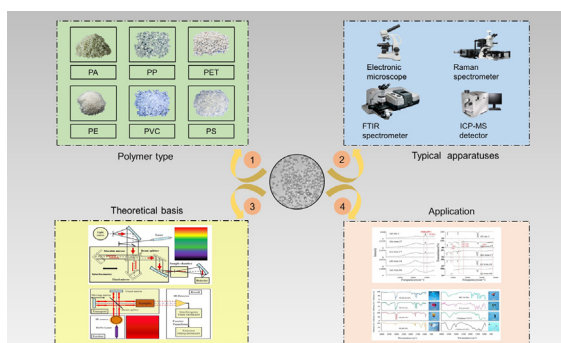Review

The development and application of advanced analytical methods in microplastics contamination detection: A critical review

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HIGHLIGHTS

- The Migration, polymer type, source, and harm of microplastics are concluded.
- The analysis methods are presented and compared in detail.
- The progress of the analysis method and application are demonstrated first.
- The development direction of chemical analysis methods is concluded
- The prospect of detection of microplastics is suggested.

GRAPHICAL ABSTRACT

ARTICLE INFO

ABSTRACT

Microplastics have gradually become emerging environmental contaminants for their extensive distribution, small particle size, and harmful effects on organisms. Therefore, finding accurate, efficient, and rapid analytical methods for detecting microplastics pollution has become an urgent problem. We reviewed the derivation, transport, and classification of microplastics and then highlighted the harmfulness of microplastics which would bring microplastics pollution to the environment and potential damage to organisms. Further, various analytical methods were classified into the thermal analytical method, spectral analytical approach, and other analytical methods based on detection principles. In addition, the application of each analytical method in sea and soil was concluded in detail, and the promising development prospect of each analytical method was discussed. In the end, the chemical analytical method was proposed to explore further in the direction of no sample preparation, nondestructive analysis, low detection limit and it is crucial to establish a unified detection and identification method for microplastics in different environments.

Contents

1. Introduction

Microplastics, which refer to plastic particles greater than or equal to 1 μm and less than 5 mm, were first proposed in 2004 (Thompson et al., 2004; Cole and Galloway, 2015; Hartmann et al., 2019). Research indicated that 4.8 million to 12.8 million tons of microplastics are released into nature each year by humans (Jambeck et al., 2015). Microplastics always exist in water (McCormick et al., 2014) and soil (Sarker et al., 2020), which are filled with intensive activities of humankind and might transport between water and soil (Bank and Hansson, 2019). For instance, microplastics could reach the sea by wind transport, marine activities, and path flow, and they probably enter soil by air floating, air deposition, and irrigation (Liu et al., 2019). Furthermore, microplastics were categorized into primary and secondary microplastics based on the source (Wang et al., 2021). Primary microplastics are related to plastic particles less than 5 mm, such as plastic microbeads (Gregory, 1996), which could find in toothpaste, soap, facial cleanser (Magni et al., 2019), textiles, and shower gel (Cole et al., 2011). Secondary microplastics refer to the large-scale plastics discarded in the environment and might transfer into less than 5 mm (Andrady, 2011) through degradation, such as solar radiation and biological reaction (Galgani et al., 2013). Numerous statistical results indicated that mostly microplastics, mainly from industry and wastes (Eriksen et al., 2013) are secondary microplastics. Additionally, based on the composition, microplastics were divided into polystyrene (PS), polypropylene (PP), polyethylene (PE), polyamide (PA), polyethylene terephthalate (PET), polyvinyl chloride (PVC), and so on. Especially, PP and PE are the most affluent polymer types in the environment (Tong et al., 2020). The main methods for determining the type of microplastics are building the characteristic wave numbers of microplastics and spectral data combined with machine learning method (Fan et al., 2021; Vidal and Pasquini, 2021). Besides, microplastics have the properties of small particle size, large specific surface area (Setala et al., 2014), hydrophobic surface, and strong fluidity (Teuten et al., 2007). Unfortunately, microplastics have strong adsorption and accumulation capacity for their large specific surface area, which provides a rich contact site for other toxic substances, such as additives, heavy metal elements, organic pollutants, and plasticizers (Frere et al., 2018; Wang et al., 2017a; Koelmans et al., 2016). What's worse, the hydrophobic properties of their surface make microplastics have a high affinity for hydrophobic

chemical pollutants. At present, as a late-model environmental pollutant, microplastics have drawn global academic attention gradually (Carbery et al., 2018).

Microplastics are harmful to some marine organisms because microplastics with small particle sizes could be adsorbed on the surface of cells, limiting the transfer of energy and substance, and then inhibiting their cells' growth. The smaller the particles, the greater the harm they have (Zhang et al., 2017). On one hand, under natural conditions, microplastics are often easily ingested by organisms for the small size and difficulty to degrade, injuring their life and health directly (Wright et al., 2013). On the other hand, microplastics tend to be adsorbed in aquatic plants and bound to toxic chemicals (Abidli et al., 2017), which indirectly harm organisms' life activities. For example, in the sea, microplastics ingested by aquatic organisms have a continuous negative impact on cell activity, organ integrity, digestive tract, and growth rate. (Galloway and Lewis, 2016). Additionally, microplastics negatively affect the sustainability of aquatic ecosystems (Besseling et al., 2014). In the soil, random disposal of domestic wastes, agricultural residues in the ground, and the use of soil amendments harm soil quality and soil biota (Ma et al., 2018). Worse still, microplastics may transfer to higher nutrient levels through the circulation of the food chain (Farrell and Nelson, 2013) and harm human health finally (Van Cauwenberghe and Janssen, 2014). Studies have shown that humans are potentially ingesting microplastics with a quantity of 74,000 tons per year (Driedger et al., 2015). Consequently, the detection of microplastics pollution in the environment is of great significance to safeguard the environment and human health. The relevance between the transport and harm of microplastics is schematically shown in Fig. 1.

Visual inspection method could select, classify microplastics, and observe tested object color and size by naked eyes or a microscope (Fahrenfeld et al., 2019), including direct visual method, optical microscope observation, and electronic microscope observation method (Karlsson et al., 2017), but this method is laborious and with low accuracy (Hidalgo-Ruz et al., 2012). Microplastics whose plastic particles with a diameter of less than 1 mm are easily overlooked or miscounted. Moreover, the results showed that the error rate is negatively correlated with the particle size when using this approach (Filella, 2015). Even with a microscope, it is still hard to detect microplastics less than 100 μm in size (Hanvey et al., 2017). Therefore, it is necessary to find more effective and accurate methods for the detection of microplastics.
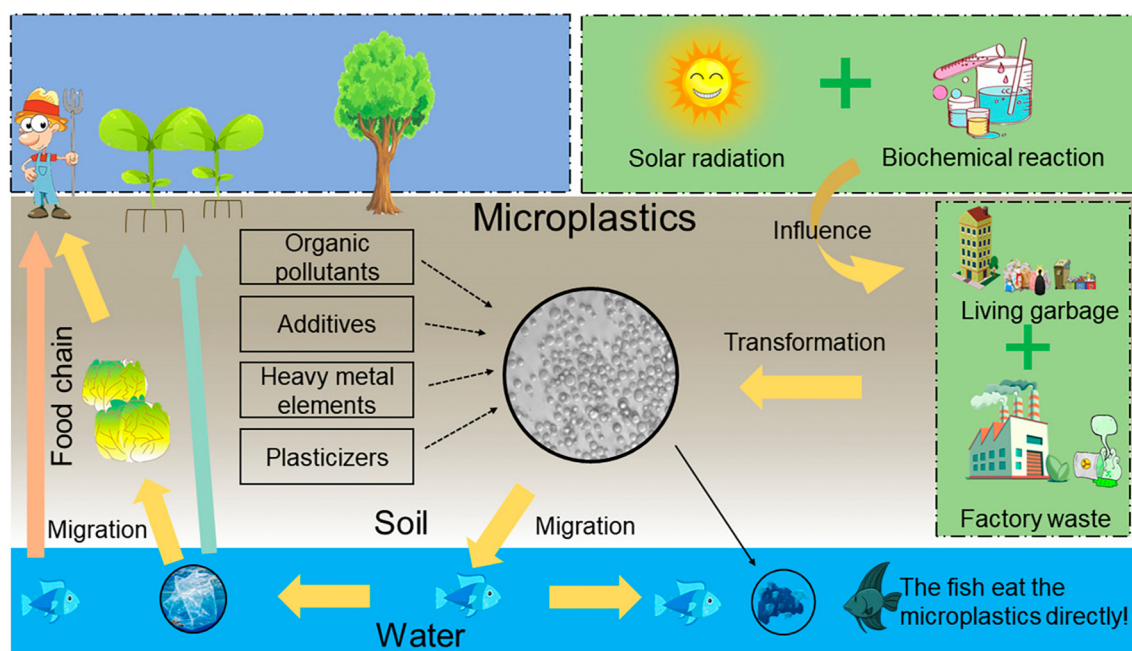
Fig. 1. the source, migration, and harms of microplastics.

