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Thermal stability of adsorbents used for gas chromatography in space exploration

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Abstract

For analytical purpose, thermal desorption is now used in gas chromatographs developed to analyse the chemical composition of planetary environments. Due to technical constraints, the thermal desorption cannot be as finely controlled as in the laboratory resulting in possible thermal alteration of the adsorbents used. For these reasons, the influence of heat on physical and chemical properties of various adsorbents, either used or that could be used in gas chromatographs for space exploration, is studied. If the adsorbents made of carbon molecular sieves and graphitised carbon black that were tested show a very high thermal stability up to 800°C, the porous polymers tested are highly degraded from a minimum temperature that depends on the nature of the polymer. Poly-2,6-diphenylphenylene oxide is shown to be the more thermally robust as it is degraded at higher temperatures, confirming it is currently the best choice for analysing organic molecules with a space instrument. Finally, the products of degradation of the porous polymers tested were analysed after heating the porous polymers at 400°C and 800°C. They were identified and listed as potential contaminants of analyses performed with this type of adsorbent. If the exposure to the higher temperature produces numerous organic compounds, mainly aromatic ones, a few ones are also detected at the lower temperature tested, meaning they should be considered as potential contaminants. Again poly-2,6-diphenylphenylene oxide should be preferred because it releases less organic compounds, the structure of which is completely specific to the adsorbent composition.

Highlights

Thermal evolution of adsorbents used for GC in space exploration is studied up to 800°C

Graphitised carbon blacks and molecular sieves are thermally stable

Porous polymers are drastically degraded by the heat

Potential organic contaminants produced by porous polymers are tentatively identified and listed

Keywords

Gas chromatography
Thermal desorption
Adsorbents
Thermal stability
Space exploration

1. Introduction

Gas chromatography has been used for decades for space exploration [1]. Due to its robustness and relative technical simplicity, this instrumentation has been part of the scientific payload of several space probes that explored Venus [2], Mars [3, 4], comets [5] and even Titan [6]. It is used for the analysis of the chemical composition of the atmospheres, and of condensed materials collected at the surface or in the atmospheres of these bodies. It is favoured to characterize the molecular composition of complex samples containing, or releasing, numerous gaseous compounds which cannot be directly identified with spectrometry alone (e.g. [7]). Through time, the complexity of space experiments increased to get more and more information from the analysed samples.

In particular, the preparation of samples (mainly the solid ones) has become more and more complex for gas chromatography in space exploration, to reach the ambitious scientific goals of the instruments, and to meet the technical constraints imposed by the flight of the space probes and the *in situ* operations. For the last chromatographs we built to explore the surface of Mars, this results in quite long times of transfer from the sampling system to the gas chromatographs. For this reason, our team transposed the thermal desorption technique, commonly used in the laboratory to analyse breath samples [8] or to monitor air composition [9], to space application. During the sampling phase, it allows to trap the maximum amount of analytes (enrichment) and spatially focalize them for the transfer duration. During the injection phase, it allows to transfer the trapped chemical species into the chromatographic columns as fast as possible. The whole process is assumed to ensure to have the best possible separation of the analytes with the best detection sensitivity. We did it first successfully for the Sample Analysis at Mars (SAM) experiment onboard the Curiosity rover currently exploring the Mars surface [3], and we will improve it for future missions, as Exomars 2020 [10].

In this frame, adsorbents of different natures are used, depending on the chemical species to be analysed. For example, in SAM, Carbosieve is used to trap the most volatile species and Tenax® (TA and GR) for the other volatile compounds. Some of these adsorbents have an upper temperature of thermal stability quite close to their usual recommended operational temperature (400°C as the limit temperature against about 300 °C for operating Tenax®). Moreover, as on Earth, despite their interest for trapping the analytes, adsorbent can be a source of organic molecules which are finally observed in the chromatograms with the analytes released by the sample (see [11] for an example). Then, the compounds released by the adsorbent can be contaminants of the analysis and it is important to limit their contribution, and to clearly identify them in order to discriminate them from the analytes present in the samples. The knowledge of the nature of these possible contaminants prior to the *in situ* measurement is of high importance because the operation limitations of space instruments usually do not allow to perform systematic blank runs to identify background contributions.

Usually, these by-products are produced through thermal decomposition or alteration of the adsorbent. For space exploration, the need for building light, sturdy and relatively simple instruments, added to the fact that environmental conditions of the instrument cannot be perfectly stabilized, results in a much less accurate thermal control of the desorption unit compared to laboratory instrumentation. As a consequence, some adsorbent present in the trap could be submitted to a thermal stress (e.g. maximum temperature overshoot) sufficient to lead to an alteration of the adsorbent. These are the main reasons why we performed a systematic study of the behaviour of various adsorbents of interest for space application, when submitted to temperatures up to 800°C. This article presents observed changes of physical and chemical features of different adsorbents commonly used in analytical chemistry when submitted to thermal stress, and the lessons learned for their use in space instrumentation specifically.

2. Material and methods

2.1. Adsorbents

Three main types of adsorbents are commonly used for thermal desorption injection with gas chromatography: i. carbon black for organic molecules of low to medium weight; ii. porous polymers for organic molecules of medium to heavy weights; iii. and molecular sieves rather devoted to small molecules and noble gases. In this work, we studied these all three types of adsorbent materials which are listed in Table 1. We studied the all three categories of adsorbents, and we selected at least two different adsorbents of each type to compare their behaviour when submitted to thermal treatment.

For graphitized carbon blacks (GCB), Carbopack B is the more commonly used today but we also tested Carbopack C. For porous polymer, Tenax® TA is a critical adsorbent for analysing the trapping and injection of organic molecules in the experiments developed to explore the surface of Mars [3, 10], and an adsorbent commonly used to monitor the Earth atmosphere composition [12]. This is the reason why in addition to its nature, we also studied the influence of the size of Tenax® TA particles on its thermal behaviour. Tenax® GR is a mixture of Tenax® TA and GCB, and it is used for trapping lower molecular weight compounds. Both Tenax® adsorbents are used in the SAM experiment [3]. Porapak Q is another type of porous polymer that could be used in a gas analyser onboard a future Russian landing probe to the moon surface named Luna Resours [13]. Finally, among the molecular sieves, we studied Carbosieve SIII which is also used in the SAM instrument on Mars, and Molsieve 5A which is of different chemical composition and could have an interest for future applications in space exploration, especially for analysing very volatile organic and inorganic molecules, as well as noble gases.

Adsorbent commercial name	Type of adsorbent	Density ($g.mL^{-1}$)	Specific area ($m^2.g^{-1}$)	Particle size (mesh)	Maximum operating temperature (°C)
Carbopack C	Graphitized carbon black	0.64	10	80-100	400
Carbopack B	Graphitized carbon black	0.38	100	60-80	400
Tenax® TA	Porous polymer	0.25	35	60-80	350
Tenax® TA	Porous polymer	0.29	35	80-100	350
Tenax® GR	Porous polymer	0.40	25	n.a.***	350
Porapak Q	Porous polymer	0.66	550	50-80	250
Carbosieve SIII*	Molecular sieve	0.72	975	n.a.	400
Molsieve 5A**	Molecular sieve	0.34	n.a.	80-120	300

*Table 1 : Adsorbents used in this study and their main characteristics. Data from suppliers (Supelco, Sigma-Aldrich). *Carbosieve SIII is a graphitized carbon black but its specific area makes places it in the molecular sieves category; **Molsieve 5A is a zeolite carbon molecular sieve; ***Not available.*

2.2. Scanning Electron Microscopy

In order to physically characterize each adsorbent studied and their possible evolution when submitted to pyrolytic conditions, Scanning Electron Microscopy (SEM) was used. With this aim, a few particles of each adsorbent, either taken from their original vial, or collected in the pyrolysis cup after their heating, have been deposited on a double-sided tape composed of carbon to ensure the

electric conduction required for performing SEM measurements. The adsorbents were analysed in low vacuum mode at a 0.45 torr pressure with an acceleration voltage of 15 kV. The particles of adsorbent were observed in an Environmental Scanning Electron Microscope (ESEM FEI Quanta 200).

2.3. Thermal Gravimetry Analysis and Evolved Gas Analysis

Thermal evolution study of most of the adsorbents selected were carried out using Thermal Gravimetry Analysis (TGA). Among the thermal analysis techniques, TGA is commonly used for characterizing the thermal properties of both inorganic and organic materials. It allows to measure the sample mass loss as a function of the sample temperature and time. TGA analyses were performed using a SENSYS evo (Setaram) TGA instrument, using a CALISTO software for data recording and treatment. The samples were placed in a 100 µL platinum crucible. The average sample mass put in the crucible was approximately 20 mg for each analysis. The samples were heated from the ambient temperature (~20°C) to 1000°C at a 10°C.min^{-1} heating rate and in an argon (chemically inert) atmosphere to prevent any reactivity of the sample with the carrier gas. Once the maximum temperature was reached, the samples were kept for one hour at the final pyrolysis temperature.

