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Analysis of Microplastic Polymer Using Pyrolysis GC/MS

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Introduction

Microplastics (MPs) encompass fine plastic particles with sizes ranging from several µm to about 5 mm; their effect on ecosystems in the marine environment as well as other environmental compartments is of concern as the mass of microplastics in aquatic habitats will surpass that of the fish by 2050 (Pico and Barcelo, 2019). In addition to the negative impact from plastic ingestion, organisms can also bioaccumulate contaminants sorbed on MPs. There is a need for comprehensive analytical workflows to characterize microplastics, including major and trace components and sorbed contaminants, with the ultimate goal of understanding the fate and toxicity of MP in the environment.

Pyrolysis gas chromatography/mass spectrometry (Py-GC/MS) based methods are a tool of choice for qualitative and quantitative analysis of MP in complex environmental samples. High sensitive detection of the distinctive pyrolysis products of each polymer can be achieved. This poster demonstrates the performance of the Shimadzu GCMS-QP2020 NX with Frontier PY-3030D with AS-1020 Autoshot for characterizing a mixture of MPs.

Figure 1: Shimadzu GCMS-QP2020 NX with Frontier pyrolysis unit PY-3030D with AS-1020E auto-shot sampler

Instrumental Conditions

Py conditions	
Furnace temp	600°C
Interface temp	300°C
GC conditions	
Inlet	300°C
Column	40°C (2min) → 10°C/min → 320°C (16min)
Carrier gas	Helium
Linear velocity	36.1cm/min
Injection mode	Split (1:50)
Purge flow rate	3mL/min
MS conditions	
Interface temp	300°C
Ion source temp	230°C
Ionization method	EI
Measurement mode	Scan/SIM (m/z 29-700)
Scan event time	0.3s
SIM event time	0.15s

Table 1: Analytical conditions for Py-GC/MS system

Experimental Approach

A MP standard was created in-house to mimic a representative environmental sample. Four types of commercially-available polymer samples (PE, PP, PS, PVC) each weighing approximately 0.05 mg were introduced into a sample cup with about 1 mg of wool above to prevent scattering.

The Py unit was run in the single-shot mode by loading the sample cups into the autosampler for automatic loading and removal of the sample. The Py unit sits on top of a standard split/splitless inlet on the GC/MS equipped with an Ultra Alloy metal column. This column was chosen due to its ability to handle high temperature applications. To be able to identify the representative pyrolysis products, it was determined that using the simultaneous Scan/SIM mode was best. The Scan/SIM mode allows for the collection of a both the full scan over a set of masses as well as looking at specific times for specific masses. The ions of interest for the polymers studied can be seen in Table 2. These ions are well known as the main pyrolysis products of these polymers.

Polymer	Pyrolysis product	Retention time (min)	SIM monitoring ion
PE	C20, alkane	20.937	99, 85
	C20, α-alkene	20.879	97, 83
	C20, α, ω-alkene	20.817	95, 82
PP	2,4-dimethylhept-1-ene	5.231	126, 70
	2,4,6,8-tetramethyl-1-undecene	12.908	111, 69
	2,4,6,8-tetramethyl-1-undecene	13.027	111, 69
	2,4,6,8-tetramethyl-1-undecene	13.145	111, 69
PS	Styrene	6.17	104, 78
	3-butene-1,3-diyldibenzene	18.136	208, 91
	5-hexene-1,3,5-triyltribenzene	25.032	312, 207
PVC	Benzene	2.498	78, 51
	1-Chloroindan	8.874	116, 115
	Dihydronaphthalene	10.835	130, 115
	Azulene	11.145	128, 102

Table 2: Pyrolysis products and analytical conditions for detection of listed polymers

Results

The total ion chromatogram (TIC) obtained by analyzing the mixed sample containing multiple polymers is shown in Figure 2. As it can be seen in this traditional scan, numerous peaks can be identified. Peak positive identification of standards in Scan mode can be easily done. However, the positive peak identification of complex environmental samples containing MPs and other interfering compounds is easier by acquiring data in SIM mode as individual products can be identified. The ion chromatograms shown in Figure 3 represent the pyrolysis products from PE, PP, PS and PVC.

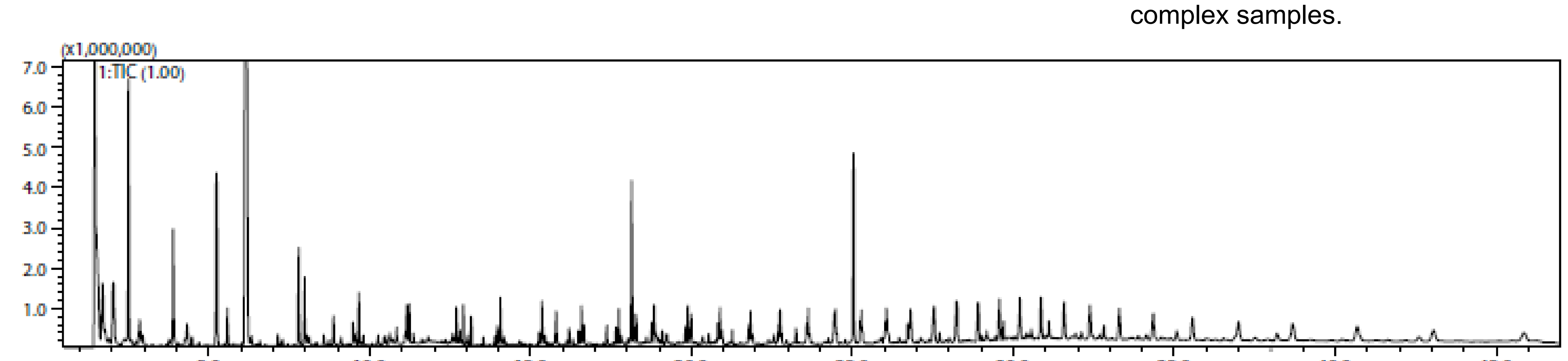

Figure 2: TIC Chromatogram Obtained by Analysis of Mixed Polymer Sample by Py-GC/MS

