Application note | 003970

Environmental

Comprehensive profiling of plastic polymers using pyrolysis coupled to GC-MS

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Keywords

Plastic polymers, microplastics (MPs), pyrolysis, gas chromatography, Py-GC-MS, TRACE 1610 GC, single quadrupole mass spectrometry, ISQ 7610 GC-MS

Goal

The aim of this study is to demonstrate the suitability of pyrolysis coupled to GC-MS (Py-GC-MS) for the identification and quantitation of the 12 most common polymer types within a single GC-MS run as well as qualitative analysis of plastic samples collected on the beach.

Introduction

Microplastics (MPs) are solid particles of polymeric materials, with regular or irregular shape and typical size ranging from 1 µm to 5 mm, of either primary or secondary manufacturing origin, which are insoluble in water.[1]

Each year, around 42,000 tons of microplastics are released into the environment.[2] They come from a variety of sources including debris from larger plastic pieces, clothing, construction, renovation, food packaging, and industrial processes. Another common form of microplastics are microbeads, which are very tiny pieces of manufactured polyethylene that are added as exfoliants to health and beauty products, such as some cleansers and toothpastes.[3]

MPs have been found in marine, freshwater, and terrestrial ecosystems as well as in food and drinking water.[2] Once in the environment, microplastics do not biodegrade, but accumulate in animals and are consequently consumed as food by humans. Exposure to microplastics is linked to a range of negative (eco)toxic and physical effects on living organisms.[2]

With increasing awareness of the detrimental effects of microplastics on the environment, countries worldwide are now advocating for the removal and ban of microplastics from various products.[4]

In the US, some states have taken action to mitigate the negative effects of microplastics in the environment.[5] One such campaign is "Beat the Microbead," which focuses on removing plastics from personal care products.[6]

Illinois was the first US state to ban cosmetics containing microplastics, whereas the Microbead-Free Waters Act[7] was introduced at a federal level in 2015. This law prohibits the addition of plastic microbeads in the manufacturing of certain personal care products, such as toothpaste, to reduce water pollution caused by these products. Manufacture of microbead-containing products was prohibited in July 2017, and retail sales are prohibited as of July 2018.

Alongside Fourier Transform Infrared Spectroscopy (FTIR), Raman spectroscopy, and electron microscopy, pyrolysis of polymers followed by mass spectrometric analysis is commonly used to analyze plastics since it can provide important information about polymer structure, molecular weight, degree of polymerization, main functional groups, and end group structure.[8]

In particular, pyrolysis coupled to gas chromatography–mass spectrometry (Py-GC-MS) is a typical technique applied for the identification of plastic polymers. A polymer is made up of a repetitive structure of molecules (monomers) that are covalently bonded, forming a long molecular chain or macromolecule. In analytical pyrolysis, these molecular chains of a polymer are broken up under a rapid temperature increase (usually to about 600 °C) in an inert atmosphere, which leads to thermal degradation of the polymer. The composition of the polymer is investigated by introducing the degradation products (pyrolyzates) into an analytical instrument such as a GC-MS. A schematic of the pyrolysis workflow is reported in Figure 1.

The Multi-Shot Pyrolyzer™ EGA/PY-3030D (Frontier Laboratories Ltd.) is a furnace-type pyrolyzer in which a sample placed in a sample cup is dropped (free fall) into a preheated furnace. It provides a fast and reliable material characterization of practically any kind of organic sample. Insoluble, non-volatile, solid and liquid samples can be analyzed directly without complex sample preparation by enabling multiple analysis modes, such as evolved gas analysis (EGA), single-shot analysis, double-shot analysis, and heart-cut EGA analysis (HC/EGA). Additionally, it can be coupled to the Auto-Shot Sampler AS-2020E (Frontier Laboratories Ltd.) for continuous analysis of up to 48 samples.

In this study, a single-shot Py-GC-MS method for the detection and identification of common polymers was evaluated for performance and reliability by assessing linearity, method detection limits (MDLs), and absolute peak area repeatability (%RSD). Additionally, the developed method was used to analyze plastic debris collected on a Mediterranean beach.

Microplastics contained in samples are thermally degraded at 600 °C in an oxygen-free environment such as inert gas (He or N_2).

The degraded polymers produce a large amount of thermal degradation products that are transferred to the GC-MS system.

The thermal degradation products are identified based on spectral library search.

Figure 1. Schematic of Py-GC-MS workflow

Experimental

A Multi-Shot Pyrolyzer EGA/PY-3030D equipped with the Auto-Shot Sampler AS-2020E autosampler was coupled to a Thermo Scientific™ TRACE™ 1610 GC, configured with a Thermo Scientific™ iConnect™ split/splitless injector (iConnect-SSL), and connected to a Thermo Scientific™ ISQ™ 7610 single quadrupole mass spectrometer.

The SSL injector was equipped with dedicated hot injection adapter (P/N 19050733), allowing for connection to the pyrolyzer and ensuring efficient analyte transfer.

The separation of the pyrolysis products was achieved using a Thermo Scientific™ TraceGOLD™ TG-5 SILMS capillary column 30 m x 0.25 mm × 0.25 µm, with 5 m integrated SafeGuard column (P/N 26096-1425). This column provided high inertness and thermal stability for consistency of results over time. Additionally, the integrated SafeGuard offers the benefit of an extended column lifetime.

Instrument parameters are reported in Table 1.

Data acquisition, processing, and reporting

The Thermo Scientific™ Chromeleon™ Chromatography Data System (CDS) software, version 7.3, was used for data acquisition, processing, and reporting. Pyrolysis parameters were set using Frontier Laboratories' pyrolyzer control software, which provides an intuitive interface for easy method set-up. Each analytical mode (EGA, single-shot analysis, double-shot analysis, and HC/EGA) comes with a set of optimized conditions that can be used to start acquiring samples. Characteristic fragmentation products were used for polymer detection and identification based on comparison with commercial spectral libraries. Additionally, the F-Search MPs 2.1 Analytical Software for Microplastics Analysis (Frontier Laboratories Ltd.) allowed confident polymer identification based on the mass spectra comparison of unknown samples with the reference polymer in the library.

