**REVIEW ARTICLE**

# Analysis of aged microplastics: a review

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## Abstract

Microplastics are emerging contaminants that undergo progressive aging under environmental conditions such as sunlight irradiation, mechanical forces, temperature variations, and the presence of biological organisms. Since aging modifies microplastic properties, such as their own toxicity and the toxicity of trapped pollutants, advanced methods to analyze microplastics are required. Here we review methods to analyze microplastic aging with focus on the aging process, qualitative identification, quantitative characterization, and chemometrics. Qualitative identification is done by mechanical techniques, thermal techniques, e.g., thermal degradation and gas chromatography–mass spectrometry, and spectral techniques, e.g., infrared, Raman, fluorescent, and laser techniques. Quantitative characterization is done by microscopy and mass spectrometry. Microplastic aging results in a series of surface physical changes, biofilm formation, chemical oxidation, thermal alternation, and mechanical deterioration. Changes in mechanical and thermal properties allow to differentiate aged microplastics. Infrared and Raman spectroscopy are rapid and sensitive for chemical identification of microplastics in complex environmental samples. Combining two techniques is preferable for accurate detection and categorization.

**Keywords** Microplastics · Identification · Quantification · Aging · Detection method · Chemometrics

## Abbreviations

| | |
|---|---|
| 3D EEM | Three-dimensional excitation–emission mode |
| ABS | Acrylonitrile–butadiene–styrene copolymer |
| CARS | Coherent anti-Stokes Raman scattering |
| FTIR | Fourier transform infrared |
| HDPE | High-density polyethylene |
| HPLC–MS/MS | High-performance liquid chromatography–tandem mass spectrometry |
| LC-HRMS | Liquid chromatography–high-resolution mass spectrometry |
| LDPE | Low-density polyethylene |
| LIBS | Laser-induced breakdown spectroscopy |
| MALDI-TOF MS | Matrix-assisted laser desorption/ionization time-of-flight mass spectrometry |
| MCR-ALS | Multivariate curve resolution-alternating least squares |
| μFTIR | Micro-Fourier transform infrared spectroscopy |
| PA | Polyamide |
| PBAT | Polybutylene adipate terephthalate |
| PBT | Polybutylene terephthalate |
| PC | Polycarbonate |
| PE | Polyethylene |
| PET | Polyethylene terephthalate |
| PLA | Polylactic acid |
| PMMA | Polymethyl methacrylate |
| PP | Polypropylene |
| PPE | Polyphenylene oxide |
| POM | Polyoxymethylene |
| PS | Polystyrene |

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| PU | Polyurethane |
| PVA | Polyvinyl alcohol |
| PVC | Polyvinyl chloride |
| Pyr-GC/MS | Pyrolysis gas chromatography–mass spectrometry |
| SERS | Surface-enhanced Raman scattering |
| TED-GC/MS | Thermal extraction-desorption gas chromatography–mass spectrometry |
| $TiO_2$ | Titanium dioxide |

## Introduction

Improper plastic waste management affects the ultimate disposal of plastics. The natural weathering process stimulates abundant smaller-size secondary plastics split from commercial plastic products, making microplastics ubiquitous in the environment. There is a rising concern regarding the accumulation of microplastics in different areas worldwide (Drummond et al. 2022; Ding et al. 2023; He et al. 2023; Kim et al. 2023; Sharma et al. 2023; Chen et al. 2023; Osman et al. 2023). The aging process of microplastics initiates gradually upon exposure to the environment, encompassing photo-radiation, thermal radiation, biodegradation, and mechanical fragmentation processes (Liu et al. 2020; MacLeod et al. 2021). The lateral and vertical transport over long distances through wind, atmosphere, overland runoff, ocean currents, and food chain forms an extensive global microplastics cycle. The prevalence of aged microplastics has become a cause for concern, which has become a global plastic toxicity problem (Rillig et al. 2021).

A great deal of previous research about aged microplastics has focused on their characteristic changes after various aging processes simulated in the laboratory (Liu et al. 2019a, 2019c; Chamradová et al. 2021; Wu et al. 2021b; Shan et al. 2022; Shi et al. 2023c). As the issue of microplastics gains more attention, there is an increasing need for research on their qualitative and quantitative characteristics. In response to the need, several studies have been conducted to explore various techniques for the detection and analysis of microplastics, including physical and chemical identification and quantification (Rowenczyk et al. 2020; Zhang et al. 2021b; Huang et al. 2023). Ivleva (2021) deliberated on the applicability and complementarity of diverse mass-based and particle-based methodologies for microplastics. However, a systematic summarization of innovative techniques for identifying and quantifying aged microplastics to evaluate the risk of complicated microplastic mixture has not yet been established.

This review aims to provide an overview of the current state of research on aged microplastics and their detection technologies in environmental matrices in Fig. 1 using spectral-based, thermal-based, and mechanical-based qualitative techniques and microscopy-based and mass spectrometry-based quantitative methods. Furthermore, the review also highlights the advantages and limitations of each detection technique, as well as their potential for investigating aged microplastics. This review article serves as a valuable resource for researchers working in the field of microplastics and provides insights into the current state of research on aged microplastics and the techniques available for their detection and characterization.

## Aging reshapes microplastics

The natural aging process is regarded as the simultaneous complexion of photoaging, thermo-aging, and biological and mechanical aging processes. Laboratory studies often focus on the mechanistic effects induced by individual aging processes due to their manipulability and simplicity. Under different aging conditions, the physical and chemical properties of microplastics change a lot. Firstly, it is obvious that the surface morphology of microplastics undergoes great changes after extraneous contact or autologous peeling as microplastic particle size decreases (Song et al. 2017). Several reports have shown that surface roughness increases with the generation of lots of cracks, fractures, notching, pores, depressions, and protrusions and many small fragments or debris after a period of aging when subjected to ultraviolet light and mechanical abrasion (Song et al. 2017; Shi et al. 2023c). Biofouling on microplastics are those colonized by living organisms, a complex microbial community comprising heterotrophs, autotrophs, predators, and symbionts, which is referred to as the "Plastisphere" (Zettler et al. 2013). The adhesion of microorganisms can increase microplastic surface hydrophilicity, density, and surface roughness during biofilm formation (Nauendorf et al. 2016; Shabbir et al. 2020; Huang et al. 2022; Shan et al. 2022). For example, Pete et al. (2023) explored that microorganisms can form biofilms on the surface of microplastics, and the highly surface-active biosurfactant of *Alcanivorax* can modify the wettability of microplastics, causing the sinking of microplastics. Typical aged plastic–biofilm combinations exhibit unique effects and environmental risks.

After exposure to various stimuli, such as successive illumination (Ren et al. 2021), chemical contacts (Liu et al. 2019a, 2019c; Wu et al. 2020b; Ren et al. 2021), high temperature (Gardette et al. 2013; Karlsson et al. 2018; Ding et al. 2020), and microbial colonization (Tu et al. 2020; Shan et al. 2022), element variation is predominant, especially in the change of oxygen content of the polyolefin plastics. Commonly, the aging process increases the oxygen content and changes the structure of polymer chains during degradation and oxidation. The substantial rise of oxygen-contained functional groups indicates the accumulation of many
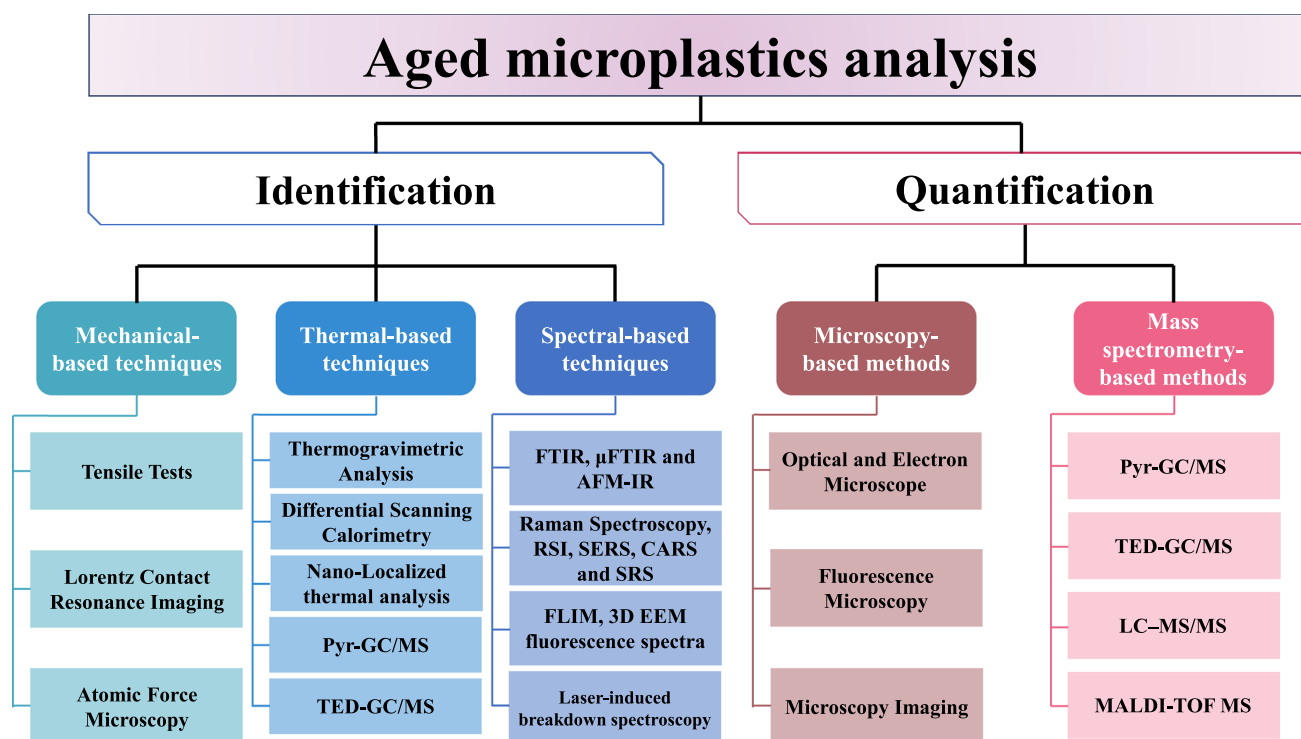
# Aged microplastics analysis

## Identification

### Mechanical-based techniques

- Tensile Tests
- Lorentz Contact Resonance Imaging
- Atomic Force Microscopy

### Thermal-based techniques

- Thermogravimetric Analysis
- Differential Scanning Calorimetry
- Nano-Localized thermal analysis
- Pyr-GC/MS
- TED-GC/MS

### Spectral-based techniques

- FTIR, µFTIR and AFM-IR
- Raman Spectroscopy, RSI, SERS, CARS and SRS
- FLIM, 3D EEM fluorescence spectra
- Laser-induced breakdown spectroscopy

## Quantification

### Microscopy-based methods

- Optical and Electron Microscope
- Fluorescence Microscopy
- Microscopy Imaging

### Mass spectrometry-based methods

- Pyr-GC/MS
- TED-GC/MS
- LC–MS/MS
- MALDI-TOF MS

**Fig. 1** Methods for qualification and quantification of aged microplastics. 3D EEM, three-dimensional excitation–emission-mode; AFM-IR, atomic force microscopy coupled with IR spectroscopy; CARS, coherent anti-Stokes Raman scattering; FLIM, fluorescence lifetime imaging microscopy; FTIR, Fourier transform infrared; HPLC–MS/MS, high-performance liquid chromatography–tandem mass spectrometry; MALDI-TOF MS, matrix-assisted laser desorption/ionization time-of-flight mass spectrometry; MCR-ALS, multivariate curve resolution-alternating least squares; µFTIR, micro-Fourier transform infrared spectroscopy; Pyr-GC/MS, pyrolysis gas chromatography–mass spectrometry; RSI, Raman spectral imaging; SERS, surface-enhanced Raman scattering; SRS, stimulated Raman scattering; TED-GC/MS, thermal extraction-desorption gas chromatography–mass spectrometry

conjugation units with electron-withdrawing substituents such as carbonyl and carboxyl groups (Shi et al. 2023c). The formation of conjugated bonds, enabling electron transition with minimum energy expenditure, results in heightened fluorescence in photoaged microplastics (Wang et al. 2023a). Aged microplastics with different surface structures reveal different environmental fate.

