Quantification and Identification of Microplastics in Air Using Pyrolysis-GC/MS

An easier to implement, efficient technique for measuring plastic pollutants in the air

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INTRODUCTION

As the use of plastics increases, so does the presence of microplastics in the environment. These tiny particles are less than 5 mm in diameter and can pollute a variety of environmental compartments, including the air we breathe. Microplastics travel long distances when carried by the wind and are present in the home, as well as in the workplace. For this reason, screening for microplastics has become a pressing issue.

While the scientific community has developed several analytical methods for the identification and quantitation of these pollutants, many of these methods struggle to quantitate microplastics in complex matrices, require complex sample preparation steps, and are not amenable to automation. This paper introduces a novel analytical system configuration with simple and easy-to-follow workflows. The system uses the micro-furnace pyrolysis-gas chromatography-mass spectrometry (pyrolysis-GC/MS), a powerful analytical technique, in combination with cryogenic milling and specialized software. With the workflows described herein, scientists will be able to accurately identify and measure microplastics in shorter timeframes and with simpler sample preparation protocols compared to other available methods.

THE WORKFLOW

The three main components of the workflow are sample preparation, pyrolysis measurement, and data analysis. Analysts can easily prepare samples by exposing pre-conditioned quartz filters to the air in the room. In this case, there is no need for solvent extraction, but if there are proteins or other organic materials present in the target matrix, they must be removed. The filter is ground using a cryogenic mill, a few milligrams of the ground sample is placed into an inert sample cup, and a small amount of quartz wool is placed over the sample to prevent it from scattering out.

THE PYROLYSIS MEASUREMENT SYSTEM

The main components of this system include the Frontier EGA/PY-3030D micro-furnace multi-functional pyrolyzer, Frontier Auto-Shot Sampler, a packed GC glass insert, a specialized GC column kit, the Frontier Microplastics Calibration Standards (MPCS) kit set of calibration standards, the Frontier IQ Mill 2070 cryogenic mill device, and Frontier F-Search MP software. The system requires the Frontier Splitless Sampler and Frontier MicroJet Cryo-Trap accessories if performing splitless pyrolysis (**FIGURE 1**). The micro-furnace connects directly to the GC inlet without a transfer line. The sample is held near ambient temperature which eliminates evaporation, degradation, or thermosetting of the sample before the analysis. The micro-furnace deposits all the pyrolyzates directly and continuously on the GC column. It generates reproducible results with +/- 0.1 °C precision and is compatible with GCs from major manufacturers. Users can configure the micro-furnace to perform evolved gas analysis (EGA) with a deactivated EGA tube, or they can switch to the separation column for single and double shot runs, as well as thermal desorption and heart cutting.

The recommended GC column is Frontier Laboratories' Ultra ALLOY® Metal Capillary column kit, which improves the quantitative separation of compound peaks. This column kit can separate pyrolyzates that co-elute, such as C8 from PE and cyclopentanone from N66. In addition, users can further improve the peak shapes obtained with this column kit by using packed glass inserts with it.

Another accessory that can be used depending on the application of interest is the multi-functional splitless sampler, which has backflushing capabilities to prevent column contamination and shortens analysis times of high boiling pyrolyzates (**FIGURE 2**). It can also vent solvent or derivatization agents to protect the column and the detector.

To crate calibration curves, the Frontier MPCS kit includes a mixture of 12 commonly targeted polymers in a matrix of either $CaCO_3$ or SiO_2 at concentrations that allow analysts to weigh a few milligrams of MPCS on a semi-micro balance to obtain a few micrograms of the polymers. The polymers included are polyethylene (PE), polypropylene (PP), polyvinylchloride

