

Pyrolysis GC-MS characterization of plastic debris from the Northern Gulf of Alaska shorelines.

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ABSTRACT:

Plastics and their breakdown components are accumulating at alarming rates in global ecosystems, including the Gulf of Alaska. Obtaining knowledge of the chemical composition of plastics is important because different types of plastics are manufactured using different types of polymers and copolymers for specialized applications. We employed pyrolysis GC-MS for the chemical characterization of 115 plastic debris samples of different physical and optical properties non-randomly collected from shorelines in the northern Gulf of Alaska. A two-tier approach of peak fingerprinting and mass spectral data of marker peaks provided higher confidence in the data. The analyses did not appear to be compromised by the physical properties, optical properties, or weathering conditions of the debris. Polyethylene and polypropylene, the low-density floating plastics possibly of oceanic origins, were some of the most frequently detected polymers in the Katmai National Park and Preserve and Kenai Fjords National Park. Interestingly, a more diverse composition of polyethylene, polypropylene, polystyrene, polyethylene terephthalate, and polyvinyl chloride was detected in Western Prince William Sound shorelines, possibly of oceanic as well as terrestrial origins. Additional benefits of the pyrolysis GC-MS method included the detection of copolymers and plastic additives in the same analytical runs.

KEYWORDS

Plastic Pollution, Northern Gulf of Alaska, Chemical Characterization, Pyrolysis GC-MS, Polymers, Co-Polymers, Additives

SYNOPSIS

Few studies exist on the nature of plastic debris in Alaska. We used pyrolysis GC-MS for the analyses of polymers, co-polymers, and chemical additives in non-randomly collected samples.

INTRODUCTION

It is an unfortunate paradox that the extremely remote, beautiful, and picturesque shorelines of the Gulf of Alaska (GOA) continue to be inundated with enormous amounts of debris carried by winter storm events, ocean currents, and wind. While local sources play a part, a significant

contribution is likely from the Western Pacific nations with under-developed waste management systems¹⁻⁵. The Tohoku earthquake of 2011 and the resulting tsunami sharply increased the debris on northern Gulf of Alaska beaches in the years immediately following the event. Polasek et al.¹ reported marine debris at all 28 beaches surveyed from the five coastal National Park Service units in Alaska, where plastic containing foam, ropes, nets, and hard plastics contributed to 60% of the total weight of the debris. Rope and netting (14.6%) were found in a greater proportion of the weight than foam (13.3%) from all beaches. The Gulf of Alaska Keeper⁵ reported that besides the plastics, other types of debris of concern on Alaskan beaches include the containers of pharmaceuticals, cleansers, bleach, medical waste, coolants, industrial chemicals, lubricants, engine oil, and creosote-treated lumber.

Plastics, once generally perceived to be benign, are now recognized as contaminants of worldwide concern. The weathering forces of storms, surf, and sun further disintegrate the plastic debris into 5 mm or smaller microplastics. As these microplastic particles can appear similar to aquatic prey items, fish, birds, and other marine taxa can mistakenly ingest them. Debris littered on the sensitive coastal habitats of Alaska can thus potentially affect the health and quality of the vegetation, spawning streams, wildlife, fisheries, and aquaculture facilities. Clean up of plastic pollution, control of future releases, and monitoring of status and trends are the logical and most critical steps in restoring healthy ecosystems, sustainable fisheries, and the blue economy.

Different types of plastics exhibit different density-dependent distribution patterns in aquatic environments, contain different additives, adsorb different amounts of chemical contaminants from the water column, and exert different toxicities in marine organisms. Understanding the nature of plastic debris being washed on Alaskan beaches is critical to identifying, regulating, and mitigating sources of plastics. Team members from Gulf Watch Alaska, a nearshore marine monitoring program in the northern GOA, collected a non-random array of different types of weathered and non-weathered plastics from their long-term study sites for us to test the utility of pyrolysis GC-MS for plastic identification. We analyzed 115 different plastic samples for the identification of polymers, co-polymers, and plastic additives. The results of the analyses are reported here.

MATERIALS AND METHODS

Field Collection. The Nearshore Ecosystem Monitoring Group of the Gulf Watch Alaska Program collected the samples of plastic debris from the three sampling regions: Katmai National Park and Preserve (n=36), Kenai Fjords National Park (n=56), and Western Prince William Sound (n=23) (Figure 1). The field team non-randomly selected 3-5 shorelines from each of the sampling regions during the summer months of 2017. The shorelines were selected based on

accessibility by a small skiff and their walkability. Not all accessible shorelines were searched and not all shorelines were equal in length.

Up to ten small pieces of different types of plastics were targeted from each shoreline along the high tide line and storm tide line, resulting in a total of 115 samples. An effort was made to collect an array of visually different types of plastics, but the amount of each type of plastic was not quantified because it was not intended to be an exhaustive collection. The plastic debris of various shapes, sizes, densities, hardness, color, opacities, and degradation conditions was comprised of fragments, foams, ropes, caps, wraps, a belt, broken bottles, a cigar tip, and a butane lighter. A few examples of the sizes of the plastic debris pieces are depicted along with a ruler in Figure S20. The debris sizes ranged from about 0.5 cm in width to about 15 cm in length. The plastic cap diameter was as wide as about 7.5 cm. Three caps that had Asian-language inscriptions, could have either originated from local discards or based on the literature, from long-range transports from Pacific Asian countries.

The field collectors had no prior knowledge of the polymer chemistries of the plastics they were collecting. The goal of their non-random sampling was to simply collect different types of visually interesting plastic pieces of different colors, forms, or shapes. The non-randomly collected samples thus may not represent all plastic types from the northern shorelines of the Gulf of Alaska in terms of their polymer compositions. One field note indicated that only five samples could be collected on Ninagiak Island in Hallo Bay from Katmai National Park and Preserve due to the presence of grizzly bears on the beach.

Plastic samples were stored, grouped by collection location, at ambient temperature until shipment to the NOAA Sandy Hook Laboratory for analysis. All samples were analyzed as received in their raw natural environmental states without any additional chemical, enzymatic, or physical treatment, except for cutting a small piece of the sample required for the pyrolysis GC-MS analysis.

Pyrolysis GC-MS Methods. Pyrolysis GC-MS was employed for the chemical characterization of constituent polymers, copolymers, and additives in plastics of different morphological and optical properties and in plastics in different weathering conditions. Pyrolysis GC-MS is recognized as one of the most promising and accurate techniques in the field of polymer analyses.