Semi-crystalline and amorphous polymers have different properties, presenting different effects in their aging condition. In general, the degradation rate of amorphous polymer is faster than the crystal one, because of the disorder. The degree of crystallinity is related to the level of long-chain alignment in a macromolecule, influencing the mechanical properties of polymers, such as rigidity (Guo and Wang 2019). Amorphous plastics like polycarbonate (PC), polystyrene (PS), and polyvinyl chloride (PVC) exhibit temperature resistance through their glass transition temperature (Sorolla-Rosario et al. 2022). After aging processes, the decrease of glass transition temperature corresponds with the decline of molecular weight, degradation of long chain, and generation of rotatable single chains, enhancing the internal free space and mobility of molecular segments

(Artham and Doble 2009; Pye et al. 2010; Zhang et al. 2020; Shi et al. 2021). Semi-crystalline plastics like polyethylene (PE), polypropylene (PP), polyethylene terephthalate (PET), and polyamide (PA) were identified by particular melting point temperatures (Sorolla-Rosario et al. 2022). The crystallinity of plastics is calculated using melting enthalpy and increases due to the degradation of amorphous component and the chemi-crystallization through photo- or thermo-oxidation (De La Orden et al. 2015; Guo and Wang 2019; Zhou et al. 2020; Yu et al. 2022). Moreover, the mechanical characteristics of aged microplastics undergo dramatic changes, possibly due to alterations in carbon chain molecules (Yu et al. 2022). The aging process alters the physicochemical properties of microplastics, facilitates the leaching of additives and degradation products, and ultimately poses ecotoxicological risks to humans and the environment.

It is worth noting that aging in an open environment makes it a challenge to be identified and quantified, due to the modified properties and the coating of natural organic matter and pollutants on the surface of microplastics and nanoplastics. Pristine and aged microplastics and nanoplastics can interact with allochthonous natural organic matters,

i.e., cellulose, humic acid, dissolved black carbon, and fulvic acid; and autochthonous natural organic matters, i.e., extracellular polymeric substances secreted from algae, bacteria, and fungi; and anthropogenic natural organic matters, i.e., septic systems, wastewater treatment plants, and agricultural, industrial and stormwater drainage runoff (Ali et al. 2022). These mixtures can form an eco-corona film or aggregation, changing the physicochemical characteristics of microplastics and affecting their bioreactivity, transport, aggregation, and fate in the environment (Ali et al. 2022). Microplastics are potential vectors of persistent organic pollutants and their ability to sorb and concentrate persistent organic pollutants increases after aging (Ricardo et al. 2021). Therefore, digestion protocols and other pretreatment are indispensable to explore microplastics qualitatively and quantitatively in complex environment matrixes.

## Qualitative identification of aged microplastics

Most of the current literature on aged microplastics paid particular attention to their specific properties with distinct changes. However, it is hard to distinguish the aged microplastics from pristine ones through the changes, such as surface morphology, hydrophobic and hydrophilic performance, and molecular weight. Methods are indispensable for identifying different types and different aging degrees of microplastics, according to special properties present in characterization. In this study, we reviewed various mechanical-, thermal-, and spectral-based techniques to explore and identify different kinds of aged microplastics according to their different characteristics.

### Mechanical-based techniques

Mechanical-based techniques cannot give information about the identification of the type of polymers. However, changes in mechanical properties are powerful evidence for the influence of aging, which is also reflected in tensile strength and the brittle/ductile transition. Tensile tests were conducted to reveal the changes in the mechanical properties of microplastics during aging process. Ainali et al. (2021) pointed out that almost all mechanical properties of low-density polyethylene (LDPE), high-density polyethylene (HDPE), polypropylene (PP), and polystyrene (PS), namely tensile strength at yield point and at break point (MPa), as well as elongation at break (%) exhibited a distinct decline utilizing an Instron Dynamometer after a period of ultraviolet exposure with the continuous embrittlement of the samples. Fracture strain (MPa) or elongation at break (%), represents how well a plastic item can maintain its shape without cracking (Zhang et al.

2021a). Plastics with lower fracture elongation values are more prone to break under the influence of external tensile forces. The brittle–ductile transition for various levels of hydrolysis degradation has been tested using a 10-kN capacity Instron machine (Arhant et al. 2019). For the unaged PET sample and aged ones after 1–3 days of hydrolysis, there was a ductile transition followed by necking, showing a ductile failure. The narrow neck-like sections are related to yield deformation. However, after a longer time of aging, stress declined significantly, and sample failed in a brittle manner. The brittle–ductile transition is the condition of microplastic formation. This embrittlement was accompanied by the decline of the maximum stress under different temperatures. Besides the aging process in the laboratory, Yu et al. (2022) found the tensile strength of landfill shopping bags and food bags tested by the universal testing machine were weakened significantly compared to the original ones. However, the relationship between the sample's stress value and landfill age had subtle and irregular changes. The mechanical alteration ultimately caused the formation of cracks and imperfections on the surface of the examined samples (Ainali et al. 2021). Thus, it is more susceptible to the rupture of polymer chains and accumulation of microplastics under prolonged external forces.

Aging process of microplastics can also lead to changes in stiffness and elasticity. The stiffness of the microplastics sample affected the oscillation amplitude of the cantilever in the mechanical spectra, and a higher frequency value correlated with a stiffer sample of microplastics (Luo et al. 2020, 2021b). Lorentz contact resonance imaging measurements were performed in the research of Luo et al. (2020) to quantify the mechanical characteristics of each phase in microplastics. The resonance variations of the two characteristic peaks between pristine and photoaged low-density polyethylene (LDPE) microplastics were significant. Unaged microplastics showed two typical peaks at the resonance frequencies of 299 and 645 kHz, while aged ones showed those of 311 and 670 kHz, respectively. The aging process resulted in a considerably stiffer surface characteristic, as seen by the frequency differences between the two peaks for aged and unaged microplastics (Luo et al. 2020). During the heating process, the burned polypropylene (PP) also experienced physical degradation, resulting in a regionally inhomogeneous surface (Hu et al. 2021). Julienne et al. (2019) utilized atomic force microscopy to study the elastic mechanical properties of the thin film surface and small fragments. The film elastic modulus of unaged low-density polyethylene (LDPE) was determined to be 0.17 GPa (Jee and Lee 2010; Julienne et al. 2019). Surface hardening of the film shown by an increase in elastic modulus is evident in both air and water after 25 weeks of xenon lamp weathering to varying extents. Compared to air aging, the aquatic environment

prevented the enhancement of the surface rigidity, but meanwhile accelerated the crack propagation of polymers (Julienne et al. 2019).

As discussed above, mechanical properties are not competent for the identification of different types of microplastics; nonetheless, it is qualified for distinguishing the aged microplastics from pristine ones. The embrittlement and changes in tensile strength, elongation at break, stiffness, and compressive strength of microplastics resulted from chain scission, molar mass decrease, and chemi-crystallization of polymers. The complicated and sluggish process of environmental weathering makes the deterioration of plastics tricky. However, the changes in the mechanical properties under different conditions make it possible to generate more microplastics and nanoplastics from abundant waste plastics.

## Thermal-based techniques

Thermal analysis is an effective way to determine the properties of polymers that typically do not require any sample pretreatment. Two thermal techniques are commonly used: thermogravimetric analysis and differential scanning calorimetry (Sorolla-Rosario et al. 2022). Additionally, gas products released through sample pyrolysis can be analyzed by mass spectrometry analysis, after passing through a chromatographic column, such as pyrolysis gas chromatography–mass spectrometry (Pyr-GC/MS) or thermal extraction-desorption gas chromatography–mass spectrometry (TED-GC/MS) to identify microplastics.

### Temperature indices

Thermal analysis provides information on particular properties of plastic polymers and has been utilized to identify different types of pristine and aged microplastics with identical decomposition temperature, melting point temperature and glass transition temperature. Thermogravimetric analysis is applied to measure mass changes of polymers during thermal treatment indicating the degradation of the material. Thermogravimetric analysis is an effective method to monitor the decomposition of all types of individual polymers. However, it is challenging to use this approach to identify and measure polymers in multicomponent mixtures since the decomposition temperature of most polymers overlaps, ranging 400–480 °C (Sorolla-Rosario et al. 2022). The only exception is polyvinyl chloride (PVC), which decomposes in two stages and may be easily identified from other microplastics due to a low-temperature breakdown step of 310 °C (Stromberg et al. 1959; Sorolla-Rosario et al. 2022). This phase is caused by the weak C–Cl bond breaking (Wu et al. 2014; Sorolla-Rosario et al. 2022).

Differential scanning calorimetry determines how temperature affects the heat capacity of a material, detecting the alterations in polymer structures, such as phase transitions or melting (Sorolla-Rosario et al. 2022). Semi-crystalline and amorphous polymers have different softness, elasticity, strength, and fatigue resistance, making different sense in their aging behaviors (Guo and Wang 2019). Therefore, different indexes should be applied for identifying polymers with different crystalline states. Sorolla-Rosario et al. (2022) found that it is possible to identify both polyvinyl chloride (PVC) and polystyrene (PS) amorphous polymers accurately by using the glass transition temperature in differential scanning calorimetry. glass transition temperature represents the minimum temperature at which amorphous polymer macromolecular chain segments become mobile. Meanwhile, semi-crystalline polymers such as polyamide (PA), polyethylene terephthalate (PET), polypropylene (PP), high-density polyethylene (HDPE), and low-density polyethylene (LDPE) can be identified by comparing the melting temperature.

