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Determination of Microplastics using Pyrolysis Gas Chromatography Mass Spectrometry

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

Abstract

Plastics, micro- and nanoplastics 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 through drain disposal since they are not always efficiently removed in the waste water treatment process.

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

This work shows the application of pyrolysis (GERSTEL PYRO) in combination with gas chromatography mass spectrometry for the identification of plastic pollution samples collected from the Great Lakes and from personal care products.

Introduction

The GERSTEL Multipurpose Sampler (MPS) in combination with the GERSTEL Thermal Desorption Unit (TDU 2) and GERSTEL Cooled Injection System (CIS 4) programmable temperature vaporizer (PTV) inlet, provides the user with a multitude of analytical options to utilize for sample analysis. A pyrolysis insert, GERSTEL PYRO, is available for the TDU. The PYRO in combination with the MPS offers efficient automation along with a variety of modes including standard pulsed, sequential, fractionated, and smart ramped pyrolysis. In combination with PYRO, the CIS 4 can be used to cryofocus analytes in the inlet or as a hot split interface for direct transfer to the GC column.

This study describes the use of the GERSTEL MPS Robotic Sampler with CIS, TDU, and PYRO pyrolysis module for analysis of microplastic samples from the Great Lakes and for determination of microplastics in commercial products.

Experimental

Instrumentation.

Analysis conditions

Column:	DB-5MS UI (Agilent) di = 0.25 mm, df = 0.25µm, L = 30 m
Pneumatics:	He, Pi = 7.1 psi (MSD) Constant flow = 1.0 ml/min
Oven:	40°C (2.0 min), 10°C/min, 320°C (5 min)

Thermal Desorption Conditions

TDU	Splitless: 40 °C (0 min), 300 °C/min, 300 °C (2.02 min)
CIS 4:	Solvent vent (50 ml/min) Split Transfer 75:1 -120° (0 min), 12° C/sec, 325° C (3 min)

Pyrolysis (Microplastics Samples):

Lead Time:	0.00 min
Follow up Time:	0.25 min
Initial Time:	0.00 min
Initial Temp:	300°C (0 min), 5.0 °C/s, 800 °C (0.10 min)

Pyrolysis (Facial Scrub):

Lead Time:	0.25 min
Follow up Time:	0.25 min
Initial Time:	1.00 min (120 and 300 °C); 0.33 min (600 °C)
Initial Temp:	120 °C, 300 °C, or 600 °C
TDU (120 °C)	40 °C (0 min), 60 °C/min, 120 °C (1.5 min); Xfer Temp = 130 °C
TDU (300 °C)	40 °C (0 min), 160 °C/min, 300 °C (1.5 min); Xfer Temp = 300 oC
TDU (600 °C)	40 °C (0 min), 720 °C/min, 300 °C (0.85 min); Xfer Temp = 300 °C

Sample Preparation

Pyrolysis –A small piece, less than one milligram of sample, was put into a quartz tube pyrolysis vessel on top of a small piece of quartz wool. 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 it is 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. Slow temperature ramping, relative to pulsed pyrolysis, reduces or eliminates the formation of secondary pyrolysis products producing chromatograms that are similar to those obtained when pyrolyzing at optimial temperature in pulsed pyrolysis mode. As a result, only a single sample run is required to achieve an optimal 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. Individual pieces of the red, green, white and black materials seen were analyzed separately.

Figure 1: Plastic Sample GL13 #13

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 #13 White	Polypropylene

Table 1: "Plastic" Sample Results

Table 1 lists the plastic types identified in individual samples using pyrolysis GC/MS. The samples are identified by name. Different color particles from the same "sample" were analyzed separately.

Figure 2 shows a chromatogram resulting from SRP pyrolysis of sample GL13 #13 (Green) exhibiting a typical polyethylene pattern.

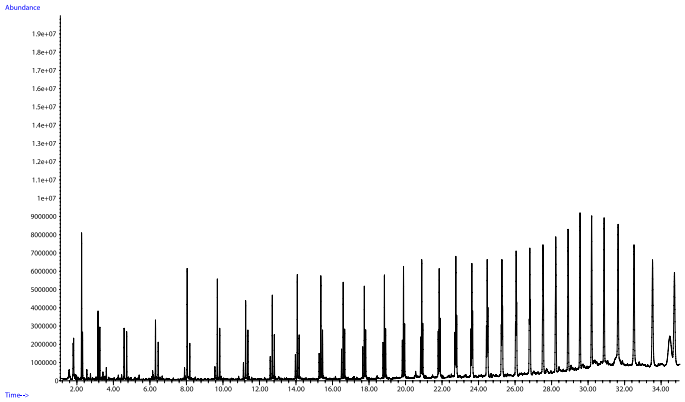

Figure 2: Total Ion Chromatogram for Sample GL13 #13 (Green)

Figure 3 shows a chromatogram for Sample GL13 #14 (white) with a typical polypropylene pattern.

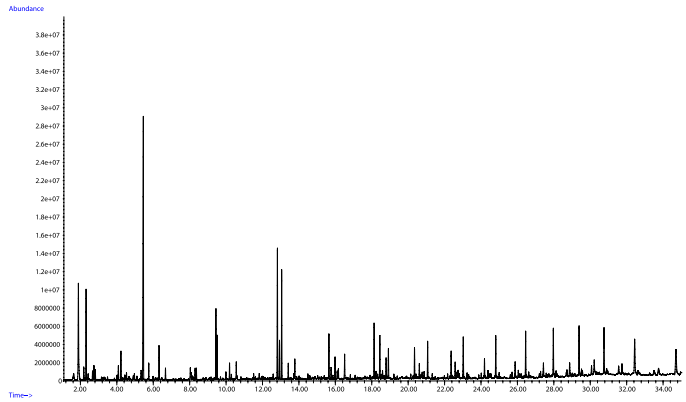

Figure 3: Total Ion Chromatogram for Sample GL13 #14 (White)

The polymers identified in the samples were polyethylene and polypropylene. Samples GL13 #13 and GL13 #10 contained both polymers.

