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Sensitivity and resolution optimization in gas chromatography coupled to mass spectrometry analyses of volatile organic compounds present in vacuum environment

Ninette Abou Mrad^{1,2}, Steven Werner¹, Julie Mouzay¹ and Grégoire Danger^{1,*}

1. Aix-Marseille Université, CNRS, PIIM, UMR 7345, 13013 Marseille, France.

2. Université Paris-Sud 11, LETIAM, IUT d'Orsay, Plateau de Moulon, 91400 Orsay, France

*E-mail gregoire.danger@univ-amu.fr, phone number : +33491288285

Abstract

The gaseous phase analyses of *volatile organic compounds* (VOCs) are an important challenge especially when these organics are formed in high vacuum environments (10^{-8} mbar) *reproducing the environment of astrophysical ices formation and processing*. Several analytical techniques have been developed to identify the molecular diversity formed from the processing of these ices. Among them, the coupling of a GC-MS to the vacuum chamber where ices are processed highlighted the interesting chemical diversity of such processed ices. These analyses were possible due to the development of a specific system, the VAHIIA interface that enables the preconcentration of VOCs at low pressure (10^{-8} mbar) and their transfer at higher pressure to the injection unit of a GC for their subsequent analyses. This system showed sufficient repeatability (13%) and low detection limits (nmol) for simple ices [1], but presents limits when ice mixtures are complex (*such as multi-component ices including water, methanol and ammonia*). In this contribution, we present the optimization of our previous VAHIIA system by implementing a cryofocusing system in the GC oven and by improving the recovery yield of VOCs from the vacuum chamber to the VAHIIA interface. The cryofocusing provides an improvement of efficiencies leading to higher resolution and signal to noise ratio, while the addition of argon in the vacuum chamber during the VOC recovery allows increasing the amount of molecules recovered by a factor of ~200. The coupling of both approaches provides an increase of sensitivity of a factor ~400. At the end, experiments on astrophysical ices are shown demonstrating the interest of such optimizations for VOC analyses.

Keywords

Volatile Organic Compounds, Vacuum environment, GC-MS, cryofocusing, ice analogs

1. Introduction

Direct and online analysis of Volatile Organic Compounds (VOCs) in vacuum environments using chromatographic techniques is quiet problematic, mainly due to pressure differences between their formation environments and the analytical instruments used for their analysis, to the compound dilution that prevents direct analysis but also to delicate logistics to ensure online analysis preserving the representativeness of samples. We addressed this issue in 2014 through the development of a

specific interface (referred to as VAHIIA) answering the main analytical challenges encountered in such analysis, with a particular case application for VOCs coming from the photo and thermal processing of astrophysical ice analogs formed in vacuum chambers mimicking the interstellar medium [1]. We have earlier proposed to analyze qualitatively and quantitatively these VOCs by gas chromatography coupled to mass spectrometry (GC-MS) [1,2], using the developed VAHIIA interface that directly *connects* the vacuum chamber where compounds are formed (10^{-8} mbar) to the GC injector (*higher than the atmospheric pressure*).

This VAHIIA interface is *composed* of two units. One is devoted to the VOCs recovery and their preconcentration and is formed of a preconcentration loop (2.5 mL) *immersed* in liquid nitrogen. The second unit allows the gaseous sample resulting from the preconcentration loop heating to be introduced into the GC injector, and is constituted of gaseous injection loops (i.e. 500 μ L volume). The VOCs transfer from the first unit to the second is realized following a controlled pressure gradient, performed by increasing the pressure in the preconcentration loop after its warming relatively to the injection loop through the addition of helium gas. Gaseous samples are then injected via the GC injector. The VOC transfer from the vacuum chamber mimicking the interstellar medium to the GC is reproducible (variability below 13%) with detection limits in the range of nanomolars [1].

This VAHIIA interface was first used to characterize VOCs released in the gaseous phase from the processing of a pure methanol ice. It enabled the detection of various compounds having different chemical functions [2]. Thirty nine molecules having one to six carbon atoms were identified among the hundred detected. However, the increase of the molecular diversity resulting from the increase of the number of molecules composing the initial ice [3,4] brings up new challenges to overcome, both for qualitative and quantitative measurements. Indeed, we observed low column theoretical plates for peaks at low retention times, which implies low chromatographic resolution and column peak capacity. In addition, the injection of a large sample volume (500 μ L) is a source of peak broadening and therefore a decrease of efficiency.