Standard preparation

Calibration curve preparation

Microplastic calibration standard set (P/N B51007372) containing 12 plastic polymers—polystyrene (PS), polyethylene (PE), polypropylene (PP), polyvinylchloride (PVC), polyethylene terephthalate (PET), polycarbonate (PC), polyurethane (PU), Nylon 6 (N-6), Nylon 66 (N-66), polymethyl methacrylate (PMMA), styrene-butadiene copolymer (SBR), and acrylonitrile butadiene styrene copolymer (ABS)—was used to prepare a 5-point calibration curve. Different aliquots (0.2, 0.5, 1.0, 2.0, and 4.0 mg) of the MPs-$CaCO_3$ mixture were accurately weighted into the pyrolysis cup (P/N B51007380) using a microbalance (Mettler Toledo XPR6UD5). Each cup was covered with quartz wool to prevent the loss of the mixture of microplastics. Each calibration level was prepared in duplicate.

Precision in weighing samples on a microbalance is crucial to ensure accurate and reliable experimental results, as even the smallest deviations can significantly impact the outcome and validity of the data.

Sample preparation

Transparent and colored plastic samples collected on a Mediterranean beach were cut into small pieces, and an aliquot (weight = 0.5 mg) was placed into the pyrolysis cups and covered with glass wool for analysis.

Table 1. Py-GC-MS parameter settings

Multi-Shot Pyrolyzer EGA/PY-3030D parameters	
Analysis type	Single shot analysis
Initial temperature (°C)	600
Initial (min)	0.2
Interface temperature (°C):	300
TRACE 1610 GC parameters	
iC-SSL	
Inlet module	SSL with hot injection adapter
Injection mode	Split
Injection temperature (°C)	300
Split flow (mL/min)	50
Split ratio	50:1
Purge flow (mL/min)	5.0
Carrier gas, flow (mL/min)	He, 1.0
Oven temperature program	
Temperature (°C)	40
Hold time (min)	2.0
Rate (ºC/min)	20
Temperature 2 (°C)	280
Hold time (min)	10.0
Rate 2 (ºC/min)	40
Temperature 3 (°C)	320
Hold time 2 (min)	15
GC run time (min)	40.0
Oven equilibration time (min)	0.20
Analytical column	
TraceGOLD TG-5SILMS guard column	30 m × 0.25 mm × 0.25 µm (P/N 26096-1425)
ISQ 7610 mass spectrometer parameters	
Transfer line temperature (°C)	320
Ion source type and temperature (°C)	Thermo Scientific™ ExtractaBrite™ ion source, 320
Ionization type	EI
Emission current (µA)	50
Tuning parameters	SmartTune
Aquisition mode	Full Scan
Mass range (*m/z*)	29–350

Results and discussion

Chromatography

A pyrogram is a total ion chromatogram (TIC) in which each peak represents a smaller fragment (pyrolyzate) derived from the decomposition of a polymer. The identification of the native polymers was carried out by extracting the characteristic ions of the typical pyrolyzate pattern for each polymer and comparing the mass spectra with the commercially available NIST 2023 spectral library using Chromeleon CDS.

An example of the pyrogram (full scan chromatogram) as well as the extracted characteristic ion traces (XIC) of a MP standard mixture (weight = 2.0 mg) is shown in Figure 2. The typical pyrolyzates of the 12 most common polymers could be detected in one single GC-MS run. Appendix 1 summarizes the pyrolyzate pattern of each polymer with the characteristic monitored ions.

Additional confirmation of the native polymers was obtained by importing the pyrograms in F-Search MPs software and comparing the acquired MS spectra with the MP libraries embedded in the software, as shown in Figure 3. The value in the "Prob. [%]" column represents the match quality between the summation mass spectrum of each polymer from the sample and the summation mass spectrum in the library. The closer the value is to 100%, the higher the probability that the polymer is present.

