

Hyphenation (TG-GC/MS)

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Analysis of Microplastics in Suspended Solids with TG-GC/MS

Introduction

Microplastics are a major concern due to their impact on the environment. There is growing research into microplastics, typically submillimeter in size, and which

often end up in waterways and oceans. They remain in a suspended state and can be ingested by marine organisms; thereby entering and accumulating within the food chain.

This application note describes a powerful analytical technique to measure constituents of microplastics, the most common being polyethylene (PE), polypropylene (PP) and polystyrene (PS).

Material thermal decomposition analysis is commonly done by mass spectrometry in decoupled mode. The products are accumulated and analyzed indirectly thereafter. Unfortunately, this often results in insufficient information on the identity of the degradation products and little to no information on when degradation products are formed.

Hyphenated thermogravimetric analysis (TGA) and gas chromatography mass spectrometry (GC/MS), referred to as TG-GC/MS, enables in-depth characterization of evolved gases through real-time analysis of the products resulting from the thermal decomposition of the suspended microplastic matter. This results in greater information on the identity of the degradation products as well as details on when the degradation products are formed.

Experimental Setup

A hyphenated TG-GC/MS system is used, consisting of:

- PerkinElmer TGA 8000™
- PerkinElmer TL 8500e transfer line
- PerkinElmer Clarus® 690 GC/SQ8 MS

Table 1. Parameters used for the TGA system.

TGA Parameters (TGA 8000)	
Start Temperature	30 °C
End Temperature	700 °C
Heating Rate	20 °C/min
Purge Gas	Nitrogen 35 mL/min
Sample Pan/Mass	PerkinElmer Ceramic Pan Part.no. N5370464
TL8500e Temperature	280 °C

The TGA 8000 heated adapter valve is intrinsically immune to over-pressure with flow control and an exhaust tube at the bottom of the furnace. The sniffer tube is located next to the sample pan to reach the native gas, preventing gas condensation on the furnace walls. The TGA 8000 furnace design results in negligible dead volume. Additionally, the valve design permits it to be easily closed enabling the TGA 8000 to run as a stand-alone instrument.

Dead Volume is the unmoving, stagnant or un-swept volume of gas trapped in the TGA furnace space. Over time the stagnant gas deposits over the surfaces and can deleteriously affect the TGA balance mechanism, creating problems for the normal TGA function. Passive systems often lead to both furnace temperature and pressure increases, that can result in:

- Sample destruction, resulting in the loss of valuable data from the GC/MS instruments;
- Damage to the TGA furnace itself; and
- Even risk of injury to personal using the instrument.

Table 2. Parameters used for the GC/MS system.

GC Parameters – Clarus 690	
Injector Type	Sample loop 100 µl Volume
Carrier Gas	Helium
Carrier Gas Flow Rate	2.0 mL/min
Temperature Program	
Initial Oven Temperature	30 °C
Oven Hold	4 min (isotherm) @30 °C
Ramp 1	50 °C/min to 80 °C
Ramp 2	5 °C/min to 280 °C
Oven Hold	5 min (isotherm) @ 280 °C
Column	PerkinElmer Elite-624ms Capillary Column (30m x 0.25mm, 1.40µm) Part No. N9315068 This column provides excellent peak shape for a wide range of compounds used.
MS Parameters – SQ8	
Mass Range (amu)	30 – 300 amu
GC Inlet Line Temp	280°C
Ion Source Temp	Electron Ionization
Ion Energy	70 V

The best means of addressing dead volume is through active hyphenation (figure 1) combined with optimal TGA furnace design. An **active hyphenation** system sucks gas partially from the TGA furnace and leaves a little amount to the exhaust outlet. The TGA 8000 Dead Volume is deemed negligible compared to other TGA instrument at 100ml.