That the polymer types found were mainly polypropylene and polyethylene is not surprising, as the samples were collected by netting and the densities of these two polymers would most likely cause them to be found in the water column.

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 100 µl volumes 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 before being analyzed using pyrolysis in SRP mode and GC/MS.

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

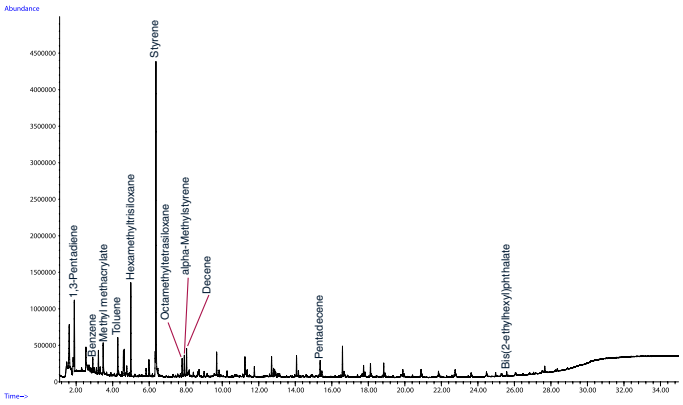

Figure 4: Total Ion Chromatogram for Sample ER-60

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.

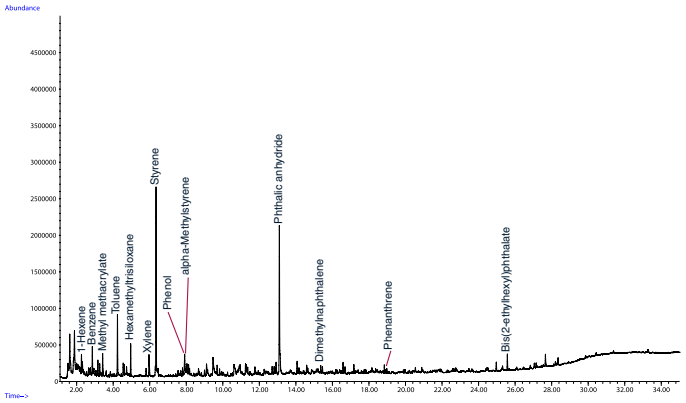

Figure 5: Total Ion Chromatogram for Sample ER-07

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

Table 2: Sediment Sample Results

Table 2 summarizes the results from the analysis of the sediment samples. Styrene and Bis(2-ethylhexyl) phthalate are common to all samples analyzed.

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.

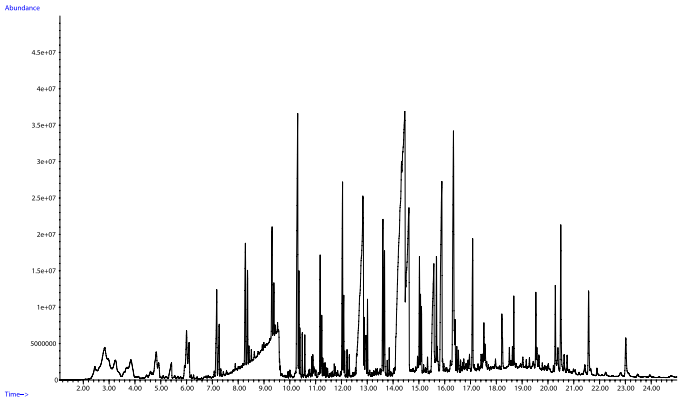

Figure 6: Total Ion Chromatogram for Facial Scrub Sample

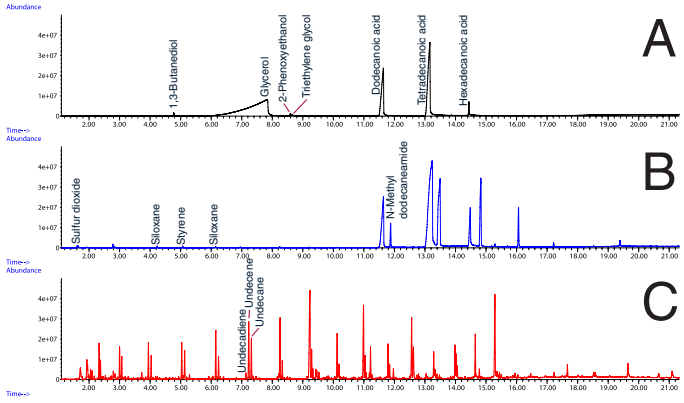

Figure 7: Stacked View of Facial Scrub Sample; 100 °C (Top), 300 °C (Middle), 600 °C (Bottom)

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, resulting from heating the sample to 120 °C, a large glycerol peak is present. The compound 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, run after heating the sample to 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.

Conclusions

The GERSTEL MPS Robotic/TDU/CIS fitted with the PYRO insert can be used for the identification of microplastics in environmental samples. Smart Ramped Pyrolysis mode can be used in order to simplify method development, especially for unknown samples, and in case only a limited amount of sample is available.. Fractionated pyrolysis can be used in order to separate compounds from complex samples into multiple chromatograms, simplifying the interpretation and helping to identify microplastics in commercial products.

GERSTEL AppNote

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