Chapter 4
Methodology of Assessing Microplastics and Nanoplastics in the Environment: Recent Advances in the Practical Approaches

Dayakar Govindu, Radhika Tippani, Mahendar Porika, and Syam Prasad Sura

Abstract Microplastics (MPs) and nanoplastics (NLPs) have emerged as emergent particle anthropogenic contaminants, quickly gaining scientific and popular attention. These microscopic plastic particles have been identified in the nature, portable water, and foodstuff all around the world, raising worries about their effects on the environment and human health. Reliable information on MP and NLP concentrations in the environment is required to fully address these challenges. MP and NLP particles, on the other side, vary greatly in shape, density, size, polymer type, surface characteristics, and other factors. While particle concentrations in various mediums may range by up to ten orders of magnitude, analysing these complex samples might seem like looking for a needle in a haystack. This emphasises the vital need of using the right methodologies to identify, quantify, and characterise MP and NLPs with an emphasis on sensitivity and detection limits.

Keywords Microplastics (MPs) · Anthropogenic contaminants · Nanoplastics (NLPs) · Polymer type

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4.1 Introduction

Environmental plastic pollution has a significant influence on the development, growth, and longevity of a variety of living species, including humans, prompting scientists to design novel monitoring and purification methods. Despite the many benefits of plastic materials in everyday life, their limited biodegradability, incorrect usage, and ineffective disposal contribute to increased environmental contamination. Plastic derivatives are exposed to the environment, which stimulates chemical, physical, and biological degradation processes, resulting in the accretion of tiny plastic particles in both aquatic and terrestrial environments, such as soil (Li et al., 2020), freshwater, air (Prata, 2018), foodstuff, and sediments.

Microplastics (MPs, 5 mm) and nanoplastics (NLPs, 1 nm to 1 mm) are small particles of synthetic polymers that can be discharged into the environment (soils, water (sea, fresh, and drinking), biota, food, air, and sediments) and are thus recognised as evolving particulate anthropogenic contaminants (Dehaut et al., 2019; Hale et al., 2020; Delgado-Gallardo et al., 2021). Thompson et al. (2004) used the term microplastics to describe microscopic plastic pieces found in the ocean. Arthur et al. (2010) recommended a microplastics size limit of 5 mm in 2009. NP and MP are now defined as plastic particles and fibres smaller than 1 μm and in the size range of 1 μm to 1 mm, respectively (Gigault et al., 2018). Large microplastics are defined as fragments with a diameter of 15 mm or more. In the following, we'll use the acronyms MPs for microplastics, NPLs for nanoplastics (rather than NPs to prevent misperception with nanoparticles), and NMPs for both nanoplastics and microplastics when discussing microscopic plastic particles and fibres in general. In complex environmental samples, MPs and NPLs are found. This study does not cover micro- and nanoplastic analyses in full; however a few essential topics are worth mentioning (Fig. 4.1).

Aside from the fact that plastic materials increase the standard of lifespan for millions of individuals throughout the world wide by rendering it easier, harmless, and additional pleasurable. They are lightweight, adaptable, durable, formable, corrosion- and flame-resistant, and so on. On the other hand, as soon as plastics end up in nature or in food, it raises global worries. While plastic output in Europe has decreased somewhat (61.8 Mt in 2018 and 59.7 Mt in 2019), worldwide production has increased year after year, reaching 368 Mt in 2019. Production of thermoplastics like polyethylene (PE) of high density (HDPE) and low density (LDPE), polypropylene (PP), polystyrene (PS), polyvinyl chloride (PVC), and polyethylene terephthalate (PET) is an indicator of the extent to which MP pollution is present in freshwater and drinking water, for example (Koelmans et al., 2019).

Bioplastics are manufactured in addition to traditional polymers such as those described above, as well as poly(methyl methacrylate) (PMMA), polyurethane (PUR), and polyamide (PA). Food packaging (e.g., polylactide, PLA) and agriculture are increasingly using the latter (e.g., polybutylene adipate-co-terephthalate, PBAT). Tire wear particles (TWP), which comprise 40–60% synthetic polymers (e.g., styrene-butadiene rubber, SBR) and paint particles/surface coatings, are also

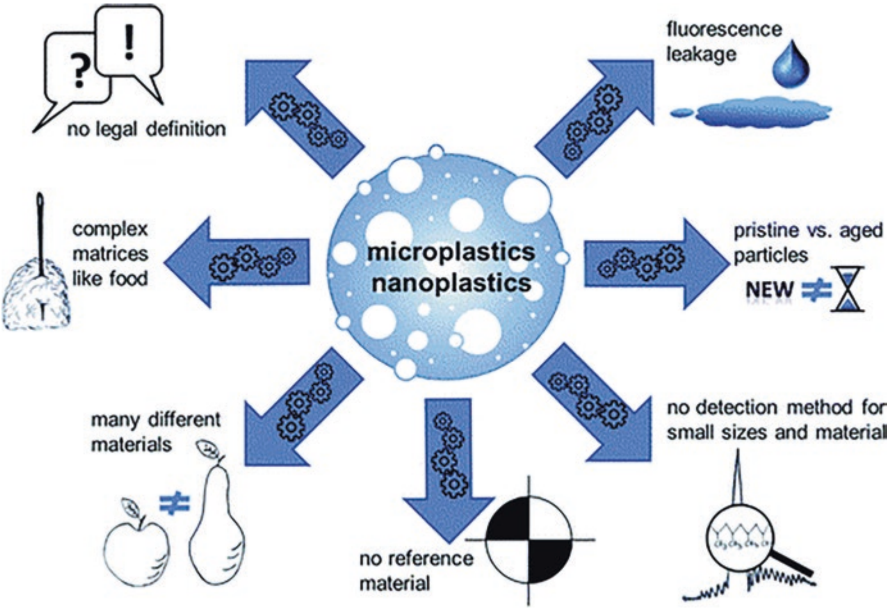


Fig. 4.1 Obstacles and opportunities in the realm of MP and NPLs study. (Adapted from Paul et al., 2020)

attributed to MPs, according to a new definition (Hartmann et al., 2019). In these systems, synthetic polymers act as film formers and are mixed with binders and fillers (Hartmann et al., 2019).

"Primary" and "secondary" origin nanomicroplastics are distinguishable. "Primary": it is possible to use nano microplastics in diverse ways (e.g., pellets for industrial production, industrial cleaners, and nano- and microbeads for personal care products). Plastic waste in the environment is fragmented and degraded by mechanical, UV, and microbiological degradation (Frias & Nash, 2019) to create secondary nano microplastic particles and fibres.

Across the globe, MPs are discovered in deep-sea sediments (Cunningham et al., 2020) and even on Mount Everest (PES fibres were identified at 8440 m) (Napper et al., 2020). The many reports of MP occurrence globally sparked several issues about MP consequences on biota. Leaching of monomers and additives may have undesirable effects, some of which are poisonous, carcinogenic, or endocrine disruptive (Tian et al., 2021). Also, oxidative photodegradation of plastic trash may produce toxic volatile organic compounds (VOCs) such as acrolein and benzene (Lomonaco et al., 2020). The MPs may also function as a vector for harmful and/or antibiotic-resistant microbes (Bakir et al., 2014; Brennecke et al., 2016; Bank et al., 2020).

There is a wide range of MP effects on biota recorded thus far: negative (including deadly), neutral, or even detoxifying. Many of these investigations used MP particle concentrations that were 102–107 times higher than those found in the environment. This observation emphasises the value of MP exposure research at actual concentrations (Lenz et al., 2016). While NPLs have been shown to cross the blood-brain barrier in fish (Mattsson et al., 2017), quantifiable data on their environmental incidence is lacking. The extent of human exposures to MPs through water, food, and air is currently being examined (Catarino et al., 2018; Paul et al., 2020). While MPs have been detected in a variety of foods (Van Cauwenberghe & Janssen, 2014; Kirstein et al., 2021), inhalation is thought to be the main source of exposure (Cox et al., 2019). Smaller MPs are predicted to have greater harmful impacts. However, NPLs have been found to pass the gut barrier (Lehner et al., 2019).

To estimate real nano microplastic dangers, accurate data on particle presence in ambient and dietary samples is required. Since just 1.4% of particles that looked like MPs were found to be made of synthetic polymers, (Löder et al., 2015), accurate chemical characterization of nano microplastics is critical.

Micro- and nanoplastics can enter the human body via the mouth. Following oral consumption, particles are affected by interactions with digestive fluids, intestinal cells, absorption and transit in the gut and liver, and excretion. Figure 4.2 shows an example.

Because plastic sources, use patterns, emission channels, and material qualities vary widely, so do nano microplastic particles (Koelmans et al., 2019; Hale, 201; Zarfl, 2019). This analyte is one among the most difficult to identify, quantify, and characterise in the environment and food.