Differential scanning calorimetry tests can also provide important messages for distinguishing different aging degrees of microplastics. According to differential scanning calorimetry measurements by Shi et al. (2021), with different aging times, the glass transition temperature of polycarbonate (PC) microplastics dropped from 147.6 °C (0 h) to 126.4 °C (640 h), most likely due to photodegradation, which caused the polymer chain structure to start separating and the side chain proportion to gradually increase (Artham and Doble 2009). More rotatable single chains increased chain flexibility and migration rate, ultimately causing glass transition temperature to be offset to a lower temperature (Claude et al. 2004; Artham and Doble 2009; Jiang et al. 2018). Changes in the molecular weight may also explain the differences in glass transition temperature between pristine and aged polycarbonate (PC) microplastics. Ainali et al. (2021) demonstrated that ultraviolet irradiation affected the melting point temperature of single low-density polyethylene (LDPE), high-density polyethylene (HDPE), and polypropylene (PP), analyzed by a differential scanning calorimetry instrument. The shortening of the average polymer chain length due to the chain scission and the decrease of the average molecular weight resulted in the decline of melting point and the widening of the peak. Interestingly, the polypropylene (PP) melting behavior displayed double endotherm curves as a result of recrystallization or rearrangement during heating. Similarly, as with the exothermic peak, the melting peak of the waste polyethylene (PE) plastic in the landfill decreased when compared to the original samples (Yu et al. 2022). Furthermore, the polyethylene (PE) in landfills for 27 years presented a double shoulder peak in the melting area. Two peaks were also showed in the differential scanning calorimetry thermograms of polypropylene (PP) bread foil after 5 years of natural degradation in a waste landfill (Potrykus et al. 2021). However, the melting point of polypropylene (PP) food bags showed an increasing trend as the

landfill time increased, which corresponds with the crystallinity of polymers. The changes in different polymers agreed to their intrinsic properties. The chain scission and rearrangement of polyethylene (PE) macromolecules made the lower crystallinity, while the vulnerable amorphous region of polypropylene (PP) influences the changes in the crystallinity (Yu et al. 2022).

Nano-localized thermal analysis is one of the most common procedures for determining nanoscale thermal analysis of unaged and aged microplastics. After aging treatment, the average glass transition temperature of low-density polyethylene (LDPE) masterbatch microplastics dropped by 114.6 °C (from $209.5 \pm 11.5$ to $94.9 \pm 4.4$ °C). It was determined that glass transition temperature of the continuous phase of low-density polyethylene (LDPE) was shown to be predominantly lowered after aging process of microplastics (Luo et al. 2020). Luo et al. (2021a) verified that over a longer photocatalytic period, the average softening temperature of artificially titanium dioxide ($TiO_2$)-coated polypropylene (PP) microplastics steadily dropped. And the closer to aged microplastics were to the nano-$TiO_2$ particle, the deeper the surface oxidation on them, which was likely induced by nano-$TiO_2$ photocatalytic degradation of the plastic polymers. The glass transition temperature of low-density polyethylene (LDPE) microplastics also decreased after oxidation treatments except the Fenton system, showing a reduced capacity to withstand high temperatures (Luo et al. 2021b). It is recognized that some factors are partially responsible for the changes in the glass transition temperature. The less flexible carbon chain, lower intermolecular force, or smaller molecular weight of the polymer affected the lower glass transition temperature.

Thermal changes after aging provide significant insight into distinguishing aged microplastics in the environment. Thermogravimetric analysis, differential scanning calorimetry, and nano-localized thermal analysis reveal unique polymer thermal properties. Discovering changes in the thermal properties of polymers after aging is crucial to guarantee the existence of microplastics in complex environments. In addition, for comprehensive insights, thermal techniques should be complemented by other analytical approaches when characterizing aged microplastics in environmental samples, thereby preventing the misidentification of different types.

## Thermal degradation combined with gas chromatography-mass spectrometry

Pyrolysis mechanisms and thermal behavior of different plastic polymers have been extensively studied. Combining pyrolysis techniques with mass analysis, the main products can be considered as thermal degradation markers of structural information about macromolecule plastics. Due to its multiple advantages and prospective employments,

Pyr-GC/MS has received increased attention in microplastic qualitative analysis in recent years (Fischer and Scholz-Böttcher 2017; Okoffo et al. 2022; Rosso et al. 2023). Pyrolytic markers are widely utilized nowadays in microplastic qualification analysis. Pyr-GC/MS demonstrate the primary depolymerization mechanism for low-density polyethylene (LDPE), high-density polyethylene (HDPE), polypropylene (PP), and polystyrene (PS) (Ainali et al. 2021). Besides, it can analyze the effect of photo-irradiation on their decomposition route. Thus, it is also regarded as an indicative technique to determine their oxidation situation (Ainali et al. 2021). The formation of linear ketones, monounsaturated and saturated aldehydes, esters, carboxylic acids, and lactones can be recorded according to different structures with irradiation time increasing (Ainali et al. 2021). Rosso et al. (2023) detected tire wear particles by employing indicators specific to the primary rubbers commonly utilized in tire manufacturing, namely natural rubber, isoprene rubber, butadiene rubber, and styrene–butadiene rubber. It is important to note that certain monomers and dimers of these rubbers could originate from diverse sources, including styrene, 1,3-butadiene, isoprene, 4-vinyl cyclohexene, and limonene (1-methyl-4-(1-methylethenyl)-cyclohexene, also known as dipentene) (Unice et al. 2012; Rauert et al. 2021).

Furthermore, pristine and aged plastics can be recognized by identifying potential chemical markers of polyurethane (PU) foam degradation in remarkable Pyr-GC/MS fingerprints (Lattuati-Derieux et al. 2011). As the aging period progressed, the isocyanate hard component of polyester-based foam altered in chromatographic fingerprints. A dramatic increase was observed in glycol derivatives, which were decomposition products of the polyether polyol soft component caused by artificial light aging. The existence of many breakdown products might be regarded as an indicator of the status of foam deterioration. The Pyr-GC/MS fingerprints of foams naturally aged were very similar to those obtained from the artificially aged polyester-based foam, therefore the presence of the compounds detected can be considered as degradation markers of this type of plastic polymers (Lattuati-Derieux et al. 2011). Li et al. (2023) developed a novel extraction method for Pyr-GC/MS identification of small solid-embedded microplastics and nanoplastics that combined tetramethylammonium hydroxide digestion with dichloromethane dissolution under sonication. Samples from soil, sediment, and sludge contained polyvinyl chloride (PVC), polyethylene (PE), polyethylene terephthalate (PET), polypropylene (PP), and polystyrene (PS) but not polymethyl methacrylate (PMMA), suggesting the widespread presence of small microplastics and nanoplastics in the solid matrix. Therefore, it is necessary to build Pyr-GC–MS databases for pyrolytic products linked with polymers that have undergone environmental weathering processes found in nature even in organisms.

New methods were developed to address potential contamination of a transfer capillary and limited sample masses (more than 0.5 mg) in Pyr-GC/MS (Dümichen et al. 2017; Klöckner et al. 2020; Sorolla-Rosario et al. 2023). TED-GC/MS enable the measurement of complex environmental matrices that are heterogeneous on a small scale (Duemichen et al. 2014). Using the thermal decomposition method, it is possible to analyze a considerable number of samples (up to 100 mg) quickly (in about 2–3 h) (Dümichen et al. 2017). The distinctive thermal breakdown products of significant types of polymers like polyethylene (PE), polypropylene (PP) and polystyrene (PS), polyethylene terephthalate (PET), and polyamide (PA) are identified. At least one distinct and specific decomposition product can be found for each polymer. These markers are then applied to recognize microplastics in actual environmental samples from the aquatic (three different rivers) and the terrestrial (biogas plant) systems (Dümichen et al. 2017). Through conducting TED-GC/MS measurements, a breakthrough was achieved in measuring microplastics from both thermoplastics and tire wear abrasion in real environmental samples from street runoff at the same time (Eisentraut et al. 2018). The drawback was that this study did not account for various factors such as the type of car and tires, the wear rate, the level of elastomers, the additive composition in tires, and the regional variations in vehicle usage. Generally, Pyr-GC/MS and TED-GC/MS represent distinctive methodologies for identifying microplastic polymers through the analysis of their thermal degradation products with high recognition rate.

## Spectral-based techniques

### Infrared and Raman spectroscopy

Table 1 shows that different spectroscopy types have different size limitations, drawbacks, and advantages in the application of aged microplastics qualification. Infrared and Raman spectroscopy, both of which involve radiation interaction with molecular vibrations, can be used to study microplastics and nanoplastics from wastewater (Simon et al. 2018; Van Do et al. 2022; Yang et al. 2023a), drinking water (Koelmans et al. 2019; Jung et al. 2022), freshwater (Koelmans et al. 2019; Campanale et al. 2023; Yang et al. 2023a), marine environment (Abaroa-Pérez et al. 2022; Melo-Agustín et al. 2022; Yang et al. 2023a), soil and sediment (Jia et al. 2022; Jiang et al. 2022), and atmosphere (Chen et al. 2022; Xie et al. 2022).

Fourier transform infrared (FTIR) is widely used to identify microplastic types, tracing back to the first study about microscope plastic debris (Thompson et al. 2004). Micro-FTIR spectroscopy (μFTIR), an FTIR spectrometer connected to an optical microscope, has gained popularity for recognizing and characterizing microplastic particles by library matching (Rowenczyk et al. 2020). FTIR is also an effective way of evaluating the degradation degree by determining the surface chemical compositions at specific wavelengths. Different indicators are used to determine the oxidation level of polymers, including the carbonyl index and hydroxyl index. Carbonyl index is calculated by the intensity of the carbonyl peak (1779–1680 $cm^{-1}$) to that of reference peak such as methylene peak (1490–1420 $cm^{-1}$ (ter Halle et al. 2017; Zhang et al. 2021b) or 2992–2874 $cm^{-1}$ (Liu et al. 2019c; Jiang et al. 2022)), while hydroxyl index refers to the maximum absorbance ratio of hydroxyl groups (3700–3100 $cm^{-1}$) to the reference peak (Yu et al. 2022; Wang et al. 2023b). The carbonyl index and hydroxyl index are proven to be positively correlated with the aging degree (Zhang et al. 2021b; Yu et al. 2023). Carbonyl index is not suitable for the evaluation of non-olefin microplastics due to the presence of oxygen atoms in the pristine polymer structure; nevertheless, it is appropriate for studying the newly generated surface oxygen-containing moieties of polyolefin microplastics perfectly like polyethylene (PE) (Zhang et al. 2021b; Yu et al. 2023), polypropylene (PP) (Wu et al. 2021a, 2021b), polystyrene (PS) (Wang et al. 2021, 2023b; Liu et al. 2022), and polyvinyl chloride (PVC) (Miranda et al. 2021; Wang et al. 2023b).

Although the presence of absorption peaks linked to oxidation in those polymers makes it easier for infrared analysis to identify aging effects in microplastics, those same peaks due to the aging process, the fouling attachment, and applied additives can overlap with specific vibrational modes that reduce the identification efficiency of the plastic (Phan et al. 2022). Particularly, it is referred that polyvinyl chloride (PVC) is sensitive to ultraviolet radiation, causing dechlorination at the first step and generation of conjugated double bonds in the polyene polymer (C=C stretching) and hydrogen chloride (Gewert et al. 2015). Thus, the infrared spectra of aged polyvinyl chloride (PVC) in the environment resemble those of aged PE with the emergence of ketones, carboxylic acids, and carbon double bonds. It is noteworthy that in real environmental conditions, aged microplastics can be misidentified when compared to conventional polymer libraries.

Therefore, it is necessary to set up a customized thorough spectra database including pristine and aged plastic polymers (Filgueiras et al. 2019; Lee and Chae 2021; Fernández-González et al. 2022). Filgueiras et al. (2019) identified three plastic types including aged polystyrene (PS), polyamide (PA), and polymethyl methacrylate (PMMA) in surface sediments along the Spanish Mediterranean continental shelf through PerkinElmer spectra libraries and a customized polymer database. Renner et al. (2017) developed a robust "microplastics identification" method with a success rate of 96.1% to recognize and characterize heavily aged and contaminated microplastics without any cleaning pretreatment.