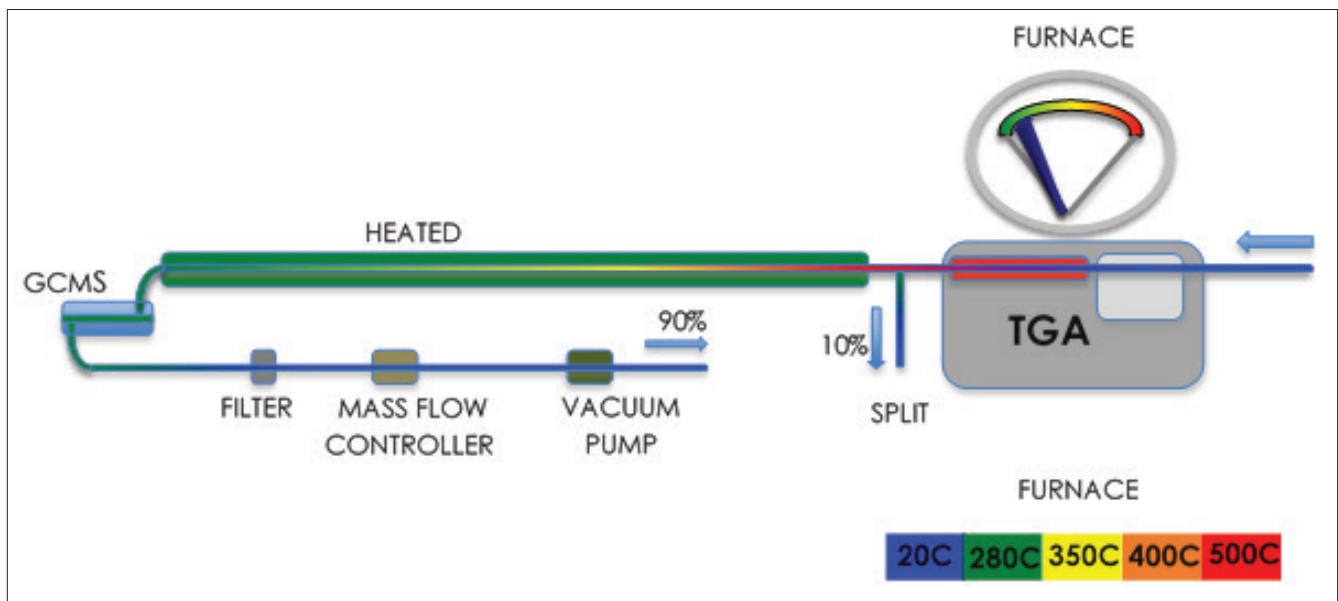


Figure 1. Schematic showing Active Hyphenation flow control instead of the pressure, the Transfer Line is constantly heated up to a max 350°C.



Figure 2. TG-GC/MS system.

The TG-GC/MS transfer line (TL 8500e) enables gases evolved in the heating of a sample in a TGA system to be transferred to a GC/MS instrument for identification and quantification. The advanced digital control unit incorporates temperature controlling devices, mass flow controller (MFC), flow smoothing system, filters and pump with exhaust line. The heated high-temperature transfer line uses the principle of active balanced flow to prevent condensation and gas deposits along the path. The double valve block of the transfer system is an external oven installed over the GC next to the FID position. The high temperature valve block enables the isolation of the GC/MS during stand-by mode or when the TGA furnace is open or not in use. Evolved gases are injected with a sampling loop into the GC column and then passed through the MS only when set by the trigger. There is the

option to switch to MS online directly through the valve and controller configuration without any manual changes. The mass spectrometer is flushed continuously with helium (a different carrier gas can also be used). The unique PerkinElmer design ensures no cold spots, no carry over, and no capillary clogging. Smart trigger mechanism enables automatic triggering by time or weight loss. The temperature ramp in the transfer line reduces the risk of a secondary degradation and preserves volatile sample integrity. The FAST GC capability enables the analysis of 2 events in a single run; $\geq 80\%$ time saving. The TGA can be used as a standalone instrument without decoupling from the system, allowing use of the system for multiple purposes. The TGA 8000 designed for Evolved Gas Analysis (EGA) hyphenation is equipped with an autosampler leading to additional time-savings.

Approach

The initial goal is the examination of the pure polymers in order to define the parameters used for the experiment. Therefore, the decomposition characteristics of the frequently used polymer (PE, PP, PS) in the packaging industries is investigated. A pre-run analysis of the pure thermoplastics is examined thermogravimetrically and the decomposition temperatures are determined. For each polymer a temperature range for the release of decomposition gases can be defined (Figure 3).