To overcome these drawbacks, we present herein the optimization of our previous VAHIIA system by implementing a cryofocusing system inside the GC oven to limit the diffusion inherent to the injection. Furthermore, to improve qualitative and quantitative aspects, we worked on the optimization of the VOCs recovery from the vacuum chamber to the GC-MS by modifying the pressure inside the chamber.

2. Materials and Methods

2.1 Experimental set-up

The basic equipment and techniques employed for the formation and the follow up of ice analogs have been previously reported [1]. A brief description of the overall system is provided herein. All

experiments described were performed in a high vacuum chamber presenting a pressure of $5 \cdot 10^{-8}$ mbar at 295 K and 10^{-8} mbar at 20 K. The gaseous methanol was deposited at a rate of 6×10^{-1} mol min⁻¹ on a copper-plated surface kept at 20 K with a closed helium cycle model 21 CTI cold head. In these conditions an ice of methanol is formed on the sample holder. Control of sample is provided by infrared spectroscopy [1]. The warming up of the ice mixture to room temperature was performed by stopping the cryogenic system. For the VOC analysis, the chamber is connected to a GC-MS (GC Trace **1310** and MS ion trap ITQ 900 from Thermofisher) with stainless steel tubes. *To test the impact of the cryofocusing system, compounds were introduced in the gaseous form directly into the preconcentration loop of the VAHIA interface and were not pumped from the vacuum chamber as described in the introduction section. Details of the procedure are given elsewhere [1].*

The GC split/splitless (SSL) injector was maintained at 250 °C, and a split mode injection with a ratio of 10 was conducted which ensures a good compromise between a high sensitivity while avoiding column saturation. Separation of target analytes was achieved using a Rxi®-624 Sil MS (60 m × 0.25 mm i.d. × 1.4 µm d.f.) capillary column purchased from Restek, and using helium (alpha gaz 2) as the carrier gas with a 1.18 mL min⁻¹ constant flow rate. The temperature program started at 45 °C and was held for 3 min. The temperature was then increased up to 150°C at a rate of 5°C min⁻¹, then to 220°C at a rate of 20°C min⁻¹. The temperature of the transfer line from GC to MS was set at 250 °C. The ion trap mass spectrometer was used in the electron impact ionization mode (ionization energy of 70 eV). The ion source temperature was set to 250 °C and the maximum ion time in the trap was of 25 ms. The signal was collected with a full scan mode in the mass range between 15 and 300 *u*. and a scan event time of 0.16 s. For this study, the GC has been modified due to the addition of a gaseous sample injection unit mainly constituted of sample loops detailed further in reference [1]. In addition, both injectors have also been modified to allow gaseous sample injection. The first modification allows the carrier gas to flush the sample injection loop at the injector level, and the second modification consists of adding a stainless steel tube in the injector that brings the sample from the injection loop to the injector [1]. The whole interest of having both these modified SSL injectors in our instrument is to make possible the use of multiple columns for the analysis of molecular species having different physical and chemical properties. Furthermore, column swapping is facilitated due to the use of a vent-free GC/MS adapter (Frontier Laboratories LTD) (i.d. 0.15 mm, length ca 50 cm, column ultra-ALLOY metal capillary) in the interface between the GC and the MS which limits the air flow into the MS at values lower than 0.5 mL/min during the switching of columns. A MicroJet Cryo-Trap MJT-1035E from Frontier Laboratories LTD was implemented on a 20 cm x 0.25 mm i.d. Rxi guard column from Restek. The cryogenic point was set at 10 cm from the head of the separative column. Liquid nitrogen was used as a trapping gas allowing a cooling at the precolumn point around -190°C.

2.2 Chemicals

The VAHIA system was optimized using compounds belonging to different chemical classes *having the main functional groups expected in the ice photoprocessing experiment*. For the laboratory experiments, the standards of diethyl ether (anhydrous, assay $\geq 99\%$, ACS reagent), acetaldehyde (puriss. p.a, anhydrous, assay $\geq 99.5\%$ (GC), Fluka), methyl acetate (anhydrous, assay 99.5%), methanol (for pesticide residue analysis, Fluka Analytical), absolute methanol and acetonitrile (for pesticide residue analysis, Fluka Analytical) were purchased from Sigma Aldrich, Saint Quentin Fallavier, France.