**Table 1** Principle, advantages, disadvantages, and size range of spectroscopic methods for microplastic identification

| Techniques | Principle | Size | Advantages | Disadvantages | References |
|---|---|---|---|---|---|
| Fourier transform infrared spectroscopy (FTIR, including Micro-FTIR spectroscopy (µFTIR)) | The identification of functional groups within molecules where such groups vibrate (either through stretching or bending in various ways) when irradiated with specific wavelengths of light | Microscale | 1. Can evaluate the degradation degree such as carbonyl index and hydroxyl index 2. Well-developed spectra libraries or custom polymer databases for aged polymers | Misidentification of aged polyvinyl chloride (PVC) and pristine polyethylene (PE) | (Thompson et al. 2004; Renner et al. 2017, 2019; ter Halle et al. 2017; Filgueiras et al. 2019; Chabuka and Kalivas 2020; Chen et al. 2020; Rowenczyk et al. 2020; Cowger et al. 2021; Zhang et al. 2021b; dos Santos et al. 2022; Fernández-González et al. 2022; Jiang et al. 2022; Phan et al. 2022, 2023) |
| Atomic force microscopy coupled with infrared spectroscopy | Based on the thermal expansion of the sample area beneath the AFM tip triggered by the absorption of radiation from a pulsed wavelength-tunable IR laser | Nanoscale | Allows for infrared spectroscopy to be performed at the nanometer spatial resolution scale | Cannot achieve quantification of nanoplastics | (Dazzi 2010; Dazzi and Prater 2017; Chen et al. 2020; dos Santos et al. 2022) |
| Raman spectroscopy | Provides molecular fingerprint spectra based on inelastic scattering of monochromatic laser | Microscale and nanoscale | 1. Raman spectral imaging provides qualitative identification and synchronous characterization 2. Successful detection of nanoplastics using tweezers or random forest algorithm 3. Surface-enhanced Raman scattering improves sensitivity for the detection of particles at low concentration levels | 1. Interferes with additive impurities and biological matrices 2. Cannot differentiate unaged and aged microplastics 3. Not good at identifying polymers with high fluorescence | (Frère et al. 2016; Erni-Cassola et al. 2017; Araujo et al. 2018; Cai et al. 2018; Gillibert et al. 2019; Levermore et al. 2020; Xu et al. 2020; Lê et al. 2021; Yin et al. 2021; Jin et al. 2022; Li et al. 2022a; Phan et al. 2022; Stark 2022; Tian et al. 2022; Vélez-Escamilla and Contreras-Torres 2022; Yang et al. 2022; Dey 2023; Pořízka et al. 2023; Xie et al. 2023a, 2023b) |
| Coherent anti-Stokes Raman scattering (CARS) | A nonlinear optical process where two laser beams interact with molecular vibrations in the sample, generating a coherent anti-Stokes signal at a different frequency | Microscale | 1. No need for any digestion processes 2. Will not disturbed by highly fluorescent substances 3. Rapid detection and identification | Not enough CARS spectral libraries | (Rhee et al. 2024) |
| Stimulated Raman scattering microscopy | The coherent interaction of two different laser beams with vibrational states in the molecules of the sample | Microscale and nanoscale | 1. Provides high-throughput identification at single-particle level 2. chemical specificity by selectively probing molecular vibrations | 1. One-shot stimulated Raman scattering images only display a specific resonance Raman peak 2. The expansion of the plastic library needs further improvement | (Ao et al. 2023; Qian et al. 2024) |

**Table 1** (continued)

| Techniques | Principle | Size | Advantages | Disadvantages | References |
|---|---|---|---|---|---|
| Fluorescence lifetime imaging microscopy | Multispectral autofluorescence signatures and morphology | Microscale and nanoscale | 1. Has potential for lifetime heterogeneity, visualization, and differentiation of unaged and aged microplastics without staining or other pretreatments 2. Can distinguish microplastics in the plastic mixture and sediments with size, shape, spatial distributions, and interactions of microplastics with the environment | 1. Different response for microplastics of different sizes 2. Difficult in distinguishing overlapped phasor clusters | (Monteleone et al. 2021a, 2021b; Zhou et al. 2022) |
| Three-dimensional excitation–emission-mode (3D EEM) fluorescence spectroscopy and confocal laser scanning microscopy | Autofluorescence for aged nanoplastics | Microscale and nanoscale | Fluorescently visualize the movement and migration of nanoplastics in aquatic species without modifying them with exogenous molecules | Cannot identify the nanoplastic types | (Wang et al. 2023a) |
| Laser-induced breakdown spectroscopy | Detecting heteroatoms and intensity ratios of elemental emission lines or molecular bands | Microscale | 1. Can identify polymer types and polymers containing additives and developed biofilm 2. Reveal the oxidation degree through layer-by-layer analysis 3. No need for pretreatment 4. Can combine with FTIR/Raman System | 1. Difficult to differentiate microplastics solely, 2. Need to combine statistical methods with spectral library and chemometric tools | (Anzano et al. 2008; Yu et al. 2014; Pořízka et al. 2018, 2023; Legnaioli et al. 2020; Chamradová et al. 2021; Gajarska et al. 2021; Zeng et al. 2021; Giugliano et al. 2022; Sommer et al. 2022) |
| Hyperspectral imaging | All physical objects emit radiation on different wavelengths in the electromagnetic spectrum due to their chemical composition | Microscale | 1. High-throughput screening 2. Minimum sample preparation 3. Obtain spectral along with spatial information of the sample under analysis | 1. Size detection limit and underestimate black or dark particles 2. Need to combine with the machine learning method | (Primpke et al. 2020; Su et al. 2022) |

The new mode, which can be used when slightly and even heavily aged microplastics correspond with polymer references, adopts a novel chemometric approach based on vibrational band area ratios combining noise and matrix signals, compared to the conventional library searching procedure (Renner et al. 2017). The modification of the "microplastics Identification" method is suitable for microplastic identification by µFTIR and improves the accuracy by up to 98% when identifying real microplastics from a beach sample (Renner et al. 2019). In a recent study, Open Specy (www.openspecy.org) was established as an open-source community that enables the identification of microplastics using an onboard reference library and matching correlation-based criteria (Cowger et al. 2021). To increase the precision of spectral identification for microplastic research, Open Specy contains a variety of spectra from various materials including aged ones (Chabuka and Kalivas 2020). Considering the limitation of the micrometer spatial resolution scale of µFTIR, atomic force microscopy coupled with infrared spectroscopy is a highly effective method for nanoplastic detection and analysis (Dazzi and Prater 2017; Chen et al. 2020; dos Santos et al. 2022).

Raman spectroscopy is a nondestructive technique that provides molecular fingerprint spectra based on inelastic scattering of monochromatic laser (Araujo et al. 2018). It is always regarded as the complementary approach of infrared spectroscopy for microplastic identification because of its higher spatial resolution and submicron or nanometer scale detection even in trace samples (Frère et al. 2016). Raman spectral imaging can identify the molecular species present in the sample and reflect them on the two-dimensional image without any prelabeling of microplastic particles (Levermore et al. 2020). Combined with chemometric analysis and library search, Raman spectral imaging provides the theoretical basis and practical method for qualitative identification and simultaneous characterization of the particle size distribution of microplastics in complex environmental media (Tian et al. 2022). One of the most challenging problems is that micro-sized plastic additives with similar chemical responses are incapable of being distinguished from microplastics by Raman spectroscopy. That's why preprocessing is indispensable (Erni-Cassola et al. 2017; Stark 2022). Li et al. (2022a) applied alcohol pretreatment to prevent the interference of the chemical additives during microplastic release and degradation by facilitating particle separation and individual analysis.

According to the research of Cai et al. (2018), the changes in Raman spectra of microplastics were not distinct after the aging process. Jin et al. (2022) demonstrated that Raman spectrum of microplastics under exposure to various oxidation treatments changed significantly based on the one-dimension score and loading plots of principal components analysis–linear discriminant analysis.

However, the principal components analysis used in Raman technique similarly didn't play a positive role in the classification of unaged and aged microplastics (Pořízka et al. 2023). Thus, the Raman technique is beneficial for distinguishing the polymer types, but it is not useful for assessing the extent of plastic degradation (Araujo et al. 2018; Phan et al. 2022). Moreover, the presence of biological matrices and additive impurities in the plastic products may amplify the drawbacks of Raman spectroscopy, such as weak signal and fluorescence interference (Araujo et al. 2018; Jin et al. 2022; Pořízka et al. 2023). To overcome these shortcomings, novel Raman techniques are developed to enlarge the detecting scale. Raman Tweezers (optical tweezers combined with Raman spectroscopy) were utilized to optically trap and chemically detect sub-20 µm, down to 50 nm range of both model particles in distilled and seawater, and fragmented particles in naturally aged environmental samples (Gillibert et al. 2019). Nanoplastics with various impure materials may be clearly identified chemically using Raman Tweezers, even in the presence of biosurfactant organic overlays. Recently, Xie et al. (2023b) combined Raman spectroscopy with a random forest algorithm to overcome the limitations of low-quality nanoplastic Raman spectra and the interference of complex environmental impurities. The application of a tap water spiked sample achieved over 97% identification accuracy, and the confirmatory experiment demonstrated the successful detection of polystyrene (PS) and polyvinyl chloride (PVC) nanoplastics in rainwater (Xie et al. 2023b).

Surface-enhanced Raman scattering (SERS) is a nanomaterial-enhanced technique derived from Raman spectroscopy that improves sensitivity for the detection of a wide range of particles present at low concentration levels (Vélez-Escamilla and Contreras-Torres 2022; Dey 2023). SERS has been used for many years to identify and target microplastics and nanoplastics in the real environment and everyday consumer products through continuously enhancing the potential of system optimization and resolution improvement. But most of studies focused on SERS detection of targeted polystyrene (PS) nanospheres of standard size to verify the excellent signal intensity (Lê et al. 2021; Yin et al. 2021; Yang et al. 2022). It would be ideal to develop SERS substrates that would respond favorably to a range of plastic materials (Xie et al. 2023a). Xu et al. (2020) accomplished the detection and identification of polyethylene terephthalate (PET) and polystyrene (PS) microplastics and nanoplastics by using SERS with Klarite substrates with sizes down to 450 nm in ambient air. So far, the SERS identification has depended on manual matching or library searching according to specific spectra characteristics of conventional plastics. It is necessary to apply a special machine algorithm to the SERS detection system to expand the environmentally efficient identification to nanoscale and optimize

accurate distinction of additive effects and low-concentration influence.

Coherent anti-Stokes Raman scattering (CARS) is a non-linear optical process where two laser beams interact with molecular vibrations in the sample, generating a coherent anti-Stokes signal at a different frequency. In the CARS spectroscopic mode, the range of observable spectra is specifically constrained to 2800–3200 $cm^{-1}$ within the C–H stretching frequency region, which is attributed to the narrower pump bandwidth (Rhee et al. 2024). Recently, Rhee et al. (2024) illustrated the efficacy of employing broadband CARS micro-spectroscopy for the fast identification of poly-ethylene (PE), polystyrene (PS), polymethyl methacrylate (PMMA), and polyamide 12 (PA 12) within natural soil, eliminating the need for any digestion processes. The C–H bond-specific CARS imaging and spectral analysis not only facilitate a rapid search for microplastic particles but also enable chemical identification, even when disturbed by residual particles and highly fluorescent substances in the soil (Rhee et al. 2024).

