Microplastics identification by Py-GC/MS: method optimization and validation

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Introduction

Plastic pollution has gained a large interest in the scientific community because plastic particles are found in marine environments. Moreover, ingestion of microplastics (MPs) particles (<5 mm) by numerous seafood products (bivalves and fish) has been demonstrated. However, some studies performed the identification of plastic polymer with reliable methods such as Fourrier Transform infrared, Raman spectoscopy or Pyrolysis-GC/MS (Py-GC/MS).

Py-GC/MS has been recently used for microplastics identification and it has the advantage to be relevant to identify plastic polymers.

The purpose of this work was to optimize and validate a method using Pyrolysis-GC/MS to characterize microplastics.

Material and methods

1. Optimisation

Polyethylene (PE) microspheres were used to perform this step.

Optimisation was carried out by varying 3 parameters: pyrolysis and injector temperature and split ratio (Figure 1).

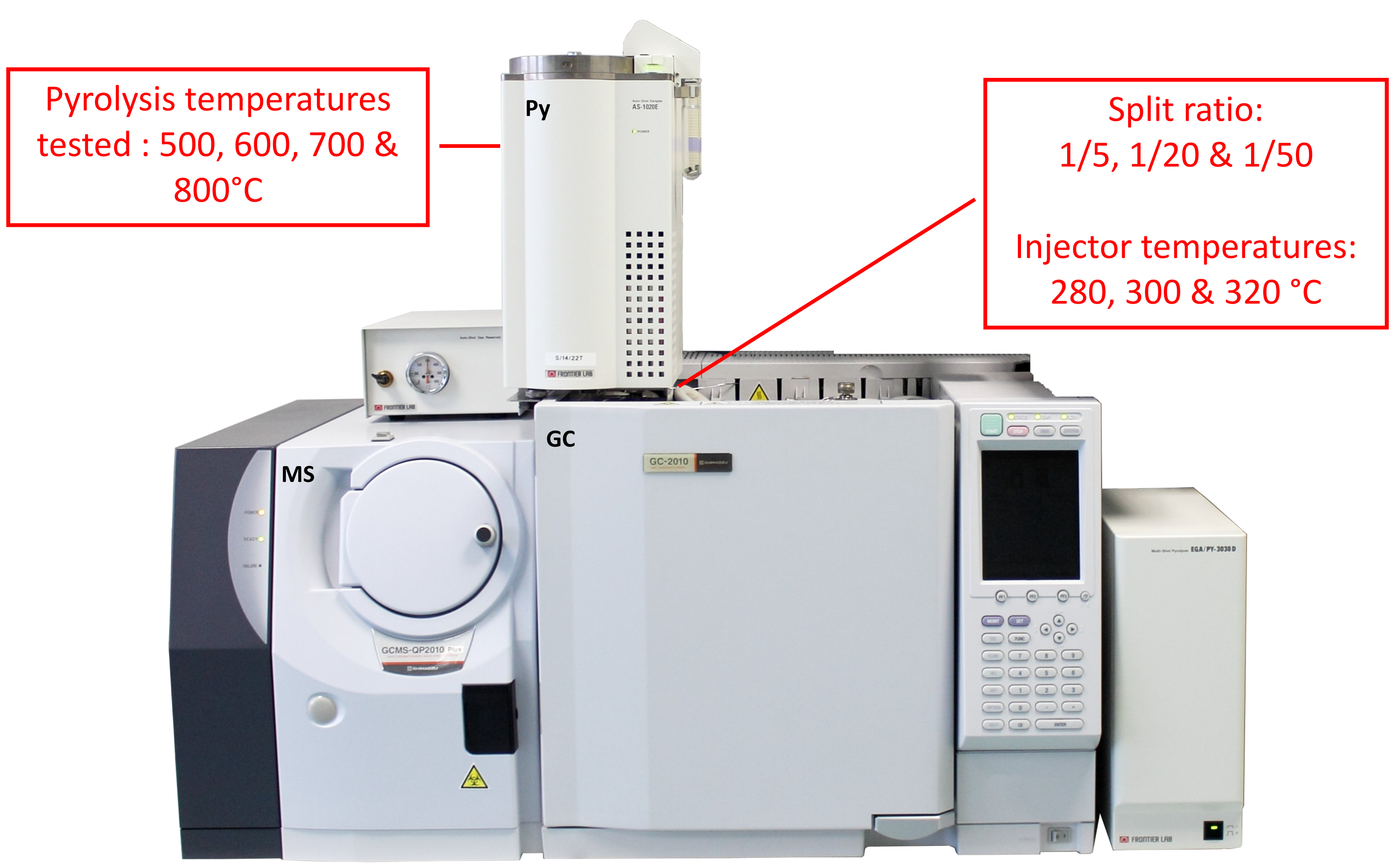

Figure 1: Picture of the Py-GC/MS system used for the study. Red squares highlight the parameters submitted to optimisation.

2. Validation

PE, Polystyrene (PS) and poly(methyl methacrylate) (PMMA) microspheres were used to perform this step.

Repeatability tests were carried out on 10 replicated analysis per polymer (single day).

Reproductibility tests were carried out on 5 replicated analysis (0,2 and 3 weeks).

Confirmation was performed on n=7 samples already identified by Raman spectroscopy (Figure 2A-B)

3. Application on environmental particles

Unknown particles recovered from bivalves (mussels and cockles) were analysed using the developped method. Some of these particles (n=14) were previously identified as « pigment » (Figure 2C) by Raman spectroscopy.

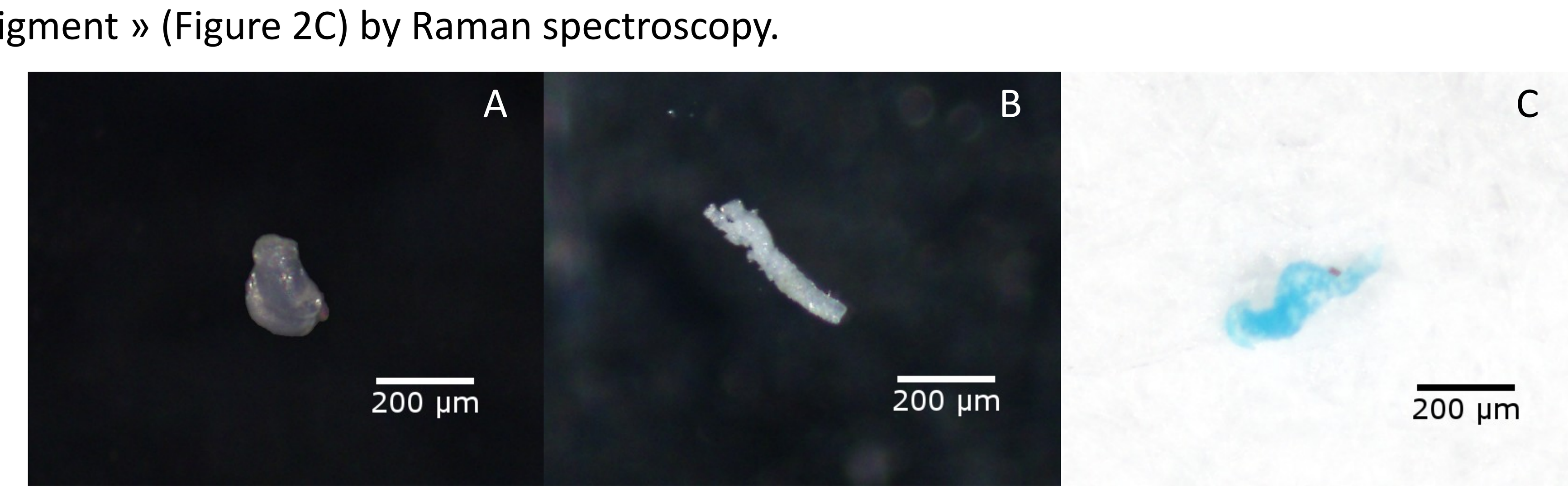

Figure 2: Pictures of particles recovered from mussels and cockles samples successfully identified (A-B) and partialy (C) by Raman spectroscopy.

