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Carbon sorbents for the retention of thermodecomposition compounds from microplastics

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Abstract

Carbon sorbents have been tested in this study to improve the retention of microplastics thermodecomposition compounds in Thermoextraction-Desorption Gas Chromatography-Mass Spectrometry (TED-GC-MS) technique and has been demonstrated an optimal behavior for this application, highlighting two main advantages with regard to conventional PDMS sorbents; On the one hand, carbons present slit-type pores, being optimal for retaining the aromatic compounds released from most polymers. In addition, those materials have shown to have a greater retention capacity than PDMS being between 1.25 and 25 times more efficient. Combination of PDMS+Carbon sorbents increases retention of the most representative compounds for each polymer up to 1.7 times with regard to only carbon, increasing sensitivity, but with an experimental procedure more complicated, because two desorption process must be done.

On the other hand, carbon materials can retain the chlorinated compounds released by thermodecomposition of PVC, while conventional PDMS sorbent is not effective for these compounds.

Key words

Microplastic, TED-GC-MS, thermodecomposition, carbon, sorbent.

1.- INTRODUCTION.

The increase in the production of plastic materials has also brought a relevant generation of plastic waste, being today an increasing global environmental problem.

The presence of plastics and microplastics (MP) in the environment has motivated the scientific research, increasing the number of publications in the recent decades due to their potentially harmful health effects[1,2].

The sources of MP are very diverse. In residential areas, washing machines can produce more than 1900 fibers in one wash cycle[1], personal care products can discharge huge amounts of MP into sewer system after use[3] and waterborne paints, electronics, coatings, medical applications, and adhesives can also produce high amounts of MP after friction and decomposition[1,3]. Because of the huge amount of MP in wastewater treatment plants and industries, those particles end up in soils, rivers, lakes and oceans.

To better understanding the distribution and effects of MPs, many analytical methods have been developed and investigated, but a standardized method, ranging from sampling to pretreatment and analysis itself, for conducting these studies has not yet been established, so the results from different laboratories can be very different and difficult to compare.

One of the analytical methods that is offering the most promising results are thermal techniques, such as Pyrolysis coupled to gas chromatography/mass spectrometry (Pyr-GC-MS) or Thermal Extraction-Desorption coupled to gas chromatography/mass spectrometry (TED-GC-MS). In this kind of technics, microplastics are thermally decomposed and the products generated are analyzed by chromatography to determine the polymer where they come from.

Gas chromatography/mass spectrometry is a powerful tool to analyze microplastic decomposition products, since different compounds in a complex mixture may be separated and analyzed, and the chromatogram obtained is a fingerprint of the parent polymer.

Different studies have used TED-GC-MS to study microplastics[4–7], where microplastics are first filtered from a water source. A portion of this waste-containing filter is placed in a Thermogravimetric analysis equipment (TGA) crucible and is pyrolyzed in an inert atmosphere, trapping thermodecomposition products in a solid sorbent, usually based on polydimethylsiloxane (PDMS). Once the decomposition products are concentrated into the sorbent, they are thermal desorbed and analysed by gas chromatography/mass spectrometry.

The TGA equipment has the drawback that it uses very small crucibles, so only a very small portion of the filter can be analysed. This can cause two big problems; on the one hand, handling of the filters can give rise to mass losses and, on the other hand, it must be taken into account that microplastics are solid particles that are suspended, not dissolved, in the medium, and when filtering the sample, the filtrated is not homogeneous, so the results depend on the portion of filter analysed.

Our previous studies have demonstrated the benefits of less sample handling and higher analysis sensitivity by pyrolyzing the entire filter using a tubular furnace instead of using a TGA thermobalance[8].

Another key step to improve in this technic is the sorbent material where thermodecomposition compounds are trapped.

The pyrolysis of the waste-containing filter, either in a furnace or in a thermobalance, yields thermodecomposition gas products that are traditionally trapped on a PDMS-coated Gerstel twister stir bar, being mainly suitable for non-polar compounds[4,6,7,9,10].

Thermodecomposition products from microplastics are mostly non-polar, but some products from some polymers may have certain polarity and are not properly retained in a PDMS sorbent.

As an example, PVC is one of the most found polymers in the environment, and to better identify it, following chlorinated compounds is the best option, because chlorine is a characteristic element of this polymer, and PDMS is not capable of retaining this type of compounds.

There is a need to improve the retention of thermodecomposition compounds and to find a material that optimally retains all the compounds, including chlorinated compounds, so we consider carbon materials to be good candidates.

The adsorption properties of carbon materials are very well known, and these properties are also expected to be useful for the retention of MP thermodecomposition gas products. Carbon materials usually have slit-type pores that are optimal for the adsorption of aromatic compounds, like most decomposition products of microplastic. Furthermore, carbon materials retain compounds by adsorption/physisorption, while PDMS retention is based on absorption. Differences in the behavior of carbon and PDMS are therefore expected for the application under study.

The main goal of this study is to analyze the utilization of commercial carbon materials as sorbent in the analysis of microplastics by TED-GC-MS. The behavior of carbon sorbents is compared with that of PDMS, which is classically used for this application. To test the proper behavior of carbon sorbents for the retention of the thermodecomposition products of microplastics, the most commonly found polymers in the environment were tested, including Polyethylene (PE), Polystyrene (PS), Polyamide (PA), Polyethylene terephthalate (PET), Polypropylene (PP) and Polyvinylchloride (PVC).

2.- MATERIALS AND METHODS.

2.1. Reference microplastics.

Reference plastic materials purchased to Sigma-Aldrich were chosen to cover the most abundant types in freshwater systems. The set of reference plastics studied include the following, where the physical-chemical properties are those reported by the supplier:

- Polystyrene (PS): Pellets, average M_w (molecular weight) ~192,000 g/mol.

- Polyamide (PA): Powder with a particle size between 50 and 160 μm.

- Polypropylene (PP): Isotactic polypropylene granules, melting temperature 157 ° C, density 0.9 g / ml at 25 ° C and average M_w ~12,000 g/mol.

- Polyvinyl chloride (PVC): Powder. Density 1.4 g / ml at 25 ° C, average M_w ~48,000 g/mol.

- Polyethylene terephthalate (PET): Granulate with 30% glass particles as reinforcer, density 1.68 g / ml at 25 ° C, melting temperature between 250 and 255 ° C.

- High-density polyethylene (HDPE): Powder with particle size between 40 and 48 μm, melting temperature of 144 ° C, density 0.94 g / ml at 25 ° C.