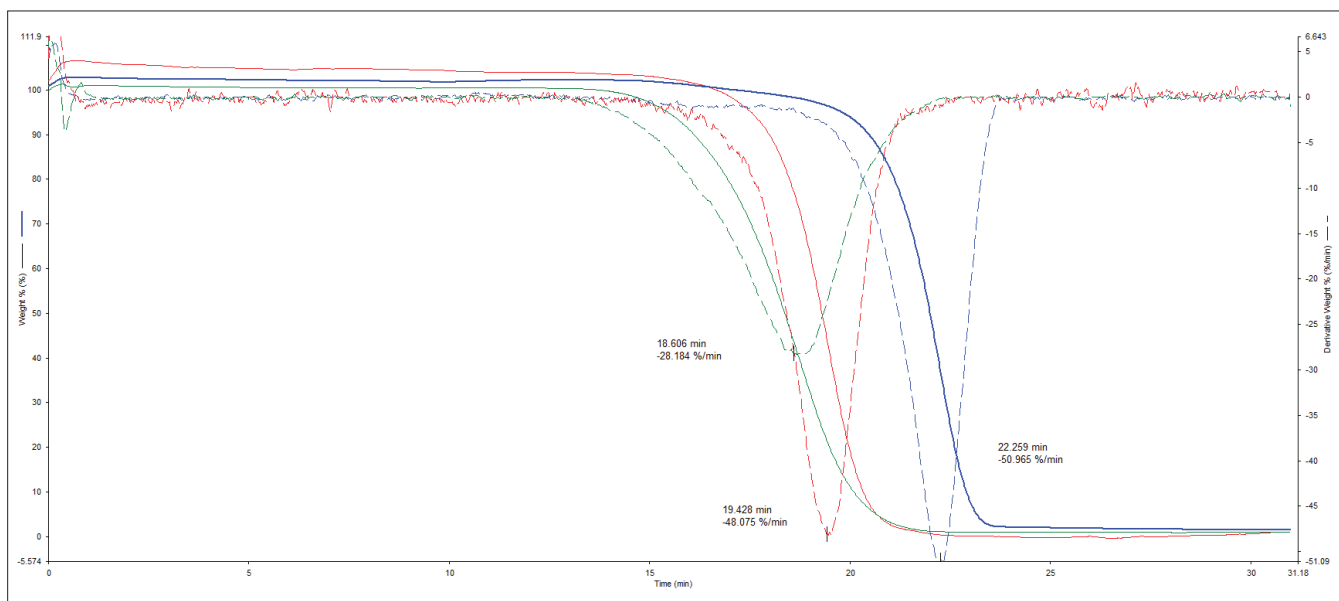


Figure 3. Different decomposition temperature areas for pure samples.

Table 3. Table with TGA curve legend and decomposition temperatures areas.

	Color of TGA Curve	Different Decomposition Temperature Areas for Pure Samples
PE	blue	440 – 490°C
PS	red	390 – 430°C
PP	green	360 – 430°C

Mixing the three polymers of interest together yields a thermogram where the whole degradation takes place in around 4 minutes (between 18 and 22 min depending on heating rate). Upon closer inspection two trigger points are set at 19 and 22 min for collecting two times a 100µl gas volume assuring to get all three samples and injected it on the column head. Both injections are trapped on the GC column at low temperature (see Table 2), before running. Therefore, the time interval used on the GC is about 3 to 4 minutes. During this time, the sample must be trapped on the GC column at a low temperature (see GC temperature program).

A simulated soil sample contaminated with microplastic was mixed and analyzed with TG-GC/MS to determine if the known contaminants could be identified. The composition of the sample is shown in Table 4.

Table 4. Absolute weights of the analytes.

Absolute Weight in mg		
Simulated Matrix	12.50	94.2%
PE	0.28	2.1%
PS	0.26	2.0%
PP	0.22	1.7%

