Analysis of Microplastic Samples using Pyrolysis Gas Chromatography Mass Spectrometry

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Abstract

Plastics, micro- and nanoplastic pollution in oceans, lakes and other water sources is a well documented issue. Uptake of these particles by shellfish and fish is one avenue for the pollutants to enter the food chain and cause possible adverse effects. Micro- and nanoplastics are commonly used in commercially available products as abrasives. They end up in the environment from down the drain disposal. They are not efficiently removed in the waste water treatment process.

Raman and infrared spectroscopy are often used for identification, but dyes used in the plastic can sometimes hamper identification using these techniques.

This work will show the application of the GERSTEL pyrolyzer in combination with gas chromatography mass spectrometry for the identification of plastic pollution samples collected from the Great Lakes and from personal care products.

Keywords

Pyrolysis, smart ramped pyrolysis, fractionated pyrolysis, gas chromatography, mass spectrometry

Introduction

The GERSTEL Multipurpose Sampler (MPS) in combination with the GERSTEL Thermal Desorption Unit (TDU 2) and programmable temperature vaporizer (PTV) inlet, the CIS 4, provides the user with a multitude of analytical options to utilize for sample analysis. A pyrolysis insert, GERSTEL TDU PYRO, is also available for the TDU. The TDU PYRO offers efficient automation and a variety of modes including standard pulsed, sequential, and fractionated pyrolysis. The CIS 4 can be used to cryofocus analytes in the inlet or be used as a hot split interface for direct transfer to the column. This study describes the use of the GERSTEL MPS Robotic Sampler with CIS, TDU, and TDU Pyrolysis module for analysis of microplastic samples from the Great Lakes and commercial products.

Experimental

Instrumentation.

Analysis conditions.	
CIS 4:	solvent vent (50 mL/min), split transfer 75:1 -120°C; 12°C/sec; 325°C (3min)
Pneumatics:	He, constant flow, 1 mL/min
Column:	30m DB-5MS UI (Agilent) d_i=0.25 mm d_f=0.25 µm
Oven:	40°C (2 min); 10°C/min; 320°C (5 min)

Analysis conditions Smart Ramped Pyrolysis (SRP).	
Pyrolysis:	Lead Time: 0.00 min Follow up Time: 0.25 min Initial Time: 0.00 min Initial Temp: 300°C; 5.0°C/s; 800°C (0.1 min)
TDU:	splitless 40°C; 300°C/min; 300°C (2.02 min)

Analysis conditions fractionated pyrolysis.	
All fractions	
Pyrolysis:	Lead Time: 0.25 min Follow up Time: 0.25 min
TDU:	splitless
120°C fraction	
Pyrolysis:	Initial Time: 1.00 min Initial Temp: 120°C
TDU:	40°C; 60°C/min; 120°C (1.5 min) Transfertemp: 130°C
300°C fraction	
Pyrolysis:	Initial Time: 1.00 min Initial Temp: 300°C
TDU:	40°C; 160°C/min; 300°C (1.5 min) Transfertemp: 300°C
600°C fraction	
Pyrolysis:	Initial Time: 0.33 min Initial Temp: 600°C
TDU:	40°C; 720°C/min; 300°C (0.85 min) Transfertemp: 300°C

Sample Preparation Pyrolysis. Approximately less than one milligram of sample were weighed into a short, quartz test tube shaped pyrolysis vessel. The quartz tubes were connected to pyrolysis adapters and placed into a 40 position pyrolysis tray.

Results and Discussion

Five plastic samples and five sediment samples from the Great Lakes were obtained from Professor Sherri Mason, Penn State Behrend, Erie, PA. The sediment samples were aqueous with suspended strands and particles. The plastic samples were non-homogenous plastic particles.

Method development for flash pyrolysis GC/MS usually consists of running several pieces of the same sample at different pyrolysis temperatures and evaluating the chromatograms for secondary pyrolysis products in order to choose the optimum pyrolysis temperature for that particular sample. This can be a time consuming process and not practical when the amount of sample is limited.