2.2 Adsorbents/absorbents.

Two different solid phase commercial sorbents were used:

- Twister/Stir Bar Sorptive Extraction SBSE (Gerstel): The Gerstel Twister® bar consists of a 10mmx3.2mm magnetic stir bar covered by a 1 mm layer of polydimethylsiloxane (PDMS).
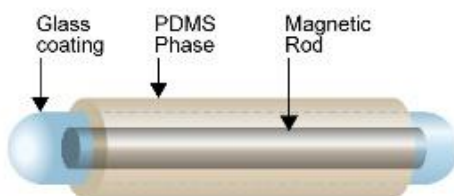
Figure 1.- Schematic representation of the twister stir bar used as conventional absorbent in TED-GC-MS techniques.

- Desorption liners for thermodesorption unit (TDU) packed with Carbopack C+B and Carbosieve S-III (Gerstel) carbon adsorbents: 60mm termodesorption tubes, external diameter of 6mm and internal diameter of 4mm, filled with triple layer of carbon materials (Carbopack C+B and Carbosieve SIII), conditioned and marketed by Gerstel.
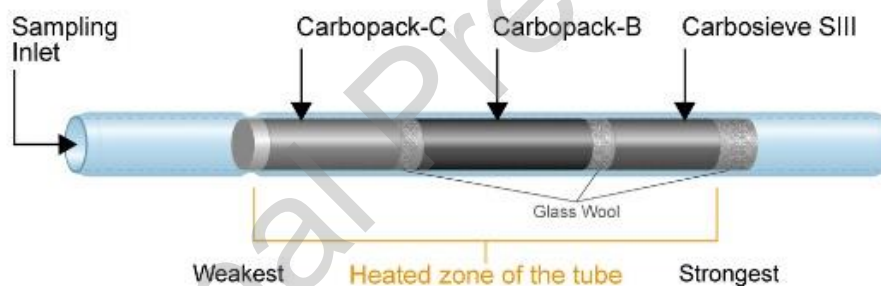
Figure 2: Schematic representation of thermodesorption tubes filled with triple layer of carbon material.

2.3 Characterization

Different characterization techniques were carried out to study the physical-chemical properties of the sorbent materials used.

- **N_2 adsorption at -196 ºC.**

    N_2 adsorption isotherms were carried out at -196 ºC in a 3FLEX equipment (MICROMERITICS) equipped with 0.1 Torr sensors that allow obtention of high-resolution isotherms.

    The specific surface area of the different sorbents was calculated by the BET method.

- **FTIR analysis**

    A JASCO FTIR 4700 spectrometer was used to obtain infrared spectra of the PDMS and carbon sorbents working with a resolution of 0.5 cm^{-1}. It has a medium IR source, a Germanium encapsulated KBr beam splitter and a DLaTGS detector. A range of frequencies between 500 and 4000 cm^{-1} was swept.

- **TGA Characterization.**

    A NETZSCH STA 449F5 thermobalance with a DSC-TGA standard module was used, which allows working from room temperature up to 1600 °C with a base noise of 3 μg.

    Experiments were performed in an alumina crucible n first using an Ar flow rate of 50 ml/min and a temperature gradient from 20 to 850 °C with a heating rate of 10 °C/min. After holding the temperature for 5 minutes at 850 ºC, the innert gas was replaced by a 50:50 O_2/Ar mixture and the temperature was raised to 1000 ºC with a heating rate of 10 °C/min.

    The outlet gas composition was monitored during the thermal treatment by a quadrupole mass spectrometer model Aeolos QMS 403 Quadro of the brand NETZSCH.

    In the case of carbon materials, the 18, 28 and 44 m/z ratios, which correspond to H_2O, CO and CO_2 respectively, have been followed. For PDMS the gases have been analysed in scan mode.

2.4 TED-GC-MS protocol.

In the TED-GC-MS technique, three stages can be distinguished: (i) Filtration, (ii) thermal decomposition and retention of the released MPs thermodecomposition gases (iii) Desorption of the retained gases and analysis by Gas chromatography/Mass spectrometry.

- **Filtration**

To simulate MPs collection from real water samples, water suspensions of the individual microplastics were prepared. To isolate MP particles, the water samples were filtered in a vacuum filtration system using a 2 μm pore size quartz filter. To avoid moisture, the filters were dried in a silica desiccator at least for 48 hours.

The filters must be made of quartz to withstand the high temperature in the furnace during the further pyrolysis process without generating interfering compounds.

- **Thermal decomposition and retention** of the released MPs thermodecomposition gases**.**

This is a key step in TED-GC-MS, where polymers are thermally degraded and decomposition gas products are trapped in a solid phase sorbent at room temperature.

The whole MPs-containing filter was introduced into a quartz reactor and was subjected to a controlled temperature program, from 25 to 600 °C, with a heating rate of 10 °C/min in a nitrogen flow rate of 90 ml/min.

A solid phase sorbent was placed at the gas outlet, and for this study three different combinations of sorbents were compared:

Option 1 - PDMS Gerstel twister stir bar.

Option 2 - Desorption liners for TDU filled with Carbopack C+B and Carbosieve S-III.

Option 3 -Combination of both sorbents placed in series at the exit of the furnace gases (first PDMS and carbon beds downstream).

A diagram of the extraction setup is exposed in figure 3.
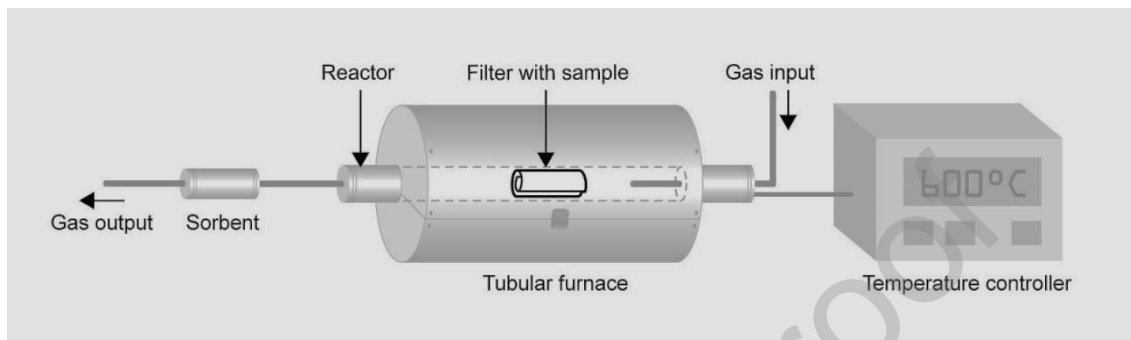
Figure 3.- Extraction experimental setup.

- **Desorption-Gas chromatography/Mass spectrometry.**

Once the decomposition products have been trapped in the solid sorbent, the sorbent is introduced into a commercial thermodesorption unit (TDU, Gerstel), mounted on a cooling injection system (CIS 4. Gerstel) used as a cryotrap and coupled to a gas chromatograph (GC) with mass spectrometry (MS) detection.

