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A review on challenges and developments of analytical pyrolysis and other thermoanalytical techniques for the quali-quantitative determination of microplastics

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ABSTRACT

Environmental pollution from microplastics (MPs) and the associated health and environmental risks are the focus of intense multidisciplinary research. In fact, that there is an urgent need to produce quantitative and qualitative data on the amount and types of MPs in environmental matrices, organisms, and commodities, and to perform spatial and temporal comparisons. This has led to the development, optimization and application of analytical methods to characterize MPs in aquatic, terrestrial or biological samples.

Instrumental analytical techniques based on analytical pyrolysis and thermal analyses provide qualitative and mass-based quantitative information and have a high potential to become of general use in the analysis of MPs.

This paper reviews the research carried out to date in the analysis of MPs by analytical thermal and pyrolysis techniques. The aim is to provide a detailed and comprehensive critical examination of recent quantitative analysis developments, integrated with a brief historical excursus.

The main analytical issues and limitations are described with practical detail, to provide an overview of the rapid ongoing development of this sector of analytical chemistry, and to contribute to the activities aimed at evaluating, comparing and standardising analytical techniques and analytical data in MP research.

1. Introduction

In the last decade the issues related to the pollution from microplastics in all environmental compartments [1–3] and the associated health and environmental risks [4] have been the focus of intense social, media and political attention, and of multidisciplinary research worldwide [5,6].

Microplastics (MPs) have been defined as synthetic solid particles or polymeric matrix of any shape in the 1 µm-5 mm size range [7], however a harmonised and internationally accepted definition is not yet available at present. Some studies only investigate particles < 1 mm as microplastics, defining particles > 1 mm as visible plastic debris [8]. A more detailed classification has been suggested by the *Technical Subgroup on Marine Litter* for the implementation of the European Marine Strategy Framework Directive, according to which particles < 1 mm are small microplastics, while the visible size fraction (> 1 mm) are divided into large microplastics (1 – 5 mm), mesoplastics (5 – 25 mm) and macroplastics (> 25 mm) [9].

Although the term *plastic* refers to polymers that can be shaped (moulded, extruded, etc.) into a definite solid form (thermoplastic and thermosetting polymers), the term *microplastics* has been extended to other types of polymers that constitute a significant source of solid particles in the environment, such as elastomers (represented by rubbers) and fibres. Water soluble polymers such as poly(vinylpyrrolidone) and poly(vinylacrylate), liquid polymers such as certain polysiloxanes, have not often been considered in MP studies, despite being identified in environmental samples (see for instance [10]).

In summary, the following attributes are considered relevant for MPs: synthetic, solid, in the form of appropriately sized particles, and persistent (resistant to bio/degradation). These attributes are relevant in establishing a regulatory definition for intentionally-added MPs that may contribute to the primary MP pool when released into the environment.

Primary MPs are introduced into the biosphere mainly through release into the aquatic environment of the discharge of the washing of textile fibres [5] or from the discharge of cosmetic formulations which contain them [11]. Another major source of MPs is the mechanical, photo-oxidative and biological degradation of larger plastic items such

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as floating marine litter. The degradation of plastic debris under the effect of UV-light and moisture is responsible for the fragmentation into small particles (secondary MPs) [12].

There is increasing scientific concern regarding the effects of MPs on aquatic life [4] as they persist in the marine environment and have been reported to retain contaminants as persistent organic pollutants [13]. In fact, MPs are considered a vector for introducing bacteria and hazardous chemicals into organisms through ingestion [14], such as organic additives [15] or residual monomers [16], with potential toxic effects for the aquatic biota. These aspects are fundamental for human health since MPs ingested by fish and shellfish have recently been suspected to contaminate the human food chain [13,17].

Environmental scientists, regulators and other interested parties have highlighted the urgent need for quantitative and qualitative data on the amount and types of MPs, in order to evaluate their sources and distribution in environmental matrices [18], organisms, and in commodities for human use [13,17,19], and to perform scale spatial and temporal comparisons.

