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Jérôme Randon

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1	Hyphenation of short monolithic silica capillary column with
2	vacuum ultraviolet spectroscopy detector for light
3	hydrocarbons separation
4	
5	Huian Liu ¹ , Guy Raffin ¹ , Guillaume Trutt ² , Vincent Dugas ¹ , Claire Demesmay ¹ ,
6	Jérôme Randon ¹
7	
8	1 - Univ Lyon, CNRS, Université Claude Bernard Lyon 1, Institut des Sciences
9	Analytiques, UMR 5280, 5 rue de la Doua, F-69100 VILLEURBANNE, France
10	2 - Antelia, ZA des Grandes Terres – 1305 Route de Lozanne – 69380
11	DOMMARTIN, France
12	
13	Corresponding author : randon@univ-lyon1.fr
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 conventionnal 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 27other hand, informative detectors such as mass spectrometer are valuable but 28 low maintenance detectors are prefered. 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 be 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 intrument, 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 loadability. As an alternative choice, silica monolithic capillary columns (75 µm 69 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 perfomances 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 μ m on silica monoliths and 15 80 value reported was 25 μmon 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 4

84 low as 16 µm. Furthermore, owing to the macropore size of monoliths (in the 85 range from 2 to 4 μ m), these columns were commonly of rather low permeability [9-17], and a very high inlet pressure was mandatory which can be as high as 86 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 occur all along the monolithic column. 95

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].

So, hyphenation of monolithic columns with VUV detector (mono-VUV) could 113 be an elite candidate to design a new fast and efficient separative tool with 114 115informative detector for industrial separation of light hydrocarbons. However, several constraints have to be taken into account during hyphenation starting 116 117 from the injection value 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 122capillary column connected to fast FID. Then the monolithic capillary column 123has been hyphenated to a VUV detector and such GC-monolith-VUV device 124 has been optimized (efficiency and sensitivity) according to column and 125detector characteristics.

126

127 **2. Experimental**

128 **2.1** Fabrication of monolithic columns

Monolithic columns were fabricated following the procedure proposed by El-129 130 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 132acid solution containing 1.9 g PEG 10,000 and 4.05 g urea. Then the sol mixture 133was stirred at 0°C for 30 min and next the temperature was increased to 40°C. 134The mixture was loaded into a 75 µm I.D. fused-silica capillary (Polymicro 135Technologies USA) and the capillary was introduced into a 40°C oven overnight for gelification completion. Mesopores were formed by urea decomposition 136 137 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 (0.075 mm internal diameter) used was finally cut to the required length 30 cm. 140

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 152meter ADM1000 was from Agilent Technologies (Paris, France) and was calibrated by France Metrologie (Paris, France). VGA-100 VUV detector was 153154from VUV Analytics, inc. (Cedar Park TX, USA), VUV cell length was 10 cm and 155cell volume was 80 µL. Argon from Air Liquide (Paris, France) was used as both 156carrier gas for chromatographic separation and make-up gas for VUV detector. The so-called BC gas sample was from Air Liquide (Paris, France) and contains 157 158hydrogen (15 mol %), carbon monoxide (15 mol %), carbon dioxide (15 mol %), 159methane (15 mol %) and ethane (15 mol %) in nitrogen as a balance gas.

160

161 **3. Results and Discussions**

In order to obtain an effective separation/detection instrument based on monolithic silica capillary columns hyphenated to VUV detector for on-line separation of light hydrocarbon mixtures, injection band broadening and detection band broadening have to be reduced to the minimum value in order to keep the observed column efficiency at the maximum value, and detector
 parameters can then also be tuned to lead to suitable limits of detection and
 deconvolution.

169 **3.1 Preliminary evaluations**

Flame ionization detector is a very sensitive and broadly used detector in gas chromatography, and despite the fact that FID is not able to provide any spectrometric information, it is a reliable tool to measure column efficiency in relation to the very low band broadening created by such detector using short time constant (50 ms). In order to anticipate the hyphenation with VUV detector, argon was used as carrier gas and so column performance was reported here 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 injection band broadening to a value significantly lower than the column band 185

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 evaluated by measuring the vent flow and the column flow and then calculating 189 their ratio. Fig.1 shows the effect of split ratio in the range from 2 to 50 on the 190 observed height equivalent to a theoretical plate number (HETPobs) of ethane 191 192 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 cm.s⁻¹).