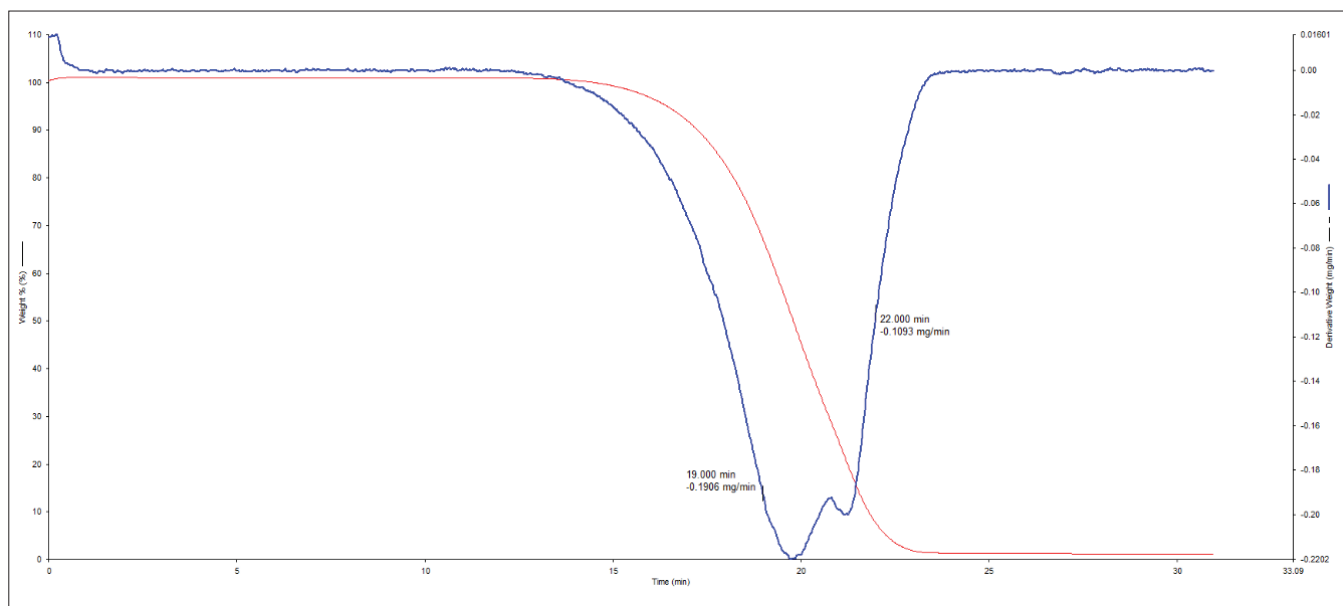


Figure 4. Setting trigger points, gas volume is drawn at 2 trigger points, depending on TGA heating rate. Trigger points used are 19 and 22 min.

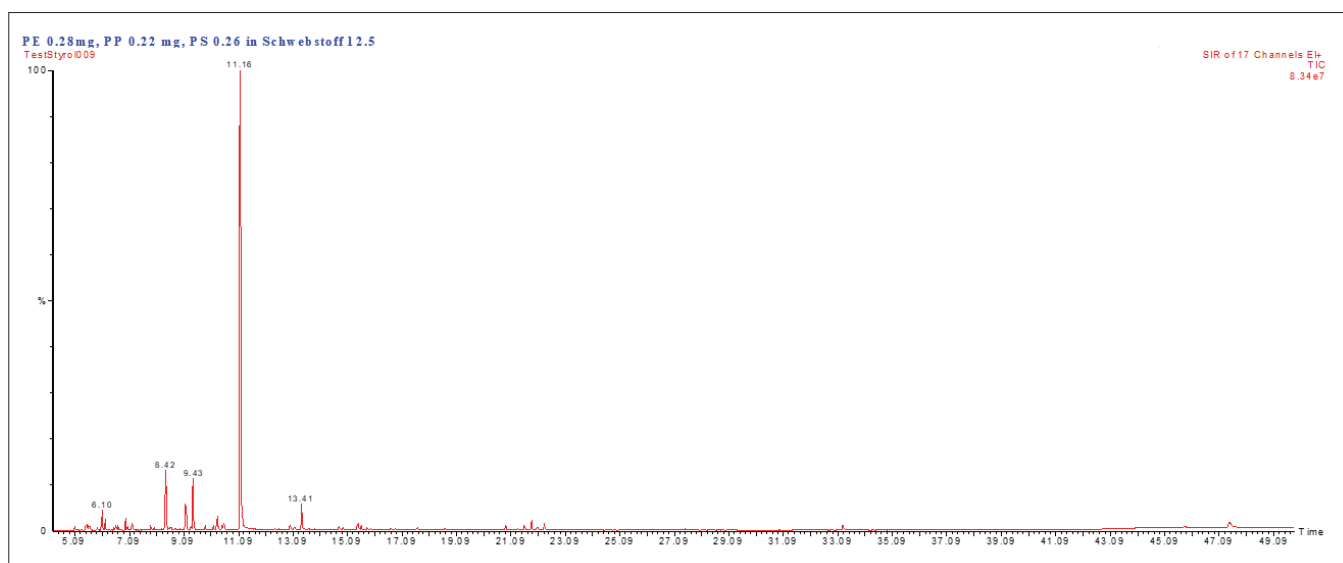


Figure 5. Total Ion Chromatogram (TIC) of PE, PP, PS in a simulated matrix.

