GL Sciences

Application note: 137

Pyrolysis–GC–MS for Microplastic Analysis Using the OPTIC-4 Pyrolyzer; polyethylene terephthalate

Keywords

Pyrolysis, OPTIC, LINEX, Py–GC–MS

1. Introduction

Polyethylene terephthalate (PET) is a commonly used plastic in packaging, textiles, and other consumer goods. PET microplastics, generated from the breakdown of larger plastic materials in the environment, have raised significant environmental concerns due to their persistence and potential toxicological effects. Understanding the chemical composition and degradation behavior of PET microplastics is crucial for assessing their environmental impact and advancing recycling technologies.

Pyrolysis-GC-MS is a powerful analytical technique that allows for the detailed analysis of polymer degradation products. The OPTIC-4 thermal desorption system provides precise control over the pyrolysis process, and when coupled with the LINEX Liner Exchanger, it facilitates automated and reproducible sample introduction. This automation is especially valuable for the analysis of microplastics, where consistent sample handling and high throughput are essential.

The OPTIC-4 Pyrolyzer, paired with the LINEX automatic liner exchanger, facilitates precise and reproducible pyrolysis, while the ChromIdent software ensures reliable pyrogram identification and analysis.

This application note demonstrates the analysis of PET microplastics using Pyrolysis-GC-MS with the OPTIC-4 and LINEX Liner Exchanger, offering a rapid and reliable method for characterizing the thermal degradation products of PET microplastics.

2. Instrumentation

OPTIC-4 Pyrolizer – : A high-precision pyrolysis unit capable of rapid and efficient heating, offering a range of temperature control settings for different materials. The OPTIC-4 Pyrolyzer ensures that polypropylene is broken down into its constituent monomers and other pyrolysis products at controlled temperatures up to 700°C.

LINEX Automatic Liner Exchanger – The LINEX system automates the exchange of pyrolysis liners, ensuring a contamination- and oxygen-free sample introduction and maintaining reproducibility between sample runs. It is particularly useful when analyzing multiple samples of microplastics in a high-throughput setting.

GC–MS System – The GC is equipped with a non-polar column for optimal separation of pyrolysis products. The Mass Spectrometer operates in electron impact (EI) ionization mode for the identification of the pyrolyzed products.

ChromIdent Software – ChromIdent software is specifically designed for pyrogram analysis. It helps identify the chemical structures of pyrolysis products based on their

mass spectra and chromatographic retention times. ChromIdent also supports data interpretation and compares results with libraries of known pyrolysis products.

3. Experimental

A small amount of microplastic sample is weighed into a µ-vial . Following the µ-vial is put in a quartz liner, getting placed in a sample rack of the PAL3 xyz-autosampler. Once the GC–MS system is ready for analysis, the LINEX head for automatic tube exchanges opens and gives access to the OPTIC-4 Pyrolyzer. The PAL3, equipped with a LINEX Tool places the tube into the OPTIC-4 Pyrolyzer, after which the LINEX head closes. After closing the LINEX head, the tube is purged with carrier gas during 30 seconds at 50 ml/min. Once purging is finished, the tube is rapidly heated with 60°C/sec to 700°C, where it is held during 10 seconds. The pyrolysis products are transferred to the capillary column with a split flow of 100 ml/min. For GC separation of the pyrolysis products, the GC oven starts at 40°C where it is held during 2.0 minutes. Then, the GC oven is ramped with 10°C/min to 350°C where it is held during 3.0 minutes. The capillary column is a 30 m × 0.25 mm × 0.25µm InertCap 5HT from GL Sciences with 5 m ProGuard capillary, The ProGuard prevents for bleeding products from the head of the capillary being connected to the OPTIC-4 Pyrolyzer. The helium column flow is constant at 1.5 ml/min. The mass spectrometer is running in scan mode in the mass range 29 – 800 amu, after a delay of 1.5 minutes. Figure 1 gives a schematic overview of the LINEX on top of the OPTIC-4 Pyrolyzer with the connected capillary column. All analytical conditions are summarised in Table 1. Figure 2 gives an impression of the workflow.

