. The system has
34 been optimized by adjusting split ratio at high pressure and by tuning two main
35 VUV detector parameters ("average number" linked to data point averaging and
36 make-up gas pressure) to decrease the limit of quantification. The optimization
37 stage led to a set of experimental parameters which is a good compromise
38 between signal-to-noise ratio and chromatographic efficiency. Finally, the
39 hyphenated monolithic column has been used to partially separate a mixture of
40 methane, ethane, carbon monoxide and carbon dioxide within 15 seconds, and
41 the VUV deconvolution capabilities have been exploited to overcome coelution

42 and finally separate individual signals.

43

44 **1. Introduction**

45 Gas chromatography (GC) has been broadly applied in refinery and natural gas
46 industry for the separation of light hydrocarbons (LHs) due to its exceptional
47 separation capabilities [1]. Several gas chromatographic columns have been
48 used in order to boost the speed and chromatographic efficiency of such
49 separation [2][3] and have been hyphenated to conventional thermal
50 conductivity (TCD), flame ionization (FID), photoionization (PID) or mass
51 spectrometry (MS) detectors. At the same time, to perform on-line analysis,
52 miniaturized GC devices have been introduced and widely spread in industry,
53 mainly based on thermal conductivity detector. However, fast and efficient
54 separative tools with informative detector for on-line analysis of light
55 hydrocarbons mixtures are still required to control more efficiently the industrial
56 processes. Such kind of tools have to take into account experimental and
57 analytical constraints such as high sample pressure, high sample temperature,
58 reduced facilities, low maintenance, ATEX directives, sampling rate, sample
59 volume... So, in order to design an innovative analytical instrument, sampling,
60 columns and detectors have to be carefully selected and hyphenated in an
61 effective tool.

62 In general, porous layer open tubular (PLOT) columns using highly retentive
63 stationary phases such as silica [4] and alumina [5] are able to separate light
64 hydrocarbons with fulfilling efficiency. On the other hand, packed columns
65 deliver a lower efficiency but offer a higher sample loadability compared to
66 PLOT columns [6]. Some research groups have also carried out light
67 hydrocarbon separation on micro-packed columns [7] and have stated that it
68 could be a good compromise between relatively high efficiency and high sample
69 loadability. As an alternative choice, silica monolithic capillary columns (75 μ m
70 I.D) have been recently introduced to achieve the separation of light
71 hydrocarbons within very short analysis time [8-10]. Silica based monolithic
72 columns are porous rod-type structures characterized by a micrometric
73 skeleton, mesopores and interconnected macropores. Even if this porous
74 material exhibits higher flow resistance compared to open tubular (OT) columns,
75 these monolithic columns showed very favorable separation ability towards
76 different analytes such as light hydrocarbon mixtures. Such performances were
77 related to a very high efficiency per unit of column length, leading to extremely
78 fast separations using short columns. Kurganov et al. have carried out a series
79 of experiments on different monolithic columns [11-14] and the minimum HETP
80 value reported was 25 μ m on silica monoliths and 15 μ m on
81 polydivinylbenzene monoliths, using CO₂ as carrier gas under optimum
82 conditions. More recently, Maniquet et al. have performed light hydrocarbons
83 separations on monolithic silica based columns [15-16] with HETP values as

84 low as 16 μm . Furthermore, owing to the macropore size of monoliths (in the
85 range from 2 to 4 μm), these columns were commonly of rather low permeability
86 [9-17], and a very high inlet pressure was mandatory which can be as high as
87 60 bar for 30 cm long columns. This high carrier gas pressure constraint
88 becomes a real advantage for on-line industrial analysis operating on high
89 pressure reactors. Usually, sample at high pressure cannot be directly
90 introduced in the column head via a multiport valve because the sample
91 decompression in the column head creates a large injection band broadening.
92 With monolithic columns operating at inlet pressure higher than sample
93 pressure, the sampling process is dramatically simplified because sample
94 decompression is not anymore required before the injection stage and will
95 occur all along the monolithic column.