In complement to TGA, Evolved Gas Analyses (EGA) were performed to follow the chemical species released by the adsorbents as a function of temperature throughout their heating. With this aim we used an EGA/PY-3030D micro-oven pyrolyser (Frontier Lab), installed on the split/splitless injector of a gas chromatograph (GC/Trace GC Ultra, Thermo Scientific) coupled to a quadrupole mass spectrometer (MS/ISQ LT, Thermo Scientific). A short-deactivated (Siltek™ process of silicon layer deposition, Restek) tube (2.5 m long, 0.10 mm internal diameter) made of stainless steel was installed between the injector and the MS. This geometry is used to ensure a fast transfer of the sample from the injector to the MS, and thus making the correlation between the sample temperature and the volatile species detected with MS easy. Moreover, the gas flow restriction induced by the capillary tube allows to maintain the pressure in the MS sufficiently low to operate it. The main operating conditions of the GC-MS instrument were set as follows: the injector was used in the split mode at a temperature of 250°C; the column temperature was kept at 250°C and the carrier gas (Helium, 99.9999% purity, Air Liquide) flow rate was set constant to 0.5 mL.min^{-1} with a split flow rate of 10 mL.min^{-1}. The GC to MS transfer line was heated at 250°C as the electron ionization ion source. The ionization energy was 70 eV and the ions produced were scanned in the 12 to 650 m/z range.

For pyrolysis, we applied the following program of temperature to all the adsorbents: 280°C for 30 min, then heating at 10°C.min^{-1} up to 800°C that was maintained for 5 min. The total time of the sequence was 82 min during which the mass spectrometer recorded the signal. Knowing the program of temperature of the pyrolyser as a function of time, the EGA curves representing the MS response as a function of the sample temperature can have been simply obtained by converting the time of analysis in temperature. A mass of 5.0±0.1 mg of each adsorbent was pyrolyzed. It was chosen as a trade-off between the sensitivity of the method and the saturation of the MS signal.

2.4. Gas Chromatography-Mass Spectrometry analysis of the products of decomposition of the adsorbents

The goal of this measurement is the identification of the products of degradation of the adsorbents, if they exist, as they can be possible contaminants in the chromatograms. With this aim, the same experimental set-up as described for the EGA measurements was used. Only the deactivated tube was replaced by a MXT-5 (Restek) chromatographic column with the following

geometry: 30 m long, 0.25 mm internal diameter and 0.25 µm stationary phase film thickness. This is a metallic column (Siltek™ process) with a stationary phase made of poly diphenyl (5%) dimethyl (95%) siloxane bonded to the deactivated inner wall of the column. The operating conditions were similar except the flow rate that was set to 1.0 mL.min^{-1} constant, and the program of temperature was 35°C for 2 min then heating at 10°C.min^{-1} up to 300°C maintained for 3 min. The MS was used in the full scan mode to detect all the ions in the 10-450 m/z range. The mass spectrum of the chemical species detected were compared to those of the National Institute of Standards and Technology (NIST) reference mass spectra library for identification. The less retained compounds (up to about 20 min retention) are identified with a significant degree of confidence. The more retained compounds have a more complex structure and usually a lower signal to noise ratio that increase the uncertainty of the mass spectra. The identification of the corresponding chemical species can be considered as essentially tentative. But the chemical structures given should be quite similar to the detected molecule's one.

As the adsorbents are heated too slowly to perform a brief injection of the gases released into the chromatographic column, a cryofocusing system (Frontier) was used to cool down the head of the column at the liquid dinitrogen temperature throughout the pyrolysis, and then to inject the species condensed in a small volume by stopping the cryocooling and heating the column. For each adsorbent studied, a specific program of temperature was used for pyrolysis. The different pyrolysis steps are summarized in Table 2 for each adsorbent. After each step, the molecular species released after reaching the final temperature were analysed with GC-MS. Prior to perform the pyrolysis itself, a first step consisted in desorbing the species trapped on the adsorbent by heating them at 280°C for 20 min, temperature to which the tested adsorbents are not decomposed, as observed on the EGA and TGA analyses (even if Porapak Q could be slightly degraded), and because 280°C is very close to the upper temperatures (300-350°C) usually used to clean the adsorbents in order to limit the possible contamination [14-16].

For this study, we focused only on the main materials that were observed to decompose thermally, meaning Tenax® TA (60-80 mesh) and Porapak Q. Figure 1 shows the chemical structure of these two organic polymers. Tenax® GR was not studied as it is composed in part of Tenax® TA which is the source of the mass loss observed using TGA. 5.0±0.1 mg of material was introduced in the pyrolyser for Tenax® TA (60-80 mesh) and Carbosieve SIII, and 1.0±0.1 mg of material for Porapak Q.

Adsorbent	Initial temperature	First pyrolysis step	Second pyrolysis step
Carbosieve SIII	80°C (5 min)	10°C.min^{-1} up to 300°C (5 min)	10°C.min^{-1} up to 800°C (3 min)
Tenax® TA (60-80 mesh)	280°C (5 min)	10°C.min^{-1} up to 400°C (3 min)	10°C.min^{-1} up to 800°C (3 min)
Porapak Q	280°C (5 min)	10°C.min^{-1} up to 400°C (5 min)	10°C.min^{-1} up to 800°C (3 min)

Table 2 : Pyrolysis steps used to characterize the nature of the molecules released by the adsorbents when they decompose into volatile molecules. For Tenax® TA and Porapak™ Q were first heated at 280°C for desorbing the species trapped on the adsorbents, before starting the pyrolysis.

3. Results and discussion

3.1. Thermal decomposition

TGA analysis

The use of TGA allowed to follow the mass loss of each sample of adsorbent as a function of the temperature. The results obtained for all the tested adsorbents are presented in Figure 2.

On Figure 2, we can observe two general trends. First, there are adsorbents keeping their mass almost constant up to 1000°C, the maximum temperature. This behaviour is representative of materials which are very stable to the temperature. The corresponding adsorbents are the molecular

sieves and the graphitized carbon blacks. The mass loss observed at the lowest temperatures (from the ambient to ≈200°C) for Molsieve 5A is attributed to the desorption of atmospheric gases which are efficiently trapped by this material. It is not observed for the carbon molecular sieves tested which are not efficient to trap these low mass species (see [17] as an example for an application to space science). This is not fully surprising to observe such a stability as the materials produced to make these adsorbents are usually obtained by controlled pyrolytic processes occurring usually at temperatures up to 700- 800°C. Now, when looking more carefully at the curves, we observe a small loss of mass for these materials (≈4% for Carbopack B, ≈5% for Carbosieve SIII, and ≈2% for Molsieve 5A), the loss occurring rather at the highest temperatures (typically above 800°C). This indicates a very limited decomposition that should impact the superficial part of the adsorbent only or this could be ascribed to moisture vaporization [18, 19].

Then, we observe that the adsorbents made of porous polymers are resistant to the increase of temperature up to a threshold temperature for which they are subjects to a significant mass loss of tens of percent. This corresponds to a massive thermal decomposition that should be accompanied by an outgassing of volatile molecules. Once this large mass loss is finished, we observe at the higher temperatures that the adsorbents still lose mass but at a much lower rate. It is interesting to notice that the massive mass loss is observed at the same temperature for Tenax® TA and Tenax® GR, as the material decomposing for both adsorbents is the same, *i.e.* Tenax® TA. It shows that the presence of graphitized carbon black in Tenax® GR does not catalyse the thermal decomposition of Tenax® TA. Moreover, the mass loss of Tenax® GR (≈45%) is about 30% less important than for Tenax® TA (≈55%) as there is only 70%wt of Tenax® TA in Tenax® GR. The results obtained are therefore consistent with the composition of Tenax® GR. For Porapak Q, we observe that the temperature of massive mass loss is lower than for Tenax® TA (450°C instead of 550°C), in a range of temperatures similar to those observed in previous studies [20], and that the mass loss is much more significant (≈ 80%). As for Tenax®, after the massive mass loss, Porapak Q continues to lose mass but at a much lower rate, down to ≈95%. These observations demonstrate that Porapak Q is made of a material much more fragile to the heat than Tenax® TA.

Evolved Gas Analysis

On Figure 3 is plotted the evolution of total ion current of the mass spectrometer detector as a function of the temperature for each adsorbent. All the adsorbents were submitted to this diagnostic. Two main behaviours are observed.

First, all the adsorbents based on porous polymers show a significant outgassing observed when MS detector response significantly increase. For all three Tenax® adsorbents tested, this outgassing is observed from about 475°C to 800°C with a maximum observed at 570°C. The major part of the gases are shown to be released from 475°C to 677°C. The major ion observed throughout the outgassing has m/z=246, which is typical of the m/z value of the ion formed from 2,6-diphenyl-p-phenylene oxide which is the monomer of the material composing Tenax®. For Porapak Q, the outgassing occurs at lower temperatures, basically from 300°C to about 750°C with a maximum gas release observed around 450°C. The major ions observed throughout the outgassing have m/z=117 and 132. These m/z values are typical from methylstyrene and ethylstyrene ions respectively. The peak observed is broader than those observed for Tenax® and most of the outgassing occurs from 350°C to 600°C. This may due to the fact that Porapak Q is made of a copolymer of ethylvinylbenzene/divinylbenzene, making its decomposition slower than for pure 2,6-diphenyl-p-phenylene oxide polymer. Therefore, it can be concluded that porous polymers are not chemically stable when heated up to 800°C, resulting in a probable loss of their adsorption properties and a possible contamination of the analytical set up with the gaseous molecular species produced if the minimum temperature at which they decompose is reached. As Porapak Q releases gases at lower

temperature than Tenax®, it means it is more fragile when submitted to thermal stress. This explains why its maximum operating temperature recommended by the suppliers is much lower for Porapak Q compared to Tenax® (Table 1). It can be noticed that these maximum operating temperatures are effectively lower than the minimum temperatures at which the porous polymers start to release gases. It must also be underlined that results obtained with EGA are in agreement with the TGA measurements.