As another coherent nonlinear optical techniques, stimulated Raman scattering microscopy introduces an innovative approach to amplify Raman signals (Genchi et al. 2023). This breakthrough enables the attainment of high-speed, three-dimensional imaging with exceptional chemical specificity and sensitivity, effectively overcoming previous limitations in the Raman field (Saar et al. 2010; Ao et al. 2023). Upon conducting density separation of a sediment sample derived from the Rhine estuary, Zada et al. (2018) efficiently surveyed a 1 $cm^2$-area of the filter surface in less than five hours. In this examination, a total of 88 microplastics were successfully identified, including Nylon, polyethylene terephthalate (PET), polystyrene (PS), polypropylene (PP) and polyethylene (PE), indicating a concentration of 12,000 particles per kilogram of dry weight. In atmospheric environmental samples, a range of microplastics and nanoplastics, encompassing polypropylene (PP), polyethylene (PE), polymethyl methacrylate (PMMA), and cellulose plastics, were identified, without the interference from other impurities during the analysis (Ao et al. 2023).

Therefore, infrared and Raman spectroscopy, both based on radiation interaction with molecular vibrations, are used to study microplastics and nanoplastics in various environments. FTIR is commonly used for identifying microplastic types and evaluating degradation degree by analyzing surface chemical compositions. To address the issue of reduced identification efficiency caused by overlapping with specific vibrational modes, it is crucial to establish a comprehensive and customized spectral database containing both pristine and aged plastic polymers. Raman spectroscopy, providing molecular fingerprint spectra, is useful for distinguishing polymer types but not for assessing microplastic degradation extent. CARS and stimulated Raman scattering microscopy offer innovative approaches for rapid and sensitive chemical identification of microplastics in complex environmental samples, overcoming previous limitations in Raman spectroscopy.

## Fluorescent responses

Fluorescence visualization has been widely utilized in the microplastics research. Fluorescently labeled particles using different dyes or fibers utilizing the compound spinning method were especially applied to trace their fate in the organisms (Karakolis et al. 2019; Li et al. 2020; Ma et al. 2021). The artificial exogenous fluorescent additive methods are tricky to control the consistency and have the risk of leaching, making secondary pollution. Nonetheless, microplastics' intrinsic fluorescence can be used to differentiate them from other particles and achieve classification in a complex environment by utilizing their morphology and multispectral autofluorescence fingerprints.

The fluorescence lifetime ($\tau$) made microplastics competent for the identification and characterization using fluorescence lifetime imaging microscopy. Monteleone et al. (2021a) demonstrate that using a laser pulse repetition frequency of 40 MHz, phasor analysis for fluorescence lifetime imaging microscopy was capable of generating specific locations and being color-coded in the phasor plot for the plastics for fast distinction, such as acrylonitrile–butadiene–styrene copolymer (ABS) at 3.019 ns, polyphenylene oxide (PPE) at 6.239 ns, polyethylene terephthalates (PET) bottles from Germany at 2.703 ns, and polyethylene terephthalates (PET) bottles from USA at 2.711 ns of $\tau$ (Monteleone et al. 2021b). The autofluorescence spectra of microplastics were also analyzed using the fluorescence lifetime imaging microscopy with a femtosecond pulsed laser to excite continuous excitation lines to determine the detection range of microplastics (Zhou et al. 2022). Phasor analysis for fluorescence lifetime imaging microscopy is a nondestructive approach that has the potential for lifetime heterogeneity, visualization, and differentiation of microplastics and aged ones. Zhou et al. (2022) established that microplastics "phasor fingerprint libraries" relying on multiple phasor fingerprints shown by specific phasor clusters in each phasor image, contained phasor cluster positions and quick fluorescence lifetime information. The results revealed obvious spatial distances of different kinds of microplastics in the "phasor fingerprint database", which makes it simple and intuitive to differentiate them even in the plastic mixtures and sediments (Zhou et al. 2022). The advantage of utilizing autofluorescence phasor mapping is that it may also provide size and shape information, the spatial distributions of microplastics, and their interactions with the environment. Although integration of thermally treated plastics appears to make plastic separation more challenging, the majority of the tested

polymers with the heat treatment are located in the right half of the phasor plot representing shorter fluorescence lifetimes (Monteleone et al. 2021a).

Recently, Wang et al. (2023a) demonstrated that artificial and naturally photoaged nanoplastics have the potential to function as fluorescent tracers without the need for external fluorescent materials, through the further results of confocal laser scanning microscopy and three-dimensional excitation–emission-mode fluorescence spectra. It showed newly generated fluorescence and optical absorption centers in aged nanoplastic polymers in three-dimensional excitation–emission-mode fluorescence spectra after ultraviolet and sunlight irradiation, with aged polyvinyl chloride (PVC) and polystyrene (PS) nanoplastics exhibiting stronger fluorescence than polypropylene (PP) and polyethylene (PE) nanoplastics. Without modifying with exogenous molecules, fluorescent nanoplastics may be produced after artificial or natural sun irradiation and are useful for fluorescently visualizing the mobility and migration of nanoplastics in aquatic species.

## Laser-based techniques

Laser-induced breakdown spectroscopy (LIBS) is a novel elemental analysis technique with the advantage of high analytical speed in various industries including plastic-recycling factories (Yu et al. 2014; Legnaioli et al. 2020; Zeng et al. 2021). The identification of polymer types is always connected to the detection of heteroatoms and intensity ratios of elemental emission lines or molecular bands. The $C_2$ Swan system (516.0 nm), the carbon–nitrogen (C–N) band (388.0 nm), carbon (247.9 nm), hydrogen Balmer alpha line (656.3 nm), oxygen (777.2 nm), and nitrogen (746.8 nm) were the prominent emission lines (Anzano et al. 2008). Through determining the major elemental ratios in polymers, the most crucial one for identifying the plastics was H/C ratio, followed by the $C_2/C_1$ ratio which relates the number of carbon–carbon bonds and carbon atoms. However, considering most polymers have similar elemental compositions, their LIBS spectra are highly comparable, making it difficult to differentiate, particularly for the polyolefins (Anzano et al. 2008; Zeng et al. 2021). Nonetheless, there are minor changes in signal intensities resulting from distinct stoichiometric ratios of polymeric molecules. Therefore, statistical methods with spectral library and chemometric tools have been carried out to give more information from obtained spectra and to enhance the discrimination ability.

The principal components analysis has been regarded as the most prevalent and effective machine learning approach that is suitable for analyzing LIBS spectroscopic data over the past decade (Pořízka et al. 2018). Chamradová et al. (2021) succeeded in the separation of aliphatic and aromatic polymers representing different polymer structures with or

without heterogeneous atoms, i.e., polypropylene (PP), polyamide 66 (PA 66), polyoxymethylene (POM), polystyrene (PS), and acrylonitrile–butadiene–styrene copolymer (ABS), with the greatest polymer ablation effect under air and argon atmospheres through LIBS and principal components analysis. It also demonstrated the possibility for the identification of 20 different virgin polymer types and polymers containing additives using LIBS combined with k-nearest neighbors, principal components analysis, and hierarchical cluster analysis multivariate analysis, providing technical support for the recognition of real-life samples (Gajarska et al. 2021).

To explore the potential application of LIBS in aged plastics, Sommer et al. (2022) examined the oxidation degree of PS based on the oxygen emission line at 777.3 nm. As the oxidation time increased, oxygen absorption peaks formed and increased. Meanwhile, depth profile analysis was carried out to evaluate the penetration depth of the oxidation layer and to collect information about the stratification of structure inside the polymer matrix. Interestingly, it was found that weathered samples showed the oxidation penetration depth of up to $58.0 \pm 6.4$ μm (Sommer et al. 2022). The LIBS technique with principal components statistical analyses showed the function of quick polymer identification from a large sample of different kinds of plastics in a marine environment (Giugliano et al. 2022). LIBS has also proved as a reliable method for the identification and characterization of aged microplastics with developed biofilm without any pretreatment (Pořízka et al. 2023). Principal components analysis was utilized to illustrate the capacity of LIBS to distinguish with several microplastic types by matching wavelengths with relevant information about the sample, including polyamide (PA), polyethylene (PE), polyethylene terephthalate (PET), polypropylene (PP), and polyvinyl chloride (PVC). In the score plot, it is possible to discriminate between unaged and aged microplastics in freshwater and wastewater. The current findings reveal that it is feasible to identify and characterize aged microplastics coated by biofilms utilizing enhanced laser-based methods regardless of the aging time and primary biotic components of the biofilm layer (Pořízka et al. 2023). As a result, these advanced approaches have the potential to significantly supplement traditional analytical methods and provide novel insights into changes in the molecular composition and characteristics of aged microplastics.

Layer-by-layer analysis of LIBS does not require any sample pretreatment with no limitation of water existence compared to FTIR analysis, despite the minor damaging property due to laser ablation (Sommer et al. 2022). Therefore, both can be regarded as complementary spectral techniques that can determine and verify the characteristics of plastic samples. Near-infrared spectroscopy is proven to have problems identifying opaque plastics, especially black plastics (Zeng et al. 2021). Given this, LIBS is capable to

identify and quantify black plastics after the initial screening using near-infrared spectroscopy (Liang et al. 2017; Zeng et al. 2021). Raman spectroscopy can provide a particular molecular "fingerprint" but is not good at identifying polymers with high fluorescence or scattering due to the presence of additives like organic and inorganic dyes and fillers. In addition, a hybrid pulsed laser-based LIBS-Raman system is constructed to obtain a comprehensive description of elemental, structural and molecular information, proving that the two methods complement each other perfectly (Shameem et al. 2017; Zeng et al. 2021). Therefore, a combined system exploiting the complementarity of two spectral-based technologies is more beneficial than a system based on one or the other alone for a comprehensive detection and categorization of various types of plastics.

## Quantitative characterization of aged microplastics

Laboratory aging experiments provide a test basis for the quantitative study of aging plastics in environmental samples, while it is difficult to distinguish the aging degree of microplastics when counting the amount. Therefore, in this study, we reviewed some novel techniques to calculate the overall number of microplastics in laboratory and environmental samples, including optical and electron microscopes, microscope spectrometers and mass spectrometry-based methods (Table 2). The size detection scope was compared except for mass spectrometry-based techniques, which are regardless of microplastics size and shape (Fig. 2). These techniques provide ways of visual and mass aspects to quantify unaged and aged microplastics. The most regularly used units in water samples are microplastics per cubic meter (Primpke et al. 2020) and microplastics per liter (Rosso et al. 2023; Yang et al. 2023b) according to the abundance per water volume as well as gram items per liter (Rosso et al. 2023) according to mass per water volume. A significant number of studies were reported to use units such as microplastics per kg dry weight in sediment samples (Thompson et al. 2004; Filgueiras et al. 2019; Lin et al. 2021) and microplastics per cubic meter in airborne samples (Liu et al. 2019b; Levermore et al. 2020; O'Brien et al. 2023).