Smart Ramped Pyrolysis (SRP) mode uses a temperature ramp of 5°C/s from 300 to 800°C. The slow temperature ramp, relative to pulsed pyrolysis, avoids the formation of secondary pyrolysis products. This mode produces chromatograms similar to those obtained using an optimized pulsed temperature. The result is the need to only run a single sample to achieve an optimum pyrogram. The plastic samples and sediment samples were analyzed using the Smart Ramped Pyrolysis (SRP) mode.

Figure 1 shows a photo of one of the plastic samples, GL13 #13. A variety of shapes and colors are found in this sample. For this sample, individual pieces of the red, green, white and black were run separately.

Figure 1. *Plastic sample GL13 #13.*

Table 1 shows the plastic identified for each of the "plastic" samples using pyrolysis GC/MS. The samples are identified by name. Different color particles were analyzed from the same "sample".

Table 1. *"Plastic" sample results.*

Sample Name	Plastic Identity
GL13 #3	Polypropylene
GL13 #10 Brown	Polypropylene
GL13 #10 Black	Polyethylene
GL13 #12	Mixed PE/PP
GL13 #13 Black	Polyethylene
GL13 #13 Green	Polyethylene
GL13 #13 Red	Polypropylene
GL13 #13 White	Polyethylene
GL13 #14 Red	Polypropylene
GL13 #14 White	Polypropylene

Figure 2 shows a chromatogram for Sample GL13 #13 (Green) showing a typical polyethylene pattern. Figure 3 shows a chromatogram for Sample GL13 #14 (white) showing a typical polypropylene pattern. The polymers identified in the samples were polyethylene and polypropylene. Samples GL13 #13 and GL13 #10 contained both polymers. The samples mainly being polypropylene and polyethylene is not surprising, as these samples were collected by netting and the densities of these two polymers would cause them to be most likely found in the water column.