The chemical detection method detects microplastics based on the chemical properties of plastics (Song et al., 2015), which mainly includes the thermal analytical method (Kaeppler et al., 2018) and vibratory spectral method (Bonhomme et al., 2003). The thermal analytical method mainly includes Pyrolysis gas chromatography–mass spectrometry (Pyr-GC–MS) (Duemichen et al., 2017), Thermal extraction desorption gas chromatography–mass spectrometry (TED-GC–MS) (Eisentraut et al., 2018), and Differential scanning calorimetry (DSC). The thermal analytical method, which measures the relationship between physical properties and temperature of microplastics under specific temperature conditions, is an effective analytical method for detecting the components of microplastics by using the characteristic pyrolysis spectra of polymers. Despite the reliable detection results, but it needs tedious pre-processing for the relatively small quality of samples. What's worse, impurities in samples could seriously influence the analytical results(Silva et al., 2018). Besides, these methods have disadvantages such as high reaction temperature (Chialanza et al., 2018), which would cause damage to samples and even people (Zhang et al., 2020). Therefore, another advanced and helpful method is strongly needed. The vibration spectral method is mainly represented by Raman spectroscopy (Raman) (Wang and Wang, 2018) and Fourier transform infrared spectroscopy (FTIR) (Nam et al., 2018). Vibratory spectroscopy is used to detect and identify polymers in environment samples through specific absorption spectra, which will not cause damage to pieces (Rocha-Santos and Duarte, 2015). In addition, it is always applied in the detection of microplastics due to its high accuracy and reliability (Song et al., 2015). Besides, terahertz spectroscopy (THz) (Li et al., 2020), hyperspectral imaging (HSI) (Shan et al., 2018), scanning electron microscopy energy dispersive spectroscopy (SEM-EDS) and high-performance liquid chromatography (HPLC) (Shui and Leong, 2002) possess the strengths of strong penetration, online monitoring, determining the elemental composition, and the high sensitivity respectively and have been gradually used in the detection of microplastics. Especially, SEM images will help to observe the form of the microplastics.(Wang et al., 2017b).

It is worth pointing that the combination of the visual inspection and the chemical detection methods would make a difference in the detection of microplastics. For example, FTIR combined with a microscope could improve the detection limit from 20 μm to 10 μm (Imhof et al.,

2012), which means the smaller microplastics would be detected. And μ-Raman spectroscopy has a high spatial resolution of less than 1 μm (Lenz et al., 2015), which may be used to detect Nano-plastics.

Furthermore, the measuring method of microplastics is also a direction for further study. Brunauer–Emmett–Teller (BET) is a reliable and widely used analytical technique that could measure the surface of microplastics (Rozman et al., 2021; Zhao et al., 2021). X-ray Photoelectron Spectroscopy (XPS) method is a highly sensitive and specific method that measures the elements present on the surface of a sample, except H and He. What's more, it provides not only chemical information on the overall aspect; but also information on the surface, small areas, and depth distribution when analyzing electronic materials and it is widely used in the detection of microplastics (Fang et al., 2021; Kedzierski et al., 2020). X-ray diffraction (XRD) is the most basic and vital structure testing and measuring physical properties such as composition. However, such a technique needs a dried sample for the detection, acting as a complementary role (Miranda et al., 2021). Atomic absorption is widely applied in element analysis due to its strong selectivity, high sensitivity, and wide range of analyses. And the technique should analyze the metal element in an aqueous sample (Kutralam-Muniasamy et al., 2021). Inductively coupled plasma mass spectrometry (ICP-MS) is a technique to detect heavy metal elements in the wort, water, and even the surface of microplastics (Lee et al., 2021). To conclude, these methods were mainly used as an auxiliary in the detection of microplastics in recent years because the detection of microplastics focuses on the particle size and abundance rather than the surface area, composition, and the metal elements on the surface of the microplastics. The specific classification, measure method, and typical apparatuses are shown in Fig. 2.

This review aims to analyze the advantages and disadvantages of modern identification methods of microplastics and the research of modern chemical identification methods in microplastics identification so that we can put forward corresponding suggestions for the improvement of modern identification methods of microplastics and contribute to the research of microplastics detection using modern chemical detection methods. The first part of this review introduces the pollution sources, classification, and hazards of microplastics; Then, we review the theoretical basis of modern detection methods grouped by the principle of each technique; In the third part, the application research
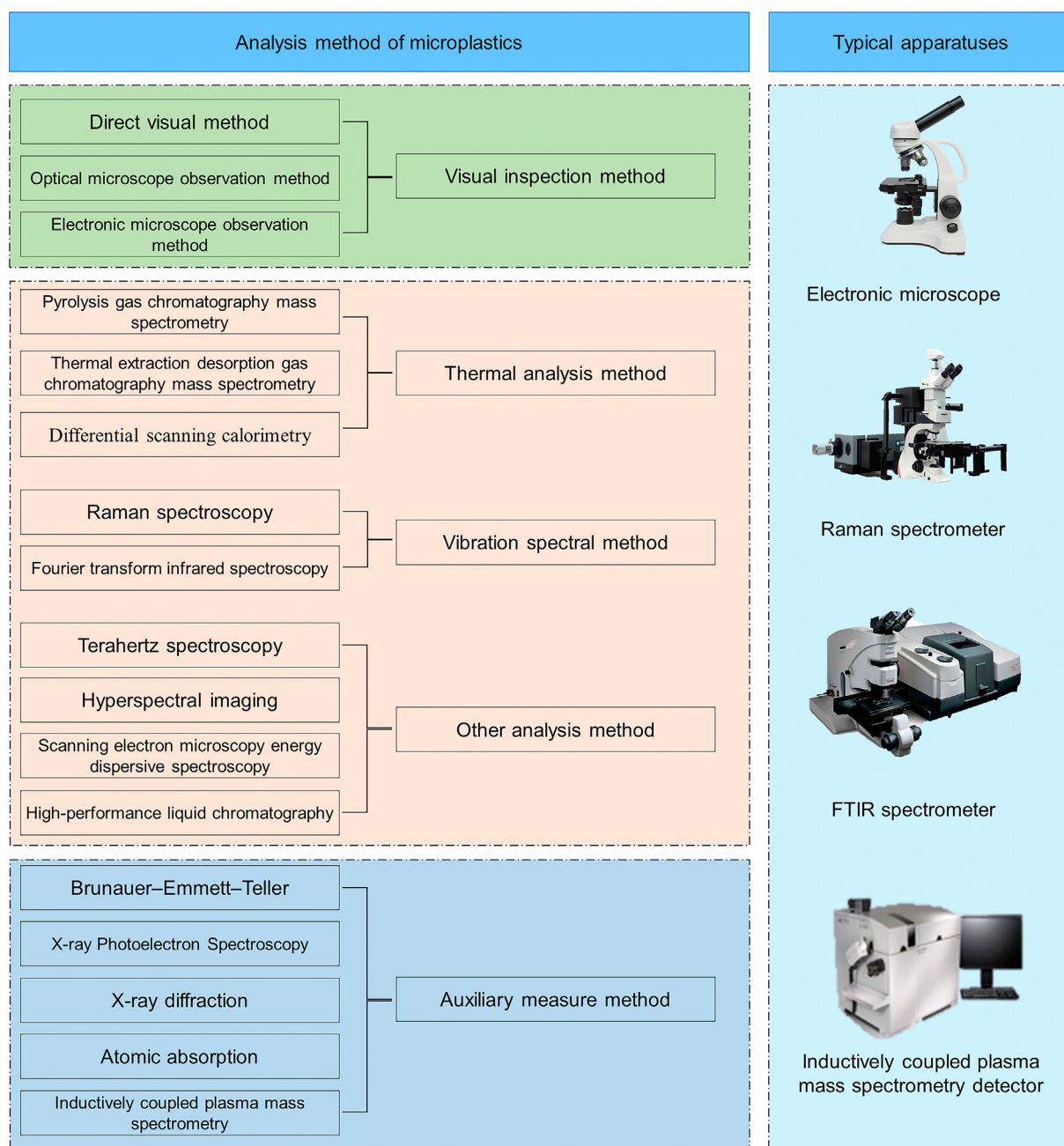
Fig. 2. Classification, measure method, and some typical apparatuses.

and progress of modern detection methods in microplastics detection are introduced in detail; In the last part, to provide a reference for the future research direction of microplastics detection, the modern identification methods have prospected based on summarizing the existing research.

2. Theoretical basis of the chemical detection method

The detection process of microplastics is usually divided into three parts: extraction, separation and purification (Tagg et al., 2015), and analysis. The first two steps are to extract relatively pure microplastics from the microplastics liquid (Isobe et al., 2015). The third step is to conduct qualitative and quantitative analysis based on the characteristics of microplastics (Zettler et al., 2013). This review is focused on the study of microplastics using the chemical detection method and especially the step of detection.