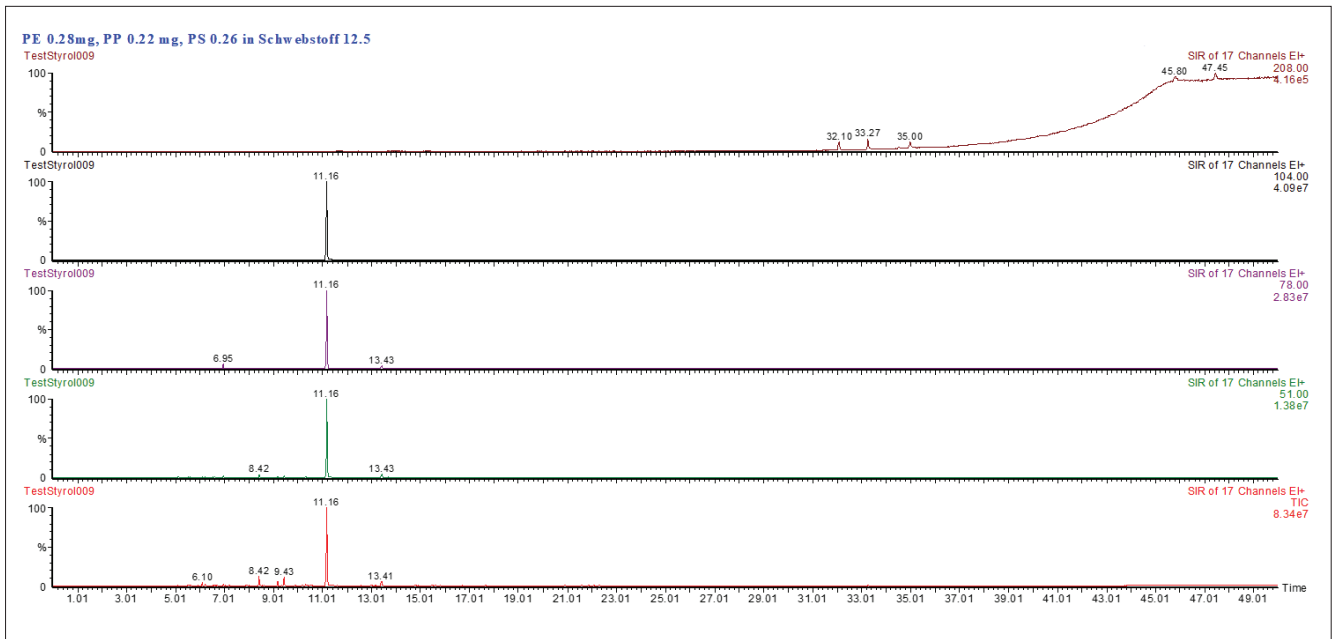


Figure 6. Detection of polystyrene over the individual masses 51, 78, 104. It shows that all PS mass fragments are found. The top trace shows the dimers on mass 208.

The next step is detection of the TGA signal of the substances in a run from simulated and samples from a lake near Berlin, Germany provided by the German Environment Agency (UBA), sometimes referred to as the German EPA. The analytes are mixed in similar parts with a simulated suspended matter matrix and searched for a suitable location in the thermogram, where a maximum of two samples on the GC column, the sample can be detected as a whole.

Table 5. Masses used for the analysis.

Analyte	Target Mass SIR m/z *				
PE – Polyethylene	55	69	95		
PS – Polystyrene	104	51	91	78 (208)	
PP – Polypropylene	69	111	97	85	Triplet