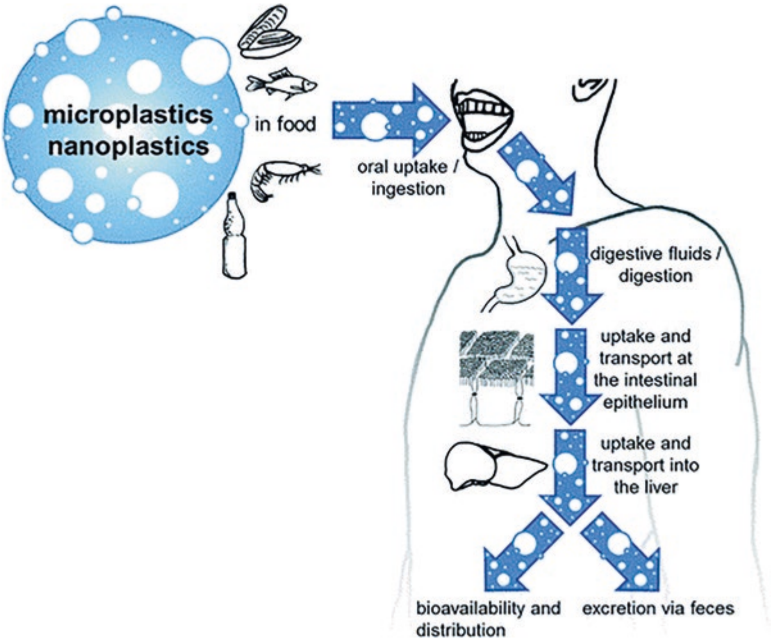


Fig. 4.2 Human exposure and micro- and nanoplastic particle pathways. (Adapted from Paul et al., 2020)

The main goals of this chapter include: (i) draw attention to the difficulties in studying micro and nanoplastics, (ii) that may be utilised to perform a trustworthy and exact chemical evaluation of particles, and (iii) to share viewpoints both inside and beyond the area of nano microplastic research. As a result, the benefits and drawbacks of both mass-based and particle-based methodologies for identifying and quantifying MPs are explored first, with an emphasis on sensitivity and lower detection size limits, and also automation and high-throughput analysis. New and promising approaches are given alongside well-evolved techniques for the examination of model and actual samples, as well as their applications. The complementary nature of several analytical approaches for thorough MP characterisation is next emphasised. A special section of the study is dedicated to the rapidly evolving subject of nanoplastic research, with an emphasis on NPLs with tiny masses and sizes. Finally, attempts to validate, harmonise, and standardise nano microplastic investigations are discussed, as well as the future uses of sophisticated technologies for the examination of plastic and non-plastic micro nanoparticles.

4.2 Analysis of Microplastics

4.2.1 Mass-Based Analysis

(a) *Thermal Degradation/GC/MS Combination*

Thermal degradation approaches have been revealed to be particularly successful in identifying and quantifying plastic pollution in food stuff and environment. These technologies depend on breakdown products created at certain temperatures in the absence of oxygen. After gas chromatographic (GC) separation, the pyrogram displays the fingerprint of the specific polymer. The volatile breakdown products may then be detected on a molecular level using mass spectrometry (MS). The measurement of polymer mass can be done based on particular pyrolysis products, allowing for concurrent detection and quantification of distinct MP in complicated environmental samples. For mass balances and modelling, and also future regulation, this knowledge for various polymers is essential. Moreover, such approaches enable the identification of plastic-associated additives and also degradation by products and so provide the information required for a meaningful risk analysis of MP for the habitat and human safety. These mass-related data, on the other hand, must be regarded as large quantities of a specific plastic type, such as PS, regardless of whether it is a pure polymer or a component of a copolymer, and are unaffected by particle properties like size, shape, form, and so on (Primpke et al., 2020).

De Leeuw et al. (1986) were the first to disclose the presence of PS as an anthropogenic contaminant in sediment and soil studied by Py-GC/MS. In another study, the Py-GC/MS examination of PS and PVC in coastal sediments, and also polybutadiene (PB), poly(vinyl acetate) (PVA), block (SBS) copolymers, poly(acrylonitrile-costyrene-co-butadiene) (ABS), and styrenebutadiene random (SBR) (Fabbri et al., 2000; Fabbri, 2001). These approaches are commonly used in marine and freshwater environments (sediments, (Fries et al., 2013; Hermabessiere et al., 2018; Käppler et al., 2018; Dierkes et al., 2019; Ceccarini et al., 2018); Hermabessiere et al., 2018) water (Primpke et al., 2020; McCormick et al., 2016; Ravit et al., 2019; Dümichen et al., 2017; Hendrickson et al., 2018) biota (Hermabessiere et al., 2018; Dehaut et al., 2016; Dümichen et al., 2015), sewage sludge, (Dierkes et al., 2019; El Hayany et al., 2020) airborne emissions from laundry dryers, soil, (Watteau et al., 2018; Steinmetz et al., 2020) and commercial sea salt, (Fischer et al., 2019). Py-GC/MS has recently been shown to be capable of evaluating nanoplastics in both model and actual samples (Sullivan et al., 2020).

There are two kinds of pyrolysis units and their connection with gas chromatographs in terms of applicable instrumentation: I Py-GC/MS and (ii) TED (thermo-extraction and desorption) GC/MS.

(i) *Pyrolysis-Based Methods*

Py-GC/MS can be used in a variety of ways, including (I) single-shot analysis, (ii) double-shot (or “multi-shot”) analysis, (iii) evolved gas analysis (EGA-MS), and (iv) reactive or thermochemolysis Py-GC/MS (Picó & Barceló, 2020). Pyrolysis is carried out in “single-shot” mode at a certain temperature, generally over 500 °C. The sample temperature is quickly raised from ambient to pyrolysis temperature (<20 ms for contemporary systems). The macromolecules are virtually instantaneously broken in the pyrolyzer, and the pyrolysis products are separated in the GC column and utilised for MS-based polymer(s) and additive identification (Primpke et al., 2020; Käppler et al., 2018).

Double-shot mode, also known as thermal desorption (TD) Py-GC/MS, is a way to analyse various kinds of compounds at different times. For example, volatile compounds that are released at low temperatures during a thermal desorption step can be analysed in the same way as the decomposition fragments of the larger macromolecules that are formed at high temperatures during pyrolysis. This is a good way to find out about the different types of polymer additives that are both volatile and nonvolatile (Herrera et al., 2003; Jansson et al., 2007) and even sorbed organic compounds (Reichel et al., 2020) pooled with the detection of polymer(s) based on the investigation of pyrolysis products (Fries et al., 2013; Dekiff et al., 2014). Also, before pyrolysis, the “double-shot” mode may be employed to eliminate organic molecules that can impede with identifying and quantifying MP breakdown products from complicated organic-rich materials (Okoffo et al., 2020).

EGA-MS is a type of chromatography that doesn’t use a chromatographic column. Instead, it uses a short and narrow (2.5 m, 0.15 mm i.d.) deactivated silica capillary tube without a stationary phase to connect the GC injector and the MS detector directly (Picó & Barceló, 2020). Thermal chemistry Py-GC/MS involves adding a derivatization agent, like tetramethylammonium hydroxide (TMAH) solution, which causes an ester and ether to be broken down and then methylated (Primpke et al., 2020; Picó & Barceló, 2020). Individual plastic particles or a small amount of a sample are put into a pyrolyzer target for the Py-GC/MS method of identifying polymers, which is how it works. Each pyrolyzer has a different size and can process a different number of samples at a time (Fries et al., 2013; Nuelle et al., 2014; Funck et al., 2020) placed in a platinum coil. CP pyrolyzers utilize semi-closed ferromagnetic targets (typical dimensions ⌀ 2 mm, 8 mm height) (Fischer & Scholz-Böttcher, 2017). MF pyrolyzers use stainless steel cups (typical dimensions approximately ⌀ 4 mm, 8 mm height (Fischer et al., 2019). Heating the sample to a certain temperature in an inert gas (generally He or N2) is done in each case. This gas is also used as a carrier gas for GC separation (Primpke et al., 2020). A quadrupole mass spectrometer is usually used to make sure that the polymers made from decomposition products can be identified and counted with a high level of accuracy. A new study by Sullivan et al. shows that GC time-of-flight mass spectrometry (Py-GC/ToF) can significantly increase the amount of information that can be found (Sullivan et al., 2020).

Based on the pyrolysis product complexity and how quickly they break down, the pyrograms of different types of polymers look very different. The pyrogram of a single polymer can be very complicated (e.g., PE, PP, PET) over moderate (e.g., PS) to simple (e.g., PMMA) (Primpke et al., 2020; Fotopoulou & Karapanagioti, 2017).

Identification of Particles and Additives

Py-GC/MS has been used by a lot of different groups to find individual (plastic) particles that have been isolated from marine and river sediments, surface water, and biological samples (Hermabessiere et al., 2018; Hendrickson et al., 2018; Dehaut et al., 2016). Using "double-shot" mode (TD-Py-GC/MS), Fries and coworkers investigated marine microplastic particles down to 100 nm. These researchers could identify many plastics (PE, PP, PS), as well as numerous additives (benzophenone, 1,2-benzenedicarboxylic acid, dimethyl phthalate, diethylhexyl phthalate, dibutoxyphthalate, dibutyl phthalate, phenol, and 2,4-di-tert-butylphenol) (Fries et al., 2013; Dekiff et al., 2014). Py-GC/MS can be used to correctly determine particles and get more useful details about additives and copolymers, but it takes a long time. Each GC-MS run can take up to half an hour or more. FTIR and Raman microspectroscopy data were recently compared with Py-GC/MS findings by Käppler et al. (2018) and Hermabessiere et al. (2018). Thus, Py-GC/MS and spectroscopic approaches may be used together to analyse individual particles. EGA-MS may also be used to quickly identify additives and polymers. While Py-GC/MS can analyse individual particles, its true ability for simultaneous MP identification and quantification in complicated materials has lately been discovered (Kirstein et al., 2021; Fischer et al., 2019; Dibke et al., 2021).

Simultaneous Identification and Quantification of Polymers from Complex Samples

Analysing samples immediately (Funck et al., 2020) or after one or more sample preparation steps may involve chemical and enzymatic digestion of organic matrix and elimination of inorganic matrix by density separation (Kirstein et al., 2021; Primpke et al., 2020). Soluble extraction (Dierkes et al., 2019; Okoffo et al., 2020) and pressurised liquid extraction (PLE) may also be used to preconcentrate polymers from complicated matrices prior to Py-GC/MS. CPE has also been used to preconcentrate nanoplastics from water samples (Zhou et al., 2018). Watteau et al. (2018) found MPs in bulk soil and soil factions. Using a 0.5–1 mg sample permits identification of plastic characteristics (e.g., typical for PS) that vary from soil organic matter. Funk et al. used Py-GC/MS to identify and quantify MPs in wastewater after cascade filtering with no sample preparation other than extraction and drying. PS and PE LOQs were 0.03 μg and 1 μg absolute, respectively (Funck et al., 2020).