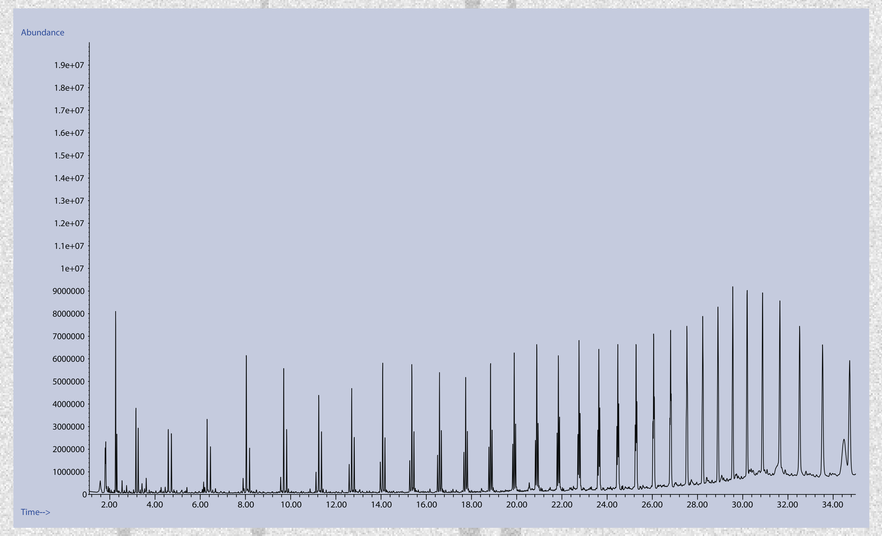

Figure 2. *Total ion chromatogram for sample GL13 #13 (green).*

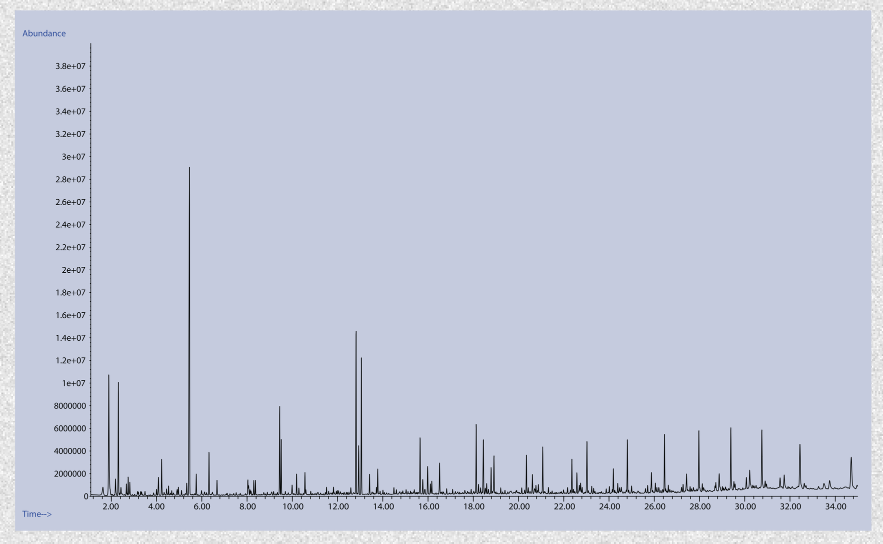

Figure 3. *Total ion chromatogram for sample GL13 #14 (white).*

The sediment samples presented a separate challenge as they were mainly aqueous solutions with suspended strands and particles. It was decided to use an open ended quartz pyrolysis tube with quartz wool to filter the samples. The bottom end of the quartz tube was set on a Kimwipe®. A 100 µL pipettor was used to add two by 100 µL of sample to the top of the tube. The water passed through the tube by capillary action and collected on the Kimwipe®. The suspended strands and particles were trapped on the quartz wool in the tube. The tubes were then dried in an oven for 30 minutes at 100°C to remove any remaining water. The samples were allowed to cool to room temperature and then analysed using SRP mode GC/MS.

Figure 4 shows a chromatogram for sample ER-60. Peaks of interest are labelled in the chromatogram. These include styrene (polystyrene), polyethylene series of peaks, methyl methacrylate (polyacrylate), siloxanes and a plasticizer, Bis(2-ethylhexyl) phthalate.

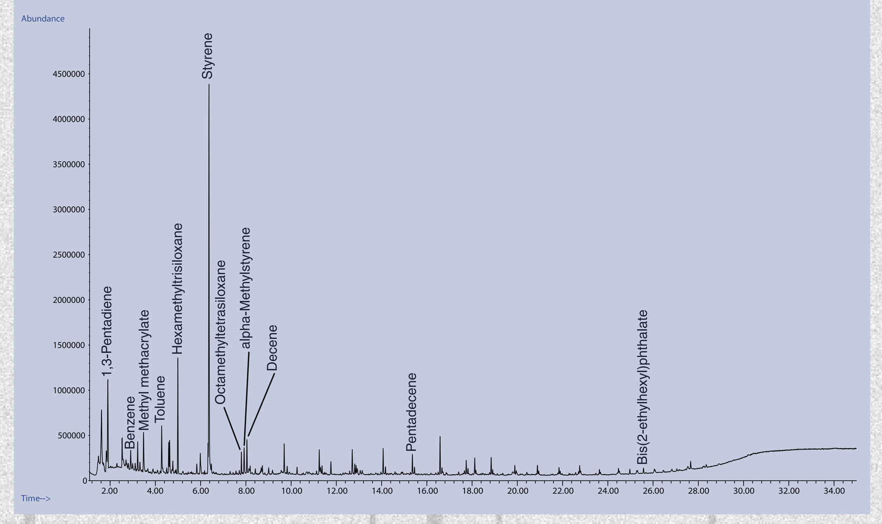

Figure 4. *Total ion chromatogram for sample ER-60.*

Figure 5 shows a chromatogram for Sample ER-07. Similar compounds are seen as in ER-60 such as methyl methacrylate, styrene, siloxanes and Bis(2-ethylhexyl) phthalate. In addition, phenol (polyphenol) and phthalic anhydride (polyester) are identified. Table 2 summarizes the results from the analysis of the sediment samples. Styrene and Bis(2-ethylhexyl) phthalate are common to all the samples.

