HIGH SCHOOL EDITION
Journal of Student Research
Volume 13 Issue 4 (2024)

Microplastic Analysis of the Marine Environment in Ras Tanura

Sooyoung Choi[1] and Elizabeth Rodostianos[#]

[1]The American School in Switzerland (TASIS), Switzerland
[#]Advisor

ABSTRACT

As the amount of plastic waste continues to increase with humanity's extravagant use of it, the problem of microplastic pollution arises. Microplastics are minuscule plastic particles that have decomposed, and their sizes range from 1 micrometer to 5000 micrometers. Recently, scientists have found that microplastics have infested almost all of Earth's marine ecosystems. As such, water samples from the local beach of Ras Tanura in Saudi Arabia were analyzed using Gas Chromatography-Mass Spectrometry (GC-MS) and Fourier Transform Infrared (FT-IR) Spectroscopy for microplastic particle detection.. The local beach was chosen because many people perform activities there such as swimming and fishing, and there are lots of oil tankers that dock at a nearby port, so analyzing the water from this beach will give results on which microplastics are the most abundant in these settings. The results of the analysis using FT-IR states that particles of polyamide (PA), polyethylene (PE), polymethyl methacrylate (PMMA), polytetrafluoroethylene (PTFE), polyurethane (PU), and rayon were detected in the water samples. However, due to the limitations of GC-MS regarding microplastic concentration threshold, the results came out very vague The analysis of the Ras Tanura beach water shows the extent of how easily microplastic pollution can spread. Additionally, it emphasizes the importance of improvement in the limitations of analysis methodologies, such as the case of GC-MS and the minimum concentration threshold. Another improvement that should be made is the standardization of microplastic analysis, specifically the development of a clear-cut line between safe and dangerous microplastic concentrations in water.

Introduction

Plastic, due to its versatility and cheap production costs, is one of the most used materials in the world currently. This category includes polyethylene terephthalate (PET) for plastic bottles, polypropylene for straws and food containers, and polystyrene, commonly known as styrofoam.

OECD states in 2019, 461 million tonnes of plastic were produced around the globe, of which 353 million tonnes went to waste (OECD 2022). This is a significant surge in plastic production since 1950, at that period only 2 million tonnes were generated (UNEP 2022). 33 billion tonnes of plastic will accumulate in landfills by 2050 if the trend of increasing plastic waste stays consistent.

Around 9% of the waste gets properly recycled, and the mismanagement of plastic waste is a huge issue as lots of the waste finds their way to marine environments, which affects the food and water we consume. As of 2019, around 6 million tonnes of plastic waste were dumped into rivers alone, increasing the total number of plastic in rivers to approximately 110 million tonnes (OECD 2022). In the oceanic environments, around 10 million tonnes of plastic waste gets unleashed into them. When these plastic wastes break down into particles with sizes ranging from 1 micrometer to 5000 micrometers, they are considered microplastics. Due to their high surface-area-to-volume ratio, they tend to absorb substances perilous to humans. The harmful nature of microplastics paired with their sheer abundance in our planet makes microplastic pollution one of the biggest rising global issues.

Ras Tanura Beach is on the East Coast of Saudi Arabia, and several activities are performed on the water, such as swimming, paddle boating, kayaking, and fishing. It is also relatively close to an industrial port where oil tankers frequently dock. I analyzed four water samples, 1 liter each, using Gas Chromatography-Mass Spectrometry (GC-MS) and Fourier Transform Infrared Spectroscopy (FT-IR).

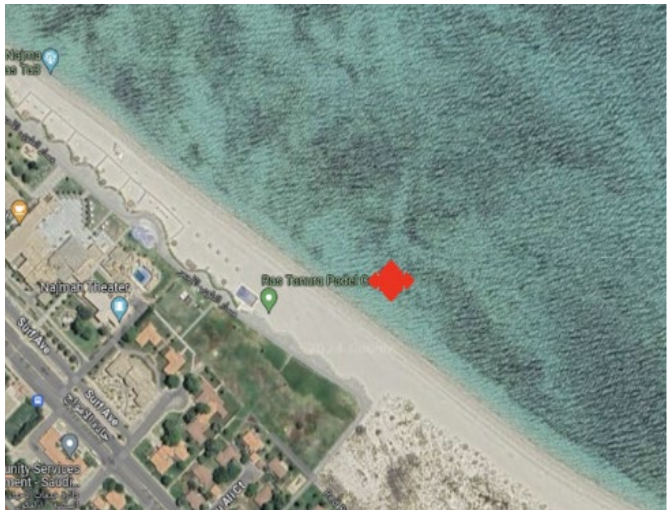

Figure 1. The location where the water samples were taken

Methods

Gas Chromatography – Mass Spectrometry (GC-MS)