*see References section

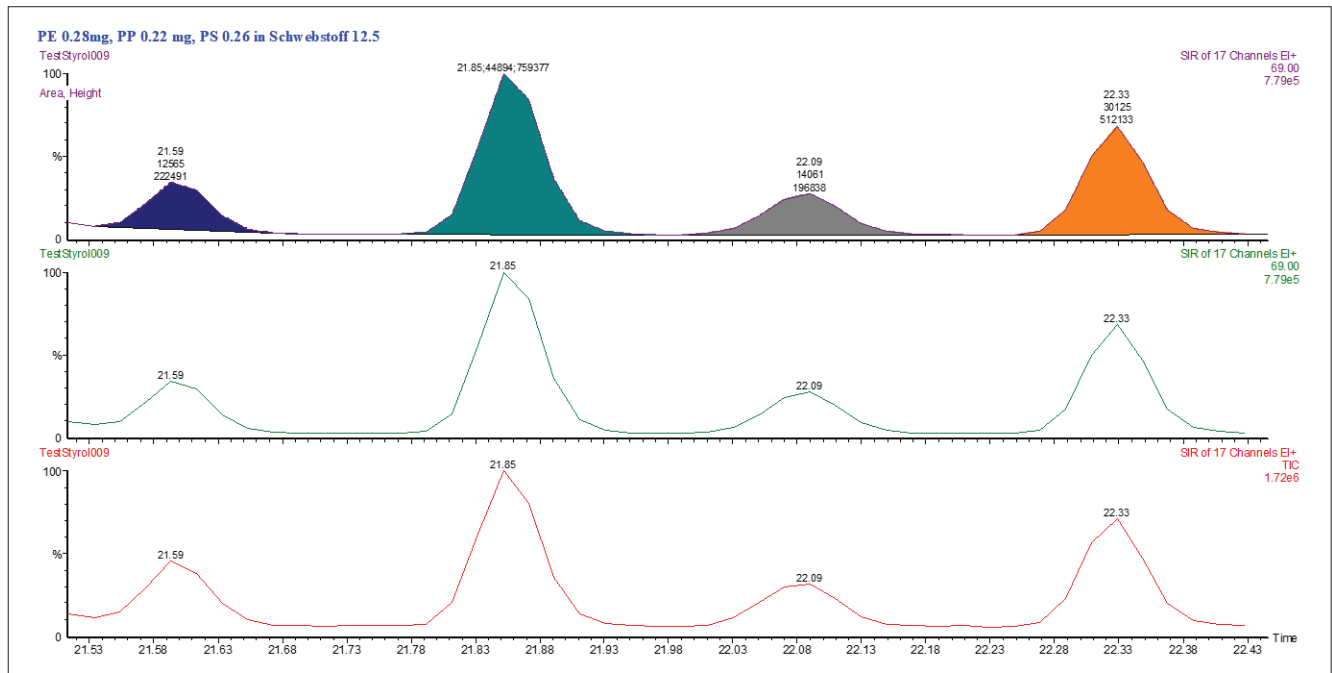


Figure 7. Detection of the polypropylene via triplet with mass 69. It shows clearly the specific triplet structure of PP. In addition, no overlays of other mass fragments can be seen.

Figure 8 shows MS data. Upon closer inspection, we see that all three analytes in the mixture are detected.

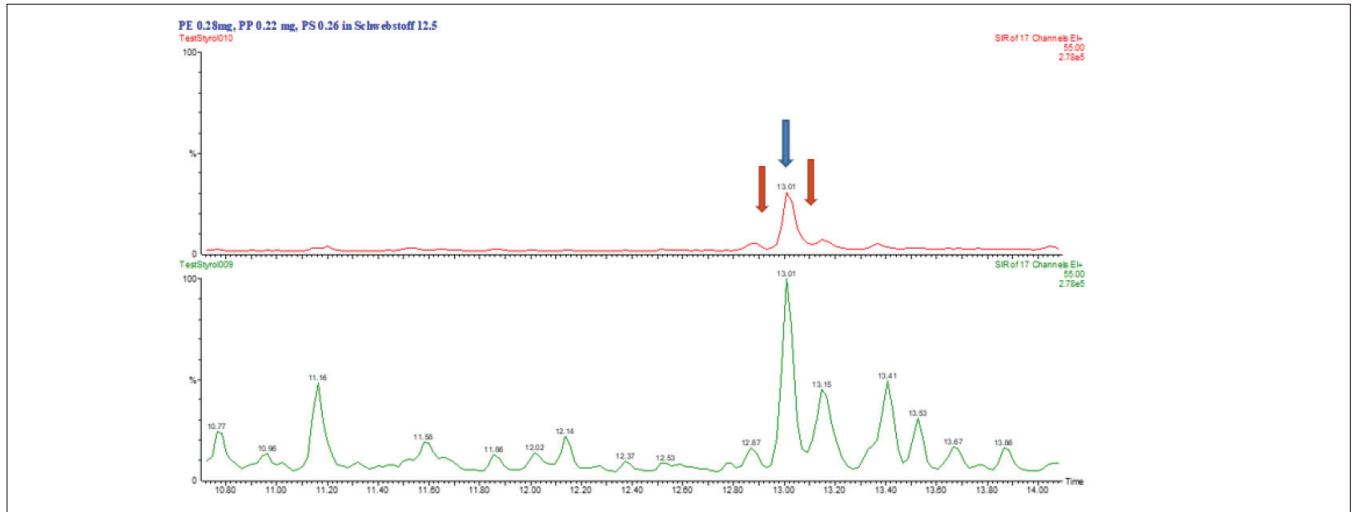


Figure 8. Detection of the polyethylene by mass 55, the triad of alkane, alkene and alkyne is crucial. The top trace shows PE in the mixture of pure substances, bottom trace in a simulated matrix.