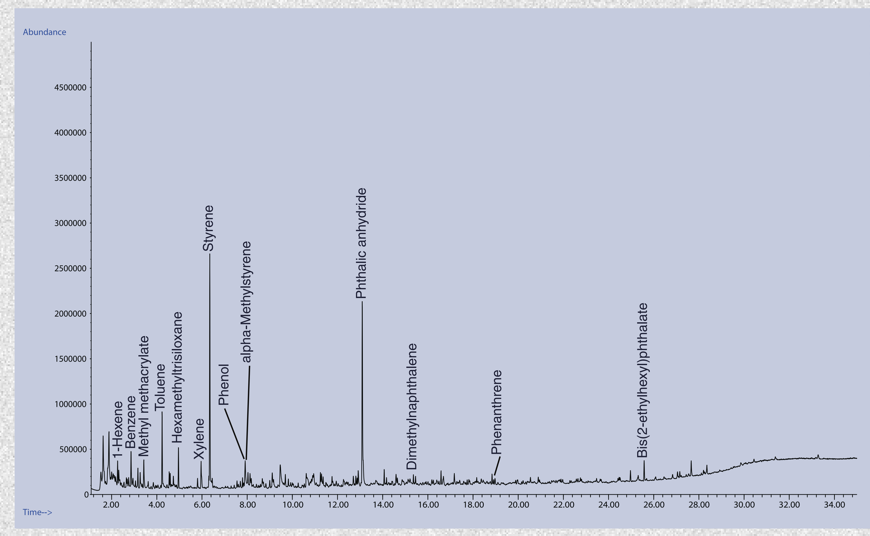

Figure 5. *Total ion chromatogram for sample ER-07.*

Table 2. *Sediment sample results.*

Sample	Compounds
ER-02	Styrene, methyl methacrylate, siloxanes, Bis(2-ethylhexyl) phthalate
ER-02 4-6 cm	Styrene, siloxane, creosol, Levoglucosan, Bis(2-ethylhexyl) phthalate
ER-07	Styrene, methyl methacrylate, siloxanes, Bis(2-ethylhexyl) phthalate, phthalic anhydride, phenol
ER-60	Styrene, methyl methacrylate, siloxanes, Bis(2-ethylhexyl) phthalate, polyethylene
ER-109	Styrene, methyl methacrylate, siloxanes, Bis(2-ethylhexyl) phthalate, wax

Microplastics in the environment can come from several sources including tires, marine coatings, dust, plastics, and personal care products, among others. Personal care products which contain microplastics include toothpaste, facial cleaners, scrubs, wipes and bath products.

In this last example, pyrolysis GC/MS is used to analyze a commercial facial wash product for microplastics. A small amount of the product was placed in an open ended quartz pyrolysis tube and analyzed using SRP mode. Figure 6 shows the resulting chromatogram. The chromatogram is complex and important peaks may be obscured.