Now focusing on the different Tenax® adsorbents studied, we observe that the outgassing is similar for both adsorbents. The only difference observed is the peak area with more material outgassed for Tenax® TA (60-80 mesh) and the less observed for Tenax® GR. As the mass of adsorbent sampled is the same, it means there are chemical differences that should explain this observation. As said for interpreting TGA data, Tenax® GR contains 70% of Tenax® TA and 30% of graphitized carbon black, this last adsorbent being stable with the temperature. It thus results that the Tenax® GR sample has 30% less material that can decompose compared to pure Tenax® TA and this explains why the amount of gases observed to be released by Tenax® GR is the lowest one, the corresponding peak area being ≈77% of the pure Tenax® TA peak area. Concerning the two pure Tenax® TA samples, we observe that the adsorbent with bigger particles (60-80 mesh) releases more gases than the adsorbent with smaller particles (80-100 mesh). It thus indicates that there is a particle size effect in the release of products of degradation and bigger particles are more subject to decompose than smaller ones.

On Figure 3, the second behaviour observed is an absence of gases released by the molecular sieves and graphitized carbon blacks, whatever the temperature is. This confirms the results obtained with TGA that shows that these adsorbents are all thermally stable up to 800°C. The only exception to this rule is Carbopack C which shows a low outgassing around 550°C (major ions observed have m/z=91, 105 and 119, typical from alkylated aromatic species as toluene, or dimethylbenzene). This degassing may be due to the fact that the surface area is smaller for this adsorbent than for the other two.

3.2. Evolution of the adsorbent grains morphology

As we demonstrated the heating of adsorbents up to 800°C could have a significant effect on adsorbents, we tried to follow the physical evolution of the adsorbent particles with temperature. We limited this approach to Porapak Q, Tenax® TA and Carbosieve SIII as they are representative of the main behaviour observed for adsorbent to thermal stress and described above.

Figure 4 shows images obtained before and after heating Porapak Q adsorbent particles up to 800°C. It can be observed that the particle size drastically decreased from ~230 µm down to ~80 µm, but the particles keep a roughly spherical shape. This size decrease is compatible with the significant mass loss of material observed both with TGA and EGA measurements. Looking at a given particle, the soft and homogenous spherical shape observed before thermal treatment, changed to a multi-faces carved surface. If we have no information about surface roughness of the particles with SEM, the decrease of the size of the particle should drastically limit its specific surface, and then its adsorption power. As an organic polymer, Porapak Q material should have significantly graphitized at the temperatures used for the pyrolysis, resulting in a modification of the adsorption properties.

Figure 5 shows images obtained before and after heating Tenax® TA (60-80 mesh) adsorbent particles to 800°C. As for Porapak Q, the particle size drastically decreased by a factor of about 2, but the particles roughly kept their initial shape. This size decrease is compatible with the significant mass loss of material observed with TGA and EGA measurements. Looking at a given particle, the surface globally looks like similar before and after the heating. But looking closer to the surface, it

seems that the highly porous and sinuous surface observed initially, was flattened by the thermal stress. This could indicate a decrease of the porosity of the adsorbent which could induce a loss of adsorption efficiency. Similarly, to Porapak Q, the decrease of the size of the particles, and the likely graphitization of the polymer should drastically limit its adsorption properties.

Figure 6 shows images obtained before and after heating Carbosieve SIII adsorbent particles to 800°C. In this case, the particles keep their original size and shape after heating them up to 800°C. This is consistent with the absence of mass loss observed with TGA and EGA measurements. The only change observed is related to the surface roughness of the particles. Indeed, if initially the particle surface is flat and soft, after heating up to 800°C, we observe a fluffier material. This shows that if Carbosieve SIII is globally thermally resistant, its structure is modified by the thermal treatment. And this change should modify its adsorption properties as the manufacturer recommend not to use it at temperatures higher than 400°C (Table 1).

3.3. Volatile products of degradation

The programs of temperatures used to heat the different adsorbents were defined from the results obtained with TGA and EGA analyses. The different ranges of temperature defined correspond to different steps of mass loss from the adsorbents observed with TGA, which may correspond to steps of decomposition releasing different volatile molecules. By sharing the pyrolysis in steps, we wanted to test this assumption.

Figure 7 shows the chromatograms obtained when analysing the gases released by Carbosieve SIII after the pyrolysis. It can be observed that only a few compounds are detected. If we except the peaks attributed to column bleeding, only methanol, water and carbon dioxide are detected. Methanol and water are mostly observed at the lowest temperatures the adsorbent is heated, meaning these chemical species should be mainly desorbed from the adsorbent, and that they are not products of decomposition of Carbosieve SIII. Water comes from the atmosphere whereas methanol probably comes from residual solvent used to clean the material used to prepare the sample for pyrolysis. Carbon dioxide is observed on both chromatograms. This is compatible with background CO_2 present in the carrier gas which is trapped by the cold trap. This analysis confirms that Carbosieve SIII does not decompose into volatile species when heated to high temperatures, as already shown by TGA.

Figure 8 shows the chromatograms obtained after analysing the products of pyrolysis of Tenax® TA (60-80 mesh) for the two steps of the pyrolysis it was submitted to. Most of the chemical species identified in these chromatograms are listed in Table 3.

For the lower pyrolysis temperatures range (from 280 to 400°C), water and carbon dioxide mainly coming from the air present in the background of the carrier gas are detected. In addition to products of decomposition of the column's stationary phase, a few polyaromatic compounds are observed late in the chromatogram. These polyaromatic molecules tentatively identified from their mass spectra, have a structure which is compatible with products of degradation from Tenax® TA because they include aromatic and cyclic structures that bear oxygen atoms. In spite of the detection of these degradation products, we can notice that they are limited in number, and that they have a really characteristic molecular structure compared to usual organic molecules targeted by the chromatographs used for space exploration. This demonstrates that Tenax® TA is quite thermally stable up to 400°C, confirming the observations done with TGA and EGA analyses. This also in accordance with the maximum recommended operating temperature given by the supplier (350°C), which should be the temperature around which these compounds should start to be released by Tenax® TA.

For the higher pyrolysis temperature range (Figure 8b), numerous organic compounds are detected in addition to air and products of degradation of the column stationary phase (Table 3). Most of these compounds are monoaromatic or polyaromatic compounds bearing oxygen or not. The two compounds the more retained detected after the low range of temperature pyrolysis are not present in this chromatogram. This is likely due to the higher temperatures used in this case that should prevent the formation of these species, or that could degrade them in lighter ones. The most abundant compounds detected in the chromatogram is the alcohol derived from 2,6-diphenyl-p-phenylene oxide (peak #14 in Figure b). This observation is in agreement with the TGA measurements. But many other molecules are observed in various abundances, with molecular structures which can be easily derived from the decomposition or rearrangement of 2,6-diphenylphenylene oxide. Then, the detected molecules must be released by Tenax® TA. This experiment shows the dramatic effect of heating Tenax® TA at temperatures higher than 400°C because the number and the amount of degradation compounds produced is significant. In addition to the certain alteration of its adsorption properties, this result shows that this adsorbent must not be heated at temperatures higher than 400°C because it can produce numerous organic molecules that can interfere with the detection and identification of molecules present in the analysed sample. Indeed, many of the degradation products detected (like benzene or phenol) are not strictly characteristic of the adsorbent because these chemical species can be found in many environments, including planetary ones [21]. Then their presence in the chromatograms measured *in situ* would lead to confusing situations for the identification of molecules indigenous to the probed environment.

As a conclusion, this study shows that Tenax® TA is quite stable when heated up to about 400°C, releasing only a low amount of polyaromatic molecules very specific to the polymer, but Tenax® TA is significantly degraded when heating it up 800°C, leading to the massive release of numerous molecules susceptible to contaminate the analysis.

280-400°C first pyrolysis step (desorption)		**400-800°C second pyrolysis step (degradation)**	
Retention time (min)	**Compounds name**	**Retention time (min)**	**Identified compounds name**
3.1	[1]CO_2	3.3	[1]CO_2
3.7	[2]H_2O	5.0/B[a]	[2]H_2O
13.7	[*]Stationary phase fragment	6.8/B	[3]benzene
18.4	Stationary phase fragment	11.4/B	[4]toluene
21.2	Stationary phase fragment	13.8	[*]Stationary phase fragment
23.7	Stationary phase fragment	15.2	[5]ethylbenzene
26.0	Stationary phase fragment	15.7	ethynylbenzene
28.0	Stationary phase fragment	16.2	[6]styrene
29.5	*1,1,3,3 tetramethylbutyl phen-2-ol*[b]	17.0	methylethyl-benzene isomer
34.4	*m-tertphenyl-2-ol*	17.6	propenylbenzene
40.3/B	[3]not identified	17.8	propylbenzene
49.3/B	[4]not identified	18.2	benzaldehyde
		18.4	[*]Stationary phase fragment
		18.5	phenol
		18.6	propenyl-2-benzene
		18.9	benzofuran

