

Accelerated Determination of Microplastics in Environmental Samples Using Thermal Extraction Desorption-Gas Chromatography/Mass Spectrometry (TED-GC/MS)

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Abstract

There is growing interest in quantifying microplastics in environmental samples. This application note presents a thermal extraction desorption-gas chromatography/mass spectrometry (TED-GC/MS) method that is well suited to automation and increased sample throughput. The method is also able to detect all particle sizes in the sample as long as the limit of detection (LOD) is reached and allows analysis of larger samples of 15 to 25 mg or more. Samples were decomposed by thermogravimetric analysis (TGA), and the gaseous decomposition products were trapped on a solid-phase sorbent, followed by thermal desorption-gas chromatography/mass spectrometry (TD-GC/MS) using an Agilent 5977B GC/MSD coupled to an Agilent 7890B GC. Target microplastic particle (MP) polymers were identified in environmental samples including surface water, finished compost, house dust, and drinking water. Quantification of MP polymers in environmental samples provided LODs of 0.06 to 2.2 μg , allowing the detection of MPs in trace amounts with sample weights of up to 1 g. Method repeatability was adequate for reliable quantification with RSDs of approximately 6 to 12%.

Introduction

Microplastic particles (MPs) are defined as any solid plastic particles insoluble in water with any dimension between 1 μm and 1,000 μm (ISO/TC 21960). Consisting mainly of synthetic polymers, MPs are observed nearly everywhere in the environment. Though, the systematic occurrence of MPs in environmental samples has not yet been sufficiently investigated, it is necessary to fully understand their relevant sources and entry pathways into the food and environmental ecosystem and to initiate sustainable prevention strategies. MPs are mainly formed in the environment by fragmentation of macroplastics, and remain for an uncertain length of time. This persistence increases the likelihood that MPs will be ingested and accumulated in organisms, the risks of which are unclear and the subject of controversy. As a result, there is increased interest in determining MPs in environmental samples such as soils, water, air, and organic matter.

MP analysis commonly relies on spectroscopic imaging techniques, such as infrared (IR) or Raman microscopy that provide particle numbers, and polymer chemical identity, geometry, and size distributions.¹ The disadvantage of these techniques is that they are often time-consuming and require extensive sample preparation. Small particles (<10 μm) cannot directly be analyzed by spectroscopic imaging, but are expected to be the relevant fraction for toxicology. Quantification of MPs in environmental samples using traditional GC/MS or LC/MS methods has been challenging, because of their very high molecular weights and poor solubility in most solvents.

Thermo-analytical methods offer an alternative. Complementary to imaging techniques, they provide information on mass content that can be essential for regulatory and monitoring purposes. As temperature is increased, pyrolytic decomposition of polymers occurs, forming smaller molecules that can be analyzed using spectroscopic techniques such as IR spectrometry and mass spectrometry. In addition, the thermal decomposition products formed can generate structural information about the polymer analyzed. However using such evolved gas analysis tools for environmental samples produces unspecific signals, which cannot be unambiguously related to specific MP type. Pressurized liquid extraction in combination with pyrolysis-gas chromatography/mass spectrometry (Py-GC/MS) can provide reliable determination of MPs in environmental samples, however large quantities of solvents, some of which are not environmentally friendly, must be used and the additional extraction step carries the risk of particle loss or contamination.^{2,3}

Another approach, TED-GC/MS, is better suited to automation and increased sample throughput without an additional sample preparation step, including reproducible automated analysis of polymer decomposition processes.^{4,6} A further advantage of TED-GC/MS is its ability to detect all particle sizes in the sample as long as the limit of detection is reached. In this approach, the sample is decomposed by TGA and the gaseous decomposition products are trapped on a solid-phase sorbent, followed by TD-GC/MS. MP samples can be very heterogeneous. By using a TGA furnace with a relatively large oven, TED-GC/MS

allows analysis of larger samples of 15 to 25 mg or more, resulting in a more representative sample and eliminating the need to take multiple samples. This is in contrast to Py-GC/MS, where sample sizes are typically ten times less and thus require running ten times the samples to achieve the same degree of representation, while also potentially not covering a large enough sample volume to achieve homogeneity.