FIGURE 1: Micro-Furnace Pyrolysis-GC/MS for Microplastics Analysis

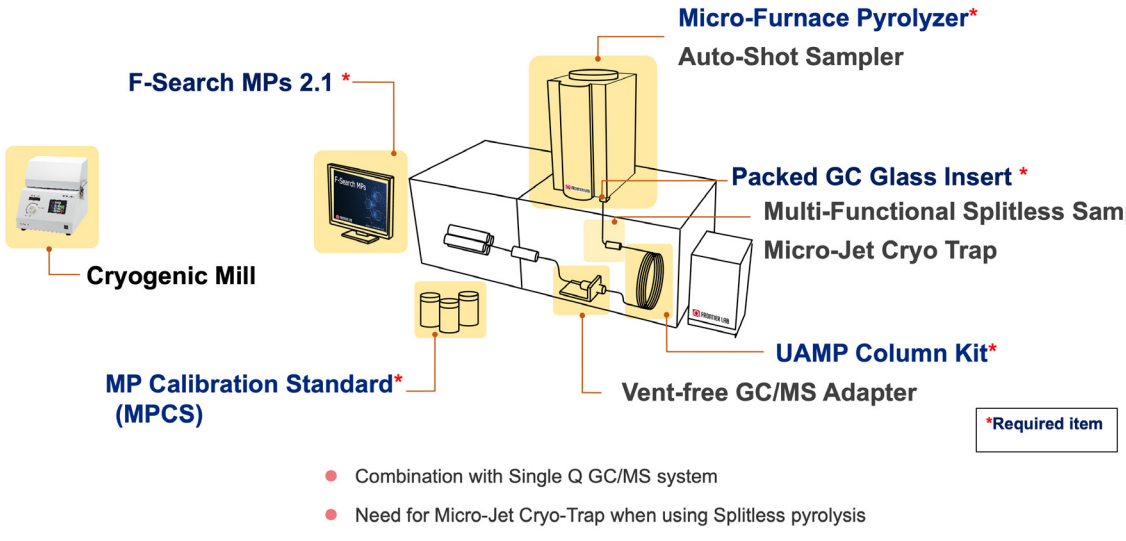
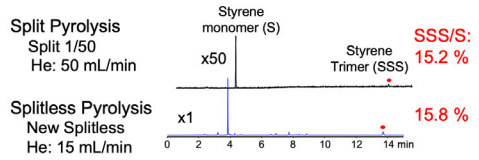
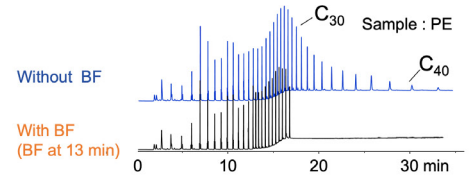


FIGURE 2: Multi-Functional Splitless Sampler Features

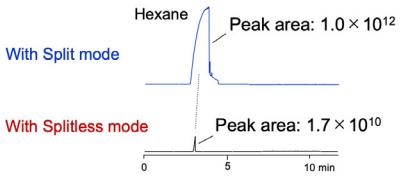
- **New Splitless Pyrolysis**
  High-sensitivity detection of trace pyrolyzates.
  New Splitless is useful for trace analysis such as microplastic analysis.



- **Backflushing (BF)**
  To prevent contamination of a separation column as well as detector by pre-column.
  BF is useful to shorten analysis time with high boiling pyrolyzates such as pyrolysis of polyethylene.



- **Solvent cut**
  To vent solvent (or derivatization reagent), and protect a separation column and detector.