		19.4	ethenylmethylbenzene isomer
		19.6	ethenylmethylbenzene isomer
		19.8	propynylbenzene isomer
		19.9	methylphenol isomer
		20.2	acetophenone
		20.9	methylbenzofuran isomer
		21.2	*Stationary phase fragment
		21.7	methylindene isomer
		21.8	*4-methylbenzylvinylether*
		21.9	methylindene isomer
		22.3	[7]Naphtalene
		22.7	3-phenyl-3buten-2-one
		22.8	*2,3 dihydro-3-methyl Inden-1-one*
		23.7	*Stationary phase fragment
		23.9	methyl naphthalene isomer
		24.3	methyl naphthalene isomer
		25.0	*4-phenyl 3-butene-2-one*
		25.3/B	[8]biphenyl
		25.8	diphenylmethane
		26.6	methylbiphenyl isomer
		26.7	methylbiphenyl isomer
		27.1	[9]hydroxybiphenyl isomer
		27.2	*dibenzofuran*
		27.9	*methylphenylphenol isomer*
		27.95	*phenalene isomer*
		28.0	*4-phenyl-4-cyclopentene-1,3-dione*
		28.2	*methylphenylphenol isomer*
		29.3/B	[10]hydroxybiphenyl
		30.3	phenanthrene
		30.8	[11]biphenyldiol isomer
		30.9	*9-vinylanthracene*
		31.0	*2-dibenzofuranol*
		31.1	terphenyl isomer
		32.2	[12]phenylnaphtalene isomer
		33.7	phenylmethyl naphthalene isomer
		33.9/B	[13]tertphenyl isomer
		35.3/B	[14]*m-tertphenyl-2-ol*
		35.6	phenyldibenzofuran isomer
		35.7	[15]phenyldibenzofuran isomer
		37.5/B	[16]*tertphenylol isomer*
		38.1/B	[17]*4,4 hydroxyphenoxybiphenyl*
		38.8/B	[18]not identified
		39.4	*9-phenyl-9-fluorenol*
		41.4	terphenyl-phenyl isomer
		42.1	*4-triphenylmethylphenol*

		43.3	*Triphenylphenol msse 322 proeminente*
		44.4	*Triphenylphenol*
		48.6	*Triphenylphenol*
		50.6	*Triphenylphenol*

Table 3 : Retention time and name of each compound released by Tenax® TA (60-80 mesh) after each heating step applied to the adsorbent. Indices refer to the peak attribution given in Figure 8. [a]B is indicated when the corresponding peak is broad in the chromatogram .[b]Chemical species written in italics are tentatively identified only, with NIST match score typically below 800.

Figure 9 shows the chromatograms obtained after analysing the products of pyrolysis of Porapak Q for the two steps of the pyrolysis it was submitted to. Most of the chemical species identified in these chromatograms are listed in Table 4.

For the lower pyrolysis temperatures range (from 280 to 400°C, Figure 9a), water and carbon dioxide mainly coming from the air present in the background of the carrier gas are detected. In addition to products of decomposition of the column's stationary phase, several aromatic and cyclic organic molecules are observed in the chromatogram. The detected molecules are mostly monoaromatic molecules which are either ramified or associated to a cyclic structure (aromatic or not). Such molecular structures are compatible with the pyrolysis of the ethylvinylbenzene-divinylbenzene copolymer that leads to the production of a monoaromatic motifs, combined with products of the alteration or modification of the linear carbon chain of the polymer. Then, for this organic polymer, the number and the amount of compounds released at relatively low temperature is significant. Moreover, the nature of the compounds, even if they are specific to the copolymer, can be difficult to discriminate from organic molecules indigenous to samples that can be analysed in planetary environments, like on Titan that is a medium rich in hydrocarbons (see [22-24] for instance). Therefore, Porapak Q is an adsorbent relatively thermally weak at 400°C, producing several organic molecules that can interfere with the analysis of a sample. This explains why its maximum recommended operating temperature given by the supplier (250°C) is lower than for Tenax® TA.

For the higher pyrolysis temperature range (Figure 9b), numerous organic compounds are detected in addition to air and products of degradation of the column stationary phase (Table 4). As for low temperature pyrolysis, the majority of the detected compounds are monoaromatic alkylated hydrocarbons. A few biphenylic hydrocarbons are probably present in the last part of the chromatogram, but the uncertainty in the attribution of the chemical species from comparison with the NIST mass spectra library prevents their strict identification, as numerous peaks in this region of the chromatogram (for retention times longer ~than 30 min). These molecular groups being characteristic from those of ethylvinylbenzene-divinylbenzene, the detected molecules must be released by Porapak Q. As for Tenax® TA, this experiment shows the dramatic effect of heating this adsorbent to temperatures higher than 400°C because the number and the amount of degradation compounds produced is significant. In addition to the certain alteration of its adsorption properties, this result shows that this adsorbent must not be heated at temperatures higher than 400°C because it can produce numerous organic molecules that can interfere with the detection and identification of molecules present in the analysed sample. It can also be noticed that the number of species detected when pyrolyzing Porapak Q to 800°C is significantly higher than for Tenax® TA, showing that ethylvinylbenzene-divinylbenzene can produce a larger variety of molecules compared to 2,6-diphenylphenylene oxide.

As a conclusion, this study shows that Porapak Q is relatively unstable when thermally stressed. Its use requires to limit strictly its heating to relatively low temperatures (250°C from the supplier) whether it should start to produce many organic molecules susceptible to contaminate the analysis.

449

450

280-400°C first pyrolysis step (desorption)		400-800°C second pyrolysis step (degradation)	
Retention time (min)	**Identified compounds name**	**Retention time (min)**	**Identified compounds name**
3.1	[1]CO_2	3.2	[1]CO_2
3.8	[2]H_2O	3.4	butene isomer
13.6	[*] Stationary phase fragment	4.1/B[a]	[2]H_2O
16.0	[3]styrene	5.4	isobutyronitrile
17.9	ethylmethylbenzene isomer	6.2	[3]benzene
18.4	Stationary phase fragment	11.1	[4]toluene
18.7	[4]propenyl-2-benzene	13.7	[*] Stationary phase fragment
20.5/B	[5]ethenylethylbenzene isomer	15.1	ethylbenzene
20,7/B	[5]ethenylethylbenzene isomer		
21.0	diethenylbenzene isomer	15.5/B	[5]xylene isomer
21.3	diethenylbenzene isomer	16.3/B	[6]styrene
21.8	*methylbutenylbenzene*[b]	17.9/B	[7]ethylmethylbenzene isomer
22.2	[6]not identified	18.5	[*] Stationary phase fragment
22.4	not identified	18.9	[8] propenyl-2-benzene
22.7	not identified	19.4	methylmethylethylbenzene isomer
23.4	*ethylphenylethanone isomer*	19.8	diethylbenzene isomer
23.7	[7] *phenylbutenone isomer*	20.0	diethylbenzene isomer
24.0	*phenylbutenone isomer*	20.8/B	[9] ethenylethylbenzene isomer
32.2	not identified	21.4	diethenylbenzene isomer
32.4	not identified	21.5	*methylbutenylbenzene*
32.6	not identified	21.9	*ethenyltrimethylbenzene isomer*
		22.1	not identified
		22.2	*ethenyltrimethylbenzene isomer*
		22.3	not identified
		22.5	[10]not identified
		22.8	*ethylindene*
		23.1	*methyleneethylmethylbenzene isomer*
		23.4	*ethylmethylethylbenzene isomer*
		23.6	*bismethylethenylbenzene isomer*
		23.8/B	[11] *phenylbutenone isomer*
		24.1/B	[12] *phenylbutenone isomer*
		24.9	[13]*methylethenylphenylethanone isomer*
		25.1	*phenylbutenone isomer*
		25.2	not attributed
		25.3	*methylethenylphenylethanone isomer*
		25.4	*vinylbenzoic acid isomer*
		25.9	biphenyl

		26.5	*methylbiphenyl isomer*
		27.0	*methylbiphenyl isomer*
		From 28 to 41	Numerous peaks which cannot be identified from their spectrum. But their spectrum contains ions typical from monoaromatic fragments for most of them
		30.5	*bisphenylmethylpropane*
		31.0	*diphenylpentene*

Table 4: Retention time and name for each compound released by Porapak Q after each heating step applied to the adsorbent. Indices refer to the peak attribution given in Figure 9. [a]B is indicated when the corresponding peak is broad in the chromatogram .[b]Chemical species written in italics are tentatively identified only, with NIST match score typically below 800.

4. Conclusion

Among the adsorbents used, or that could be potentially used, in the development of instruments for space exploration, this study shows that carbon molecular sieves and graphitized carbon blacks are mechanically and chemically inert materials when submitted to temperatures usually used for thermal desorption (~300°C) and pyrolysis (800°C). Without presuming about the effect of thermal treatment on the adsorption properties of these materials, this result proves that these adsorbents can be used without any risk of contamination or degradation of the analytical system. Concerning the porous polymers tested, both are fragile materials when submitted to temperatures higher than ~300°C but Tenax® TA is more robust as a significant degradation is observed only from 600°C. As these adsorbents have similar adsorption properties, this means that Tenax® TA should be preferred as it is more able to resist to local or global overheats that can occur in space instrumentation. Moreover, Porapak Q produces more organic degradation products than Tenax® TA, which should be difficult to discriminate from analytes because they are mostly common monoaromatic hydrocarbons. Tenax® TA produces volatile degradation products which can be more easily identified due to their specific molecular structure, at least at reasonable temperatures relevant to thermal desorption (~300°C). These results therefore strengthen the choice of adsorbents that were, or are still used for thermal desorption in space instrumentation, and they will be useful for the development of new instruments, and for the interpretation of the data collected in the planetary environments explored.

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References

[1] R. Sternberg, F. Raulin, C. Szopa, A. Buch, C. Vidal-Madjar, GAS CHROMATOGRAPHY | Gas Chromatography in Space Exploration, in: I.D. Wilson (Ed.) Encyclopedia of Separation Science, Academic Press, Oxford, 2007, pp. 1-13.