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

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

198
$$HETP_{obs} = \frac{L}{N_{obs}} = L.\frac{\sigma_{obs}^2}{t_R^2}$$
 (2)

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

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

After the study of the injection part, the FID was removed and the monolithic 208 209 column was then connected to the tranfer 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 2µL), band broadening due to the 212 tranfer 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 rapidely 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

3.2 Optimized design for monolithic column directly connected to VUV detector
 On VUV detector, the transfer line was originally designed to connect
 11

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 configuration (fig. 2), the transfer line has been removed, so that additional 230 231 connections have been avoided and the dead volume of transfer line has been 232 definitively eliminated. Since the separation of carbon monoxide, methane carbon dioxide and ethane can be performed at room temperature using silica 233 234 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

The effect of VUV make-up gas pressure on observed efficiency has been studied using ethane as a test compound. As shown in fig.3, the effect of VUV make-up gas pressure (P_m on fig.2) on observed HETP value, under the same experimental conditions as for FID detection, has been investigated. The higher the make-up gas pressure, the lower was the HETP value, and a value comparable to the one obtained with FID hyphenation was observed for the highest make-up gas pressure. That could be explained as the higher make-up 12 gas pressure brings higher flow in the flow cell, which substantially reduces the band-broadening occurring in the cell. So, to get the maximum efficiency value using monolith columns, the make-up gas pressure must be tuned at the highest possible value. Such high make-up gas pressure (flow) was not required with conventional open tubular columns with internal diameter of 250 µm because the column broadening was higher and only a small make-up pressure (flow) was then necessary to avoid detector band broadening.

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

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

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

264

In the set of experiments reported here, an increase in make-up gas pressure increased the total flow through the cell F_{cell} by increasing the make-up flow. 13 Because the pressure drop through the column did not change significantly (P_i was constant 59,5 bar / 863 psi, P_m varied from 1 to 5 psi, so ΔP varied from 862 to 858 psi), the column flow was constant for all the experiments, and the dilution factor for the compound eluting from the column increased according to the make-up gas pressure. Therefore, the peak height was lowered when the make-up pressure increased.

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

276

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.

In VUV detection software, there is a parameter called "Average" which defines 288 289 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, the sampling period was 220 ms (fig.5). Interestingly, when the average number 294 was increased from 5 to 20, a smoothed baseline has been observed, the 295 standard deviation of the noise has been reduced from 126.10⁻⁶ AU to 55.10⁻⁶ 296 AU, roughly by a factor 2 (the number of points has increased by a factor of 297 4=20/5, the standard deviation of the noise was expected to be reduced by a 298 299 factor $\sqrt{4}$). When higher average number was used, the signal was averaged 300 during a longer time, so the baseline appeared to be smoothened, and the signal to noise ratio was successfully enhanced. However, for fast separation 301 302 (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 value is set to 50 (sampling period 550 ms), only 2 points are recorded to 305 306 describe the peak, which is not enough for an accurate peak surface measurement. So, a compromise has to be found in such system according to 307

the targeted application (an average value of 20 can be applied for CO, CH₄,
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 becomes much more informative than that with FID detector. As shown in fig.6 314 315 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 to VUV absorption are reported in supplementary document. As described in 324 325 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**

The analysis of light hydrocarbons was performed on a modified GC-VUV using 330 331 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

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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

capilary column I.D 75 $\mu m,$ length 30 cm.FID, time constant 50 ms.

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

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

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

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

Fig.6 Deconvolution of co-eluted peaks corresponding to the initial chromatogram top-left (three different wavelength ranges). Signal intensity for ethane was higher than for other compounds and is related to right side axis. 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



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





Figure 2



Figure 3.











Figure 6.