The whole debris sample was not pyrolyzed. A scalpel knife was used to cut a smaller piece of the fragment for the pyrolysis GC-MS analysis. For the colored/multicolored debris, a random piece was cut for the analysis with the assumption that the colors will minimally interfere with

the analyses. The dyes used for coloring the plastics usually have high molecular extinction coefficients, and therefore the amount of dye needed to give a bright color to the plastic is comparatively minuscule. The mass spectral signals of pyrolyzed products generated from the tiny amounts of dyes were therefore expected to be proportionately much smaller than the polymer signal and hidden in the baseline of the mass spectrum.

In the pyrolysis GC-MS procedure, a quartz tube (2.5 mm OD/1.9 mm ID x 25mm L) was heat-cleaned 3 times for 20 seconds each at 1200°C before a small piece of plastic debris was placed inside. The goal was to use about 0.2 cm long plastic piece for the analysis. The quartz tube was placed in a platinum coil (6.35 mm OD x 25 mm L) of a CDS-2000 Pyroprobe. The pyroprobe was inserted into a CDS-1500 Valved GC Interface maintained at 320°C. The sample in the quartz tube was pyrolyzed by heating the platinum filament at 750°C for 2 seconds in the presence of hydrogen. Hydrogen generated from a Parker Balston Hydrogen Generator Model H2-300NA was also used as a carrier gas for the Agilent 6890N GC. The intense heat in the pyroprobe breaks down the large plastic polymer chains into smaller fragments, and the resulting pyrolytic fragmentation patterns are reproducible and unique to a given polymer type. The pyrolyzed fragments were transferred to and separated on a DB-5 (0.25 mm OD x 60 m length; 0.25 μ film thickness) fused-silica capillary column. The CDS-1500 GC Interface valve was closed after one min. The column oven temperature was initially held at 45°C for 2 min and then ramped to 320°C at a rate of 20°C/min. The column oven was then held at 320°C for 19 min resulting in a total run time of 34.75 min. The flow rate for the hydrogen carrier gas for the GC column was 1.2 ml/min in constant flow mode. The inlet and mass spectrometer transfer line heater were maintained at 320°C. The whole pyrolyzed sample mixture was not analyzed by the GC-MS. The inlet split ratio was 50:1. The mixture entering the GC inlet was not trapped in any way, but it was transferred directly to the GC column.

Plastic Identification. Marker peaks were identified by using an Agilent 5973 Mass Selective Detector. Data acquisition was performed in full-scan mode from 29-600 m/z by using Agilent ChemStation Software. The mass spectrometer quadrupole and source temperatures were held at 150°C and 230°C respectively. The electron multiplier auto-tune voltage was adjusted by 200V above the auto-tune voltage. The pyrograms of the collected plastics were compared with pyrograms in a pyrolysis GC-MS library created in-house for some of the most common polymers in commercial plastics products. Identification of unknown pyrograms beyond our library collection was based on the information available on the internet, application notes, a book¹⁰, and published literature.

The samples of plastic debris we analyzed were typically greater than the 0.5 cm size used for the definition of microplastics. When the debris was cut into a smaller piece for the pyrolysis

GC-MS analysis, it was below 0.5 cm and it was like analyzing a microplastic fragment. We thus actually analyzed the microplastics, although the original samples were of greater sizes.

The Use of Hydrogen for Pyrolysis GC-MS Analyses. Watanabe et al.⁶ compared the use of nitrogen, helium, and hydrogen for the pyrolysis GC-MS analyses. The authors first compared the chromatographic properties of the gases. They noted that both hydrogen and helium exhibit a broad minimum on the van Deemter curve, and the separating power of the chromatographic column does not change appreciably as the carrier gas linear velocity increases. The authors stated that hydrogen has the lowest viscosity, and it thus provides the highest mobile phase velocity that produces the required separation in the shortest time. Despite the desirable properties of hydrogen as a carrier gas, the authors cautioned about its use due to its flammability issue. In our laboratory, we used a hydrogen generator that produced only the required amount of hydrogen, and as needed. This produced hydrogen is used immediately and it is not stored anywhere. The hydrogen generator also has a feature that shuts itself off in case of a pressure drop due to a leak somewhere along the gas line.

Watanabe et al.⁶ compared the pyrograms of 24 polymer samples using helium and hydrogen. The authors stated that the differences in the pyrograms by using helium and hydrogen were due to the hydrogenation reactions occurring during the pyrolysis as well as in the electron ionization source of the mass spectrometer. The authors however found that the effect of the hydrogenation reaction on the library search results was negligible for most polymer samples with polar and nonpolar monomer units. The authors concluded that using hydrogen as a carrier gas will not adversely affect the match quality of a library search, although caution is needed whenever helium-based libraries are used to identify components in radically different chemical environments. Watanabe et al.⁶ stated that Moldoveanu⁷ reported that pyrolysis in a hydrogen atmosphere proceeds, in most cases, like pyrolysis in an inert gas such as helium and nitrogen. They stated that this is because many molecules are less reactive in molecular hydrogen. The hydrogen generator provided in-house, high-quality hydrogen safely, and the chromatography was equivalent to or theoretically superior to helium. The use of the hydrogen generator also resulted in substantial cost savings for this project.

Nitrogen could be another interesting option for consideration for conducting pyrolysis experiments in an inert atmosphere. It would be probably cost-effective to use nitrogen for pyrolysis and use hydrogen or helium for the gas chromatography. Such a combination of two different gases will also require the modification of the GC plumbing, and it could be a great potential topic for future studies.

RESULTS

Physical Properties of Plastics Analyzed. As shown in Figures S1-S4, plastic pieces were comprised of fragments, foams, ropes, caps, wraps, a belt, broken bottles, a cigar tip, and a butane lighter. These figures show that the field samplers non-randomly collected unique plastic pieces of various shapes, sizes, densities, hardness, colors, and opacities. It was also visually evident that different plastics were in the environment for different durations and perhaps underwent different weathering degradation stages. While most plastic pieces were parts from unidentifiable sources, some plastics were easily identifiable. For example, in the collection, we found intact bottle caps, bottle parts, ropes, nets, tape, and a butane lighter. It is interesting to note that the three bottle caps had inscriptions of Pacific Asian languages.

Pyrograms of Unweathered Plastics. Figures S5-S7 depict standard pyrograms of some of the commonly used polymers in commercial plastic products. Each pyrogram appears to have a distinctly different signature pattern. In addition to the distinct fingerprints, the mass spectral data for different marker peaks within a given pyrogram provided additional confirmation for the chemical composition of the polymers.