An instrument system developed by the Bundesanstalt für Materialforschung und -prüfung (BAM) in cooperation with GERSTEL GmbH & Co. KG adds a heated coupling device that enables a sample robot to transfer thermal desorption tubes from the pyrolysis gas flow of the TGA furnace to the TD-GC/MS system for automated analyses.⁴ This application note describes use of a 5977B GC/MSD coupled to a 7890B GC as part a complete automated TED-GC/MS system, which is exclusively available through GERSTEL and Agilent. Further details about the experimental setup and methodology are provided in the publications by Dümichen *et al.*,⁴ Altmann *et al.*,⁵ and Eisentraut *et al.*⁶

Experimental

TED-GC/MS instrumentation

TGA heats the sample in an inert atmosphere, during which measurements of mass versus temperature can be made. The technique is convenient, reliable, and robust for analysis of sample weights up to 1 g and temperatures up to 1,000 °C. TGA was performed using a thermogravimetric furnace equipped with an autosampler (TGA2, METTLER TOLEDO) and 150 µL alumina crucibles. Dümichen *et al* determined that a TGA purge gas flow rate of 30 mL/min N₂ is the best compromise between analyte response and contamination, and that a heating rate of 10 °C/min provides the best average response.⁴ The TGA parameters are provided in Table 1.

Connected directly behind the TGA furnace as an extension of the exhaust, the coupling device enables the vertical sample transfer required by the sample robot. The coupling was maintained at its maximum temperature of 240 °C and required two independent 3 mL/min N₂ flows to avoid contamination. Separating the TGA from the GC/MSD minimizes or eliminates contamination and overloading of the GC/MS from the relatively large amounts of natural organic matter or MPs that are decomposed during TGA, which is a concern with traditional Py-GC/MS.

Because nonpolar or semipolar compounds are the most important compounds released during polymer decomposition in MP analysis, poly(dimethylsiloxane) (PDMS) (Sorb-Star, ENVEA GmbH) was used as solid-phase sorbent agent to capture the components purged from the TGA furnace for subsequent TD-GC/MS analysis. Designed specifically for chemical analysis, the cylindrical PDMS adsorption bar was 2 mm by 20 mm (diameter by length). If desired,

GERSTEL's PDMS Twister devices may be used for similar results.

A Thermal Desorption Unit (TDU 2, GERSTEL) performed the thermal extraction step. It was mounted on top of the coupling device, allowing the TD tube to be automatically transferred by the sample robot based on the time program. Another TDU attached to the GC/MS performed the thermal desorption step.

The GC/MS system was a 7890B GC coupled to a 5977B GC/MSD. The 7890B GC was equipped with cryo-injection (CIS 4, GERSTEL). The analytes were cryo-focused in the cooling trap (CIS) at -100 °C using liquid nitrogen. When the thermal desorption process was completed, the trapped analytes were quickly reheated, separated, and analyzed by GC/MS. The TD-GC/MS parameters are presented in Table 2.

Table 1. TGA parameters for TED-GC/MS.

Parameter	Value
Model	METTLER TOLEDO large furnace TGA 2
Sample Mass	20 mg (standard conditions; but up to 1,000 mg possible)
Purge Gas	30 mL/min N ₂
Heating Rate	10 °C/min
Total Exhaust Flow	56 mL/min
Heating Range	25 to 600 °C

Table 2. TD-GC/MS parameters for TED-GC/MS.

Parameter	Value
Thermal Desorption	
Model	GERSTEL TDU 2
Mode	Splitless
Total Flow	24 mL/min He
Temperature Program	50 to 200 °C at 40 °C/min Hold at 200 °C for 5 min
Cryofocus And Injection	
Model	GERSTEL CIS 4
Mode	Solvent Vent
Temperature Program	-100 to 270 °C at 12 °C/s Hold at 270 °C for 3 min
Gas Chromatograph	
Model	Agilent 7890B gas chromatograph
Column	Agilent HP-5MS, 30 m × 250 µm, 0.25 µm
Flow Rate	1 mL/min He
Temperature Program	Hold at 40 °C for 1 min, 40 to 300 °C at 5 °C/min, hold at 300 °C for 3 min
Mass Spectrometer	
Model	Agilent 5977B GC/MSD
Interface Temperature	300 °C
Ion Source Temperature	230 °C
Quadrupole Temperature	150 °C
Ionization Mode	EI, 70 eV
Mode	Scan, 35 to 350 m/z (under specific circumstances 25 to 450 m/z for PE)