96 In the field of GC detectors, FID has been widely used as a reference tool,
97 owing to its good sensitivity towards organic compounds as well as its wide
98 linear range, easy calibration, quantification and robustness [18]. Beside of it,
99 even with a lower sensitivity compared to FID, TCD is a very attractive detector
100 for on-line analysis because it does not require additional gas facilities and does
101 not create an hot spot such as a flame. However, FID and TCD cannot provide
102 any information for peak identification or deconvolution when co-elution occurs.
103 For identification of compounds, mass spectrometry is remarkably interesting
104 and very sensitive towards trace quantitative analysis [19]. However, this

105 technology requires a high instrumental maintenance which is not easily
106 performed in on-line environment. Recently, vacuum ultraviolet (VUV) detector
107 has emerged for gas chromatography [20]. It was designed to overcome the
108 issue of sensitivity and detection capabilities, especially when the performance
109 of mass spectrometry (GC-MS) is limited. As for MS detector, the VUV detector
110 has a strong ability for deconvolution of co-eluted compounds since all chemical
111 species absorb and have unique gas phase absorption cross sections in 120-
112 240 nm wavelength range (VUV spectral range) [20].

113 So, hyphenation of monolithic columns with VUV detector (mono-VUV) could
114 be an elite candidate to design a new fast and efficient separative tool with
115 informative detector for industrial separation of light hydrocarbons. However,
116 several constraints have to be taken into account during hyphenation starting
117 from the injection valve to the detector : band broadening has to be avoided all
118 along the instrument, and sensitivity has to be kept high enough according to
119 the targeted application. In order to overcome these constraints and design an
120 effective separation/detection instrument, sample injection and monolithic
121 column efficiency have been first of all evaluated using a short monolithic
122 capillary column connected to fast FID. Then the monolithic capillary column
123 has been hyphenated to a VUV detector and such GC-monolith-VUV device
124 has been optimized (efficiency and sensitivity) according to column and
125 detector characteristics.

126

127 **2. Experimental**

128 2.1 Fabrication of monolithic columns

129 Monolithic columns were fabricated following the procedure proposed by El-
130 debs et al. [21]. All chemical compounds were from Sigma-Aldrich (France). 18
131 mL of mixture of TMOS/MTMS (85/15 v/v) was added to 40 mL, 0.01 M acetic
132 acid solution containing 1.9 g PEG 10,000 and 4.05 g urea. Then the sol mixture
133 was stirred at 0°C for 30 min and next the temperature was increased to 40°C.
134 The mixture was loaded into a 75 μ m I.D. fused-silica capillary (Polymicro
135 Technologies USA) and the capillary was introduced into a 40°C oven overnight
136 for gelification completion. Mesopores were formed by urea decomposition
137 slowly raising the capillary temperature at 0.5°C/min up to 120°C and then
138 maintained for 4 hours. After cooling, the monolithic column was washed with
139 methanol during 3 h with 50 bar constant pressure. The monolithic column
140 (0.075 mm internal diameter) used was finally cut to the required length 30 cm.

141 2.2 Materials

142 Chromatographic studies were all carried out on the Clarus 590 gas
143 chromatograph (Perkin Elmer, France) with an injection valve from VICI Valco
144 (Switzerland) having an internal sample loop of 0.06 μ L and a pressure limit
145 of 69 bar/1000 psi with valve actuation performed with helium. Such

146 configuration was applied because macropores of monolithic backbones do not
147 bring a large permeability to the column, so correspondingly, the inlet pressure
148 had to be much higher (up to 60 bar) than for conventional GC using open
149 tubular columns. Between the valve and the column, an open tubular silica
150 capillary (10 cm L, 50 μm I.D) and a T-shape split with 50 μm I.D. from Antelia
151 (France) were placed in order to reduce the injection band broadening. Flow
152 meter ADM1000 was from Agilent Technologies (Paris, France) and was
153 calibrated by France Metrologie (Paris, France). VGA-100 VUV detector was
154 from VUV Analytics, inc. (Cedar Park TX, USA), VUV cell length was 10 cm and
155 cell volume was 80 μL . Argon from Air Liquide (Paris, France) was used as both
156 carrier gas for chromatographic separation and make-up gas for VUV detector.
157 The so-called BC gas sample was from Air Liquide (Paris, France) and contains
158 hydrogen (15 mol %), carbon monoxide (15 mol %), carbon dioxide (15 mol %),
159 methane (15 mol %) and ethane (15 mol %) in nitrogen as a balance gas.

160

161 **3. Results and Discussions**

162 In order to obtain an effective separation/detection instrument based on
163 monolithic silica capillary columns hyphenated to VUV detector for on-line
164 separation of light hydrocarbon mixtures, injection band broadening and
165 detection band broadening have to be reduced to the minimum value in order

166 to keep the observed column efficiency at the maximum value, and detector
167 parameters can then also be tuned to lead to suitable limits of detection and
168 deconvolution.

