Analytical Methods for Plastic (Microplastic) Determination in Environmental Samples

G. Dierkes, T. Lauschke, and C. Földi

Contents

Abstract Beside several studies about the occurrence of microplastic (MP) there is still a huge gap of knowledge regarding the dynamic processes of MP distribution and fate. Consequently, there is a need for reliable, fast, and robust analytical methods for MP monitoring. However, due to the physicochemical attributes of plastic, new analytical approaches fundamentally different from those for most other environmental contaminants are required. Promising strategies include spectroscopic and thermo-analytical methods. The two vibrational spectroscopic methods, Fourier-transform infrared spectroscopy (FT-IR) and Raman spectroscopy, have been implemented for MP detection. Especially in combination with particle finding software or a focal plane array (FPA) detector, they enable reliable determination of MP particle numbers in environmental samples. In recent years, different thermo-analytical techniques, such as pyrolysis (Py), thermogravimetric analysis (TGA), and differential scanning calorimetry (DSC) have been adapted for MP detection. All thermo-analytical methods are based upon measurement of physical or chemical changes of the polymer under thermal treatment. While DSC measures differences in

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heat flux caused by phase transitions of the polymer, TGA-MS is based upon detection of specific thermal degradation products. By means of a gas chromatographic separation step, an enhanced detection of the marker compounds is possible, enabling a more sensitive MP detection even in complex matrices. The extent of analytical information obtained as well as the complexity and effort of the methods increase by TGA-DSC < TGA-MS < Py-GC-MS/TED-GC-MS. The results are comparable to those of spectroscopic methods (FT-IR, Raman), but both techniques have different benefits and limitations. While thermo-analytical methods require minor sample pretreatment and reveal mass concentrations, spectroscopic methods are non-destructive and yield particle numbers and size distribution by imaging techniques. Whichever is the most suitable method depends on the scientific question and what kind of information is required.

Keywords Microplastic analysis, Spectroscopy, Thermo-analytical methods

1 Introduction

Coming along with the emerging awareness of microplastics (MP) as a meaningful contaminant in aquatic systems, there is a need for reliable, fast, and robust analytical methods for MP monitoring [1]. However, due to the high molecular masses of the polymers, they are not suitable for direct analysis by standard techniques in environmental science such as liquid chromatography (LC) or gas chromatography (GC) coupled to mass spectrometry (MS). The physicochemical attributes of plastics ask for new analytical approaches fundamentally different from those for most other environmental contaminants. In order to solve this issue, intensive scientific development work was done worldwide during the last decade [2–9]. Different strategies were developed, among which thermo-analytical methods and spectroscopic methods are the most promising.

Synthetic polymers consist of one or more types of small organic molecules, the so-called monomers, linked by covalent bonds. During different kinds of polymerization reactions, the monomers are polymerized to macromolecules with molecular weights of several thousand g/mol. The particular polymer types vary in composition and arrangement of a large number of available monomers. For the characterization of a polymer, the building monomers have to be identified and their order in the molecular chain has to be elucidated. Beside spectroscopic methods, thermo-analytical methods are standard applications for the characterization of synthetic polymers in polymer science [10–12].

Microscopy coupled with vibrational spectroscopy for chemical characterization enables visualization and identification of small particles such as MP. Identification is based upon comparison of recorded spectra to those in spectra libraries. Sample imaging techniques can provide morphological parameters such as particle size, shape, and color. By scanning of a representative sample surface, MP particle numbers and a rough estimation of MP mass can be determined.

In recent years, different thermo-analytical techniques (pyrolysis, thermogravimetry, and differential scanning calorimetry) have been adapted for MP detection [3, 9, 13]. These methods can be applied for qualitative and quantitative MP detection in environmental samples. Therefore, thermo-analytical methods are a good alternative or complement to the widely used spectroscopic methods [14]. Today there is no harmonization of the existing analytical methods and only a few comparative studies exist [15, 16]. Consequently, comparison between results of different studies is limited.

In the following sections, the different techniques for the analytical investigation of MP are introduced and benefits and challenges are discussed. Furthermore, a comparison of the benefits and limitations of the different methods is drawn.

2 Description of Different Methods

In contrast to other contaminants, MP do not occur dissolved or sorbed to solids in the environment, but as discrete particles visual for the naked eye or by microscopy. This may lead to the misjudgment that MP determination could be done by visual sorting and counting. However, optical microscopy is not suitable for reliable identification of MP in environmental samples. Classification especially of small particles (<100 μm) by properties such as color, shape, and hardness is prone to errors and leads to false estimation of MP burden [17, 18]. Accuracy can be improved by use of staining with fluorescence dyes such as Nile Red [19–21]. Nile red adsorbs to lipophilic surfaces like those of MP, while hydrophilic and inorganic surfaces are not stained [22]. Under a UV-lamp or a fluorescence microscope MP can be identified by fluorescence. For distinct results and identification of the polymer types, a chemical characterization of the MP particles is necessary [23]. This can be realized by spectroscopic or thermo-analytical methods.

2.1 Spectroscopic Methods

FT-IR and Raman spectroscopy are widespread used methods for MP identification. Both spectroscopic methods are based upon excitation of intramolecular vibrations by electromagnetic radiation. In FT-IR-spectroscopy, the absorption of IR light (wavenumbers between 400 and 4,000 cm^{-1}) is measured. Positions and intensities of the absorption bands depend on the resonance frequencies of vibrations and the magnitude change of the atomic bond's permanent dipole moment. In contrast, Raman spectroscopy is based on measurement of a shift in the wavelength of a scattered laser beam. Interaction of the photons and the sample molecules is related to a change in the polarizability of chemical bonds. Due to these fundamental