[2] V.I. Oyama, G.C. Carle, F. Woeller, J.B. Pollack, Laboratory Corroboration of the Pioneer Venus Gas Chromatograph Analyses, Science, 205 (1979) 52.

[3] P. Mahaffy, C. Webster, M. Cabane, P. Conrad, P. Coll, S. Atreya, R. Arvey, M. Barciniak, M. Benna, L. Bleacher, W. Brinckerhoff, J. Eigenbrode, D. Carignan, M. Cascia, R. Chalmers, J. Dworkin, T. Errigo, P. Everson, H. Franz, R. Farley, S. Feng, G. Frazier, C. Freissinet, D. Glavin, D. Harpold, D. Hawk, V.

Holmes, C. Johnson, A. Jones, P. Jordan, J. Kellogg, J. Lewis, E. Lyness, C. Malespin, D. Martin, J. Maurer, A. McAdam, D. McLennan, T. Nolan, M. Noriega, A. Pavlov, B. Prats, E. Raaen, O. Sheinman, D. Sheppard, J. Smith, J. Stern, F. Tan, M. Trainer, D. Ming, R. Morris, J. Jones, C. Gundersen, A. Steele, J. Wray, O. Botta, L. Leshin, T. Owen, S. Battel, B. Jakosky, H. Manning, S. Squyres, R. Navarro-GonzÃ¡lez, C. McKay, F. Raulin, R. Sternberg, A. Buch, P. Sorensen, R. Kline-Schoder, D. Coscia, C. Szopa, S. Teinturier, C. Baffes, J. Feldman, G. Flesch, S. Forouhar, R. Garcia, D. Keymeulen, S. Woodward, B. Block, K. Arnett, R. Miller, C. Edmonson, S. Gorevan, E. Mumm, The Sample Analysis at Mars Investigation and Instrument Suite, Space Science Reviews, 170 (2012) 401-478.

[4] D.R. Rushneck, A.V. Diaz, D.W. Howarth, J. Rampacek, K.W. Olson, W.D. Dencker, P. Smith, L. McDavid, A. Tomassian, M. Harris, K. Bulota, K. Biemann, A.L. LaFleur, J.E. Biller, T. Owen, Viking gas chromatograph-mass spectrometer, Rev. Sci. Instrum., 49 (1978) 817-834.

[5] F. Goesmann, H. Rosenbauer, R. Roll, C. Szopa, F. Raulin, R. Sternberg, G. Israel, U.J. Meierhenrich, W.H.P. Thiemann, G. Munoz-Caro, COSAC, the cometary sampling and composition experiment on Philae, Space Science Reviews, 128 (2007) 257-280.

[6] H. Niemann, S.K. Atreya, S.J. Bauer, K. Biemann, B. Block, G.R. Carignan, T.M. Donahue, R.L. Frost, D. Gautier, J.A. Haberman, D. Harpold, D.M. Hunten, G. Israel, J.I. Lunine, K. Mauersberger, T.C. Owen, F. Raulin, J.E. Richards, S.H. Way, The Gas Chromatograph Mass Spectrometer for the Huygens Probe, Space Science Review, 104 (2002) 551-590.

[7] C. Freissinet, D.P. Glavin, P.R. Mahaffy, K.E. Miller, J.L. Eigenbrode, R.E. Summons, A.E. Brunner, A. Buch, C. Szopa, P.D. Archer, H.B. Franz, S.K. Atreya, W.B. Brinckerhoff, M. Cabane, P. Coll, P.G. Conrad, D.J. Des Marais, J.P. Dworkin, A.G. Fairén, P. François, J.P. Grotzinger, S. Kashyap, I.L. ten Kate, L.A. Leshin, C.A. Malespin, M.G. Martin, F.J. Martin-Torres, A.C. McAdam, D.W. Ming, R. Navarro-González, A.A. Pavlov, B.D. Prats, S.W. Squyres, A. Steele, J.C. Stern, D.Y. Sumner, B. Sutter, M.P. Zorzano, M.S.L.S.T. the, Organic molecules in the Sheepbed Mudstone, Gale Crater, Mars, Journal of Geophysical Research: Planets, 120 (2015) 2014JE004737.

[8] M. Xu, Z. Tang, Y. Duan, Y. Liu, GC-Based Techniques for Breath Analysis: Current Status, Challenges, and Prospects, Critical Reviews in Analytical Chemistry, 46 (2016) 291-304.

[9] A. Cecinato, C. Balducci, D. Mastroianni, M. Perilli, Sampling and analytical methods for assessing the levels of organic pollutants in the atmosphere: PAH, phthalates and psychotropic substances: a short review, Environmental Science and Pollution Research, 19 (2012) 1915-1926.

[10] F. Goesmann, W.B. Brinckerhoff, F. Raulin, W. Goetz, R.M. Danell, S.A. Getty, S. Siljeström, H. Mißbach, H. Steininger, R.D. Arevalo, A. Buch, C. Freissinet, A. Grubisic, U.J. Meierhenrich, V.T. Pinnick, F. Stalport, C. Szopa, J.L. Vago, R. Lindner, M.D. Schulte, J.R. Brucato, D.P. Glavin, N. Grand, X. Li, F.H.W. van Amerom, M.S.T. the, The Mars Organic Molecule Analyzer (MOMA) Instrument: Characterization of Organic Material in Martian Sediments, Astrobiology, 17 (2017) 655-685.

[11] P. Axel Clausen, P. Wolkoff, Degradation products of Tenax TA formed during sampling and thermal desorption analysis: Indicators of reactive species indoors, Atmospheric Environment, 31 (1997) 715-725.

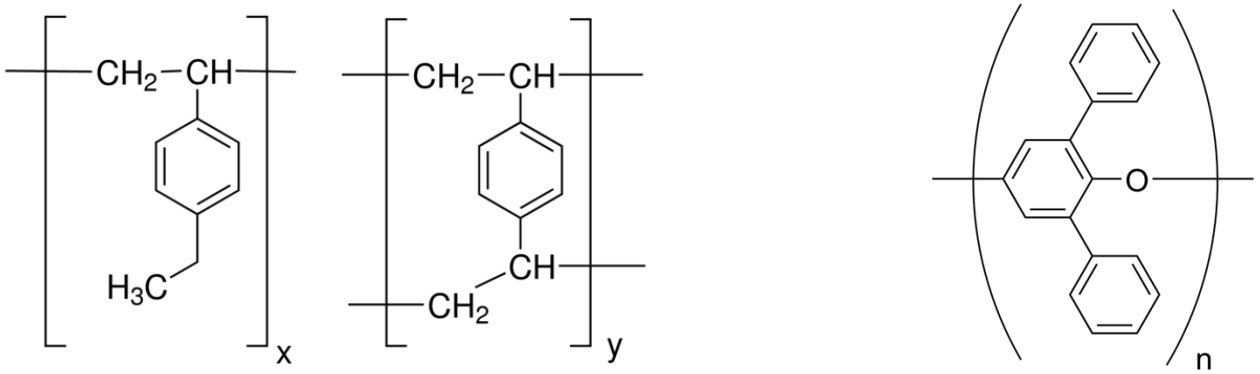
[12] A. Kumar, I. Víden, Volatile Organic Compounds: Sampling Methods and Their Worldwide Profile in Ambient Air, Environ Monit Assess, 131 (2007) 301-321.

[13] L. Hofer, P. Wurz, A. Buch, M. Cabane, P. Coll, D. Coscia, M. Gerasimov, D. Lasi, A. Sapgir, C. Szopa, M. Tulej, Prototype of the gas chromatograph–mass spectrometer to investigate volatile species in the lunar soil for the Luna-Resurs mission, Planetary and Space Science, 111 (2015) 126-133.

[14] A. Sonnette, M. Millet, R. Ocampo, L. Alleman, P. Coddeville, Tenax-TA Spiking Approach of Thermal Desorption Coupled to GC–MSMS for the Quantification of PAHs in Indoor Air and Dust, Polycyclic Aromatic Compounds, 37 (2017) 170-177.

[15] L. Chu, S. Deng, R. Zhao, J. Deng, X. Kang, Comparison of Adsorption/Desorption of Volatile Organic Compounds (VOCs) on Electrospun Nanofibers with Tenax TA for Potential Application in Sampling, PLOS ONE, 11 (2016) e0163388.