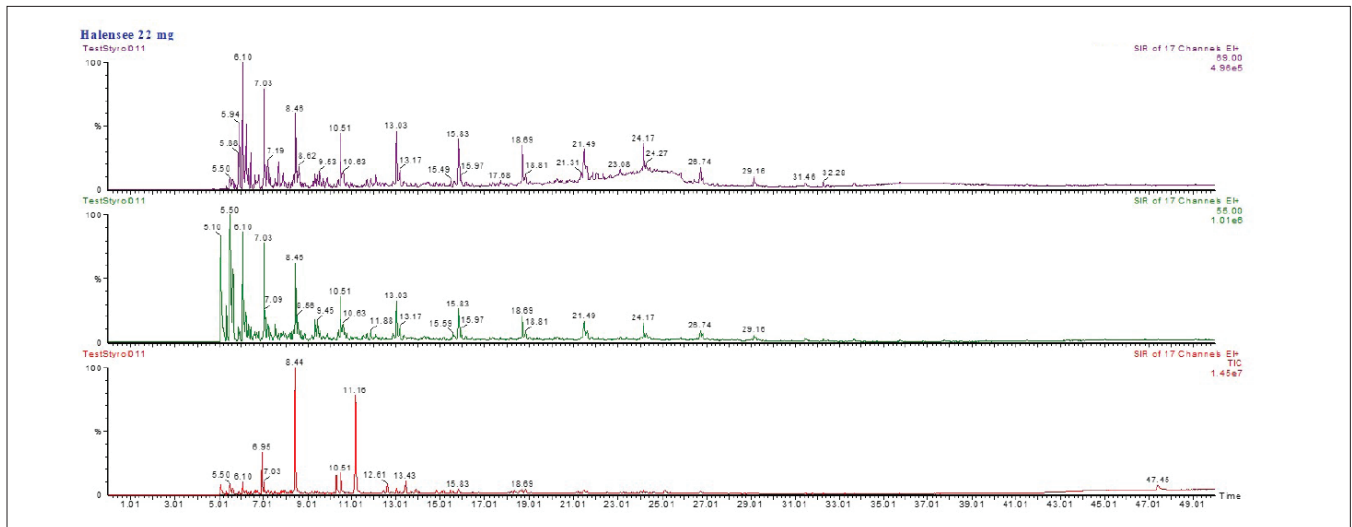


Figure 9. Detection of masses 55 and 69 provide proof that the Berlin lake sample contains PE.

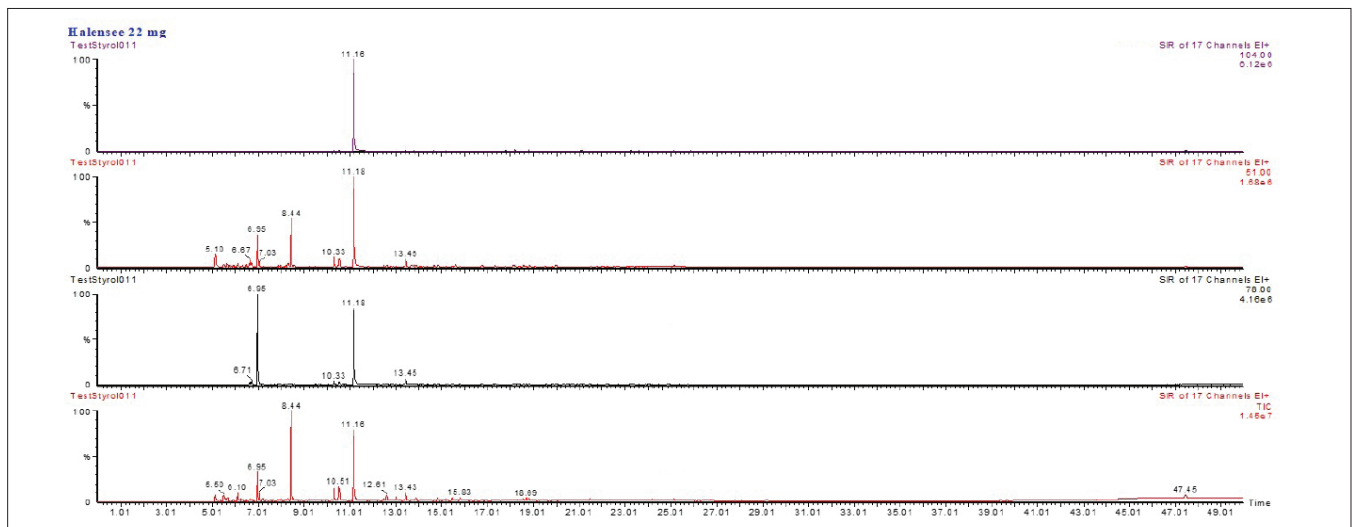


Figure 10. Detection of the ions at masses 51 and 78 giving proof that the Berlin lake sample contains PS.