169 3.1 Preliminary evaluations

170 Flame ionization detector is a very sensitive and broadly used detector in gas
171 chromatography, and despite the fact that FID is not able to provide any
172 spectrometric information, it is a reliable tool to measure column efficiency in
173 relation to the very low band broadening created by such detector using short
174 time constant (50 ms). In order to anticipate the hyphenation with VUV detector,
175 argon was used as carrier gas and so column performance was reported here
176 for this specific gas.

177 3.1.1 Injection broadening evaluation using monolith-FID

178 To perform separation using monolithic columns, due to the low permeability of
179 monoliths, an inlet carrier gas pressure as high as 60 bar has to be applied. So
180 an appropriate injection valve from Valco, which can withstand such high
181 pressure, was introduced (internal sample loop volume 60 nL). Schematic
182 representation of GC system can be found with more details in ref [15]. Because
183 of the very small column dimensions, the column band broadening was very
184 low and a split had to be installed after the injection valve in order to reduce the
185 injection band broadening to a value significantly lower than the column band

186 broadening. The split ratio was so controlled by using several open tubular silica
187 capillaries with different dimensions (length and internal diameter, typically 10-
188 30 cm long, 10-75 μm I.ID) in order to tune the vent flow. The split ratio was
189 evaluated by measuring the vent flow and the column flow and then calculating
190 their ratio. Fig.1 shows the effect of split ratio in the range from 2 to 50 on the
191 observed height equivalent to a theoretical plate number (HETP_{obs}) of ethane
192 for a separation performed on a 30 cm long monolithic capillary column at 30°C
193 using a 59 bar argon inlet pressure corresponding to the optimum velocity of
194 this column (4 $\text{cm}\cdot\text{s}^{-1}$).

195 Larger split ratio led to lower injection band broadening σ_{inj}^2 and so to lower
196 observed HETP values as expected from equation 1 and 2.

197
$$\sigma_{obs}^2 = \sigma_{col}^2 + \sigma_{inj}^2 + \sigma_{det}^2 \quad (1)$$

198
$$\text{HETP}_{obs} = \frac{L}{N_{obs}} = L \cdot \frac{\sigma_{obs}^2}{t_R^2} \quad (2)$$

199 With high split ratio, the observed HETP was only related to column band
200 broadening, because σ_{inj}^2 was minimized and σ_{det}^2 was negligible using FID
201 with small time constant (50 ms). In these conditions, the minimum HETP value
202 obtained for the optimal velocity was 53 μm using argon as carrier gas (5660
203 plates for a 30 cm long column). Obviously, by increasing the split ratio, the
204 injected amount into the column was reduced. So for further experiments, a
205 split ratio of 20 has been used to introduce the maximum of sample and to keep

206 the observed HETP at a minimum value.

207 3.1.2 Monolith-VUV hyphenation with extra make-up flow

208 After the study of the injection part, the FID was removed and the monolithic
209 column was then connected to the transfer line of the VUV detector (capillary
210 from the GC oven to the make-up T of the detection cell). Using a monolithic
211 column with such low volume (less than 2 μ L), band broadening due to the
212 transfer line was too large compared to the column band broadening and led to
213 very poor separation. So, in order to guarantee that eluted compounds coming
214 out from the column were able to flow rapidly through the transfer line until the
215 VUV detection cell, another argon make-up gas was added at the exit of the
216 column (i.e. entrance of the transfer line, in the GC oven). Separation of BC
217 sample was performed with such configuration and two peaks appeared to be
218 well separated within 15 s but with a very poor signal-to-noise ratio. Even if the
219 feasibility of this hyphenation has been demonstrated here, with the addition of
220 an extra make-up gas, the dilution factor of the sample has been dramatically
221 increased which reduced the sensitivity of the method since VUV detector is a
222 concentration-dependent detector [22].

223

224 3.2 Optimized design for monolithic column directly connected to VUV detector

225 On VUV detector, the transfer line was originally designed to connect

226 conventional open tubular columns to the VUV cell. However, in case of
227 monolithic column, the transfer line volume appeared to be too large compared
228 to the monolith column volume and an extra make-up gas line was necessary
229 but led to poor sensitivity of such hyphenated instrument. In the new
230 configuration (fig. 2), the transfer line has been removed, so that additional
231 connections have been avoided and the dead volume of transfer line has been
232 definitively eliminated. Since the separation of carbon monoxide, methane
233 carbon dioxide and ethane can be performed at room temperature using silica
234 monolithic columns, the GC oven has been initially removed and the column
235 left at room temperature. So the monolithic column was directly connected to
236 the entrance of flow cell of VUV detector (to the make-up gas line with a T-type
237 connector).