### Microscopy-based methods

### Optical and electron microscopy

An optical microscope is commonly used to visually count microplastics (Hanvey et al. 2017). Shi et al. (2023c) quantified fiber numbers on the gridded filtration membrane, then manually scaled up based on the sample volume acquired before filtering to calculate the overall amount of microplastic fibers. However, visual counting just considers the restricted view field and measurement frame. The number of microplastics could be drastically overestimated or underestimated due to the neglect of the nanosize range of plastics in the environment samples and the possibility of treating non-plastic particles as plastics without identification.

The optical particle shape and size analyzer combines a unique integrated vacuum dispenser with an ultra-high-resolution optical bench, which empowers it to measure particle size, shape, and concentration. Because microplastic fibers have a special shape (length-to-width ratio larger than 3), the analyzer can differentiate them from microplastic particles (Shi et al. 2023a). This method has a sufficient dispersion, high representativeness of test results, quick analysis speed, and broad applicability of particles with different shapes, which helps it overcome the shortcomings of existing image analyzers. But simultaneous identification is also indispensable for multiple particle analysis.

Scanning electron microscope is the most widely used method to evaluate the length and size of microplastics and is also applied in the quantification procedure. Instead of accounting for the entire filter, previous research estimated an approximate count of microplastics by randomly selecting a portion of the membrane filter area, which caused a miscount of the sum of microplastics. De Falco et al. (2018) created a novel counting method by taking 21 electron micrographs along the two orthogonal diameters of the circular filter. The number of microplastics on the entire filter membrane surface is calculated according to the average number of microplastics per unit area, the rectangular area of each micrograph and the total area of the filter. Since the procedure is general, accuracy cannot be guaranteed due to biased estimations and human errors. A fast-random forests algorithm is used to identify the inhomogeneous load of filtered microplastics (Liu et al. 2024). The unique microplastic aggregation forms highly varied patches on filtered substrates, which is governed by interfacial apportionment and redistribution of microdroplets due to surface tension changes. The aggregation mode can be influenced by the weathering state and ambient substances. Pattern-resolved calibration is suggested for traditional region-of-interest quantitative microplastic analyses, unless using microfluidic investigation (Liu et al. 2024).

Fluorescence microscope is an alternative to scanning electron microscope and a normal optical microscope. Staining dyes are well-established in the identification of microplastics because they make it easier to separate microplastics from mineral and organic ingredients in samples by adding color or fluorescence agents. Compared to other dyes like Basic Blue 24, Crystal Violet, and Acridine Orange, Nile Red has a stronger affinity for many synthetic polymers, although some textile fibers also present weak even with no

**Table 2** Comparison of quantitative techniques to characterize aged microplastics

| | Techniques | Size | Limit of quantification | Advantages | Disadvantages | References |
|---|---|---|---|---|---|---|
| Optical and electron microscope | Optical microscope | – | – | Convenient | Limited view field, measurement frame, and misidentification | (Hanvey et al. 2017; Shi et al. 2023c) |
| | Optical particle shape and size analyzer | 800 nm | – | 1. Can measure particle size, shape, and concentration<br>2. Can distinguish microplastic fibers and microplastic particles | Unable to identify the types and aging degrees | (Tse et al. 2022; Shi et al. 2023c) |
| | Scanning electron microscope (SEM) | 800 nm | – | Can evaluate the length and size of microplastics | Limited view field, measurement frame, and misidentification | (De Falco et al. 2018) |
| | Fluorescence microscope | 10 μm | – | 1. Can distinguish plastics using staining dyes<br>2. Automated quantification | 1. Chemical digestion may be necessary<br>2. Difficult to identify the types and aging degree of microplastics | (Prata et al. 2019; Leonard et al. 2022; Liu et al. 2023a; Zhang et al. 2023a, 2023b) |
| | Sensitive fluorescence video microscopy | 45 nm | – | 1. Can determine the size of individual plastic particles and concentrations simultaneously<br>2. Directly applicable to contaminated water samples | Not provide information on the chemical nature of the particles | (Molenaar et al. 2021) |
| Microscope spectrometers | Micro-FTIR spectroscopy (μFTIR) | 5 μm | – | Simultaneous identification and quantification | Pretreatment is indispensable | (Rosso et al. 2023; Yang et al. 2023a, 2023b) |
| | Raman spectral imaging | 100 nm | – | 1. Simultaneous identification and quantification<br>2. A higher spectral coverage with a highly specific fingerprint spectrum and less interference from water than FTIR<br>3. Have a better lateral resolution | 1. Pretreatment is indispensable<br>2. Time-consuming | (Araujo et al. 2018; Cabernard et al. 2018; Schymanski et al. 2018; Sobhani et al. 2019, 2020) |
| | Stimulated Raman scattering microscopy | 100 nm | – | 1. Enables high label-free 3D imaging speed<br>2. Provides high throughput at single-particle level | 1. One-shot stimulated Raman scattering images only display a specific resonance Raman peak<br>2. The expansion of the plastic library needs further improvement | (Ao et al. 2023; Qian et al. 2024) |

**Table 2** (continued)

| Techniques | | Size | Limit of quantification | Advantages | Disadvantages | References |
|---|---|---|---|---|---|---|
| Advanced microscope techniques | Tunable external cavity quantum cascade laser microscope | – | – | 1. Higher sensitivity and accuracy toward small-scale microplastics 2. Timesaving | – | (Primpke et al. 2020) |
| | Optical-photothermal infrared micro-spectroscopy | 600 nm | – | Identification and quantification of microplastics and nanoplastics | Potential interference of decomposed products | (Su et al. 2022) |
| Mass spectrometry-based methods | Pyrolysis gas chromatography–mass spectrometry (Pyr-GC/MS) | – | pg level | 1. Absence of sample preparation processes 2. Quantify microplastics and nanoplastics in real environments | Destructive | (Velimirovic et al. 2021; Xu et al. 2022, 2023; Gregoris et al. 2023; Hernandez et al. 2023; Li et al. 2023; Lou et al. 2023; Okoffo et al. 2023; Sheng et al. 2023) |
| | Thermoextraction and desorption coupled with gas chromatography–mass spectroscopy (TED-GC/MS) | – | µg level | 1. Assess larger sample quantities within one measurement than Pyr-GC/MS 2. Complex matrix components have little effect on lower limit of detection values of non-biodegradable microplastics | The interactions of complex chemicals could increase the limit of detection value of biodegradable polymers | (Dümichen et al. 2017; Kittner et al. 2023) |
| | High-performance liquid chromatography–tandem mass spectrometry (HPLC-MS/MS) | – | pg level | High sensitivity and robustness, low limit of detection and limit of quantification | Need to optimize using appropriate ionization sources and columns | (Wang et al. 2017; Zhang et al. 2019a, 2019b; Peng et al. 2020; Di Renzo et al. 2021) |
| | Matrix-assisted laser desorption/ionization time-of-flight mass spectrometry (MALDI-TOF MS) | – | ng level | Can effectively and accurately analyze fresh and aged microplastics and nanoplastics | Have different responses depending on the nature of the polymer, lower sensitivity | (Schirinzi et al. 2019) |
| | Ambient ionization approaches such as desorption electrospray ionization and direct analysis real-time | – | – | Rapid identification and quantification of microplastics | Not suitable for the ionization of molecules with MW higher than 1500–2000 Da and non-polar polymers such as PS | (Schirinzi et al. 2019) |
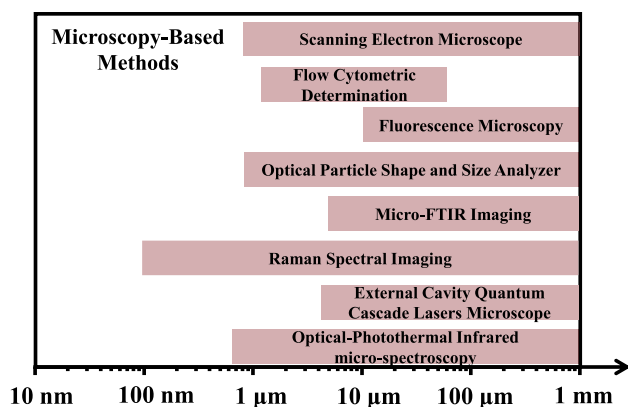
**Fig. 2** Size range of methods for microplastic detection

fluorescence (Prata et al. 2019). The most common application is Nile Red fluorescence tagging, combined with fluorescence microscopy, based on morphology assessment and quantification based on ImageJ and statistical analysis (Kukkola et al. 2023). Automated quantification has advanced gradually in recent years to enhance sample throughput and remove the operator-dependent subjective variance. Prata et al. (2019) applied Nile Red with the automated software "Microplastics Visual Analysis Tool" for the quantification of fluorescent microplastics. Different kind of plastics has different fluorescent responses under different wavelength. As the effectiveness of dying changes due to the polarity of the different polymer surfaces, it also makes a difference on aged plastics. For example, fluorescence can be observed in weathered high-density polyethylene (HDPE), polypropylene (PP), expandable polystyrene and cellulose acetate stained with Nile Red at 254 nm but not both fragmentary and fibrous weathered polyethylene (PE). It is suggested that chemical digestion may be necessary to eliminate organic matter in complicated matrices when applying the "Microplastics Visual Analysis Tool" on real river water and sediment samples (Prata et al. 2019).

Recently, advanced fluorescence tracking techniques have been developed. For example, Zhang et al. (2023b) constructed the microchannel, a polymethyl methacrylate (PMMA)-based microfluidic device, to facilitate the dispersion and transportation of Nile Red-stained microplastic particles in the carrier fluid. The entire process of microplastics moving through the microchannel was captured and recorded on a fluorescence microscope. Finally, the microplastic particles were automatically counted and measured by the software using the camera data. A video containing 253 frames was created by pumping 700 µL of a polyvinyl alcohol (PVA) solution containing suspended microplastics via the microchannel. 221 microplastic particles were found and examined. It offers a way to realize high throughput and precision in particle counting and size

determination, and minimal time cost without requiring the use of highly sophisticated instruments and chemical reagents (Zhang et al. 2023b). The method was employed successfully in the sample detection from river water, sediments, and fish gastrointestinal tract (Zhang et al. 2023a). Another opti-mechanical attachment on a smartphone-based fluorescence microscope is employed to measure the strained microplastics as small as 10 µm (Leonard et al. 2022). The algorithm-based smartphone quantification eliminates the need for laborious digestion procedures and tedious manual counting, allowing for the quick assessment of microplastic concentration in environmental samples. High-content screening combines high-resolution imaging, high-throughput detection, and automated quantification of microplastics (20–1000 µm) in small-volume liquid samples to test the released particles from contact lenses (Liu et al. 2023a). Molenaar et al. (2021) demonstrated that it was possible to measure particle diameters as small as 45 nm and estimated the number concentrations as 2000 nanoplastics per liter using sensitive fluorescence video microscopy, combined with Nile Red staining and single-particle tracking. Although recent studies have developed novel microscope techniques to automatically count microplastics with high accuracy and efficiency even in complicated environmental samples, the identification of types and aging status of microplastics requires the complement of other subsequent investigative methods.