Pyrograms of Plastics from the Northern Shoreline of the Gulf of Alaska. Figures S8-S18 are shown as representative examples of different plastic polymers that were detected in the northern shoreline of the Gulf of Alaska. The signature pattern specific to a given plastic polymer appeared to be evident in each pyrogram regardless of the physical properties, optical properties, or degradation condition of a given plastic sample. As in the standard pyrograms, the mass spectral data provided additional corroborations for the identification of the polymers and copolymers in the unknown plastics. Identification of plastic additives in the same pyrolysis run was an added benefit of the pyrolysis GC-MS method.

Polyethylene and Polypropylene Debris in Katmai National Park and Kenai Fjords National Park. Polyethylene (PE) and polypropylene (PP) were some of the most frequently detected polymers in the debris samples from the Katmai National Park and Preserve (n=36; PE=16, PP=14) and Kenai Fjords National Park (n=56; PE=16, PP=32) (Figures 2A-2C, Table S1), but PE and PP did not occur as dominantly in the Western Prince William Sound. Interestingly, a more diverse composition of PE, PP, polystyrene (PS), polyethylene terephthalate (PET), and polyvinyl chloride (PVC) was detected in samples from the Western Prince William Sound shorelines (n=23; PE=6, PP=4, PS=3, PET=3, PVC=3) (Figures 2A-2C, Table S1). The presence of evenly spaced triplets containing dienes, monoenes, and saturated alkanes suggested the presence of PE (Figure S16A and Figure S16B). PP was recognized by the presence of a marker peak corresponding to the compound 2,4-Dimethyl-1-heptene (Figure S8A). The number of plastics

identified as PP and PE was about the same in Katmai National Park (Figure 2A), but the number identified as PP was twice as high as the number identified as PE in Kenai Fjords National Park (Figure 2B).

Diverse Plastics Debris on the Western Prince William Sound Shoreline.

Interestingly, the plastics collected in the Western Prince William Sound were comprised of diverse chemistries (Figure 2C). In addition to PE and PP, we also detected plastics made of polyvinyl chloride (PVC), polystyrene (PS), and polyethylene terephthalate (PET) at this location. The pyrogram of PVC contained the marker peaks of hydrochloric acid and aromatic compounds (Figure S13A). The pyrogram of PS contained the marker peaks of styrene, styrene dimer, and styrene trimer (Figure S11B). PET was recognized by the presence of marker peaks of acetaldehyde, benzoic acid, and 4-(vinylloxycarbonyl) benzoic acid (Figure S9A).

Detection of Polymers Other Than PE, PP, PVC, PS, and PET. Polymers other than PE, PP, PVC, PS, and PET, that were detected on beaches in Alaska included nylon-6, polyoxymethylene (POM), and polyurethane (PU). Nylon was rather easy to confirm because we had previously analyzed plastics made of nylon-6 and nylon-6,6. Detection of ϵ -caprolactam in the pyrogram suggested the presence of nylon-6 and not nylon-6,6 (Figure S8B). We had not previously analyzed POM-based plastics. A literature search suggested that POM could be the constituent polymer of the butane lighter³¹. The pyrogram and mass spectral data were therefore examined to confirm the presence of POM (Figure S14A). The presence of PU was suggested based on the mass spectral peaks like aniline, p-toluidine, and 4,4'-diaminodiphenylmethane⁸⁻¹⁰ (Figure S10A). The diisocyanate compound peak was not found in the pyrogram. The mechanistic explanation is provided by Hiltz⁹, in which the diisocyanate compound is converted into 4,4'-diaminodiphenylmethane during the pyrolysis. One blue triangular plastic piece from Prince William Sound/Herring Bay contained the marker compounds of PU and PE (Figure S18). The quality of the PE peaks was not very good because the peak intensities were small. The pattern of evenly spaced clusters of peaks suggested the presence of PE.

Detection of Copolymers. In the plastics debris collected on the beaches in Alaska, we also detected the presence of copolymers such as PE/PP, PE/polyvinyl acetate (PVA), PVC/polyacrylonitrile (PAN)/polyurethane (PU), PU/hexaethyl cellulose (HEC), PVC/PET, PVC/PET/benzoguanamine-formaldehyde resin (BFR), and PE/PU. While we had analyzed PE/PP and PE/PVA copolymers before, we were unfamiliar with the other copolymers. The presence of the PE/PP copolymer was suggested based on the pyrogram peak of 2,4-Dimethyl-1-heptene (a marker peak for PP) and the presence of evenly spaced triplets containing dienes, monoenes, and saturated alkanes (Figure S11A). For the PE/PVA copolymer, the presence of evenly spaced triplets containing dienes, monoenes, and saturated alkanes suggested the presence of PE, and

the pyrogram peak of acetic acid suggested the presence of PVA (Figure S15C). For the PVC/PAN/PU copolymer, the pyrogram peaks of hydrochloric acid and aromatic compounds suggested the presence of PVC, the peak of methyl acrylonitrile suggested the presence of PAN, and the peak of 2,4-diisocyanato-1-methylbenzene suggested the presence of PU (Figure S12B). For the HEC/PU copolymer, the pyrogram peaks of carbon dioxide, acetaldehyde, propylene glycol, and triethylene glycol suggested the presence of HEC, and the peaks of aniline, p-toluidine, and 4,4'-diaminodiphenylmethane suggested the presence of PU^{8,9} (Figure S9B). For the PVC/PET copolymer, the pyrogram peak of hydrochloric acid suggested the presence of PVC, while the peaks of acetaldehyde, vinyl benzoate, and benzoic acid suggested the presence of PET (Figure S17B). Benzene and other aromatic hydrocarbons were not as conspicuous in this pyrogram as found in the pyrogram of the PVC standard in Figure S6. For the PVC/PET/BFR copolymer, the pyrogram peaks of hydrochloric acid and aromatic compounds suggested the presence of PVC, the peak of benzoguanamine suggested the presence of BFR³², and the peak of ethan-1,2-diyl divinyl diterephthalate suggested the presence of PET (Figure S15A). The benzoguanamine peak was confirmed by using the NIST Library Search Protocol (Figure S15B). The probability of the presence of benzoguanamine was 88.8% and it improved to as high as 97.5% after the background subtraction. Benzoguanamine in this pyrogram could also arise from a polyurethane polymer based on the polymerization reaction including benzoguanamine, 2-phenyl-4,6-dihydroxy-s-triazine, and certain diisocyanates¹¹.