Results

1. Optimisation

First, optimisation was performed on the pyrolysis temperature. Area of the main peak of the PE increased with the increase of pyrolysis temperature with the exception for 800 °C (Figure 3A). Significant differences were found (Kruskal-Wallis Post-hoc, p<0.05), the higher area was recorded at 700 °C. Then, increasing split ratio (Figure 3B) decreased significantly peak areas (Kruskal-Wallis, p<0.05). Moreover, with a split ratio of 5, peak areas were significantly different (Kruskal-Wallis Post-hoc, p<0.05) with higher area recorded with an injector temperature fixed at 300 °C.

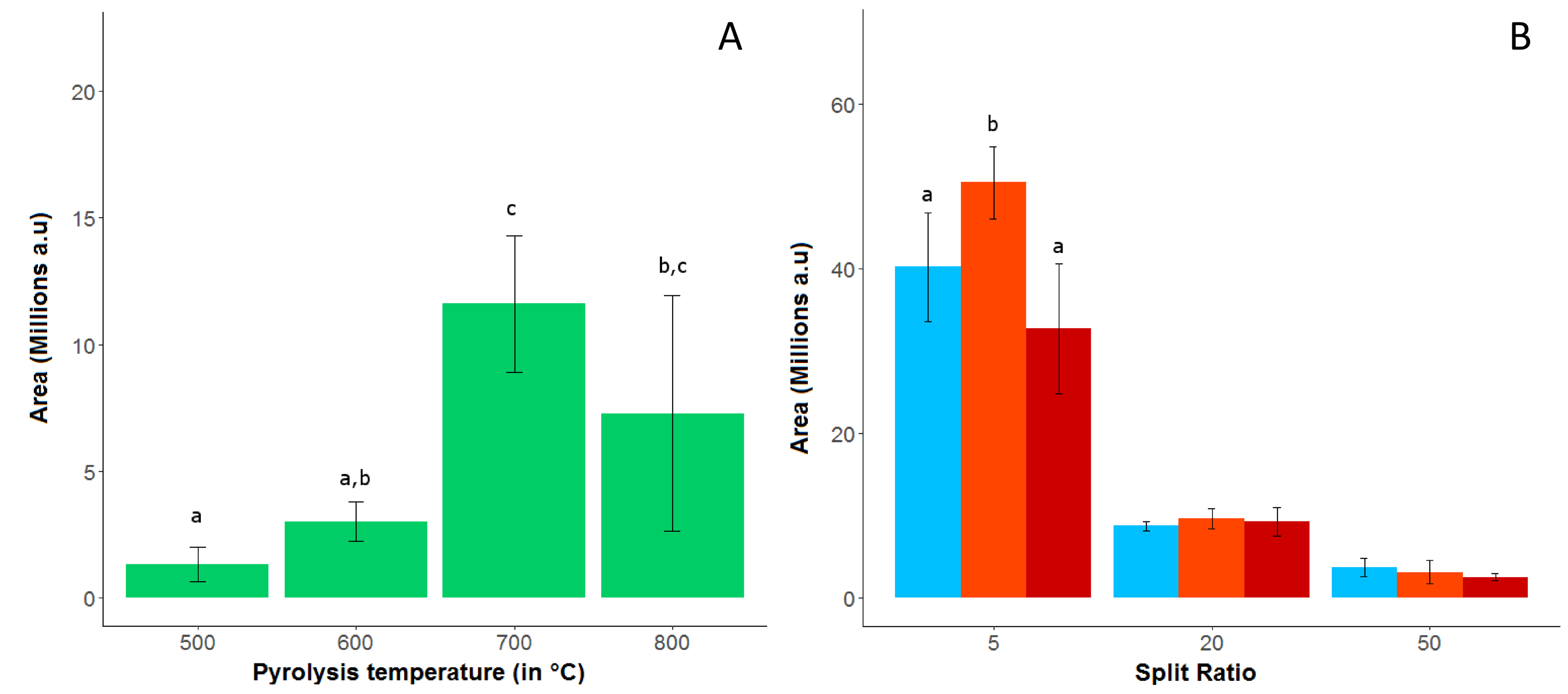