Gas Chromatography-Mass Spectrometry (GC-MS) is an widespread method of analyzing microplastics. As the name suggests, the spectrometer is composed of two parts: gas chromatography and mass spectrometry. For the identification of microplastics and polymers, the Pyrolysis-GC-MS (Py-GC-MS) is typically used (TechNet 2021).

The process starts with the sample being put in an analysis cup. The cup with the sample inside is then placed inside the pyrolysis chamber, where it is heated until 600-650 degrees celsius and the sample reaches thermal decomposition (Wikipedia 2023). This is the process of pyrolysis. Different products are made during the disintegration of the sample, which are then dropped to the gas chromatography chamber. Here, the products are separated based on their interactions with the stationary phase and their volatility (how easily the substance vaporizes), and polarity. Each chemical compound will react differently to the stationary phase and will reach the end of the tube at different times. After the separation, the products are then fed to the mass spectrometer. This is where a graph is produced for each compound based on their chemical structures and properties. The graph is called the pyrometer, and it is used to identify the substance that was present in the sample. The compounds in the sample are also quantified (Agilent 2022).

One great advantage over other methods of spectroscopy is that Py-GC-MS provides quantifications with mass percentages, instead of just the number of molecules each sample contains. This is a great and easy method for comparing the weight composition of the substances. There is also no size limit for Py-GC-MS. For Raman spectroscopy, the size limit is from 2 micrometers to 100 micrometers, while for ATR FT-IR spectroscopy, it is much larger, at 500 micrometers to 5000 micrometers. Without the size limit, a wider range of samples can be analyzed with Py-GC-MS. Barely any sample preparation is needed for this analysis method because the pyrolysis breaks down the compound. Unlike FT-IR, the solid samples do not have to be a pellet to be analyzed by Py-GC-MS – it could be in the form of powder as well. There isn't a specific limit on the amount needed for the sample to be detected, meaning that the spectrometer can detect substances that are in very small quantities (Measurlabs 2023).

There are certain disadvantages that the Py-GC-MS has. The major one is the fact that it is destructive. The sample goes through decomposition, which is an irreversible change done to the sample. Due to this, the sample cannot be used again for additional tests or re-analysis, which is a problem if there is a limited amount of substances available for testing. Another issue with this method is that analysis involving heterogeneous mixtures may be inaccurate. If the products of two or more substances produced during pyrolysis overlap, the analysis will not be as accurate as other spectroscopies (EAG 2022). Another disadvantage comes from the way Py-GC-MS quantifies the substances. Because the quantification process is by a mass spectrometer, it is provided in the unit of micrograms per liter instead of the number of molecules in the sample (Measurlabs 2023).

Figure 2. GC-MS at the King Fahad University of Petroleum and Minerals

Fourier Transform Infrared (FT-IR) Spectroscopy

The Fourier Transform Infrared Spectroscopy is the analysis of microplastic substances based on the sample's interaction with infrared radiation, which has wavelengths ranging from 760 nm to 100,000 nm (NCBI 2017). In particular, wavelengths of 2500 nm to 25000 nm are the most used wavelengths of FT-IR spectroscopy. Upon contact with an infrared beam and a substance, specific frequencies of the radiation are absorbed by the sample, causing vibrational movements in bonds between atoms within the molecules. The absorbed frequencies are different for every bond type (LibreTexts 2022). To identify the substances in the sample, the fingerprint region of the infrared spectrum is analyzed. Like each human being has unique fingerprints, every chemical substance has a distinctive fingerprint region. This region takes place in the 1500 to 500 cm-1range of the wavenumbers on the spectrum. Absorptions in the higher wavenumbers indicate functional groups present in the molecules, such as carbonyl groups (C=O) and hydroxyl groups (O-H) (LibreTexts 2022). Generally, an FT-IR spectrometer has a source, interferometer, beam splitter, fixed mirror, adjustable mirror, sample compartment, and a detector (ResearchGate 2010).