Detection of Plastic Additives and Other Chemicals. In addition to the characterization of polymers and copolymers in a given plastic, we were also able to occasionally detect plastic additives and other chemicals in the same pyrolysis GC-MS runs. Additives and other chemicals are treated to the same intense pyrolysis heat as the plastic polymers in a given pyrolysis GC-MS run. However, being simple and non-polymeric chemicals, they do not seem to degrade as severely as long-chain polymers. The resulting peaks essentially appeared to be the normal electron impact mass spectra that matched well with the mass spectral libraries.

2,4-Di-tert-butylphenol was the most frequently detected additive in this study. It was detected in 54 of 115 samples (~47%). This additive is used as a UV stabilizer and an antioxidant³³. As an example, the pyrogram of a blue triangular plastic piece from Prince William Sound/Herring Bay showed a peak of 2,4-di-tert-butylphenol (Figure S18A).

Bis(2-ethylhexyl) phthalate (DEHP) was the next frequently detected phthalate additive. Phthalates are a group of chemicals that are added to plastics to enhance their flexibility, durability, and longevity³⁴. DEHP was detected in 16 of 115 samples (~14%). This additive was usually found in PVC-based plastics (Figure S13A), but we also found it in a POM-based butane lighter, a PE-based hard plastic piece, and a PVC/BFR copolymer-based red foam (Figures S14A,

S14B, and S15A). We also detected other phthalates like dibutyl phthalate in one sample and bis(2-hydroxyethyl) phthalate in another sample.

A PVC/PAN/PU copolymer-based copper-colored foam and a PE blue tape contained a mixture of isomers of tricresyl phosphate (Phosflex), which is used as a plasticizer and a flame retardant (Figures S12B and S13B).

One PE-based plastic contained 2,4-ditert-butyl-6-(5-chlorobenzotriazol-2-yl) phenol (Uvazol 237), which is used as a UV Stabilizer (Figure S10B). One PE-based plastic contained a chemical tentatively identified as a trimethylsilyl derivative of cannabinol (Figure S17A). One PET/PVC-based plastic contained a tentatively identified pharmaceutical Nirvanol which is used as an anticonvulsive drug (Figure S17B).

DISCUSSION

Pyrolysis GC-MS. Pyrolysis GC-MS is a very mature technique¹⁰ with well-known applications for the analyses of a wide range of solid materials, including synthetic polymers, forensics, art materials, paints, adhesives, fibers, microorganisms, rubber, soil, sediment, organic matter, museum artifacts, petrochemical fuels, coal, and biofuels^{8,12-14}. In reviewing the chronology of milestones of pyrolysis GC-MS, Tsuge et al.¹⁰ described that the experiments on analytical pyrolysis began in the late 1940s. The major milestones in the development of pyrolysis GC-MS were the availability of gas chromatographs in the early 1950s, the availability of GC-MS in the mid-to-late 1960s, and the availability of fused silica capillary columns in the late 1970s. Although used widely in a variety of other applications, pyrolysis GC-MS was less commonly used in the characterization of marine plastics. Visual and microscopic examination, FT-IR, and Raman spectroscopy have been the primary methods of plastic analyses until recent times. Fries et al.¹⁵ were some of the early researchers who reported the utility of pyrolysis GC-MS in the analyses of marine microplastics. Although the foundational approach of pyrolysis GC-MS appears to be not yet fully utilized by marine scientists, the interest appears to be growing steadily.

Hyphenation of a pyroprobe with a gas chromatograph and a mass spectrometer provides marine scientists with a highly powerful tool for the positive characterization of plastics in the littoral and aquatic environments. The two-tiered confirmation approach based on unique peak fingerprints and the mass spectral data for the marker peaks provides the most accurate and unequivocal identification of polymers, copolymers, and allied chemicals in the same analytical run. Because the analysis is based purely on the masses of the fragment ions, the data quality is negligibly compromised by the shape, density, texture, surface deformities, color, fluorescence,

or brightness of the plastic material. Additionally, the huge mass spectral database library of over 300,000 compounds facilitates the easy identification of pyrolysis product mixtures.

There are other similar methods such as double shot pyrolysis-GC-MS³⁵ and thermogravimetric analysis-Fourier transform infrared-GC-MS (TGA-FTIR-GC-MS)^{36,37} which have been applied to the analyses of microplastics and plastics debris. Okoffo et al.³⁵ reported the use of pressurized liquid extraction combined with double-shot pyrolysis GC-MS for the identification and quantification of polyethylene, polypropylene, polyvinyl chloride, polystyrene, and poly-(methyl methacrylate) in biosolids. Nel et al.³⁶ used TGA-FTIR-GC-MS for the characterization of both the physical and chemical properties of the environmental samples of mesoplastics collected from the beaches in the U.K. and South Africa. Liu et al.³⁷ used TGA-FTIR-GC-MS for the detection, identification, and quantification of microplastics in marine mussels, *Mytilus edulis*, from six locations along the coast of China.

Other comparable techniques such as FTIR and Raman spectroscopy are highly powerful as well, but the identification is based only on a one-dimensional data set consisting of peak patterns. Spectroscopic methods require additional sample purification step(s) and the data quality can be prone to potential challenges related to surface aberrations, dark colors, and fluorescence, which can limit their application. The dyes used for coloring the plastics usually have high molecular extinction coefficients, and therefore the amount of dye needed to give a bright color to the plastic is comparatively minuscule. The strong color can however cause interferences in the spectroscopic analyses, and sometimes even overwhelm the polymer spectrum. The mass spectral data quality is rarely degraded because of the presence of dyes. The mass spectral signals of pyrolyzed products generated from the tiny amounts of dyes are proportionately much smaller than the polymer signal, and although present, they are invariably inconspicuous and hidden in the baseline of the mass spectrum. We would argue that pyrolysis GC-MS is perhaps the only method suitable for the analysis of dark-colored, non-volatile, and solvent-insoluble polymeric substances.

Compared to the high procurement costs of spectroscopic instrumentation, pyrolysis GC-MS involves the low-cost addition of pyrolysis capability to a mass spectrometer, which many laboratories already possess. It is important to note that the mass spectrometer depends upon the availability of sufficient mass of the sample. Pyrolysis GC-MS can become challenging and less useful as the particle size becomes smaller and smaller from the low microgram to nanogram range. A combination of a highly sensitive mass spectrometer and high-end spectroscopic techniques can be potential candidates for the analyses of plastics in this ultra-low mass range.

