GERSTEL
MAKING LABS WORK

GERSTEL AppNote 232

Identification of Microplastics in Water by Pyrolysis Gas Chromatography Mass Spectrometry

John R. Stuff, Jaqueline A. Whitecavage, and Nicole C. Kfoury

GERSTEL, Inc., 701 Digital Drive, Suite J, Linthicum, MD 21090, USA

Keywords

Microplastics, filtration, pyrolysis, fractionated pyrolysis, gas chromatography, mass spectrometry

Abstract

Micro- and nanoplastics pollution in oceans, lakes and other water sources is an on-going and well-documented issue. Sources and entry ways of these plastics include grey water, surface runoff, and litter. Grey water is defined as the relatively clean wastewater from sources such as baths, sinks, washing machines and dishwashers. The very small plastic particle size precludes efficient removal during the wastewater treatment process. As a result, fish and other aquatic life ingest the plastics, which introduces them into the food chain and causes possible adverse effects. This work will show the identification of plastics in various water sources after filtration followed by analysis by the GERSTEL PYRO Core system in combination with gas chromatography mass spectrometry.

Introduction

Following visual inspection of plastic particles in a sample, analysis of micro- and nanoplastics is primarily performed by Fourier transform infrared (FT-IR) spectroscopy with imaging software, which can count particles and confirm the polymer type of the detected plastics. However, in terms of mass content, spectroscopic techniques lack accuracy and precision, cannot detect particles smaller than 10 μm, and are influenced by complex matrices. Furthermore, spectroscopic techniques cannot detect tire abrasion particles due to high levels of carbon black, which absorbs all light. Tire abrasion can constitute up to 50% by mass of microplastics introduced to the environment depending on the geographic region, mainly the synthetic SBR rubber used for car tires. Pyrolysis gas chromatography mass spectrometry provides a promising solution for analyzing plastics too small to detect by other methods, especially when present in a complex matrix.

The GERSTEL pyrolizer heats the sample using an advanced dual coil platinum wire that allows it to operate in a variety of pyrolysis modes including standard pulsed, sequential, and fractionated. In addition, lower temperatures can be used to perform thermal desorption before pyrolysis. The unique heating system provides uniform sample heating and unmatched reproducibility. The system has an integrated GERSTEL CIS 4 inlet that can be used to cryofocus analytes in the inlet or be used as a hot split interface for direct transfer to the column. An also integrated GERSTEL MultiPurpose Sampler MPS allows for complete automation of the analysis.

This study describes the use of the GERSTEL PYRO Core system for analysis of microplastics in water samples. The samples were first filtered, the filtrates then analyzed by pyrolysis GC-MS.

GERSTEL AppNote 232

Experimental

Instrumentation

GERSTEL PYRO Core system on Agilent 8890 GC with Agilent 5977B MSD.

Analysis Conditions PYRO Core System

PYRO	Microplastic Samples	
	Lead time	0.00 min
	Follow up time	0.50 min
	Initial time	0.00 min
	Temp	300 °C, 5.0 °C/s to 800 °C
CIS 4	Split 25:1	
	300 °C isothermal	

PYRO	Facial Scrub	
	Lead time	0.25 min
	Follow up time	0.25 min
	Initial time	5.00 min (120 and 300 °C)
		0.33 min (600 °C)
	Temp	120 °C, 300 °C, or 600 °C
CIS 4	Split 50:1	
	300 °C isothermal	

Analysis Conditions Agilent 8890 GC

Column	30 m DB-5MS UI (Agilent)
	d_i = 0.25 mm, d_f = 0.25 µm
Pneumatics	He, P_i = 7.1 psi (MSD)
	Constant flow = 1.0 mL/min
Oven	40 °C (1.0 min), 15 °C/min to 320 °C (15 min)

Sample Preparation

Samples – Pond water and surface runoff samples were collected locally. A facial scrub with polyethylene was created for proof of concept. Polyethylene was cryomilled in a SPEX Sample Prep 6775 Freezer/Mill and then added to the facial scrub at a level of 1 wt %. The particle size range for the cryogrinding conditions used is typically 200-500 microns. A simulated grey water sample was created by adding 1 g of the facial scrub to 1 L of bottled water. Bottled water was purchased locally.