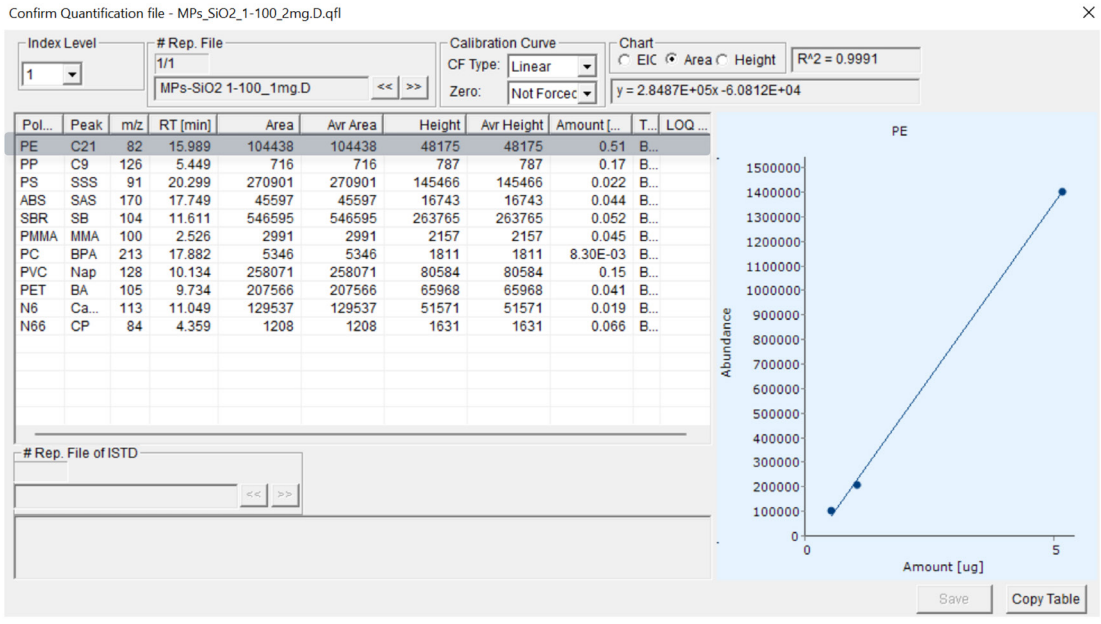
(PVC), polycarbonate (PC), polyethylene terephthalate (PET), poly methyl methacrylate (PMMA), nylon-6 (N-6), polystyrene (PS), acrylonitrile-butadiene-styrene copolymer (ABS), styrene-butadiene rubber (SBR), nylon-6,6 (N-66), and MDI-polyurethane (PU). Users must select the MPCS matrix based on their target polymers, as the SiO_2 matrix is not compatible with PU because of unwanted reactions with PET and N-66 pyrolyzates; the $CaCO_3$ matrix has low sensitivity for PET.

For the data analysis, Frontier Laboratories has developed proprietary analytical software, F-Search MPs 2.1, that performs not only the calibration steps but is an integral part of the identification and quantitation of unknown microplastics (**FIGURE 3**). It is a sophisticated search program that uses a library of microplastics for their accurate identification. A four-step process develops the necessary calibration curves and identifies the unknown microplastics. In the first step, the software adjusts the retention indices (RI) of the microplastics, based on their pyrolyzates. In the second step, it creates a calibration file (QFL) based on the MPCS pyrograms. The third step is the quantitative and qualitative analysis of actual microplastics. Finally, the fourth step involves the interpretation and review of the results. The check points for this review are peak shape, retention time, mass spectrum, and peak integrated area.

APPLICATION EXAMPLE: ANALYSIS OF MICROPLASTICS IN AIR SAMPLES

For this example, the passive sampling method was used in three separate rooms. The samples were homogenized by being ground in the cryogenic mill and aliquots were weighed into inert sampling cups. Solvent extractions did not have to be used with the samples. For the quantification and identification, the main components of the Micro-furnace Pyrolysis-GC/MS configuration were used including the micro-furnace pyrolyzer (EGA/PY-3030D), auto-shot sampler, the packed GC glass insert liner, UAMP column kit, MPCS kit, multi-functional splitless sampler, and the vent-free GC/MS adapter. For the data analysis and quantification, the F-search MPs 2.1 software was used.