Plastics in the Northern Shorelines of the Gulf of Alaska. Pyrolysis GC-MS provided a proof-of-concept for the accurate and reliable confirmation of polymers, copolymers, and additive chemicals in the complex environmental samples from the Alaskan beaches. We also demonstrated that prior chemical, enzymatic, or physical treatments are probably unnecessary in these analyses. Pyrolysis GC-MS characterization of unknown plastics from the northern shorelines of the Gulf of Alaska was almost 100% successful and every debris sample we analyzed turned out to be some kind of plastic. The pyrolysis GC-MS method provided the two-tier identification method comprised of peak fingerprints and mass spectra of the marker peaks, which resulted in additional confidence in the data quality. We detected familiar as well as unfamiliar polymers, copolymers (Figures 2A-C, Table S1), and other chemicals, including additives. Positive identification without the additional chemical, enzymatic, or physical treatment of the sample demonstrated the high power of mass spectrometry.

Overall, plastics made from PE and PP were most commonly detected in the present study (Figure 2D). Both these plastic types are considered commodity plastics, and thus they are manufactured in high volumes for making a wide range of products. As an example, the global production of PE was 116 million tons in 2015, out of which 97 million tons (83.6%) were estimated to be discarded as primary waste¹⁶ (Figure S19). Similarly, the global production of PP in 2015 was 68 million tons, out of which 55 million tons (80.9%) were estimated to be discarded as primary waste¹⁶. PE and PP production was followed by PVC (38 million tons), PET (33 million tons), polyurethane (PU) (27 million tons), and PS (25 million tons). The estimated primary wastes of PVC, PET, PU, and PS were 15 million tons (39.5%), 32 million tons (97%), 16 million tons (59.3%), and 17 million tons (68%) respectively. The higher levels of production of PE and PP plastics presumably resulted in higher levels of plastic waste, and this pattern was reflected very well in our chemical analyses.

Origins of Plastics in the Northern Gulf of Alaska. Jambeck et al.¹⁷ suggested that the majority of waste plastics enter the ocean from a relatively smaller geographic area of the Asia-Pacific, and that over half of the plastic waste comes from just the five rapidly growing economies, namely, China, Indonesia, Philippines, Thailand, and Vietnam. The pace of economic development of these countries seems to be advancing far more rapidly than their waste-management capabilities. China leads the world nations in mismanaged plastic waste with 8.82 million tons/year or 27.7% of the total global mismanaged plastic waste. Jambeck et al.¹⁷ estimated that the plastic marine debris originating from China ranged from 1.32–3.53 million tons/year, followed by Indonesia (0.48–1.29 million tons/year), Philippines (0.28–0.75 million tons/year), Vietnam (0.28–0.73 million tons/year), Sri Lanka (0.24–0.64 million tons/year), and Thailand (0.15–0.41 million tons/year). Northwest Arctic debris has been documented to also include small quantities of debris from Russia, Korea, Japan, and China³. Debris from a broader

range of international countries such as Argentina, China, Japan, Korea, Russia, Singapore, Greece, Netherlands, the U.A.E., and South Africa is also found in the Gulf of Alaska parks.

Impacts of the 2011 Tohoku Earthquake and Resulting Tsunami on Plastics in Alaska. The 2011 Tohoku earthquake and resulting tsunami increased the volumes of Styrofoam and urethane debris on northern Gulf of Alaska beaches by multiple times in the years immediately following the event⁵. Tsunami-generated debris began arriving on the coasts of the United States and Canada in late 2011 and NOAA expected that the debris will continue to arrive for several years¹⁸. However, there were no reliable estimates as to how much tsunami debris will ultimately reach Alaska. NOAA estimated an increase of up to one thousand times greater debris of light plastic and polystyrene in some areas of Alaska than in pre-tsunami baselines¹⁹. The Alaska Department of Environmental Conservation conducted an aerial survey of debris and found high densities of light, high-floating materials along Alaska beaches¹⁹. Comparisons of pre- and post-tsunami debris using aerial survey imagery provided evidence of a 10-fold increase in marine debris on beaches in southeast Alaska, the outer coast of the Kenai Peninsula and Kodiak Island, and numerous islands in Prince William Sound²⁰. The Gulf of Alaska Keeper estimated that the 2011 tsunami doubled the debris volume on the Northern Gulf of Alaska shoreline⁵. Styrofoam % of total weight also more than doubled starting after the 2011 Tsunami and this trend continued through 2014⁵.

Howell et al.² suggested that while single events such as the 2011 Japanese tsunami can generate extensive marine debris, the debris that arrives in Alaska is usually caused by more routine and common means such as lost shipping containers, derelict fishing gear, upstream littering, and other anthropogenic activities, both locally and far from Alaska. This debris is then transported to Alaska by winter storm events, ocean currents, and wind. Each year, thousands of tons of new debris washes up on the Alaska coast, and dense pockets of marine debris are common along the northern Gulf of Alaska coast. The Gulf of Alaska Keeper estimates that the high-concentration beaches, such as Gore Point and Montague Island on the outer coast hold 20 to 30 tons of plastic debris per mile⁵. Based on plastic bits in animal scat, many mammals, from small rodents to bears, are thought to potentially ingest plastic debris⁵. Storms and surf along Alaska's high-energy coast also break down the foam debris into small particles which can be potentially ingested by fish, birds, and smaller marine organisms.

Significance of Occurrence of Polyethylene and Polypropylene. Just as different plastics have different chemical compositions, different plastics also possess different densities (Table S1). The density of PE ranges from 0.89–0.98, and the density of PP ranges from 0.85–0.92²¹. PE and PP are lighter than seawater which has a density of 1.02²¹. This means that plastic debris composed of PE and PP would likely float at the surface and therefore be the most likely

candidates for long-range transport from Asia-Pacific countries to Alaska via surface currents, wind, and storms. The results of our analyses showed exactly that pattern. Even though the field sampling crew non-randomly collected uniquely different pieces of plastics without any bias (Figures S1-S4), PE and PP still dominated the plastics we analyzed (Figure 2D). A combination of the remoteness of Alaska National Parks and the lighter densities of PE and PP suggested that the occurrence of plastics made with PE and PP would be primarily of oceanic origin and less of the local human littering. As the densities of PE and PP are lower than the density of seawater, these plastics were probably dislodged from surface waters on the beaches, particularly during storm events and high tides. Although the non-randomly collected samples may not be a true representation of all plastics from the northern shorelines of the Gulf of Alaska, in terms of their polymer compositions, the plastics from Katmai National Park and Preserve and Kenai Fjords National Park may have been the low-density floating PE and PP plastics of oceanic origins. Many other plastics are heavier than seawater. For example, the densities of PS, polyamides (PA) (nylons), PVC, PU, polyester, PAN, and PVA are 1.04, 1.12–1.15, 1.38–1.41, 1.20–1.26, 1.10–1.40, 1.18, and 1.19 respectively (Table S1). The diverse composition of plastics from the Western Prince William Sound shorelines could indicate combinations of oceanic as well as terrestrial origins.