Figure 3: Mean peak area (arbitrary unit) depending on the Pyrolysis temperature (A), on split ratio and injector temperature (blue: 280°C, orange: 300°C and red: 320°C) (B) of the 1-decene (PE). Error bars correspond to the CI95% and letters to the differences after post-hoc using Fisher's least significant difference with Bonferroni correction.

2. Validation

Repeatability tests demonstrated that pyrolysis for PE and PMMA were acceptable with a relative standard deviation (RSD) of 10%. However, RSD were above 20% with PS microspheres.

Reproductibility over time did not showed significant differences for PE, PS or PMMA (Figure 4).

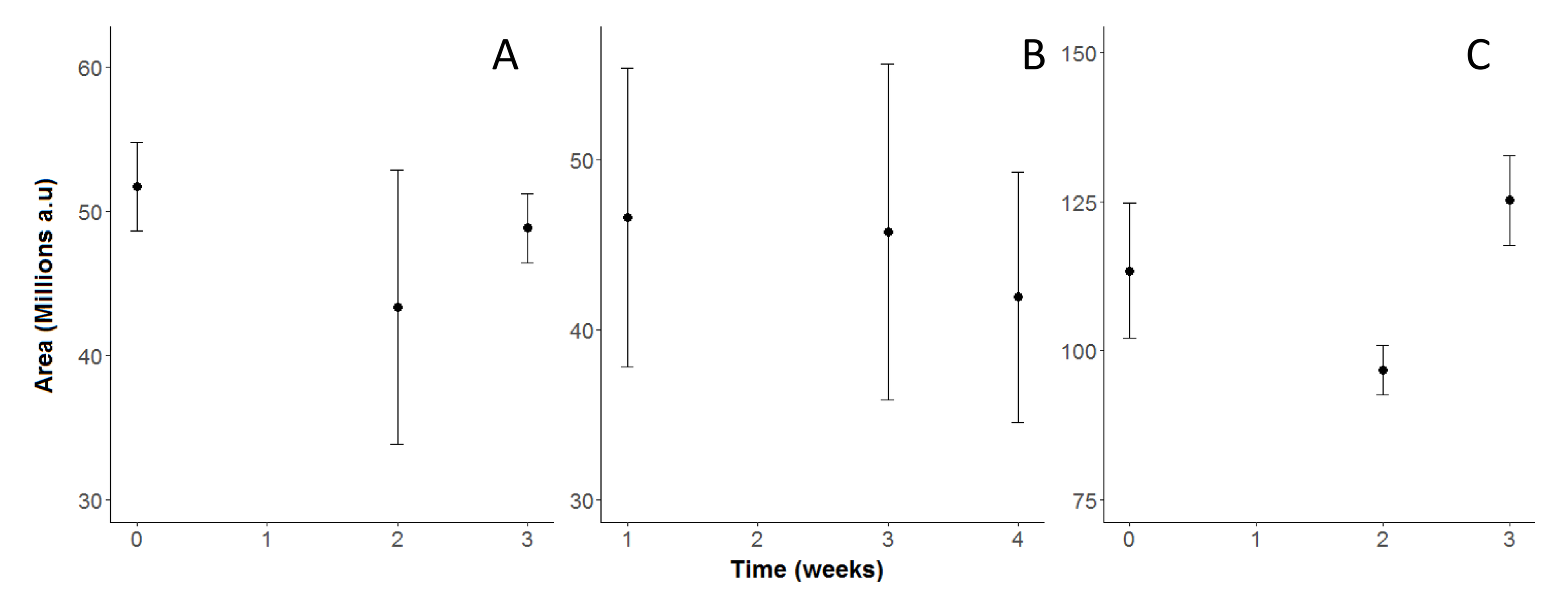

Figure 3: Mean peak area (arbitrary unit) over time (in weeks) for the mains peaks of PE (A), PS (B) and PMMA (C). Errors bars correspond to the CI95%.

