Quantitative Analysis of Microplastics Using the Pyroprobe with GC-MS

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Application Note
Environmental

Abstract
This application note demonstrates quantitative analysis of microplastics by pyrolyzing the sample into a GC-MS.

Introduction
Over 300 million tons of plastics are being manufactured every year and the scale of production is growing at a faster pace[1]. Studies showed that >10% of plastics eventually entered and contaminated the ocean[2,3]. Beside the traditional topics on cleaning macro plastic pollution in the sea, a growing attention on microplastics in sea water with <5 mm diameter size has been rising[4]. Many of the existing scientific surveys on the microplastics in ocean were using FT-IR and Raman techniques. Automation was recently achieved by optic method[5] to improve testing speed. However, such technique could only provide limited information on polymer type and size and is not capable in offering an accurate weight percentage of the pollutants. PY-GC-MS technique was introduced for this purpose[6].

In the previous publication[7], Pyroprobe was shown to identify microplastics in the sea water over ppm concentration when coupling to a mainstream GC-MS. This application note is a continued study to further quantify the microplastics concentration.

Experimental Setup
Five different plastics, which include PP, PET, PVC, PS and PE, were mixed at a random ratio. The mixing sample, 100 μg, was weighed and loaded into a DISC tube to mimic a complex sample concentrated from sea water. This simulant was then analyzed by a CDS 6150 Pyroprobe with a GC-MS. The system parameters are listed below:

Experimental Parameters

6150 Pyroprobe		GC-MS:	
DISC:	700°C	Column:	5% phenyl (30m x 0.25mm)
Ramp Rate:	20°C per ms	Carrier:	Helium 1.00 mL/min, 50:1 split
DISC Interface:	300°C	Injector:	360°C
Transfer Line:	300°C	Oven:	40°C for 2 minutes 12°C/min to 320°C (10min)
Valve Oven:	300°C	Ion Source:	230°C
		Mass Range:	35-600amu

Results and Discussion
Figure 1 is the pyrogram of the plastic mixture sample. All five polymers were all correctly identified. Table 1 listed each of the identified polymer with its marked peak. Figure 2 further displayed all the marked peaks for each polymer.

After polymer identification, a calibration curve was drawn on polystyrene only to demonstrate the feasibility of mass quantification on each component. The calibration curve was composed of four points.

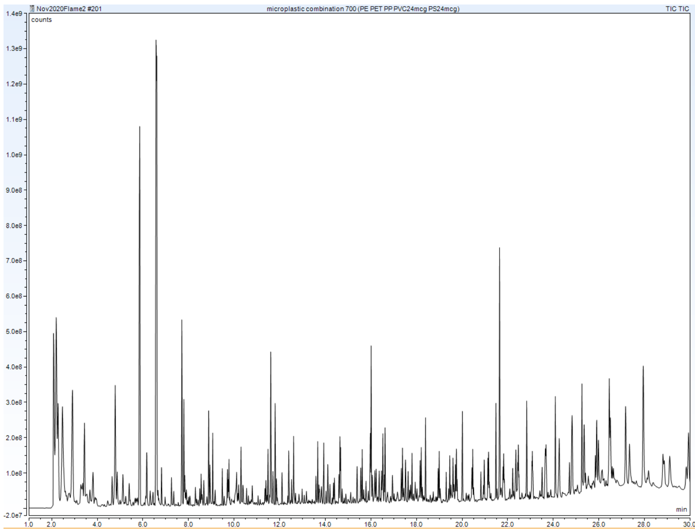
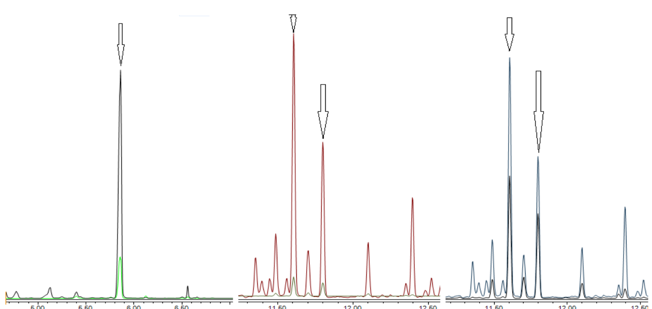


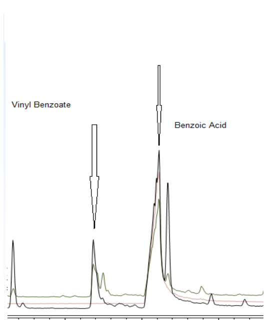
Figure 1. Pyrogram of mixed plastics, containing polypropylene, polyethylene terephthalate, polyvinyl chloride, polystyrene, and polyethylene.