[16] B. Glas, B. Stenberg, H. Stenlund, A.-L. Sunesson, A novel approach to evaluation of adsorbents for sampling indoor volatile organic compounds associated with symptom reports, Journal of Environmental Monitoring, 10 (2008) 1297-1303.
[17] S.A. Aseev, M.V. Gerasimov, M.A. Zaitsev, A.G. Sapgir, Analysis of volatile lunar compounds: The study of gas retention time on Carbosieve SIII adsorbent with respect to temperature, Cosmic Research, 54 (2016) 358-365.
[18] F. Cataldo, A study on the thermal stability to 1000°C of various carbon allotropes and carbonaceous matter both under nitrogen and in air, Fullerenes, Nanotubes and Carbon Nanostructures, 10 (2002) 293-311.
[19] F. Cataldo, A study on the thermal stability of the. photopolymer, the ozopolymer, and the photochlorinated derivative of C60 fullerene, Fullerene Science and Technology, 9 (2001) 55-61.
[20] C.N. Caşcaval, V. Neagu, The thermal degradation of copolymers of vinyltoluene and divinylbenzene, Polymer Degradation and Stability, 45 (1994) 423-427.
[21] S. Vinatier, B. Schmitt, B. Bézard, P. Rannou, C. Dauphin, R. de Kok, D.E. Jennings, F.M. Flasar, Study of Titan's fall southern stratospheric polar cloud composition with Cassini/CIRS: Detection of benzene ice, Icarus, 310 (2018) 89-104.
[22] C.M. Anderson, R.E. Samuelson, D. Nna-Mvondo, Organic Ices in Titan's Stratosphere, Space Science Reviews, 214 (2018) 125.
[23] M.L. Cable, S.M. Horst, R. Hodyss, P.M. Beauchamp, M.A. Smith, P.A. Willis, Titan Tholins: Simulating Titan Organic Chemistry in the Cassini-Huygens Era, Chem. Rev., 112 (2012) 1882-1909.
[24] M. Morisson, C. Szopa, N. Carrasco, A. Buch, T. Gautier, Titan's organic aerosols: Molecular composition and structure of laboratory analogues inferred from pyrolysis gas chromatography mass spectrometry analysis, Icarus, 277 (2016) 442-454.



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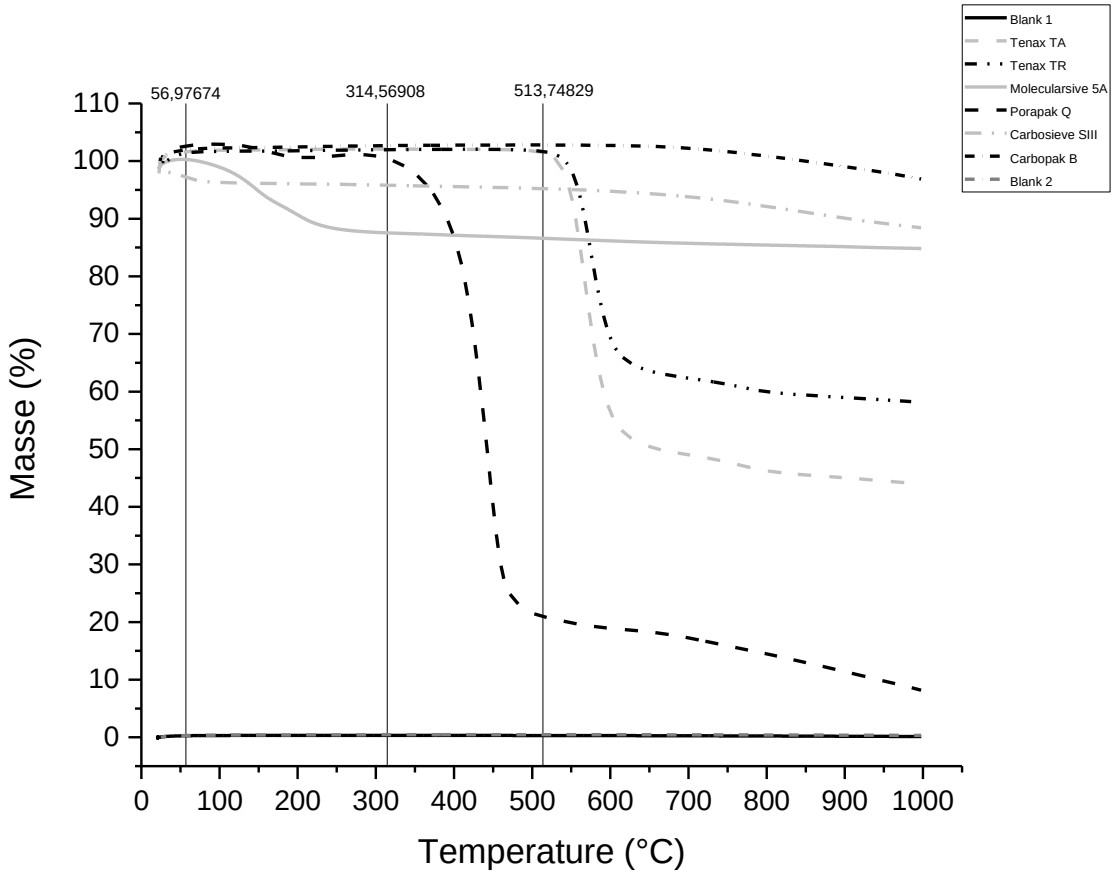
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513,74829
Blank 1
Tenax TA
Tenax TR
Molecularsive 5A
Porapak Q
Carbosieve SIII
Carbopak B
Blank 2
Masse (%)
Temperature (°C)
110
100
90
80
70
60
50
40
30
20
10
0
0
100
200
300
400
500
600
700
800
900
1000

Figure 2

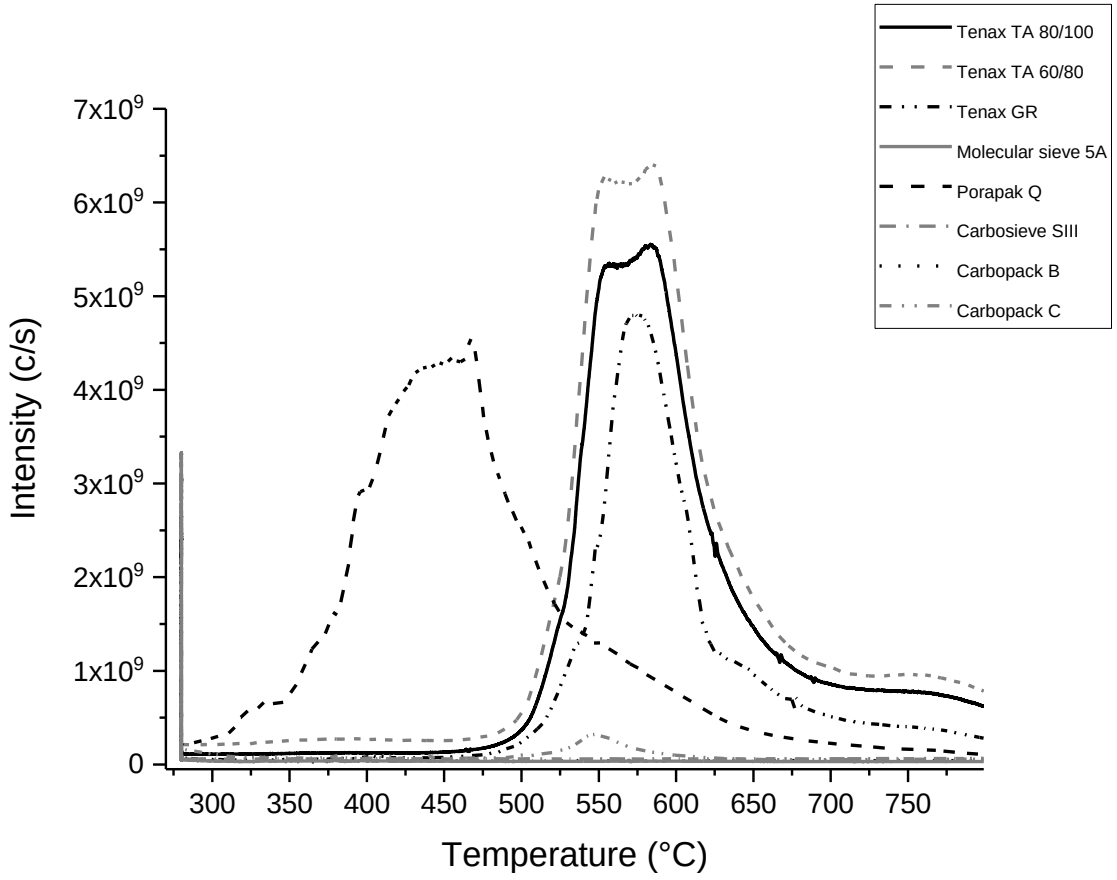
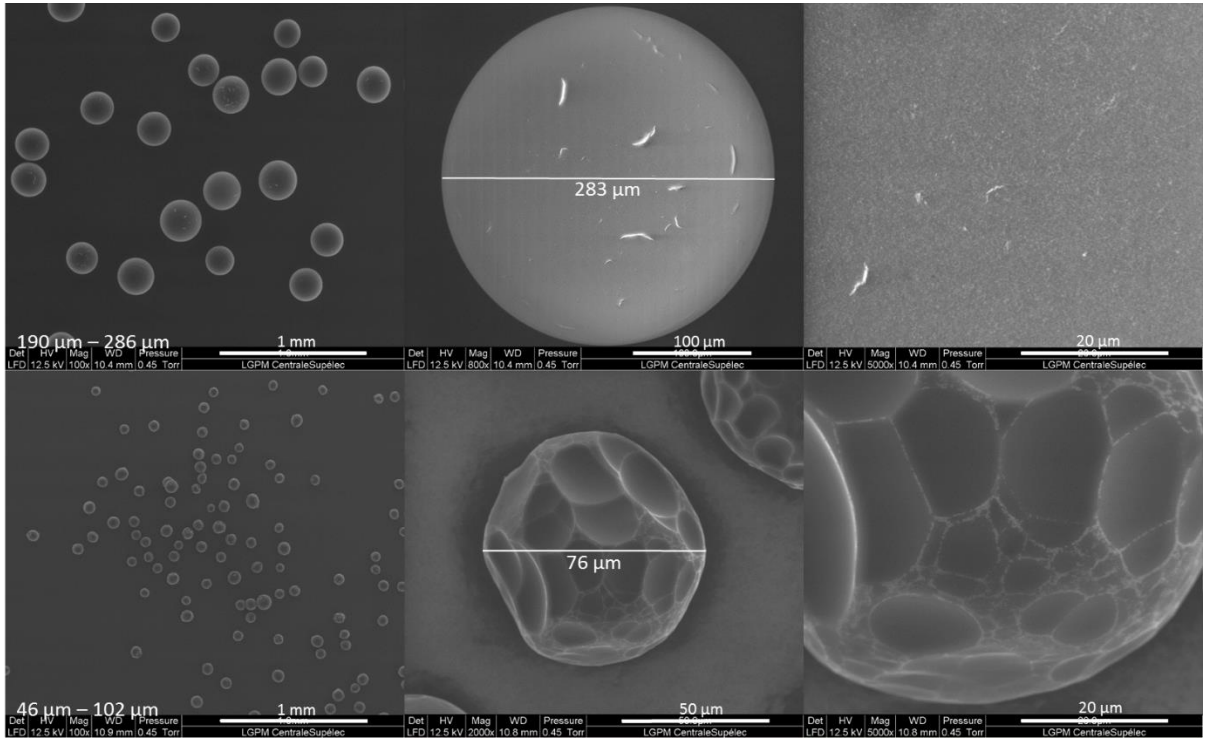