The elimination of organic and inorganic matrices has shown to be effective in increasing the sensitivity of Py-GC/MS for the measurement of various polymers in complicated samples. MPs deposited on a filter are pyrolyzed after sample preparation and drying; for this, fragments or even the complete glass fibre filter with a diameter of 15 mm may be immediately introduced into the pyrolyzer for analysis (Kirstein et al., 2021).

Before Py-GC/MS analysis, liquid extraction of soluble polymers may be used to preconcentrate polymers from complicated matrices (Okoffo et al., 2020). For MP measurement in environmental samples, Dierkes et al. (2019) devised a technique that combines PLE with Py-GC/MS. A pre-extraction process with methanol is used to decrease matrix effects before a PLE with tetrahydrofuran is used (THF). LOQs as low as 0.007 mg/g have been obtained for the most commonly used synthetic polymers (PE, PP, and PS). For the detection and enumeration of PP, PET, PS, PVC, PE, PMMA, and PC in biosolids, Okoffo et al. coupled PLE (using dichloromethane, DCM) with “double-shot” Py-GC/MS (treated sewage sludge). For MP analysis in complex organic-rich samples, thermal desorption of possibly interfering coextracted chemicals before pyrolysis has been shown to be particularly effective. The method’s validation demonstrated a linear range of polymer absolute between 0.01 μg and 2 μg, with MP pollution of biosolids ranging from 0.1 mg/g to 4.1 mg/g dry weight across samples. Moreover, the use of 1,2,4-trichlorobenzene (TCB) for dissolving PE, PP, and PS in soil for Py-GC/MS analysis has been shown, with the technique detection limits being 1–86 g/g, while the instrumental detection limits are 186 ng absolute (Steinmetz et al., 2020). A combination of solvent extraction (using DCM) followed by gel permeation chromatography (GPC) to distinguish higher and lower molecular weight fractions was described by Ceccarini et al. (2018) as a method for characterising MPs and their degradation products in coastal sediments. In one kilogramme of sand, the researchers discovered up to 30 mg MPs.

Cloud point extraction in conjunction with Py-GC/MS has recently been proved to be effective for the study of nanoplastics in ambient waters. PS (about 65 nm) and PMMA (roughly 85 nm) Nanoplastics were enriched factored up to 500 utilizing Triton X-45-based CPE, without affecting their original shape or sizes (Zhou et al., 2018).

While adequate sample preparation may help Py-GC/MS analysis perform better, the accurate identification and quantification of polymers in complicated mixtures remains a difficult but necessary element. Specific pyrograms of distinctive and selective breakdown products representing various polymers may be used to identify them. The relative strength of indicator chemicals varies from polymer to polymer, which has a big impact on detection sensitivity. Ion chromatograms are often used for the identification of polymers in complicated samples because they may increase detection sensitivity (Dibke et al., 2021). The ion chromatograms show the ion current over time as calculated from mass spectrometric data for a specific fragment ion of an indicator molecule. In this scenario, choosing typical indicator products and their corresponding ions for each polymer based on their intensity and specificity becomes critical, with the latter being crucial for appropriate polymer identification and quantification (Primpke et al., 2020). PS has two preferred indicator compounds, styrene and its trimer, which are distinct in terms of specificity and quantity. The former is plentiful but generic, while the latter is the polar opposite. As a result, styrene is an excellent PS indicator chemical in matrix-free samples. It may be made from a variety of artificial polymers and natural chemicals, such as chitin, in natural matrices. As a result, in this scenario, using a less intensive styrene trimer is more dependable since its creation can be traced back to the presence of PS in the sample without a doubt (Primpke et al., 2020). Matrix interfered n-alkanes and n-alkenes are good choices for PE identification and quantification. Furthermore, when the carbon number, n-alkenes, rises, the interferences diminish dramatically. Polymer identification is often ensured by the presence of additional polymer-specific breakdown products (Primpke et al., 2020). The rider is directed to a recent article by Primpke et al. for an expanded list of indicator chemicals and related indicator ions that allow for the simultaneous identification and measurement of various kinds of plastics utilising thermal breakdown procedures (Primpke et al., 2020). The area beneath the signals of the indicator ions coincides with the mass of the polymer contained in the sample vessel, resulting in an ion chromatogram when pyrolysis is done under repeatable circumstances. This relationship is linear throughout a system-dependent concentration range and may be utilised for external polymer calibration. The implementation of an internal standard (or standards) will enhance data quality even more. Deuterated molecules (styrene (Funck et al., 2020) polystyrene (Eisentraut et al., 2018) and chlorobenzene (Sullivan et al., 2020) or a combination of 9-dodecyl-1,2,3,4,5,6,7,8-octahydro anthracene, anthracene-d10, androstane, and cholanic acid may be (Fischer et al., 2019; Gobmann et al., 2021).

Retrospective analysis of the pyrograms generated may detect new polymer indicator ions despite thermal degradation methods‘destructive character, which prevents any further observations. Even semiquantitative information on these novel polymers may be gained by using internal standards (Primpke et al., 2020). The Py-GC/MS data for complex environmental samples like freshwater, marine sediments, road dust, blue mussels, and marine salts were recently analysed retrospectively by Gobmann et al. (2021) to determine the pollution with tyre wear particles, which are assumed to be the major source of habitat MPs. The authors discovered that in all samples studied, automobile tyre wear mass loads dominated truck tyre wear mass loads (ratios of car to truck tyre wear were up to 16 to 1). There was a substantial difference in TWP concentrations in road dust and thermoplastic (PE) MP (about 5 g of TWP vs 0.3 g of MP per kg road dust, dry weight), while TWP contamination was reduced or absent in samples collected further away from TWP sources. Nevertheless, thermoplastic polymers were still widely used (Gobmann et al., 2021).

The sensitivity of various polymer detection in complex mixtures is determined by indicator product relative intensities. A broad backdrop and any interference are quantified as well. Also, the solubility of the polymers directly affects the calibration range. Calibration of the soluble PS, for example, may be done down to 0.01 m. The LOD (S/N-ratio > 3) for the conspicuous, but unspecific pyrolysis product styrene monomer and the extremely specific but substantially weaker styrene-trimer, respectively, was derived from this calibration. The comparable LOQ values are 16 and 282 ng, respectively (S/N-ratio > 10). Lower calibration points for PP and PA 6 have been reported as 0.3 μg and 0.5 μg, respectively (Fischer et al., 2019). When working with solid standards, the LOQ for Py-GC/MS may be determined by the available balance and varies between 0.7 and 1 μg absolute, depending on the polymer type (Primpke et al., 2020). Consequently, depending on the polymer type and pyrolysis unit, Py-GC/MS analysis may be carried out with a LOQ of 0.01–1 μg. (Braun et al., 2020). It should be noted that the direct pyrolytic products of various polymers (e.g., PET and PC) exhibit a significant degree of variety and polarity, resulting in poor chromatography and limited sensitivity. Thermochemolysis, for example, by adding TMAH, may be used to boost the method's sensitivity for these polymers. The latter causes an ester and ether cleavage process, which is then followed by methylation. PET and PC have more specific thermochemolysis products, resulting in increased sensitivity for these polymers. Simultaneously, most other polymers' pyrolytic behaviour was unchanged. Using online pyrolytic derivatization, it is possible to effectively quantify PE, PP, PS, PET, PVC, PMMA, PC, PA 6, and methylene-diphenyldiisocyanate-PUR (Primpke et al., 2020; Fischer & Scholz-Böttcher, 2017). The initial sample volume needs to be adjusted for MP quantification with Py-GC-MS using the preconcentration process, taking into consideration the pyrolyzer's maximum sample capacity (g-range), as well as the predicted content of MPs and the appropriate calibration range (s).

The use of thermoextraction and desorption (TED) GC/MS allows for the analysis of much higher sample amounts (mgrange).

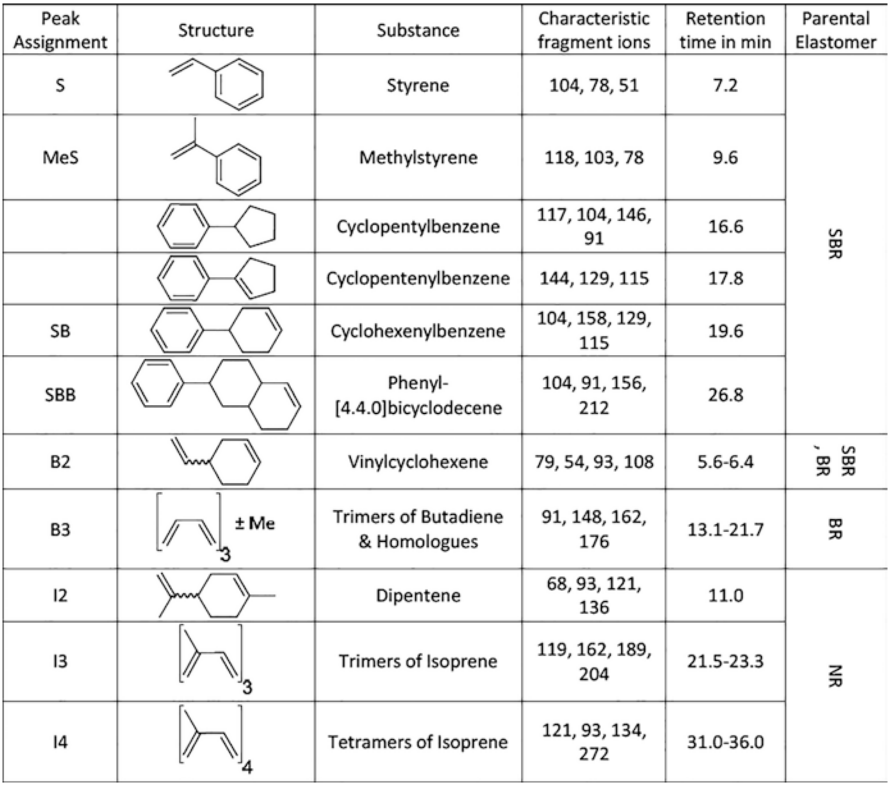
(ii) *TED-GC/MS*

In the TED-GC/MS method, the material is pyrolyzed using a thermogravimetric analyzer (TGA) under inert gas (typically N2) and temperature-ramped conditions up to 600 °C. The breakdown products are purged from the TGA and transported to a solid-phase adsorber bar (containing, for example, polydimethylsiloxane, PDMS), which is only linked to the decomposition product gas flow in a certain temperature range (s). The trapped gases' temperature range may be set ahead of time, for example, 25–650 °C or 350–600 °C. All volatile pyrolysis products are represented in the first range. The second is typical of most common polymers with degradation temperatures over 350 °C; however it leaves out a significant portion of pyrolysis products produced by thermo-labile organic matrix components (Primpke et al., 2020; Eisentraut et al., 2018). The adsorber is moved to a thermal desorption unit (TDU) of the GC/MS instrument after the solid phase is filled with an extract of the breakdown products (Eisentraut et al., 2018; Dümichen et al., 2019). The breakdown products are thermally desorbed and mobilised in the TDU unit and then cryo-focused in a chilled injection system, separated using a GC column, and quantified using MS (Eisentraut et al., 2018).