238

239 3.2.1 make-up gas effect on efficiency and dilution

240 The effect of VUV make-up gas pressure on observed efficiency has been
241 studied using ethane as a test compound. As shown in fig.3, the effect of VUV
242 make-up gas pressure (P_m on fig.2) on observed HETP value, under the same
243 experimental conditions as for FID detection, has been investigated. The higher
244 the make-up gas pressure, the lower was the HETP value, and a value
245 comparable to the one obtained with FID hyphenation was observed for the
246 highest make-up gas pressure. That could be explained as the higher make-up

247 gas pressure brings higher flow in the flow cell, which substantially reduces the
248 band-broadening occurring in the cell. So, to get the maximum efficiency value
249 using monolith columns, the make-up gas pressure must be tuned at the
250 highest possible value. Such high make-up gas pressure (flow) was not
251 required with conventional open tubular columns with internal diameter of 250
252 μm because the column broadening was higher and only a small make-up
253 pressure (flow) was then necessary to avoid detector band broadening.

254 On the other side, VUV detector being a concentration dependent detector, the
255 detector response is proportional to the concentration of the sample component
256 in the cell. The maximum of the peak height ($h_{c,dil}$) can be described by equation
257 3, taking into account the dilution effect generated by the make-up gas [24].

$$258 \quad h_{c,dil} = S \cdot \frac{C_{inj} \cdot V_{inj}}{\sqrt{2\pi}} \cdot \frac{\sqrt{N_{col}}}{V_r} \cdot \frac{F}{F_{cell}} \quad (3)$$

259 Where S is the sensitivity of the detector for the eluted compound, C_{inj} the
260 concentration of the injection compound, V_{inj} the injected volume, N_{col} the
261 column efficiency, V_r the retention volume, F the column flow, and F_{cell} the total
262 gas flow through the detection cell. Fig.4 illustrates the effect of make-up gas
263 pressure on peak height for ethane.

264

265 In the set of experiments reported here, an increase in make-up gas pressure
266 increased the total flow through the cell F_{cell} by increasing the make-up flow.

267 Because the pressure drop through the column did not change significantly (P_i
268 was constant 59,5 bar / 863 psi, P_m varied from 1 to 5 psi, so ΔP varied from
269 862 to 858 psi), the column flow was constant for all the experiments, and the
270 dilution factor for the compound eluting from the column increased according
271 to the make-up gas pressure. Therefore, the peak height was lowered when the
272 make-up pressure increased.

273 Thus, in case of low sample pressure or concentration, there must be a
274 compromise between signal intensity and efficiency in order to keep the signal
275 intensity as high as possible and to limit band broadening in the detector cell.

276

277 3.2.2 Noise reduction

278 To lower the limit of detection or quantification, the signal intensity (peak height)
279 has to be maximized as described in the previous section, and/or the signal
280 noise has to be minimized. For most chromatographic detectors, the signal
281 noise can be smoothed using a parameter called "time constant", and the
282 acquisition frequency can be selected independently of the time constant
283 parameter. With these two parameters, it is then possible to select the
284 acquisition frequency in order to have a number of points high enough (i.e. 20)
285 to describe the chromatographic peak, and to increase the time constant to
286 minimize the noise taking into account that a too large time constant value will

287 create band broadening of the recorded chromatographic peak.