3. Results and Discussion

3.1 Cryofocusing to enhance resolution

The main analytical challenge in the photo and thermal processing of astrophysical ice analogs comes from the high molecular diversity obtained in such experiments. *As previously reported, the photoprocessing of a pure methanol ice led to the formation of numerous alcohols, esters, ethers, acids, ketones and aldehydes presenting a wide variability in volatility* [2]. Consequently, at the minimum temperature of our GC oven (45°C), some molecules are not focused at the column head and start to diffuse in the analytical column. These compounds present large peak widths implying weak resolutions [5]. Furthermore, large sample volumes ($500\ \mu\text{L}$) are injected contributing to peak broadening due to the extra-column dispersion effect. The objective is thus to trap analytes on a pre-column in order to minimize peak broadening and increase peak capacity. Several techniques are used to cryo-trap analytes in gas chromatography [6–9]. In the present work, the head of the *guard-column* is cooled down to $77\ \text{K}$ *with a cryogenic controller injecting* a liquid nitrogen jet leading to the cryo-focusing of analytes. If the cryogenic time is sufficient all analytes would be focalized. When trapping is completed, analytes should be released from the *guard column* and introduced in a sharp band at the head of the analytical column that would lead to higher column efficiency and better peak resolution.

The first step is to optimize the cryogenic time, which corresponds to the period during which the liquid nitrogen flow is opened. For this purpose, three standards covering a range of saturated vapor pressures *were introduced separately and directly into the preconcentration loop*: acetaldehyde (t_r : $5.68\ \text{min}$), ethanol (t_r : $8.55\ \text{min}$) and ethyl acetate (t_r : $11.66\ \text{min}$) with various cryofocusing periods. The evolutions of areas are statistically homogeneous (three injections for each period, $n=3$ with a same injected quantity for each compound) whatever the cryo-focusing periods are, implying that the system modification does not impact the compound recovery. Table 1 displays the evolution of thermodynamic and kinetic factors as a function of the cryofocusing period. *The increase of retention times observed with the cryofocusing compared to the non cryofocusing experiment is due to the lapse of time where compounds are stacked at the cryogenic point on the guard column. This cryofocusing time is the added to t_r , and t_0 explaining this increase*. As shown by the evolution of capacity factors (k'), compounds' retention on the stationary phase is not impacted by the

cryofocusing process since k' of all compounds are constant whatever cryogenic times are. Inversely, data highlight an increase of column theoretical plates (N) with the increase of the cryofocusing period, a phenomenon which is intimately related to the peak sharpening with cryofocusing. It is more pronounced for analytes with low retention times since N of acetaldehyde increases by a factor of 11 while those of ethanol and ethyl acetate increase only by a factor of 4.5 and 2.5 respectively. The difference observed between acetaldehyde and the two other compounds is due to their difference in volatility. All compounds eluting between 4.3 min (column dead time) and 7.3 min (end of the 45°C isotherm) are too volatile to get focused on the column head during the 3 min of isotherm at 45°C, which is the case of acetaldehyde (5.68 min). These analytes diffuse and therefore present peak broadening as observed in Figure 1. Once the cryofocusing operates, all analytes are trapped into a thin plug at 77 K just after the injection. This phenomenon prevents the diffusion observed at 45°C, which considerably increases N due to peak sharpening.

Table 1 – Data related to the injection of specific standards to estimate the impact of the cryofocusing on thermodynamic (capacity factor, k') and kinetic (column theoretical plates, N) factors. t_0 is obtained from the air peak and RSD are obtained from 3 replicates ($n=3$). S/N_1 is the signal to noise ratio. k' is obtained by subtracting the cryofocusing time to the reduced retention time in order to only consider the retention on the separative column.

We pursue our investigation by monitoring the evolution of the S/N_1 ratio as a function of the cryofocusing period (Table 1). Data also show an S/N_1 increase once the cryofocusing is turned on until it reaches a plateau at 45 s, which is related to N improvements. We then estimate a limit of detection (LOD) by focusing on the lowest quantity (123 nmol, average RSD of 7% for triplicates) of compounds injectable into the VAHIIA system (Table 2). By considering a S/N_1 of 3 at the LOD value, estimated LOD were extrapolated for the 45s and the non-cryofocusing experiments. Estimated LOD range from 0.3 to 6.2 nmol. The cryofocusing allows an average S/N_1 increase of 2 compared to the non cryofocusing method, resulting in lower detection limits.