Biofouling^{22,23}, mineral adsorption²⁴, incorporation of microplastics into fecal pellets²⁵, and marine aggregates²⁶ can decrease the buoyancy of PE and PP²⁷, and these plastics would then be less available for surface transport. Biofilm formation varies with the season, geographical location, and plastic substrate type²⁸. The bio-fouled plastics are hypothesized to undergo yo-yo types of vertical movements in the water column^{29,30}. The bio-fouled plastics and other plastic types being heavier than seawater may not appreciably make the long journey to Alaska.

Unique Plastic Objects in Alaska National Parks. The field collectors found three caps on the northern Gulf of Alaska shorelines that had inscriptions of Asian languages on them. The two caps in the Katmai National Park (Hallo Bay, Figure S8A and Figure S18B) were identified as made of PP and PE, and one cap in Kenai Fjords National Park (Verdant Cove, Figure S12A) was identified as made of PP.

Incidentally, some pyrograms of polypropylene are tricky to interpret like the one in Figure S8A. It appears that there are repeat units giving a sense of the potential presence of polyethylene. This can cause quite a confusion. Upon close examination of the peaks, however, we realized that these apparent polyethylene peaks do not show the characteristic repeat patterns of triplets containing double-bonded, single-bonded, and saturated hydrocarbons. For example, all peaks in the supposed triplet group between 9.1–9.3 min were apparently identified as one compound: 1-heptadecene. The next group between 10.5–11 min showed the presence of a

branched alcohol (2-hexyl-1-dodecanol) and an unsaturated hydrocarbon alcohol ((Z)-13-Docosen-1-ol). The first two major peaks in the next group between 11.8-12.3 min showed the presence of a branched alcohol (2-hexyl-1-Decanol) which was the same as in the previous group, and an unsaturated hydrocarbon alcohol ((Z)-13-docosen-1-ol) which was also the same as in the previous group. Visually the peak pattern looked like a possible polyethylene copolymer. The mass spectral analyses however showed the absence of polyethylene's evenly spaced peak pattern as well as triplet peak pattern. The presence of polyethylene as a copolymer in Figure S8A thus could not be corroborated.

The fact that PE and PP are lighter than seawater and the overwhelming evidence on plastics and other wastes being washed to Alaska's shores from faraway countries suggested that the origins of these caps could have been in the Asia-Pacific region. One would argue that these caps could also have resulted from the local discards. Plenty of travelers from Asian countries visit Alaska, possibly losing their trash post-arrival. There are many large containers and other vessels that lose trash overboard on routes that take them through the Aleutian Islands to the west of Katmai. In addition, as stated, collections were non-random, so personnel might have targeted the caps with Asian writing because they seemed more interesting than the regular debris.

Future Studies. The sample size of this study was not too small, but it was not too comprehensive either. Not all plastics were sampled or analyzed from a given location. The field collectors had no prior knowledge of the polymer chemistries of the plastics they had collected. The goal of their non-random sampling was to collect different types of visually interesting plastic pieces of different colors, forms, or shapes found on the Alaskan beaches. Because the samples were non-randomly collected and the collections were not comprehensive of all available plastics on the shorelines, the differences in polymer occurrences among different sites were probably not representative of the true polymer population, which in itself could be changing dynamically due to different likely debris types being dislodged on Alaskan beaches from different storm events. It is therefore difficult to predict whether the PE and PP domination patterns we found would repeat if an order of magnitude or more samples were analyzed. Given the enormous extent of plastic pollution in Alaska, the characterization of all littered plastic pieces would be highly cost-prohibitive, time-intensive, imprudent, and a huge logistical nightmare. A modest rationalized approach to future spatial and temporal monitoring would be to analyze certain percentages of different collections that could be beneficial in the assessment of types of plastic pollution and also that could be indicative of their sources of oceanic or terrestrial origins. Sources tracking would be critically important in the control and mitigation of plastic pollution in Alaska.

Supporting Information. The materials supplied as supporting information include the photos of the plastic debris from the northern Gulf of Alaska shorelines along with their polymer identifications, pyrolysis GC-MS pyrograms of commonly used plastic polymers, the example pyrograms of plastics from the northern Gulf of Alaska shorelines, global production and waste estimate graph of different plastic polymers, a few examples of the sizes of plastic debris found on the shorelines of the northern Gulf of Alaska, and a table of densities of different polymers and seawater. “This supporting information is available free of charge via the internet at <http://pubs.acs.org>.”

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Table S1 in Supplementary Material <https://ars.els-cdn.com/content/image/1-s2.0-S0304389419301979-mmc1.pdf>

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Table 1. Results of pyrolysis GC-MS characterization of plastics from the northern shoreline of the Gulf of Alaska.

Location	PE	PP	PS	PET	Nylon 6	PE/ PP	PU	PVC	E/VA	BFR	PVC/ PAN/ PU	POM	PU/ HEC	PE/ PU	Total
Katmai National Park (KATM)															
Hallo Bay	1	1		2	1										
Kukak	5	5													
Little Mink Island	10	8	1			1	1								
Total	16	14	1	2	1	1	1	0	0	0	0	0	0	0	36
Kenai Fjords National Park (KEFJ)															
Harris Spit	1	1	1												
Verdant Cove	1	2													
Nuka Bay		3													
McArthur Pass	12	21	2	1				1	1	1					
Harris Bay	2	5		1											
Total	16	32	3	2	0	0	0	1	1	1	0	0	0	0	56
Western Prince William Sound (WPWS)															
Herring Bay		1									1			1	
Johnson	3	2	2	1				1				1			
Near Iktua	3	1	1	2				2					1		
Total	6	4	3	3	0	0	0	3	0	0	1	1	1	1	23
Total for All Locations	38	50	7	7	1	1	1	4	1	1	1	1	1	1	115

Figure 1. Locations for the collection of plastic debris samples along the shorelines of the northern Gulf of Alaska. WPWS = Western Prince William Sound, KEFJ = Kenai Fjords National Park, and KATM = Katmai National Park and Preserve.