Filtration – One liter of aqueous sample was vacuumed filtered through a 10 µM PTFE filter (ADVANTEC 47 mm PTFE Filter, Cole-Parmer #36240-08). The filters were allowed to air dry at room temperature overnight.

Pyrolysis – Approximately one milligram of sample was placed into an open-ended quartz pyrolysis tube with quartz wool. The quartz tubes were connected to pyrolysis transport adapters and placed into individually sealed sample positions in a 40 position PYRO tray. For punch samples, a 1.2 mm punch (Harris Uni-Core 1.20) was used to sample the filters. The whole punch was placed into the quartz pyrolysis tubes.

Results and Discussion

Figure 1 shows the filtrate samples prior to drying. A beige filtrate is seen for the grey water, black for the runoff sample, green for the pond sample and clear for the bottled water sample.

Grey water | Runoff | Pond water | Bottled water

Figure 1: Filtrate samples, prior to drying.

GERSTEL AppNote 232

Figures 2 shows fractionated pyrolysis of a sample of the spiked facial scrub. Fractionated pyrolysis uses multiple steps for a sample under varying conditions. It typically involves a thermal desorption step followed by a pyrolysis step. It can be used for removal or separate determination of interfering volatiles. It allows clear differentiation of adsorbed volatiles and pyrolysis products and usually results in a simpler pyrogram which makes data interpretation more accurate.