FIGURE 3: Create Calibration Curve Using F-Search MPs Software



For calibration purposes, the microplastics calibration in SiO_2 was used. The SiO_2 matrix is not compatible with PU, so this polymer was not targeted in the study. The calibration curves created by the F-Search program were all excellent, with correlation coefficients (R^2) all greater than 0.99. **FIGURE 4** shows the specific compounds expected from the pyrolysis of the MPCS polymers, along with their characteristic ions. This information is central to the analysis as it represents the targets that the software will use for its library search. The software shows the results of the search in tabular form with a probability value for each of the potential targets and the amount detected in µg (**FIGURE 5**). Analysts use two criteria for confirming the presence of a given microplastic: probability close to 100% (at least > 87%) and measured amount sufficiently greater than the system's limit of quantitation (LOQ), which is determined by the F-Search software. In the case of Room #1, the microplastics that met these criteria were N66, PE, PET, and N6. It is recommended to run a second MS test on the selected peaks to confirm that the software selected the correct microplastics. In this case, the confirmation runs showed that for PE, the chosen peak was for a linear hydrocarbon that would be present even in the absence of PE. Furthermore, the detailed extracted ion chromatogram (EIC) for m/z 55 and 57 of the sample, characteristic of PE, did not match that of the MPCS and thus it was concluded that PE was not present.

Using the same approach, the presence of PET, N6, and N66 in Room #1 was confirmed. Finally, the analysis of samples from Room #2 and Room #3 confirmed the presence of all four polymers. With this information in hand, it was possible to calculate an important parameter for risk assessment, which is the amount of microplastics/m^2/day in each room. Looking at the weight of the samples, the collection time, and the area of the rooms, it was shown that PE, although not present in Room #1, was the most abundant of the microplastics measured (**FIGURE 6**). The actual amounts varied from 1 to 1.6 mg/m^2/day for PE, while the other microplastics were present at lower levels, from 0.04 to 1.1 mg/m^2/day.

FIGURE 4: Characteristic Compounds for 11 Polymers and their Characteristic Ions

Polymer	Target compound	Abbrev.	m/z
PE	1,20-Heneicosadiene	C21"	82
PP	2,4-Dimethyl-1-heptene	C9'	126
PS	Styrene trimer	SSS	91
ABS	2-Phenethyl-4-phenylpent -4-enenitrile	SAS	170
SBR	4-Phenylcyclohexene	SB	104
PMMA	Methyl methacrylate	MMA	100
PC	Bisphenol A	BPA	213
PVC	Naphthalene	Nap	128
PET	Benzoic acid	BA	122
N6	ε-Caprolactam	Capro	113
N66	Cyclopentanone	CP	84