Desorption occurs in two stages. In the first stage, the analytes are released in the TDU from 70 to 300°C maintaining this temperature for 8 minutes for complete desorption of all analytes from the solid phase. The evolved species are transferred through a heated capillary to the cryogenic trap. This transfer should always be at a temperature higher than the highest TDU temperature (preferably 20-30 °C above) to ensure complete transfer of all analytes to the cryogenic trap.

Once all the analytes have been adequately desorbed from the solid sorbent, the cryo-focuser is cooled to -50°C to retain all the compounds. After this cooling the temperature rises rapidly, heating with a ramp of 12 ºC/s to 300°C and maintaining this temperature for 8 minutes, to transfer all the analytes to the GC column with minimal loss of sample. With this technique 99% of the analytes are desorbed during the first seconds.

The GC/MS system was a 6890N GC coupled to a 5973 MSD (Agilent). Data acquisition was performed in scan mode from m/z 35 to 380.

Data analysis was performed with MassHunter Workstation (Qualitative Analysis) version 10.0 software from Agilent Technologies.

The identification of the compounds was carried out considering the retention time (Tr) and the characteristic ions (m/z) of each compound. The identification was completed with a fit ≥80% in NIST14 and/or Wiley 11th Edition/NIST 2017 (W11N17).

In the third option, in which the two types of sorbents were combined, a sequential desorption was carried out in the TDU. In a first step, the PDMS twister was desorbed, and the gas products were trapped in the cryo-focusing unit. Then, the desorption tubes filled with carbon material were desorbed and their retained gases were also collected in the cryo-focusing unit. Once all products extracted from both sorbents were in the injection system CIS, they were transferred together to the chromatographic column, managing to concentrate the products extracted by both adsorbents in a single chromatogram, thus minimizing the potential losses that can occur in the extraction by using a single adsorbent, either by saturation or by its limited affinity with a certain product.

4.- RESULTS AND DISCUSSION.

4.1 Characterization results

- **N$_2$ adsorption at -196 ºC**

Figure 4 shows N$_2$ adsorption-desorption isotherms recorded at -196 ºC for PDMS and carbon materials. To estimate surface area of each material, Brunauer-Emmett-Teller (BET) method was used, and the results are summarized in Table 1.
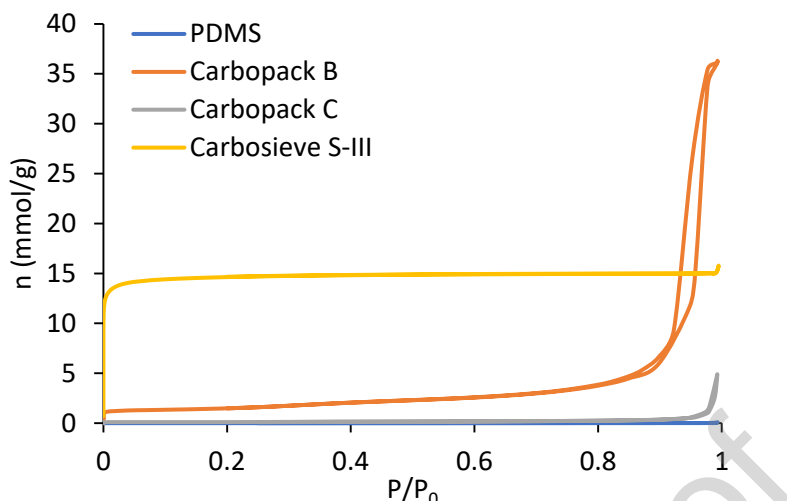
Figure 4.- N_2 adsorption-desorption isotherms at -196 ºC for the sorbents used in this study: PDMS, Carbopack B, Carbopack C and Carbosieve S-III.

N_2 adsorption is not observed at any pressure for PDMS, which is expected for a non-porous polymeric material. This is in agreement with the fact that the gas retention mechanism is based on absorption for this material, ruling out relevant physisorption in this case.

On the contrary, carbon sorbents are porous materials and each of them has a different porosity. Carbopack C is a slightly porous material with certain macroporosity, while Carbopack B presents a mesoporous/macroporous characteristic isotherm with a considerable hysteresis loop above 0.9 P/P_0 approximately. Finally, Carbosieve S-III is a microporous material with a typical Type I isotherm with high N_2 adsorption at low partial pressures, leading to a high specific surface area (1270 m^2/g; Table 1).

Table 1.- Specific surface area of the studied sorbents.

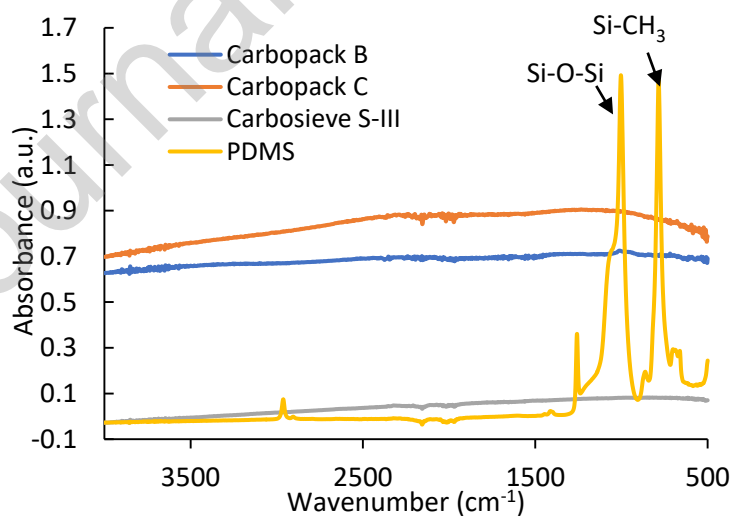| MATERIAL	PDMS	Carbopack C	Carbopack B	Carbosieve S-III
$S_{B.E.T.}$ (m^2/g)	0	8	120	1270

Figure 5 shows a scheme of the retention mechanism of compounds in both materials, where it can be seen how in carbon materials the retention of compounds is through surface adsorption and in the case of PDMS retention occurs within the material.
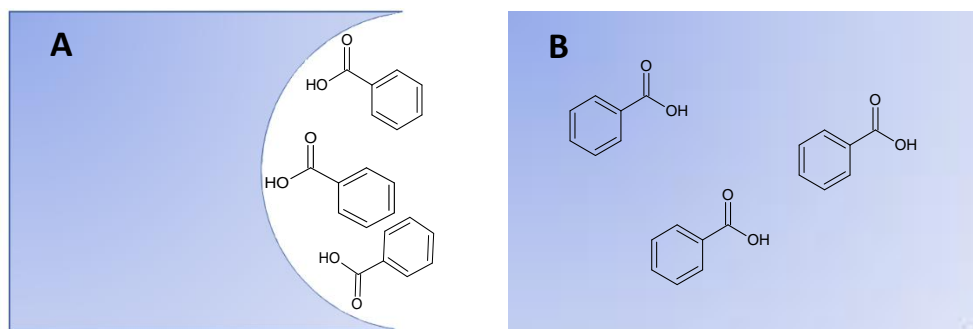
Figure 5.- Scheme of the sorption mechanism for; A) Adsorption in carbon materials, B) Absorption on PDMS.