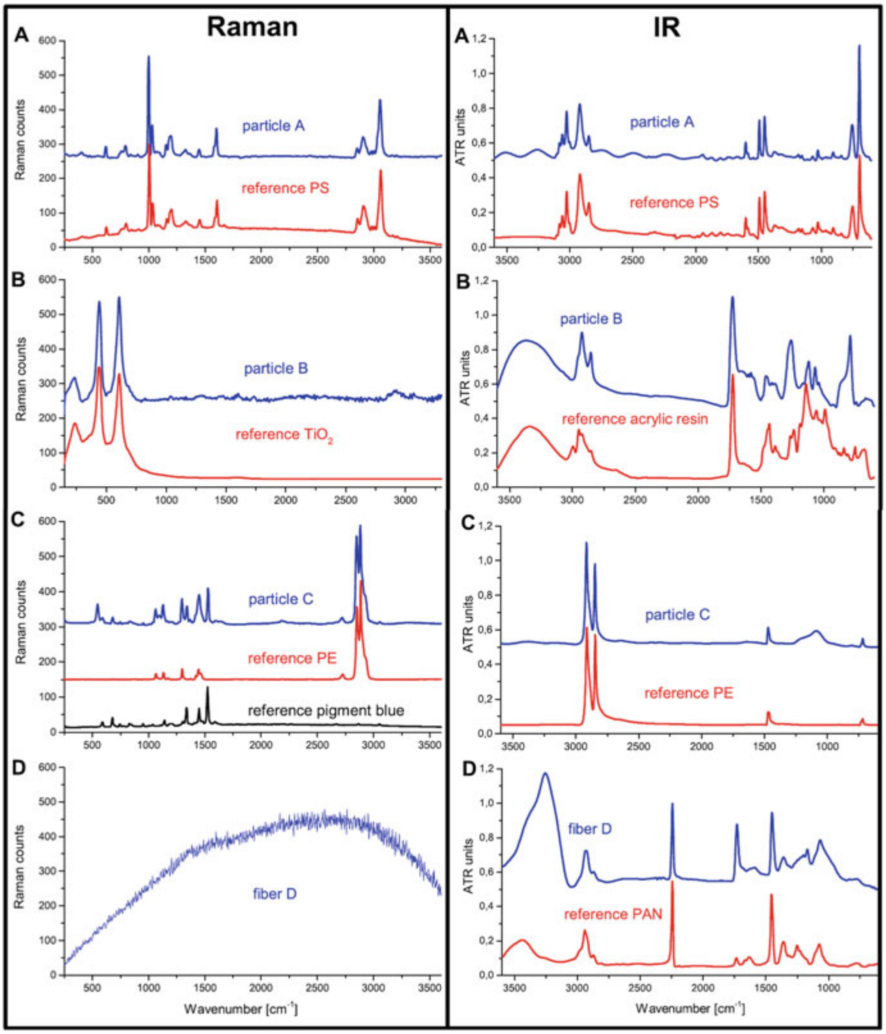

Fig. 1 Raman spectra (left) and ATR-FTIR spectra (right) of MP (blue) each in comparison with a reference (red) (Reprinted by permission from Springer Nature, Anal Bioanal Chem, Käppler et al. [24], 2016)

differences in the physical principles of the absorption processes, both spectroscopic methods are complementary, since some kinds of vibrations are IR active while Raman inactive and vice versa (Fig. 1). In both cases, the resulting spectra consist of characteristic bands for the functional groups in the molecules and are like a chemical fingerprint of the substances. Thus, characterization of the chemical structure and identification of polymers by comparison with reference spectra is possible [24]. By employing spectra libraries and matching software identification can be done by automated routines. The success of matching depends upon the comprehensiveness of the library and the matching algorithms of the software.

For MP identification in environmental samples, a division into two size fractions is recommended: (1) particles >300 μm which can be handled manually and (2) particles <300 μm which are too small for manual picking. For identification of the larger particles, FT-IR in attenuated total reflection (ATR) mode is the best choice [25–27]. The isolated particles are put upon a crystal probe and IR spectra from the near surface region of the sample are recorded. Due to the direct contact between sample and crystal and the poor penetration depth, strongly contaminated particle surfaces may lead to cross contamination and adulterated spectra. Therefore, MP isolated from environmental samples may need cleaning of the polymer surface by acids, bases, or oxidants such as H_2O_2 to remove biofilms or other contaminants. Advanced weathering of polymers leads to chemical modifications of the surface and consequently to an alteration of the IR spectra hampering the identification. Consequently, databases of pristine polymers have to be complemented by spectra of weathered polymers [3].

For analysis of the <300 μm fraction, the particles have to be isolated from the matrix (e.g., by density separation) and purified by chemical or enzymatic digestion of the organic matter (see Stock et al. [28]). Subsequently, they are concentrated onto filters. Coupling a vibrational spectrometer to a microscope enables direct identification of single particles on filters [26, 29]. The filter choice depends on the requirements of the used spectroscopic method. If FT-IR is used in transmission mode, the filters have to be translucent for IR radiation, such as aluminum oxide, silicon, or metal covered polycarbonate [30–32]. For Raman spectroscopy, filters that do not induce background fluorescence are required, such as quartz fiber, polytetrafluoroethylene (PTFE), or silicon filters [31, 33, 34]. The minimum detectable particle size is 10 μm for FT-IR, whereas Raman microscopy can detect particles down to 1 μm. In environmental samples MP are highly outnumbered by natural particles (e.g., clay minerals or organic substances). Such contaminants can hamper the detection of MP by agglomeration and alteration of spectra or strong fluorescence. Therefore, decrease of natural particles and organic contamination by extensive sample pretreatment protocols is essential (see Stock et al. [28]).

There are three different options for particle identification: (1) manual selection of single particles, (2) automated selection by particle finder approaches, and (3) chemical imaging of the filter surface. The manual step-by-step analysis of all particles is very time-consuming. Hence, not the whole filter area is analyzed, but often only less than 10%. The accuracy of the extrapolation depends on the representativeness of the chosen measurement area [3]. More efficient are approaches using particle finding software [33], where high-resolution dark-field images of the whole filter are scanned for particles and a map of all particles is created. Spectra are collected only at those dedicated points [34, 35]. Since numbers of particles in complex environmental samples are very high, particles may be not well separated and agglomerates of small particles may be mistaken for larger particles. Furthermore, analysis of all particles is not possible in a reasonable time. Hence, a diluted sample aliquot or a randomly chosen subset representative for all particles has to be analyzed. The minimal needed number of particles depends on the total number of particles, the ratio of MP to natural particles, and the accepted analysis error. Using a method called "simple random sample of units selected without replacement," Anger et al. [33] calculated a minimum of particle measurements of approx. 6,000 assuming a total particle number of 10^6 containing 0.5% MP and with an accepted error of 20%. Assuming typical measurement times of Raman setups capable of measuring particles between 1 and 5 μm in the range of 10 s per particle, this leads to a total measuring time of approx. 17 h per sample. To reduce the number of the needed particle measurements, Erni-Cassola et al. [19] used the fluorescent dye Nile red for selective staining of MP particles. By fluorescence imaging, the stained particles are mapped and are exclusively considered for chemical identification via spectroscopy. Another approach to reduce measuring time is the use of an IR laser instead of a classical light source in FT-IR. In the so-called Laser Direct Infrared (LDIR) chemical imaging method, very short measuring times of 1 s per spectrum can be realized by focusing a bright laser source onto the particles. The fast spectra acquisition in combination with optical particle finding enables identification of a huge number of particles scattered over a wide area in comparatively short time. Unfortunately, spectral range is limited to 975 to 1,800 cm^{-1} which could be a handicap in polymer identification.

Another option is the automatic chemical imaging of the full area by focal plane array (FPA) detectors [30, 36–38] or Raman imaging [24, 35]. FPA detectors are capable of recording several thousand spectra simultaneously while Raman imaging is realized by time-consuming point-by-point analysis. MP particles are detected by selected bands such as carbon–hydrogen stretch vibration (2,980–2,780 cm^{-1}) in FT-IR. Detected particles are counted and identified automatically by comparison of full spectra. By measuring the full filter area, the bias resulting from extrapolation is circumvented. However, this advantage comes at the costs of long measuring times especially in Raman spectrometry and huge data amounts. Spectral correlations of millions of spectra lead to data analysis times of 4–48 h depending on the used software and hardware [39].