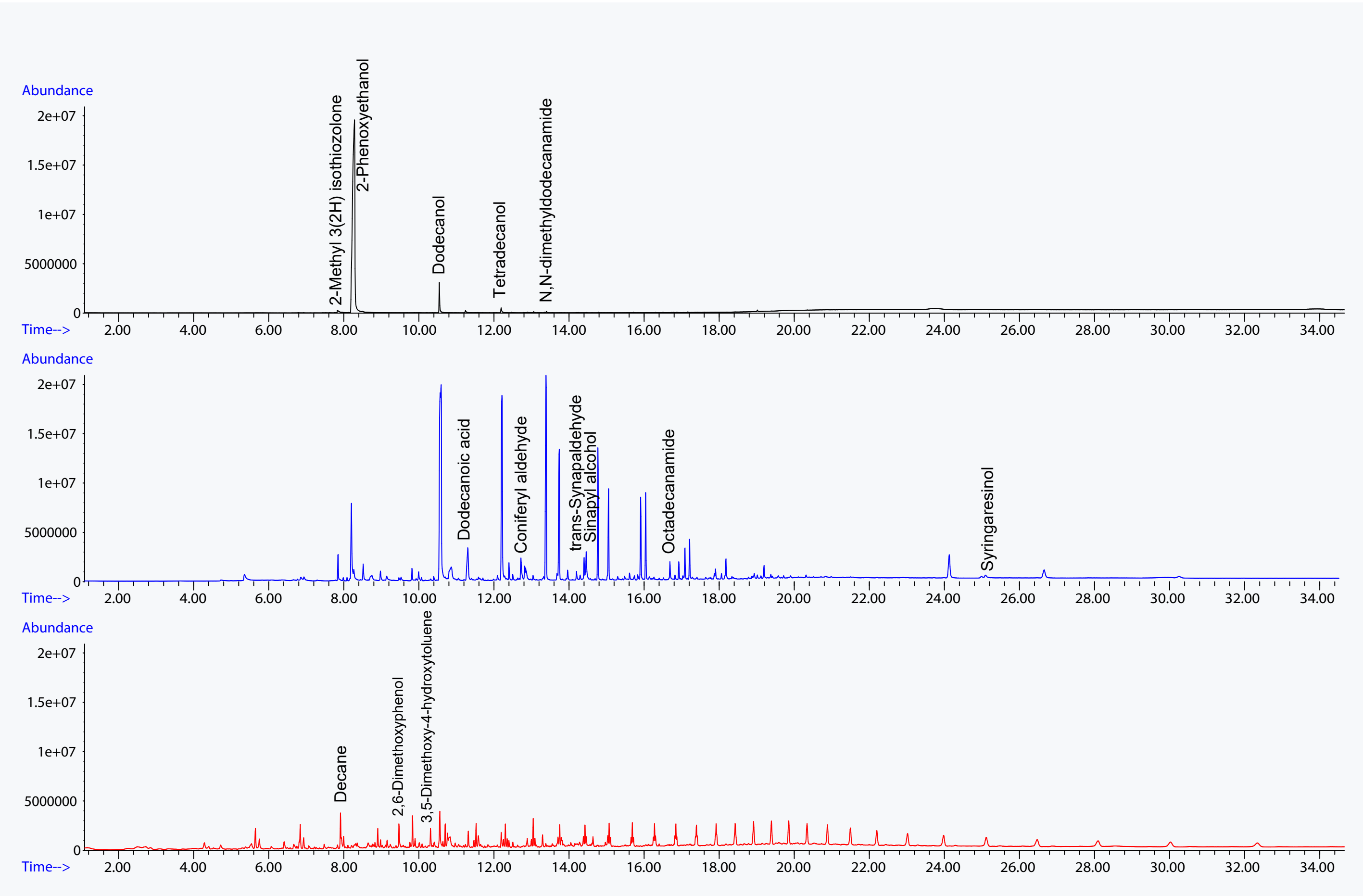

Figure 2: Stacked view of total ion chromatograms for facial scrub extracted at 120 °C (top), facial scrub extracted at 300 °C (middle) and pyrogram for facial scrub pulsed to 600 °C (bottom).

The top chromatogram in figure 2, shows the facial scrub sample extracted at 120 °C for 5 minutes. Several compounds can be seen in the chromatogram including 2-methyl 3(2H) isothiozolone which is added as a biocide, long chain alcohols added as emollients, N,N-dimethyldodecanamide added as a surfactant, and the largest peak, 2-phenoxy ethanol added as a preservative.

The middle chromatogram in figure 2, shows the extraction of the facial scrub at 300 °C for 5 minutes. This chromatogram contains several long chain amides used as emulsifiers, long chain acids used as moisturizers and anti-microbial agents, and skin conditioning agents such as coniferyl aldehyde, trans-synapaldehyde and syringaresinol.

The bottom chromatogram in figure 2 shows how well the fractionation technique works in providing a clean pyrogram for the polyethylene particles contained in the facial scrub. The chromatogram also shows peaks for 3,5-dimethoxy-4-hydroxytoluene and 2,6-dimethoxyphenol which may be byproducts of the pyrolysis of the nutshell powder used in this formulation.

GERSTEL
MAKING LABS WORK

GERSTEL AppNote 232

Figure 3 shows the resulting pyrogram for a 1.2 mm punch of an unused PTFE filter. The pyrogram is relatively clean. The large peak at the beginning of the chromatogram is mainly C_2F_6 and some other fluorinated alkanes formed from the pyrolysis of the PTFE. The levoglucosan and squalene are background peaks.

No pyrogram is shown for the bottled water filtrate, as no peaks beside hexafluoroethane were seen.