- **FTIR analysis**

Figure 6 shows the FTIR spectra for PDMS and carbon sorbents, where it can be observed that carbon materials do not present surface groups while PDMS shows two bands at 780 and 1000 cm^{-1} approximately that correspond to Si-CH$_3$ and Si-O-Si bonds respectively.

Figure 6.- FTIR spectra for Carbopack B, Carbopack C, Carbosieve S-II and PDMS.

- **TGA Characterization.**
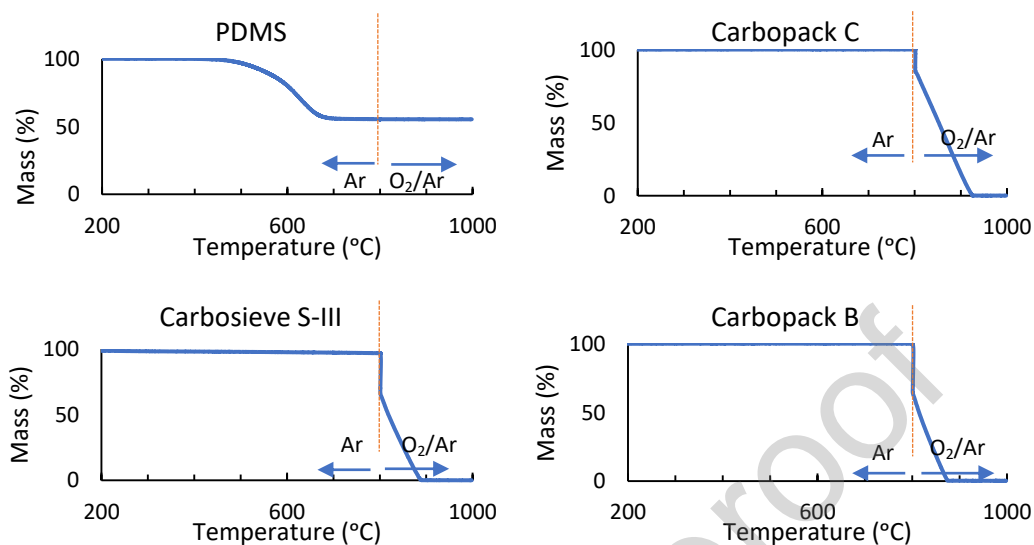
Figure 7.- Thermograms for PDMS, Carbopack C, Carbopack B and Carbosieve S-III in Ar atmosphere until 850 °C, hold time of 5 minutes and Ar-Ox atmosphere until 1000 °C.
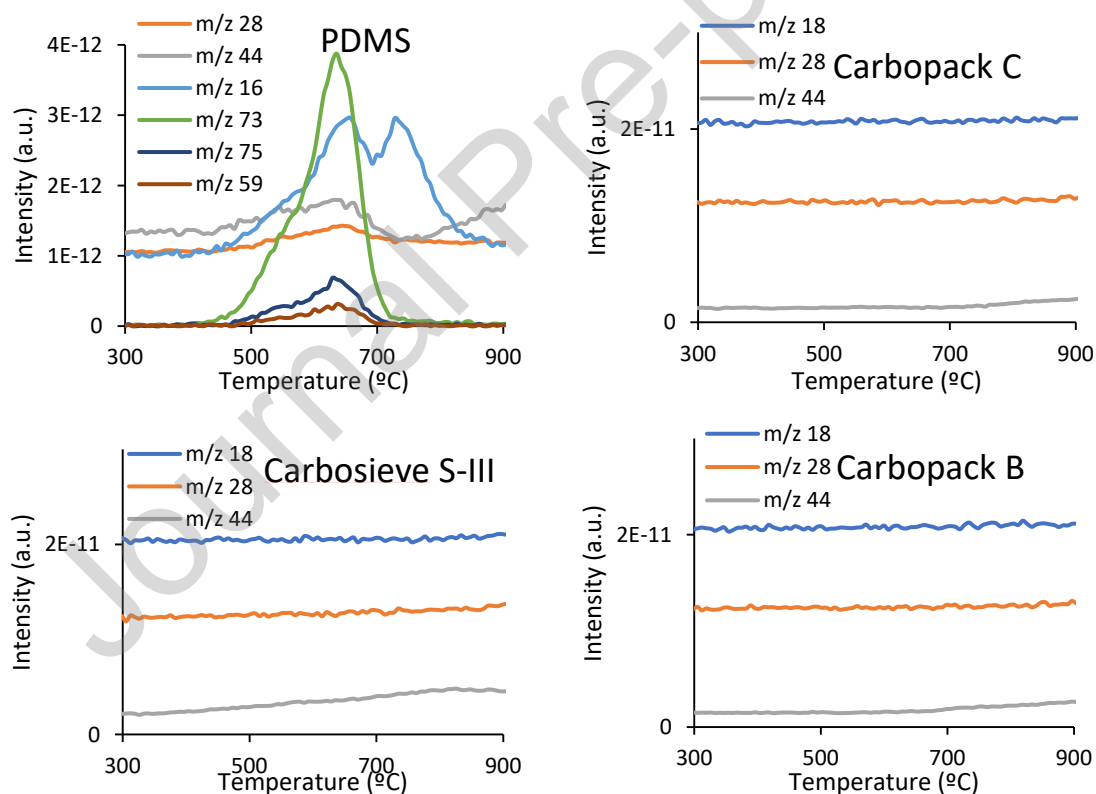
Thermograms for PDMS, Carbopack C, Carbopack B and Carbosieve S-III are shown for Ar atmosphere until 850 °C, and O_2/Ar from 850 to 1000 °C. This protocol allows quantification of the moisture, volatile matter and ashes on the different materials.

The PDMS onset decomposition temperature is approximately 450 °C, losing approximately 47% of its mass.

On the contrary, 100 % weight loss is observed for carbon materials under O_2/Ar, evidencing that they are ash-free carbons, while the weigh remains stable under N_2 until 850 ºC, indicating that the presence of surface oxygen groups is negligible. This is confirmed by the gases released analysis by mass spectrometry, summarizing the spectra in the Figure 8. The 18, 28 and 44 m/z ratios have been followed, corresponding to H_2O, CO and CO_2 respectively.

The mass spectra of these carbon materials do not show any peak in any of the ions followed, which shows that they do not generate any of these compounds when exposed to these temperatures in an inert atmosphere.