By measuring the dimensions of the identified MP particles, a rough estimation of the mass is possible [38]. More suitable for determination of mass concentrations of MP are near-infrared (NIR) and FT-IR spectroscopic methods in combination with chemometrics [40–42]. By measuring bulk samples mixed spectra of all components are generated. Using multivariate calibration models spectral information about the different polymers can be isolated and used for quantification. So, MP at levels above 0.5 to 1.0 g/100 g depending on the polymer can be detected and classified very rapidly in bulk samples without any chemical pretreatment. Limits of detection are rather high, and applicability of the chemometric model for other matrices and particle sizes than those used for the calibration has yet to be tested. Furthermore, these bulk methods deliver no information about particle sizes and shapes.

Peez, Janiska [43] developed a nuclear magnetic resonance spectroscopy (^{1}H NMR) method for quantitative MP detection. After dissolving the particular polymers in an appropriate solvent, ^{1}H NMR spectra of the polymers are recorded. Quantification is based upon integration of signals showing a polymer specific

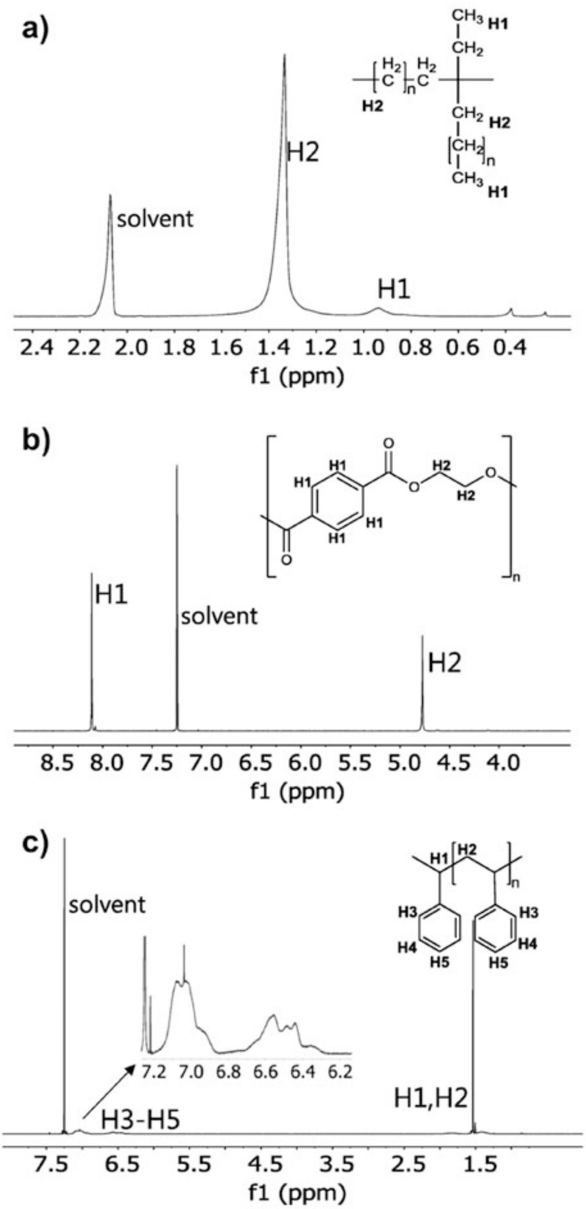

Fig. 2 1H NMR spectra of MP particles and their structural formulas. (**a**) PE granule measured in toluene-d8 at 60°C. (**b**) PET fibers measured in CDCl3/ TFA 4:1 at 25°C. (**c**) PS beads measured in CDCl3 at 25°C. In addition, the enlarged range of 7.20–6.20 ppm is shown (Reprinted by permission from Springer Nature, Anal Bioanal Chem, Peez et al. [43], 2018)

chemical shift (ref. Fig. 2). Limits of detection are in the range of 20–84 μg/mL [43, 44]. Applicability for environmental samples was shown for PET [45]. After chemical digestion, to reduce organic matrix compounds and dissolution in $CDCl_3$ selective determination of PET was realized in water, biofilms, and invertebrates.

The disadvantage of this method is the need of specific solvents for the different polymers and due to the dissolution step information about particle size gets lost.

2.2 Thermo-Analytical Methods

All thermo-analytical methods are based upon measuring physical or chemical changes of the polymer under thermal treatment. At elevated temperatures, polymers undergo phase transitions such as changes in crystal structure and melting. These processes can be observed by differential scanning calorimetry (DSC). During DSC analysis, the difference in heat flow between the sample and a reference is measured over a controlled temperature gradient using a defined heating rate. The result of a DSC experiment is a curve of heat flux versus temperature containing peaks at substance's specific temperatures. These peaks represent the temperature of thermal transitions such as the glass transition temperature, crystallization temperature, and melting temperature. Majewsky et al. [46] determined characteristic endothermic phase transition temperatures for seven polymer types using thermogravimetric analysis (TGA) coupled to DSC (Fig. 3). By integration of the associated peaks, a qualitative and quantitative analysis method for PE and PP was developed. The method was applied for analysis of wastewater samples. However, due to overlapping transition temperatures, the method is not reliable for other polymers [46]. Furthermore, transition temperatures are highly affected by product specific attributes such as fillers, additives, length and branching of the polymer chain. Even

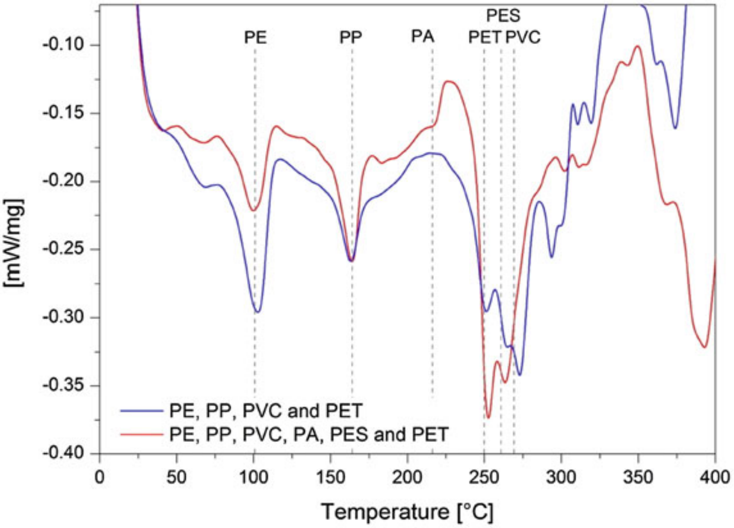

Fig. 3 DSC signals of a mixture of pure polymers. PE and PP show discrete peaks, while the other signals overlap (Reprinted by permission from Elsevier, Sci total Environ, Majewsky et al. [46], 2016)

particle size is a critical parameter, since larger particles can cause interferences by lagged response in terms of an unfavorable mass to surface ratio [3, 47].