Tenax TA 80/100
Tenax TA 60/80
Tenax GR
Molecular sieve 5A
Porapak Q
Carbosieve SIII
Carbopack B
Carbopack C
Intensity (c/s)
7x10^9
6x10^9
5x10^9
4x10^9
3x10^9
2x10^9
1x10^9
0
300
350
400
450
500
550
600
650
700
750
Temperature (°C)

Figure 3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100 µm
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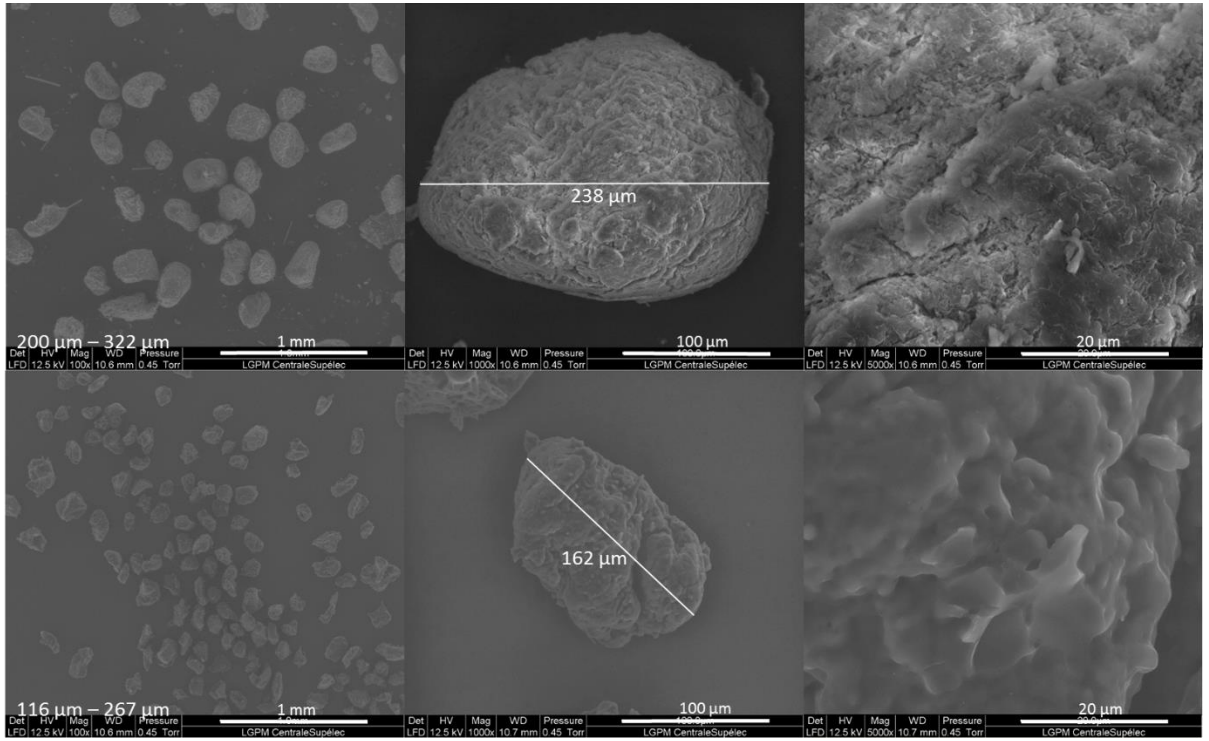
20 µm
46 µm – 102 µm
1 mm
50 µm
76 µm
20 µm

Figure 4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LGPM CentraleSupélec
238 µm
100 µm
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LFD 12.5 kV 1000x 10.6 mm 0.45 Torr
LGPM CentraleSupélec
20 µm
Det HV Mag WD Pressure
LFD 12.5 kV 5000x 10.6 mm 0.45 Torr
LGPM CentraleSupélec
116 µm – 267 µm
1 mm
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LFD 12.5 kV 100x 10.6 mm 0.45 Torr
LGPM CentraleSupélec
162 µm
100 µm
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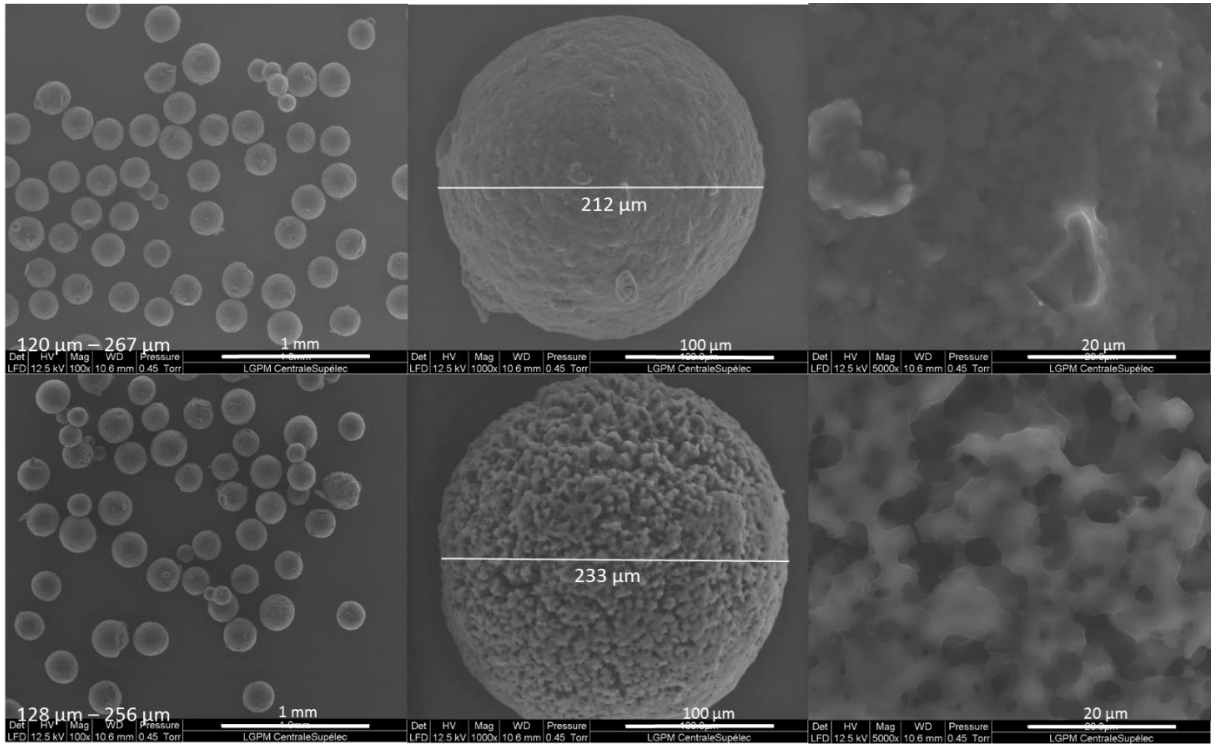
Figure 5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212 µm
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20 µm
128 µm – 256 µm
1 mm
233 µm
100 µm
20 µm
Det HV Mag WD Pressure
LFD 12.5 kV 100x 10.6 mm 0.45 Torr
LGPM CentraleSupélec
Det HV Mag WD Pressure
LFD 12.5 kV 1000x 10.6 mm 0.45 Torr
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Det HV Mag WD Pressure
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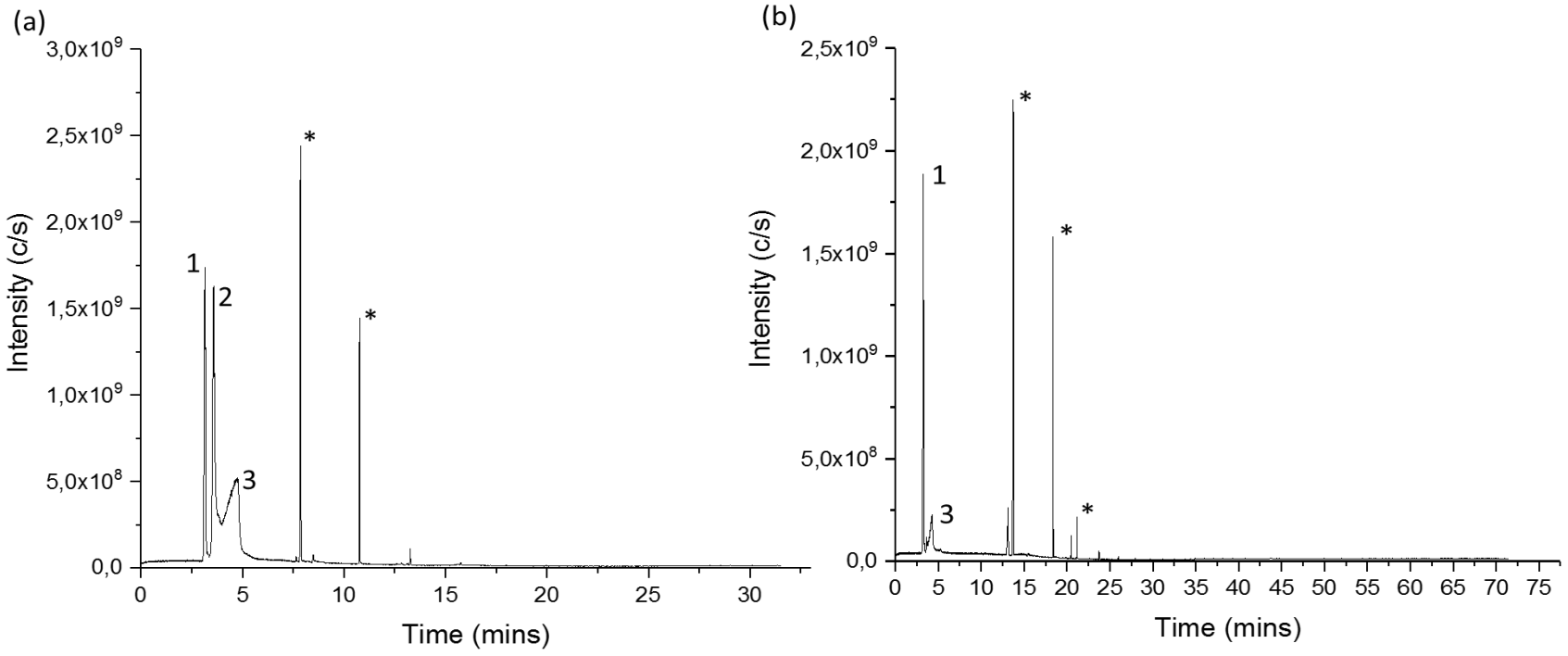
Figure 6