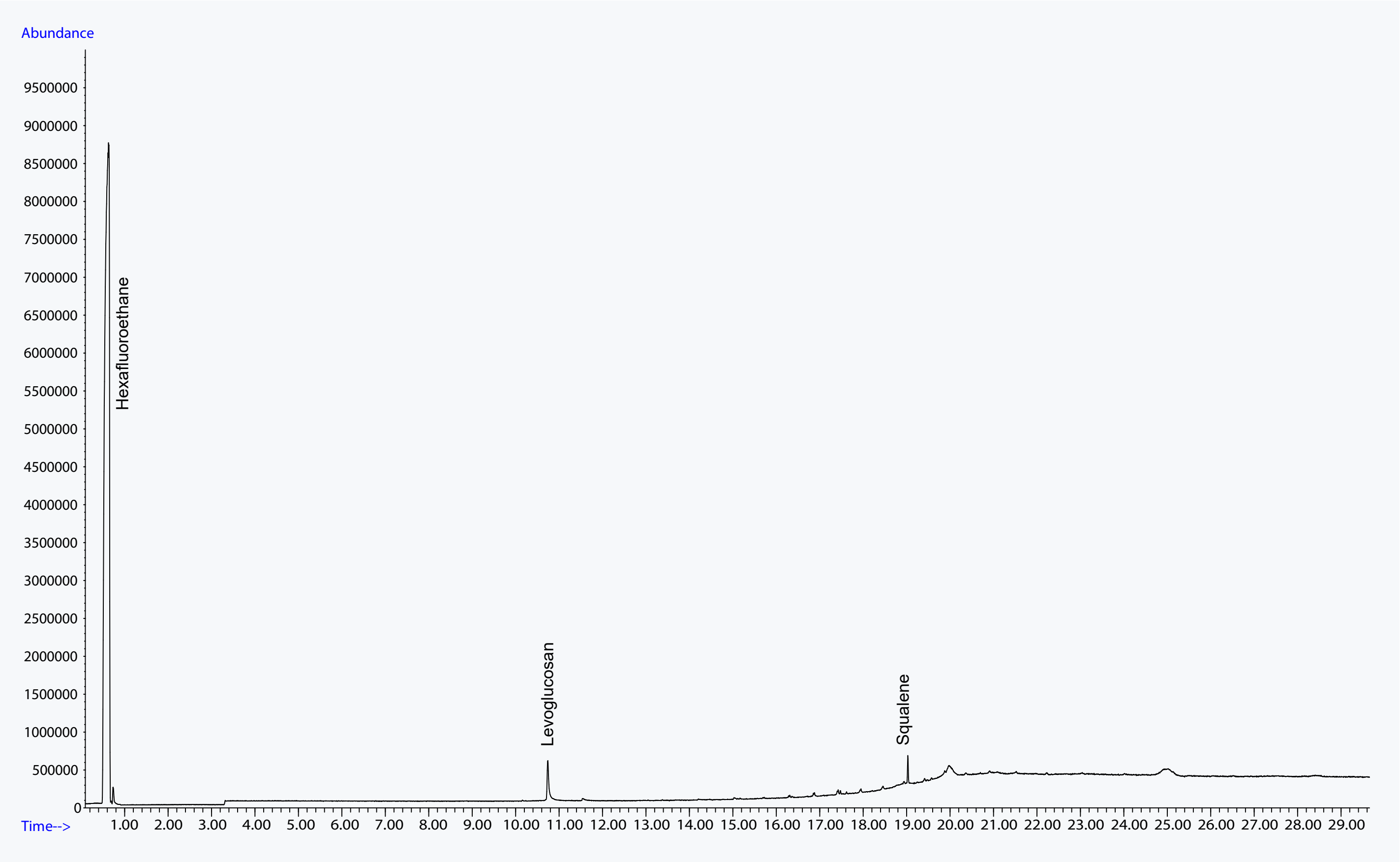

Figure 3: Pyrogram for punch of an unused Teflon filter; SRP mode.

Figure 4 shows the pyrogram of a 1.2 mm punch of the simulated grey water. The pattern for the polyethylene is clearly seen indicating that the PE particles were trapped by the filter. Styrene is also present, which may be from other components in the facial scrub formulation. Other components from the facial scrub are dissolved in the water and not trapped by the filter.

