Detection of Plastic Pollution by the Pyroprobe

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Application Note
Environmental

Abstract
This application note demonstrated the feasibility of detecting environmental plastic contamination by Pyroprobe at different concentrations.

Introduction
Inexpensive and durable, plastic production is at its highest rate. Unfortunately, plastic is resistant to degradation, leading to an accumulation in the environment. This pollution has been known to adversely affect both wildlife and humans. Analysis of plastics in general can prove to be difficult. Non-volatile, and often insoluble, they cannot be analyzed by HPLC or GC. However, py-GC/MS is perfect for extending the use of a gas chromatograph for plastic analysis.The identification of the presence and types of plastic is possible, whether it be polyester, polyethylene, polyvinyl chloride, or polypropylene, in environmental samples.

Experimental Setup:
Two liters of seawater was passed through a 10μm PTFE membrane. The sediment from this membrane, 4mg, was added to a Drop-In-Sample Chamber (DISC) tube, and run using a multi-step sequence of 300°C and 600°C, to look at the organic profile. The chromatograms were summarized in Figure 1.

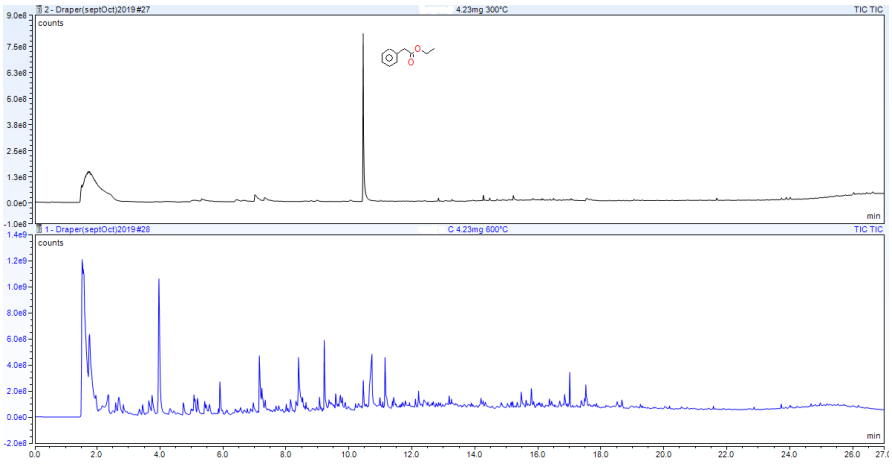

Figure 1. Seawater sediment run at 300°C (top), then 600°C (bottom).

A fresh sample of sediment was then spiked with high density polyethylene (HDPE) microplastic at a 1% level (wt/wt), and run at the same multi-step sequence (Figure 2). HDPE overwhelms the signal from the sediment alone, not approaching the detection limit of a single quad MS. In Figure 3, sediment in a DISC tube was spiked with 0.4% HDPE, the signature for the plastic is still evident amongst the organic signature of the oceanwater sediment.

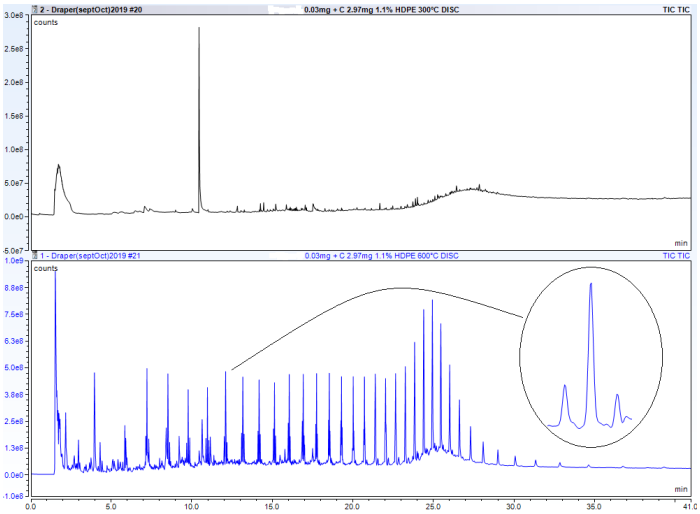

Figure 2. Seawater sediment with 1% HDPE spike, run at 300°C (top), then 600°C (bottom).

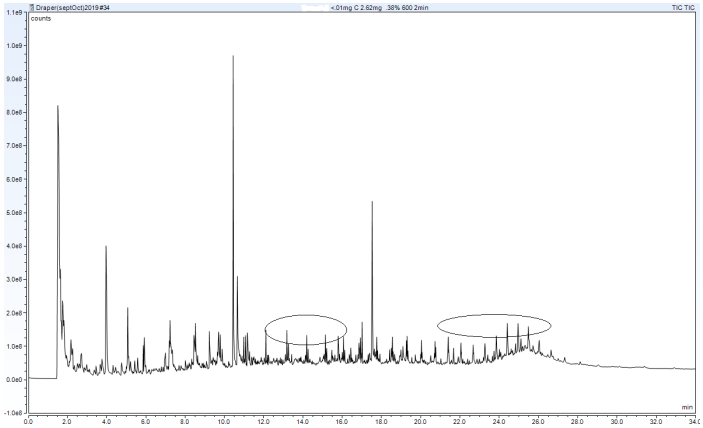

Figure 3. Seawater sediment with 0.4% HDPE spike, run at 600°C.

