Identification and Quantification of Different Microplastics in Soil using Pyrolysis-GC-MS

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Application Note
Environmental

Abstract
This application note demonstrates quantitative pyrolysis of microplastics in soil.

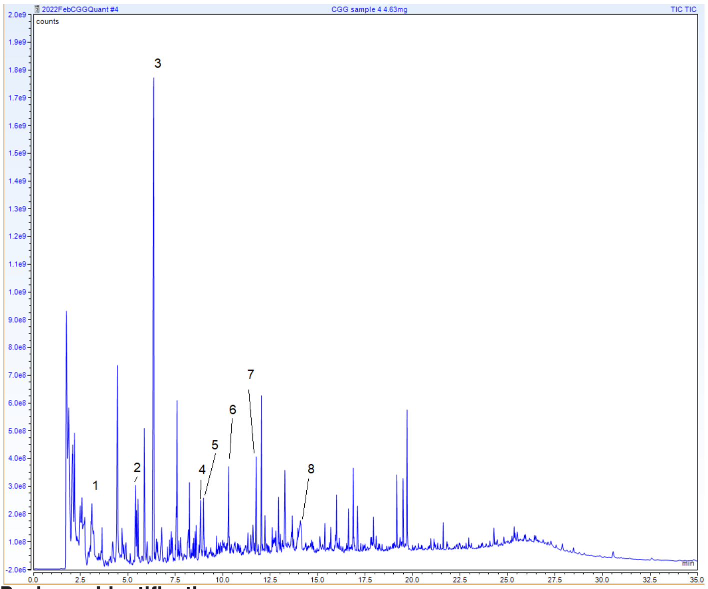
Introduction
Microplastics are a major contributor to plastic pollution and draws global attention as a critical environmental issue. Analytical pyrolysis naturally lends itself to the identification of microplastics environmental matrices. In previous publications[1,2,3], a Pyroprobe has been used to identify microplastics in various natural matrices, and in a complex mixed microplastic sample using diagnostic marker peaks. This application note is a continued study to identify microplastics in soil using marker peaks followed by quantification, using Pyroprobe 6150 interfaced to a GC-MS.

Experiment Setup
A Drop In Sample Chamber (DISC) tube was tared on a balance, and 4.63mg of soil was added. The tube was then analyzed with a Pyroprobe 6150 interfaced to a GC-MS.

Pyroprobe		GC-MS	
DISC:		Column:	5% phenyl (30m x 0.25mm)
Dry:	150°C 120s	Carrier:	Helium 1.25mL/min, 50:1 split
Pyrolysis:	700°C 30s	Injector:	360°C
		Oven:	40°C for 2 minutes
Interface:	300°C		12°C/min to 320°C (10min)
Transfer Line:	325°C	Ion Source:	230°C
Valve Oven:	300°C	Mass Range:	35-600amu

Results and Discussion
Soil was pyrolyzed at 700°C (Figure 1). While some much of its content may be inorganic, soil still contains plenty of natural organic matter from plants, animals, fruits and vegetables[4], which will have their own pyrolysis products. Natural occuring compounds include methoxy phenols and furans from lignocellulosic material. Microplastics in soil were identified by looking for diagnostic marker peaks, shown in Table 1. The diagnostic marker peaks were obtained by analyzing polymer standards. The soil was found to have markers for polypropylene (Figure 2), polybutadiene (Figure 3), and polystyrene (Figure 4). After identification of these polymers, the amount of polystyrene in the soil was quantified. As polystyrene's monomer, styrene is produced from thermal degradation of many natural substances (1), or other plastics (2), the amount of polystyrene in this soil sample was quantified using the area of polystyrene trimer peak, which is 5-hexene-1,3,5-tryltribenzene.

To make the calibration curve, a calibration stock solution was first prepared by dissolving polystyrene in toluene, resulting in a final polystyrene concentration of 7.4 μg/μL. Aliquots of 0.4, 0.6, 0.8, and 1.0 μL stock solution with an absolute mass



Peak	Identification
1	1-hydroxy 2-propanol
2	3-furanaldehyde
3	styrene
4	methyl phenol
5	2-methoxy phenol
6	2-methoxy-5-vinyl phenol
7	D-allose

Figure 1. Soil pyrolyzed at 700°C, Total Ion Chromatogram.