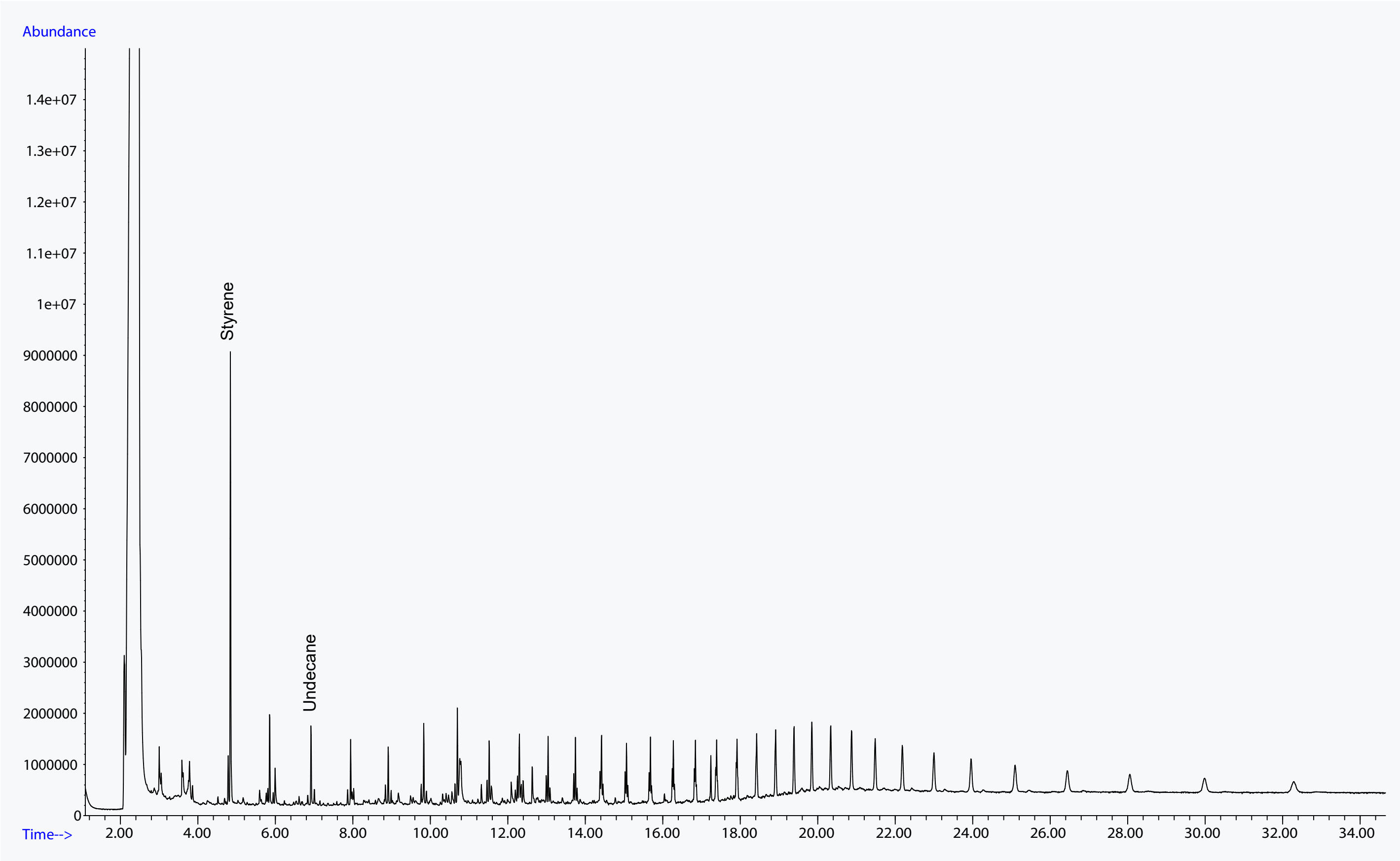

Figure 4: Pyrogram for punch of grey water filtrate; SRP mode.

GERSTEL AppNote 232

Figure 5 shows the pyrogram for a 1.2 mm punch of the pond water filtrate. Peaks for the plasticizers bis(2-ethylhexyl) phthalate and di-isononyl phthalate are seen in the figure. Styrene and alpha-methyl styrene are present indicating polystyrene in the water. Phthalic anhydride is also seen, which is a possible pyrolysis product of polyester.