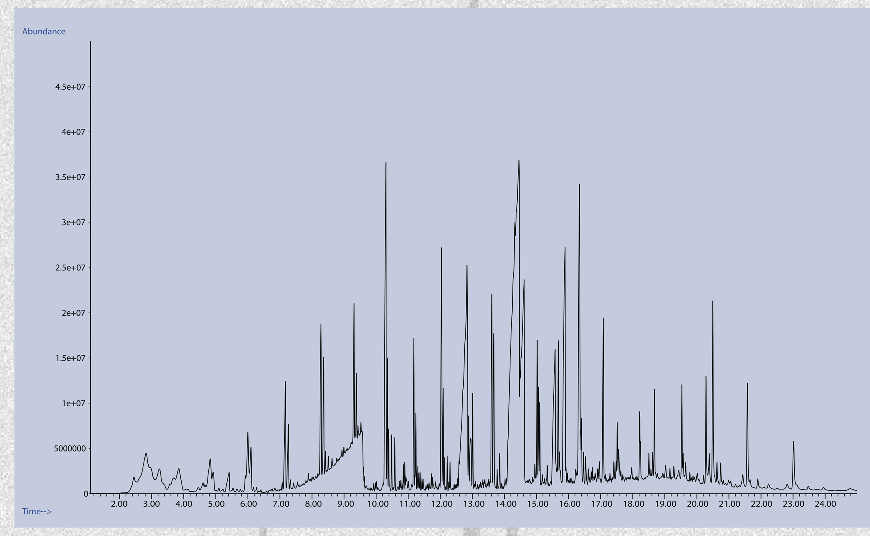

Figure 6. *Total ion chromatogram for facial scrub sample.*

One way to simplify this analysis is to perform fractionated pyrolysis of the sample. In this mode, an aliquot of the sample is analyzed three times at increasing temperatures. For this analysis, temperatures of 120, 300 and 600°C were chosen. Figure 7 shows a stacked view of the three chromatograms obtained at these temperatures. The fractionated approach simplifies the analysis. In the top chromatogram, 100°C, a large glycerol peak is present which is added to the product to increase skin smoothness and aid in moisture retention. 1,3-butanediol is a skin conditioner and stabilizer, 2-phenoxyethanol is added as a preservative and the long chain acids are added as moisturizers and anti-microbial agents. The middle chromatogram, 300°C, shows more of the long chain acids along with long chain amides, used as emulsifiers, siloxanes and sulfur dioxide. Sulfur dioxide can be a thermal degradation product of dextran sulfate which is commonly added to cosmetics as a binder/skin conditioning agent. The bottom chromatogram shows a pattern for polyethylene, most likely from beads added as an exfoliant.

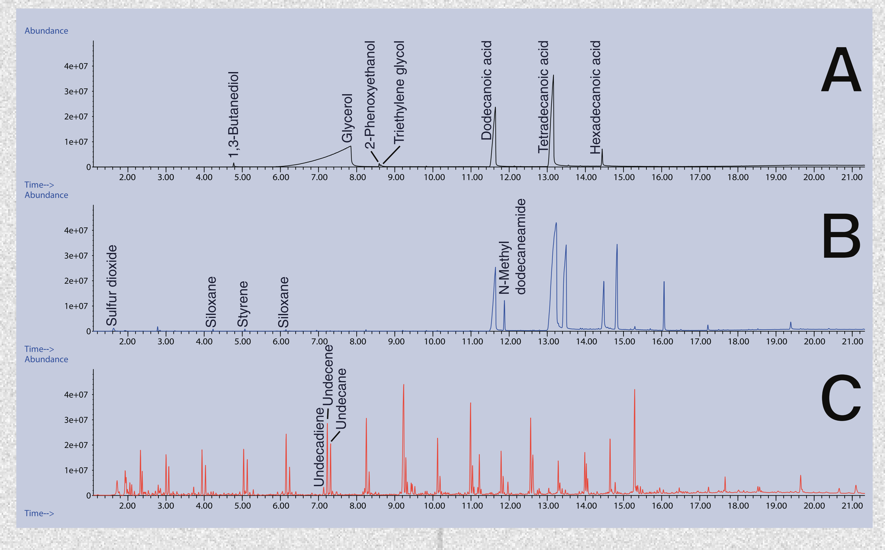

Figure 7. *Stacked view of facial scrub sample; 100°C (A), 300°C (B), 600°C (C).*

Conclusions

The GERSTEL MPS Robotic/TDU/CIS with the TDU PYRO insert can be used for the identification of microplastic samples from the environment. Smart Ramped Pyrolysis mode can be used in order to simplify methods development, especially for unknown samples and where a sample may be limited. Fractionated pyrolysis can be used in order to simplify a complex chromatogram and identify microplastics in commercial products.

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