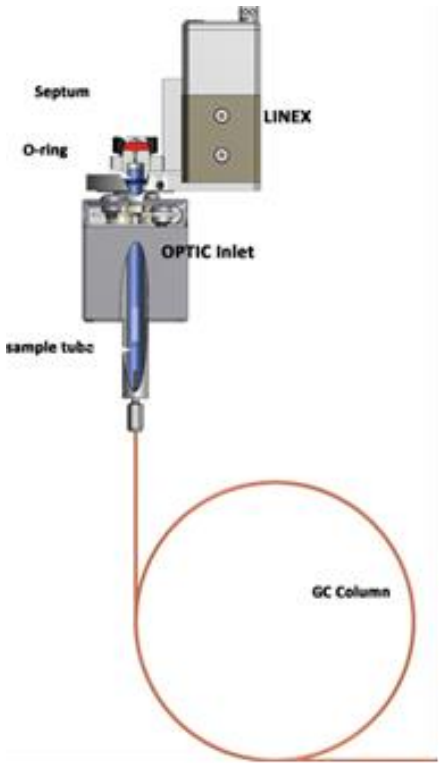

Figure 1: Hardware setup. The LINEX opens/closes the head of the OPTIC automatically to enable the placement/removal of the sample tube, containing a µ-vial with the microplastic sample.

Table 1: Analytical conditions.

Parameter	Setting
OPTIC-4 Pyrolyzer	
Sample	1 mg Polyethylene terephthalate
Tube	Quartz DMI Liner [2414-1018] containing a µ-vial [2406-1020]
Purge flow	50 ml/min
Temperature	40°C(10 sec) – 60°C/sec – 700°C(10 sec)
Column flow	1.5 ml/min
Gas Chromatograph	
Temperature	40°C(2.0 min) – 10°C/min – 350°C(3 min)
Capillary column	InertCap 5HT ProGuard 5m, 30+5m × 0.25 mm × 0.25µm [1010-90926]
Mass Specrometer	
Delay	1.5 minutes
Mass Range	29 – 800 amu

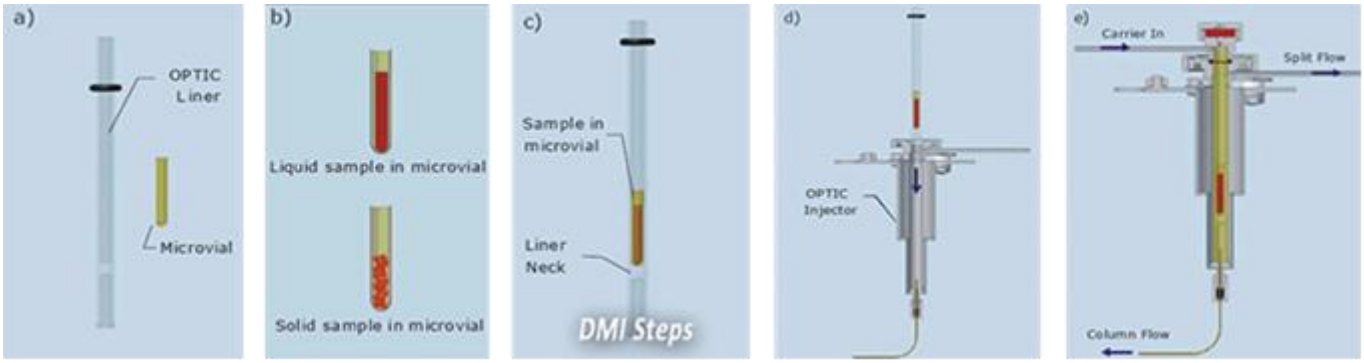

Figure 2: Impression of the workflow.

4. Results

The thermal degradation of PET microplastics produced a range of degradation products, primarily consisting of the monomers ethylene glycol and terephthalic acid. Other significant products included oligomers and smaller volatile organic compounds, such as benzene and toluene, which are typical of the degradation of aromatic polyesters like PET. The analysis revealed that, as expected, the pyrolysis of PET microplastics predominantly leads to the formation of smaller aromatic and aliphatic hydrocarbons, reflecting the breakdown of the polymer's ester linkages.

The pyrolysis products were successfully separated using the InertCap 5HT ProGuard column, which provided high resolution for the volatile degradation products. A characteristic series of peaks was observed, corresponding to both

monomers and smaller oligomeric compounds. The mass spectra of these compounds were consistent with the degradation products reported for PET, with well-defined peaks matching known fragmentation patterns.

The use of the LINEX Liner Exchanger for automated sample introduction enhanced the throughput and reproducibility of the analysis. Automated liner exchange reduced the potential for contamination between samples and ensured that each sample was introduced in a consistent manner. This automation is particularly beneficial for high-throughput analyses, such as those required for environmental monitoring or large-scale studies of microplastics.

The total analysis time per sample was approximately 30 minutes, including pyrolysis, chromatographic separation, and mass spectrometric detection. This rapid analysis time makes the system ideal for analyzing large numbers of PET microplastic samples in a relatively short period. The LINEX Liner Exchanger further optimized sample handling, allowing for automated sample introduction and reducing manual intervention.