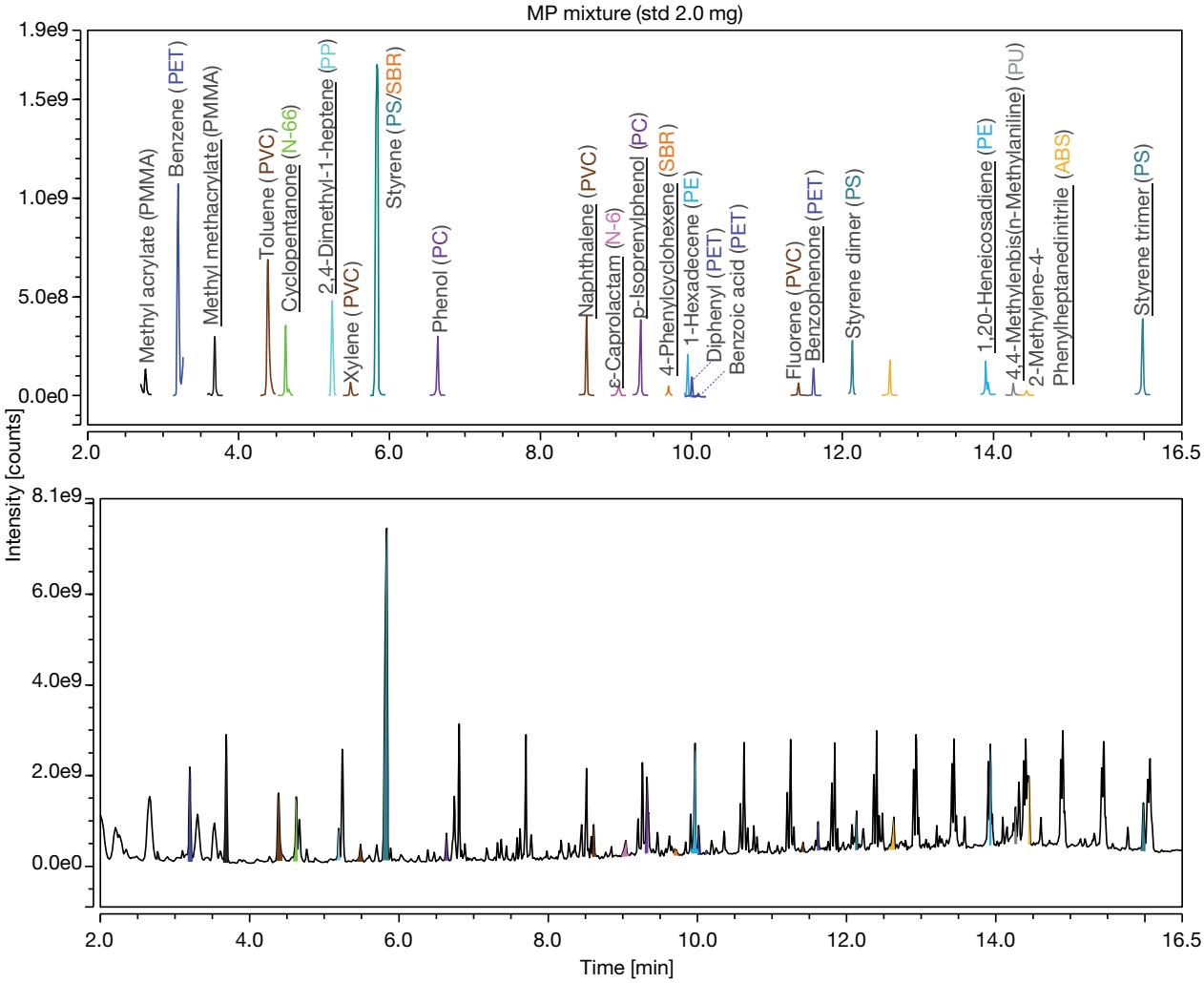

Figure 2. Example of pyrogram (bottom) and XIC of pyrolyzates (top) obtained by pyrolyzing a MP-$CaCO_3$ standard mixture (weight = 2.0 mg). In the top trace, the typical pyrolyzate pattern for each native polymer is shown with the native polymers reported in parentheses. The most representative pyrolyzate of each polymer is underlined.

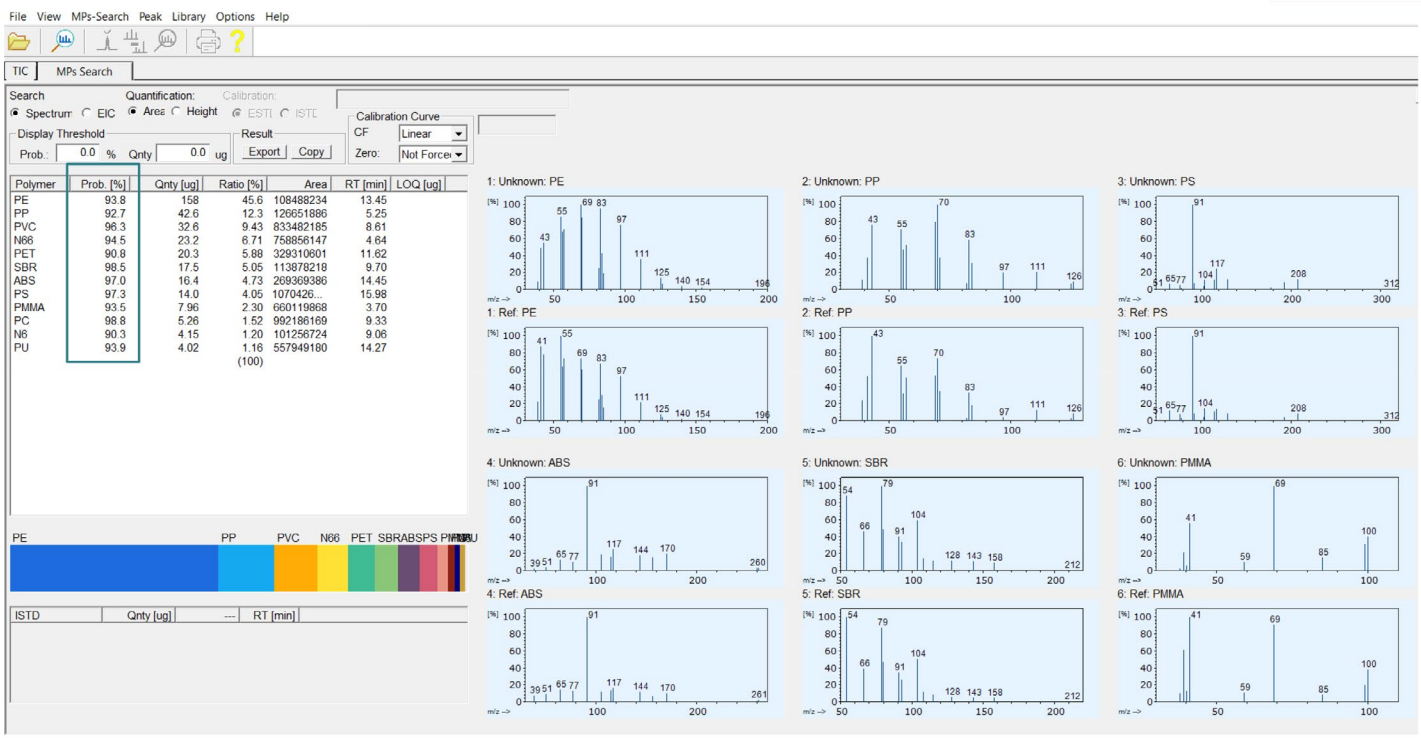

Figure 3. F-Search MPs software result browser showing an example of the comparison between acquired spectra and MP library spectra. The closer the "Prob. [%]" value in the highlighted table column is to 100%, the higher the probability that the polymer is present in the analyzed sample.