Table 1. Microplastic Marker Peaks

Polymer	Marker Peaks	Retention times	Ions
Polypropylene	trimer	5.86	70, 126
(PP)	tetramer	8.86, 8.90	69, 111
	pentamer	11.58,11.77	69, 111
Polyethylene terephthalate	vinyl benzoate	9.66	77, 105
(PET)	benzoic acid	10.24	105, 122
Polyvinyl chloride	HCl	2.08	36
(PVC)	naphthalene	10.38	128
Polystyrene	monomer	6.58	104
(PS)	dimer	16.01	208
	trimer	21.64	312
Polyethylene	C10 diene	7.8	55, 81
(PE)	C10 alkene	7.69	55, 140
	C20 diene	18.16	55,109
	C20 alkene	18.21	55,111
Polybutadiene	monomer	1.9	54
	dimer	5.5	79

of polystyrene at 3.0, 4.5, 6.0, and 7.4 μg respectively were added in duplicate to individual DISC tubes. Each calibration standard was pyrolyzed at the same condition as the soil. Figure 5 shows a pyrogram of the soil and the 4.5μg level standard. The area of styrene trimer plotted against the absolute mass of polystyrene, resulted in a R^2 of 0.99 (Figure 6). Using this calibration curve, 4.63mg of soil was found to have 4.16μg of polystyrene, a concentration of 0.9μg/mg.

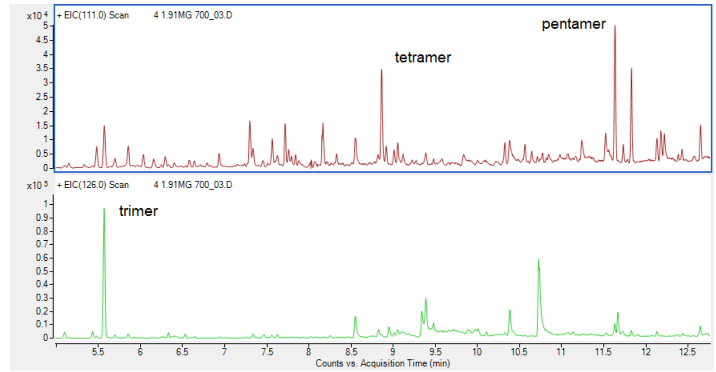


Figure 2. Extracted Ions of 111 (top), and 126 (bottom) to show markers for polypropylene.

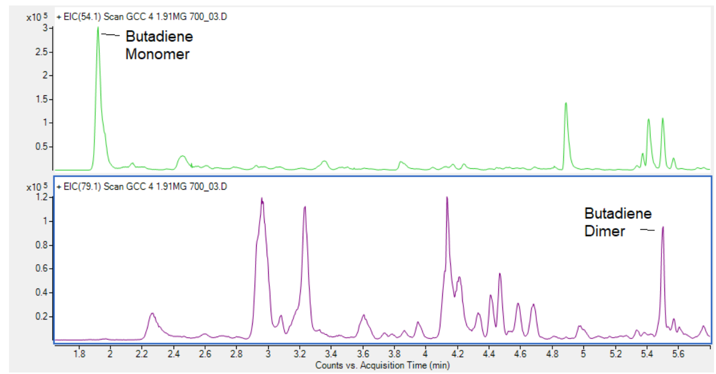


Figure 3. Extracted Ions of 54 (top), and 79 (bottom) to show markers for polybutadiene.