The Fourier Transform method of analyzing microplastics has clear advantages over other spectroscopies. FT-IR provides a non-destructive analysis – meaning that the sample's chemical properties and structure is not altered during the process (ChemLabGenius 2021). Unlike destructive methods such as GC-MS spectroscopy, FT-IR preserves the sample integrity and allows for better experimental reproducibility. The fixed and adjustable mirrors direct beams of multiple frequencies at the sample simultaneously, resulting in a reduction in the time of analysis (Measurlabs 2023). Certainly, there are limitations to the FT-IR spectrometer. The most prominent issue is the long and meticulous process of the sample preparation. There are further problems with data collection if the sample is aqueous: as water is IR-active, water molecules also absorb infrared radiation, causing inaccuracies in the analysis. Additionally, because FT-IR measures the change in the dipole moment of the molecule, non-polar molecules will not be detected directly by infrared spectroscopy (Ruhr University 2022). With nonpolar microplastics such as polystyrene, the interactions the microplastics have with other substances are analyzed with FT-IR to identify them. Another way to detect nonpolar molecules is through different sampling methods of FT-IR such as Attenuated Total Reflectance (ATR) FT-IR, which is the most favored configuration of infrared spectroscopy for identifying microplastics. Another disadvantage of FT-IR is the size limit. For ATR FT-IR, the minimum size that a sample can have is 200 micrometers, which is large compared to other methods such as Raman spectroscopy, which can detect substances down to 2 micrometers (ResearchGate 2020).