288 In VUV detection software, there is a parameter called "Average" which defines
289 the number of measurements before recording the signal. If the average
290 number was assigned to 5, with a fixed detector exposure time (11 ms in our
291 VUV instrument), the sampling period was 5 times the detector exposure time:
292 the sampling period was 55 ms, so the detector recorded one point on
293 chromatogram every 55 ms. Accordingly, when the average number was 20,
294 the sampling period was 220 ms (fig.5). Interestingly, when the average number
295 was increased from 5 to 20, a smoothed baseline has been observed, the
296 standard deviation of the noise has been reduced from $126 \cdot 10^{-6}$ AU to $55 \cdot 10^{-6}$
297 AU, roughly by a factor 2 (the number of points has increased by a factor of
298 $4=20/5$, the standard deviation of the noise was expected to be reduced by a
299 factor $\sqrt{4}$). When higher average number was used, the signal was averaged
300 during a longer time, so the baseline appeared to be smoothed, and the
301 signal to noise ratio was successfully enhanced. However, for fast separation
302 (i.e. small peak width), the average number could not be tuned too high,
303 otherwise the system would not be able to collect enough points to precisely
304 describe a peak. For very fast separation, i.e. peak width about 1s, if average
305 value is set to 50 (sampling period 550 ms), only 2 points are recorded to
306 describe the peak, which is not enough for an accurate peak surface
307 measurement. So, a compromise has to be found in such system according to

308 the targeted application (an average value of 20 can be applied for CO, CH₄,
309 CO₂, C₂H₆ separation).

310

311 3.2.3 Identification and deconvolution

312 The most remarkable and promising property of VUV detector is its ability of
313 deconvolution of co-eluted peaks [23–26]. So, the separation on mono-VUV
314 becomes much more informative than that with FID detector. As shown in **fig.6**
315 **upper left side**, for a separation of BC sample (CO, CH₄, CO₂, C₂H₆) on
316 monolith-VUV, only some classical chromatographic information (retention time,
317 peak area and height) of two peaks can be obtained (the different colors are
318 related to different wavelength ranges). Using VUV detector software, it was
319 moreover possible to obtain the spectrometric information of each peak [25].
320 Since basically all chemicals absorb in ultraviolet wavelength range and there
321 is a comprehensive database in the VUV spectra library, it was possible to
322 perform peak identification and then signal deconvolution. Spectra of the four
323 compounds in our sample (CO, CO₂, CH₄ and C₂H₆) contributing substantially
324 to VUV absorption are reported in supplementary document. As described in
325 the main screen of fig.6, the first peak consisted of methane and carbon
326 monoxide, and similarly the second peak was the overlapping chromatogram
327 of ethane and carbon dioxide.

328

329 **4. Conclusion**

330 The analysis of light hydrocarbons was performed on a modified GC-VUV using
331 short silica monolithic columns. The effect of make-up gas pressure on
332 efficiency and on signal intensity has been studied according to the
333 concentration sensitive property of VUV detector and the “average” number of
334 VUV detector has been adjusted to obtain the lower noise to improve the limit
335 of quantification. Mixture in BC sample (methane, ethane, carbon monoxide
336 and carbon dioxide mixture) has been partially separated within 15 s using a
337 silica monolithic column and chromatographic peaks have been then
338 deconvoluted using spectral information of VUV detector. With such
339 configuration, quantification was possible in a concentration range of percent
340 and was in agreement with the other original requirements (introduction of
341 sample without depressurization stage). So, the hyphenation of monolithic silica
342 capillary column (fast separation) with high pressure carrier gas (on-line
343 analysis) connected to VUV detector (spectrometric information) appears to be
344 an efficient analytical tool and will be extended to other applications.

345

346

347 **Acknowledgment**

348 The authors are grateful to VUV Analytics for the loan of VUV-100 detector.

349

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432 ultraviolet spectroscopy - A tutorial. *Anal Chim Acta.* 8 (2017) 10-22

433

434

435 **Figure caption**

436 Fig. 1 : Effect of split ratio on observed HETP of ethane. Carrier gas Argon, inlet
437 pressure 59.5 bar, GC oven 30 °C. BC Sample, pressure 3 bar. Monolithic silica
438 capillary column I.D 75 µm, length 30 cm.FID, time constant 50 ms.

439 Fig.2. Configuration of **monolithic column** directly connected to VUV detector.

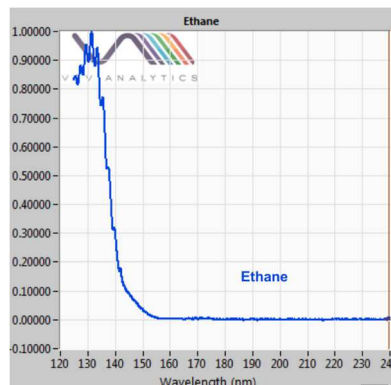
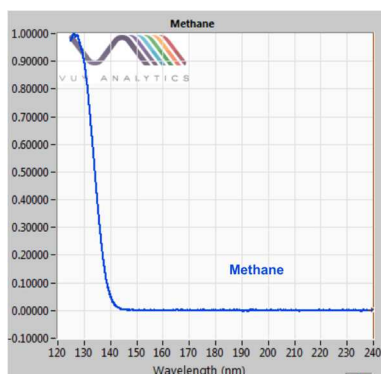
440 Fig.3. Observed HETP value of ethane as a function of make-up gas pressure.
441 Carrier gas Argon, inlet pressure 59.5 bar, BC Sample, pressure 3 bar.
442 Monolithic silica capillary column I.D 75 μm , length 30 cm.