Table 2 – Estimated LOD extrapolated from the lowest concentration (123 nmol) injectable in the VAHIIA interface. S/N_1 at this concentration is displayed for diethyl ether, acetaldehyde and methanol as well as the corresponding RSD ($n=3$). The estimated LOD is obtained by taking $S/N_1 = 3$ and assuming a linear relation between our 123 nmol data and the $S/N_1 = 3$. The average RSD on areas is 7% showing a sufficient robustness.

To evaluate the impact of cryofocusing on the separation of VOCs, a mixture of six compounds (3 couples of compounds having close retention times) was injected using different cryofocusing periods (from 0 s to 60 s, Figure 1). With no cryofocusing, column efficiencies for the first peaks are low (Table 3) providing low resolution (0.42 between compounds 2 and 3, 1.00 between compounds 4 and 5, and 0.17 between compounds 6 and 7). When the cryofocusing is applied during 15 s, column

efficiencies for all compounds are highly increased with a higher impact for low retention time peaks. Resolutions increase from 0.42 to 1.33 for compounds 2 and 3 and from 1.00 to 1.27 for compounds 4 and 5. At 45 s of cryogenic trapping, a significant improvement is observed with a complete resolution reached between compounds 4 and 5. No improvements are observed at higher cryogenic times (60 s, Figure 1). ***Our results pinpoint also the lower impact of cryofocusing on “high” retention time compounds tested in this study***, as observed for acetonitrile and methyl acetate which remain co-eluted even though peak sharpening can be noted. Furthermore, the S/N_1 improvement with cryofocusing allowed the detection of residual water for the first time. It is noticeable also that the atmospheric carbon dioxide can also be resolved from the column dead time using cryofocusing even if it does not interact with the column stationary phase. This resolution is only due to the retention of carbon dioxide at 77 K at the cryofocusing position.

Figure 1 – Effect of the duration of the cryofocusing on a standard mixture. Resolutions are calculated from extracted ions of each compound. 1: O_2/N_2 column dead time, 2: acetaldehyde (m/z 43 u), 3: methanol (m/z 31 u), 4: ethanol (m/z 45 u), 5: diethylether (m/z 59 u), 6: acetonitrile (m/z 41 u), 7: methyl acetate (m/z 74 u). Note: Baselines of the different chromatograms are artificially shifted. Same amounts of standards were injected at each experiment.

Table 3 – Data related to Figure 1 displaying retention times (t_r), column theoretical plates (N) and resolution (R_s) between acetaldehyde/methanol, ethanol/diethyl ether, acetonitrile/methyl acetate. R_s and N are obtained from extracted ions: acetaldehyde (43), methanol (31), ethanol (45), diethyl ether (59), acetonitrile (41), methyl acetate (74).

All these results demonstrate the impact of adding a cryofocusing trap to the VAHIA system. It allows an important improvement of efficiencies, leading to better resolution and sensitivity.

3.2 To improve the COV recovery from the vacuum chamber

At another level, increasing the sensitivity of the VAHIA system required an improvement of the VOC recovery yield from the vacuum chamber *where* ices are processed to the preconcentration loop where VOCs are concentrated at 77 K. For this purpose, we investigated the impact of the pressure inside the vacuum chamber on VOCs recovery. The experiment designed consisted of introducing 4 μ mol of gaseous methanol inside the vacuum chamber (10^{-8} mbar), which condensed on the sample holder maintained at 20 K. Once the vacuum chamber was isolated from the pumping system and the sample holder warmed up to 300 K, the pressure in the vacuum chamber raised up to 10^{-3} mbar. Ultrapure Argon was then added to reach various pressures in the chamber, and the resulting VOCs recovery was monitored. Argon was used since it presents no chemical reactivity and since its freezing temperature is of 40 K which prevents its condensation in the preconcentration loop at 77 K. Argon was added to obtain a total pressure in the chamber of 10^{-2} , 10^{-1} , 1 or 10 mbar. Three experiments were

performed at each pressure to obtain an insight on the variability of VOCs recovery at a given pressure. At 10^{-3} and 10^{-2} mbar, the area of methanol detected with the GC-MS is statistically equivalent (Figure 2) and corresponds to a methanol recovery of 0.4%. However, once the pressure in the chamber is increased to 10^{-1} mbar, the quantity of methanol recovered increases by a factor of 180 giving a 50% recovery of the initial methanol amount deposited in the vacuum chamber. The recovery is even higher with a total pressure of 1 mbar, showing a 270-enhancement factor relatively to 10^{-3} mbar, and remains stable with pressures higher than 1 mbar. At this total pressure in the vacuum chamber around 80% of the initial amount of methanol is recovered.