2.1. Thermal analytical method

2.1.1. Pyrolysis gas chromatography–mass spectrometry

Pyrolysis gas chromatography–mass spectrometry (Pyr-GC–MS) is the combination of pyrolysis and GC–MS. This method is for pyrolysis of samples without oxygen to decompose the polymer into volatile small molecules, which are then introduced into the GC–MS system to determine the combustion or pyrolysis products (Xu et al., 2019). Individual microplastic particle is fed into a reaction tube for pyrolysis and the pyrolysis products of some polymers are usually known to us. Then, the gaseous compounds released after the reaction are cold-injected, captured by the system, and transferred to a GC column coupled to the mass spectrometer. In the end, the obtained spectrum of pyrolysis products is compared with the spectrum database of common plastic types to complete the detection of microplastics.

Pyr-GC–MS can accurately identify various polymer types, and provide information about toxic organic plastics additives (OPA) potentially (Fries et al., 2013). More than that, Pyr-GC–MS can also be used to analyze the chemical composition and structural characteristics by detecting the pyrolysis products of high molecular weight polymers, which could provide a complete sample description and assess the actual chemical properties of the samples accurately (Tianniam et al., 2010).

2.1.2. Thermal extraction desorption gas chromatography–mass spectrometry

Thermal extraction desorption gas chromatography–mass spectrometry (TED-GC–MS) is an improved thermal analytical method that combines thermogravimetric analytical solid phase extraction (TGA-SPE) and thermal desorption gas chromatography–mass spectrometry (TDS-GC–MS) (Duemichen et al., 2015). The sample is first pyrolyzed in TGA at a temperature of up to 1000 °C and then adsorbed on solid-phase reagents for extraction. Then the degradation products are transferred to a thermal desorption device and desorbed by increasing the temperature. Subsequently, the sample was separated from a chromatographic column and then characterized using mass spectrometry. This method reduces analysis time for high sample size and increases sample weight to 100 mg. In addition, this method overcomes the limitation of blocking the reaction tube by high-molecular-weight pyrolysis products (Duemichen et al., 2019) and does not need to pretreat the sample (Elert et al., 2017).

2.1.3. Differential scanning calorimetry

Differential scanning calorimetry (DSC) identifies chemicals by detecting the melting temperature of the plastic sample when heated over a range of temperatures (Chialanza et al., 2018). This method can provide qualitative and quantitative information on gaseous products of microplastics samples. At present, DSC is widely used to study the thermal properties of polymer materials. As high levels of exploration method, it is cheap and simple. Nevertheless, since each plastic product has different DSC characteristics, reference material is needed to determine the types of polymer. Moreover, large particles cause disturbance because the ratio of mass to surface area is higher than that of small particles (Huppertsberg and Knepper, 2018). The transition temperature is affected by production parameters including additives, impurities, and part of polymerization chains. Another disadvantage of DSC is that DSC signals are dependent on the particle size of microplastics exceedingly, so the samples should be pretreated before testing. To make matters worse, when the melting point of the polymer mixture is similar, or some polymers have low thermal conductivity due to the low sensitivity the DSC sensors have. These disadvantages limit its rapid application in the detection of microplastics.

It is found that thermogravimetric analysis differential scanning calorimetry (TGA-DSC) could accurately identify PE and PP in environmental samples. However, phase change signals of other types of MPs cannot be recognized due to the much overlap of phase change signals. Meanwhile, the peak area will increase while the resolution will decrease due to the increase in sample size, leading to inaccurate measurement results.

2.2. Spectral analytical method

The Spectral analytical method provides more accurate information than visual recognition alone (Song et al., 2015). So far, spectroscopic methods can not only identify microplastics; but also ensure their composition. That is because different microplastics produce unique characteristic peaks, which are reflected in the spectral signal. FTIR and Raman have been used to identify polymer types for microplastic particles with a minimum particle size of 10 μm and 1 μm respectively.

2.2.1. Raman spectroscopy

Raman spectroscopy (Raman) is a vibration technique based on inelastic scattering of light (Schymanski et al., 2018). By analyzing the scattering spectrum, which is different from the frequency of incident light, the information of molecular vibration and rotation can be obtained to achieve the molecular structure of the material. Raman has a high spatial resolution (less than 1 μm) (Lenz et al., 2015), high sensitivity, high precision, and high specificity of the fingerprint spectrum. In addition, this method has the advantages of no sample preparation, no staining, no requirement for sample thickness, and no damage to the sample. At present, it has been rapidly processed to identify organic chemistry and polymer materials. Because of the inherent resonance fluorescence phenomenon, Raman scattering is easily disturbed by the fluorescence background caused by inorganic substances, organic substances, and colored additives (Dehaut et al., 2019; Zarfl, 2019). What's worse, the Raman signal is usually weak, which makes it hard to reach an accurate identification.

Due to the high signal-to-noise ratio of the spectral data and the absence of fluorescence interference (Borman, 1982), the nonlinear Raman spectroscopy technology is emerging in the field of microplastics detection (Galloway et al., 2017). Meanwhile, surface-enhanced Raman spectroscopy is also gradually developing microplastics detection because of its high sensitivity and unique molecular specificity. Raman spectroscopy method can overcome the difficulty of target detection in liquid and provide the possibility for rapid in-situ detection of microplastics in water in the future.

2.2.2. Fourier transform infrared spectroscopy

As Raman's complimentary spectrum, Fourier transform infrared spectroscopy (FTIR) uses the chemical bond information of the identifiers to conduct the identification. Different chemical bond structures will produce different peak patterns and form specific maps. Thus, the constituent materials of particles can be determined, and then the purpose of detection can be achieved by comparing with the standard library (Mai et al., 2018). For the time being, although the spatial resolution of FTIR is as low as 20 μm (Lee and Chae, 2021), the drawback of long-time processing should be considered. FTIR is easily disturbed by water and has low horizontal resolution and complex spectrums; when detecting wet samples, so drying the sample is of great significance. μ-FTIR is the combination of microscopy and FTIR for the characterization of MPs (Imhof et al., 2012), whose detection limit is less than 10 μm. This method can be used for the detection of microplastics in the environment because of the strengths of characteristics of small sample size, high throughput screening (Loeder et al., 2015), and environmental friendliness (Araujo et al., 2018). However, this method usually produces a weak signal for microplastics of small size, which may result in a mass of false negatives or false positives (Sobhani et al., 2020). Moreover, this method has specific requirements on the thickness and characteristics of microplastics.

2.3. Other analytical methods

2.3.1. Scanning electron microscopy energy dispersive spectrometer

Scanning electron microscopy energy dispersive spectroscopy (SEM-EDS) is an analytical method combining scanning electron microscopy (SEM) and energy dispersive spectroscopy (EDS). Scanning electron microscopy (SEM) is a means of microstructure observation between the transmission electron microscopy and optical microscope, which can be directly used for microscopic imaging according to the composition of the surface material. With the clear and high magnification, it could provide images of the surface properties of microplastic particles (Mahon et al., 2017), which makes it convenient to distinguish the microplastic and other organic matter particles. However, this method can only obtain the image of the surface morphology of the material, so it is necessary to combine the surface characteristics of plastic particles and elemental analysis to identify the microplastics better. At present, the elemental composition information of microplastics is often analyzed with energy dispersive spectroscopy (EDS) to characterize the surface morphology of microplastics and obtain the elemental

composition information of microplastics. SEM-EDS can be used to characterize the surface morphology of microplastics, and determine the elemental composition of polymers by diffraction and reflection based on the surface emission radiation of microplastics (Vianello et al., 2013), and it has a sample capacity ranging from 5 to 10 mg. Currently, this method is commonly used to characterize Nano-plastics, but the disadvantage is that no chemical information would be provided.

2.3.2. High-performance liquid chromatography

High-performance liquid chromatography (HPLC) is commonly used to separate, identify, and quantify organic compounds in liquid. This method works by injecting the sample with a solvent (as a mobile phase) and pumping it into a column containing a filler of small porous particles (as a stationary phase). And then the separation of these components is caused by the different flow rates of each component from the column due to the different solubility and polarity of the sample components in the mobile and stationary phase. Liquid absorbance measurements for other retention times are subsequently compared with standard calibration curves to calculate the concentration of each component. HPLC has high sensitivity and low detection limit and it is often used as a terminal detection method. What's more, it is more suitable for the identification of large, polar, and thermally unstable (Fu et al., 2020), related to microplastics. Nevertheless, it could be destructive to the sample as it shows the chemical composition of the sample (Wu et al., 2020).

2.4. Summary

From the above content, it can be concluded that modern chemical identification methods have their advantages and disadvantages. The advantages and disadvantages and some important properties are summarized in Table 1.

3. Research progress of modern analytical method

3.1. Application of the thermal analytical method in the detection of microplastics

The thermal analytical method mainly includes Pyr-GC–MS, TED-GC–MS, and DSC, which plays an important role in detecting microplastics in

the environment due to their high detection accuracy. This section mainly analyzes the detection of microplastics in soil and water.