The last step is the investigation of a Berlin lake sample with unknown polymers and concentration.

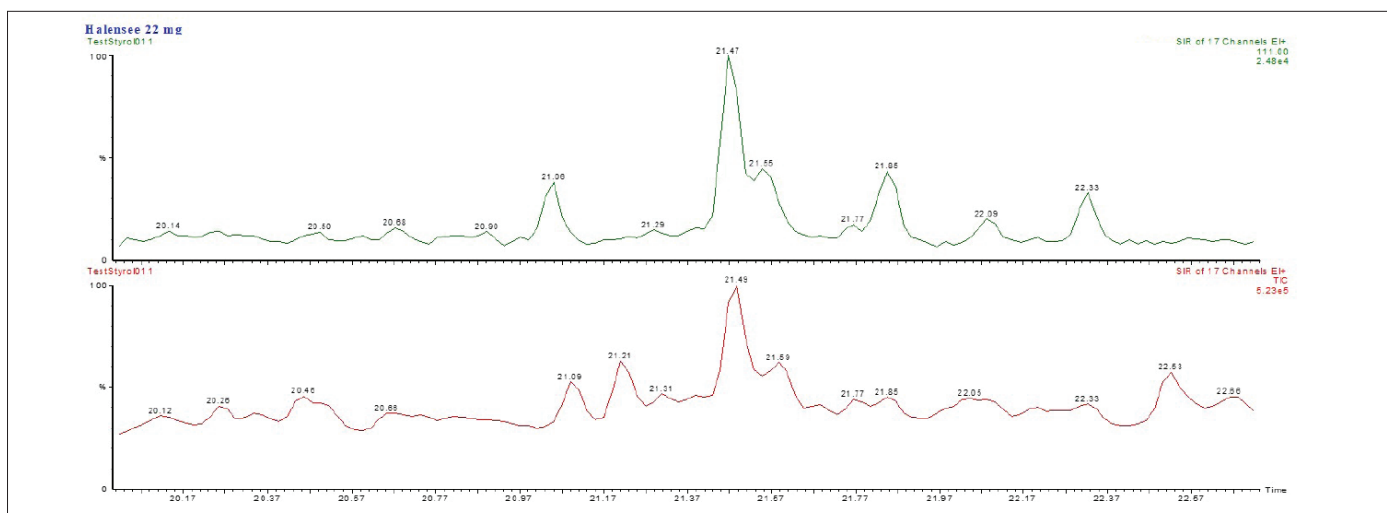


Figure 11. Berlin lake sample contains small amounts of PP.

Conclusion

This method demonstrates that without extensive sample preparation, the detection of microplastics in a matrix can be performed in a few hours of analysis time. The above examples demonstrate the advantages of a hyphenated TG-GC/MS system to analyze complex sample relationships. TG-GC/MS hyphenation technique is sensitive enough to carry out measurements without the need to perform additional sample separation or enrichment, in contrast to existing conventional methods. With the TG-GC/MS system, there is no need for an additional thermal desorption or lengthy measurement times as the GC/MS analysis has already started during the thermogram. The TG-GC/MS hyphenation technique provides greater detail and higher-resolution results. Matrix effects and overlapping events are irrelevant, since we concentrate on the release area of the analytes.

In addition, data can be obtained at more target times that have greater relevance to the analysis (if the thermogram shows "excitation"). The sample can also be taken several times and "isothermally" parked on the GC column (as shown in the example), start an isothermal GC run with multi-triggering (e.g. every 30 seconds) and record the degradation profile in the GC/MS (if there are only a few relevant components) or use Fast GC to start several independent GC runs at different times in the thermogram.

This offers significantly more options than currently available systems. Using the chromatography collected, we can separate gas mixtures without any confusion compared to inline/online measurement TG-MS or pyrolysis and therefore get a greater

resolution of the multicomponent mixtures contained in the gas phase. This makes it possible to analyze different weight losses with a coherent GC run. It is important to identify the analytes with the appropriate Selected Ion Recording (SIR) masses.

TG-GC/MS is a sequential analysis which resolves overlapping events, moisture and most of matrix (SPM) are split off. In parallel, it is possible to carry out a TG/MS without system re-configuration, which allows an overview of the entire thermogram. With both operating modes in one system and controlled by the thermobalance, this allows many combination variants enabling in-depth characterization of evolved gases.

References

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