Figure 2 – Impact of the pressure inside the vacuum chamber on the amount of methanol recovered. Error bars were calculated based on the standard deviation of methanol areas from replicates (n=3).

The increase in the amount of methanol recovered once the pressure in the chamber increases could be related to the free molecular flow regime of gas that can occur at pressures below 10^{-2} – 10^{-3} mbar. Once the pressure increases above 10^{-2} mbar, the free molecular flow evolves to a laminar flow where argon drives a large part of gaseous species from the vacuum chamber to the preconcentration loop.

After both developments on VOCs recovery from the vacuum environment and VOCs cryofocusing on the chromatographic column, we can estimate a total increase of the methanol sensitivity of a factor about 400.

3.3 Application to VOCs analysis coming from the photo- and thermal processing of a pure methanol ice

To test the impact of the previous optimizations on VOCs analysis, an ice of methanol was irradiated during 24 h.

Figure 3 – GC-MS analyses of the gases sublimated from a methanol ice sample after its irradiation during 24 h. Chromatograms showing the impact of cryofocusing and pressure chamber increase are displayed. 1: O₂/N₂ column dead time, 2: methanol, 4: acetone, 5: dimethyl ether, 6: acetaldehyde. Note: Baselines of the different chromatograms are artificially shifted. *For a better reading, peaks 1, CO₂ and 2 were manually truncated in the bottom and middle chromatograms. From 8.5 min the intensity of the signal is multiplied by 3 in order to have a better insight on the remaining compounds.*

The VOCs formed after the photo-processing of the methanol ice were transferred to the GC-MS through the VAHIA interface using the new developments described in the previous section (Figure 3). In a first experiment, VOCs were recovered with no addition of Argon (final pressure after ice warming of 10^{-3} mbar in the vacuum chamber) while using the cryofocusing (45 s). In comparison to

the experiment conducted with no cryofocusing published elsewhere [5], the cryofocusing allowed the resolution of CO₂ from the column dead time and enabled the detection of H₂O. The second experiment consisted in recovering VOCs with a 10 mbar pressure in the vacuum chamber with no cryofocusing. An impressive increase in the number of detected compounds was observed as depicted in the chromatogram (9-19 min) in Figure 3, with identifications of ethanol and acetone, next to H₂O and methanol. As for the non photo-processed methanol used during the recovery optimization, the VOCs recovery from samples presenting an important molecular diversity is also highly enhanced by increasing the pressure in the vacuum chamber. The last experiment combined cryofocusing and chamber pressure increase, resulting in a high number of detected species and a significant improvement in sensitivity and resolution.

4. Conclusion

The introduction of cryofocusing to the VAHIA experimental set-up combined to the modification of chamber pressure during VOCs recovery contribute clearly to enhance the detection sensitivity and to improve chromatographic resolution. Consequently, our ability to detect new compounds in such experiments increased in comparison to what has been developed previously. Indeed, our experimental results pinpoint the presence of numerous new compounds that have not been previously observed, but their identification is out of the scope of this work. Besides, the improvement of chromatographic resolution enables the most possible non-ambiguous identification with mono dimensional chromatography and low resolution mass spectrometry, and inevitably a reliable quantification. This method optimization proved its effectiveness in the analysis of VOCs coming from a pure methanol ice, and its contribution to the analysis of VOCs coming from the processing of complex ices is without a doubt crucial to enlighten us on the composition of such gaseous samples.