The complete TED-GC/MS instrument setup is shown in Figure 1. Water filtrate, air filter samples, neat polymers, soil, compost, and other materials filled into heat-resistant conventional or smart filter crucibles can be measured directly without additional sample preparation. In this approach, the total TED-GC/MS measurement time is approximately two hours and 30 minutes: one hour for TGA, one hour for GC/MS analysis, and about 30 minutes for GC cool down and TGA device bake out. After the thermal extraction step and during the GC/MS run, the TGA furnace can be cleaned by heating to 1,000 °C under oxidizing atmosphere. A new sample measurement can then be started after completion of the GC/MS measurement. Complete automation allows measurement of up to ten samples per day, including blank runs between measurements. In general, a sample mass of 20 mg is sufficient, but if needed, masses up to 1 g can be investigated.

Agilent MassHunter GC/MS Acquisition Software revision B.07.04.2260 was used for data acquisition. Agilent Enhanced ChemStation software revision F.01.03.2357 was used for data analysis.

Samples

TED-GC/MS allows routine determination of the polymers commonly used in manufacturing, and thus of environmental concern, including those in tire materials. Polymers determined in this study were polyethylene (PE), polypropylene (PP), polystyrene (PS), poly(ethylene terephthalate) (PET), polyamide (PA), poly(methyl methacrylate) (PMMA), and styrene-butadiene rubber (SBR), which is associated with tire materials. Several different types of samples were analyzed to demonstrate method applicability to MP detection:



Figure 1. Complete TED-GC/MS instrument setup with the TGA furnace (right) and coupling device (top). The TD-GC/MS system based on the Agilent 5977B GC/MSD (left), and sample robot. The patented smart filter crucible is shown bottom right. Photos courtesy of BAM.

- Fractions of filtered surface water
- Finished compost
- House dust
- Drinking water in PET bottles

The technique is versatile and allows other experiments, such as the analysis of a PE/PP blend with unknown relative weight mass⁵ and the determination of adsorbed pollutants on activated carbon from wastewater treatment filters that were analyzed per Dittmann *et al.*⁷

Polymer identification

The polymers in the MP samples were identified via detection of the

characteristic fragment ions associated with their decomposition products and retention times (t_R) (Table 3). Polystyrene deuterated on the benzene ring (d_5 PS) was used as an internal standard to provide a relative reference value for measurement quality control. One decomposition product of the internal standard is the deuterated dimer of styrene d_{10} -(2,4-diphenyl-1-butene) with the characteristic fragment ions m/z 96 and 218, which can be distinguished from the decomposition product of PS (2,4-diphenyl-1-butene) at m/z 91 and 208 using MS, but also by chromatographic separation.

Table 3. Specific polymer markers and characteristic fragment ions.

Polymer	Polymer Marker (Decomposition Product)	t_R (min)	Characteristic Fragment Ion(s) (m/z)
PE	1,14-Pentadecadiene	23.4	55 or 81
PP	2,4,6,8-Tetramethyl-10-undecene	18.8	111
PS	2,4-Diphenyl-1-butene	28.7	91 or 208
PET	Ethyl benzoate	15.3	105
SBR	Cyclohexenylbenzene	19.6	104
PA 6	Caprolactam	18.0	113
PMMA	Methyl methacrylate	3.7	69 or 100

Polymer quantification

Quantification of polymers is typically performed using standard addition. By rerunning samples after adding polymer standards in known amounts (available from BAM), the change in peak response was used to determine polymer mass contents.

A faster alternative is the use of response factors obtained from one-point calibration experiments or external calibration where polymers in various levels are added to suitable plastic-free matrices. It was determined that for samples from the same or similar origin, a standard addition for a single, carefully selected sample was suitable for quantification of the entire set of samples.

In the fractions of filtered surface water, PE and SBR were dominant, but small amounts of PP and PS were also found. A component of tires, SBR is mainly

identified in the fractions <100 μm . A total of 73 $\mu\text{g/L}$ of target polymers was found in the surface water.