Linearity, limits of detection (LODs), and limits of quantitation (LOQs)

Linearity was assessed by analyzing five different concentrations of the MP-$CaCO_3$ mixture. Calibration curves were generated by extracting the characteristic ions of the most representative pyrolyzate for each polymer (Figure 2, underlined compounds). The generated calibration curves were fitted using a linear type, and the response values of each calibration level were averaged before curve fitting. All 12 investigated polymers showed a linear trend with coefficient of determination (R^2) > 0.990, and average calibration factor (AvCF) %RSD <10. Full range calibration curves for the target polymers are shown in Figure 4. The extracted ion chromatogram of the most representative pyrolyzates at the lowest calibration point (weight = 0.2 mg), except for PU for which the lowest calibration point is 0.5 mg, is reported as an example in Figure 5.

LODs and LOQs were calculated based on the standard deviation of the responses and the slope of the calibration curve applying Equations 1 and 2. They are summarized in Table 2 together with other method characteristic parameters, such as calibration ranges, calculated R^2, and AvCF %RSD.

Equation 1 $LOD = 3.3 \cdot \sigma / S$

Equation 2 $LOQ = 10 \cdot \sigma / S$

Where:

σ = standard deviation of the responses

S = slope of the calibration curve

Repeatability

The repeatability of the analytical system was evaluated by analyzing n=9 MP-$CaCO_3$ mixture (weight = 0.5 mg). The precise control of the pyrolysis process with accurate and controlled heating rate (±0.1 °C) combined with the inertness of the sample path allowed for reliable repeated analysis with absolute peak area %RSD < 15.0 as reported in Figure 6.

Table 2. Retention times (RT), calibration ranges, calculated R^2, AvCF %RSD, LODs, and LOQs for the target polymers

Native polymer	RT (min)	Calibration range (µg)	Coefficient of determination (R^2)	Av CF %RSD	Calculated LODs (µg)	Calculated LOQs (µg)
PMMA	3.685	0.39–7.90	0.994	7.3	0.87	2.64
N-66	4.675	1.20–24.10	0.996	6.8	2.27	6.88
PP	5.240	2.23–44.60	0.990	9.8	6.18	18.73
PVC	8.610	1.66–33.20	1.000	1.9	0.84	2.56
N-6	9.050	0.20–4.10	0.997	6.5	0.32	0.98
PC	9.324	0.26–5.20	0.999	3.7	0.22	0.67
SBR	9.698	0.86–17.20	0.991	10.2	2.28	6.91
PET	11.617	1.00–20.10	0.997	6.7	1.49	4.52
PE	12.899	7.55–151.00	0.993	9.2	17.30	52.43
PU	14.259	0.47–3.80	0.997	6.1	0.32	0.96
ABS	14.440	0.82–16.40	0.998	5.0	1.05	3.20
PS	15.977	0.62–12.40	0.995	7.1	1.31	3.97