Temperatures higher than the decompositions temperature of the polymers lead to fragmentation of the macromolecules and generation of smaller volatile molecules. The resulting mass reduction as a function of the temperature can be monitored by a thermobalance. David et al. [48] developed a thermogravimetric method for MP quantification in soils without sample pre-separations or pre-treatments. The method is based upon mass losses at selected temperatures specific for the particular polymers. To compensate interfering mass losses by the soil matrix they used the so-called soil universal model which was calculated from previously determined relationships between typically observed mass losses and soil properties. The method revealed quantification of PET, PS, and PVC with limits of detection in the range of 0.3–2.2 wt%. For PE determination the method was not suitable, due to overlapping temperature ranges of PE and soil organic matter degradation [48]. Altogether, the method does not enable specific MP detection, and applicability for different kinds of matrices has yet to be tested. More specific detection of MP can be realized by analyzing specific degradation products.

Decomposition of polymers at elevated temperatures is a complex process of different types of reactions, the most common ones being eliminations and rearrangements [49]. Consequently, there is not only one decomposition product, but a pattern of several products. Under standardized conditions (time, temperature, atmosphere), the decomposition process is reproducible and a characteristic product pattern can be obtained for the particular polymers [50, 51]. The fragments of the initial compound are volatile and can be analyzed in the gas phase. FT-IR [52] and mass spectrometry (MS) [53] are the most frequently used detection techniques for analysis of decomposition gases in the so-called evolved gas analysis (EGA-FTIR, EGA-MS) [49]. The fragment pattern is like a fingerprint of the different polymers and can be used for identification, especially in combination with TGA [52–54]. David et al. [54] developed a method for the qualitative and quantitative determination of polyethylene terephthalate (PET) using specific ion fragments of decomposition products resulting from PET (vinyl benzene and benzoic acid). In Fig. 4 typical output for determination of PET in soil is displayed. At the degradation temperature of PET (300–650°C) a clear signal for the PET decomposition compound vinyl benzene can be observed. However, due to interferences by matrix compounds, detection limits of the method are rather high (600 μg/g).

Unfortunately, in most cases the EGA is dominated by small unspecific molecules like H_2O, CO_2, and NH_3, hampering the identification of more complex and specific decomposition products. This disadvantage can be evaded by an additional separation step such as gas chromatography (GC). GC provides separation of the compounds and facilitates identification by provision of retention times and undisturbed mass spectra. Coupling of pyrolysis and GC can be done on-line and off-line. In on-line Py-GC/MS the pyrolysis chamber (filament, micro furnace, or Curie Point pyrolyzer) is directly coupled to the injection system by a heated transfer line or interface and pyrolysis products are directly transferred onto the separation column [10, 55–61]. Major differences between the different techniques lay in

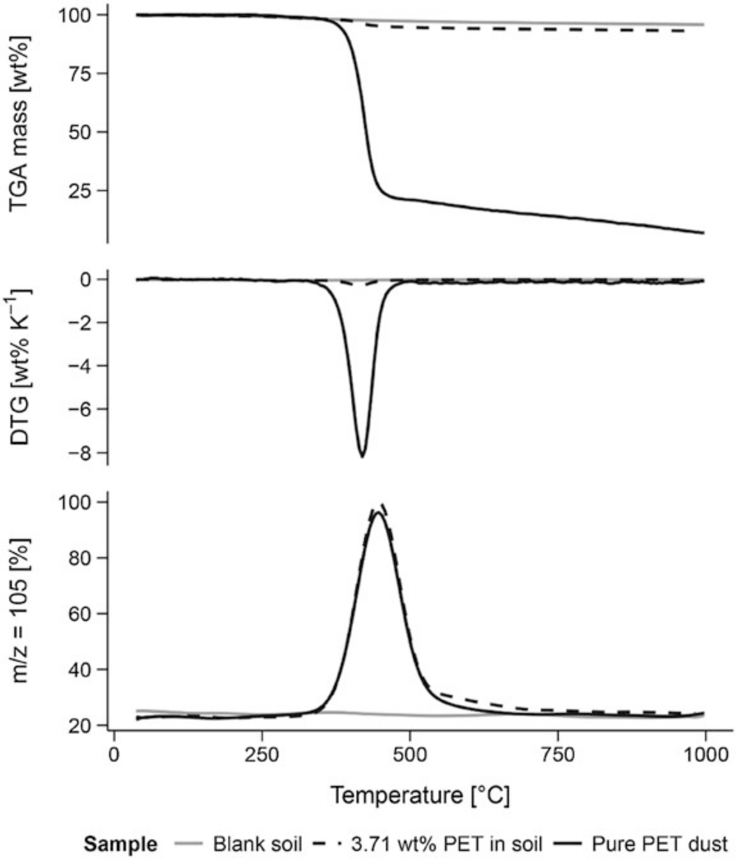

Fig. 4 Output of TGA-MS analysis of PET (Reprinted by permission from ACS Publications, David et al. [54], 2018)

heating rates and sample capacity [62]. Off-line coupling can be realized by trapping the pyrolysate on a sorbent (TED-GC/MS) [63–66] or in a cooled solvent trap [67]. Pyrolysis products are transferred onto separation column by thermal desorption and liquid injection, respectively.

Polymer identification can be based upon specific pyrolysis products or the peak pattern of the pyrogram. Thermal decomposition of some polymers such as polystyrene (PS) results in a small number of specific degradation products, and, therefore, in simple pyrograms with few discrete peaks (ref. Fig. 5a). The pyrogram of polyethylene (PE), for example, is much more complex. It consists of a series of triplets originating from homologous series of alkanes, alkenes, and alkadienes (ref. Fig. 5b). The interpretation of pyrograms of cross-linked polymers like varnishes and resins is very complex and identification of individual decomposition products is very difficult (ref. Fig. 5c). However, identification of the polymers is possible by comparison of the pyrograms with those of reference materials or comprehensive libraries [10, 60, 68, 69].