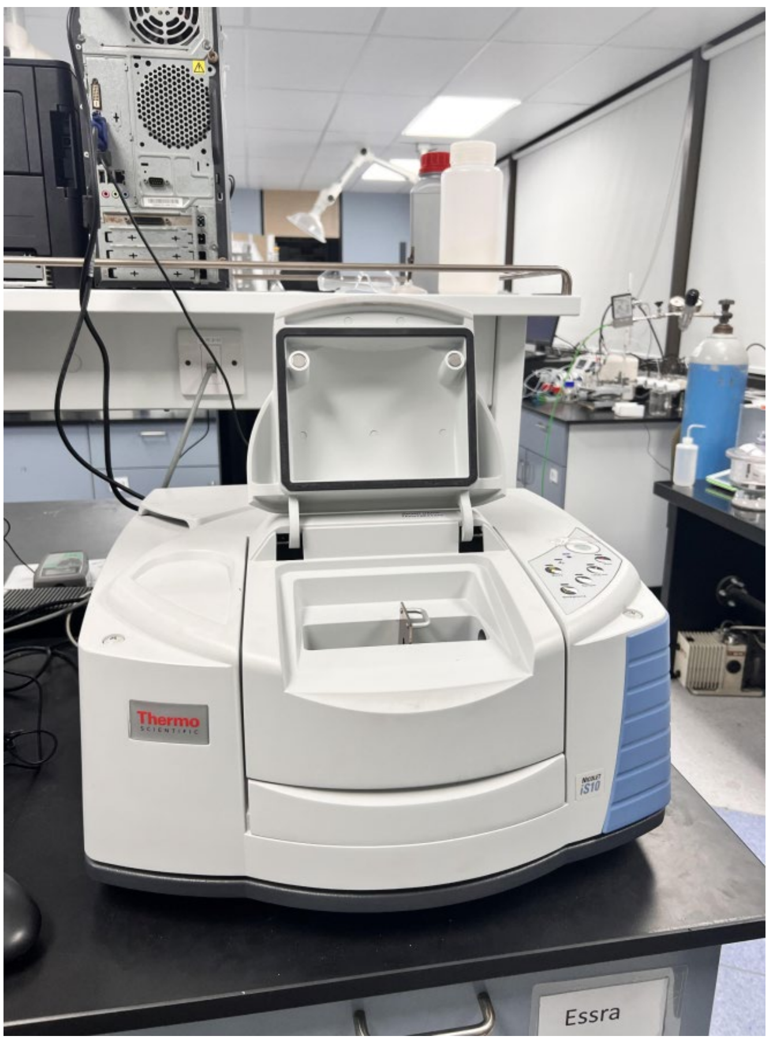

Figure 3. FT-IR at the King Fahad University of Petroleum and Mineral

Results

Gas Chromatography – Mass Spectrometry (GC-MS) Analysis Results

Two 1-liter samples were analyzed using the Gas Chromatography-Mass Spectrometry (GC-MS) method. GC-MS was chosen because it gives its results in the context of mass – milligrams – rather than quantifying the microplastics by particles. This means that GC-MS will provide another perspective of the amount of microplastics in the sample.

With the GC-MS, there is a certain threshold of microplastic weight, in milligrams, for the detection of each type of microplastic, which is listed under the column LOR (limit of reporting).

Table 1. GC-MS Limit of Reporting (LOR) based on plastic types

METHOD CODE	PARAMETER DESCRIPTION	UNIT	LOR
Microplastics Polymer Types			
Pyrolysis GCMS	Acrylonitrile Butadiene Styrene Copolymer (ABS)	µg	4.0
Pyrolysis GCMS	Nylon-6 (N-6)	µg	2.0
Pyrolysis GCMS	Nylon-6,6 (N-66)	µg	6.0
Pyrolysis GCMS	Polycarbonate (PC)	µg	3.0
Pyrolysis GCMS	Polyethylene (PE)	µg	18.0
Pyrolysis GCMS	Polyethylene Terephthalate (PET)	µg	6.0
Pyrolysis GCMS	Polymethyl Methacrylate (PMMA)	µg	3.0
Pyrolysis GCMS	Polypropylene (PP)	µg	8.0
Pyrolysis GCMS	Polystyrene (PS)	µg	2.0
Pyrolysis GCMS	Polyurethane (PU)	µg	1.0
Pyrolysis GCMS	Polyvinyl Chloride (PVC)	µg	10.0
Pyrolysis GCMS	Styrene Butadiene Rubber (SBRR	µg	4.0

For example, there would have to be a minimum of 18.0 micrograms of polyethylene (PE) per liter of the sample for it to be properly detected. However, neither of the samples that were analyzed met the requirements for the minimum detection concentration, leading to the results being vague.

Table 2. GC-MS analysis results for two water samples

Volume 13 Issue 4 (2024)

	DA2405537-001	DA2405537-002
	Water 001	**Water 002**
	WATER	WATER
	8/6/2024 0:00	45510.00
Acrylonitrile Butadiene Styrene Copolymer (ABS)	<4.0	<4.0
Nylon-6 (N-6)	<2.0	<2.0
Nylon-6,6 (N-66)	<6.0	<6.0
Polycarbonate (PC)	<3.0	<3.0
Polyethylene (PE)	<18.0	<18.0
Polyethylene Terephthalate (PET)	<6.0	<6.0
Polymethyl Methacrylate (PMMA)	<3.0	<3.0
Polypropylene (PP)	<8.0	<8.0
Polystyrene (PS)	<2.0	<2.0
Polyurethane (PU)	<1.0	<1.0
Polyvinyl Chloride (PVC)	<10.0	<10.0
Styrene Butadiene Rubber (SBRR	<4.0	<4.0

The table does not give a specific value of the concentration of each microplastic type, rather, it states that the samples met none of the thresholds of detection. This highlights the need for a high concentration for microplastic diagnosis as a limitation of Py-GC-MS relative to other analysis methods such as RAMAN spectroscopy and FT-IR spectroscopy.

Fourier Transform Infrared (FT-IR) Spectroscopy Analysis Results

Two 1-liter samples were also analyzed with Fourier Transform Infrared (FT-IR) spectroscopy. FT-IR was used because it is the most used and oldest microplastic analysis, so it has the most amount of standardized basis in the methodology.

Because there is not a minimum concentration threshold for FT-IR, the analysis yielded better results. However, for the FT-IR, there is a size limitation, which is that any particles under 20 micrometers will not get detected, therefore there is a chance that the concentration of each microplastic particle will be lower than the actual value in the water since there will be microplastics smaller than 20 micrometers.