This need has fostered intense research to develop, optimize, evaluate and apply analytical methods for the characterisation of MPs in aquatic, terrestrial or biological samples.

An additional crucial issue is the lack of standardisation in the sampling and analysis of MPs, and focused research actions are now tackling this fundamental task (see for instance [20]), activating massive scientific efforts in developing, optimizing and evaluating methods. Instrumental analytical techniques based on analytical pyrolysis and thermal analysis in the last years have become candidates to become of general use in the analysis of MP, as an integration to spectroscopic methods. Most of the data on MP contamination have been obtained by microscopic visualizations, which are based on the particle number and size. Although quantitation based on particle counts is important especially in ecotoxicological studies, data cannot be converted into mass by calculating the shape and density without strong approximations due to the highly variable morphology of MPs. Unlike spectroscopic methods (FTIR, Raman) which are essentially applied for polymer identification, thermochemical methods provide both qualitative and mass based quantitative information.

Thermal analysis [21–23] and analytical pyrolysis [24,25] methods are based on the thermal decomposition of polymers or polymer mixtures and on their characterisation through the analysis of the pyrolysates (Fig. 1). These approaches are recognized crucial and powerful tools for the molecular and thermal/physical characterisation of polymeric materials, thus their application to the analysis of MPs has been a natural step.

In particular, analytical pyrolysis coupled with gas chromatography and mass spectrometry has been recently considered with great attention as a means to provide molecular and mass spectral information on MP composition and degradation in the environment.

Although several reviews [26–33] have been published on the chemical analysis of MPs in various environmental matrices that mention thermochemical methods, including a specific overview on the subject [34], a detailed and comprehensive critical examination focused on a quantitative analysis integrated within a historical perspective is lacking.

This paper reviews the research carried out to date in the analysis of MPs by analytical thermal and pyrolysis techniques. This could then provide a basis for monitoring the rapid ongoing development of this sector of analytical chemistry, and also the activities aimed at evaluating, comparing and standardising analytical techniques and analytical data in MP research.

2. Pyrolysis of plastic polymers

The main pyrolysis products of common plastics are reported in Fig. 1. Thermal analyses proposed for the determination of MPs, but which do not involve the pyrolysis process were not considered in this review (e.g. TGA-DSC exploiting the endothermic solid-liquid transition of polymers [35]).

Where applicable the abbreviations used in this review are consistent with the IUPAC nomenclature for polymers (see Fig. 1) [36], analytical pyrolysis [37], and thermal analysis [38]. For analytical pyrolysis coupled with gas chromatography and mass spectrometry, the abbreviation Py-GC–MS is recommended and herein used. Fig. 2 reports the scheme of the set-up for a typical furnace Py-GC–MS system. The majority of common plastic polymers are reported to undergo full volatilisation during pyrolysis (PE, PS, PMMA, PP), while a certain amount of charred residue is reported for PC, PET and PVC (for example 23%, 9% and 6% of the starting mass for the three polymers respectively) [39].

The abbreviation TED-GC–MS is used for TGA combined with solid phase extraction (SPE and thermal desorption TDS-GC–MS) [21]. Fig. 3 reports the scheme of a TED-GC–MS system.

3. Sample pre-treatments and isolation of MPs for thermochemical analysis

3.1. General aspects

An opportune treatment of the sample is crucial in order to produce a suitable portion of material to introduce into the Py-GC–MS system. Plastic particles can be collected by visual inspection – using a microscope and tweezers – for particles with a minimum size suitable for handling, that can be approximatively estimated as > 0.1 mm in size or > 0.1 mg in weight [42].

A lower size or weight may be possible depending on the type of fragment (e.g. microfiber vs. microsphere) and polymer (e.g. high vs. low density) [43]. Plastic particles can be directly picked up from the sample and transferred into the pyrolysis holder, as reported for the sand surface [43] or stomach content of marine fish [42]. However, even when plastic particles are manually selected, a concentration/separation step from the samples is often necessary. For instance, in one study particles from surface lake water tow were sieved, treated with $Fe^{2+}/30\%H_2O_2$ to degrade labile organic matter, separated by density with NaCl, and transferred into a Nylon filter from which selected items were manually selected and transferred to Py-GC–MS for identification [42].

