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Application note: 136

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

Keywords

Pyrolysis, OPTIC, LINEX, Py–GC–MS

1. Introduction

Microplastics (MPs), particularly polypropylene (PP), are an increasing environmental concern due to their persistence and widespread contamination in ecosystems. The presence of microplastics in oceans, rivers, and soil is a global challenge, and their identification and quantification are essential for understanding their environmental impact. Py–GC–MS (Pyrolysis–Gas Chromatography–Mass Spectrometry) is a powerful analytical technique for the analysis of polymers such as polypropylene, as it breaks down the material into smaller volatile fragments that can be easily detected and identified.

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 outlines the methodology for analysing polypropylene microplastics using Py–GC–MS with the OPTIC-4 Pyrolyzer, LINEX system, and ChromIdent software for pyrogram identification.

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 hold 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.

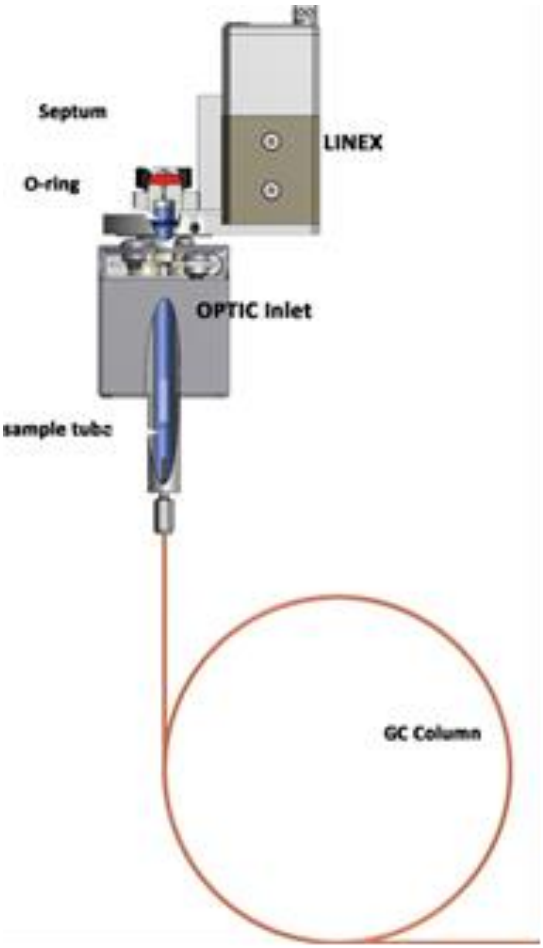

Figure 1: Hardware setup. The LINEX opens/closes the head of the OPTIC automatically to enable the placement/removal of the sample tube, containing a µ-vial with the microplastic sample.

Table 1: Analytical conditions.

Parameter	Setting
OPTIC-4 Pyrolyzer	
Sample	1 mg Polypropylene
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

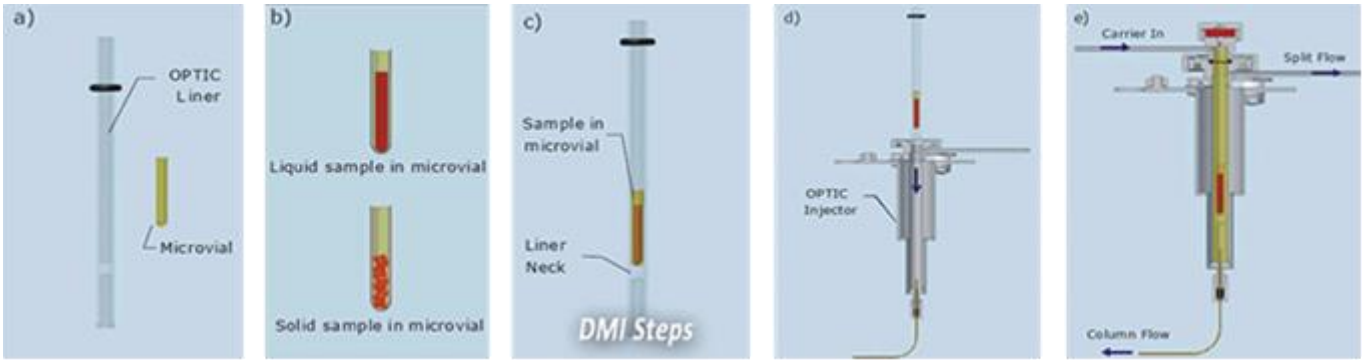

Figure 2: Impression of the workflow.