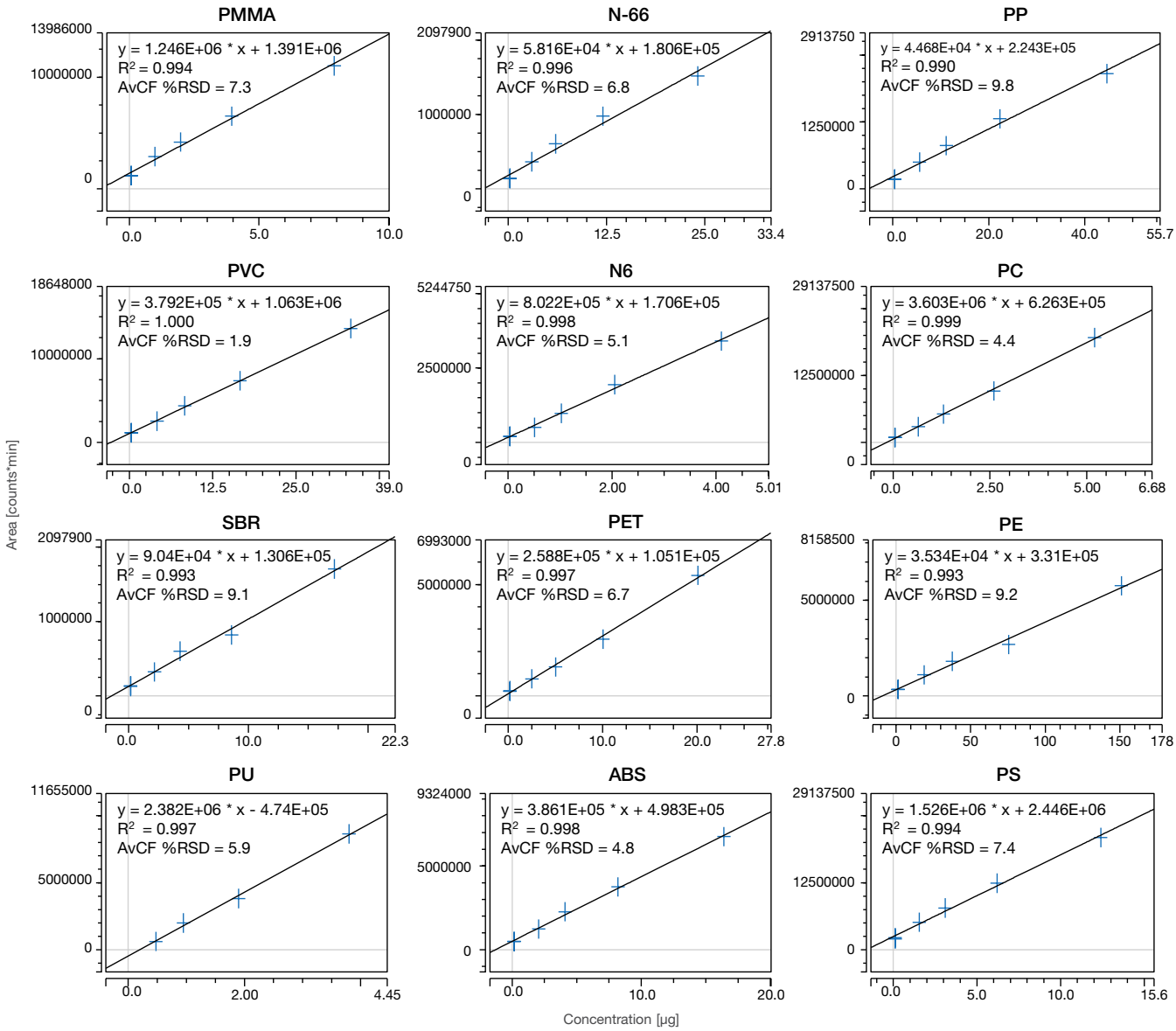

Figure 4. Full range calibration curves for the 12 investigated polymers

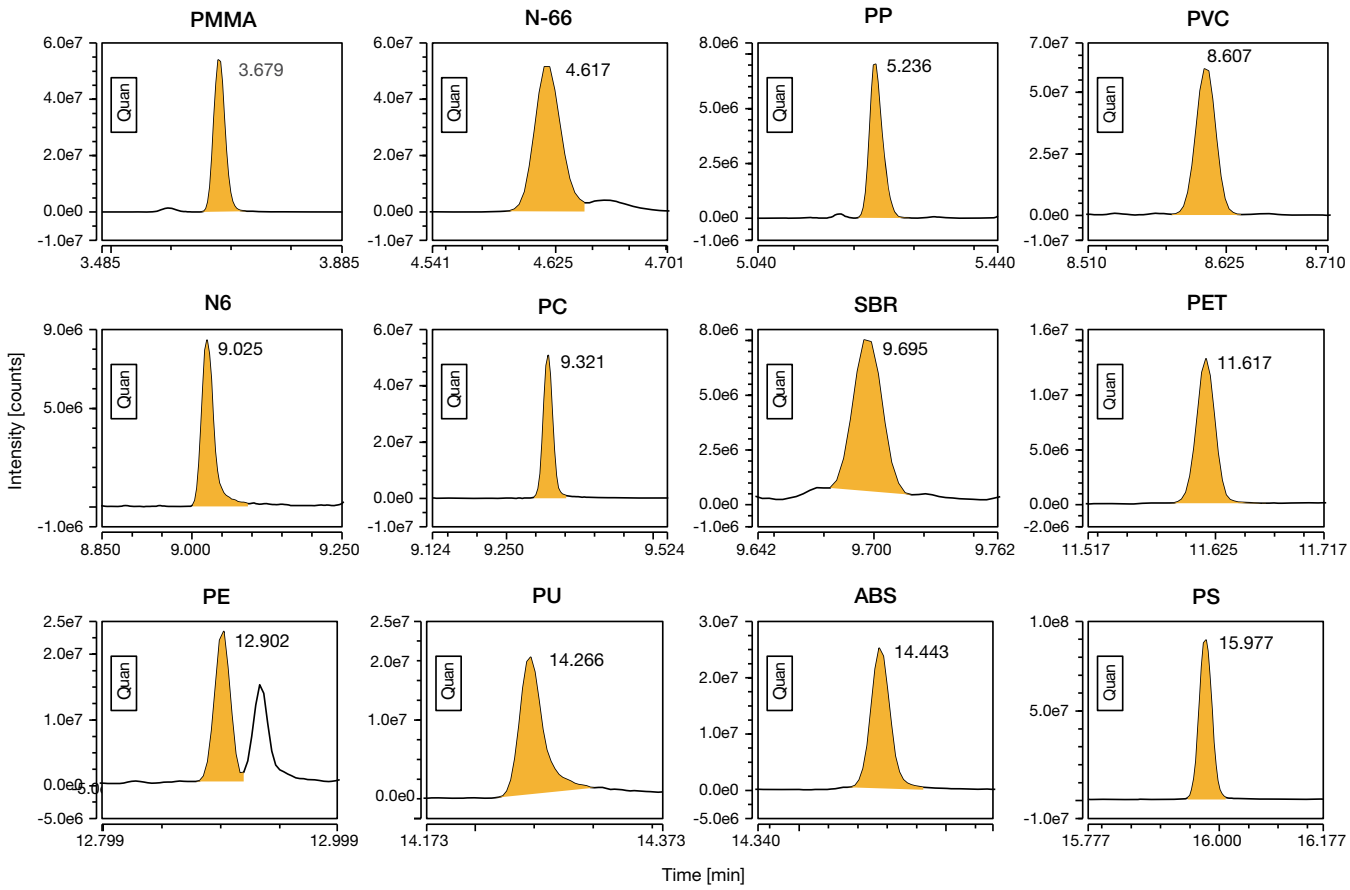

Figure 5. XICs showing the pyrolyzates at the lowest calibration point

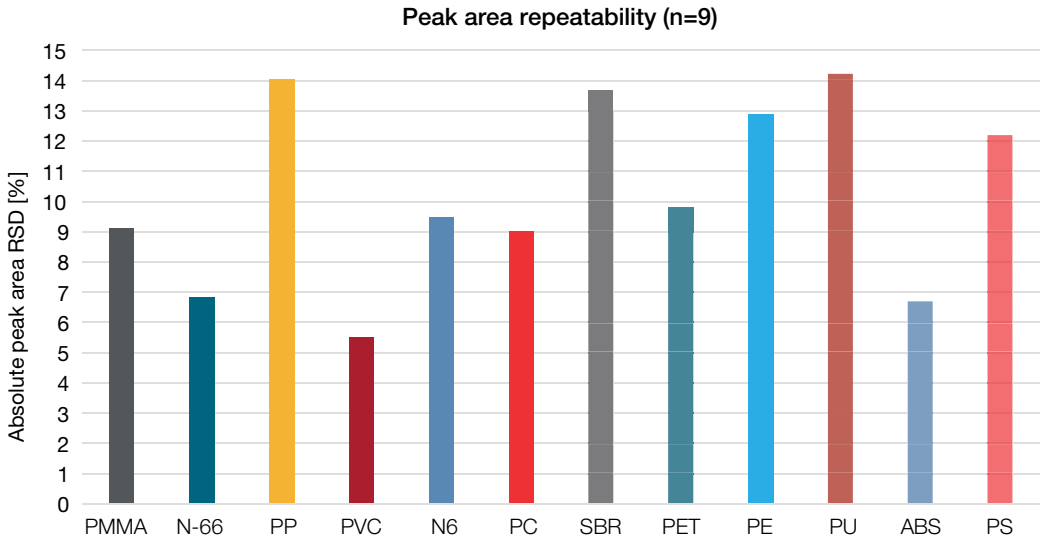

Figure 6. Absolute peak area repeatability (%RSD) obtained for n=9 MP-$CaCO_3$ mixture (weight = 0.5 mg)