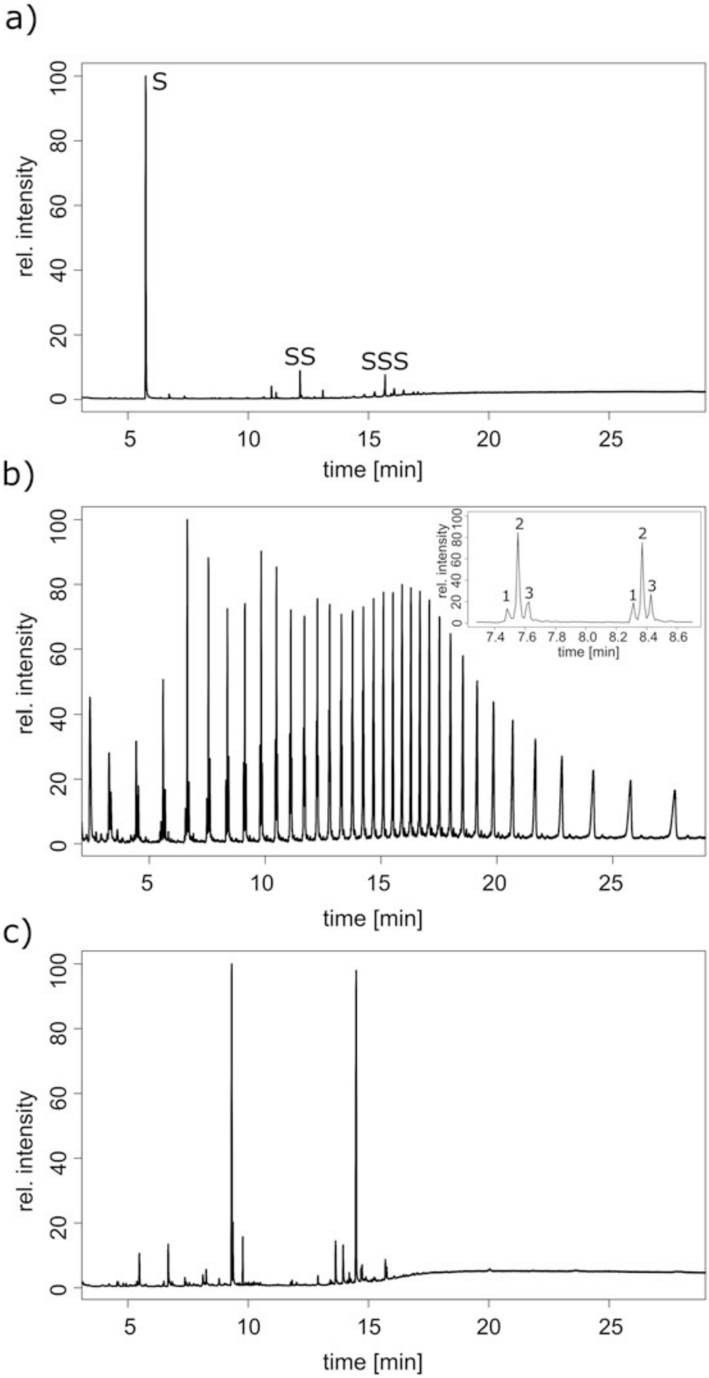

Fig. 5 Pyrograms of different polymers (**a**) Polystyrene: s = styrene, ss = dimer, sss = trimer (**b**) polyethylene: 1 = alkadiene, 2 = alkene, 3 = alkane (**c**) resin

Table 1 Specific indicator compounds for various polymers

Polymer	Indicator compound	Fragment mass	Reference
Polyethylene	α-Alkenes	97, 83	[55, 56, 70]
	α,ω-Alkadienes	95, 82	[55, 56, 70]
Polypropylene	2,4-Dimethylhept-1-ene	126, 70	[55, 56, 70]
Polystyrene	Styrene	104, 78	[55, 56, 70]
	5-Hexene-1,3,5-triyltribenzene	117, 91	[56, 70]
Polyvinylchloride	Benzene	78	[56]
	Naphthalene	128	[67]
Polyethylene terephthalate	Dimethyl terephthalate[a]	194, 163	[56]
	Vinyl benzoate	105, 77	[70]
	Ethyl benzoate	105	[67]
Polyamide	ε-Caprolactam	113, 85	[56, 70]
	N-methyl ε-caprolactam[a]	127, 70	[56]
Poly(methyl methacrylate)	Methyl methacrylate	100, 69	[56]
Styrene butadiene rubber	Vinylcyclohexene	54, 108	[59]
	Styrene	104, 78	[59]
	Cyclohexenylbenzene	104, 158, 129, 115	[66]
Natural rubber	Dipentene	136, 68	[59, 66]

Quantification of MP in environmental samples is still a major challenge for analytical chemists. Thermo-analytical methods using selected degradation products as indicator compounds are promising approaches for MP quantification [2]. These indicator compounds have to be specific for the different polymers and a linear relationship between polymer mass and the amount of indicator compound released during thermal degradation is required. By means of calibration curves, indirect quantification of the polymers is possible using the detector signal of the indicator compounds [62]. However, since some of these degradation products could also be formed from matrix ingredients present in the environmental sample, the selectivity of the indicator compounds has to be evaluated for the respective environmental matrix. Table 1 shows specific indicator compounds for the most important polymers. These compounds have been successfully used for quantification of MP in environmental samples.

Duemischen et al. [65] developed a fully automated two-step method enabling high sample throughput, the so-called thermoextraction-desorption-gas chromatography-mass spectrometry (TED-GC-MS) [65]. In this method, several mg untreated sample (soil, suspended matter) are weighed into a crucible and decomposed in a thermogravimetric analyzer (TGA). Decomposition gases originating from degradation of natural polymers and other matrix compounds in a temperature range of 100–338°C are discarded while degradation products of synthetic polymers emerging in a temperature range of 339–600°C are trapped on a solid-phase absorber. In a second step, the trapped compounds are thermally desorbed and analyzed via GC-MS. By this way PE, PP, PS, PET, PA, and SBR can be directly quantified from environmental matrices without sample pretreatment.

However, high organic contents lead to overloading of the absorber and have to be considered during sample in-weight. Low in-weights result in increased detection limits and representativeness of the analyzed sub-sample may be not given. Due to interferences of inorganic matrix compound with the pyrolysis process matrix matched calibration has to be done [61, 66]. Unice et al. [59] used deuterated internal standards to compensate these effects. However, such standards are not available for all polymers and deuterium exchange during pyrolysis limits the applicability. Therefore, sample pretreatment to reduce the inorganic and organic matrix is recommended for complex matrices. Fischer and Scholz-Böttcher used enzymatic and chemical digestion in combination with density separation for MP analysis in fish [56]. This clean-up is very effective but extreme time-consuming and hard to automate. Alternatively, the polymers can be extracted by organic solvents such as tetrahydrofuran or dichloromethane at elevated temperatures and pressure [55, 57, 58, 71]. In a first step organic matrix compounds are extracted by an organic solvent such as methanol in which most of synthetic polymers are insoluble. In a second step polymers are extracted and separated from the inorganic matrix. The extraction procedure provides high in-weights in the range of 1–10 g, reduction of organic matrix, and enrichment of the polymers. These methods are limited to polymers soluble in the particular solvent under the chosen conditions. Cross-linked polymers such as elastomers and duroplasts are scarcely soluble and currently no extraction methods exist.

Beside the polymer matrix, additives are important and environmentally relevant constituents of plastics. These low molecular substances are added to polymers to improve their attributes such as stability, flexibility, or flame resistance. They can be leached into the environment and harm organisms by toxic effects [72–75]. Pyrolysis/thermal desorption gas chromatography–mass spectrometry (Py/TD-GC–MS) allows solvent-free screening of additives and a subsequent identification of the polymer [60, 76]. In a first step, the additives are thermally desorbed from the polymer matrix at temperatures in the range of 280 and 320°C. After GC-MS analysis of the additives, the remaining polymer matrix is pyrolyzed [77]. Figure 6 shows the thermogram and pyrogram of a plastic sample. The thermogram shows the detected additives: Among others, the UV filter octrizole can be identified. In the pyrogram, however, degradation products specific for polycarbonate such as bisphenol A can be found.