4. Results

Polypropylene, being one of the most commonly used plastics, is often found as microplastics in environmental samples. Py–GC–MS using the OPTIC-4 Pyrolyzer allows for the detection of polypropylene in complex samples by analyzing the specific pyrolysis products. The pyrolysis of polypropylene generally results in a mixture of small hydrocarbons, including:

- **Monomeric Compounds** – Propylene (C_3H_6), propane (C_3H_8)
- **Oligomeric Compounds** – Dimers (C_6), trimers (C_9), cyclic oligomers
- **Alkanes** – Butane (C_4H_{10}), hexane (C_6H_{14}), decane ($C_{10}H_{22}$)
- **Alkenes** – 1-Butene, 2-butene, isobutene, 1-hexene
- **Cyclic Compounds** – Cyclohexane (C_6H_{12})
- **Aromatic Hydrocarbons** – Benzene (C_6H_6), toluene (C_7H_8), xylenes (C_8H_{10}), which are characteristic of polypropylene pyrolysis

Besides the typical pyrolysis products of polypropylene, this polymer produces a very distinctive Pyrogram. Figure 3 presents the Pyrogram of polypropylene 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.

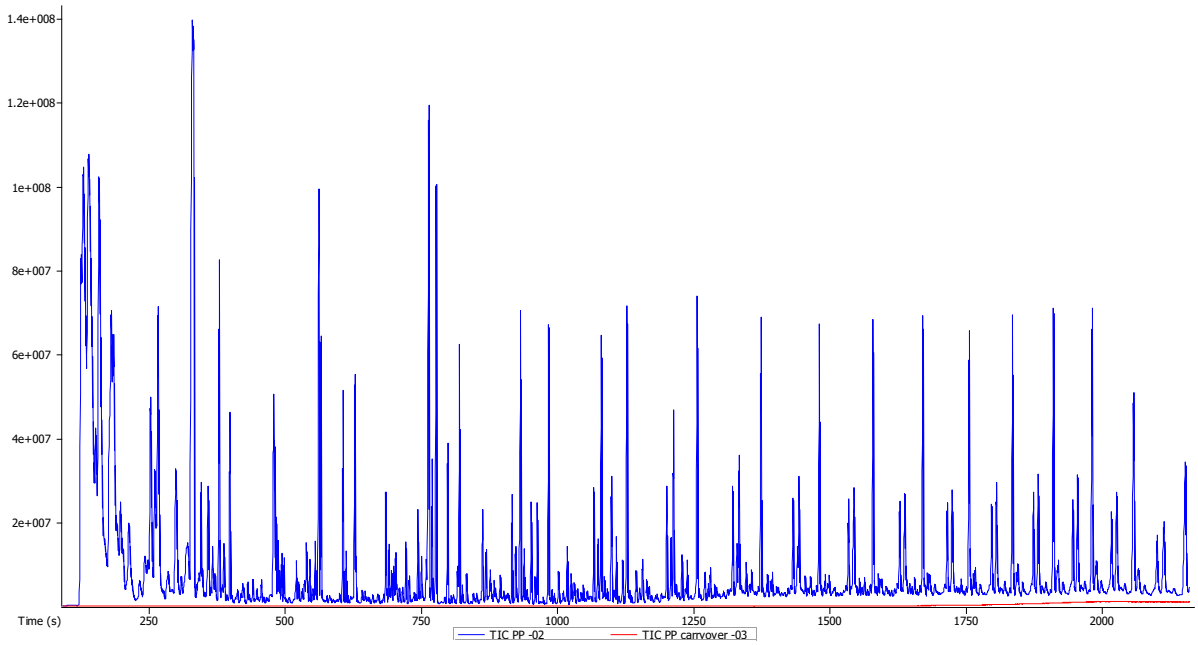

Figure 3: Pyrogram of polypropylene. Blue, Pyrogram; Red, blank run after pyrolysis-run.

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 polypropylene 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 polypropylene

5. Conclusions

- **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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