Dierkes et al. developed a method combining pressurized liquid extraction and Pyr-GC–MS for the quantitative detection of microplastics in solid substrates, such as soil and sediments, and the results found that the detection limit of microplastic samples was reduced to 0.007 mg/g (Dierkes et al., 2019). When this method was applied in the quantitative analysis of the microplastics in sewage sludge, it was found that the concentrations of PE and PP were 3.3 ± 0.3 mg/g and 0.08 ± 0.02 mg/g respectively, which may be applied to the monitoring of MPs in soils and sediments of freshwater systems in future studies. Steinmetz et al. used Pyr-GC–MS for selective quantification of PP, PE, and PS, which are the most environmentally friendly polymers in soil (Steinmetz et al., 2020), and the results showed that the limits of detection of PE (fractionation ratio 15:2), PE (fractionation ratio 17:2), PE (fractionation ratio 18:2), PP, PS (pyrolysis product Sty) and PS (pyrolysis product aMeSty) were 4800, 2500, 11,300, 43,200, 500, and 1600 μg/L respectively. The limits of quantification (LOQ) were 25,700, 38,600, 53,400, 46,700, 43,300, and 33,100 μg/L respectively. These differences may be related to the heterogeneity of soil substrates and this method has the potential for routine analysis and screening studies of agricultural systems. Additional information on particle shape and size would be probably obtained if combined with microspectroscopic techniques. El Hayany et al. used Pyr-GC–MS and Nile red dye to identify the lagoon sludge, used as a soil conditioner (El Hayany et al., 2020), the survey demonstrated that the average microplastic particles in fresh sludge and dehydrated sludge were $40.5 \pm 11.9 \times 10^3$ particles/kg and $36 \pm 9.7 \times 10^3$ particles/kg. The difference between the two may be resulting from sludge dewatering in the drying bed, which caused the small loss of MPs (<500 μm). This study provides a theory for co-composting technology, which may lead to the physical degradation of plastics and reduce their size. Peters et al. used Pyr-GC–MS to quantitatively and qualitatively analyze 43 microplastics, extracted from the stomachs of Marine fishes along the Texas Gulf Coast (Peters et al., 2018), the results showed that PVC and PET were the most common polymers followed by nylon, silica gel, and epoxy resin. It confirmed that Pyr-GC–MS was a suitable analytical tool for the polymer identification of microplastics. This survey provides a basis for the future development of polymer identification methods in fish. Hendrickson et al. assessed the extent, distribution, and common

Table 1
Comparison of modern chemical analysis methods.

Method	Type	Advantages	Disadvantages	Sample mass	Detection limit	Reference
Pyr-GC–MS [1]	Thermal analysis	Various polymer types, accurate results, high sensitivity, and no sample preprocess	Long processing time, the damage to sample, high reaction temperature, and placed manually	0.5 mg	0.007 mg/g	(Duemichen et al., 2017; Fries et al., 2013; Tianniam et al., 2010)
TED-GC–MS [2]	Thermal analysis	High sample size, high sample mass, no blocking reaction cube, and no sample preprocess	Long processing time, the damage to sample, high reaction temperature	100 mg	–	(Duemichen et al., 2019; Elert et al., 2017; Shishkin, 2006)
DSC [3]	Thermal analysis	Accurate results, widely used method, cheap and simple, comprehensive analysis	Long processing time, the damage to sample, easily influenced by substrate, and sample preprocess	3–15 mg	–	(Chialanza et al., 2018; Huppertsberg and Knepper, 2018)
FTIR [4]	Spectral analysis	Accurate results, high sensitivity, high throughput screening, and environmental friendliness	Time-consuming, easily disturbed by water, sample preprocess, low horizontal resolution	–	10 μm	(Araujo et al., 2018; Imhof et al., 2012; Loeder et al., 2015; Sobhani et al., 2020)
Raman [5]	Spectral analysis	Good spatial resolution, high precision, high sensitivity, high specificity of fingerprint spectrum, and no damage to the sample	Weak signal, the fluorescence background, sample preparation, and long processing time	–	1 μm	(Dehaut et al., 2019; Sobhani et al., 2019; Zarfl, 2019)
SEM-EDS [6]	Microscopy and element analysis	Surface morphology analysis, good results for small size sample, no damage to sample and high accuracy	No chemical information, long processing time, low sensitivity and sample preprocess	5–10 mg	–	(Vianello et al., 2013)
HPLC [7]	Chemical composition analysis	High sensitivity, low detection limit, high accuracy, high reaction rate, and widely used method	Damage to sample, sample preprocess	–	–	(Fu et al., 2020; Wu et al., 2020)

Note: [1] Pyrolysis gas chromatography mass spectrometry, [2] Thermal extraction desorption gas chromatography mass spectrometry, [3] Differential scanning calorimetry, [4] Fourier transform infrared spectroscopy, [5] Raman spectroscopy, [6] Scanning electron microscopy energy dispersive spectrometer, and [7] High-performance liquid chromatography.

polymers of microplastics pollution in the surface water of West Lake (Hendrickson et al., 2018), using Pyr-GC–MS and FTIR to quantify and identify microplastic particles, the results showed that the concentration of microplastics in the surface water of West Lake was in the range of 0–110,000 particles/km^2 (standard deviation was 28,000 particles/km^2) and the most common polymer was PVC, followed by PP and PE. This study provides a method for improving future research on microplastics in aquatic systems. Becker et al. used TED-GC–MS to quantitatively identify the suspended organic compounds in particle reinforced sediments in the freshwater (Becker et al., 2020), including PE, PS, PET, and PP, and the results showed that the LOQ of PE, PP, PS, and PET were 20.0, 5.70, 2.20 and 18.0 μg/mg respectively. This survey indicates that this method has the potential to be used as an alternative method for quantifying polymers in solid substrates.

Majewsky et al. used (Thermo gravimetric analysis) TGA combined with DSC to measure the characteristic endothermic phase change temperatures of seven kinds of plastic polymers and obtained the corresponding curves of low-density endothermic phase change heat flow and peak temperature (Majewsky et al., 2016). The results showed that the peak temperatures of PE, PP, PET, PA, PES, PVC and PU are 101 ± 2 °C, 164 ± 1 °C, 250 °C, 253 °C, 261 °C, 268 °C, 291 °C respectively, which may be related to the degree of branching of the plastic itself. On this basis, the extraction of the waste water sample was analyzed and the results showed that only PE and PP can be identified among the studied polymers while the phase transition signals of other polymers were overlapped greatly. This research provides a complementary and alternative method for the determination of PE and PP in environment samples for FTIR. Bitter et al. used DSC to detect and quantify semi-crystalline thermoplastics in wastewater (Bitter and Lackner, 2020), the results explained that concentrations of PE, PP, PA, and PET ranged from 0.5 μg/L to 35.5 μg/L. This study completed the quantification of MPs in industrial wastewater for the first time and provides a reference for the quantification of MPs in industrial wastewater in the future. Funck et al. proposed a representative microplastics sampling method combined with Pyr-GC–MS to rapidly and quantitatively study the microplastics load and mass balance of surface water and wastewater (Funck et al., 2020), the results showed that the average recovery rate of microplastics was 86% and the proposed method based on the platinum wire was simple for sample preparation. The limits of quantification of polystyrene (PS) and polyethylene (PE) were 30 μg/L and 1000 μg/L respectively. This research provides a theoretical basis for the analysis of microplastics in surface water and wastewater. Kuhn et al. evaluated the polymer composition of plastic samples from Dutch beaches using ATR-FTIR and DSC (Kuhn et al., 2018), the results showed that the size of plastic particles was 0.5–2 mm accounting for 68% of all. This research shows that it is possible to create homogenous mixtures of microplastics and provides lessons for bridging the gap between raw materials laboratory research and the real-life scenarios of weathered microplastics.

Pyr-GC–MS is the main thermal analytical method for microplastics detection, and the main disadvantages of this method are that the microplastics must be placed manually in the pyrolysis reaction tube and the sample mass is only 0.5 mg (Duemichen et al., 2017). Additionally, pyrolysis products of high molecular weight above 300 °C usually contaminate the reaction tube (Parsi et al., 2007). Compared with Pyr-GC–MS, TED-GC–MS improves the sample mass to 100 mg and overcomes the limitation of sample contamination to the reaction tube, but the temperature is high and up to 1000 °C, which means the experiment risk is high. This may be an important reason for TED-GC–MS's current slow development. As a highly exploratory method, DSC has a good prospect for the analysis of microplastics in water in the future. However, this method requires pretreatment for the samples and only has good detection results for microplastics of PE and PP types. Current studies show that the thermal analytical method has disadvantages, such as destructive experiments and the inability to meet the requirements of rapid detection of microplastic pollutants in water. Therefore, the invention of an instrument integrating the drying, testing, and data analysis of microplastics in the future is conducive to the rapid development of the thermal analytical method. The summary of the application in microplastics using the thermal analytical method is shown in Table 2.

Table 2
Summary of the application in microplastics using thermal analysis.