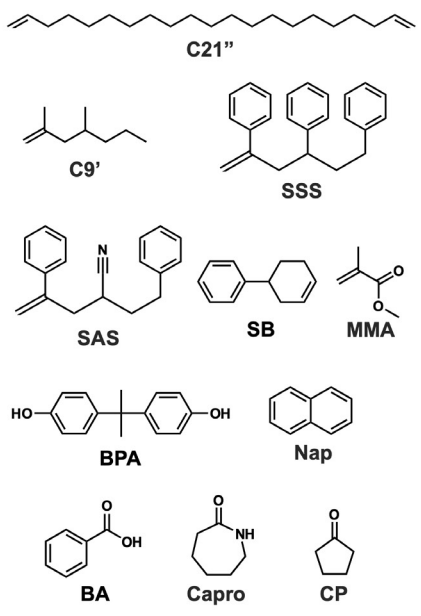


FIGURE 5: Results From F-Search MPs Library: Room #1

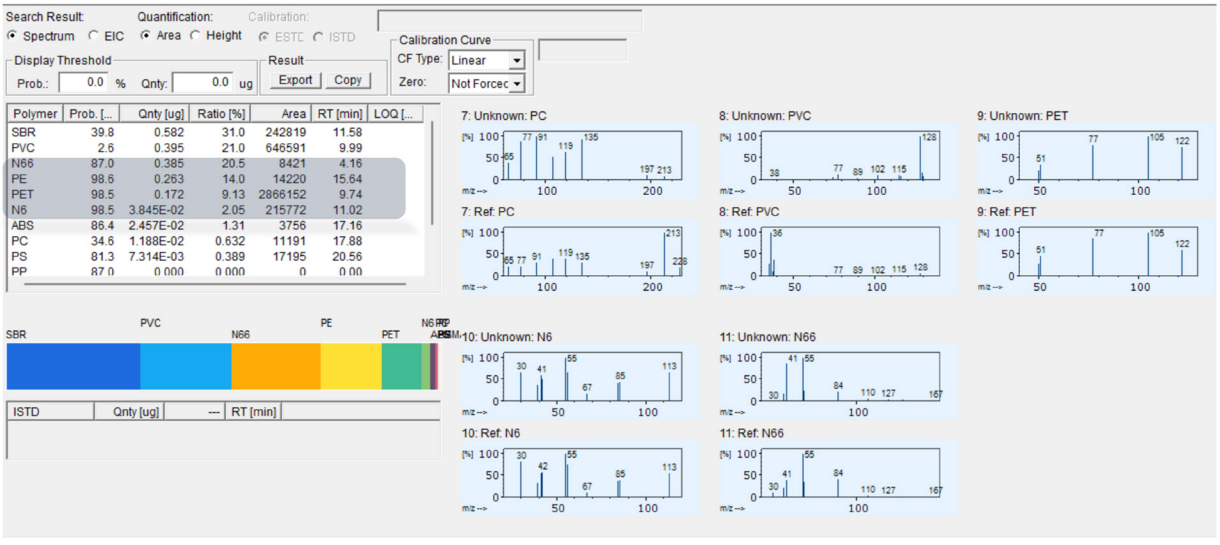
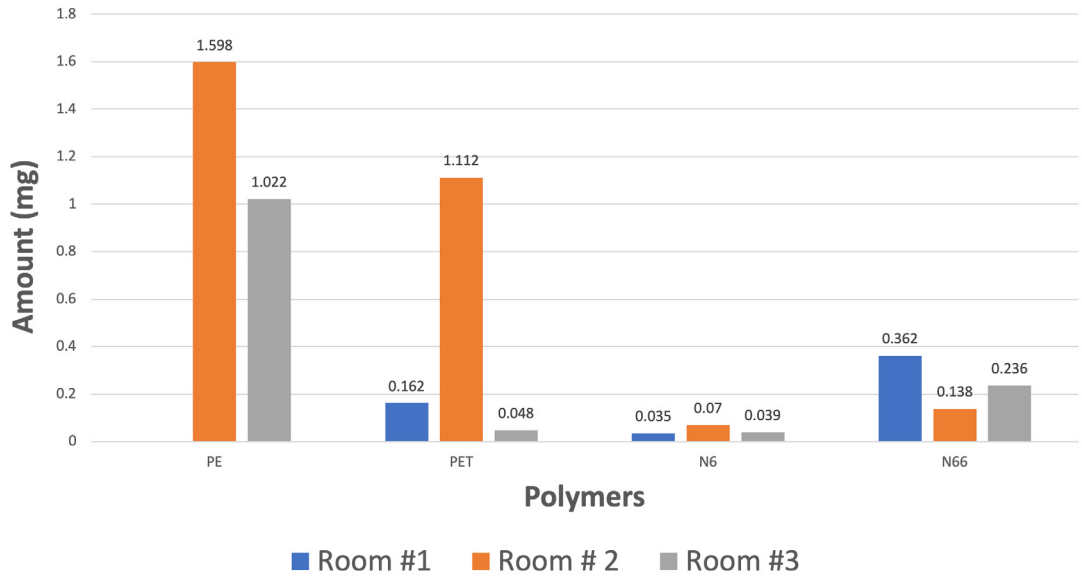


FIGURE 6: Comparison Chart - Amount of Microplastics/m^2/Day



CONCLUSIONS

Micro-Furnace Pyrolysis-GC/MS is a powerful technique for quantifying microplastics in the air, as well as other sample types. It enables analysts to develop simple workflows with easy sample preparation and analysis that deliver accurate and repeatable results. The IQ Mill 2070 cryogenic mill streamlines sample homogenization and preparation. Users can weigh the appropriate amount of sample using a semi-micro balance instead of an ultra-micro balance. The micro-furnace pyrolyzer deposits all the pyrolyzates directly and continuously on the GC column, preventing any cross contamination and dead volume. With the available reference materials, the F-Search MPs software can automatically generate calibration curves and identify target microplastics using its built-in library, as well as external libraries. This technique delivers results in much shorter timeframes than other available methods and is more amenable to automation while data accuracy and reproducibility is guaranteed.