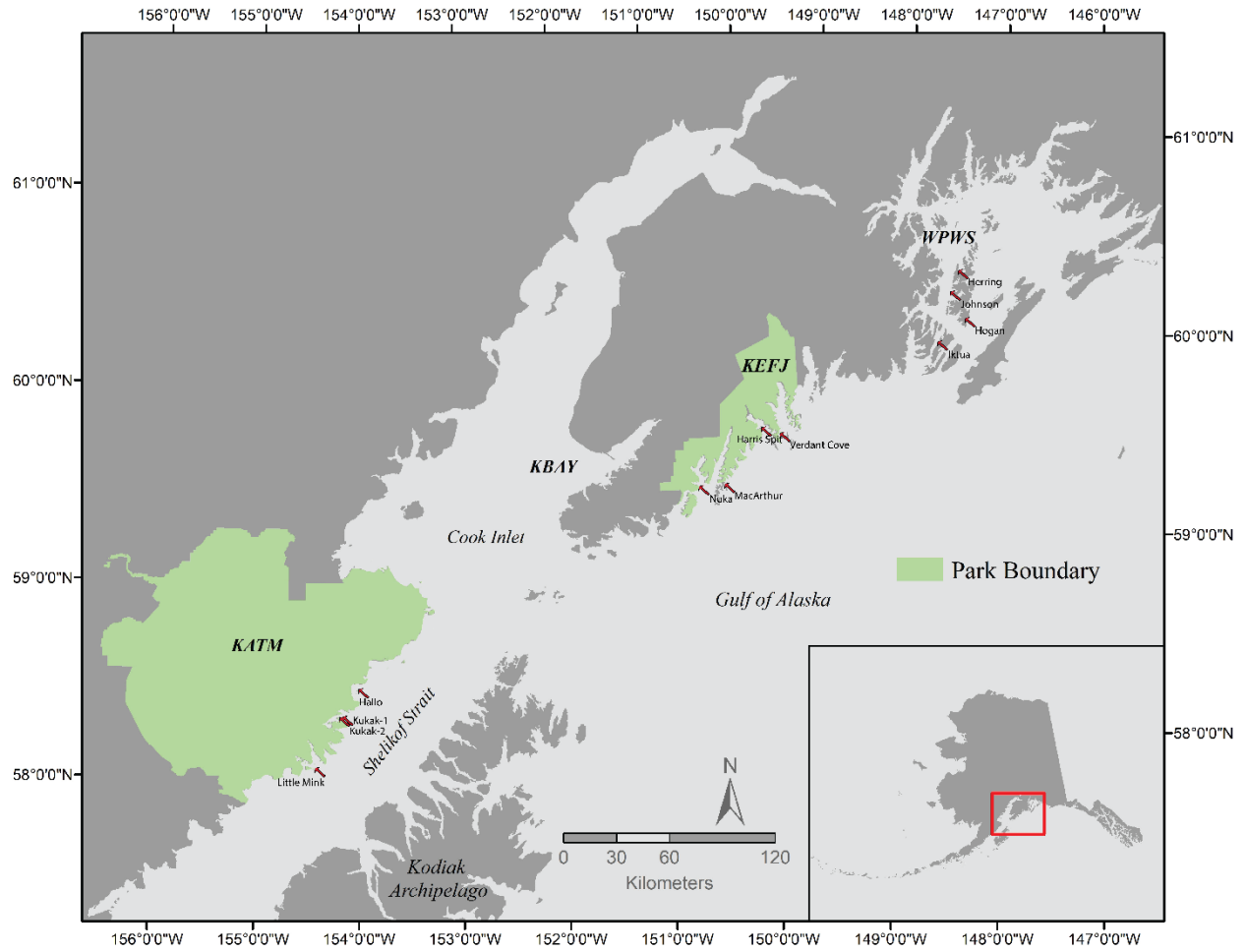
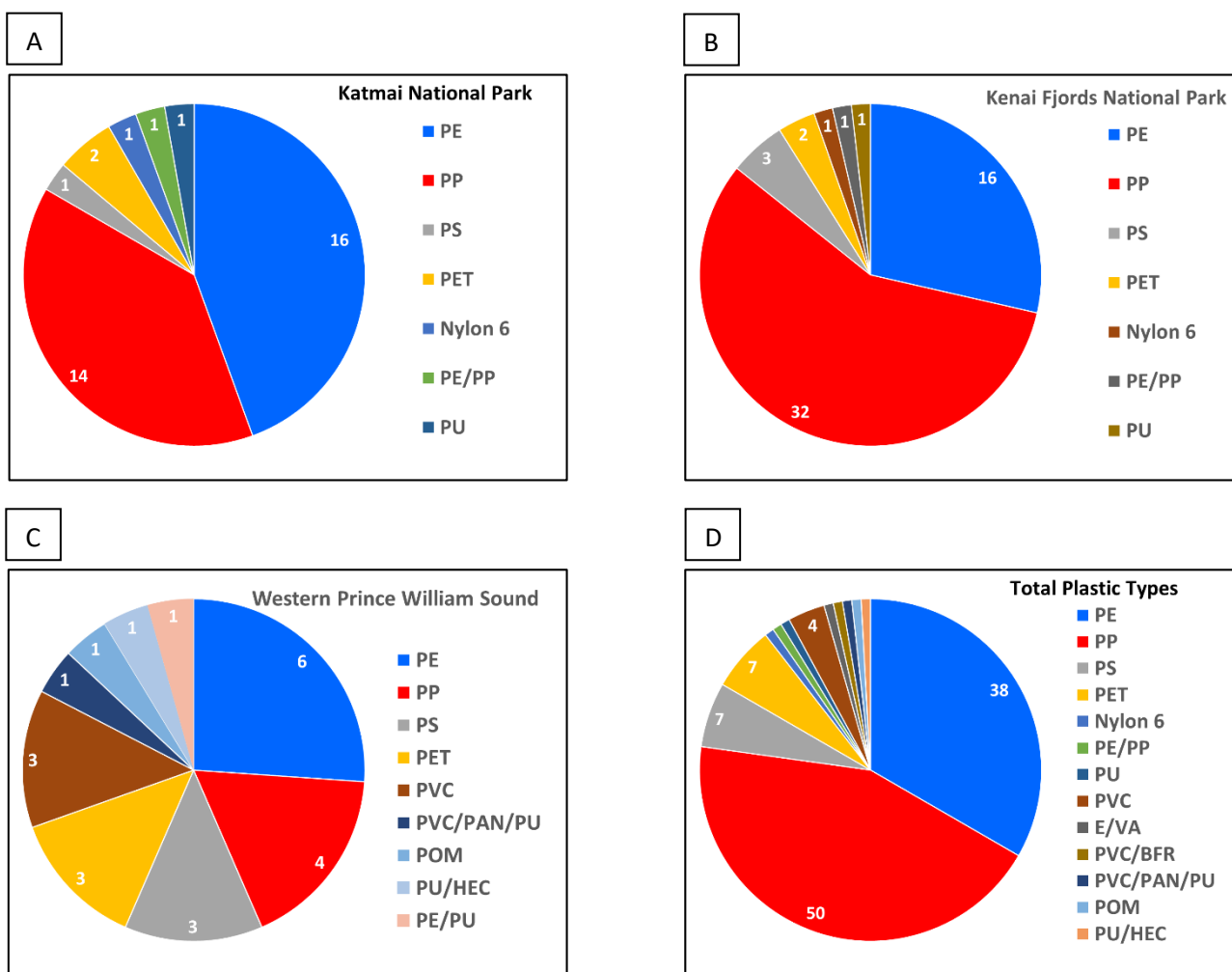
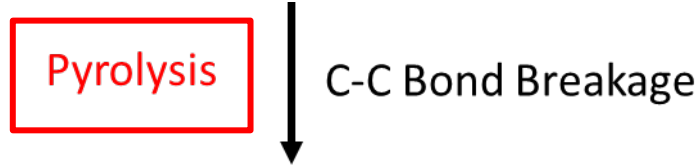
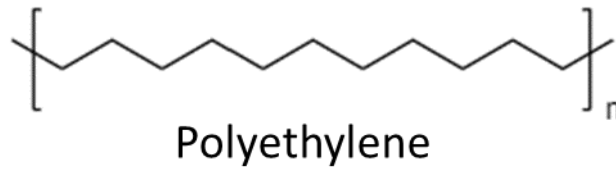