Analysis method	Sample source	Sample type	LOD	Sample abundance	Reference
Pressurized liquid extraction and Pyr-GC–MS	Soil and sediments	PE, PP	–	PE (3.3 ± 0.3 mg/g) and PP (0.08 ± 0.02 mg/g)	(Dierkes et al., 2019)
Pyr-GC–MS [1]	Soils and sediments of freshwater	PE (fractionation ratio 15:2), PE (fractionation ratio 17:2), PE (fractionation ratio 18:2), PP, PS (pyrolysis product Sty), and PS (pyrolysis product aMeSty)	PE (fractionation ratio 15:2, 4800 μg/L), PE (fractionation ratio 17:2, 2500 μg/L), PE (fractionation ratio 18:2, 11,300 μg/L), PP (43,200 μg/L), PS (pyrolysis product Sty, 500 μg/L) and PS (pyrolysis product aMeSty, 1600 μg/L)	–	(Steinmetz et al., 2020)
Pyr-GC–MS and Nile red dye	Lagoon sludge	–	–	Fresh sludge (40.5 ± 11.9 × 10^3 particles/kg) and dehydrated sludge (36 ± 9.7 × 10^3 particles/kg)	(El Hayany et al., 2020)
Pyr-GC–MS	Stomachs of Marine fishes	PVC, PET, nylon, silica gel, and epoxy resin	–	–	(Peters et al., 2018)
Pyr-GC–MS and FTIR [4]	Surface water	PVC, PP, and PE	–	0–110,000 particles/km^2	(Hendrickson et al., 2018)
TED-GC–MS [2]	freshwater	PE, PS, PET, and PP	PE (20.0 μg/mg), PP (5.70 μg/mg), PS (2.20 μg/mg) and PET (18.0 μg/mg)	–	(Becker et al., 2020)
TGA, DSC [3]	Wastewater	PE, PP, PET, PA, PES, PVC, and PU	–	–	(Majewsky et al., 2016)
DSC	Wastewater	PE, PP, PA, and PET	–	0.5–35.5 μg/L	(Bitter and Lackner, 2020)
Pyr-GC–MS	Surface water and wastewater	PS and PE	PS (30 μg/L) and PE (1000 μg/L)	–	(Funck et al., 2020)
ATR-FTIR [5] and DSC	Dutch beaches	–	–	–	(Kuhn et al., 2018)

Note: [1] Pyrolysis gas chromatography mass spectrometry, [2] Thermal extraction desorption gas chromatography mass spectrometry, [3] Differential scanning calorimetry, [4] Fourier transform infrared spectroscopy, and [5] Attenuated total refraction-Fourier transform infrared spectroscopy.

3.2. Application of the spectral analytical method in microplastic pollution

The Spectral analytical method is widely used in all directions of environmental pollution detection, such as the analysis of heavy metal pollution and polymer, due to its specific absorption spectrum characteristics and its high accuracy and reliability, making it indispensable in the detection of microplastics. At present, vibration spectroscopy is the most widely used method in the detection of microplastics along with THz and HSI. The method of FTIR has many advantages in the identification of polar groups and the combination of visual search and Fourier transform infrared spectrum library can help to reduce the misidentification rate of microplastics (Song et al., 2015). Raman has a better response to non-polar symmetric bonds (Li et al., 2018a), which has no requirement on sample thickness and does not cause damage to the sample. THz has the characteristics of high resolution and high sensitivity and its spectral data can be used to extract the material physical information directly and conveniently, such as the dielectric constant in the band. HSI is a fast, noninvasive, nondestructive, and reliable imaging method that provides direct visualization of samples through possible chemical identification. In this section, the study of microplastics in water and soil by the spectroscopic method is analyzed in two parts.

3.2.1. Research on spectroscopic method for microplastics in water

Microplastics in water have the characteristics of high specific surface area and strong fluidity, which provide a rich contact place for other toxic substances (heavy metal elements, etc.). At present, PE and PP are proven to be the richest microplastics in water. Raman is widely used in the detection of microplastics in water due to its high resolution, strong anti-interference ability to water, and high sensitivity. FTIR is often used in conjunction with Raman to detect microplastics because of its vulnerability to interference with water in microplastics.

Frere et al. used μ-Raman combined with static image analysis to identify 103 particles collected from the sea surface (Frere et al., 2016), and the success rate of analyzing microplastics reached 75%. It was found that the size distribution of different microplastics was discrepant. PS mainly existed in the range of 2–5 mm, PE in the range of 1-2 mm, and PP in the range of 0.335–1 mm. This study provides a reference for solving the problem of the specific size distribution of polymers in various environments. The results made by least squares–support vector machine (LS–SVM), support vector machine (SVM), neural network (NN), and partial least squares–discriminant analysis (PLS-DA) using underwater HSI data (PS, PET, PA, PE, and PP) were compared recently by Huang et al. and they concluded that SVM achieved the best outcome after being processed by the underwater spectral image correction model (Huang et al., 2021). In the results of the SVM (kernel type: RBF) model, the average precision, recall rate, and F1-score were 0.9839, 0.9859, and 0.9849 respectively. Besides, the accuracy of PS, PET, PA, PE, and PP was 0.9971, 0.9897, 0.9862, 0.9963, and 0.9984 respectively. Therefore, the combination of classification models and HSI would be an efficient approach to detect underwater microplastics. What's more, particles less than 0.5 mm were found and the detection limit might be extended in the future. This study proposed a method for underwater microplastics' in situ detection. Tong et al. used μ-Raman to identify and analyze tap water from 38 places in China (Tong et al., 2020), and it was found that the content of microplastics in most tap water was 440 ± 275 particles/L. The microplastics particles smaller than 50 μm were obviously dominant where PE and PP were the main components. This study fills a gap in the knowledge of microplastic pollution in tap water. Lv et al. studied microplastics in purified water and seawater through Raman and developed a SERS-based detection method for microplastics and Nanoplastics in liquid with silver colloid used as active substrate (Lv et al., 2020). It was found that the LOQ of 100 nm plastics can be detected as low as 40,000 μg/L. This study provides a method for the rapid detection of trace amounts of plastics and Nano plastics in aquatic environments. Recent research used the FTIR and microplastics pellets acquired from

SHUAN JIUH Enterprise Co., Ltd. Taiwan to determine the characteristic wave numbers of NY, PVC, PP, PET, and PE for identifying microplastics (Fan et al., 2021). 3295, 712, 841, 793, and 1472 and 1462 cm-1 are confirmed to the characteristic wave numbers of NY, PVC, PP, PET, and PE respectively using the admixtures and this study developed an identification procedure for NY, PVC, PP, PET, and PE. This study is the pioneer demonstration and valuable for future investigation on evaluating the influence of microplastics on the environment. Vinay Kumar et al. used a combination of μ-FTIR based on a focal plane array (FPA) and μ-Raman to detect mussels in Marine organisms (Vinay Kumar et al., 2021), and microplastics greater than 3 μm were found. Meanwhile, the random forest classification (RFC) method was used to separate different polymer types in the infrared spectrum analysis pipeline, which provides an important reference for commercially important biological detection of shellfish.

Loeder et al. first successfully used μ-FTIR based on FPA to detect microplastics with a particle size of around 20 μm in Marine plankton (Loeder et al., 2015) and sediment samples, which made the detection limit of microplastic particle size in environmental samples by μ-FTIR reduce to 20 μm. Tagg et al. proposed an improved FTIR technology based on FPA and verified the technology using wastewater treated by H_2O_2 in sewage treatment plants (Tagg et al., 2015). The study demonstrated that the recognition rate of microplastics reached 98.33%. Schymanski et al. tested the microplastics content of water in 22 different recyclable and disposable plastic bottles (Schymanski et al., 2018), and tiny (1–50 μm) microplastic fragments were found in each type of water and 80% of all microplastic particles were found to be between 5 and 20 μm in size. The research provides evidence that microplastic particles may be released from the bottles themselves. The method of ATR-FTIR was used to make chemical characterization of 52 microplastic particles acquired from dead Red Phalaropes base on the unique infrared spectrum of each plastic polymer (Teboul et al., 2021). The results showed that 79% of the examined particles are identified as microplastic particles and among them, PP and PE are the dominant polymer types, accounting for 29% and 53% respectively. This study highlights that seabirds may cause plastic pollution in the marine environment and a combination of analytical techniques should be made to break through the limitation that the quality of spectra might decrease when processing the interfering signals. Lenz et al. used Raman spectroscopy to evaluate the visual recognition of Marine microplasticity (Lenz et al., 2015), and the survey revealed that 68% of the visually-counted MPs ($n = 1279$) was confirmed as plastic by spectrophotometry and the percentage varied with the type, color, and size of MPs. The applicability of Raman spectroscopy for the identification of microplastic was also tested, which provided a recognizable Raman spectrum for the most common polymers in Marine MPs (PE and PP). The standard, weathering, and field composite microplastics in the marine sediment were detected and identified by Jiao et al. via building 3D Raman imaging (Jiao et al., 2021). The results showed that the miss rates of PE, PP, PS, PET, PET-fiber, PP-fiber, PE-fiber-PE, and PP-fiber-PP acquired by 3D Raman imaging (all lower than 5%) are all lower than the outcomes made by 2D Raman imaging. This study indicates 3D Raman imaging is a suitable approach to determine the composition and structure of composite microplastics and more researches should be conducted to fill the gaps of the measured and actual values. Karlsson et al. used HSI to continuously monitor MPs in real seawater (Karlsson et al., 2016). The results showed that a 100% particle recognition rate was obtained on reference plastics above 300 μm and the particle size limit of the HSI technology was determined to be 300 μm.