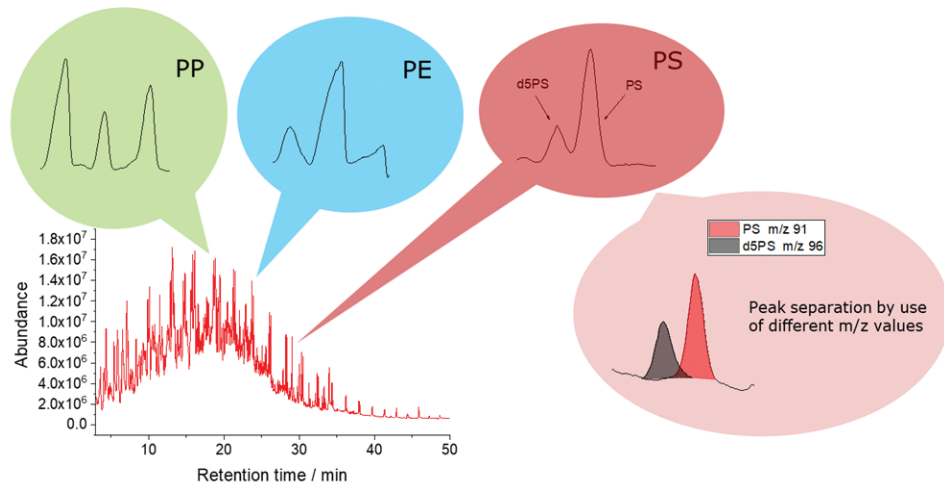


Figure 2. Total ion chromatogram (TIC) from the TED-GC/MS analysis of an environmental sample. The insets show extracted ion chromatograms that were used to identify the polymers based on their characteristic ions.

Results and discussion

Identification and quantification

Excellent separation and detection of the polymer decomposition markers of PE, PP, PS, PET, PA, acrylates, and SBR by TED-GC/MS using the 7890 GC and 5977B GC/MSD was obtained (Figure 2 total ion chromatogram, TIC). Polymer identification was achieved by analysis of the extracted ion chromatograms using the characteristic ions.

The results for the samples quantified using standard addition are presented in Figure 3. The total polymer content found in house dust and compost was 21 $\mu\text{g/mg}$ and 13 $\mu\text{g/mg}$, respectively. However, the polymer compositions of the samples differed. In house dust, the fiber polymers PET, PA, and PP were found in the highest amounts, while the compost mainly included PE and PP, which are polymers commonly used for packaging.

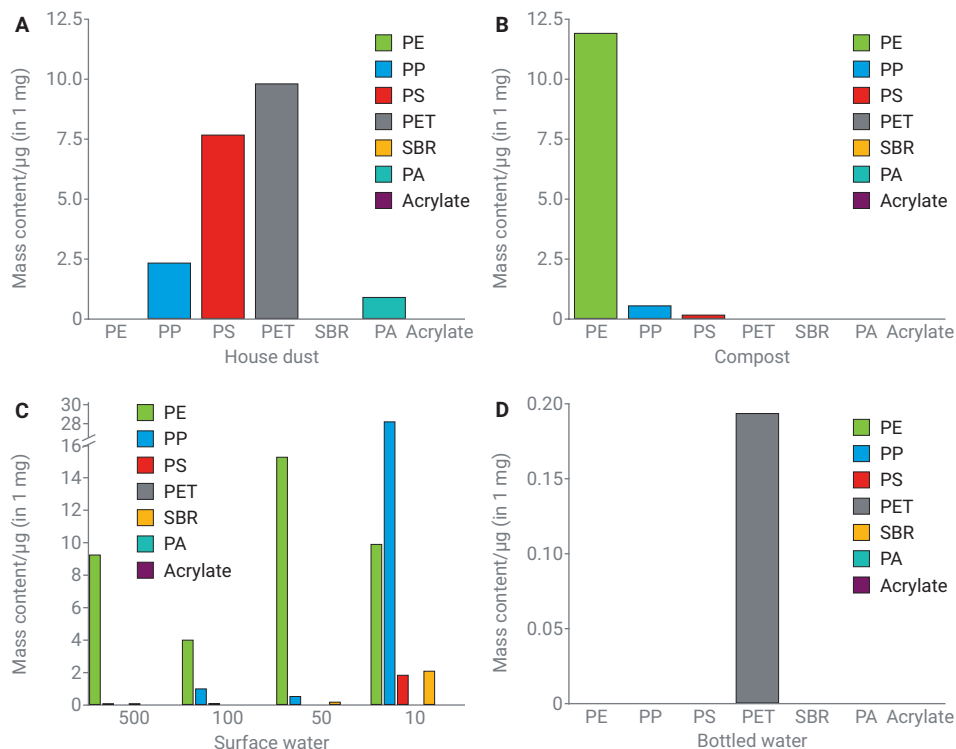


Figure 3. MP polymer content found in house dust, finished compost, surface water, and bottled water by TED-GC/MS. In the surface water analysis chart, the bars show the MP content of the different particle fractions in μm resulting from the sampling.