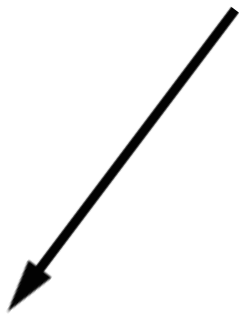
Figure 2. Pyrolysis GC-MS Characterization of Plastic Debris in (A) Katmai National Park, (B) Kenai Fjords National Park, (C) Western Prince William Sound National Park, and (D) total plastic types analyzed in this study. The number in each section indicates the number of plastic pieces identified for each type of polymer. PE=Polystyrene, PP=Polypropylene, PS=Polystyrene, PET=Polyethylene terephthalate, PE/PP=Polyethylene/Polypropylene copolymer, PU=Polyurethane, PVC=Polyvinyl chloride, E/VA=Polyethylene/Polyvinyl acetate copolymer, PVC/BFR=PVC/Benzoguanamine-formaldehyde resin (BFR) copolymer, PVC/PAN/PU=PVC/Polyacrylonitrile/Polyurethane copolymer, POM=Polyoxymethylene, PU/HEC=Polyurethane/Hexaethyl cellulose copolymer



Graphic Abstract

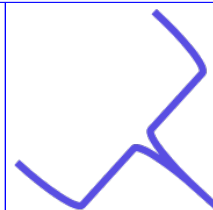
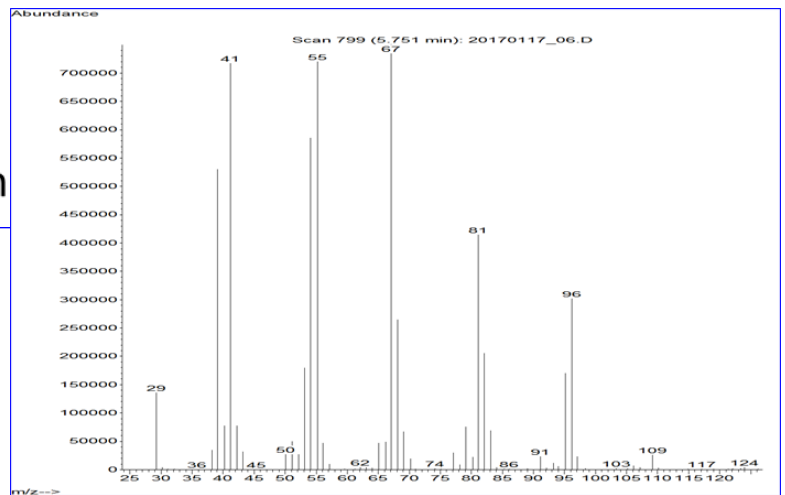
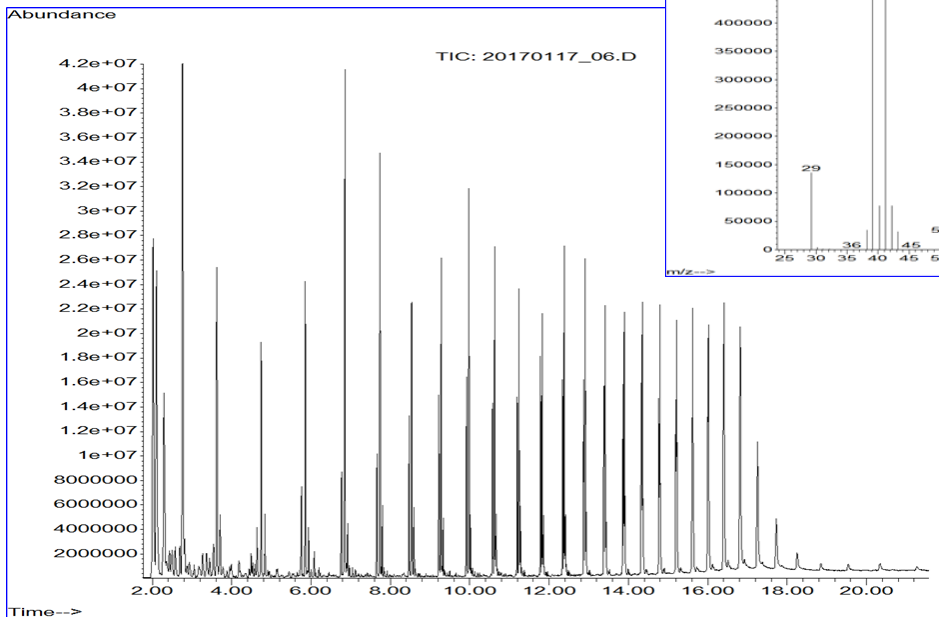


Hydrocarbon Mixture



Mass Spectrometry

Gas Chromatography Peak Pattern



Polymer ID