For the PDMS, a sweep of the gases emitted was carried out by means of mass spectrometry where the detection of several compounds at temperatures between 450 and 800 °C can be seen. Various silicon-based compounds can be distinguished, such as $(CH_3)_3$-Si-OH (m/z 75), $[(CH_3)_2$-SiO$]_5$ (m/z 73) and $(CH_3)_3$-SiH (m/z 59). The production of hydrocarbons such as methane (m/z 16) and ethylene (m/z 28) is also observed. These species come from the terminal vinyl sites of PDMS and the decomposition of Si-C_2H_3, as has been shown to occur in other organosiloxane polymers with C_2H_3-SiO as precursor[11,12]. Some production of CO and CO_2 (m/z 28 and 44) by carbothermal reduction can also be observed[13].

Figure 8.- Mass spectra for PDMS, Carbopack C, Carbopack B and Carbosieve S-III.

4.2 TED-GC-MS results

When a polymer is subjected to a temperature program in an inert atmosphere, it degrades thermally, and this degradation can be carried out fundamentally in three ways.

- Depolymerization: The end of polymer chain departs and forms low free radical which has low activity, and the polymer loses the monomer one by one.

- Random: The main chain will break down randomly, at any position, and the molecular weight decreases rapidly.

- Side group elimination: Groups that are attached to the side are held by weaker bonds than in the main chain. When the polymer is heated, the side groups are stripped off from de chain.

In addition to these general guidelines, in the case of the polymers studied in this study, particular products can be seen that are obtained after the pyrolysis of specific polymers. On numerous occasions, the breakdown mechanisms of macromolecules are not well understood, but the amounts of polymer added and the amounts of characteristic product generated are well correlated.

Some studies shown that in thermodecomposition of PVC, aromatic hydrocarbons are the main class of which the main part is benzene and chlorinated compounds represent approximately 2%[14]. Although the quantities generated of these compounds are very small, it is considered that, for the identification of PVC, following the chlorinated compounds is the best option since chlorine is a characteristic element of this polymer.

PET decompose in several products, some of them with a very well-known cracking mechanism and other products that are observed after pyrolysis, but the exact mechanism is not yet known.

To identify this polymer, a product that maintains a good relationship between the amount of polymer added and the amount of product generated must be followed, and that is a compound that does not usually appear from other polymers or other natural sources.
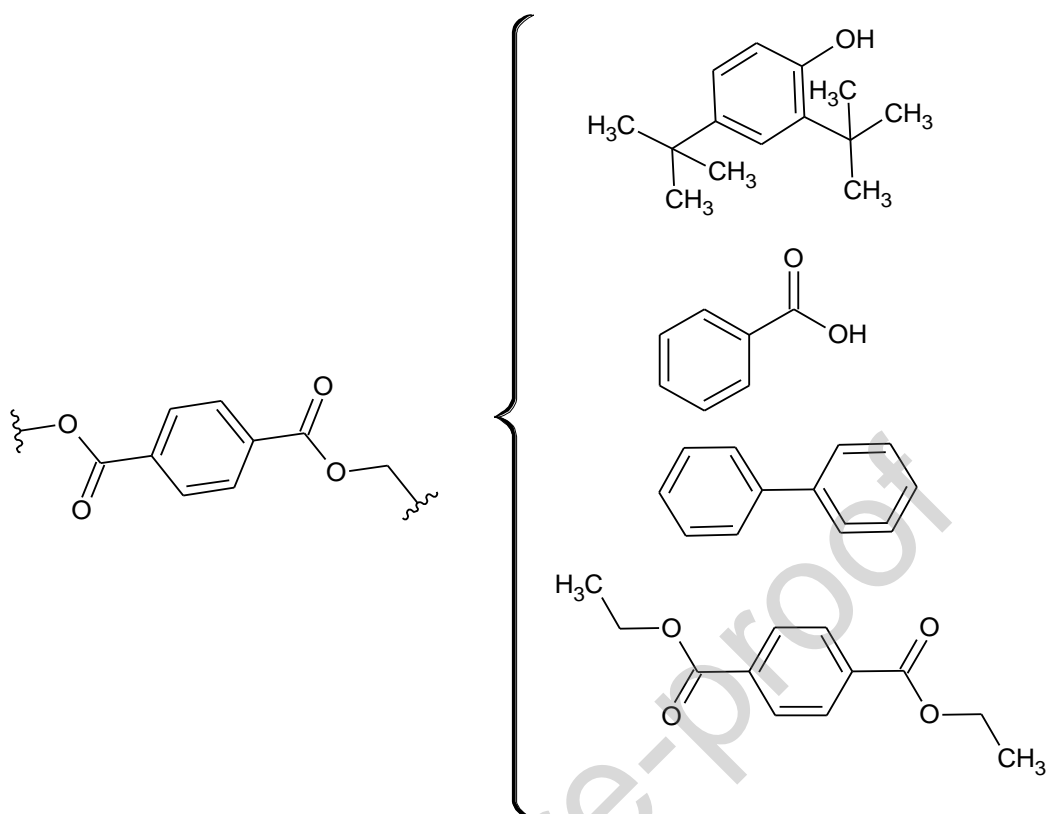
**Figure 9**.- Scheme of PET and its major thermodecomposition compounds.

Polystyrene is the typical polymer that thermodecompose in their monomers, dymers, etc. as well as polyamide, PP and PE. For a correct identification of those polymers, the products that present the most intense peaks, a good relationship between the added polymer and the amount of product generated and that usually present a good fit when the identification libraries are consulted are followed.
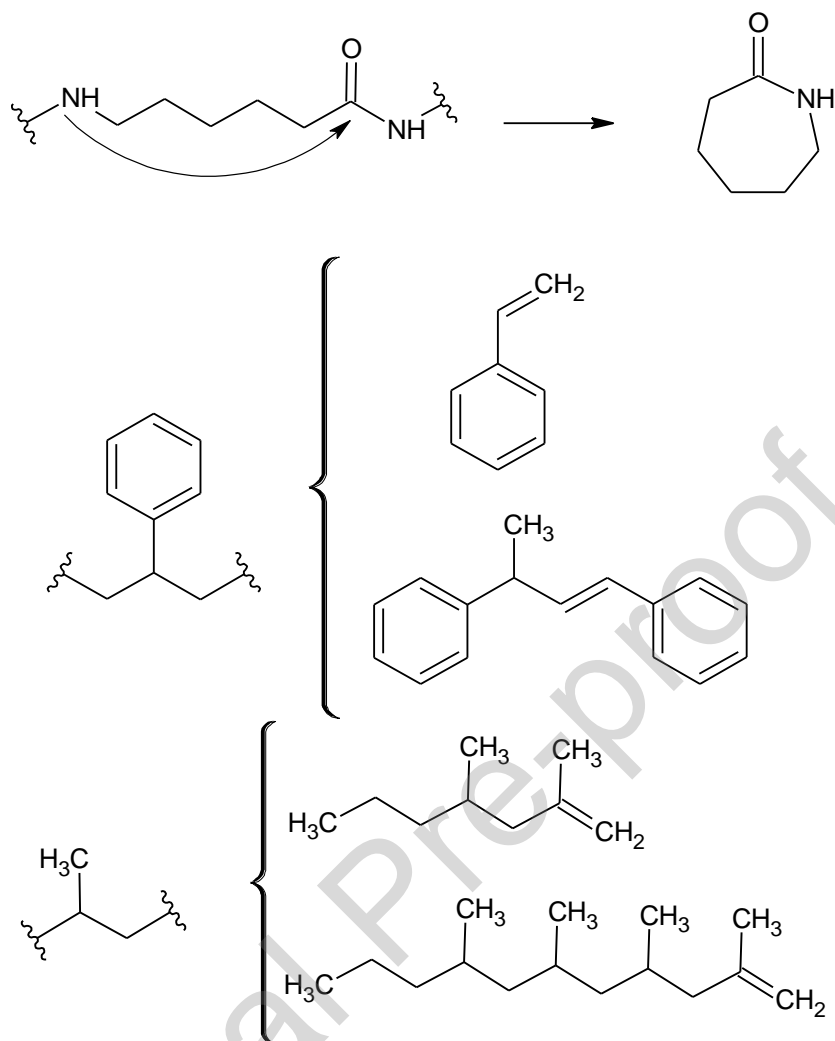
Figure 10.- Schemes of PA, PS and PP and their major thermodecomposition procucts.