443 Fig.4. The relation between make-up gas pressure and peak height of ethane.
444 Carrier gas Argon, inlet pressure 59.5 bar, BC Sample, pressure 3 bar.
445 Monolithic silica capillary column I.D 75 μm , length 30 cm. Make-up gas
446 pressure varies from 0.5 psi to 5 psi.

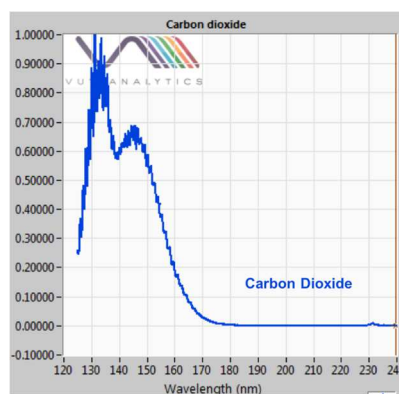
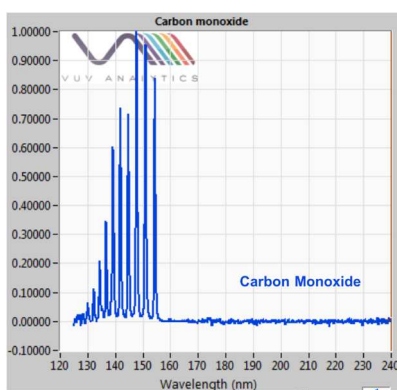
447 Fig.5. Baseline for two different values of “average” number, and standard
448 deviation of noise signal. Carrier gas Argon, inlet pressure 59.5 bar, make-up
449 gas argon, make-up pressure 2 psi. BC Sample, pressure 3 bar. Monolithic
450 silica capillary column I.D 75 μm , length 30 cm.

451 Fig.6 Deconvolution of co-eluted peaks corresponding to the initial
452 chromatogram top-left (three different wavelength ranges). Signal intensity for
453 ethane was higher than for other compounds and is related to right side axis.
454 Carrier gas Argon, inlet pressure 59.5 bar, split ratio 26. Average number 20,
455 make-up gas argon, make-up pressure 0.5 psi, BC sample, pressure 3 bar.

456 **Supplementary Documents**



457



458

459 Spectra of methane, ethane, carbon monoxide and carbon dioxide in the
460 wavelength range of 120 – 240 nm from VUV database.