The sample treatments described in the literature strongly depend on the features of the environmental matrix under investigation. The main types of matrices that have been analysed by thermoanalytical methods for MP fragment analysis include water [21,42,43], sediments [44], soil [45], and marine organisms [43,46]. Marine organisms can be sampled as whole individuals, or animal tissue, or as the content of fish stomachs. Investigating the presence of MPs in commercial food products is gaining increasing importance due to the implications for human exposure. The category of commercial food products often overlaps with marine organisms/animal tissue because it is most seafood and fish products for human consumption. Other types of food supplies derived from the marine environment, such as algae or sea salt, are also of interest [47].

Single-particle analysis is not the only application of thermochemical methods. Due to the selectivity achieved by the coupling with GC–MS, analytical pyrolysis techniques are suitable for the analysis of mixtures of different micro- and nanoplastics obtained by extraction or filtration [21,41,46,48–50], and can also be potentially exploited for the analysis of solid microportions of homogenized ground mixtures of particles of different polymers. Cryo-milling is recommended in the homogenisation of solid plastic samples in order to facilitate milling and to avoid heating and alterations in the polymers. However the effects of these types of sample pretreatment on the polymer analytical response need to be investigated further [51].

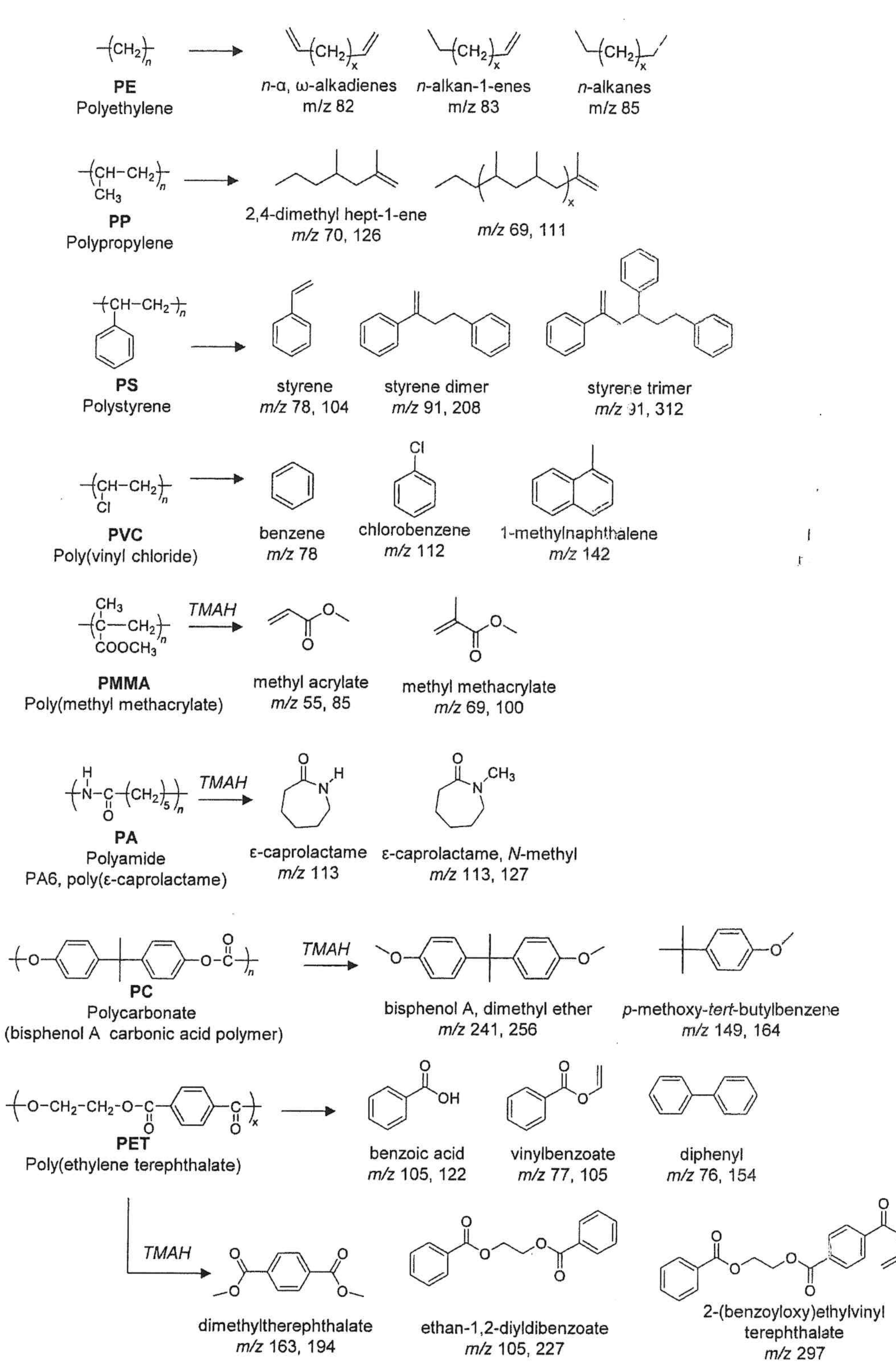

Fig. 1. Molecular structures of polymers investigated in MPs and of their main pyrolysis products, with corresponding *m/z* (TMAH: pyrolysis products produced in the presence of tetramethylammonium hydroxyde).

3.2. Filtration

MPs can be collected on filters that are subjected to Py-GC–MS or TED-GC–MS. Filtration can be directly applied to water samples (or melted ice and snow) where MPs are present as suspended particulate matter or floating fragments or from aqueous solutions derived from the last step of the isolation procedure (e.g. after density separation). Critical choices are the pore size and chemical nature of the filter to be used, and the amount of water to be filtered.

In the analysis of polluted water from a coastal lagoon on the Adriatic Sea (Italy) [52] 0.7 µm pore size quartz GF/F filters were used, and portions of filtered water of 0.5–1 l achieved amounts of filtrate in the order of mgs. Portions of 5 mg of filtrate were directly analysed in a filament pyrolyser after drying. Glass fibre filters are the most common ones used in the analysis of MPs. The filters can be cut, milled or wrapped prior to pyrolysis [53,54]. Styrene interference, probably

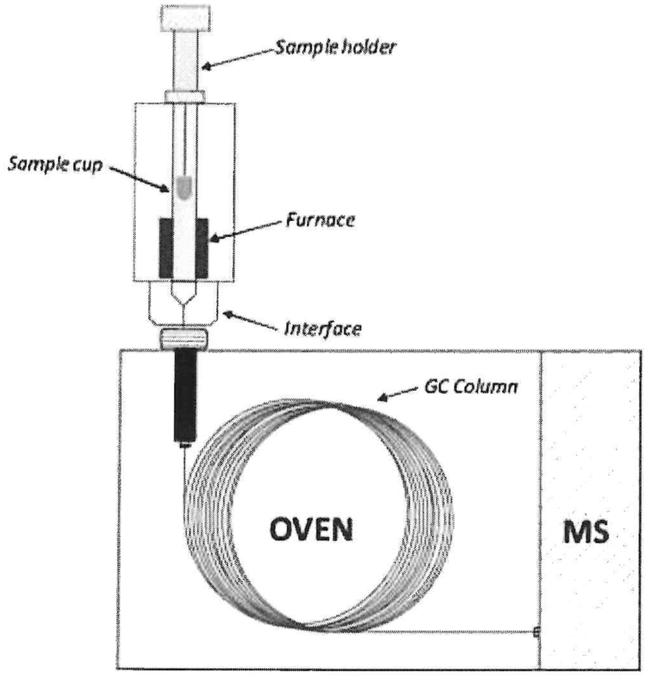

Fig. 2. Instrumental asset of a furnace PY-GC–MS system (Frontier Lab, Japan). Reprinted with permission from [40].