μ-Raman is mainly used for the detection of microplastics in water because of its low spatial resolution and high anti-interference ability to water, but this method has weak spectral signal, and low spectral signal-to-noise ratio and is susceptible to fluorescence interference caused by organic matter. Therefore, it is an important research direction to improve the SNR of Raman spectral data and the anti-fluorescence interference ability of Raman spectroscopy Fourier

transform infrared spectroscopy (FTIR) is improved by using an FPA (Primpke et al., 2017) and the method (FPA-FTIR) has a high spatial resolution (less than 10 μm) and is insensitive to sample thickness, so it requires passivation of the sample before identification (Chen et al., 2020). Therefore, the development of the pretreatment function of FTIR spectrometer is conducive to the rapid development of FTIR technology. At present, the detection limit of HSI is 300 μm (1 μm for Raman, 10 μm for FTIR). The development of HSI is slow and the detection effect for microplastics with small particle size is poor. In addition, low image quality and low scanning frame rate also hinder the development of HSI. Therefore, improving the detection limit of HSI technology in microplastics detection and the imaging quality and scanning frame rate of HSI technology are the major challenges.

3.2.2. Research on spectroscopic method for microplastics in soil

Most microplastics in soil are found in sediment and sand, where they are prone to be weathered. However, the identification of weathered polymers will degrade the quality of spectral signals and indirectly increase the complexity of the spectral analytical method. At present, the detection of plastic in the soil is mainly to reach the function of identification and classification. Besides, FTIR, Raman, THz, and HSI have been considered in this part.

Sobhani et al. used Raman spectroscopy to identify and analyze microplastic samples with sand as the background and the background recognition and visualization of MPs (PS, PET, PE, PVC, and PP) in the sand were realized (Sobhani et al., 2019). MPs as small as 1 μm can be captured by mapping the characteristic peaks and fingerprint peaks of the image. This study provides a basis for MPs recognition and visualization. Nevertheless, the quantification of MPs is not achieved, so this technique needs to be further studied. Dong et al. (Dong et al., 2020) successfully applied Raman to establish a Raman database of 124 weathered microplastics, which was used to accurately identify microplastics in the sediment environment around the waste plastic processing and recycling industry in Laizhou, Shandong Province, China. ATR-FTIR spectra of 20 fragments that were not recognized by Raman spectroscopy were collected and the results of Raman spectroscopy and ATR-FTIR identification showed that PE and PP were the main microplastic debris in the area, accounting for 45.2% and 32.9%. Subsequently, PET and PVC microplastic fragments accounted for 6.45% and 4.52%. This study shows that Raman spectroscopy has great potential in identifying naturally weathered microplastics, which combined with elemental analysis can be used to interpret microplastics degradation processes under natural conditions in the future. Wilson et al. used FTIR to analyze 1446 suspected microplastic particles from 15 coastal sites at 16 beaches in the Bristol Channel, UK (Wilson et al., 2021), the recovery rate of microplastics was 96.5%, among which the most common polymers PE and PP accounted for 61% and 26% of the total sample respectively. This study shows that microplastics are more abundant on low-energy beaches with finer sediments, highlighting the importance of sedimentary environments in determining the abundance of microplastics. The approach of μ-ATR-FTIR was applied to identify PE, PP, PET, and PS by Morgado et al. based on the selecting optimal assessed wavenumbers, spectral characteristic, and Pearson's correlation coefficient analysis and they made an MS-Excel spreadsheet used as the validation of microplastics' identification (Morgado et al., 2021). The results showed that the true positive and false-positive rates of microplastics' identification are greater than 95% and lower than 5%, respectively. This study provides a methodology for developing and validating methods to determine the type of microplastics using μ-ATR-FTIR.

Ziajahromi et al. used FTIR to measure the concentration of microplastics in the outlet water and sediments of a rainwater floating treatment wetland on the Gold Coast of Queensland (Ziajahromi et al., 2020). An average of 4.0 ± 2.4 microplastic particles/L was detected in the water phase of outlet samples while 320 ± 42 microplastic particles/kg in the dry sediments of the outlet samples. The higher

concentrations of microplastics in sediments, compared to water provide data that supports the possible role of wetlands in controlling microplastic pollution in surface water. Helcoski et al. used FTIR to identify and analyze 175 microplastic particles in habitats with different vegetation densities in tidal wetlands (Helcoski et al., 2020), and the outcomes indicate that the correct identification rate of microplastics was 81–93%, where the main polymers PS and PE accounted for 29% and 8% respectively. This study suggests that wetlands are an important place for microplastics to accumulate. De-la-Torre et al. used FTIR to statistically analyze the distribution of microplastics on four beaches in Lima, Peru (De-la-Torre et al., 2020), and the results implied that the abundance of microplastics was up to 489.7 ± 143.5 pieces/m^2, where PS was the richest plastic-type. However, this study only carried out statistical analysis on the microplastics with large size (1-5 mm) and did not involve the microplastics with small size (0.01-1 mm). Piehl et al. quantified microplastics pollution in farmland in southeastern Germany (Piehl et al., 2018). And the outcome showed that 206 large pieces of plastic could be found in each hectare of farmland and the dry weight of soil contained 0.34 ± 0.36 microplastic particles/kg. However, the report only looked at plastic pollution on congenitally treated agricultural sites, and further research is needed on the extent of pollution in areas, where agricultural fertilizers are used. A stereo microscope, FTIR, and Raman were combined to execute shape analysis and chemical identification for microplastics selecting in the sediment and the surface water based on the existed spectral database (Niu et al., 2022). The results showed that the existed forms of microplastics were fragment, fiber, and film respectively. The main polymer types in the sediment sample were PE (65%), cellulose (17%), and PP (12%), and the main polymer types in the surface water were PE (50%), cellulose (38%), and PET (11%). This study indicates that the form and type of microplastics could achieved via a microscope and spectral database and it is vital to supplement the spectral database of microplastics. Lin et al. studied the properties of microplastics using SEM-EDS and μ-FTIR (Lin et al., 2021). The results showed that the microplastic accumulation in the sediments of the East Coast had increased for several decades since the 1960s. At the same time, six synthetic polymers were identified in the sample including PP, PE, PS, PET, PVC, and PP-PE copolymer. Among them, the identification rate was 95.32%, 90.75%, 90.25%, 78.70%, 83.63%, 88.99% respectively (Fig. 3) and the proportion was 28.57%, 23.81%, 19.05%, 14.29%, 9.52%, and 4.75%. Meanwhile, the results demonstrated that this study may provide important data for the assessment and mitigation of the impact caused by microplastics in the Marine Environment. A high throughput screening method combined near-infrared hyperspectral imaging and chemometric model (SIMCA) was developed to determine the polymer type of microplastics (Vidal and Pasquini, 2021). The results showed supervised soft independent modeling of class analogy (SIMCA) model had high sensitivity and high specificity both over 99% for PE, PP, PA, PET, and PS. The method could directly measure the microplastics ranging from 150 to 300 μm, but it is difficult for the precise assessment of small microplastics' shape and size. This study shows the combination of HSI-NIR and classification models has the potential to microplastic-type characterization screening. Li et al. used THZ combined with the least square support vector machine to study the pollution levels of microplastics in the soil in different regions (Li et al., 2020), the research showed that the mean R^2 was 0.9895 and RMSE was 0.0007 for LDPE while R^2 was 0.9831 and RMSE was 0.0009 for PVC. The data shows that terahertz combined with the LS-SVM model has a good effect on predicting the degree of soil microplastic pollution. Shan et al. used HSI and stoichiometry to characterize PE particles in soil by obtaining average hyperspectral of various materials (Shan et al., 2018). Results presented that when using support vector machine (SVM), the detection accuracies were 84% and 77% respectively for white PE (the diameter of 1–5 mm and 0.5–1 mm) and 58% and 76% respectively for black PE (the diameter of 1–5 mm and 0.5–1 mm), which indicated that SVM is a suitable method to detect white PE in soil.
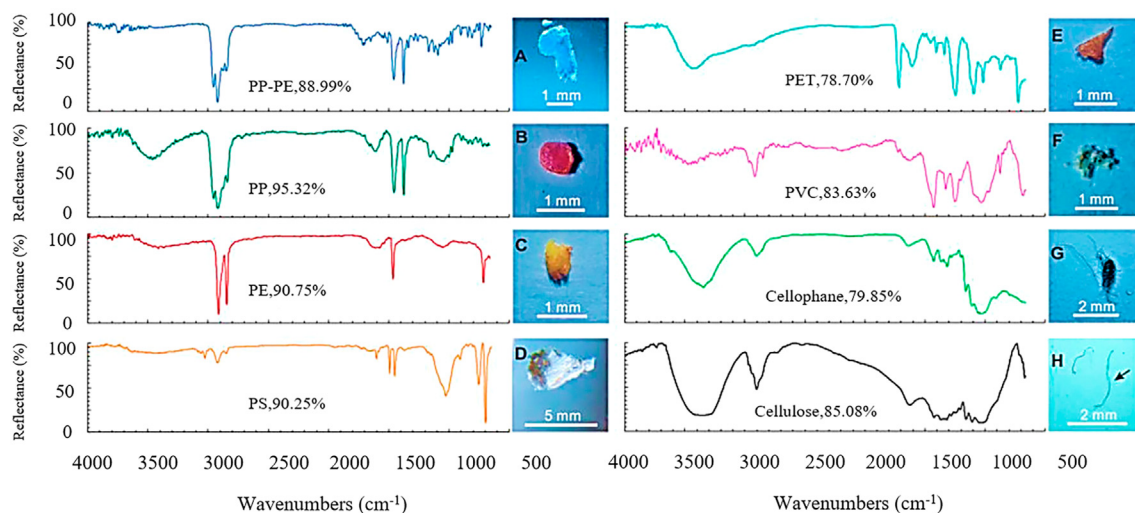
Fig. 3. The feature curve and identification rate of PP, PE, PS, PET, PVC and PP-PE copolymer (Lin et al., 2021).