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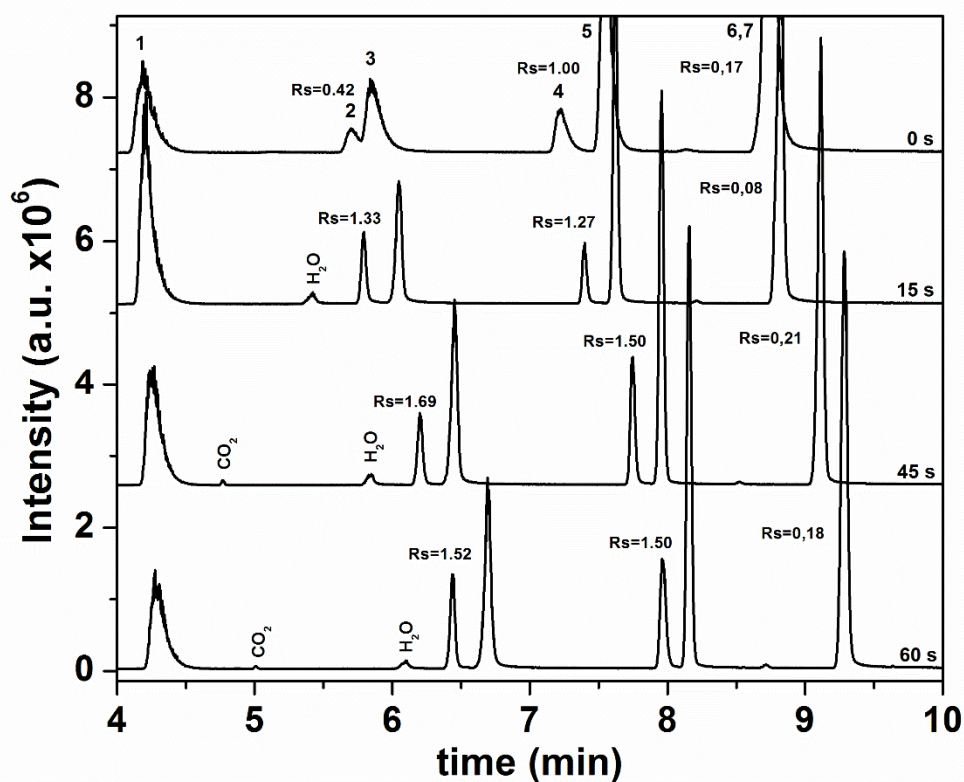


Figure 1 – Effect of the duration of the cryofocusing on a standard mixture represented by the total ion current. Resolutions are calculated from extracted ions of each compound. 1: O₂/N₂ column dead time, 2: acetaldehyde (m/z 43 u), 3: methanol (m/z 31 u), 4: ethanol (m/z 45 u), 5: diethyl ether (m/z 59 u), 6: acetonitrile (m/z 41 u), 7: methyl acetate (m/z 74 u). Note: Baselines of the different chromatograms are artificially shifted. Same amounts of standards were injected at each experiment.