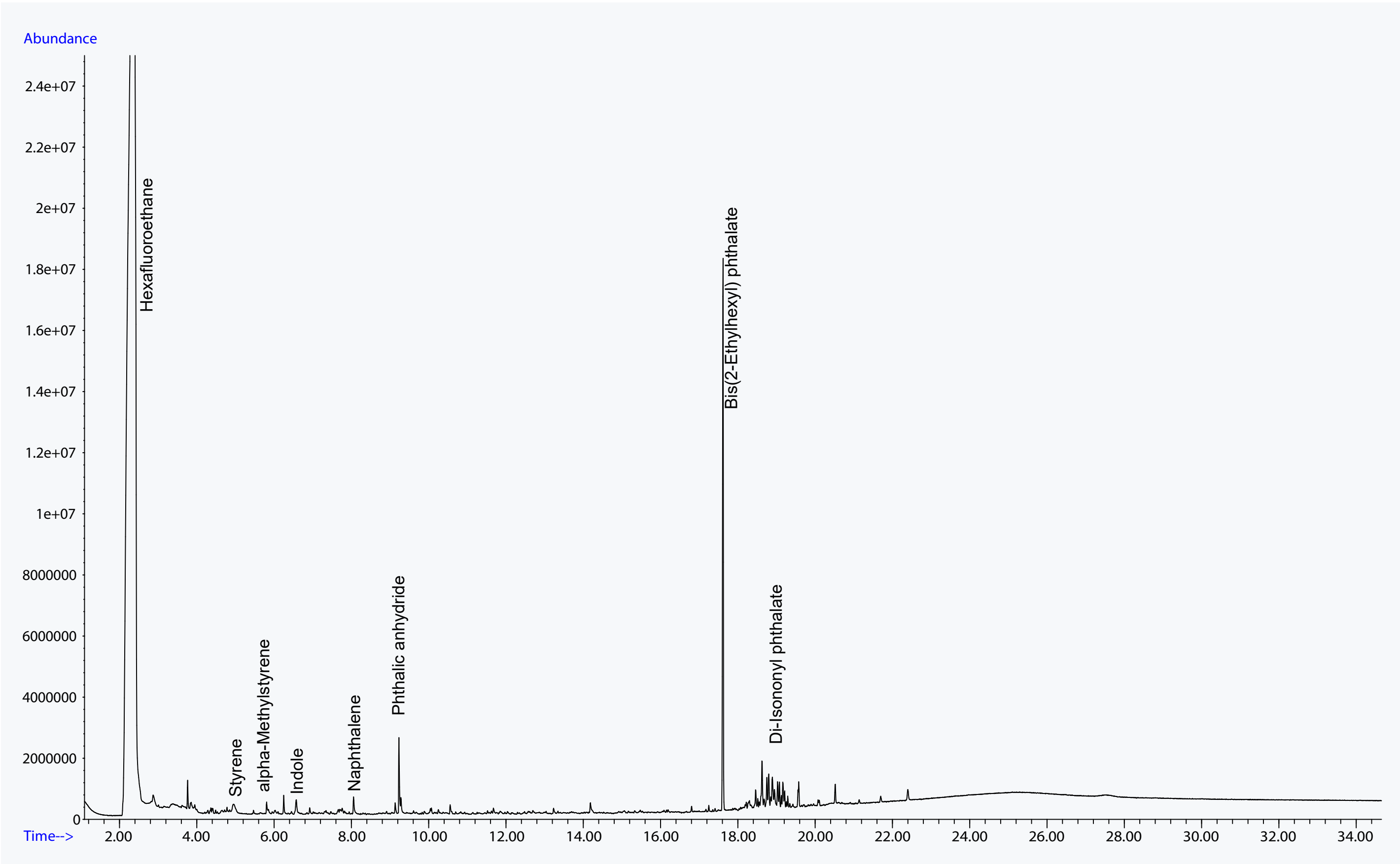

Figure 5: Pyrogram for punch of pond filtrate; SRP mode.

GERSTEL AppNote 232

A 1.2 mm punch of the runoff filtrate did not show significant amounts of pyrolysis products. Approximately ¼ of the filtrate was scraped off the filter. Figure 6 shows the pyrogram from scrapings off the runoff filtrate. The main pyrolysis products seen correspond to what would be expected from an SBR type rubber: Isoprene, styrene, isoprene dimer and 4-ethenyl cyclohexene.