Identification of native polymers using Chromeleon CDS

Plastic debris (n=8) visible by the naked eye was collected on a Mediterranean beach, cut to small pieces (weight = 0.5 mg), and analyzed by applying the method conditions reported in this study. Native polymers were identified based on their pyrolyzate patterns and by comparing the obtained spectra with the NIST23 spectral library using Chromeleon CDS. PE was identified as the main component in most of the samples together with varying amounts of PMMA and N-66. PE is the most produced plastic worldwide as it is a very versatile thermoplastic polymer suitable for a wide range of applications such as packaging, food packaging, construction, and medical. Ethylene can be copolymerized with a wide range of other monomers; common examples include linear and end-cyclized olefins, polar monomers, organosilicon monomers, and vinyl monomers such as vinyl acetate and methyl acrylate.[9] PP, the second-most widely produced commodity plastic, was predominant in sample 2. The XICs showing the characteristic pyrolyzates found in samples 1 and 2 are reported as an example in Figure 7.

Pyrograms of samples 1 and 2 were imported into F-Search MPs software for further analysis to confirm the findings (Figure 8). PE resulted in being the predominant polymer in sample 1 with a probability value of 91.2%. PP resulted in being the prevalent peak in sample 2, but despite its abundance, the qualitative match is 77.3%.

Identification of unknown pyrolyzates using F-Search MP 2.1 and MP libraries

F-Search MPs 2.1 software allows users to easily identify and quantify unknown microplastics (MPs) in the environment. It consists of a sophisticated search program with mass spectral libraries of pyrolyzates and additives. Sample 8 showed an unknown pyrolyzate that did not belong to any of the 12 polymers contained in the calibration kit. The spectral comparison of the unknown peak with NIST23 allowed putative identification of this peak as tetrafluoroethylene (RT = 2.09 min) as shown in Figure 9.

The pyrogram was imported into F-Search MPs software, and the origin of the pyrolyzate could be traced back to either polytetrafluoroethylene (PTFE) or fluorinated ethylene propylene (FEP) based on the comparison with the MP libraries included in the software as well as two additional libraries for pyrolyzates (P/N PY-1115E-221) and additives (P/N PY-1114E-221), as demonstrated in Figure 10.

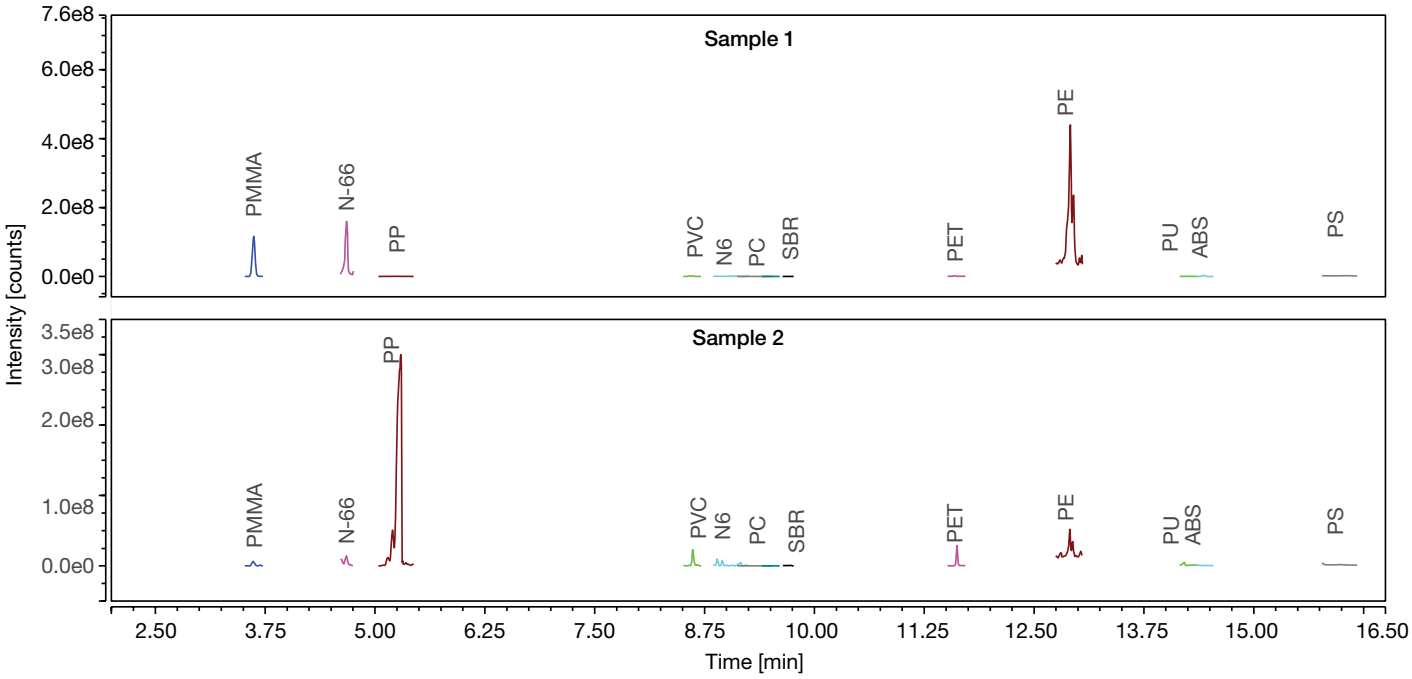

Figure 7. Examples of pyrograms and XICs for samples 1 and 2 collected. PE together with PMMA and N-66 are predominant in sample 1, whereas PP is the main component in sample 2.