TED-GC-MS experiments were carried out using PDMS twister, TD liners filled with Carbopack C+B and Carbosieve S-III and the combination of both sorbents for 6 different polymers, whose results are presented in Figure 11.
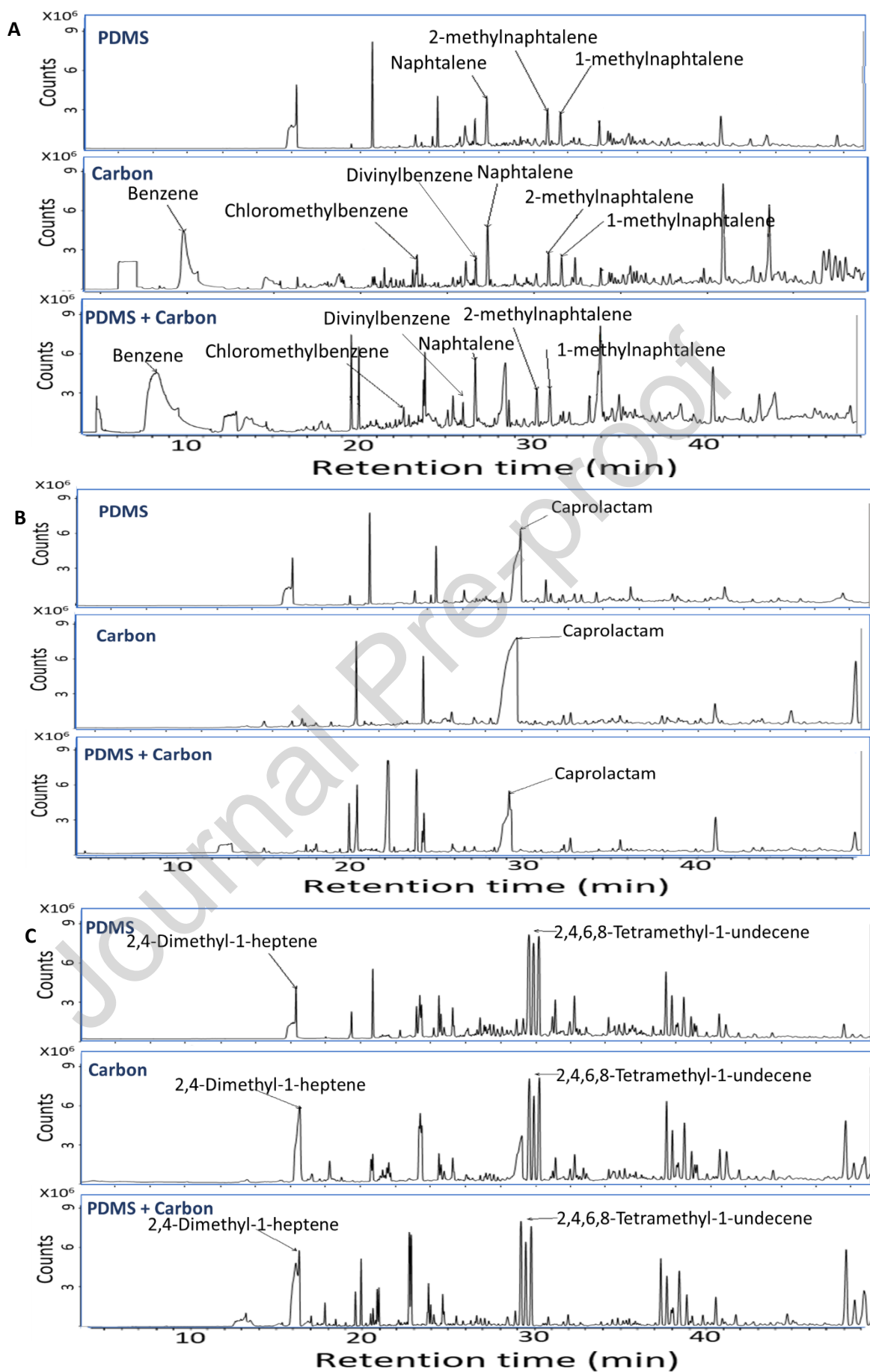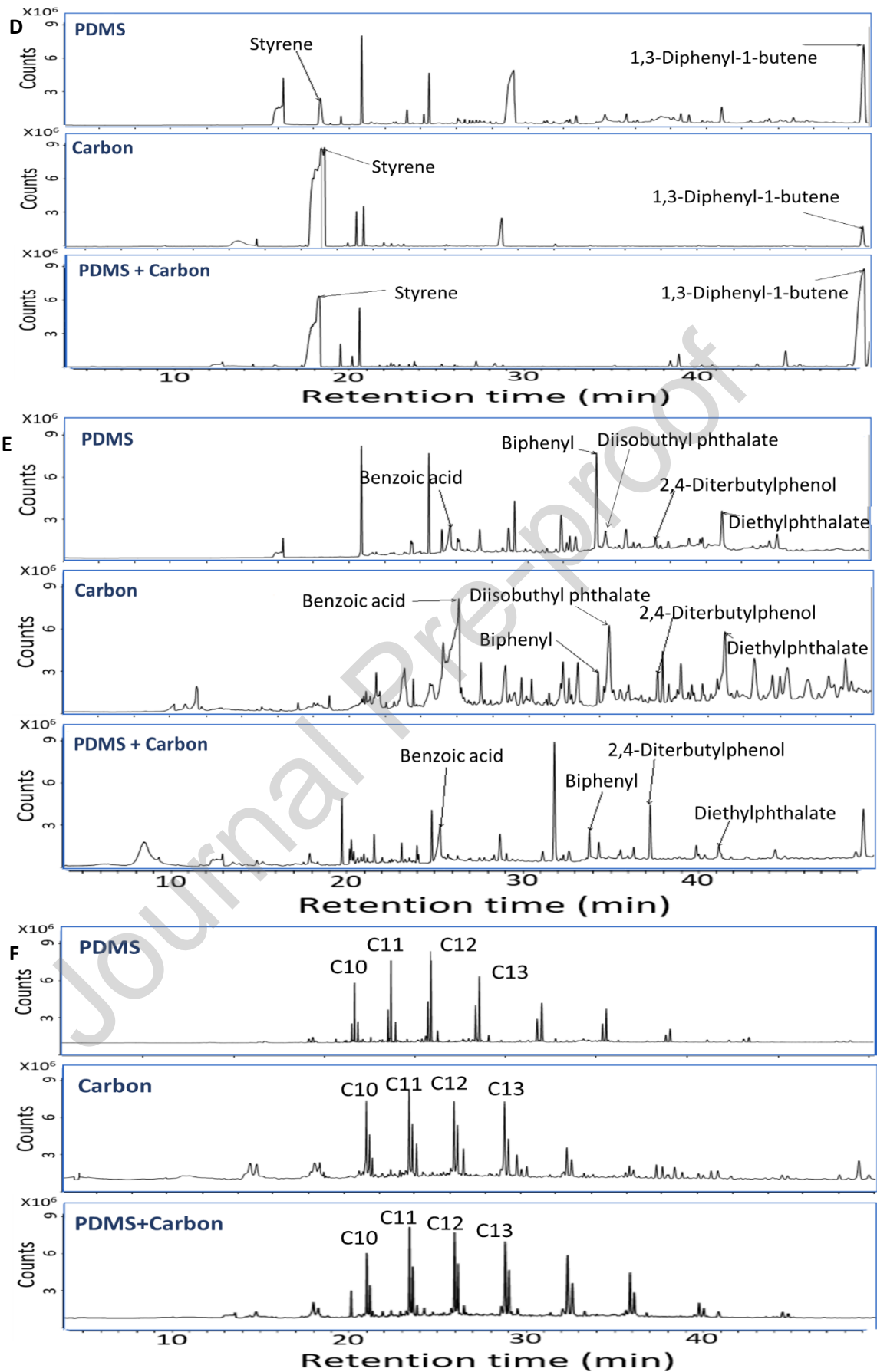
Figure 11.- Comparison of the chromatograms obtained using the three sorbent options for A) PVC, B) PA, C) PP, D) PS, E) PET and F) PE.