Table 1. Mixed Plastic Marker Peaks

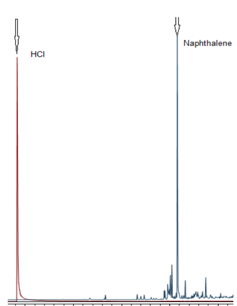
Polymer	Marker Peaks	Retention times	Ions
Polypropylene	trimer	5.86	70, 126
(PP)	tetramer	8.86, 8.90	69, 111
	pentamer	11.58,11.77	69, 111
Polyethylene terephthalate	vinyl benzoate	9.66	77, 105
(PET)	benzoic acid	10.24	105, 122
Polyvinyl chloride	HCl	2.08	36
(PVC)	naphthalene	10.38	128
Polystyrene	monomer	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



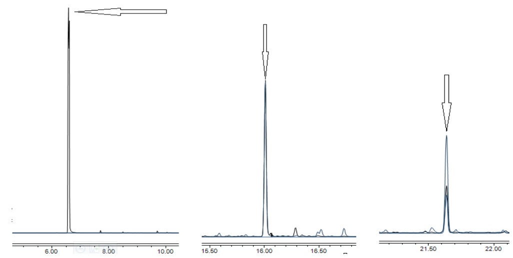
PP: trimer, tetramer, pentamer.



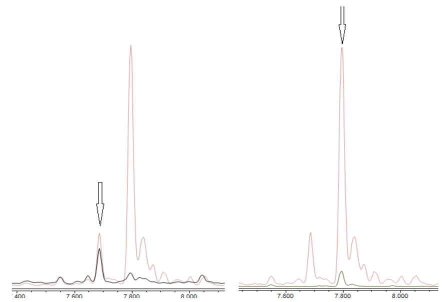
PET:vinyl benzoate, benzoic acid



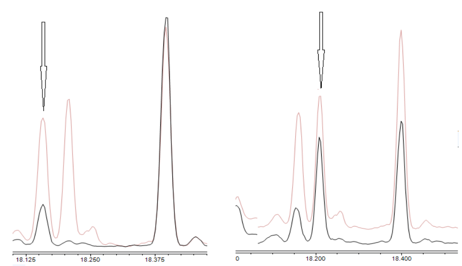
PVC: HCl, naphthalene



PS: monomer, dimer, trimer



PE: C10 diene and alkene.



PE: C20 diene and alkene

Figure 3. Extracted ion chromatograms for marker peaks in mixed plastics sample.

To make the calibration curve, a calibration stock solution was first prepared by dissolving polystyrene in toluene, resulting in a final polystyrene concentration of 11 μg/μL. Aliquots of 0.2, 0.4, 0.6, and 0.8 μL stock solution with an absolute mass of polystyrene at 2.2, 4.4, 6.6, and 8.8 μg respectively were added to 4 Drop-In-Sample-Chamber (DISC) tubes individually. Each calibration sample was pyrolyzed at the same condition, and areas of styrene monomer were plotted against the absolute mass of polystyrene. The calibration curve was then fitted with a single order polynomial in Figure 4 and the R^2 of data fitting was 0.997, which showed excellent linearity.

The area of styrene in the mixed plastic sample was calculated by integrating its monomer peak. This area was plugged into the calibration line in Figure 4 to calculate the polystyrene mass as 7.69 μg.

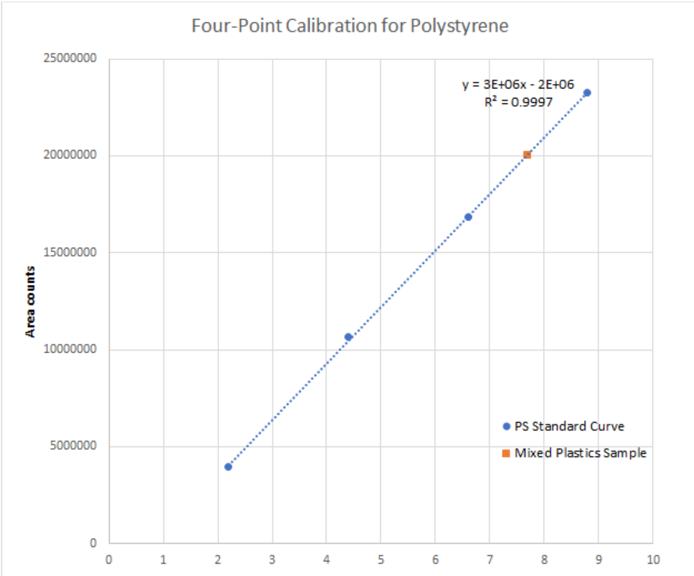


Figure 4. Polystyrene calibration.

Conclusions:

A mixture of 5 different polymers that mimics a complex environmental sample from sea water were analyzed quantitatively by Py-GC-MS method. The CDS Pyroprobe was demonstrated as a useful tool in investigating the pollution caused by microplastics.

References

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(5) Käppler, Andrea, et al. "Identification of microplastics by FTIR and Raman microscopy: a novel silicon filter substrate opens the important spectral range below 1300 cm– 1 for FTIR transmission measurements." Analytical and bioanalytical chemistry 407.22 (2015): 6791-6801

(6) Fischer, Marten, and Barbara M. Scholz-Böttcher. "Simultaneous trace identification and quantification of common types of microplastics in environmental samples by pyrolysis-gas chromatography–mass spectrometry." Environmental science & technology 51.9 (2017): 5052-5060.

(7) Sam, Karen, Detection of Plastic Pollution by the Pyroprobe, CDS App Note #214