Dümichen et al. (2015) used the TED-GC/MS for the first time to analyse environmental samples spiked with PE and identify this polymer down to 1 wt %. Meanwhile, TEDGC/MS has been shown to be a viable method for quantifying various polymers in complicated environmental matrices. PE, PP, and PS had equivalent LOQs of roughly 10, 1, and 0.2 μg, respectively (Dümichen et al., 2019). Moreover, the use of TED-GC/MS for the study of tyre wear content in environmental samples has recently been shown. (Eisentraut et al., 2018; Klöckner et al., 2019; Klöckner et al., 2020). Amounts of styrene butadiene rubber (SBR, primary component of passenger automobile tyres) discovered in highway runoff samples ranged from 3.9 to 9.3 mg/g (Fig. 4.3; Eisentraut et al., 2018). Braun et al. (2021) recently established the usefulness of TED-GC/MS for determining the MP mass content in drinks packed in plastic bottles. The scientists created a smart filter crucible as a sampling and identification instrument, allowing MPs to be filtered down to 5 μm. MP levels as low as 0.01 g/L and as high as 2 g/L were recorded, depending on the kind of beverage bottle. TED-GC/MS has a far bigger sample capacity than Py-GC/MS, up to 100 mg (approximately 200 times more than Py-GC/MS). This is beneficial for both sensitivity (albeit the LOD and LOQ for TEDGC/MS are lower than for Pyr-GC/MS) and representativity of environmental sample analysis. As a result, MP investigation of highly contaminated samples (containing more than 0.5%–1% wt % of each kind of polymer examined) may be accomplished without sample pretreatment, which might be either insufficient or difficult (e.g., for PET and PA) (Castelvetro et al., 2021). However, when using the complete temperature range of 25–650 °C, sample-dependent organic matrix may still interfere with polymer quantification, and an adsorption cutoff below 350 °C leads to losses of highly thermolabile polymers like PVC (Primpke et al., 2020).

(b) *Further Thermoanalytical Methods*

Materić et al. (2020) have suggested a novel approach for chemical characterisation of NMPs based on thermal desorption proton transfer reaction-mass spectrometry (TD-PTR/MS, where hydronium ions produced from water vapour are employed for analyte ionisation). As of now, the approach is extensively employed in environmental studies, including real-time monitoring of volatile organic compounds, semivolatiles, and organic aerosols in the air and dissolved organic matter (DOM) in water and ice (Materić et al., 2020; Peacock et al., 2018). The studies revealed a LOD of <1 ng for PS compounds found in a sample and used this approach to (semi)quantify NMPs in Alpine snow. Because of the method's great sensitivity, it was possible to utilise tiny amounts of samples (1 mL) and conduct tests without any preconcentration processes. Even when samples include mixes of other organic compounds, unique characteristics in the high-resolution mass spectrum of distinct synthetic polymers were shown to be acceptable for fingerprinting, e.g., a valid fingerprint was obtained when just 10 ng of PS was contained inside the DOM of snow. The PET, PVC, and polypropylene carbonate (PPC) were discovered in melded cores, but only PET was found after 0.2 μm filtering, showing that PET



Peak Assignment	Structure	Substance	Characteristic fragment ions	Retention time in min	Parental Elastomer
S		Styrene	104, 78, 51	7.2	SBR
MeS		Methylstyrene	118, 103, 78	9.6	
		Cyclopentylbenzene	117, 104, 146, 91	16.6	
		Cyclopentenylbenzene	144, 129, 115	17.8	
SB		Cyclohexenylbenzene	104, 158, 129, 115	19.6	
SBB		Phenyl-[4.4.0]bicyclodecene	104, 91, 156, 212	26.8	
B2		Vinylcyclohexene	79, 54, 93, 108	5.6-6.4	SBR, BR
B3	3 ± Me	Trimers of Butadiene & Homologues	91, 148, 162, 176	13.1-21.7	BR
I2		Dipentene	68, 93, 121, 136	11.0	NR
I3	3	Trimers of Isoprene	119, 162, 189, 204	21.5-23.3	
I4	4	Tetramers of Isoprene	121, 93, 134, 272	31.0-36.0	

Fig. 4.3 TED-GC-MS discovered breakdown products for elastomers and tyres. (Adapted with permission from Eisentraut et al., 2018)

fibres are the most common component of airborne pollution. Despite the low recovery rates for PS (Materić et al., 2020) and the need to account for interference from even modest contaminants emanating from various sources, the TD-PTR/MS approach seems to offer promise for sensitive NMP analysis. TGA-MS may also be used to provide a quantitative investigation of MP in complicated matrices. David et al. devised a non-pretreatment technique for quantifying PET in soil samples. The mass loss and MS signal intensity of typical PET pyrolysis products were measured, while sample mixes (ca. 50 mg) were pyrolyzed at a 5 °C/min ramp (40–1000 °C). The LOD and LOQ, respectively, were 0.07 and 1.72 wt % PET (David et al., 2018). TGAFTIR may also be used to do spectroscopic examination of the gas that is produced during TGA (Dittmann et al., 2018; Becker et al., 2020).

TGA and differential scanning calorimetry (DSC) are two thermoanalytical methods for determining MP content in complex materials (Braun et al., 2020; Castañeda et al., 2014), where endothermic phase transition temperatures may be used for polymer identification and quantification. This approach can be used to test polymers having crystalline components (PE, PP, PA, and PET), but it cannot be used to study polymers without crystalline components (e.g., PS). Majewsky et al. (2016) investigated endothermic phase transition heat fluxes and peak temperatures of LDPE, PP, PET, PES, and PA by heating them from 20 to 800 °C at a rate of 5 °C/min under N2. According to the literature, LDPE, PP, and PA have low melting points, peaking at roughly 101 ± 2 °C, 164 ± 1 °C, and 216 °C, respectively, with no overlap with the other examined plastic kinds. The other polymers' peak temperatures range from 250 to 261 °C, and they generally overlap. The authors concentrated on the determination of PE and PP since unambiguous polymer identification in the presence of numerous polymers with phase transition temperatures >200 °C is difficult. Using specific polymer combinations and a total sample weight of 10 mg, they reported LOD of 2.5 and 5 wt.% for PE and PP, respectively.

Rodríguez Chialanza et al. (2018) studied at the performance of DSC for the analysis of LDPE, HDPE, PP, and PET, as well as the effect of particle size on the DSC signal for polymer mixtures. They employed size fractions of 23–256, 256–645, and 645–1000 μm and discovered that using a 10 °C/min heating rate, the signals of four polymers were easily distinct. However, particle size had a significant impact on both polymer identification and mass quantification. As a result, the authors advocated correct sample treatment, including sieving of suspended particles for MP measurement using DSC, and evaluated this method on seawater samples spiked with polymers (Rodríguez Chialanza et al., 2018).

Bitter and Lackner recently published an expanded research for quantifying semicrystalline MP in industrial wastewaters (Bitter & Lackner, 2020). They were able to analyse the samples treated with H_2O_2 in the size ranges for small (10–1000 μm) and large (1000–5000 μm) MPs by using a modified DSC protocol proposed by Majewsky et al. (2016) (which included three steps in a N2 atmosphere: first heat-up step from 30 to 290 °C at 20 °C/min heating rate, subsequent cooling step from 290 to 0 °C at 10 °C/min cooling rate). The most prevalent polymers were PE and PP, although PA and PET were also discovered. Low mass concentrations of MPs ranging from 0.5 to 35.5 μg/L were identified at all three industrial locations, which are equivalent to the amount of organic micropollutants in municipal WWTP effluents. The removal capacity of one example industrial WWTP was found to be >99.99 percent when both influent and effluent were analysed (Bitter & Lackner, 2020).

4.3 Particle-Based Methods for Nondestructive Analysis of Microplastics

4.3.1 Vibrational Spectroscopy

It is possible to examine micro- and nanoplastic particles using infrared (IR) and Raman spectroscopy, both of which use radiation interaction with molecular vibrations. FTIR spectroscopy and Raman microspectroscopy are now frequently used because they allow for the identification of polymer type as well as the number, size/size distribution, and form of particles. The presence of plastic particles and fibres in the sample preparation and detection procedures necessitates plastic-free (or limited) working environments (Braun et al., 2020; Koelmans et al., 2019). Plastic products should be avoided throughout the procedure, and samples should be prepared in a (MP)-particle/fibre-free or MP-poor environment. In addition, protocol and experimental negative controls must be determined. Pollutions while obtaining sample, preparation of sample, and identification are all taken into account by procedural blanks values. When case preparation and detection are done in different labs, laboratory blank values become essential. These are used to identify internal MP pollutants and assist in locating and removing their origins. LOD and LOQ data for the laboratory may be derived using lab blank values (Johnson et al., 2020). At least three (ideally ten) laboratory blank values are suggested for the LOD and LOQ determinations.