Complete thermal degradation permits determination of the elemental composition (C, H, N, S, O) of polymers which differs distinctly from those of biogenic and inorganic materials. Malow et al. described an approach using elemental analysis combined with Overdetermined Equation Method (EA-OEM) based on different ratios of the elements H, C, O, N, and S in polymers and environmental matrices [78]. The method is limited to relative high MP concentrations (LOD: 33 mg/g) and matrices containing biogenic material with known and stable elemental composition. Biogenic material with high C and H contents such as fats cannot be distinguished from synthetic polymers by this method. Consequently, they have to be removed during sample preparation. The method was validated only for PE and PP, since these two polymers show the strongest differences in elemental composition

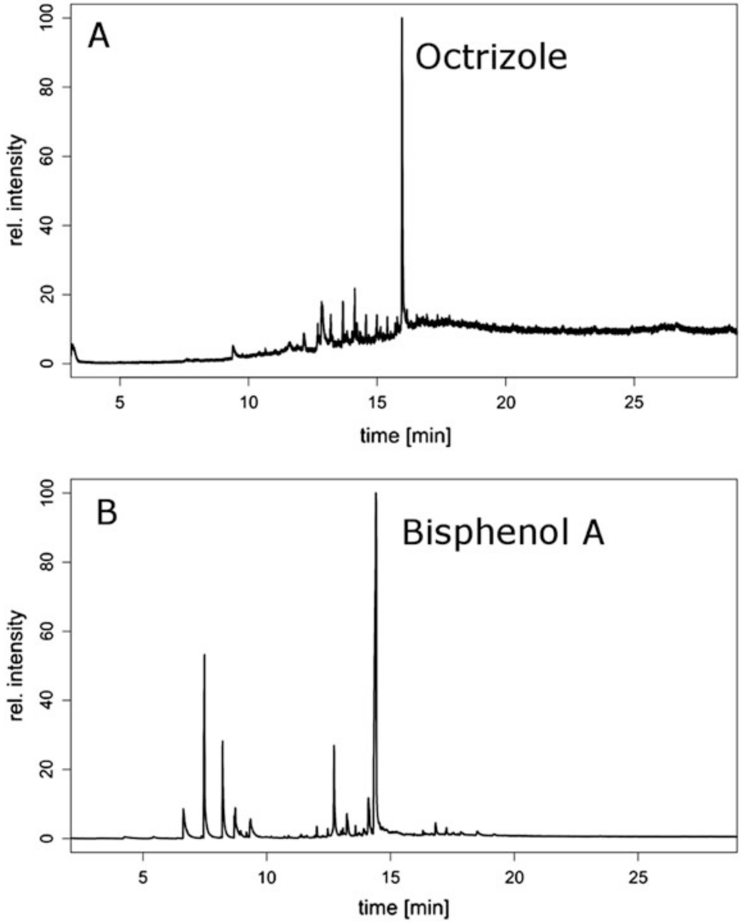

Fig. 6 (**a**) Thermogram and (**b**) pyrogram of a plastic particle

compared to biogenic material. Applicability of the method to other polymers with elemental compositions more like biogenic material such as polyesters has to be tested. However, beside these drawbacks the method reveals reliable results for PE and PP in a consistent matrix like industrial discharge.

2.3 Other Methods

Apart from thermal degradation, polyesters can be depolymerized by chemical treatment. After alkali-assisted thermal hydrolysis in butanol, polycarbonate (PC) and PET can be analyzed by LC-MS [79]. Determination is based upon detection of the emerging building blocks bisphenol A and terephthalic acid. The use of a very sensitive LC-MS-MS method enables very low detection limits in the μg/kg range. However, the suitability of terephthalic acid as specific marker for PET is questionable since it can be released from other polyesters, terephthalate plasticizers, or even natural compounds like humic acids.

3 Discussion

Spectroscopic and thermo-analytical methods are suitable for the identification of MP in environmental samples. The results of both methods are comparable, but both techniques have benefits and limitations [14]. Table 2 summarizes the differences and specifics. Spectroscopic methods are very fast and deliver identification results of isolated particles regardless of the mass. There is only a limitation in particle size (FT-IR >10 μm, Raman >1 μm) [24]. In Py-GC-MS, detection limits depend strongly on the polymer type and lie in the range of ng (e.g., PS) and μg (e.g., PE). Additionally, spectroscopic methods in combination with microscopes reveal information about particle sizes, shapes, and numbers. Another advantage is that spectroscopic methods, in opposition to thermo-analytical methods, are non-destructive and enable additional analyses using the same particle. On the other hand, identification by spectroscopic methods may be disturbed by impurities at the surface of the MP particles, such as biofilms or inorganic contaminants. Such influences are mostly negligible when using thermo-analytical methods.

Furthermore, Py-GC-MS provides a deeper insight into the molecular structure of polymers. In addition to the type of monomers building up the macromolecules, the arrangement of the monomers within the polymer can also be determined by the occurrence of specific degradation products such as oligomers. For example, in Fig. 7 an unknown polymer could be identified as styrene acrylonitrile copolymer with an alternating arrangement of the two monomers acrylonitrile and styrene. The

Table 2 Comparison of thermo-analytical and spectroscopic methods

	DSC-TGA	TGA-MS	Py-GC-MS	NIRS	Spectroscopy (FT-IR/Raman)
Identification of polymer	Limited	Yes	Yes	Yes	Yes
Arrangement of monomers	No	Limited	Yes	No	No
Additives	No	Yes	Yes	No	Severely limited
Disturbance by biofilm and inorganic contaminants	No	No	No	No	Yes
Analysis time	2.7 h	3.2 h	>30 min	5 min	6–24 h (ca. 10% of filter surface)
Non-destructive	No	No	No	Yes	Yes
Particle size distribution	No	No	No	No	Yes
Particle number	No	No	No	No	Yes
Quantification (mass concentration)	Limited	Limited	Yes	Limited	Severely limited

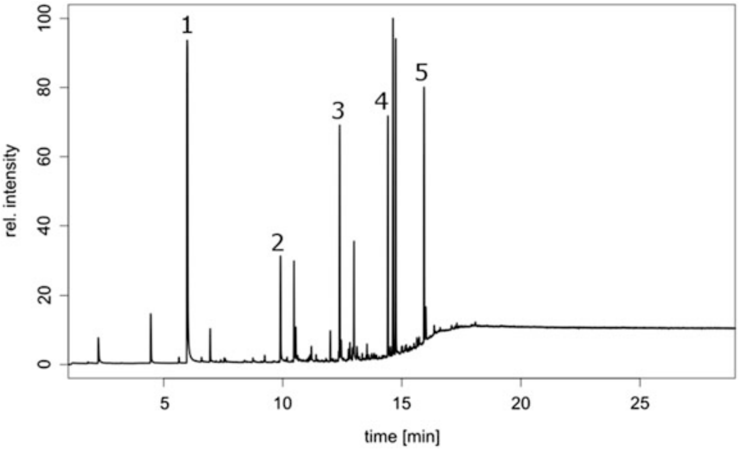

Fig. 7 Pyrogram of styrene acrylonitrile copolymer (SAN). 1: styrene, 2 + 3: S-AN dimer, 4: AN-S-AN trimer, 5: S-AN-S trimer

alternating arrangement, instead of a random or blockwise arrangement is observable by the absence of dimers and trimers consisting of only one kind of monomer and the occurrence of the trimers consisting of two acrylonitrile and one styrene or two styrene and one acrylonitrile units, respectively, in alternating order. Such detailed information can be helpful for the identification of sources of MP emissions and is not accessible by spectroscopic methods.