Table 3. FT-IR analysis results for two water samples

Polymer types	DA2405537-001	DA2405537-002
	Water 001	Water 002
Acrylonitrile Butadiene Styrene (ABS)	n.d	n.d
Polyamide (PA)	5	2
Polybutadiene/Butadiene Rubber (BR)	n.d	n.d
Polycarbonate (PC)	n.d	n.d
Polyethylene (PE)	3	1
Polyethylene Terephthalate (PET)	n.d	n.d
Polymethyl Methacrylate (PMMA)	n.d	1
Polypropylene (PP)	n.d	n.d
Polystyrene (PS)	n.d	n.d
Polytetrafluoroethylene (PTFE)	1	3
Polyurethane (PU)	n.d	1
Polyvinyl Chloride (PVC)	n.d	n.d
Rayon	4	14
Total Microplastics	**13**	**22**

The average concentration of total microplastic particles in the two samples is 17.5 particles per liter, which is considered moderately high for a relatively remote beach like Ras Tanura Beach. However, there is no clear classification of microplastic concentration as safe or dangerous due to the insufficient amount of research that has been performed yet on microplastics.

Comparing sample 1 with sample 2, sample 2 yielded a wider variety of microplastics, containing Polyurethane and Polymethyl Methacrylate while sample 1 did not, as well as a larger number of particles detected. Nonetheless, Polyamide, Polyethylene, Polytetrafluoroethylene, and Rayon were present in both samples.

Polyamide (PA)

Polyamide (PA) was detected more in sample 1, with 5 and 2 particles present in samples 1 and 2, respectively. PA is a material that can be easily found in swimming suits and activewear due to its elasticity and strength. It is also used in fishing lines because of its resilience. It can be assumed that the polyamide particles come off people's swimwear and fishing rods when they participate in such activities (AerosUSA 2020).

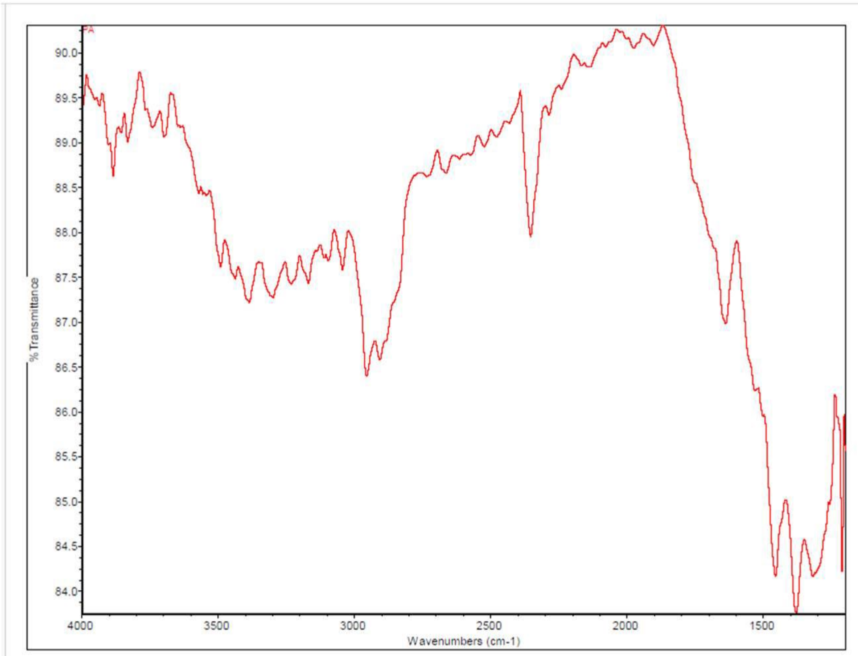

Figure 4. Transmittance spectrum of Polyamide

Polyethylene (PE)

Polyethylene (PE) is the most common type of plastic used currently – annually, around 100 million tonnes of polyethylene is produced. It is mainly used for plastic bags, bottles, and films. In water sample 1, there were 3 PE particles, while in sample 2, there was only 1 that was detected. The polyethylene microplastic particles most likely come from the wrappers and bottles of snacks, food, and drinks that people bring to the beach. To prevent this, people should focus on properly recycling their plastic waste and not littering on the beach (Britannica 2019).

