Pyrolysis-gas chromatography mass spectrometry : way forward to the low-µm and nm range plastics analysis

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1. Introduction

In recent years, the microplastics and nanoplastics pollution has gained an important interest, but methods to identify and quantify them still need to be standardized. While extensive studies have been conducted on microplastics, the growing necessity to explore the nanometer range presents a unique set of challenges. Current methods, such as µ-FTIR, face limitations below 10 µm, prompting the exploration of alternative techniques and the development of new methodologies.To overcome the size limitation problem of the µ-FTIR, the pyrolysis-gas chromatography-mass spectrometry (Py-GC-MS) can be used. This technique offers a robust solution for the detection of both micro- and nanoplastics regardless the particle size. Notably, Py-GC-MS provides mass-based information, eliminating the need for particle counting and enabling the detection of polymer quantities in the nanogram range.

This study aims to contribute to the understanding of plastics analysis by investigating the impact of particle size on the chromatographic outcomes. To achieve this, four distinct polymers, each characterized by varying particle sizes, along with a microplastics mix, were subjected to thorough analysis using Py-GC-MS. By exploring the obtained chromatograms, this research seeks to provide valuable insights into the efficacy of Py-GC-MS in elucidating the complexities of plastics at the low-µm (10-1 µm) and nm (< 1µm) ranges.

2. Materials and Methods

Polystyrene (30, 60, 90, 200, 300 and 400 nm), polyethylene (50 nm), poly(methyl methacrylate) (200 nm), polypropylene (50 nm) particles were purchased from lab261® and polystyrene (1, 2 and 5µm) particles were purchased from Bangs laboratories®. A 50 ppm acqueous suspension was prepared for each polymer and 5 to 25µL were inserted in a 40µL pyrolysis cup (Frontier lab). The samples were dried in the oven at 105°C. Once the sample dried, the cup was injected in the pyrolzer (Frontier lab) at 590°C for 18 s. The pyrolysis fragments were separated by gas chromatography (Agilent 7890B) following the oven program : 40°C (2 min) to 320°C (4min) at a rate of 20°C/min with a split ratio of 100:1 and finally detected by mass specrometry (Agilent 5977B). The ionization voltage was fixed at 70 eV and the scan range was set from m/z 40 to 550. The MPs calibration mix from Frontier lab ($CaCO_3$ as inert diluent) was used as comparison to single polymer standards. For this purpose, an amount ranging from 0.040 mg to 1 mg of the calibration mix was directly weigh in the pyrolysis cup and injected in the pyrolyzer.

3. Results and Discussion

3.1. Polymer standards analysis

Initially, acqueous suspensions of single polymers particles of different sizes have been analyzed and calibartion curves have been built. The first polymer analyzed was polystyrene. For this polymer, sizes of 30, 60, 90, 200, 300, 400 nm and 0.5, 1, 2 and 5 µm have been analyzed. The first observation that can be made is that the pyrolysis profile of polystyrene is different according to the size of the particle. examining differrent ratio between the peak areas, an increasing/decreasing tendancy, depending on the polymer type is observed according to a decrease of the particle size. Concerning the analysis of polyethylene, a peak forest is obtained. The firsrt observation being made with this polymer is the difference of LOQ compared to the other polymers. As PE brakes down in a lot of different fragments during the pyrolysis, a higher amount needs to be injected in order to be able to detect the marker compound. For the poly(methyl methacrylate), the profile is completely different as only one peak can be observed on the chromatogram and lower LOQ can be achieved.

On another hand, the different aqueous suspensions helped to determine the LOD and LOQ of the instrument as, on a practical point of view it is easier to draw an exact volume rather than weighing a solid powder.

3.2. Comparison between the MPs calibration mix and the NPs single polymers

After the single polymers, the calibration mix have been analyzed (Figure 1) and the area of the corresponding marker compound of each polymer has been used to trace a calibration curve per polymer type. The results obtained with the single polymers have been compared to the one obtained with the MPs calibration mix and the error percentage have been calculated. According to the resuls, using a calibration curve made with microplastics to quantify nanoplastics can lead to a certain error and therefore NPs standards are of importance. A mix of the NPs polymer particles has also been analyzed and the results showed a difference compared to the MPs calibration mix, confirming the fact that a distinction should be made between nano- and microsize plastic particles.
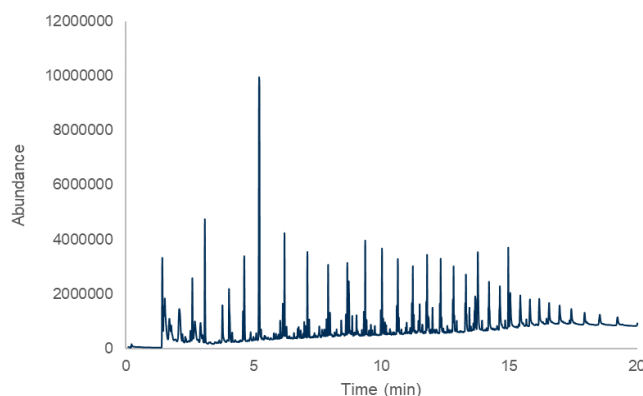

Figure 1 - Chromatogram of MPs calibration mix

4. Conclusions

To conclude, the use of pyrolysis-gas chromatography/mass spectrometry for the analysis of low-µm and nm range plastics is a promising approach as the obtained results are mass-based and not based on particles number. The analysis of different sizes, ranging from micro to nanometer, of differrent polymer standard particles show an impact of the particle size on the obtained chromatogram. These results have to be taken into account while analyzing environmental samples. As such, one of the possible solutions is a size separation step during the sample preparation procedures. However, extensives studies have still to be carry on nanoplastics to assess the deviation compared to microplastics in order to achieve a reliable quantification in environmental samples.