An interesting example in which such an extensive characterization is indispensable is the differentiation between PS and polystyrene–divinylbenzene resin (PS-DVB) [27, 80]. While PS is a widely used polymer for a multitude of applications (thermal isolation, packaging, electronic cases), PS-DVB is exclusively used for specific applications such as ion exchange materials. Due to their different fields of application, different kinds of emission sources are likely. Both polymers consist of PS chains, but in the case of PS-DVB there are crosslinks between the chains formed by incorporation of the bivalent divinylbenzene. Due to this small difference in molecular structure and the fact that both polymers contain the same chemical groups, distinguishing between both polymers is very difficult when using vibrational spectroscopy (FT-IR, Raman). In contrast, thermo-analytical methods can distinguish between PS and PS-DVB using the thermal degradation product 1,4-divinylbenzene as specific marker for PS-DVB.

Another characteristic hint to the intended use of plastic products and therefore to possible emission sources is provided by the analysis of additives. Typical concentrations of many additives lie in the range of a few mg per kg polymer which is too low for detection by spectroscopic methods. Using thermo-analytical methods, sequential determination of additives and identification of the polymer are possible in one small particle [60, 77].

In summary, both methods provide complementary results. This is especially true for determination of particle numbers and mass concentrations [3, 4, 81].

Determination of particle numbers is possible by microscopy coupled to vibrational spectroscopy. By recording spectra for each particle, reliable identification of the MP particles is provided. However, due to high particle numbers especially for particles <50 μm, measuring times lie in the range of several hours (18 h [34]) per sample. Usage of particle finding software in combination with a reduction of the analyzed particle number by statistical methods leads to a significant decrease of the analysis time. Due to an inhomogeneous distribution of the particles on the filter this approach may lead to high bias especially for minor polymers. Another approach is the analysis of the full filter by chemical mapping technics. To handle the huge amount of data, automatic analysis algorithms have to be established. To avoid a particle overload of the filter the sample volume has to be adapted to the total particle content in the sample [82]. In case of a huge number of natural particles this leads to very small sample volumes and just a few MP particles per filter. Analyzing small aliquots presumes homogeneous samples, which is in case of particle suspensions very challenging. Representativeness of the sub-sample has to be ensured and discrimination of particular particles has to be excluded during aliquoting. Measures for reduction of analysis time often come along with a decrease in spectra quality. Poor spectra characterized by high noise values or missing regions hamper the identification of the particles or lead to false classification. Evaluation of spectra quality and verification of identification by matching software are essential for generation of reliable results and unfortunately neglected in several studies in the past. It is a common practice that library matches with a quality index greater than 700 are accepted, while matches with a ranking between 550 and 700 have to be analyzed again under optimized conditions and interpreted individually [34, 83]. Spectra with an even lower matching are considered as unknown. Despite the additional effort and slowing down of the method each single particle which cannot be identified clearly should be measured under adjusted parameter (e.g., measuring time, laser energy) to render meaningful and distinct spectra for clear identification [30, 34, 83]. Organic matrix or biofilms may disturb the correct identification of the polymers, especially if automated software and libraries based on pristine polymers are relied on exclusively. Spectra in commercial and custom-made libraries usually originate from pristine polymers and may differ significantly from processed or weathered plastics. During processing polymers are blended with additives, fillers, and dyes. Such compounds lead to additional absorption bands in the spectra and may hamper the identification. Environmental stressors such as UV light, heat, or biodegradation result in chemical modifications of the polymers which are summarized in the term weathering [17]. Weathering of polymers lead to formation of polar groups by oxidation (-OH, C=O), double bounds (C=C) by elimination, and free acid groups by hydrolysis. These chemical modifications significantly alter the spectra and may prevent identification or may lead to false classification of polymers. Consequently, integration of spectra recorded from processed and weathered polymers into the libraries is an urgent value for successful identification of MP from the environment. Another aspect is to integrate spectra of widespread non-plastic materials such as inorganic particles, natural polymers (cellulose, keratin, chitin, lignin), and hydrophobic compounds (fats and waxes). Thus, materials can be easily mistaken for MP, due to analogical chemical structure of synthetic polymers and natural compounds. For example, the spectra of the natural compounds waxes and fats are dominated by the C-H vibrations and thus can be mistaken for PE [84]. Differences in the spectra are often marginal and correct identification is only possible by detailed comparison of the fingerprint region (1,500–400 cm^{-1}). To avoid such false classification the organic matrix has to be removed before chemical identification of the particles. This very time-consuming procedure extremely prolongs the analysis time (see Stock et al. [28]).

Due to the immense analytical effort per sample, a preselection of the samples by fast screening methods is advisable for routine analysis or large monitoring campaigns. Promising tools for such a screening are FT-IR or NIR spectroscopic methods for measurement of bulk samples. These methods are very time and cost efficient and reveal semiquantitative MP concentrations [41]. However, these methods are limited by very high detection limits ($>$1 wt%) and need improvements regarding robustness and reliability before being applied in environmental analysis.