Besides the typical pyrolysis products of PET, this polymer produces a very distinctive Pyrogram. Figure 3 presents the Pyrogram of PET using the OPTIC-4 Pyrolyzer. The compounds mentioned above are identified by their mass spectrum.
An additional way for microplastic identification is the summed Total-ion-current (TIC) mass spectrum, over the whole pyrogram. Figure 4 presents the summed TIC mass spectrum of the pyrogram in Figure 3.

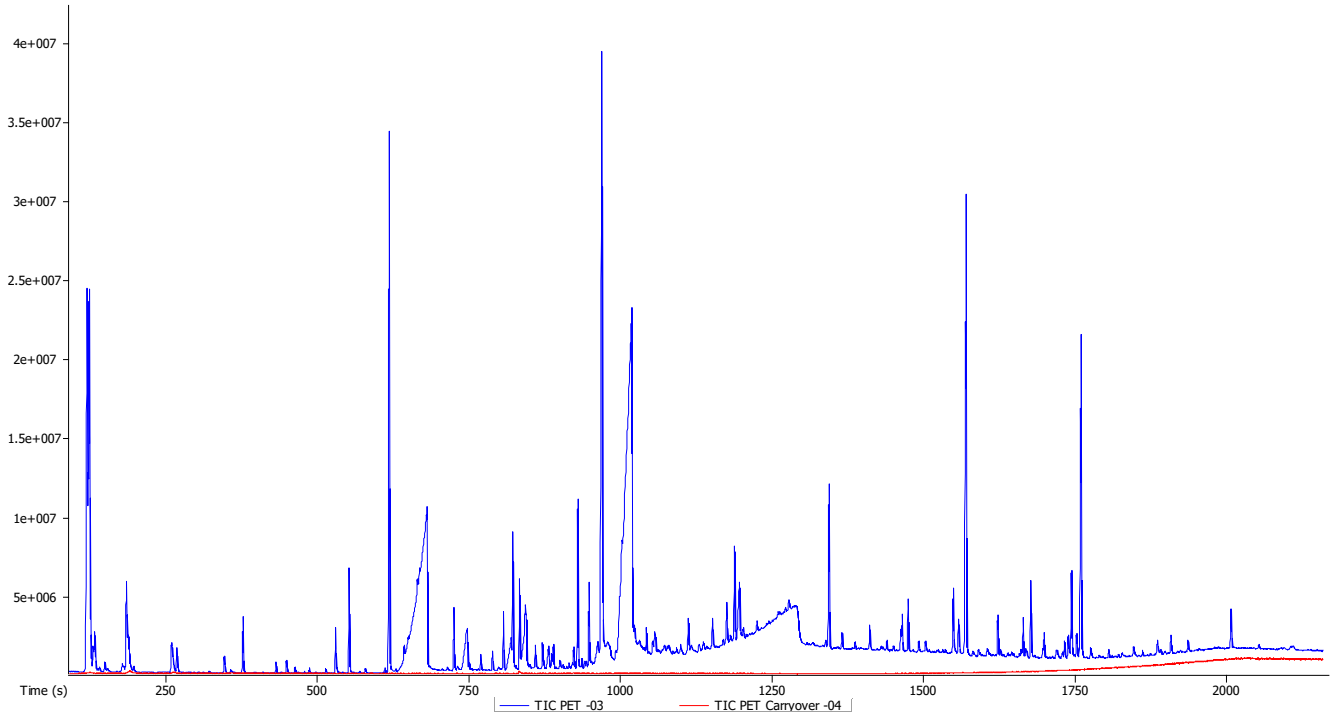

Figure 3: Pyrogram of PET. Blue, Pyrogram; Red, blank run after pyrolysis-run.

By utilizing ChromIdent software, the pyrolysis products are easily identified based on their mass spectra, and their chemical structures are confirmed through the comparison with known reference libraries. The software compares the retention times and mass spectra of the identified peaks against an internal library of known pyrolysis products. This improves the accuracy of polymer and micro-plastic identification, especially for complex mixtures, and reduces the need for manual interpretation of the pyrogram.

The amount of PET in an environmental sample can be quantified by integrating the area under the peaks corresponding to the characteristic pyrolysis products. Calibration curves can be prepared using known concentrations of pure polyethylene to convert peak areas into microplastic concentrations.