(a) *IR Spectroscopy*

The detection of MPs from marine specimens was achieved using FTIR spectroscopy in a work by Thompson et al. (2004), which was the first time the term "microplastics" was used. Since then, this method has proven to be effective for the identification, quantification, and characterization of MP pollutions in aquatic habitats (Cincinelli et al., 2017; Napper et al., 2020; Piehl et al., 2018), as well as in influents, effluents, and sludge of WWTPs (Horton et al., 2021) and ambient air (Catarino et al., 2018; Trainic et al., 2020; Pivokonsky et al., 2018; Johnson et al., 2020). IR spectroscopy is a nondestructive method that analyses molecular vibrations caused by the absorption of light in the mid-infrared (MIR) region of the electromagnetic spectrum (4000–400 cm^{-1}). Using spectrum databases (Cowger et al., 2020) or other chemometric approaches, the distinctive vibrational fingerprint spectra may be used to accurately identify the polymer type for MP as well as to assign nonplastic particles (Renner et al., 2017; Hufnagl et al., 2019). Water has extremely strong and wide IR bands, which may partly or totally overlap the spectral signature of plastic and nonplastic particles of interest; hence the samples must be dried before examination. The method's vulnerability to water is seen to be its most serious flaw. IR spectroscopy outperforms many other approaches due to the wide range of measuring options available. IR analysis may be carried out in either reflectance or transmission mode (Löder et al., 2015). IR radiation that has entered the sample is measured in transmission mode. Infrared transparent substrates or filters (e.g., aluminium oxide (Anodisc) membranes), (Primpke et al., 2018; Löder et al., 2015), silicon filters, (Käppler et al., 2016), or zinc selenide windows are necessary for this mode. Despite the fact that high-quality data is often collected and the resultant spectrum is representative for the full sample thickness (or complete particle) and hence advantageous for MP identification, this mode may be influenced by total absorption (Primpke et al., 2020). The IR beam may be partly or fully obstructed for colourful, dark, or opaque particles, resulting in low-quality spectra. This disadvantage may be overcome by using the reflectance mode, which measures the IR beam reflected by the sample (Cabernard et al., 2018; Tagg et al., 2020). Reflective surfaces, such as metal-coated (Au, Ag, Al) (Horton et al., 2021; Cabernard et al., 2018), are necessary for this sort of study. Although this mode is excellent for analysing the (aged) surface of a sample or particle, light scattering might cause the data to be distorted. Attenuated total reflection (ATR) may be used to analyse MPs efficiently. This approach has been adopted in 58% of IR research, particularly for bigger particles, since it is the most cost-effective (Primpke et al., 2020). It also doesn't need any sample preparation or complicated mathematical adjustments (which are required for transmission and (pure and diffuse) reflection modes, respectively). An ATR crystal with a high refractive index is pushed onto the sample surface for the measurement (e.g., diamond, zinc selenide, or germanium). The IR light penetrates the sample to a depth of a few micrometres (evanescent wave) after reflection at the crystal/sample contact, and the sample's IR data is acquired. ATR-FTIR is often utilised for the identification of visibly presorted particles (sizes bigger than 200–500 μm) and the characterisation of weathered MPs because information on changing particle surfaces owing to ageing may be readily collected (Primpke et al., 2020; Cabernard et al., 2018). ATR-FTIR may also be used to differentiate between natural and synthetic (micro) fibres (Dris et al., 2018). Tiny particles and fibres may be analysed directly on filters or windows using μ-ATR objective that comes into touch with the sample (Vianello et al., 2013). However, the sample might be damaged or destroyed as a result of the applied pressure, which is needed to produce the essential contact between the crystal and particle surface. Furthermore, the close contact between crystal and stiff inorganic particles (such as MPs) may cause costly μ-ATR instruments to be damaged. Furthermore, since particles must be examined one by one, the ATR-FTIR analysis takes a long time (Ivleva et al., 2017; Braun et al., 2020).

The most widely used FTIR-based approach for analysing (MP) particles is 500 mis micro-FTIR spectroscopy (μ-FTIR), in which an FTIR spectrometer is linked to an optical microscope. The spatial resolution of the study is restricted by diffraction (theoretically ca. 1.7 μm at 4000 cm^{-1} to 13 μm at 500 cm^{-1}), although particles bigger than 10 μm (Cabernard et al., 2018) or 20 μm may be easily recognised and quantified by μ-FTIR. The removal of inorganic and organic matrices is critical for IR analysis, which includes tiny particles. Density separation (Pico et al., 2019; Imhof et al., 2012) and chemical (Pico et al., 2019) or enzymatic (Löder et al., 2017) digestion are often used for this purpose.

μ-FTIR analysis may be carried out (i) for pre-selected particles or (ii) for the full filter area. Prior to IR observations, particles may be manually selected (Cunningham et al., 2020; Ziajahromi et al., 2017) or automatically selected (Brandt et al., 2020) using optical images. For Raman microspectroscopic investigation of MP particles, the preselection technique is often used. Furthermore, using staining methods for preselection and subsequent chemical identification by IR has been demonstrated to improve the identification rate and eliminate researcher bias (Shim et al., 2016). The removal of organic matrix before staining has been advised to eliminate or decrease "false-positive" identification caused by costaining of part of the natural organic material (Zarfl, 2019; Shim et al., 2016).

FTIR imaging (chemical) measures all particles in the studied region, allowing for a more detailed examination of the chemical composition of overlapping and agglomerated particles than the particle preselection option. The number of spectra that must be measured and processed, on the other hand, is much larger (Primpke et al., 2020). Chemical imaging by mercury cadmium telluride (MCT) detectors is conceivable; however measuring vast regions takes a long time. As a result, spectra are often obtained from filter subareas, such as 0.17% (3 mm^2 areas on 47 mm diameter PC membranes) (Harrison et al., 2012) or 5.6% (12 sampling unit areas of 4.5 mm^2 each on 47 mm diameter fibreglass filters) (Vianello et al., 2013). According to Johnson et al. (2020) and Horton et al. (2021), 92% of the filtration area of 11.6 mm × 11.6 mm can be studied by optimising a measuring methodology.

Recent technological developments in μ-FTIR analysis have resulted in multiple high-detail investigations on MP contamination of various ecosystems, waste management systems, (Tagg et al., 2020), and drinking water (Lorenz et al., 2019; Johnson et al., 2020). Aluminium oxide (Anodisc) filters are often employed for transmission mode measurements in FPA μ-FTIR for high-throughput analysis. Silicon filter substrates (e.g., with a pore size of 10 μm) that offer adequate transparency for the wide mid-infrared region of 4000–600 cm^{-1} may be utilised if a greater spectral range has to be monitored (Käppler et al., 2016). Au-coated PC filters were found to be adequate for measurements in reflection mode (Cabernard et al., 2018). Complementary Raman analysis is possible with both kinds of filters (Si and Au-coated PC) (Cabernard et al., 2018; Von der Esch et al., 2020). Large data sets occur from imaging-based analysis, particularly when the (automatic) FPA-FTIR option is used. These data sets must be processed to provide information on particle identification as well as other attributes (particle number, size, and shape), which are essential for the comprehensive quantitative analysis. As a result, automated data analysis procedures, such as spectrum preprocessing (baseline correction, smoothing, and so on) and assessment, are essential (Primpke et al., 2020; Renner et al., 2019). Library search is often used for spectra assignment, with search algorithms employed to build a hit quality index (Renner et al., 2019) (HQI). The HQI is a comparison of the query and reference spectrums. Despite the fact that various HQI levels (e.g., 0.7) (Yang et al., 2015) have been recommended as a threshold in different research, the HQI values created using different methods and software may not be comparable. These numbers are also heavily influenced by the database's spectral quality and sample type. It's also worth noting that reference spectra taken with various kinds of apparatus (ATR and μ-ATR, (FPA) μ-FTIR in transmittance or reflectance, detector type) and with various parameter settings (number of scans, spectral resolution) and spectral range might vary greatly (Andrade et al., 2020). As a result, the database(s) in use must be customised for specific applications, and the HQI index level utilised must be verified. Furthermore, databases must include not only the reference spectra of pure synthetic polymers (as in commercial libraries) but also the spectra of various plastic products (including additives) and weathered plastic particles (as in custom-made libraries) (Cowger et al., 2020).

Model-based classification for the automated assessment of FTIR imaging data, where labelled training data are used to predict the class affiliations of unknown data, seems to be a promising alternative to the conventional instance-based spectrum library search (Hufnagl et al., 2019; Xu et al., 2019). The main difference between traditional database searches and model-based categorization is that instead of utilising reference data to determine class membership, the latter employs a multivariate model of the actual data. Hufnagl et al. (2019) introduced a system that uses random decision forest (RDF) classifiers to discriminate between distinct polymer types and assess their abundance and size distributions with good accuracy. The approach was used to identify five different polymer kinds (i.e., PE, PP, PMMA, PS, and polyacrylonitrile, PAN). The expanded RDF technique was recently utilised to effectively identify 11 polymer classes in mussel samples evaluated by FPA-μFTIR imaging (Kumar et al., 2021). Da Silva et al. (2020) devised a model-based technique for the assessment of FPA-μFTIR hyperspectral imaging data using partial least-squares discriminant analysis (PLS-DA) and soft independent modelling of class analogy (SIMCA) models. The method worked well for classifying and quantifying MPs of <100 μm in nine of the most commonly manufactured polymers in the globe (PA, PC, PE, PET, PMMA, PP, PS, PU, PVC). PLS-DA had greater analytical performance than SIMCA models, according to the authors, and was characterised by higher sensitivity, sensibility, and reduced misclassification error. PLS-DA, on the other hand, was less affected by spectral edge effects and poorly focused particle areas (da Silva et al., 2020). It should be highlighted that the creation of classifiers (training data sets) takes time and needs expert operators; also, more work is needed to expand the number of polymer kinds (and include nonplastic analytes). However, given the fast development of hyperspectral imaging technologies, model-based approaches are becoming more appealing because they can reliably evaluate large data sets that often include spectra with poor signal-to-noise ratios.