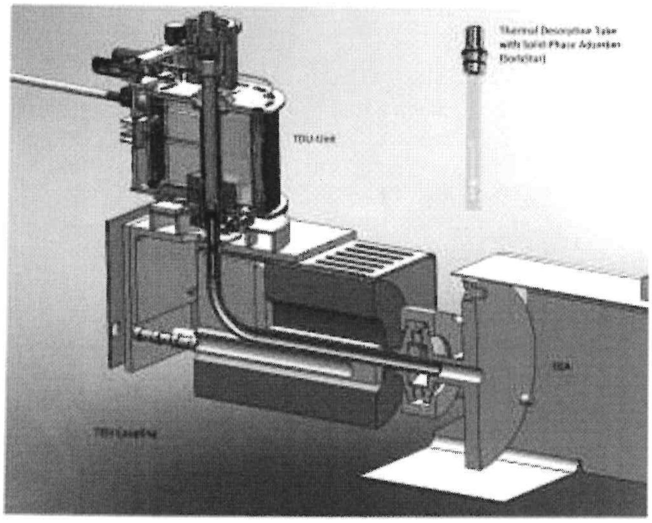

Fig. 3. Schematic drawing of the TED-GC–MS with the TED connected to the outlet of the TGA. A thermal desorption tube with a solid-phase adsorber (SorbStar®) can be placed in the thermal desorption unit of the TED for the thermal extraction process. Reprinted with permission from [41].

derived from the sizing agent of the glass filter, has been reported by Eisentraut et al. in the analysis of tire wear in street runoff by TED-GC–MS [55]. Again, styrene derived from the filter packaging made of PS was identified as a contaminant from the pyrolysis of filters [46]. Heating the filter in a muffle at 300 − 400 °C or even 590 °C is recommended to solve contamination by filters. Other aspects worth considering are the size of the filter in comparison to the maximum quantity of material that can be sampled for the pyrolytic run, as well as the need for particular care in the filtration procedure to prevent the uneven distribution of particles on the filter surface area. Gomiero et al. set up a glass adaptor to reduce the deposition area of the particles on the filter surface [53]. Filtration was combined with centrifugation under constant operation conditions to process river water samples for TED-GC–MS [21].

3.3. *Density separation*

The most common approaches to separate MP particles from large amounts of sediments are based on density separation in salt solution (flotation), exploiting the low density of the majority of polymeric materials. The most common salts used for density separation [56,57] are sodium chloride (NaCl, inexpensive, density of the saturated solution 1.2 g/cm^3 [58]), sodium bromide (NaBr, 1.46 g/cm^3 [54]) and sodium iodide (NaI, relatively more expensive, density of the saturated solution 1.8 g/cm^3 [57]). High-density (1.8 g/cm^3) salt solutions of zinc chloride [59] and sodium or zinc polytungstate [60] can be used as an alternative to enable higher density polymers to be extracted/separated (PVC, PET, density around 1.3 g/cm^3).

A major issue in the density separation of MPs from sediments is again the amount of sediment to extract. Increasing the volume of extracted sediments is clearly advantageous when the concentration of MPs is very low or very heterogeneous, in order to guarantee that a representative amount of sample is examined. However, extracting large volumes of samples with high-density salt solutions is expensive. Nuelle et al. [57] balanced this choice by proposing a two-step density separation procedure (referred to as "two-step air induced overflow extraction method") where the initial "fluidification" of the sediment was achieved in a low-cost NaCl saturated solution used to decrease the sample mass through the bubbling of air in the suspension in a device exploiting a pump to enrich the matrix in MPs. MP particles were then separated from the enriched sample through a flotation step with a saturated NaI solution. The supernatant portion was filtered using 0.45 μm nitrocellulose filters. The authors tested the recovery of the separation procedure on several types of reference polymer particles, and the approach was used to investigate the heterogeneous distribution of MPs in the < 1 mm sieved fraction starting with 1 kg portion of dry sediment from the German North Sea. After density separation, floating particles in the supernatant can be further separated into different size class fractions using steel sieves [53].