(a)
3,0x10^9
2,5x10^9
2,0x10^9
1,5x10^9
1,0x10^9
5,0x10^8
0,0
Intensity (c/s)
1
2
3
*
*
0
5
10
15
20
25
30
Time (mins)
(b)
2,5x10^9
2,0x10^9
1,5x10^9
1,0x10^9
5,0x10^8
0,0
Intensity (c/s)
1
3
*
*
*
0
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20
25
30
35
40
45
50
55
60
65
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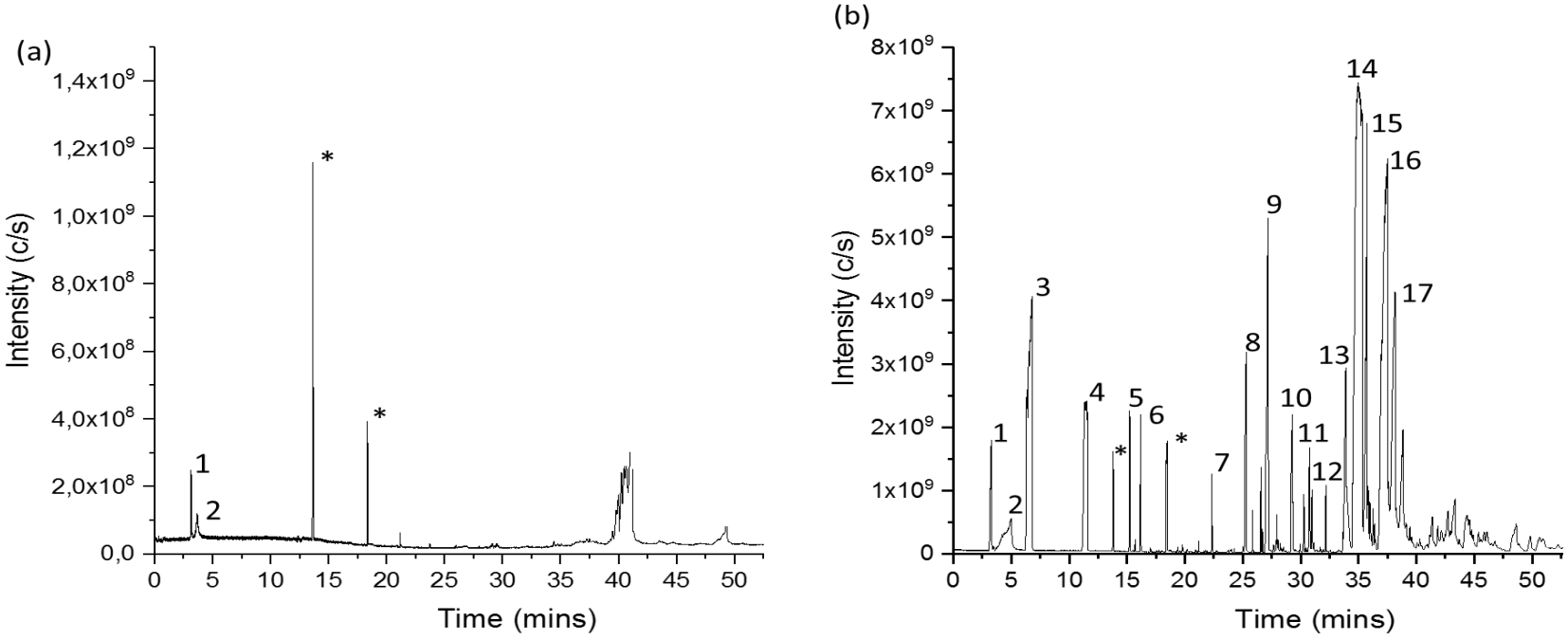
Time (mins)

Figure 7


(a)
Intensity (c/s)
Time (mins)
1
2
*
*
(b)
Intensity (c/s)
Time (mins)
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4
5
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16
17
*
*

Figure 8

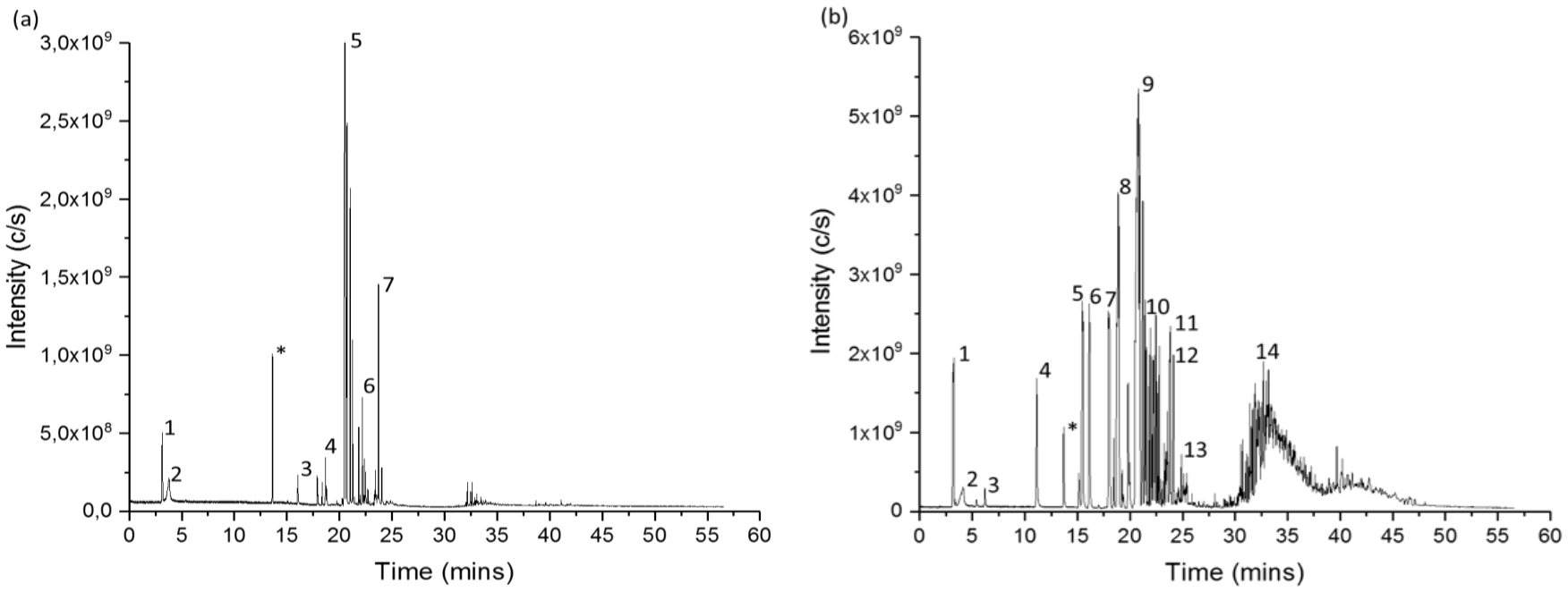

Figure 9