An exploratory investigation of FPA-μFTIR imaging data acquired from environmental microplastic samples was recently published. The multivariate similarity of spectra is used in this method to identify species or particles without the need for previous information. The dimensionality reduction using PCA and uniform manifold approximation and projection (UMAP) were used as a key idea, which increased data visual accessibility and provided a chemical two-dimensional picture of the sample. Particle spectra were isolated from blank spectra (substantially lowering the quantity of data) and analysed using PCA and UMAP. Cluster analysis utilising k-means and density-based and interactive manual clustering revealed groups of similar spectra, which were then assigned to chemical species based on reference spectra. While the acquired findings were in excellent agreement with a focused study based on automated library search, exploratory analysis highlights a set of unidentified spectra that persisted and would otherwise be disregarded (Wander et al., 2020).

Aside from FPA-μFTIR systems, Scircle et al. recently stated that an alternate technique, laser direct infrared (LDIR) analysis, seems to have a great potential for the quick and automated detection and quantification of MP particles (Scircle et al., 2020). In the aquatic environment and soil (Scircle et al., 2020; Mughini-Gras et al., 2021; Hildebrandt et al., 2020), LDIR has been used to analyse MP particles >20 μm (Scircle et al., 2020; Mughini-Gras et al., 2021; Hildebrandt et al., 2020). (Ng et al., 2021; Li et al., 2021). The light source, a customised quantum cascade laser, is the most innovative feature (QCL). The quantum cascade laser (QCL) is a semiconductor-based laser in which electrons cascade (tunnel) through a succession of quantum wells produced by thin semiconductor layers. The thickness and distribution of semiconductor layers, not the semiconductor materials, influence the wavelength of photons. The LDIR systems have been used to examine particles >20 μm, yet it is believed that in the automated mode, the size limit for studied particles might be reduced to about 10 μm (Hildebrandt et al., 2020). However, it has been noted that for tiny particles (<30 μm), the system may need to automatically refocus in order to get the best spectrum. The per-particle analysis time in this example may be as long as 8 s. The use of this approach for MP analysis of water samples revealed that LDIR detects more particles than the fluorescence-based method (Nile Red staining) (Scircle et al., 2020), albeit a more extensive comparison will be required in the future to confirm this trend. In addition, the performance of LDIR in contrast to FTIR-based approaches has yet to be determined.

(b) *Near-IR Spectroscopy*

Apart from the mid-infrared region (MIR) (4000–400 cm^{-1}) area of fundamental molecular vibrations, which is most often employed for MP identification, quantification, and characterisation, the near-infrared (NIR) region (12800–4000 cm^{-1} or 780–2500 nm) may also be used, despite the fact that NIR spectroscopy was already utilised for decades for online food quality verification and online plastic packaging sorting in recycling (Braun et al., 2020; Moroni et al., 2015). This technique has recently been identified for MP testing in various environmental materials, such as seawater (Karlsson et al., 2016; Shan et al., 2019) and surface water (Schmidt et al., 2018), biota (Zhang et al., 2019), and soil (Paul et al., 2019) has been recognized.

NIR spectra are defined by vast overlapping bands of overtone and combination vibrations for a small number of chemical vibrations, commonly of type X-H, e.g., C-H, O-H, and N-H. For NIR applications, automated statistical approaches from the area of chemometrics, as well as relevant databases, are needed. In comparison to MIR, however, using the NIR area for MP analysis has significant benefits. NIR radiation may penetrate deeper than MIR because higher overtones have lower absorption coefficients than fundamental vibrations, allowing it to handle greater sample volumes and providing fingerprints. Furthermore, the NIR area has a decreased sensitivity to water and pollutants biofilms.

In addition, the ability to use quartz materials for fibres and optical elements in NIR spectroscopy (Paul et al., 2019) leads to a wide range of instrumentation arrangements, ranging from hand-held spectrometers appropriate for in-field investigation (Crocombe, 2018) to laboratory equipment commonly used for hyperspectral imaging, as explained below. The applied equipment and analysed materials have a substantial influence on the spectral range employed, and MP particles have a smaller size limit. The lower spatial resolution of NIR analysis compared to MIR might be explained by the larger sample volume required to provide acceptable signal for weak overtone and combined vibrations. For hyperspectral investigation of MP pollution in seawater filtrates, Karlsson et al. (2016) examined three diverse imaging systems with wavelength ranges of 375–970, 960–1662, and 1000–2500 nm. They discovered that the wavelength range 1000–2500 nm, along with the PCA model technique, is the best suitable for this sort of sample, allowing them to analyse preselected MP particles down to 300 μm. (Karlsson et al., 2016). Schmidt et al. (2018) described a semiautomated approach for detecting MP particles bigger than 450 μms in surface water samples filtered via glass fibre filters. 10 complete filters with a diameter of 47 mm could be scanned in around 20 min (measurement speed, 52048 mm^2 per hour). Counting MP particles, classifying plastic kinds, and estimating particle sizes are all possible using hyperspectral pictures with a pixel size of 280 × 280 μm^2 and a spectral signature consisting of 256 spectral bands within the wavelength range of 968–2498 nm. Schmidt et al. (2018) and Paul et al. (2019) used NIR analysis in conjunction with chemometrics models such as support vector machine regression (SVR) and PLS-DA to achieve high-throughput MP identification in soil. Artificial MP/soil mixes comprising prescribed ratios of PE, PET, PP, and PS < 125 μm were utilised for calibration. Without any chemical pretreatment, accurate detection and categorization of MP at levels exceeding 0.5 to 1.0 wt%, depending on the polymer, has been shown (Paul et al., 2019). Zhang et al. (2019) showed the potential of analysing MP particles in fish digestive tracts quickly and efficiently without using any reagents (reagent-free). For the detection, identification, and characterisation of five kinds of MPs > 200 μm, the scientists used HSI in conjunction with a support vector machine classification model (Zhang et al., 2019). As a result, NIR-based technologies, particularly when combined with HSI and chemometric methods, may be highly effective for detecting MP contamination without the need for sample preparation. NIR-based monitoring might be utilised as a first step in MP prescreening (e.g., using the traffic-light approach) before doing a full study of particles <500 μm for all or just suspect samples using μ-(FT)IR or μ-Raman spectroscopy.

(c) *Raman Spectroscopy*

Raman spectroscopy is a nondestructive analytical approach that is becoming more popular, particularly for the study of tiny microplastics in a variety of environmental materials, including marine and freshwater (Cabernard et al., 2018; Trainic et al., 2020), sediments (Imhof et al., 2016; Enders et al., 2019), biota (Missawi et al., 2020; Collard et al., 2015), compost (El Hayany et al., 2020), and ambient particulate matter (Trainic et al., 2020; Levermore et al., 2020), and also in urban wastewater treatment plant effluent (Wolff et al., 2019) and in drinking (tap and bottled) water, (Weber et al., 2021; Shruti et al., 2020) beverages, and food (Karami et al., 2017). Using handmade and commercial spectrum databases, it is possible to properly identify plastic particles and certain additives and also other (in)organic and (micro)biological chemicals (Enders et al., 2015). Raman spectroscopy can analyse MP particles as well as synthetic and natural fibres (Remy et al., 2015; Wiesheu et al., 2016).

By combining Raman spectroscopy with confocal optical microscopy and using visible excitation lasers, the spatial resolution may be improved to 1 µm and even lower (~300 nm). As a result, Raman spectroscopy is recommended for examining plastic particles with sizes of 10–20 µm (Anger et al., 2018).

Fluorescence intervention caused by inorganic (clay minerals, dust particles) and organic (humic compounds) contaminants in the matrix (Ivleva et al., 2017; Anger et al., 2018), as well as some additives (pigments), is a main drawback of Raman spectroscopy, particularly when analysing MPs in habitat samples (Araujo et al., 2018; Lenz et al., 2015). Before Raman analysis, inorganic and organic nonplastic particles (Enders et al., 2020) must frequently be removed by density separation (Imhof et al., 2012; Coppock et al., 2017) and chemical (Ivleva et al., 2017; Al-Azzawi et al., 2020) or enzymatic (Löder et al., 2017). The removal of the matrix will also result in a large rise in the plastic/nonplastic particle ratio, which will enhance the MP analyses' representativity and statistical certainty. Additionally, agglomeration and overlapping of MP with natural particles may be reduced, resulting in an over- or underestimate of particle number and size (Primpke et al., 2020). To limit or prevent interferences generated by intense fluorescence, it's also crucial to choose the right measurement settings (laser wavelength and power, photo bleaching, and acquisition time, as well as objective magnification and confocal mode). It's critical to choose the right laser wavelength (Anger et al., 2018).

In general, excessively high laser power (e.g., more than 10 mW for 532 nm) should be avoided since it might induce the thermal disintegration of plastic particles and, more often, organic contaminants, as well as the formation of characteristic soot bands in Raman spectra. Additionally, photobleaching before or during Raman measurements (by using longer collection periods) may be highly effective for reducing fluorescence and therefore improving the signal-to-noise ratio. Longer acquisition durations, in particular, may assist in the accurate detection of coloured plastic and paint particles (Anger et al., 2018). The latter include pigments, film formers, curing coating systems, and physically drying systems (acryl and vinyl(co) polymers) that are generated from surface coatings (such as paints) (Hartmann et al., 2019). Because of the comparatively high (pre)resonant Raman signals of pigments (e.g., Cu phthalocyanine), spectra recorded at little acquisition periods (about 1 s) might be misattributed to paint particles, but extending acquisition time can assist to get more Raman signals of polymers. Pigments (in the absence of a strong fluorescence signal) do not generally obstruct the detection of the polymer type of MPs since pigments and polymers usually have crisp signals.