Besides sediments, density separation has been applied to other sample types including benthic fish for the elimination of sand [46], and MP particles in sea salts [47].

Innovative micro and nanoparticle extraction methods have recently been proposed by Grbic et al. [61] and Zhou et al. [62], based on the use of magnetic nanoparticles and cloud-point extraction, respectively.

3.4. *Purification from biogenic organic materials*

The flotation separation of MPs from sediments suffers from the presence of low-density biogenic natural organic matter (plant or animal parts) which floats on the surface of the salt solution, and can be difficult to visually distinguish from plastic. The elimination of biogenic organic material before the analysis is carried out through exposure to alkalis (NaOH or KOH solutions), acids (HCl, HNO_3, $HClO_4$), or an oxidising H_2O_2 solution (35%, 7 days) [57]. It is to be underlined that condensation polymers as PET or polyamides suffer destructive effects from acidic and alkaline digestion [63].

In a comparative test, the efficiency of the H_2O_2 solution was found to be higher than NaOH and HCl, however even with the H_2O_2 treatment, only 50% of the biogenic organic matter was eliminated [24].

The H_2O_2 approach was also used by Fisher et al. [46] to characterize MPs ingested by fish, and by Hendrickson et al. to characterize water tow and sediments [42].

However, some polymers are altered and or degraded by oxidising solutions of H_2O_2 [57] or by alkaline treatment [64]. In addition, coloured plastics can be discoloured by H_2O_2 treatment, impairing the visual differentiation between e.g. coloured anthropogenic fibres and colourless natural fibres.

In summary, separating MPs from biogenic natural particles remains a highly challenging task. Complete separation is often not possible, which means that the Py-GC–MS identification of the polymers needs to be based on highly specific pyrolysis markers. For example, Dümichen et al. investigated the different thermal behaviour of organic matter and MPs by TGA, identifying higher decomposition temperatures for the polymers [21]. The possible contribution of natural materials to pyrolysis profiles is an aspect to be taken into account and carefully evaluated in the analysis of MPs in environmental samples, as underlined by many authors, and more research is needed to address this issue.

3.5. Extraction with organic solvents

Isolation from sediments and soil, including sand, has been tackled in several cases by extraction with organic solvents. A few procedures are described for this purpose, and one of the most common solvents used is dichloromethane (DCM) as it dissolves most polymers present in the environment as MPs. This solvent was used by Fabbri et al. in [52,65] to extract polymers in sediments from the Adriatic Sea costal lagoon using Soxhlet-extraction in DCM of wet sediment samples (around 10 g), and subsequently precipitation in *n*-hexane, to investigate the presence of PS and PVC (following the EPA method for non-volatile organics) [66].

In 2018 extraction with DCM was adopted by Ceccarini et al. [67] using a modified Kumagawa-type apparatus enabling the sample pretreatment to be performed on 160 g of sediment. A recent evolution of solvent extraction was proposed in 2019 by Dierkes [48] based on the use of a pressurized system and on a two-step procedure, a first step using methanol to reduce the matrix effects and a second one based on the use of tetrahydrofuran to extract the MPs. The pressurized system was used by Okoffo et al. for the Py-GC–MS analysis of MPs in biosolids [68]. Trichlorobenzene has also been investigated for the extraction of PE, PP, and PS at 120 °C from soil samples [45]. Recoveries were > 70% and detection limits of 1.86 ng. The authors of this study have compared different sample treatments to solve interference by soil organic carbon.