When we compare the different sorbents, it can be observed how PDMS and carbon-filled TD tubes have in general a similar behavior, although with certain differences in terms of the affinity for the different compounds.

When we analyse the retention of the most representative thermodecomposition compounds for each studied sorbent, we can summarize:

For PDMS, it can be verified how this material does not retain chlorinated compounds from PVC. In the case of PS, the signal of 1,3-diphenyl-1-butene (styrene dimer) is much more intense than the signal of styrene, and the caprolactam signal from PA has a lower area than in the case of carbon sorbent. Signals of thermodecomposition compounds from PET are usually lower, for benzoic acid, 2,4-Diterbutylphenol and diethylphthalate. For PP, the signal for all three isomers of 2,4,6,8-Tetramathyl-1-decene has about the same intensity as for carbon materials but the signal for 2,4-Dimethyl-1-heptene is much lower. The retention of thermodecomposition compounds for PE is similar for both sorbents but with much lower signals in the case of PDMS.
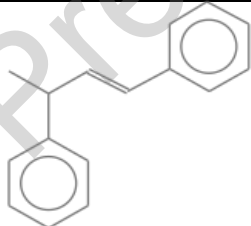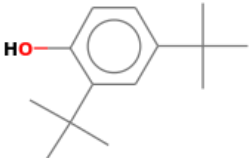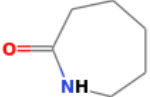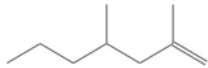
For carbon materials, it can be seen how, although with very weak signals, some chlorinated compounds, such as Chloromethylbenzene, are retained. In the case of PS, the signal of 1,3-diphenyl-1-butene (styrene dimer) is lower than the signal of styrene, the opposite of what happened in the case of PDMS. PET has, in general, more intense signals in all the compounds, more specifically for 2,4-Ditertbutylphenol, which is its most characteristic compound, as in the case of 2,4-Dimethyl-1-heptene for the analysis of PP

The largest difference observed between the two sorbents is that carbon can retain the chlorinated compounds from PVC thermodecomposition, such as benzyl chloride, while PDMS is not capable to retain this type of compounds.

Despite this suitable detection of chlorinated gases using the carbon adsorbents, the signals of these chlorinated compounds are very weak, so an improvement for the future is to design carbon materials with surface functional groups that can take advantages of the polarity of these compounds to retain them with greater efficiency.

When combining the two types of sorbents, it can be observed that it does not present any improvement in terms of the type of compounds retained, since the compounds that are capable of retaining are not complementary, but a benefit is obtained in sensitivity.

Table 2.- Comparison of the most representative peaks for the studied polymers and their relationship, calculated as area for a certain sorbent/area for carbon sorbent ratio.

	PVC	**(Naphtalene)** m/z 128		**PS**	**(1,3-Diphenyl-1-butene)** m/z 115		**PE**	**(Dodecane)** m/z 57	
	Carbon	**PDMS**	**PDMS+ Carbon**	**Carbon**	**PDMS**	**PDMS+ Carbon**	**Carbon**	**PDMS**	**PDMS+ Carbon**
TR (min)	27.4	27.4	27.4	49.8	49.8	49.8	26.1	26.1	26.1
Normalized area (a.u)	25074359	29594273	40853523	93151893	36027295	162194874	12501319	5360635	17505312
Relationship	1	1,2	1,6	1	0,4	1,7	1	0,4	1,4
	PET	**(2,4-Ditertbutylphenol)** m/z 191		**PA**	**(Caprolactam)** m/z 113		**PP**	**(2,4-Dimethyl-1-heptene)** m/z 43	
	Carbon	**PDMS**	**PDMS+ Carbon**	**Carbon**	**PDMS**	**PDMS+ Carbon**	**Carbon**	**PDMS**	**PDMS+ Carbon**
TR (min)	37.6	37.6	37.6	29.2	29.2	29.2	16.2	16.2	16.2

Normalized area (a.u)	4993538	3851147	8715042	251708228	122732699	238050630	99436362	3858944	130237499
Relationship	1	0,8	1,7	1	0,5	0,9	1	0,04	1,3

To quantitatively compare the ability to detect each compound in the case of carbon, PDMS or both sorbents placed sequentially, Table 2 shows the normalized area of the peak corresponding to the most representative compound of each polymer for the mass of polymer added and calculating the proportion of compound that is adsorbed in each of the systems using the thermodesorption tube with carbon filling as reference.