## Microscope spectrometers

FTIR spectroscopy and Raman spectroscopy coupled with imaging analysis also called µ-FTIR imaging and µ-Raman imaging have gained extensive popularity in the characterization of microplastics (Cabernard et al. 2018). This method provides microscopic counting and chemical structural analysis thereby realizing simultaneous identification and quantification. Pretreatment including digestion is indispensable to remove contaminants on the microplastic surface. Rosso et al. (2023) quantified tire wear particles in stormwater runoff via microscopic counts using µ-FTIR after ruling out fragments identified as cadmium, zinc, and barium sulfide blend, with the highest abundance of $358,915 \pm 831$ particles per liter or $40 \pm 9$ mg particles per liter. Similarly, µ-FTIR is developed for the identification and quantification of microplastics in different water samples (such as sea, fresh, and wastewater) with the highest quantity of 4203–42,000 microplastics per liter in wastewater, followed by 153–19,836 microplastics per liter in surface water or groundwater and nearly 420 microplastics per liter in seawater (Yang et al. 2023a, 2023b). According to Rosso et al. (2023), µ-FTIR is a popular technique for visualizing various microplastics with a limit of detection size down to 5 µm.

Raman spectral imaging offers less interference from water and a more distinct fingerprint spectrum with a larger spectral coverage than FTIR, in addition to having a better lateral resolution down to 1 μm even 100 nm (Sobhani et al. 2019, 2020). After microplastics identification through agglomerative hierarchical cluster analysis, Gaussian curve function, and Pearson's correlation coefficient analysis, Raman spectral imaging automatically detected the total concentration of airborne microplastics larger than 4.7 μm up to 2502 microplastics per cubic meter in 24 h $PM_{10}$ urban road-side sample in London, United Kingdom (Levermore et al. 2020). Although Raman spectral imaging enables the detection of smaller microplastics and even nanoplastics because of the smaller diameter of the laser beam, it is more time-consuming compared to μ-FTIR, even using image analysis software to identify and count particles automatically (Araujo et al. 2018). It takes 147 h per 100 L water volume to investigate microplastic particles of 1–10 μm using automated single-particle exploration coupled to μ-Raman (Cabernard et al. 2018). Schymanski et al. (2018) applied Single Particle Explorer to count and analyze microplastics released from returnable plastic bottles, and took up to 18 h just scan one filter with an area of 4.4 mm × 4.4 mm. Therefore, it is necessary to optimize spectroscopic techniques to accelerate the scanning speed for small-sized microplastics and improve identification accuracy.

## Advanced microscopic techniques

More advanced methods are developed to analyze microplastics. The hyperspectral imaging principle states that every physical item emits radiation at various electromagnetic spectrum wavelengths because of their chemical composition (Huang et al. 2021). By capturing an image across a range of wavelengths, hyperspectral imaging integrates spectroscopy with imaging. Each pixel in the image represents a spectral profile that corresponds to a specific spatial region (Huang et al. 2021). Primpke et al. (2020) proposed hyperspectral imaging combined with high brilliance infrared sources based on broadly tunable external cavity quantum cascade lasers microscope for rapid identification and quantification. The novel method displays a higher sensitivity and accuracy toward small-scale microplastics than μ-FTIR, resulting in five times more microplastics being identified and counted in the treated wastewater, deep-sea sediments, and snow samples. It also saves considerable time, over 10 times shorter compared with μ-FTIR (Primpke et al. 2020). Recently, Su et al. (2022) initiatively used optical-photothermal infrared micro-spectroscopy to trace the formation of microplastics and nanoplastics released from the steamed teats and realized to quantitatively estimate both the intake of elastomer-derived particles during bottle-feeding and the emission of those particles during the steam-disinfecting process to the environment. Optical-photothermal infrared has the potential to analyze the submicron-sized environmental microplastics (0.5–5.0 μm) mixed with a significant amount of biological matrix. It is essential to develop automated analysis to maximize the benefit of the instrument which is not affected by fluorescence (Dong et al. 2022).

Laser direct infrared spectroscopy has been recently applied to qualitatively and quantitatively analyze microplastics in bottled drinking water (Nizamali et al. 2023), air deposition samples (Nizamali et al. 2023), Mediterranean marine samples (including seawater, sediment, fish stomachs and mussels) (Ourgaud et al. 2022), beach and stormwater drain sediments (Ghanadi et al. 2023), bronchoalveolar lavage fluid (Qiu et al. 2023), human testis and semen (Zhao et al. 2023), placenta (Zhu et al. 2023) and endometrium samples (Sun et al. 2024). The simplicity and automation of laser direct infrared spectroscopy imaging make it possible to get the number and mass concentration, polymer type, and size (e.g., length, width, area, and volume) of microplastics effectively and simultaneously (Nizamali et al. 2023).

Stimulated Raman scattering microscopy has potential for detecting and three-dimension imaging of microplastics and nanoplastics at single-particle level (Ao et al. 2023). The notably increased imaging speed of stimulated Raman scattering microscopy results in efficient particle imaging with a high throughput, even detecting nanoplastics below 100 nm. A data-driven spectral matching algorithm was utilized to assist stimulated Raman scattering microscopy to estimate $240,000 \pm 130,000$ particles per liter of bottled water with nanoplastics accounting for 90% (Qian et al. 2024). This data-driven hyperspectral stimulated Raman scattering imaging platform inspires further study on single-particle imaging with nanoplastics sensitivity and plastic specificity in the environment.

In general, advanced infrared and Raman spectroscopy coupled with imaging techniques played a powerful role in developing microplastic quantification methods. Automated analysis enables enhanced efficiency, rapid processing, and advanced recognition capabilities of diverse microplastics and even nanoplastics. The subsequent enrichment of the spectra library is the goal of technological development.

## Mass spectrometry-based methods

While microscopy-based methods focus more on the number of microplastics, it is simpler to evaluate the properties of tiny plastic particles through mass-based concentrations. Thermal-based mass spectrometry applied for the quantification of different kinds of microplastics is based on characteristic pyrolysis products of polymers and their suggestive fragment ions. Different kinds of liquid chromatography–mass spectrometry rely on the distribution of ions based on their mass-to-charge ratios, providing information

about the molecular weights of the depolymerized microplastic components. These methods present high throughput, precise selectivity, exceptional sensitivity, and quantitative accuracy of microplastic analysis.

Pyr-GC/MS is paid particularly popular attention both on microplastic identification and quantification although it is destructive (Okoffo et al. 2023). The key benefits of Pyr-GC/MS include the absence of sample preparation processes, extremely low limit of detection and limit of quantification (down to ng level), and the use of a completely automated system (Velimirovic et al. 2021). The pyrograms of different polymers differ primarily in terms of respective products, signal intensity, and the associated numbers. A calibration curve is necessary to perform a correct quantification in environmental samples. The pyrolytic mechanism is distinctive regarding random chain scission, end chain scission, chain stripping, and cross-linking. The thermochemolytic pyrolysis with tetramethylammonium hydroxide plays a positive role in simultaneously detecting non-polyolefin plastics on a trace level such as polyethylene terephthalate (PET), polybutylene terephthalate (PBT), polycarbonate (PC), polymethyl methacrylate (PMMA), and polyamide 6 (PA 6), changing and enhancing the signals through the process of online esterification, transesterification, and methylation (Fischer and Scholz-Böttcher 2017).

Quantification studies have been performed to analyze microplastics in various real environmental matrices, including drinking water, sediment, wastewater, atmospheric aerosol, and table salts (Fischer and Scholz-Böttcher 2019; Gomiero et al. 2019; Kirstein et al. 2021; Li et al. 2022b; Roscher et al. 2022; Gregoris et al. 2023; Hernandez et al. 2023; Okoffo et al. 2023). Li et al. (2023) determined a total mass concentration of solid-embedded microplastics at levels of 4.6–51.4 µg per gram in six soil, sediment, and sludge samples through Pyr-GC/MS after a series of extraction procedures, even successfully quantified different microplastics in the environmental solid samples with high natural organic matter contents. Furthermore, it was discovered that based on the result from Pyr-GC/MS, the content of microplastics was correlated with that of the plastic waste and the landfill age with 7.62 kg microplastics per ton mineralized refuse in the old landfill area and 5.49 kg per ton mineralized refuse in the young one, illustrating the generation of secondary microplastics (Lou et al. 2023). An innovative approach was established for the precise quantification of polyethylene (PE) microplastics in exact atmospheric PM$_{2.5}$ utilizing Pyr-GC/MS, and notably, it does not necessitate sample pretreatment (Luo et al. 2023). The method demonstrated satisfactory recoveries (97–110%), exceptional sensitivity (limit of detection of 1 pg), and reliable precisions (relative standard deviation of 3–13%). Polylactic acid (PLA) and polybutylene adipate terephthalate (PBAT) were identified in samples of wastewater, biosolids, and sediment

using Pyr-GC/MS, with concentrations ranging from 0.07 to 0.18 mg per gram (Okoffo et al. 2022).

Recently, the quantification of nanoplastics through Pyr-GC/MS has achieved an impressive breakthrough (Xu et al. 2023; Okoffo and Thomas 2024). Pyr-GC MS detected 0.283–0.793 µg nanoplastics per liter in surface water and 0.021–0.203 µg per liter in groundwater including polyvinyl chloride (PVC), polymethyl methacrylate (PMMA), polypropylene (PP), polystyrene (PS), polyethylene (PE), and polyethylene terephthalate (PET) after undergoing ultrafiltration (100 kDa, approximately 10 nm) and H$_2$O$_2$ digestion pretreatment (Xu et al. 2022). Sheng et al. (2023) suggested a straightforward and reliable approach to estimate the concentration of polystyrene (PS) nanoplastics in the atmosphere. The results showed remarkable reproducibility and excellent sensitivity for atmospheric polystyrene (PS) nanoplastics, with a detection limit of 15 pg per cubic meter both indoors and outdoors.

TED-GC/MS is also an alternative technique to assess larger sample quantities within one measurement (Dümichen et al. 2017; Lee et al. 2023a). During the investigation of three different freshwater systems (lake sediment, fluvial suspended matter, and wastewater treatment plant activated sludge) using TED-GC/MS, eight types of polymers were analyzed (Kittner et al. 2023). These included both non-biodegradable and biodegradable types, such as polyethylene (PE), polyethylene terephthalate (PET), polypropylene (PP), polymethyl methacrylate (PMMA), polystyrene (PS), styrene–butadiene rubber, and two popular biodegradable polymers, namely, polybutylene adipate terephthalate (PBAT), and polylactic acid (PLA). It is worth noting that although complex matrix components may have an impact on detection, increased quantities of organic matter in the matrix do not necessarily affect lower limit of detection values of non-biodegradable microplastics when using TED-GC/MS. However, the interactions of complex chemicals become stronger during the decomposition of biodegradable polymers, resulting in increased limit of detection value (Kittner et al. 2023).