(d) *Nonconventional Raman Techniques*

Nonlinear Raman methods like coherent anti-Stokes Raman scattering (CARS) and stimulated Raman scattering may increase the sensitivity of Raman analysis (SRS). Only the molecular vibrational modes of curiosity give a significant signal in CARS and SRS. Thus, if fluorescing pollutants emit no light in the frequency range of interest, by removing the (in)organic and biological matrix, the fluorescence problem may be completely eliminated.

Cole et al. (2013) were the first to demonstrate the use of CARS for detecting and photographing MPs consumed by zooplankton. The scientists employed Raman bands at 2845 and 3050 cm^{-1} (aliphatic and aromatic C-H str., respectively) to see PS beads (0.4–3.8 μm) in 2D pictures scanned from 2775 to 3100 cm^{-1}. Meanwhile, CARS has been used to visualise 8 μm amino-coated and carboxylated PS beads in shore crab gills (Watts et al., 2016). CARS can therefore do 2D analysis of microscopic microplastics and even nanoplastics down to 80 nm in environmental samples. The CARS application, on the other hand, requires a complicated and costly instrumental setup as well as user skill. Furthermore, CARS may be impacted by an electronic, nonchemically specific background, like those created by solvents, making interpretation difficult (Riberio et al., 2017; Goodhead et al., 2015).

SRS microscopy is the next potential method for imaging MPs at a high speed. SRS microscopy is based on the coherent interaction of two laser beams with vibrational levels of the sample molecules. The SRS signal is created when the photon energy difference between the beams matches a molecule's vibrational state. Normally, the modulation transfer imposed on the other beam is identified by amplitude modulating one of the beams before the sample. The resultant SRS signature at various wavenumbers mimics the target analyte's spontaneous Raman spectrum (Zada et al., 2018). Zada et al. (2018) showed that this method may be used to image MPs from five different polymers, including nylon, PET, PS, PP, and PE. For the examination of particles with a spatial resolution limit of 12 μm, the spectral range from 950 to 1850 cm^{-1} was employed, and 1 cm^{2} of the filter was scanned in less than 5 h (Zada et al., 2018). Laptenok et al. (2020) recently shown the usefulness of SRS for determining natural and manufactured microfibres from environmental samples (i.e., fish gastrointestinal tract, deep-sea and coastal sediments, surface seawater, and drinking water). The majority of the studied ambient fibres are of natural origin, as predicted.

As proven by Liao et al. (2017), a fibre delivered hand-held SRS microscope may provide quick in situ imaging of MP. By temporally splitting the two ultrafast pulses travelling through the fibre and then overlaying them on a sample via a highly dispersive material, a stimulated Raman signal of PS and PMMA beads (both 5 μm in diameter) has been recorded (e.g., paper). The described system, which enables for imaging in the areas 2800–3100 cm^{-1} (CH str. vibrations) and 1550–1800 cm^{-1} with a spatial resolution of 1.4 μm, seems to be extremely promising for chemical investigation of plastic and nonplastic microparticles.

According to Zhang et al. (2017), SRS offers the potential for high-throughput single particle analysis. The newly established 32-channel multiplex stimulated Raman scattering flow cytometry (SRS-FC) technology enables for the chemical analysis of single particles (e.g., 10 μm PS and PMMA beads, and polycaprolactone, PCL) at a rate of 5 s per Raman spectra. At 0.4 m/s flow speed and a throughput of up to 11,000 particles per second, the spectral range from roughly 2800 to 3100 cm^{-1} (CH str. vibrations) was employed to discriminate between distinct particles in suspension.

Thus, SRS-based approaches offer a lot of promise for quick and sensitive MP study, but the complicated arrangement and the essential for a lot of user experience (like to CARS) are still restrictive issues for SRS's widespread application in MP investigations.

(e) *Combination of (FT) IR and Raman Analysis*

The complementary nature of (FT)IR and Raman analysis should not be overlooked. If the absorption of IR radiation results in a change in the dipole moment of the molecule during the vibration process, the molecular vibrations are said to be IR active. If the polarizability of the whole molecule's atomic electron shell changes, the vibrations become Raman active. IR and Raman spectroscopy produce various spectra with regard to vibration activities and intensities for diverse functional groups due to different selection procedures. As a result, further information on polymers and (in)organic additives may be gathered (Käppler et al., 2016; Xu et al., 2019).

Käppler et al. (2016) who analysed habitat materials using both Raman and FTIR spectroscopy offered a rigorous comparison and validation of both spectroscopic approaches with regard to MPs. The authors conclude that both approaches are acceptable for detecting MP particles in the environment in theory. However, in other situations, particularly for coloured particles, a combination of both spectroscopic approaches was required for comprehensive and consistent chemical composition determination. While acrylic resin can be identified better using FTIR spectroscopy and also characterization of particles with a high fluorescence background, μ-Raman spectroscopy can offer comprehensive pigment information. Furthermore, the scientists discovered a substantial underestimating (approximately 35%) of MP by FTIR imaging compared to Raman for particles placed on Si filter substrate (fraction <400 μm), notably in the size range <20 μm. Raman imaging, however, has shown to be much more time-consuming. As a result, the authors recommended size split of samples into two fractions at 50 μm and the use of quick FTIR imaging for particle analysis on filters (MP < 500 μm) (Käppler et al., 2016).

Kumar et al. (2021) recently utilised the suggested size split at 50 μm to the investigation of MP down to a size of 3 μm in economically relevant mussels (Kumar et al., 2021). The number of MP particles per sample discovered using FPA-FTIR imaging in the size fraction >50 m ranged from 0.13 to 2.45/g wet weight (g ww) of mussel samples, with an average of 0.63 ± 0.59 MP particles/g ww. PP (39% ± 6.3%), PET (32% ± 2.8%), PAN (8.2% ± 1.4%), and PE (7.2% ± 0.6%) were the most prevalent synthetic polymer types found. PA (40.2%), PP (16.5%), PE (14.6%), and PAN were the most prevalent synthetic polymer types in the fraction <50 μm, where 211 MP particles were discovered by Raman spectroscopy (13.2%). The findings imply that various polymer types may dominate different size fractions of MP particles, such as PP and PET or PA for particle fractions >50 μm and <50 μm, respectively (Kumar et al., 2021).

Cabernard et al. (2018) evaluated the quantification of MP particles from the aquatic environment deposited on Au-coated PC filters using FPA μ-FTIR (reflection mode) and μ-Raman coupled with automatic particle identification (Cabernard et al., 2018). They discovered that for MPs ≤ 500 μm, μ-Raman analysis quantified two times greater MP counts but took four times as long as FTIR imaging.

Furthermore, compared to the ten polymer types recognised by FTIR imaging, the µ-Raman technique allowed the identification of 19 distinct polymer kinds. Based on these findings, the authors believe that the ambient concentration of MPs ≤ 500 µm has been underestimated up to this point, which they ascribe to the unusual rise in concentration with declining MP size (Cabernard et al., 2018).

The findings show that using a combination of (FT)IR and Raman analysis to analyse MPs may yield complimentary results and allow for accurate size easily resolved chemical analysis. The evaluation of MP-related threats to the environment and human health requires extensive and reliable information on MP contamination. Small MP particles must be identified and quantified with special care, since their quantity is unknown or most likely overestimated, despite the fact that this MP fraction is the most important in terms of ecotoxicity (Cabernard et al., 2018).

Until recently, the only way to identify and measure MP fractions smaller than 10 µm was to use µ-Raman spectroscopy. The development of optical photothermal (O-PT) IR spectroscopy, on the other hand, means that noncontact IR analysis with submicrometre resolution is now possible (Hale et al., 2020). Probes for visible lasers are used to measure the photothermal response of particles that have been absorbed by a pulsed laser in the MIR range (532 nm). Furthermore, the setups allow for simultaneous IR and Raman investigation at the same location and with the same spatial resolution by detecting inelastic light scattering induced by the visible probe laser (Li et al., 2019; Marcott et al., 2020). This offers up new opportunities for future submicrometre-resolution complementary IR and Raman investigation of (plastic) particles (Hale et al., 2020; Marcott et al., 2020).

4.4 Analysis of NPLs

4.4.1 Mass-Based Methods

The knowledge on the existence of NPLs and associated mass in separate size fractions (e.g., <1 µm) can be adequate, depending on the analytical query, for example, for monitoring and modelling. The Py-GC/MS technique is still the most popular (Zhou et al., 2018). The identification of nanoplastics in the North Atlantic Subtropical Gyre (NASG) was originally published by Ter Halle et al. (2017) using Py-GC/MS. A commercial polymer database was integrated with a chemometric approach that used PCA to detect polymers. The presence of PVC, PET, PS, and PE was detected in the colloidal fraction <1.2 µm after filtering, with 70, 17, 9, and 4 percent of their anthropogenic pyrolytic fingerprints, respectively. The relative abundance of PVC and PET NPLs compared to PE, PS, and PP indicates the relative abundance of PVC and PET NPLs likened to PE, PS, and PP (Ter Halle et al., 2017). An analysis of sand water extracts from cost subjected to NASG using Py-GC/MS has revealed the presence of NPLs (PS and PVC) (Davranche et al., 2020). Citing Blancho et al. (2021), finding NPLs in complex environmental matrices remains problematic due to low concentrations of NPLs compared to NOM. The authors identified PP and PS and investigated possible environmental matrices interventions by spiking NPLs in various organic matter suspensions. Two complementary approaches were devised based on plastic composition and NOM concentration. PS NPLs must be handled first, unlike PP NPLs. H_2O_2 and UV light were employed to specifically destroy NOM and not damaging NPLs for this purpose.