The spectral analytical method is widely used in the detection of microplastics in soil because of its high sensitivity. Different spectral detection methods have different characteristics. HSI is suitable for the detection of large areas and a wide range of microplastics and THz is suitable for the detection of high thickness microplastics due to its strong penetration. Besides, Raman and FTIR are suitable for the detection of single and small microplastics and the detection limits reach 1 μm and 10 μm respectively. However, the main problem at present is to improve the detection limit of microplastics. The LOQ of Raman is 1 μm, which is the minimum value achieved by the current spectroscopic technology for the detection of microplastics. However, the spectral distortion of Raman in the detection of microplastics with a particle size of 1 μm is serious. FTIR is easily affected by the surface roughness and shape of samples (Shim et al., 2017). The development of THz, HIS, and other technologies in the detection of microplastics in the soil is still slow and the data processing method is single (SVM and SIMCA). What's worse, the research on microplastics detection using machine learning method is very rare. At present, progress has been made in the weathered microplastics in the soil, but the technology only remains in the establishment of a spectral database and optimal assessed wavenumbers. Therefore, the development of portable FTIR spectrometers, portable THz spectrometers, portable HSI spectrometers with high penetration capacity, and the optimization of spectral data processing methods are important research directions in the future.

3.3. Research on other analytical methods for microplastics

SEM-EDS and HPLC are two effective methods in the detection of microplastics. These two methods are complementary in chemical composition identification, for SEM-EDS does not provide the chemical information of the sample while HPLC only provides the chemical information. SEM-EDS can not only be used to characterize the surface morphology of microplastics; but also can be used to determine the elemental composition of polymers based on the diffraction and reflection of the surface-emission radiation of microplastics with a sample capacity of 5–10 mg. HPLC has a potential in the detection of microplastics due to the high sensitivity and low detection limit and it is often used as a terminal detection method. Nevertheless, it is destructive to the sample.

Mehdinia et al. identified microplastics samples from the Caspian Sea by SEM-EDS analytical method (Mehdinia et al., 2020), combined with observation techniques of polarized light microscope and μ-Raman. The results of the elemental analysis demonstrated that C and O were the major constituents of polymers and some other elements were also detected in the studied samples including Fe, Ba, Na, Si, Al,

and so on. This research provides data support for the truth that microplastics can be adsorbed by metal elements. Lin et al. studied the properties of microplastics using SEM-EDS and μ-FTIR (Lin et al., 2021). The SEM images of microplastics were obtained and the morphological characteristics were observed (Fig. 4 (a)). The results demonstrated that most microplastics particles exhibit cracked and porous surfaces, suggesting that the effect of weathering and fragmentation. Deng et al. used SEM-EDS to show the mechanical erosion and chemical weathering on the surface of microplastics (Fig. 4 (b)) and Cr, Zn, Pb, and Cd were observed in the elemental composition (Deng et al., 2020). The contents of Cr, Ni, Cu, Zn, Pb, As, and Cd accumulated in microplastics had no correlation with the total contents in sediments except for Hg, indicating that they may not be elements in sediments. This study proved that microplastics may be carriers of heavy metals. A combination of Raman, ATR-FTIR, and SEM-EDS was used to detect and identify the microplastics acquired from the gastrointestinal tract and gills of fishes in Malaysia coastal waters (Jaafar et al., 2021). The recovery rate of examined microplastics in the gastrointestinal tract and the gills were both greater than 85% (86% in the gastrointestinal tract and 92% in the gills). PE, PP, and PS were found in the examined microplastics using the intensity of specific absorption band (3400 cm-1, 1595 cm-1, and 1045 cm-1 for PE) and characteristic peaks (1640 cm-1 and 998 cm-1 for PS, 2950 cm-1, 1460 cm-1, and 1360 cm-1 for PP). SEM images indicated environmental exposure of microplastics would lead to the different surface characteristics and Ca, Na, Cl, Cr, and Fe were found on the surface of PE using EDS spectrum, suggesting the adherence of heavy metals. This study concludes that SEM-EDS and spectrum method are efficient at the detection and identification of microplastics. Li et al. used SEM to manifest that microplastics have different surface characteristics and different crystallinities (Li et al., 2018b). The result showed that PA had the adsorption capacity of the strongest antibiotics and the distribution coefficient was at the range of 7.36 ± 0.257–756 ± 48.0 L/kg. It reaches the conclusion that PA can be served as a carrier for antibiotics in the aquatic environment.

Hintersteiner et al. characterized the polymers by HPLC-UV (Hintersteiner et al., 2015) and the results showed that this method had a high recovery rate for microplastics, ranging from 92 to 96%. However, it acted as an auxiliary means in the detection of microplastics. Tiwari et al. used fluorescence microscopy, FTIR, and SEM-EDS technique to evaluate microplastic particles on beaches off the coast of India (Tiwari et al., 2019), and the results showed that the concentration of microplastics in beach sand ranged from 45 ± 12 particle/kg to 220 ± 50 particle/kg and the most abundant type of plastic is polyethylene (about 43%). It can also be concluded from this study that
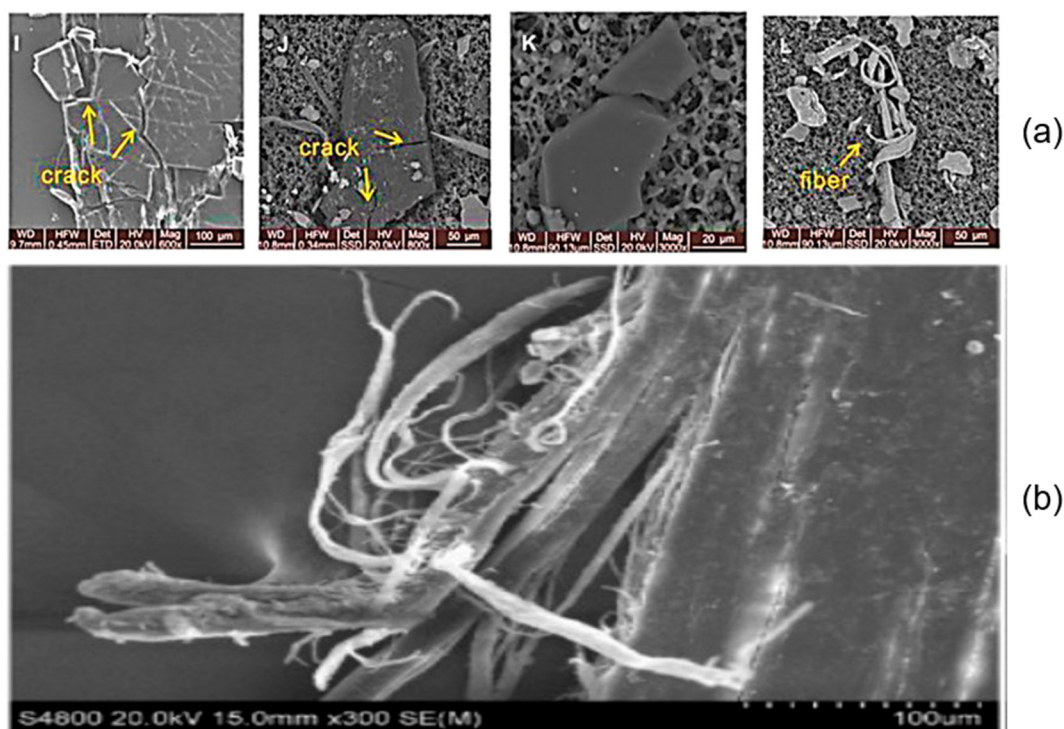
Fig. 4. The images of morphological characteristics (a) (Lin et al., 2021) and mechanical erosion (b) (Deng et al., 2020) observed by SEM.