Figure 1

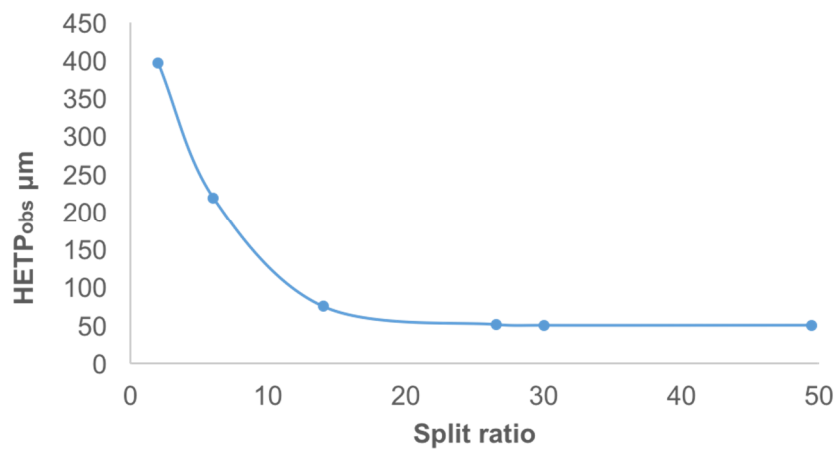


Figure 2

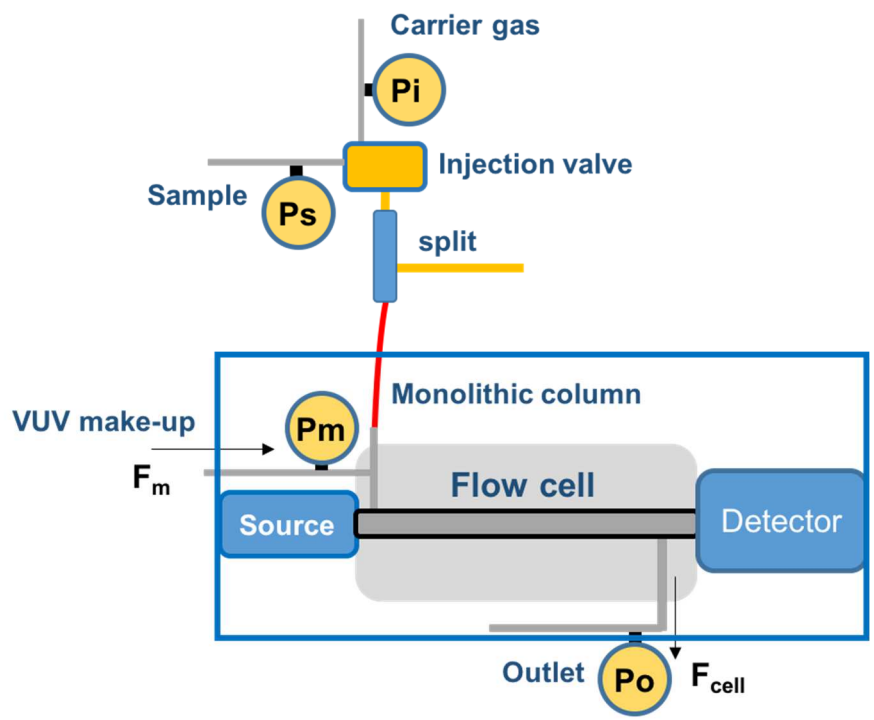


Figure 3.

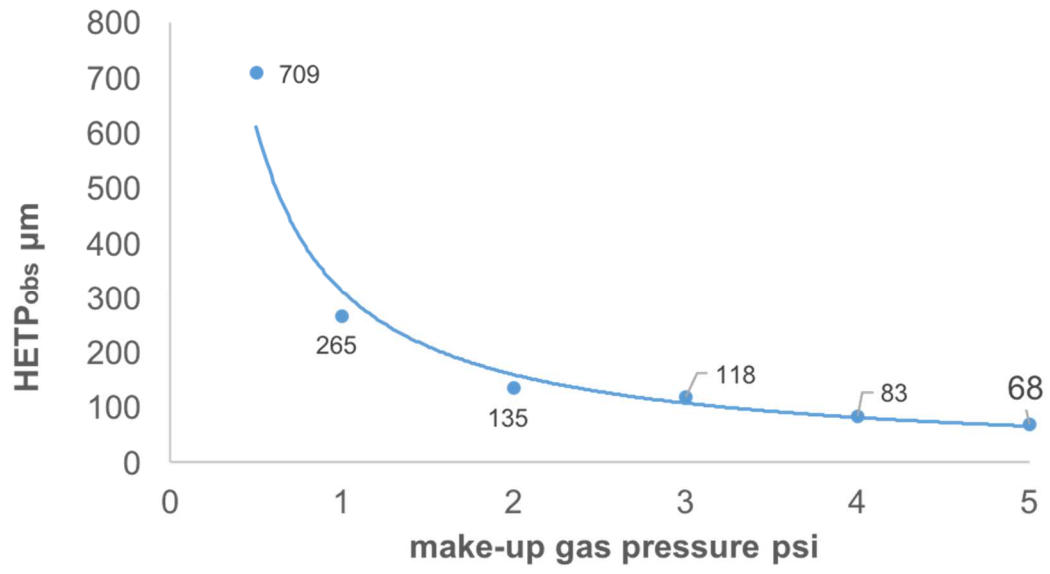


Figure 4.