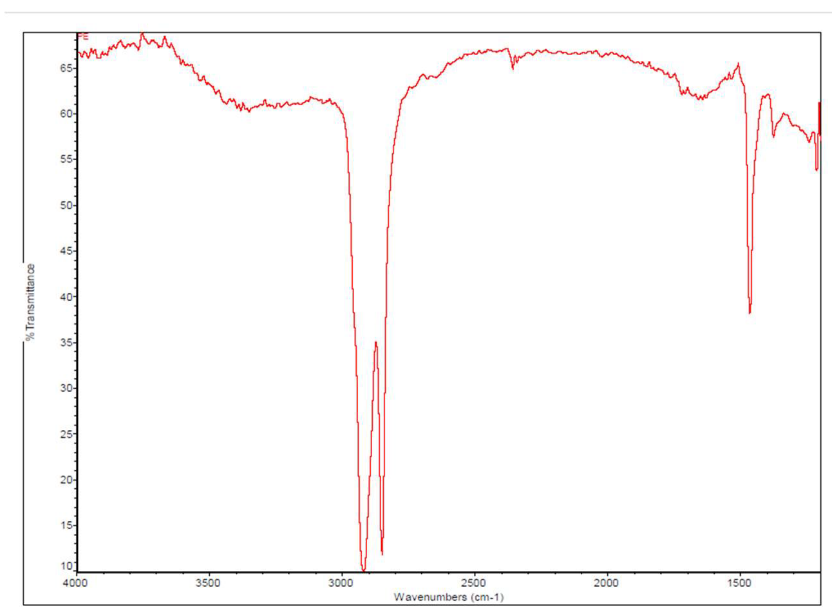

Figure 5. Transmittance spectrum of Polyethylene

Polytetrafluoroethylene (PTFE)

More Polytetrafluoroethylene (PTFE) was found in sample 2, with 3 being present, while only 1 was detected in sample 1. PTFE is more well known as Teflon, and it is a material most commonly used for coating. In the oil industry, due to its chemical resistance and stability, pipes and tanks are lined with PTFE. It is also used to package and seal liquid natural gas. The concentration of PTFE in the Ras Tanura beach water can be assumed to come from the oil tankers that dock in the port, and the oil refinery nearby (Wikipedia 2022).

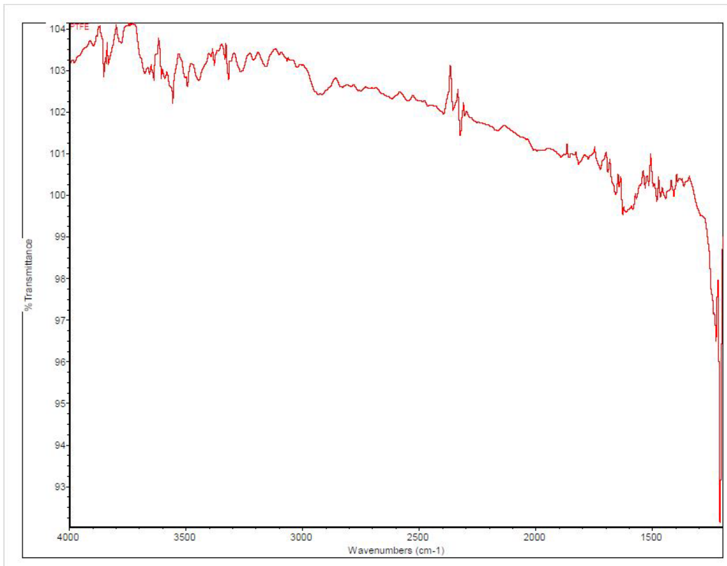

Figure 6. Transmittance spectrum of Polytetrafluoroethylene

Rayon

Rayon in sample 2 had the highest microplastic concentration detected from both water samples, with 14 particles. In sample 1, 4 rayons were detected. It is a material made of cellulose, and it is widely used in clothing, textiles, and sanitary products such as disposable wipes and napkins. These items can easily be found on beaches, hence rayon's high concentrations in the detections (McGill 2021).