Plastics which have been in the environment can fragment into smaller and smaller sizes. Very tiny plastic particles, too small to be seen with the naked eye, nanoplastics, have size range of 1-1000nm. In the next example, styrene based plastics were dissolved in both deionized water and salt water, to simulate nanoplastics. Figure 4 shows these styrene plastics at a concentrated level. Of a 45000 ppm solution, 10 microliters were added to a sample tube, automatically dried, using the “Dry” function on the Pyroprobe, and then pyrolyzed. Each polymer was detectable, showing patterns which differentiated one from the other.

A 1000ppm dilution of each solution was made, and 1 microliter was analyzed using the same method, resulting in 1 microgram of each polymer to challenge the detection limit. The largest peaks, and monomers of the polymers (Styrene and tert-butyl-Styrene) were still visible (Figure 5). As 10 microliters of water can fit into a Drop-In-Sample-Chamber (DISC) tube, the monomers of these polymers can be still be detected at a 100ppm or 0.01% level,with a split ratio of 50:1. Lowering the split ratio to 10:1 or 5:1, and working in Selected Ion Monitoring (SIM) mode, would increase this detection limit.

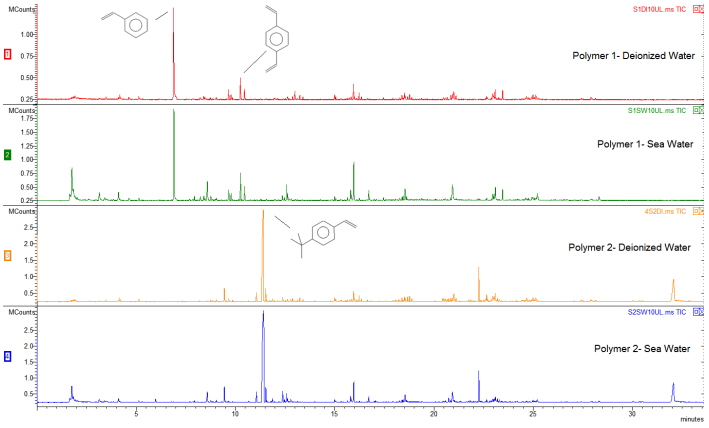

Figure 4. Styrenic plastics fresh water and salt water, 750°C.

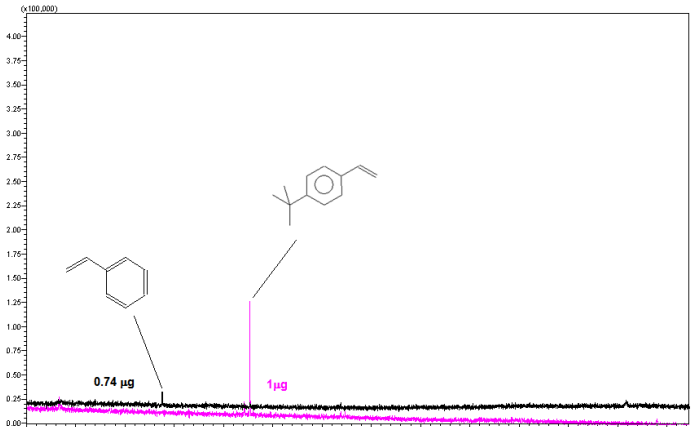

Figure 5. Styrenic polymers in water at 100ppm (0.01%), 750°C.

Plastic can also be found in our soil, arriving there either indirectly, or directly. For example, plastic film is often used as mulch, which can fragment into microplastics and accumulate in the soil. In this next example, polyethylene terephthalate was added to sandy loam soil at a 4% level. Of this soil, approximately 10mg can be added to a DISC tube, providing ample sensitivity to allow for the identification of PET. Figure 6 shows compares a PET standard to 4% PET in soil.

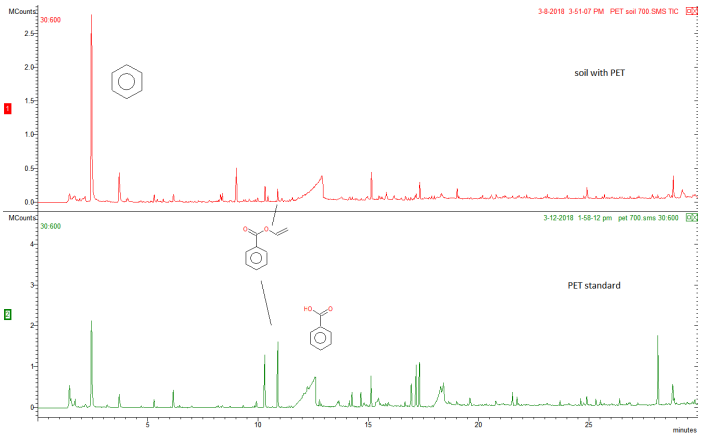

Figure 6. Sandy Loam Soil with 4% PET (top), and PET standard (bottom), 700°C.

Experimental Parameters

CDS Model 6150 Pyroprobe

Pyrolysis Dry:	200°C 2 minutes (when indicated)
Pyrolysis:	As specified in each run
Interface:	300°C
Transfer Line:	300°C
Valve Oven:	300°C

GC/MS

Column:	5% phenyl (30m x 0.25mm)
Carrier:	Helium 1.00mL/min, 50:1 split
Injector:	320°C
Oven:	40°C for 2 minutes
	10°C/min to 325°C
Ion Source:	230°C
Mass Range:	35-600amu

Results and Discussions:

From these examples, it is clear that different types of plastic pollution can be detected from natural materials such as seawater, seawater sediment, and soil. Confirmation of these plastics may be possible at a 0.1% level or lower, depending on the type of plastic and analysis conditions.