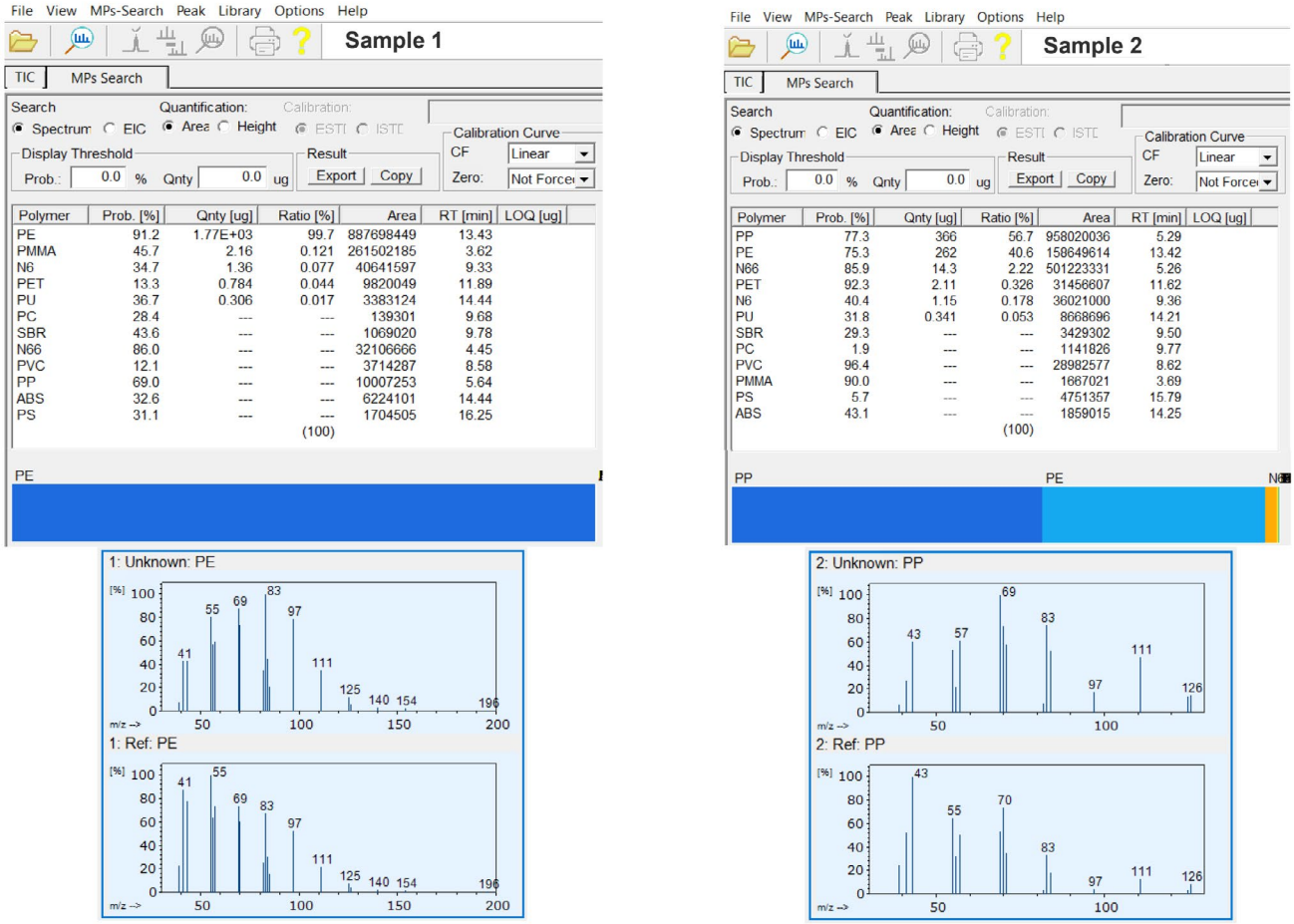

Figure 8. F-Search MPs software browser showing the polymer content in samples 1 and 2

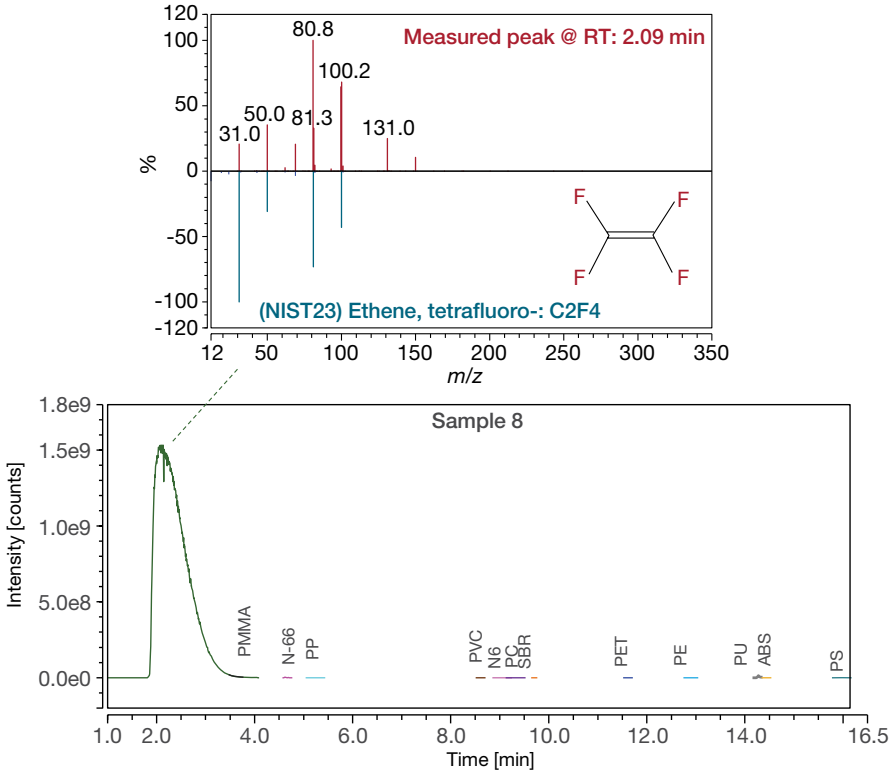

Figure 9. XICs for sample 8 showing unknown pyrolyzates with putative identification based on spectral comparison with the NIST23 library