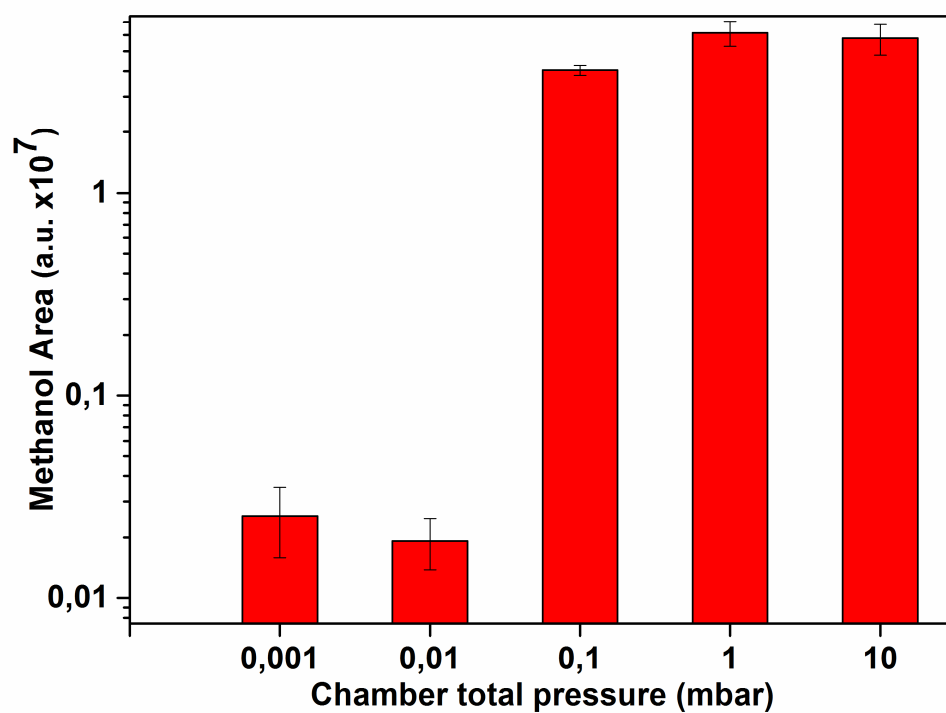


Figure 2 – Impact of the pressure inside the vacuum chamber on the amount of methanol recovered. Error bars were calculated based on the standard deviation of methanol areas from replicates (n=3).

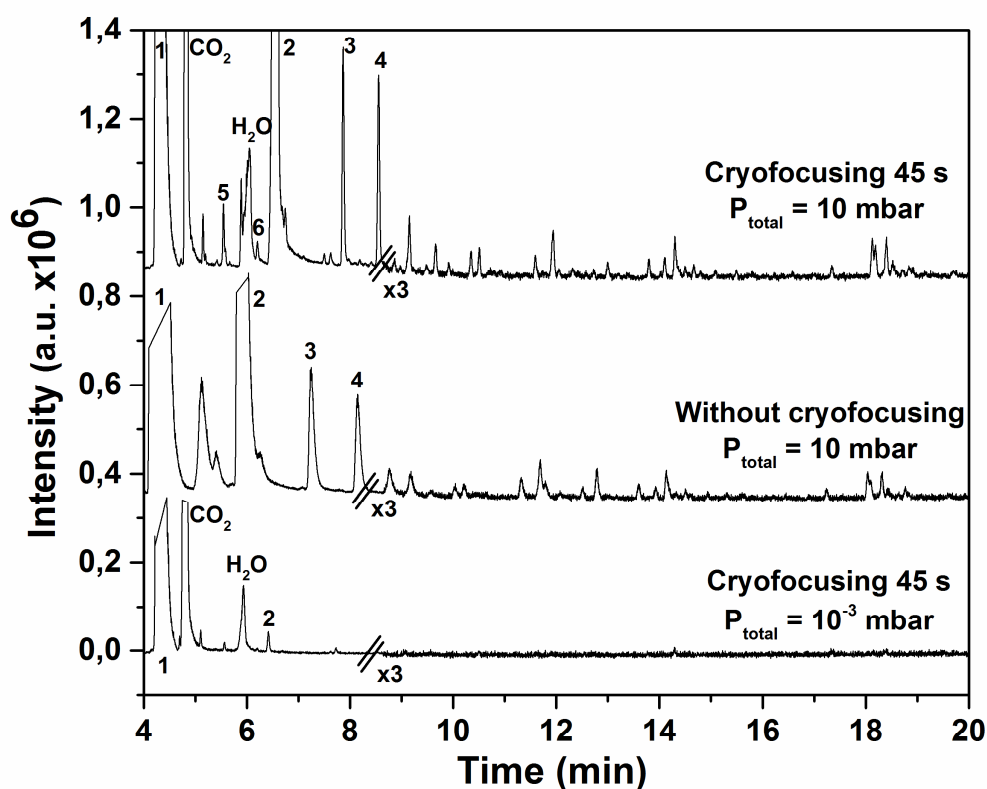


Figure 3 –GC-MS analyses of the gases sublimated from a methanol ice sample after its irradiation during 24 h. Chromatograms showing the impact of cryofocusing and pressure chamber increase are displayed. 1: O₂/N₂ column dead time, 2: methanol, 4: acetone, 5: dimethyl ether, 6: acetaldehyde. Note: Baselines of the different chromatograms are artificially shifted. **For a better reading, peaks 1, CO₂ and 2 were manually truncated in the bottom and middle chromatograms. From 8.5 min the intensity of the signal is multiplied by 3 in order to have a better insight on the remaining compounds.**

Table 1 – Data related to the injection of specific standards to estimate the impact of the cryofocusing on thermodynamic (capacity factor, k') and kinetic (column theoretical plates, N) factors. t_0 is obtained from the air peak and RSD are obtained from 3 replicates ($n=3$). S/N_1 is the signal to noise ratio. k' is obtained by subtracting the cryofocusing time to the reduced retention time in order to only consider the retention on the separative column.