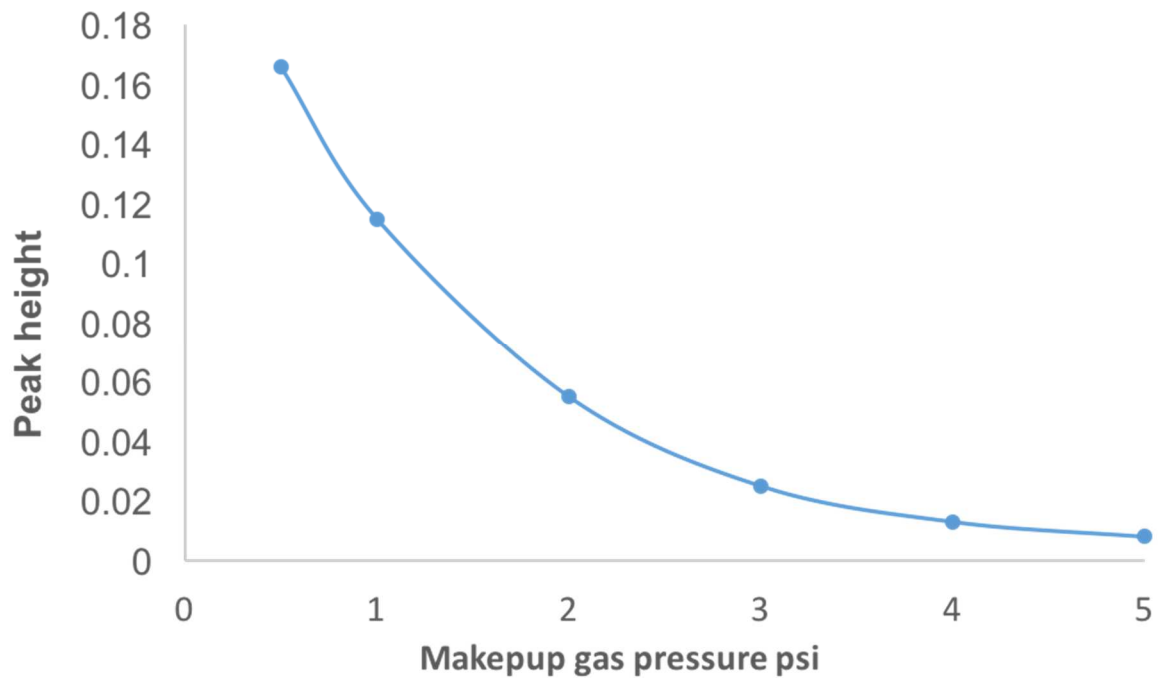


Figure 5

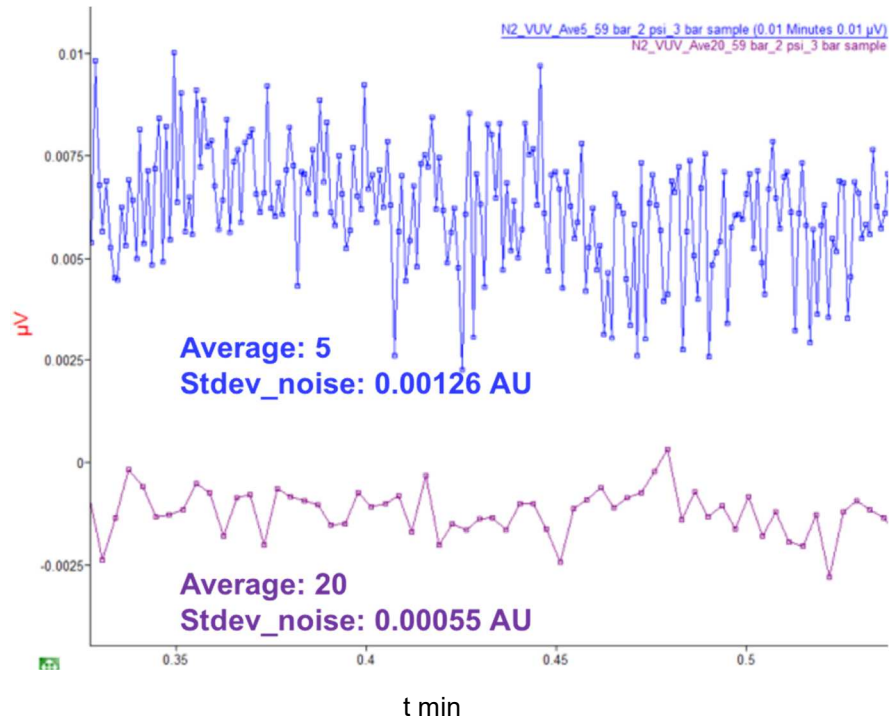


Figure 6.