The developed Py-GC/MS method identified 5 out of 7 samples already identified by Raman spectroscopy. Such confirmation must be carried out on more samples.

3. Application on environmental particles

7 out of 14 pigment samples were sucessfully identified. These Identifications correspond to 6 particles of PS and one of styrene-methyl methacrylate copolymer. (Figure 4)

3 other are suspected to be PS particles. Additional particles identification are requested.

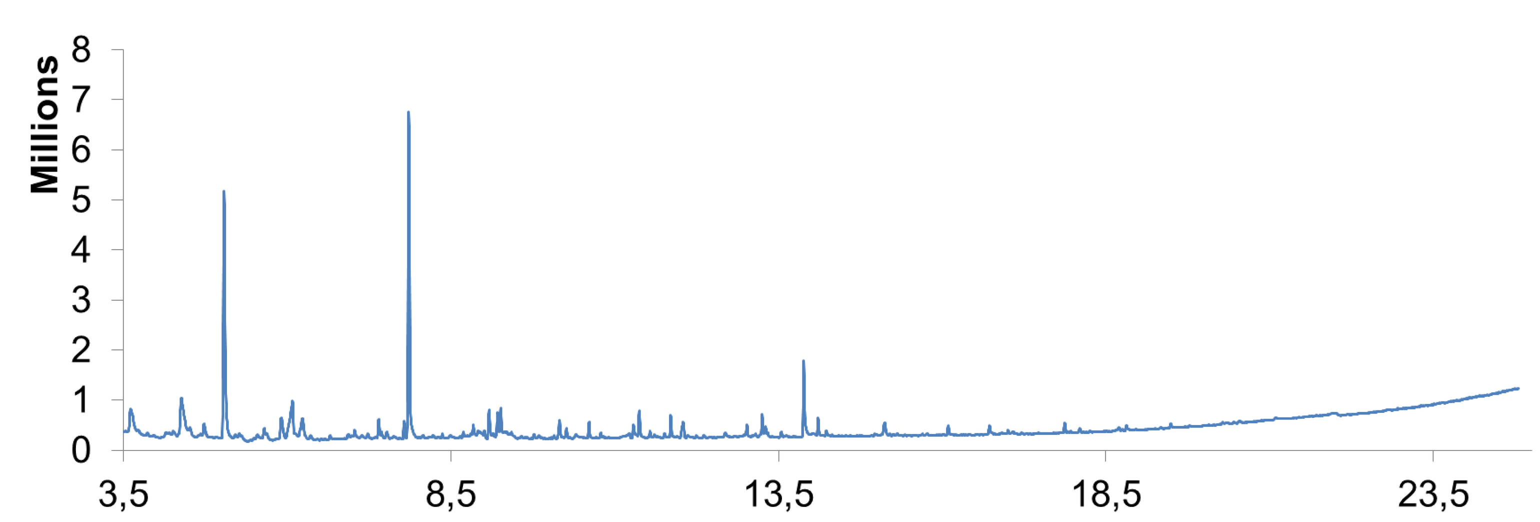

Figure 3: Pyrogram of the « pigment » identified as styrene methyl-methacrylate copolymer.

Conclusion

The new developed Py-GC/MS method uses a pyrolysis at 700 °C with an injector temperature of 300 °C and a split ratio of 1/5.
Additional confirmation on a wide number of particles are necessary, together with identifications of environmental unknown particles.

Acknowledgments

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