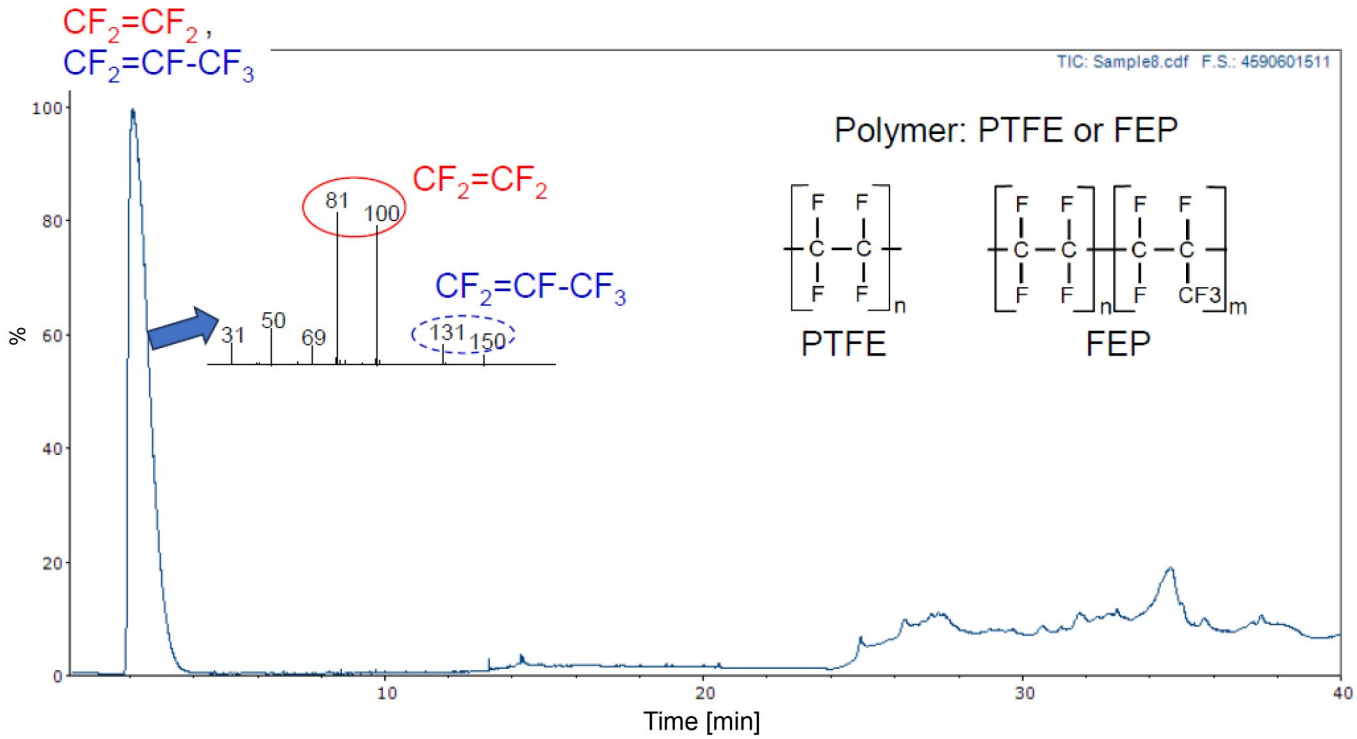

Figure 10. Identification of the native polymers based on the unknown pyrolyzate found in sample 8 by using F-Search MPs software and dedicated libraries for pyrolyzates and additives

Conclusions

The results of these experiments demonstrate that pyrolysis coupled to GC-MS provides an ideal solution for analysis of microplastics. Beyond qualitative information about the chemical nature of an unknown polymer, such as polymer type and potential additives, it also allows quantitative information to be obtained after calibration.

- Py-GC-MS can be used to identify main polymer types in plastics based on their characteristic pyrolyzates.
- Plastic polymers can be directly analyzed with minimal sample preparation consisting of cutting and weighing a few milligrams of samples into a micro cup.
- The precise control of the pyrolysis process ensures accurate quantitative performance for the investigated compounds with $R^2 \geq 0.990$, AvCF %RSD < 10.0, LODs and LOQs below 17.30 µg and 52.43 µg, respectively, and absolute peak area %RSD < 15.0.
- Plastic samples collected on a Mediterranean beach were confidently identified based on their pyrolyzate patterns by using Chromeleon CDS combined with F-Search MPs 2.1 software and dedicated libraries.

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Appendix

Table A1. Pyrolyzate pattern and characteristic monitored ions for each investigated polymer

Native polymer	Characteristic pyrolizates	Extracted ion (*m/z*)	RT (min)
PMMA	Methyl acrylate	55, 85	2.77
	Methyl methacrylate	100	3.69
N-66	Cyclopentanone	84	4.62
PP	2,4-Dimethyl-1-heptane	70	5.24
PVC	Toluene	91	4.39
	Xylene	106	5.45
	Naphthalene	128	8.61
	Fluroene	166	11.42
N-6	ε-caprolactam	85, 113	9.03
PC	Phenol	94	6.63
	p-Isopropenylphenol	134	9.32
SBR	Styrene	104	5.84
	4-Phenylcyclohexene	104	9.70
PET	Benzene	78	3.20
	Diphenyl	154	10.02
	Benzoic acid	122	10.11
	Benzophenone	182	11.62
PE	1-Hexadecene	83, 69	9.97
	1,20-Heneicosadiene (C21)	82	13.93
PU	4,4'-Methylenbis(N-methylaniline)	198	14.26
ABS	2-Methylene-4-phenylheptanedinitrile	144	12.63
	2-Phenethyl-4-phenylpent-4-enenitrile	170	14.44
PS	Styrene	104	5.84
	Styrene dimer: 3-butene-1,3-diyldibenzene	130	12.13
	Styrene trimer: 5-hexene-1,3,5-triyltribenzene	91	15.98