3.6. Analysis of MPs in biological tissues

Concerns surrounding MP contamination in the biota focus on the risks related to their ingestion from marine organisms [69] and MP accumulation through trophic levels [70]. Possible threats to humans through the consumption of seafood products are being investigated [71]. Analytical procedures that can efficiently characterize MPs present in biological tissues are thus urgently required [72]. The sample pre-treatments described in the literature for this purpose are highly heterogeneous and far from being standardized. The most common approaches to pre-treat these samples are based on alkaline [73] or acidic [74] digestion or chemical oxidation [27] of the biological materials.

The chemical integrity of the MP particles following chemical pretreatment is an important requisite to prevent analytical artefacts. In a series of experiments that compared different protocols for the digestion of biological samples for the analysis of MP contamination in fish and shellfish, Dehaut et al. [63] assessed the capacity of Py-GC–MS to identify polymers after different digestion protocols. Both Raman micro-spectroscopy and Py-GC–MS led to the correct identification of the type of polymer – in a set of 15 different plastic materials – after the application of alkaline digestion procedures (KOH 10% for 24 h at 60 °C), except in the case of cellulose acetate, which was not correctly identified after treatment with strong alkalis. The same protocol based on the use of alkaline digestion was also applied by Ter Halle et al. [49] to characterize small microplastics collected during sailing, and by Hermabessiere et al. [43] to characterize the MPs in mussels and cockles.

Enzyme treatment are milder and have no significant effect on the structure of microplastics, thus continuous enzymatic digestion and purification methods based on proteolytic enzymes [75] also find increasing application [76] for the digestion of biological matrices. However, enzymatic treatments have higher costs and a relatively lower the digestion efficiency.

Fischer and Scholz-Böttcher [46] used enzymatic degradation of biopolymers with protease, and chitinase, followed by H_2O_2 oxidation and elimination of lipids with petrol ether. Their aim was to analyse MPs in fish by Curie point Py-GC–MS. Interestingly, they observed matrix interferences for PE, PS and PVC, but not for PP, PET, PUR, PA6 and PMMA.

3.7. Direct analysis of environmental samples without separation

Only in a few cases is the analysis of MPs in environmental matrixes based on the whole matrix after homogenisation. This approach was applied by Dümichen et al. to perform a preliminary screening using TED-GC/MS of different samples from a biogas plant. The samples were homogenized by a cutting mill, subsequently cooled in liquid nitrogen, and further homogenized with a centrifugal mill and an overhead shaker [21]. Dümichen et al. also used a similar cryo-milling and direct analysis approach for the characterisation of mussels and soil samples from the Spree River (Berlin) [51]. Analysing the whole sediment sample without separation is more suitable with TED-GC/MS than with Py-GC–MS due to the amount of sample that can be used for the analysis (ca. 20 mg), which is usually around 100 times greater than the sample weight normally introduced in Py-GC–MS. The potential of TG coupled with MS [22] or FTIR [77] for the direct determination of MPs in environmental matrices has been investigated.

Off-line pyrolysis is another approach for the direct analysis, which presents the advantage to permit the analysis of high sample amounts, improving sensitivity and representativeness. Advantages and limits of off-line pyrolysis in the analysis of plastic polymers in sediment samples have been recently evaluated [78]. Off-line pyrolysis GC–MS was applied to study the accumulation of PS by mussels (*M. galloprovincialis*) exposed to different concentrations of the polymer in laboratory aquaria [79].

4. Qualitative thermochemical identification of microplastic pollution in environmental samples

According to IUPAC, qualitative analysis is the analysis in which substances are identified or classified on the basis of their chemical or physical properties. When qualitative analyses are performed by thermochemical approaches, the polymer is identified or classified on the basis of the molecular profile of the products produced in the thermal decomposition. The identification of rubbers in roadway dust was probably one of the first outcomes of analytical pyrolysis in the field of environmental contamination by synthetic polymers [80]. Since then, several studies used analytical pyrolysis to study the presence of tyre wear particles in air dust (these were reviewed by Unice et al. [81]). The main pyrolysis products indicative of the principal elastomers in passenger cars (SBR, styrene-butadiene rubber) and truck tire tread (NR, natural rubber; BR, butadiene rubber) were reported to be the monomers, styrene (SBR), isoprene (NR), butadiene (BR, SBR) and the dimers, vinylcyclohexene (BR, SBR) and dipentene (NR). In comparison to dimers, monomers were higher in abundance, but more prone to matrix interference (e.g. styrene from diesel exhaust). More recently, Eisentraut et al. described the TED-GC–MS analysis of reference elastomers for the selection of specific markers to target the characterisation of street runoff samples [55].