Alkali-assisted thermal hydrolysis combined with high-performance liquid chromatography–tandem mass spectrometry (HPLC–MS/MS) was reported for the direct quantification of polycarbonate (PC) and polyethylene terephthalate (PET) microplastics in environmentally relevant samples (e.g., sea turtles, sewage sludge, bivalve, indoor dust, sea salts, and pet food and feces (Wang et al. 2017; Zhang et al. 2019a; Zhang et al. 2019b; Di Renzo et al. 2021)) by estimating the concentrations of the depolymerized building block compounds, such as bisphenol A and p-phthalic acid. Polyamide 6 (PA 6) and polyamide 66 (PA 66) microplastics can also be depolymerized in an acid-assisted heating system to 6-aminocaproic acid and adipic acid, respectively. That can be detected by HPLC–MS/MS with the recovery ranging

from 90.8 to 98.8% of polyamide 6 (PA 6) and polyamide 66 (PA 66) microplastics in the environmental samples, i.e., indoor dust, sludge, sediment, fish gut and gill (Peng et al. 2020). Lin et al. (2020) proposed one method to quantify polystyrene (PS) microplastics and nanoplastics using thermal fragmentation and matrix-assisted laser desorption/ionization time-of-flight mass spectrometry (MALDI-TOF MS), and the fingerprint peaks on m/z 315.3 took effect on the quantification yielding a detection limit of 25 ng in 1 μL analytical sample. Moreover, unaged and even aged microplastics after weathering can be effectively and accurately analyzed by MALDI-TOF MS (Wu et al. 2020a). A strong correlation was established between normalized signal intensity and ln[polymer concentration] with a coefficient of 0.96 for low-molecular-weight polymers and 0.98 for high-molecular-weight polymers. The quantities of aged polystyrene (PS) and polyethylene terephthalate (PET) microplastics from river sediment were measured at $8.56 \pm 0.04$ mg per kilogram and $28.71 \pm 0.20$ mg per kilogram, respectively. Schirinzi et al. (2019) compared the potential for microplastics quantification of different mass spectrometry in natural waters, including MALDI-TOF MS, liquid chromatography coupled to high-resolution mass spectrometry (LC-HRMS), and the ambient ionization approaches as desorption electrospray ionization and direct analysis real-time. Among these methods, LC-HRMS equipped with an atmospheric pressure photoionization source in negative mode presented the highest sensitivity and robustness. An instrumental limit of detection of 20 pg and method limits of detection and quantification of roughly 30 pg per liter and 100 pg per liter, respectively, were achieved for the best analytical methodology. Additionally, samples from rivers and maritime coasts had recoveries of 60 and 70%, respectively (Schirinzi et al. 2019).

Microscopy-based and mass spectrometry-based methods provide different counting ways by vision and mass. Reliable analysis facilitates the research progress about aged microplastics in real environmental samples. The estimation for the prevalence of aged microplastics motivates the prediction to the amount of plastic carbon under increased plastic load. The limit of detection of mass spectrometry reaches picogram levels. The exceptional sensitivity and reliable precision of these approaches instill confidence in the ability to analyze microplastics and nanoplastics within complex environmental matrices.

## Chemometric analysis for qualification and quantification of aged microplastics

Chemometric analysis uses certain algorithms to form both qualitative and quantitative models targeting a series of data sets (Chapman et al. 2020). Chemometrics techniques can analyze both spectra and spectral imaging, including Raman spectral imaging, μ-FTIR, and hyperspectral imaging, crucial for microplastic characterization and identification (Fig. 3). Meanwhile, it also compensates for the limitation of library search in specific circumstances, such as heavily aged and contaminated microplastics (Liu et al. 2023b).

Recently, machine learning has developed to combine with Raman spectroscopy and Raman spectral imaging using unsupervised pattern recognition like principal components analysis (Levermore et al. 2020) and hierarchical cluster analysis, and supervised classification algorithms, like Gaussian curve function (Levermore et al. 2020), Pearson's correlation coefficient analysis (Levermore et al. 2020), multivariate curve resolution-alternating least squares (MCR-ALS) (Tian et al. 2022), independent component analysis (Shi et al. 2023b), support vector machine (Fischer and Scholz-Böttcher 2017), linear partial least squares regression by intervals and competitive adaptive weighted sampling (da Silva et al. 2021), and random forest algorithm (Xie et al. 2023b). Raman spectroscopy coupled with a random forest model accomplished polystyrene (PS) and polyvinyl chloride (PVC) nanoplastic detection in tap water spiked samples and rainwater with an identification accuracy of over 97% (Xie et al. 2023b). Moreover, in collaboration with MCR-ALS, Raman spectral imaging has been effectively utilized to identify microplastics in fish fecal samples and sand samples for in situ microplastics identification directly without pretreatment (Tian et al. 2022). MCR-ALS overcomes drawbacks in traditional Raman spectral analysis due to digestion and absorption in complicated biological or environmental samples (Tian et al. 2022). Photo-oxidation induced spectral alterations of microplastics did not significantly affect the source-apportionment performance of recognition of different microplastics types with a specificity of 98.1%, sensitivity of 89.5%, and accuracy of 96.8% when using the support vector machine model (Jin et al. 2022). It is worth noting that a convolutional neural network-based deep learning model achieved higher accuracy (99.33%) in automatically classifying mixtures of microplastics and natural organic matter according to their Raman spectra, compared to the conventional Raman spectral library software (6.5%) (Lee et al. 2023b). The interpretation of deep learning model improved classification accuracy, even for spectra with similar spectral shapes.

μ-FTIR is also a promising method to attach to chemometric analysis. Random decision forests for the analysis of large μ-FTIR data sets of environmental samples can discriminate between over 20 different polymer types, and are suitable for complicated matrices, such as water, sediment, soil, compost, and sewage sludge (Hufnagl et al. 2022). A robust method known as "microplastics Identification" was applied to identify aged and contaminated microplastics without any cleaning operations (Renner et al. 2017). The
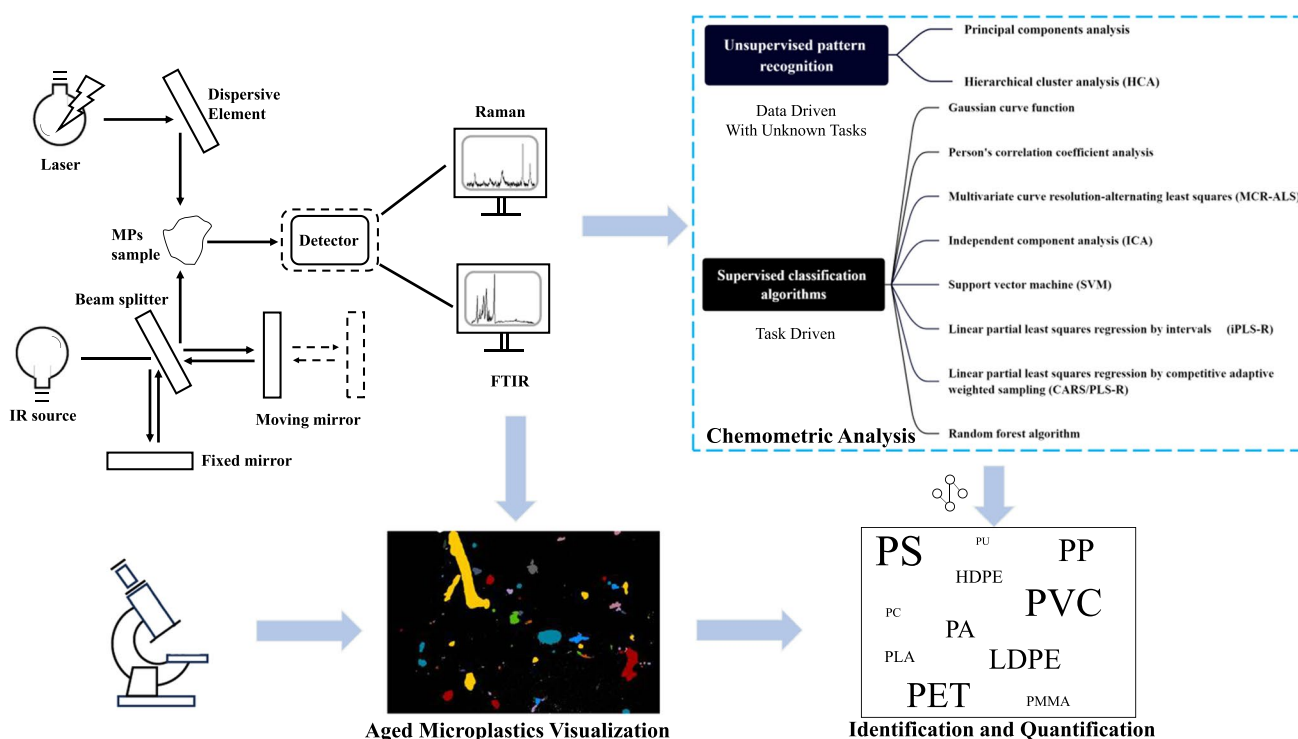
**Fig. 3** Chemometric analysis of aged microplastics qualification and quantification coupled with spectral imaging techniques. The size order of different types of plastics is determined by the search results of respective "microplastics in the environment" in the Web of Science database. HDPE, high-density polyethylene; LDPE, low-density polyethylene; PA, polyamide; PC, polycarbonate; PET, polyethylene terephthalate; PLA, polylactic acid; PMMA, polymethyl methacrylate; PP, polypropylene; PS, polystyrene; PU, polyurethane; PVC, polyvinyl chloride

concept is based on an automated curve-fitting procedure to determine a distinctive characteristic fingerprint consisting of all relevant vibrational band area ratios. Using FTIR-ATR and the "microplastics Identification" method, a total of 300 naturally aged plastic particles were identified successfully with an accuracy of 96% (Renner et al. 2017). Renner et al. (2019) extended the application of the "microplastics Identification" method on μ-FTIR data of microplastics in the presence of interfering matrices and a beach sample, with emphasis on overlapped and broad vibrational bands. Vidal and Pasquini (2021) have introduced a high-throughput screening method based on near-infrared hyperspectral imaging and multivariate supervised soft independent modeling of class analogy classification models. The method is utilized to detect and forecast constituent polymers of primary and secondary microplastics in beach sand automatically with simple sample preparation. However, it also has some drawbacks including size detection limits and underestimating black or dark particles (Vidal and Pasquini 2021).

Therefore, automated aged microplastic detection of μ-FTIR and Raman spectral imaging accompanied by chemometric analysis has demonstrated enormous prospects of automatic quantification and classification methods to identify microplastics in complex environmental matrixes.

However, to effectively address the uncertainty of microplastics in the environment, it is necessary to continue developing more advanced machine learning algorithms. Aggregation of different methods and chemometric analysis offers an effective approach to categorize and consolidate the properties of microplastics in complicated environment media.

## Conclusion

Different aging processes reshape microplastics, altering their physiochemical properties including surface morphology, chain structure, and thermal and mechanical characteristics. This review primarily summarizes advanced qualitative and quantitative techniques for aged microplastics found in the environment. Precise identification and accurate quantification of aged microplastics benefit us in assessing their impacts and understanding their environmental behaviors. Though there is no ideal identification system for aged microplastics now, the development of technologies and the application of machine learning are gradually showing hope to break through technical barriers. Currently, nanoplastic quantification is not only limited to single standard materials. Aged nanoplastic detection in the environment

is more tricky owing to its tiny size and difficult separation. Thus, further work is required to establish the viability of aged nanoplastic techniques, not only limited polymer types. An increasingly serious risk to the environment and human health regarding aged microplastics reminds us to focus on their transport, transformation, and combined effect with other pollutants. It is worth noting that plastisphere, aged microplastics and inorganic and organic pollutants are integrated with complex interaction, which increases the detection difficulties of plastic sources. The persistence and irreversibility of aged microplastics worldwide with delayed toxicological effects make the serious plastic issues focus on the need for specific removal techniques progressively.

**Code availability** Not applicable.

## Declarations

**Conflict of interest** The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

**Ethics approval** Not applicable.

**Consent to participate** Not applicable.

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