Several methods based on different physical/chemical changes during thermal treatment of polymers have been developed. The extent of the gained analytical information and sensitivity, but also the complexity and effort of the methods increase by TGA-DSC $<$ TGA-MS $<$ Py-GC-MS/TED-GC-MS. TGA-DSC is a user-friendly and cost-effective routine method. It is applicable for qualitative and quantitative analysis of known polymers in a simple sample matrix such as drinking water at high concentrations. However, its viability for trace analysis in complex matrices is severely limited. A more specific detection is given by TGA-MS using selected masses of polymer specific decomposition products. Due to disturbance by matrix compounds forming fragments with the same mass as the analytes, these methods need extensive sample preparation for the analysis of complex samples. Method performance can be improved by implementation of a gas chromatographic separation step. These Py-GC-MS or TED-GC-MS methods enable highly specific and sensitive MP determination by detection of selected marker compounds. These improvements go along with a high complexity of the methods and a weaker robustness. The used analytical instruments are more expensive and well-trained lab staff is needed. Nevertheless, Py-GC-MS and TED-GC-MS are the most promising technics for routine analysis [3]. Table 3 compares the published applications for MP quantification in different environmental matrices. Limits of detection (LOD) vary strongly for different polymers and methods. Py-GC-MS and TED-GC-MS show the lowest LODs in the range of μg/g. Other methods such as TGA-MS or TGA-DSC have LODs two or even three orders higher in magnitude. However, up to date, there is no universal method for all polymers and matrices, and MP quantification is far from standardization. Several improvements have to be done before the methods will be capable for routine analysis. One issue is the strong influence of the sample matrix and the lack of authentic internal standards for most of the polymers [13]. Thus, no universal external calibration can be used, but matrix matched calibrations or standard addition procedures have to be applied [66]. Due to the particulate behavior of the polymers and their inhomogeneous distribution in environmental samples, representativeness of the analyzed sample aliquot is an urgent

Table 3 Comparison of different MP quantification methods

Reference	Method	Polymers	Matrices	Pretreatment	LOD
David et al. [54]	TGA-MS	PET	Soil	None	600 µg/g
David et al. [48]	TGA	PET, PS, PVC	Soil	None	PET: 3.3 mg/g PS: 9.1 mg/g PVC: 22.2 mg/g
Dierkes et al. [55]	Py-GC-MS	PE, PP, PS	Soil, sediment, sewage sludge	Solvent extraction (THF)	LOQs PP: 7 µg/g PS: 8 µg/g PE: 7 µg/g
Eisentraut et al. [66]	TED-GC-MS	PE, PP, PS, SBR, NR	Soil, fish, suspended solids	None	PP: 0.44 µg PS: 0.2 µg PE: 1.6 µg SBR: 0.23 µg NR: 0.22 µg
Fischer and Scholz-Böttcher [56]	Py-GC-MS	PE, PP, PS, PET, PMMA, PA6, PVC	Fish	Enzymatic, chemical digestion	< 0.4 µg
Hahn et al. [41]	FTIRS	PE, PET	Sediment	Milling, mixing with KBr	PE: 10 mg/g PET: 10 mg/g
Majewsky et al. [46]	TGA-DSC	PE, PP	Waste water	None	PE: 25 mg/g PP: 50 mg/g
Mallow et al. [78]	EA-OEM	PE, PP	Water (>250 µm)	Chemical digestion with H2O2	PE + PP: 33 mg/g
Okoffo et al. [57]	Py-GC-MS	PE, PMMA, PS, PET, PC, PP, PVC	Biosolids	Solvent extraction (DCM)	LOQs PE: 0.03 mg/g PMMA: 0.09 mg/g PS: 0.01 mg/g PET: 0.03 mg/g PC: 0.03 mg/g PP: 0.03 mg/g PVC: 0.03 mg/g
Paul et al. [40]	NIRS	PE, PP, PS, PET	Soil	None	5–10 mg/g
Peez et al. [43]	^{1}H NMR	PE, PET, PS		Dissolution	20 µg/mL

(continued)

Table 3 (continued)

Reference	Method	Polymers	Matrices	Pretreatment	LOD
Steinmetz et al. [58]	Py-GC-MS	PE, PP, PS	Soil	Solvent extraction (TCB)	PE: 5 μg/g PP: 86 μg/g PS: 1 μg/g
Unice et al. [59]	Py-GC-MS	SBR, BR, NR	Soil, sediment	None	SBR: 6 μg/g SBR + BR: 5 μg/g NR: 2 μg/g
Wang et al. [79]	LC-MS	PC, PET	Sediment, dust, sludge, mussel, clam	Alkali-assisted thermal hydrolysis in butanol	PC: 2.8 μg/kg PET: 17.7 μg/kg

issue. Frequently used in-weights of 20–50 mg are not representative aliquots, especially if particles >100 μm are analyzed. To overcome these issues, MP has to be isolated from the matrix before analysis. Density separation and chemical or enzymatic digestion of the organic compounds are effective but time-consuming [56]. MP extraction by organic solvents is fast and can be done full automated [55, 57, 58, 71]. Solvent extraction is a widely used procedure in environmental analysis and such machines exist in most routine labs. The existing methods have to be expanded by additional polymers and tested for further matrices.

In contrast to the particle-based methods thermo-analytical methods determine the bulk content of the polymers. These methods deliver mass concentrations of the particular polymers, which is an important indicator for characterization of sources and sinks. Furthermore, for regulatory purposes and environmental thresholds mass concentrations are preferred. However, polymer masses can strongly differ from the actual mass of MPs due to additives and fillers. These plastic ingredients can account for up to 50% of the total mass of plastic objects. Consequently determination of the pure polymer masses may lead to an underestimation of the MP content. Another disadvantage is that a differentiation between homo-polymers and copolymer or polymer composites is not possible. Using styrene as indicator, for example, all styrene containing polymers such as polystyrene (PS), acrylonitrile butadiene styrene (ABS), or styrene butadiene rubber (SBR) will be summed up. On the other hand, this can be utilized for quantification of complex mixtures with known composition such as tire wear particles. Tires consist of a complex mixture of different rubbers (SBR, NR, BR) and fillers. SBR can be quantified by the specific marker compound 3-phenylcyclohexene [66]. Assuming an average SBR-content of 11.3% in the tire material SBR concentration can be transformed into tire material concentrations [85].

4 Conclusion

A realistic risk assessment and the implementation of effective measures to reduce MP emissions require a comprehensive monitoring of sources and sinks. Therefore, there is an urgent need for fast and cost-effective methods for MP determination. Whichever is the best method depends on the scientific question and what kind of information is needed [2]. FT-IR and Raman spectroscopy coupled to microscopy provide a reliable identification of MP particles. Especially in combination with automated particle finding software or an FPA detector, determination of particle numbers in complex environmental samples is possible. If mass concentrations are requested, thermo-analytical methods are the best choice. TGA-DSC and TGA-MS are fast and relatively simple methods. They give good results for MP determination at high concentrations in less complex matrices. For identification of complex polymers or MP determination at low concentrations in environmental matrices, Py-GC-MS or TED-GC-MS is the method of choice. Sample pretreatment is a critical factor regarding cost and time effectiveness. The need of time-consuming pretreatment steps such as density separation and enzymatic/chemical digestion depends on the sample matrix, the investigated polymers, and the aimed detection limits. There is a need for standardized protocols and harmonized quality standards to ensure comparability of the results. However, matrix effects and sample inhomogeneity are still great challenges which have yet to be overcome before the methods will be applied in routine analysis. The overall costs are another factor to be considered [86]. Costs and working time dramatically increase with a decrease in the lower particle size limit and detection limit, respectively. Furthermore, analytical uncertainties and error margin increase. In some cases, the gained knowledge about concentrations of very small particles (<10 μm) may not be worth the immense effort of analyzing them. On the other hand for toxicological studies especially the fraction <10 μm maybe of high interest. So, the request on the analytical methods and the resulting data should be carefully evaluated at the beginning of a study.

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