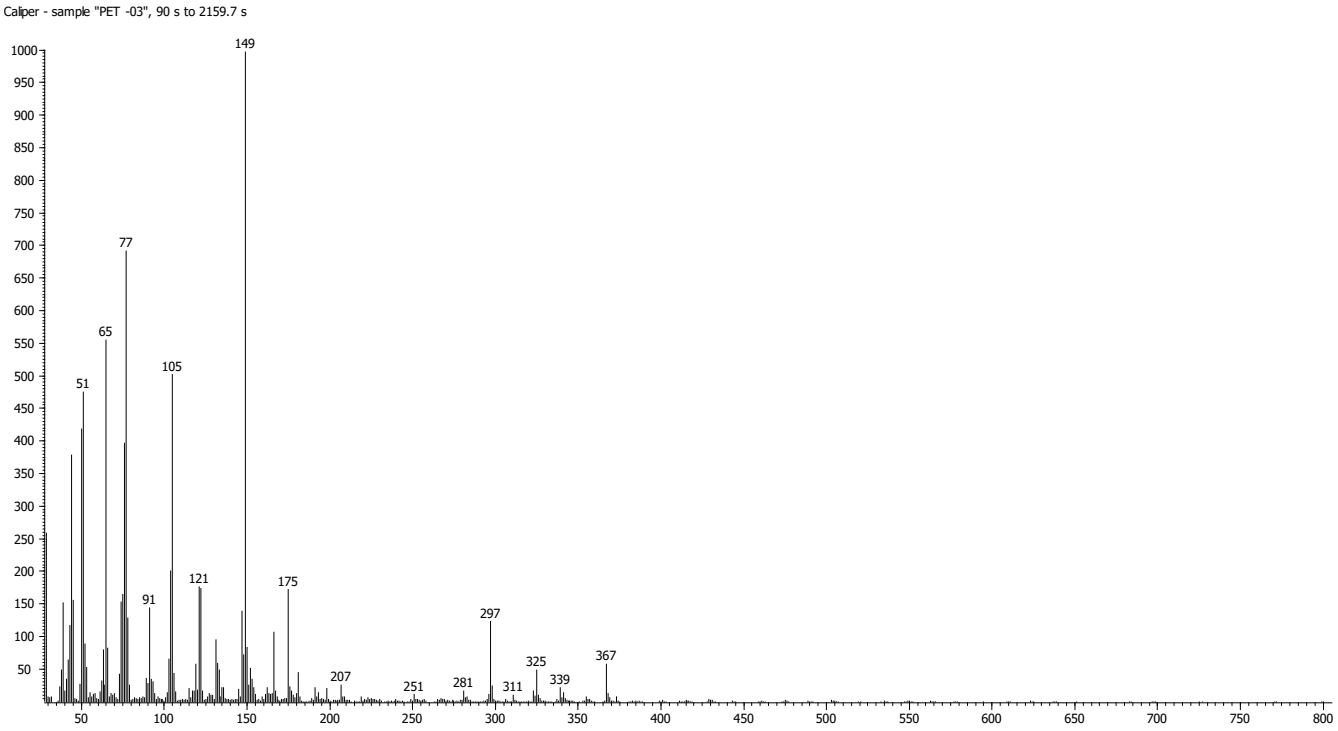

Figure 4: Summed TIC mass spectrum of PET.

5. Conclusions

The combination of the OPTIC-4 pyrolysis unit, Pyrolysis-GC-MS, and the LINEX Liner Exchanger provides an efficient and reliable method for analyzing PET microplastics and their pyrolysis products. The automated sample introduction system ensures reproducibility and eliminates the risk of contamination, while the OPTIC-4 system delivers high precision in controlling the pyrolysis process. This approach is highly suitable for the characterization of microplastic degradation products, aiding in environmental studies and advancing microplastic research.

- **Precision and Control** – The OPTIC-4 Pyrolyzer offers precise control over pyrolysis conditions, ensuring reproducibility and accuracy in the analysis of microplastics.
- **Minimal Sample Preparation** – This technique requires minimal sample preparation, allowing for the direct analysis of microplastics in environmental samples with high sensitivity.
- **Small Sample Size** – The OPTIC-4 can analyze small sample amounts (as low as a few milligrams), which is advantageous when working with limited microplastic samples.
- **No Carryover** – There is no need to run a blank between samples, since the OPTIC-4 Pyrolyzer is free of carryover, even after high sample load.
- **No thermal oxidation** – Since the sample is purged with carrier gas, all oxygen is vented prior to pyrolysis. This absolutely prevents for thermal oxidation of the sample.
- **Comprehensive Polymer Characterization** – Pyrolysis-GC-MS provides detailed molecular information, allowing for the identification of polyethylene even in complex environmental matrices.

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