fluorescence microscopy combined with ATR-FTIR and SEM-EDS is quite suitable for the characteristics of microplastics in beach sand. The abundance and surface texture of microplastics in the sediments along the Beijiang River were investigated by μ-FTIR and SEM-EDS by Wang et al., and the abundance of microplastics ranged from 178 ± 69 to 544 ± 107 particle/kg (Wang et al., 2017a, 2017b). Additionally, SEM images showed that pits, cracks, flakes, and viscous particles were common degradation patterns while EDS spectra showed differences in metal element types at different surface parts of individual microplastics, suggesting that the environment may cause the microplastics to carry the metal elements. The combination of SEM-EDS and optical microscopy was applied to screen microplastic particles selected from fish guts based on the size, morphology, and chemistry (Wang et al., 2017a, 2017b). PVC particles showed distinctive elemental signals and from the SEM images, the cracks, biofilms, radiolarians, and crustaceans were found on the surface of microplastics. This study indicates that SEM-EDS combined with optical microscopy is useful for monitoring the plastic degradation in the environment. Qin et al. used FTIR and SEM-EDS to investigate microplastic pollution in sediments of Suhai Lake, Ulan (Qin et al., 2020), and the abundance of microplastics ranged from 24 ± 7 to 14 ± 3 particles/kg. What's more, the results made by FTIR indicated that the main types of microplastics are PE, PP, and PVC and the results obtained by SEM-EDS showed that microplastics are filled with cracks and holes rather than a smooth surface. This study suggests that these microplastics may provide a site for other pollutants to attach, which may provide a reference for future research on microplastics in the freshwater environment. Zhang et al. used HPLC-MS to analyze 58 kinds of pet (cat and dog) food and 78 pet feces samples collected in Albany, New York, USA (Zhang et al., 2019), and the abundance of PET ranged from 1500 to 12,000 ng/g, which indicated that diet was also a source of PET exposure, providing suggestions for future pet food protection.

SEM-EDS generally needs to be combined with vibration spectroscopy for the detection of microplastics, which acts as an auxiliary part of the analysis. At present, there are few studies on independent detection of microplastics by SEM-EDS, possibly because this method cannot display chemical composition information (Lv et al., 2020). There are few studies on the detection of microplastics by HPLC and the existing studies do not provide accurate polymer identification information. Therefore, further study is greatly preferred. According to the strengths and drawbacks, it is concluded that the joint detection of SEM-EDS and HPLC in the future may break through the bottleneck of the current microplastics detection research. The summary of the Research on other analytical methods for microplastics is shown in Table 3.

4. Conclusion and prospect

4.1. Conclusion

At present, the primary analytical method is vibration spectroscopy, which can provide the physical and chemical characteristics of microplastics without causing damage to the sample. Furthermore, the vibration spectroscopy method mainly includes FTIR and Raman, extensively studied microplastics from water and soil. In recent years, research on airborne microplastics has gradually emerged, but most of the research published so far has focused on atmospheric deposition and a single subject. In addition, Raman is easily disturbed by the fluorescence background, which limits its rapid development. FTIR has a high spatial resolution, high spectral noise, and poor identification effect on aqueous samples. The thermal analytical method is a destructive identification method, making it impossible to obtain information on the quantity and shape of microplastics. The main disadvantage of Pyr-GC–MS is that the microplastics must be placed manually in the pyrolysis reaction tube and the sample mass is only 0.5 mg. However, the spectrum database of common plastic types should be established to complete the detection of microplastics. TED-GC–MS improves the sample mass to 100 mg and overcomes the limitation of sample contamination of the reaction tube. Still, the high temperature is up to 1000 °C and limits its development. DSC has a good prospect for the analysis of microplastics in water in the future. However, this method requires pretreatment and only has good detection results for PE and PP types microplastics. To conclude, the reaction temperature of the thermal

Table 3
Summary of the research on other analytical methods for microplastics.

Analysis method	Sample source	Sample type	Element type	Sample abundance	Reference
SEM-EDS [1], polarized light microscope and μ-Raman [2]	Caspian Sea	–	C, O, Fe, Ba, Na, Si, Al, and so on	–	(Mehdinia et al., 2020)
SEM-EDS and μ-FTIR [3]	East Coast	PP, PE, PS, PET, PVC and PP-PE copolymer	–	–	(Lin et al., 2021)
SEM-EDS	sediments	–	Cr, Ni, Cu, Zn, Pb, As, and Cd	–	(Deng et al., 2020)
SEM and XRD [4]	aquatic environment	PA, PS, PE, PP, and PVC	–	–	(Li et al., 2018b)
Fluorescence microscopy, FTIR [5] and SEM-EDS	beach	PE	–	45 ± 12 particle/kg to 220 ± 50 particles/kg	(Tiwari et al., 2019)
μ-FTIR and SEM-EDS	Beijiang River	–	–	178 ± 69 to 544 ± 107 particles/kg	(Wang et al., 2017a, 2017b)
FTIR and SEM-EDS	sediments of Suhai Lake	PE, PP, and PVC	–	24 ± 7 to 14 ± 3 particles/kg	(Qin et al., 2020)
HPLC-MS [6]	pet food	PET	–	1500 ng/g to 12,000 ng/g	(Zhang et al., 2019)

Note: [1] Scanning electron microscopy energy dispersive spectroscopy, [2] Raman spectroscopy, [3] microscope and Fourier transform infrared spectroscopy, [4] X-ray diffraction, [5] Fourier transform infrared spectroscopy, and [6] High-performance liquid chromatography mass spectrometry.

analytical method is high and the leakage of combustion products of microplastics is easy to cause environmental pollution. Terahertz spectroscopy (THz) has the characteristics of solid penetration and high sensitivity, but its spectral signal-to-noise ratio is low, and the instrument is expensive and bulky. High spectrometry imaging (HSI) can directly provide samples of visual effects, whose images contain hundreds of narrow from visible light to the infrared spectral band and tens of thousands of pixel space. Therefore, according to each pixel space, we can quickly identify the chemical composition of the microplastics, or other information such as size, shape, and so on. This method provides a new way for microplastics pollution monitoring. However, the rapid development of this method is blocked by complex operation processes and low imaging quality. Besides, the machine learning method is developed slowly in detecting microplastics combined with the spectral analytical method. SEM-EDS and HPLC are rarely used in the identification of microplastics. At present, SEM-EDS is mainly used for the identification of Nano-plastics. However, this method does not provide the chemical information of plastics. And HPLC is adaptable for the analysis of large samples. Theoretically, the chemical composition of samples can be obtained. At present, PA, PS, PE, PP, and PVC in nature have been identified by SEM-EDS, and only their absorption composition and absorption amount have been obtained. Therefore, SEM-EDS need a further development.

4.2. Prospect

It is essential to solve the fluorescence background interference of the Raman spectrum. Nowadays, unconventional Raman spectroscopy, such as nonlinear Raman spectroscopy and face-off Raman spectroscopy, can both improve the intensity of Raman and the signal-to-noise ratio of spectral data. The enhancement of signal intensity through nonlinearity, such as CARS and SRS, opens a new way for real-time analysis of MPs. In CARS and SRS, strong signals are obtained only from the molecular vibration patterns of interest. Therefore, fluorescence interference is overcome, making data analysis more accurate and the sample pretreatment becomes unnecessary. For microplastics greater than 20 μm, FTIR technology has a better effect because of its simple operation. Although the detection limit is lower than that of Raman spectroscopy, the impact is more significant than that of Raman spectroscopy. Moreover, the use of the FTIR method does not have to worry about the interference of fluorescence background in the Raman spectrum. In the future, terahertz spectroscopy (THz) technology can be developed to give play to its high sensitivity and strong penetration advantages. The invention of a portable terahertz spectrometer is a challenge for the future because of the large size of current terahertz spectrometers and raw use in detecting microplastics. The identification and qualitative method of HSI provides a new way for microplastics pollution

monitoring, but the detection limit is negative, up to 300 μm. Therefore, reducing the detection limit of HSI technology will be conducive to real-time tracking of microplastic pollution. SEM-EDS and HPLC are promising, for these two methods are complementary in the identification of chemical constituents. SEM cannot obtain the chemical composition, and HPLC can only get the chemical composition, so the two methods can be probably combined for the identification of microplastics. At present, the identification methods of microplastics in different environments do not have uniformity, so it is necessary to establish a unified detection and identification method for microplastics in different environments and achieve a unified standard of detection methods. To reduce the detection limit of the existing spectral detection methods, a variety of analytical methods and data processing methods, such as machine learning methods should be combined as far as possible for the detection and analysis of microplastics to find a non-destructive, efficient, and high-throughput detection method.

Declaration of competing interest

Authors declare that there are no conflict or interests.

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