Mintenig et al. (2018) devised a method that combines cross-flow ultrafiltration, AF4, and Py-GC/MS to analyse NPLs in aqueous environmental samples. The scientists utilised PS NPLs (50, 100, 200, 500, and 1000 nm in size) as the model particles to spike several drinking and surface water samples and obtained LODs and LOQs ranging from 50 to 250 ng. The LOD and LOQ of 4 mg/L and 410 mg/L were determined using the provided conditions and pyrolyzed quantities of 25 L. When the initial concentration of PS in watery sample was >20 g/L, it was possible to identify it by preconcentrating NPLs using cross-flow ultrafiltration. Wahl et al. (2021) recently established the viability of coupling AF4 to Py-GC/MS for the detection of NPLs in NOM-reach environmental samples, like in soil modified by plastic trash. Prior to chemical analysis, AF4-based size fractionation of aquatic extracts (0.8 m fractions) may be used to avoid the influence of organic matter on NPL detection. For the first time, PP, PS, and PVC NPLs by diameters varying from 20 to 150 nm were discovered in soil using this method. Py-GC/ToF spectrometry can be used to do sensitive examination of distinct NPL particles with a size limit of 100 nm (Sullivan et al., 2020).

Furthermore, based on thermal desorption-proton transfer reaction-mass spectrometry (TD-PTR/MS), a potential approach for highly sensitive detection and quantification of NMPs has recently been described by Materić et al. (2020). PS has an estimated LOD of less than 1 ng, and it could be detected in complex samples down to 10 ng. Following polymer extraction and depolymerization, an alternate method based on HPLC was developed (Castelvetro et al., 2021). The method with LOD and LOQ of 15.3 and 51.1 g/L for PET has been found to be appropriate for the detection and quantification of PET and PA NMPs in complicated samples. As a result, several methods for identifying and (semi)quantifying NPLs in various environmental samples have been developed and tested. Optimisation and validation of detection methods and also efficient preconcentration and enrichment for NPLs will be required to improve analytical dependability.

4.4.2 Nondestructive Spectroscopic Methods

The diffraction limit of light limits the spatial resolution of spectroscopic methods used to study microplastics. This limit is around 10 m for (FT) IR and 300 nm for Raman, which allows for the study of (almost) the entire size range of MPs. Although μ-Raman appears to be suitable for nanoscale particle analysis, recognising particles smaller than 500–1000 μm is problematic. As a consequence, SEM and Raman spectroscopy for high-resolution images and particle identification have been created and employed to examine microscopic MPs and, more recently, NPLs (Sobhani et al., 2020; Sobhani et al., 2020). Sobhani et al. (2020) showed that Raman imaging can observe and identify NPLs down to 100 nm by differentiating the laser spot, pixel size/image resolution, NPL size/position (inside a laser spot), Raman signal strength, and sample preparation. It was used to examine dust samples collected from a driveway after a vehicle's clear polyacrylic finish was hand shined. By hand-polishing an engine hood, the scientists calculated that billions of trillions of NMPs with sizes as small as 200 nm were produced (Sobhani et al., 2020). As a result of their work, the scientists have identified NPLs of sizes between 30 and 600 nm. It is possible to visualise and observe individual nanoplastics by decreasing the mapping pixel size and offsetting the colour to capture just the high-intensity component of the Raman signal generated by the laser point. It was feasible to image particles in the 30–80 nm range, but it was difficult since the Raman signal becomes extremely faint and difficult to separate from noise. Despite this, the SEM-Raman combo has shown to have a great deal of promise. Furthermore, commercially accessible devices provide correlative Raman imaging and SEM, offering up new opportunities for optimising and detailing NPL particle morphology and chemical analyses.

A recent study by Zhang et al. (2019) employed Raman imaging and SEM to directly examine NPL release from commercially recycled plastics. Several challenges must be addressed when combining SEM with Raman, such as particle carbon accumulation and destruction by the electron beam during SEM, particle switching concerns, and the need for vacuum in the SEM chamber (Primpke et al., 2020; Cardell & Guerra, 2016). A comprehensive morphological and chemical analysis of NPLs looks promising for studying small plastic particles.

The use of surface-enhanced Raman scattering (SERS) to overcome the problem of small NPL particles with weak Raman signals has recently been researched (Lv et al., 2020; Zhou et al., 2021; Lê et al., 2021). Colloids or rough surfaces that are near to or connected to nanometre-sized metallic objects (Ag or Au) have stronger Raman emissions. Electromagnetic ("localised surface plasmon resonance, LSPR") and chemical enhancement effects may produce amplification factors of 103–1011. Lv et al. (2020) have recently shown that by utilising Ag colloid as SERS medium, the Raman signal of PS beads with diameters of 100 and 500 nm may be greatly improved (up to 5 × 102 and 4 × 104, respectively). PE and PP MPs did not get as much of a boost as PS NPLs. The authors demonstrated how SERS can be used to identify NPLs in both pure water and saltwater (Lv et al., 2020). Zhou et al. (2021) publised on SERS enrichment for PS beads with a size of 50 nm using Ag colloid and used the approach to analyse model NPLs in river water, virtually simultaneously. Lê et al. (2021) created unique nanostructured Raman substrates for sensitive identification of NPLs in water in this light. They made anisotropic nanostar dimer-embedded nanopore substrates and successfully evaluated the approach for sensitive identification of PS beads with a size of 400 nm, but no substantial improvement was shown for PS NMPs with diameters of 800 nm, 2.3 m, or 4.8 m. (Lê et al., 2021).

(a) *Scanning Probe Microscopy Coupled to Spectroscopy*

While the previously stated vibrational spectroscopic approaches have been demonstrated to be effective in identifying, quantifying, and characterising MP and NPL particles, they can't overcome the diffraction limit of light's spatial resolution (Verma, 2017). Scanning probe technologies for chemical analysis at the nanoscale (Verma, 2017; Dazzi & Prater, 2017; Xiao & Schultz, 2018) shows great potential in NPL research. AFM-IR, nano-FTIR, and tip-enhanced Raman spectroscopy are some of the nanoscale methods used (TERS). It is focused on a sample at the AFM tip and tuned to an absorption band in AFM-IR. The absorbed light causes local photothermal expansion of the material, which the AFM tip detects. AFM cantilever oscillation amplitude monitoring as a function of wavelength produces local absorption spectrum with nanoscale spatial resolution (Dazzi & Prater, 2017; Xiao & Schultz, 2018; Hermann & Gordon, 2018). Felts et al. (2012) used the AFM-IR approach to successfully identify and image polymer nanostructures at the nanometre scale. They used the total internal reflection mode to examine PE and PS nanowires placed on an IR-transparent ZnSe prism, a spatial resolution of almost 100 nm. Pancani et al. (2018) claim that AFM-IR can quickly locate and chemically characterise NPLs inside a cell without any labeling. They studied macrophages treated with PLA NPLs smaller than 200 nm, which are often employed in drug delivery.

Analysing broadband IR absorption spectra of surfaces with spatial resolution of 10–20 nm is possible using nano-FTIR and scattering-type scanning near-field optical microscopy (s-SNOM). The IR beam is attentive on the near-field probe, usually a metal coated tip, in nano-FTIR investigations, and a local antenna effect provides a nanoscaled focus with the tip's dimension. During scanning of the surface with the tip, the near-field interactions between tip and sample alter. An asymmetric Michelson interferometer is then used to monitor the ensuing variations in local scattering intensity. The sample's local IR absorption bands may be connected to the amplitude and phase of scattered light, and the resulting spectra correlate well with bulk FTIR data for a broad variety of materials (Hermann & Gordon, 2018). The nano-FTIR technique has been used to analyse NPLs with success. Brehm et al. (2006) published a paper on the detection of PMMA beads with a diameter of 30–70 nm.

Huth et al. (2012) showed that PMMA samples can be chemically analysed with a spatial precision of 20 nm in this light (Huth et al., 2012). Meyns et al. (2019) examined the suitability of library-based search for the identification of distinct polymers identified by nano-FTIR using commercial and open source analytic software (siMPle). It was discovered that this technology can accurately identify polymer samples that have weathered in the environment without the need for preliminary cleaning, opening up a broad range of applications for the identification and characterisation of various polymer samples.

(b) *Optical Tweezers for Raman Analysis of Nanoplastics*

Raman analysis of NPLs and micro MPs can be done under aqueous settings since water is a feeble Raman scatterer. For this type of research, optical tweezers might be utilised, which retain the particles in the laser beam's focus and allow for spectroscopic identification. Gillibert et al. (2019) demonstrated the utility of a method that combines optical tweezers and µ-Raman spectroscopy for trapping and chemical detection of NMPs. Using 633 and 785 nm excitation lasers, plastic particles dispersed in saltwater (PE, PP, PS, PET, PVC, PMMA, and PA 6) with sizes ranging from 20 m to 50 nm were investigated. The researchers were able to distinguish plastics from organic matter and mineral deposits at the single-particle level, as well as analyse the size and shape of NMPs (beads, pieces, and fibres), with only diffraction limiting spatial resolution. The approach was evaluated on model particles as well as naturally aged environmental samples, demonstrating its ability to characterise real-world samples Gillibert et al. (2019).

Schwaferts et al. (2020) presented online connection of field-flow fractionation and Raman microspectroscopy for the investigation of NPLs using optical tweezers in this area. The authors coupled particle separation and characterisation with chemical identification using online µ-Raman spectroscopy in a flow cell. It was possible to identify particles of various reference materials (polymers and inorganic, specifically PS, PMMA, and SiO_2 at concentrations of 1 mg/L (109 particles/L) using 2D optical tweezers for particle entrapment. The new approach has a wide range of applications in nanomaterial characterisation, including NPL analysis (Schwaferts et al., 2020). It is necessary to create appropriate preconcentration and enrichment of NPLs from environmental and dietary matrices in order to get accurate and representative results. Actual reference materials are necessary for the proper development, optimization, and validation of methods for NPL detection.

4.5 Conclusions and Future Perspectives

Plastic has become the most damaging manmade trash in the environment in recent decades due to its increased production and usage by humans. However, there is a scarcity of data on the prevalence of MPs in various environmental matrices, as well as their impact on human health and the ability to detect them quickly.

There is currently no one-size-fits-all approach of identification and characterisation that can be applied to all of the cases investigated. We have described the most commonly used strategies for detecting and characterising MPs in environmental samples, as well as their benefits and drawbacks, in this study.

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