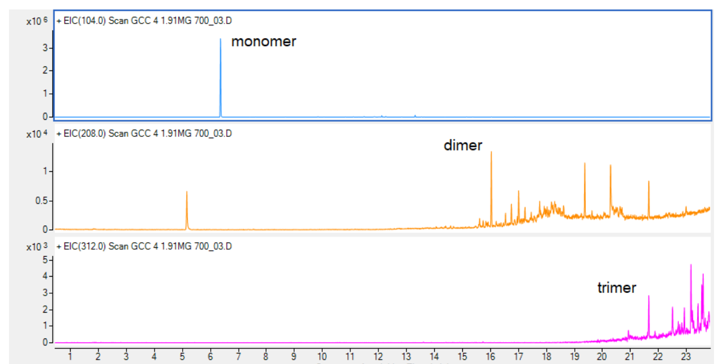
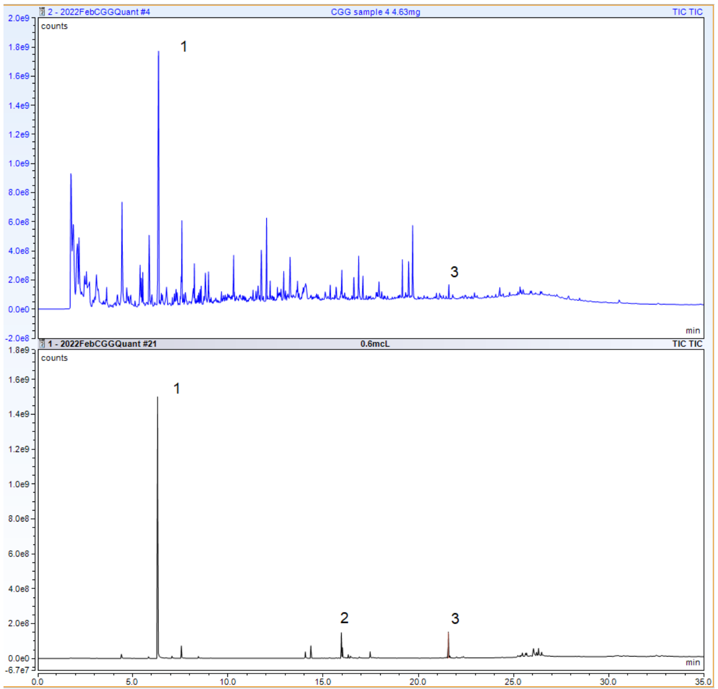


Figure 4. Extracted Ions of 104 (top), and 208 (center), and 312 (bottom) to show markers for polystyrene.

Conclusion

Three different types of microplastics were discovered in soil, including polystyrene. The amount of polystyrene was quantitatively analyzed by producing a linear calibration of polystyrene's trimer area. The CDS Pyroprobe was demonstrated as a powerful analytical tool in investigating pollution caused by microplastics.



Peak	Identification
1	styrene
2	styrene dimer
3	styrene trimer

Figure 5. Soil (top), and Calibration level (bottom).

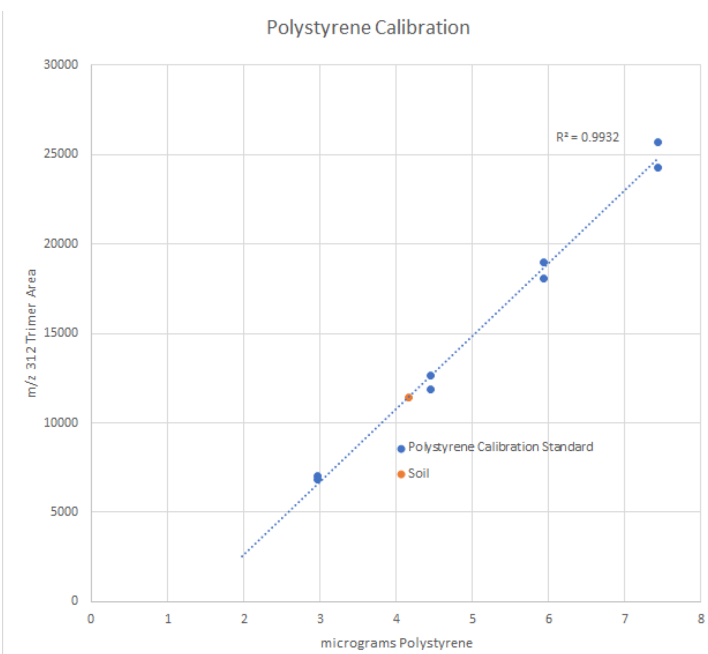


Figure 6. Calibration for Polystyrene using the trimer peak area, soil sample plugged in.

References

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2. K. Sam, Quantitative Analysis of Microplastics Using the Pyroprobe with GC-MS, CDS App Note #232

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