In the case of PVC, naphthalene has been used as a comparison product because, although chlorinated compounds are preferable for the study of this polymer, PDMS is not capable of retaining it, so we could not make the comparison with chlorinated compounds. Naphthalene was chosen instead, which although it is true that it is usually found in environmental samples very frequently from other sources, in studies in which PVC is analyzed by this technique this compound is usually used[15].

Analyzing the data exposed in the table 2, it can be seen how, in the case of PDMS, the peak area obtained is much lower than in the case of carbon, evidencing the great adsorption capacity of carbon. When the combination of PDMS plus carbon is used a larger area is obtained for each of the compounds, greatly increasing the ability to detect the thermodecomposition products. The only exception is the case of PVC, where a greater adsorption of naphthalene by PDMS can be observed, although it should be noted that this adsorbent is not capable of retaining chlorinated compounds, such as benzyl chloride, which are characteristic of this polymer.

If broader mass intervals are used, it can be observed how the line drawn by the combination of PDMS plus carbon (Figure 12-orange) is always above that of carbon alone

(Figure 12-blue) and the amount adsorbed only by PDMS is always below both options (Figure 12-grey).

In this comparison, the exception of PVC is also observed, which is slightly above the curve formed by carbon, but in no case is the adsorption capacity of PDMS and carbon together exceeded.
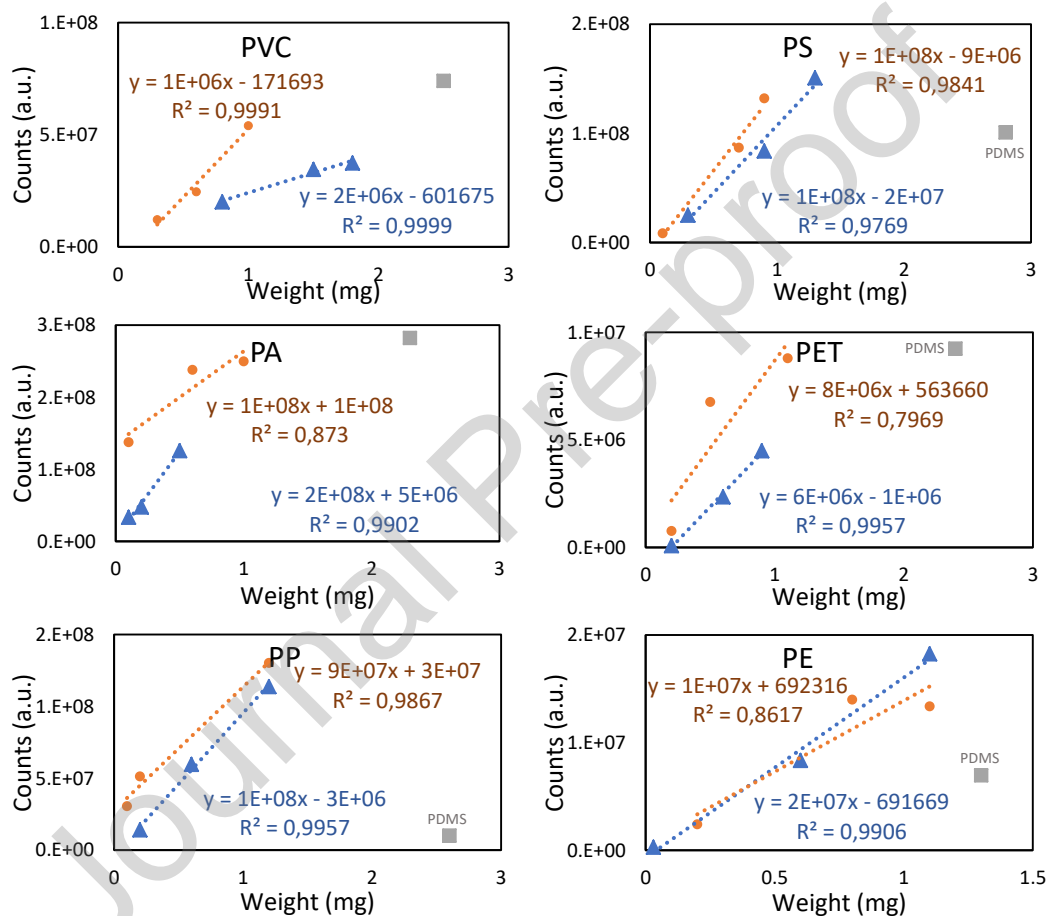
Figure 12.- Comparison in the intensity of the signals using carbon (blue triangle), PDMS (grey square) and the combination PDMS+carbon (orange circle) as sorbent.

5. CONCLUSIONS

After comparing and analyzing different commercial sorbent materials (PDMS and carbons) and strategies for the retention of the thermodecomposition compounds of the studied polymers, it can be concluded that PDMS is a non-porous material, confirming that the

gas retention mechanism is absorption-based, as shown in the literature while carbon materials tested combine porosity in the micro, meso and macroporous range, being packed in a thermodesorption tube forming three consecutive beds, thus achieving three adsorption zones and being able to retain compounds with three different molecular size ranges, although none of these materials have functional groups on their surface.

The use of carbon materials as adsorbent has demonstrated to have an optimal behavior for this application, highlighting two main advantages; On the one hand, they present slit-type pores, these are optimal for retaining the aromatic compounds that many polymers present, and on the other hand, carbon materials can retain the chlorinated compounds from PVC despite the absence of functional groups, although the intensity of the signals for these compounds is very weak.

The combined use of PDMS + carbon provides greater sensitivity, since optimally retain all the compounds, although the experimental procedure is somewhat harder, as it must analyze two sorbents for a single polymer.

_Although good results have been obtained using these commercial carbon materials, the challenge for future research is to find a carbon material with great adsorption capacity, with a surface group that improves the retention of chlorinated compounds, which would mean an improvement in the identification of PVC.

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Declaration of Competing Interest

☒ The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

☐ The authors declare the following financial interests/personal relationships which may be considered as potential competing interests:

Highlights

- Chlorinated compounds are better for PVC identification, and PDMS doesn´t hold them
- Carbon materials retain chlorinated compounds from PVC.
- Carbon materials trap all thermodecomposition products of microplastics perfectly.