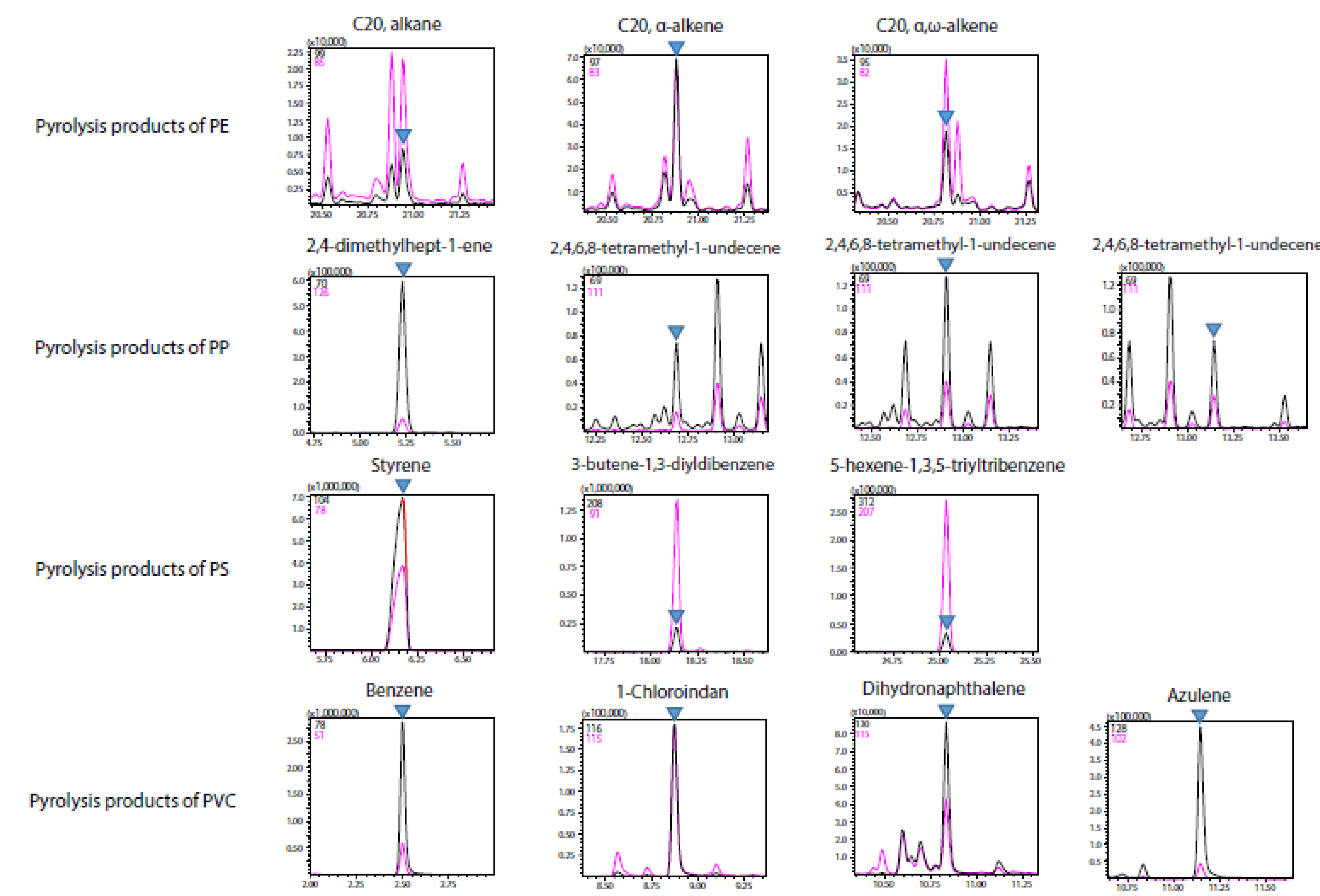

Figure 3: SIM Chromatograms of Pyrolysis Products of Polymers in a Mixed Polymer Sample

Additional tools to help with the characterization of major and trace components of MPs can be also used. These include libraries like the Wiley/NIST or a more specific polymers library like F-Search from Frontier. These tools make simpler the positive identification of pyrolysis products from MP in unknown samples.

Conclusions

In work, we established the differences between data acquisition in simultaneous Scan and SIM mode for the characterization of MPs by analyzing four model polymers (PE, PP, PS and PVC) with a Py-GCMS. While Scan mode provides a general synopsis of sample composition, it is best to monitor the pyrolysis products of the respective polymers expected in the sample in SIM mode. Simultaneous Scan/SIM mode also allows for initial identification of unknown polymers present in environmental samples. While only the qualitative method was described here, the Py-GC/MS can also be used for quantitative determination of the different polymers found in these samples. The use of Scan/SIM mode provides both the sensitivity and selectivity for characterizing MPs complex samples.

References

- Yolanda Picó and Damià Barceló. Analysis and Prevention of Microplastics Pollution in Water: Current Perspectives and Future Directions. ACS Omega 2019 4 (4), 6709-6719.
- Shimadzu Application News no. M298

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