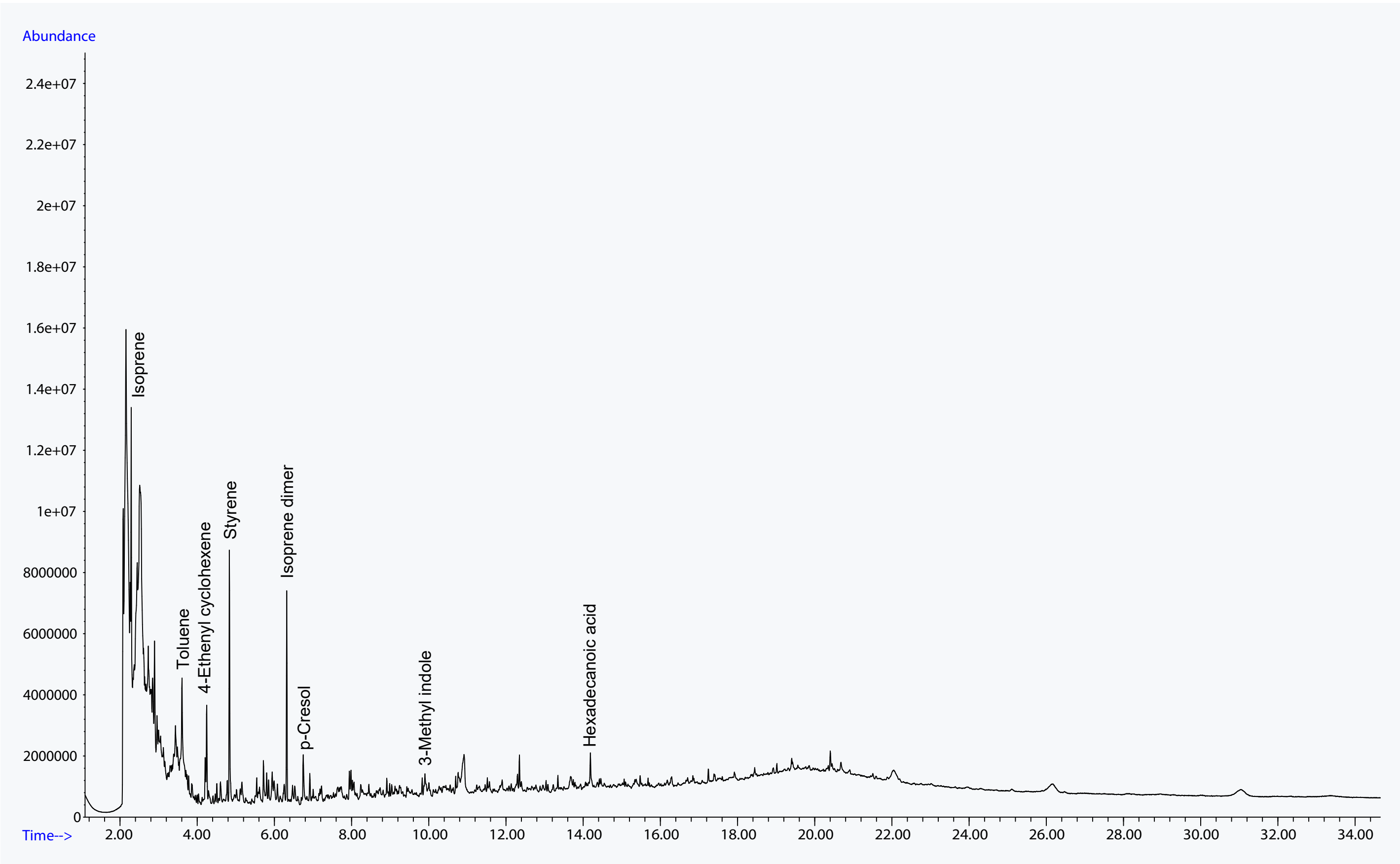

Figure 6: Pyrogram for scrapings of the runoff filtrate; SRP mode.

Conclusion

Filtration followed by pyrolysis GC-MS using the GERSTEL PYRO Core system can capture and identify polymers found in aqueous samples. The use of fractionated pyrolysis greatly simplifies data interpretation of complex samples. The polyethylene PE in the simulated grey water was easily trapped and identified. The pond sample also showed the presence of polymers and plasticizers from polymers which can potentially affect aquatic life. The runoff sample analysis result confirmed that roadways are a source of polymer pollution in terms of SBR rubber particles.