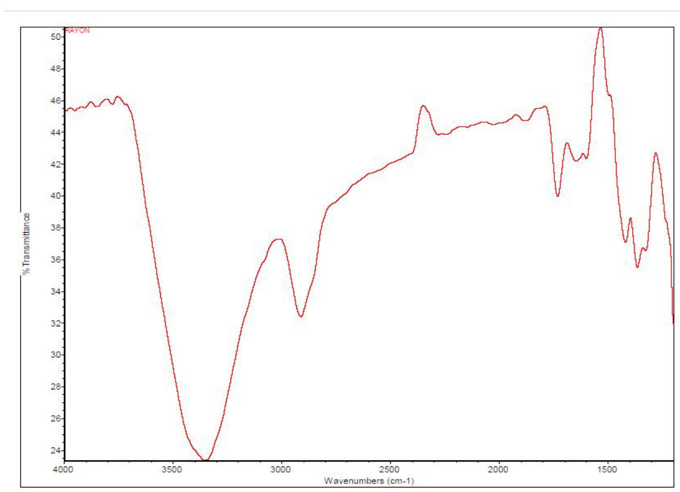

Figure 7. Transmittance spectrum of Rayon

Conclusion

As increasing amounts of plastic waste get released into the ocean, microplastic pollution rises as a global threat to marine ecosystems. An investigation was performed for the ocean water at a local beach in Saudi Arabia, Ras Tanura Beach, for the detection of microplastics and their concentrations using two methods – GC-MS and FT-IR. Due to limitations with the methodology, the GC-MS yielded poor and vague results. Nevertheless, the samples analyzed by FT-IR gave data that could properly be analyzed. Samples 1 and 2 contained 13 and 22 microplastic particles per liter. Averaging the concentration, it can be determined that 17.5 particles per liter of microplastics are moderately high for a beach like Ras Tanura, even though there is no clear-cut threshold for a low and high concentration of microplastics. A deeper look at the type of microplastics that were detected reveals that they mostly come from materials used for clothes, such as swimsuits and activewear; packaging, such as plastic wrappers, bags, and bottles; sanitary items such as wipes and napkins; and coating materials used in the oil industries. The analysis of the Ras Tanura beach water shows the extent of how easily microplastic pollution can spread. Additionally, it emphasizes the importance of improvement in the limitations of analysis methodologies, such as the case of GC-MS and the minimum concentration threshold. Another improvement that should be made is the standardization of microplastic analysis, specifically the development of a clear-cut line between safe and dangerous microplastic concentrations in water.

Acknowledgments

I would like to thank my advisor for the valuable insight provided to me on this topic.

References

"Plastic pollution is growing relentlessly as waste management and recycling fall short, says OECD." *OECD*, 22 February 2022, https://www.oecd.org/environment/plastic-pollution-is-growing-relentlessly-as-waste-ma nagement-and-recycling-fall-short.htm.

"Riverine plastic pollution." *UNEP*, https://www.unep.org/interactives/wwqa/technical-highlights/riverine-plastic-pollution.

"Pyrolysis–gas chromatography–mass spectrometry." *Wikipedia*, https://en.wikipedia.org/wiki/Pyrolysis%E2%80%93gas_chromatography%E2%80%93m ass_spectrometry.

"Gas chromatography mass spectrometry basic principles." *Agilent*, https://www.agilent.com/en/product/gas-chromatography-mass-spectrometry-gc-ms/gcms -fundamentals.

"Infrared Spectroscopy." *Chemistry LibreTexts*, 16 April 2022, https://chem.libretexts.org/Bookshelves/Physical_and_Theoretical_Chemistry_Textbook_Maps/Supplemental_Modules_(Physical_and_Theoretical_Chemistry)/Spectroscopy/Vibr ational_Spectroscopy/Infrared_Spectroscopy.

Sims, George. "Properties & Uses of Polyamide | Applications." *AerosUSA*, https://aerosusa.com/applications-properties-and-uses-of-polyamide/.

"Polyethylene (PE) | Properties, Structures, Uses, & Facts." *Britannica*, https://www.britannica.com/science/polyethylene.

"Polytetrafluoroethylene." *Wikipedia*,
https://en.wikipedia.org/wiki/Polytetrafluoroethylene.

"What is Rayon? | Office for Science and Society." *McGill University*, 19 November 2021,
https://www.mcgill.ca/oss/article/history-you-asked/what-rayon.