Because bottled water typically contains lower levels of MP, a filter crucible with 5 µm pore size was used. Up to 10 L of bottled or tap water were poured directly onto the filter and filtered using vacuum filtration with subsequent drying and analysis of the filter contents. A total of 0.193 µg/L of PET was found in the bottled water.

Limit of detection (LOD)

The LOD values for eight polymers were calculated on the basis of a quintuple signal-to-noise ratio. The LOD values were determined for the neat polymers without environmental matrix and for the respective polymer in fluvial suspended particulate matter (SPM). Six conventional standard polymers (PE, PP, PS, PET, SBR, and PMMA) were analyzed. Also analyzed were two biodegradable polymers, polylactide (PLA) and polybutylene adipate terephthalate (PBAT) with the specific decomposition products 3,6-dimethyl-1,4-dioxan-2,5-dione ($t_r = 13.9$ minutes, $m/z = 56$), and terephthalic acid dibut-3-enyl-ester ($t_r = 34.7$ minutes, $m/z = 203$).

Figure 4 presents the LODs of the neat polymers and in the presence of an environmental matrix. Method sensitivity for the various neat polymers differed as shown by their LOD values: high (LOD <0.2 µg; e.g. PP, PS, SBR, and PMMA), medium (LOD <0.5 µg; e.g. PET, PBAT, and PLA) and low (LOD >2.0 µg; e.g. PE). The addition of an environmental matrix, in this case SPM, resulted in increased LODs for all polymers analyzed. In conclusion, the matrix-induced increases in LOD were polymer-specific and probably influenced by their respective thermal decomposition mechanisms.

Repeatability

The repeatability of the TED-GC/MS method using the 5977B GC/MSD was determined by measuring specific thermal decomposition products of PP (Table 4) in seven separate runs. The mass fragments with the highest intensities were chosen for integration,

and the integration values were normalized to the sample masses. The results showed good repeatability for reliable quantitation (Figure 5). Three of the degradation products had a Relative Standard Deviation (RSD) of approximately 6% (Table 4). Repeatability results could be improved using internal standards.

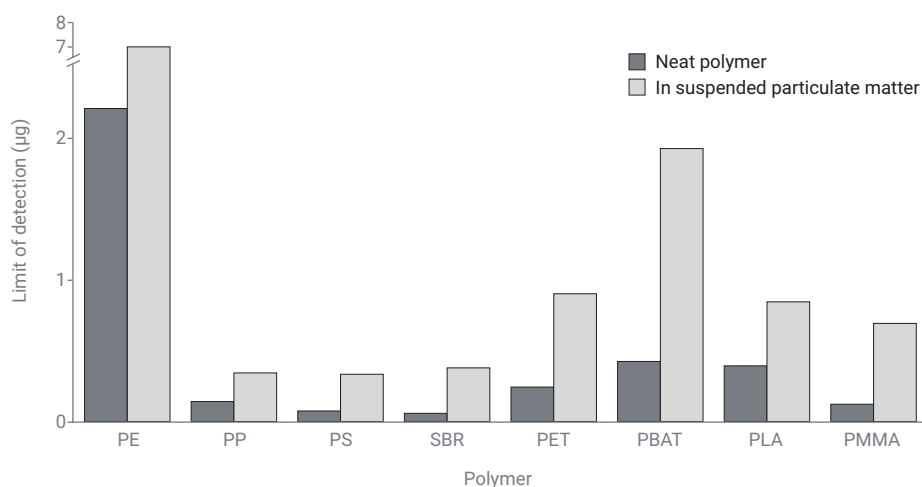


Figure 4. LOD values for the neat polymers compared to the LOD of the polymer in suspended particulate matter.

Table 4. Polymer products monitored in the repeatability experiment with %RSD.