	Cryo time (s)	t_0 ¹ (min)	t_r (min)	RSD ² (tr) (%)	k' ³	N (10 ⁶)	RSD (N) (%)	S/N_1 ⁴	RSD (S/N_1) (%)
Acetaldehyde	0	4.16	5.68	0.10	0.36	14	4	159	27
	5	4.18	5.71	0.10	0.36	30	5	450	5
	15	4.20	5.82	0.17	0.36	107	24	497	14
	30	4.22	6.06	0.19	0.35	120	18	465	14
	45	4.22	6.29	0.24	0.35	130	18	543	11
	60	4.24	6.54	0.23	0.34	155	16	561	13
Ethanol	0	4.19	7.24	0.08	0.72	23	5	230	15
	5	4.16	7.32	0.00	0.74	47	12	336	14
	15	4.17	7.41	0.00	0.73	79	10	325	7
	30	4.19	7.61	0.13	0.72	81	5	323	12
	45	4.23	7.82	0.07	0.71	101	6	313	12
	60	4.23	7.98	0.12	0.71	89	12	318	2
Methyl acetate	0	4.21	11.66	0.05	1.77	144	5	782	17
	5	4.19	11.67	0.05	1.78	306	1	1398	4
	15	4.18	11.74	0.10	1.79	356	13	1258	13
	30	4.22	11.85	0.00	1.76	333	13	1633	10
	45	4.22	11.95	0.05	1.73	365	1	1541	10

¹ t_0 is obtained from the air peak.

² RSD are obtained from 3 replicates ($n=3$).

³ k' is obtained by subtracting the cryofocusing time to the reduced retention time in order to only consider the retention on the separative column.

⁴ S/N_1 is the signal to noise ratio.

Table 2 – Estimated LOD extrapolated from the lowest concentration (123 nmol) injectable in the VAHIA interface. S/N_1 at this concentration is displayed for diethyl ether, acetaldehyde and methanol as well as the corresponding RSD (n=3). The estimated LOD is obtained by taking $S/N = 3$ and assuming a linear relation between our 123 nmol data and the $S/N_1 = 3$. The average RSD on areas is 7% showing a sufficient robustness.

	Cryofocusing	S/N_1	RSD (%)	Estimated LOD (nmol) $S/N_1 = 3$
Diethyl ether	OFF	623	9	0.6
	45 s	1250	15	0.3
Acetaldehyde	OFF	218	5	1.7
	45 s	519	8	0.7
Methanol	OFF	59	16	6.2
	45 s	99	17	3.9

Note: S/N_1 were derived from the Xcalibur software

Table 3 – Data related to Figure 1 displaying retention times (t_r), column theoretical plates (N) and resolution (Rs) between acetaldehyde/methanol, ethanol/diethyl ether, acetonitrile/methyl acetate . Rs and N are obtained from extracted ions: acetaldehyde (43), methanol (31), ethanol (45), diethyl ether (59), acetonitrile (41), methyl acetate (74).

Cryo time (s)	Compound (Extracted ion)	t_r (min)	N	Rs
0s	Acetaldehyde (43)	5.70	2140	0.42
	Methanol (31)	5.84	1380	
	Ethanol (45)	7.22	2651	1.00
	Diethyl ether (59)	7.55	2899	
	Acetonitrile (41)	8.68	3610	0.17
	Methyl acetate (74)	8.73	6755	
15s	Acetaldehyde (43)	5.79	5732	1.33
	Methanol (31)	6.05	4598	
	Ethanol (45)	7.40	9363	1.27
	Diethyl ether (59)	7.61	14259	
	Acetonitrile (41)	8.79	5089	0.08
	Methyl acetate (74)	8.81	11911	
45s	Acetaldehyde (43)	6.20	12601	1.69
	Methanol (31)	6.47	6424	
	Ethanol (45)	7.76	19739	1.50
	Diethyl ether (59)	7.97	15640	
	Acetonitrile (41)	9.40	23406	0.21
	Methyl acetate (74)	9.13	23561	
60s	Acetaldehyde (43)	6.44	15955	1.52
	Methanol (31)	6.69	5622	
	Ethanol (45)	7.94	15522	1.50
	Diethyl ether (59)	8.15	21774	
	Acetonitrile (41)	9.26	11876	0.18
	Methyl acetate (74)	9.29	24394	