Polymer	Name	Formula	t_r (min)	RSD (%)
PP1	2,4-Dimethyl-1-heptene	C ₉ H ₁₈	5.84	11.98
PP2	2,4,6-Trimethyl-1-nonene	C ₁₂ H ₂₄	12.50	5.17
PP2*	2,4,6-Trimethyl-1-nonene	C ₁₂ H ₂₄	12.62	6.85
PP3	2,4,6,8-Tetramethyl-10-undecene	C ₁₅ H ₃₀	18.97	5.89
PP3*	2,4,6,8-Tetramethyl-10-undecene	C ₁₅ H ₃₀	19.17	12.46
PP3**	2,4,6,8-Tetramethyl-10-undecene	C ₁₅ H ₃₀	19.42	8.11

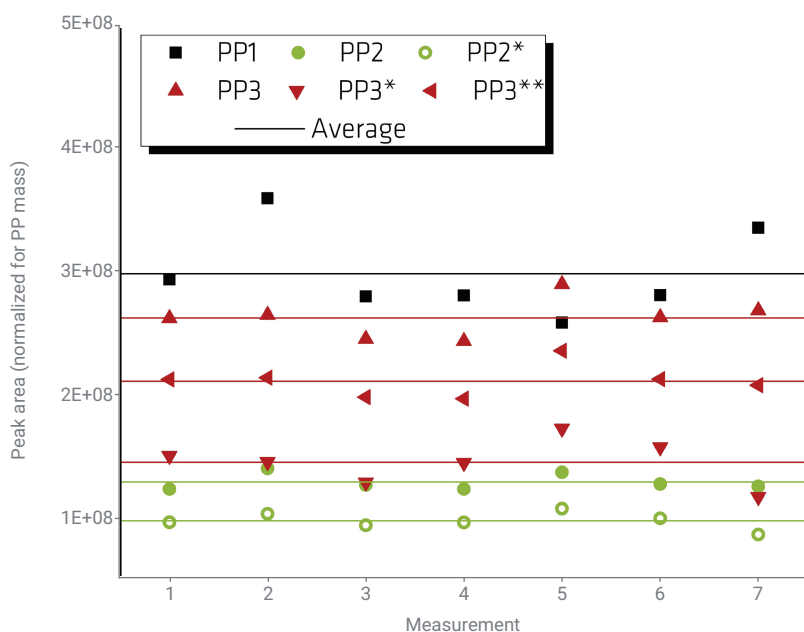


Figure 5. Integration results for the repeatability determination normalized to the sample mass for six selected decomposition product peaks. The average values are shown as a straight line.

Conclusion

Compared to other thermo-analytical approaches to MP measurement, TED-GC/MS using a thermobalance with the 7890B GC and 5977B MSD is well suited for reproducible automated analysis of polymers via their specific decomposition products. Target MP polymers were identified in a variety of environmental samples including surface water, finished compost, house dust, and drinking water. Quantification of MP polymers in environmental samples was performed by standard addition. The specific LODs of 0.06 to 2.2 µg for the different polymer types allow the detection of MPs in the trace amounts with sample weights of up to 1 g. Method repeatability was adequate for reliable quantification with RSDs of approximately 6 to 12%.

TED-GC/MS offers reproducible quantitation in addition to automation. Due to the limited capacity of the sorbent and the low desorption temperatures, the method is robust and minimizes concerns about contamination of the sensitive GC/MS equipment. The results are expressed in terms of mass contents, which enables use of the method for determination of legal limit values for regulation and monitoring. TED-GC/MS analysis is also promising for application to other scientific fields, such as the analysis of polymer blends with unknown relative weight mass and the determination of adsorbed pollutants on activated carbon from wastewater treatment filters.

Though it is possible to use Py-GC/MS for MPs determination, TED-GC/MS offers automation, simplified sample preparation, reproducible quantitation, and the ability to analyze sample weights up to 1 g by weighing samples into crucibles. Analyzing the same amount of sample by Py-GC/MS would require running multifold samples, and consequently much more analysis and data-evaluation time. The ability to analyze larger sample amounts is also important due to the heterogeneous nature of MP samples. In addition, with the limited capacity of the sorbent and low desorption temperatures, overloading the GC/MS is less likely, making the method robust and without contamination concerns for long-term usage. The fast measurements provided by TED-GC/MS provide a new path to more widespread monitoring of MP pollution.

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