The presence of non-visible traces of PS in soil samples by Py-GC–MS was described in 1986 by de Leeuw et al. [82], a pioneer research group in the application and development of analytical pyrolysis. They proposed Py-GC–MS (Curie temperature pyrolysis at 550 °C of approximately 200 µg of sample suspended in methanol) as a screening method for the rapid determination of anthropogenic pollutants directly through the analysis of soil and sediments avoiding sample pre-treatment or separation. The presence of traces of PS in a sample of polluted soil was highlighted by the identification of styrene, methylstyrenes and dimethylstyrenes among the pyrolysis products. Although the term "microplastic" was not commonly used at that time, plastic particles had already been reported as an emerging contaminant in the environment [83].

Ten years after this first result, Fabbri et al. focused on determining the presence of PS and PVC evaluating the Py-GC–MS analysis of sediment samples [65] and of extracts in organic solvent [52]. Sediment samples were withdrawn from a coastal lagoon on the Adriatic Sea (Italy) impacted by the industrial production of synthetic polymers. Py-GC–MS revealed a specific case of pollution by resin pellets. Plastic pellets are solid particles ranging in size between 1–5 mm which raised environmental concerns in the early 1990s [84] and are today referred to as primary MPs. Pyrolysis conditions were 700 °C in a quartz tube, using a filament pyrolyser. PS was identified on the basis of intense signals for styrene and α-methylstyrene, together with the presence of characteristic PS pyrolysis products (styrene-dimer, biphenyl, diphenylpropane). PVC presence was indicated by an intense benzene peak and confirmed by the presence of chlorobenzene. A critical issue was highlighted in the quantitation and also in the qualitative assessment due to the fact that the most abundant pyrolysis products of PS and PVC (styrene and benzene respectively) are poorly specific, while the most specific markers, styrene-dimer and chlorobenzene, have a low pyrolysis yield and thus their use leads to poor detection limits.

The same research group reported the identification of a larger set of synthetic polymers in the dichloromethane extracts of lagoon sediments [85] through the identification of characteristic pyrolysis products: polybutadiene (PB), poly(acrylonitrile-co-styrene-co-butadiene) (ABS), styrene-butadiene random (SBR) and block (SBS) copolymers, and polyvinyl acetate (PVA), in addition to PVC, and PS. The specific pyrolysis products exploited as markers were chlorobenzene for PVC, acetic acid for PVA, benzene-butanenitrile for ABS, and cyclohexenylbenzene for styrene–butadiene rubbers.

After these initial promising studies, Fries et al. used Py-GC–MS to analyse individual marine microplastic particles, isolated manually after density separation [58]. In particular, MPs from sediment samples from the island of Norderney (Germany) were analysed after density separation with NaCl and NaI [57], and optical microscopy selection of the potential microplastic particles.

The potential of fractionated Py and GC–MS was exploited to rapidly identify not only the polymer type, but also the associated organic plastic additives (OPAs) [58,86] in one single analytical run. Thermal desorption at 350 °C was used for the analysis of OPAs followed by pyrolysis at 700 °C of the same particle [58]. The particles were identified as PE, PP, PS, PA, chlorinated PE (CPE) and chlorosulfonated PE. The identified OPAs were phthalates, benzaldehyde and 2,4-di-*tert*-butylphenol. The analyses were complemented by scanning electron microscopy (SEM) determination of the inorganic plastic additives (IPAs). Their paper showed the first identification of MPs containing CPE and chlorosulfonated PE in a marine environment. The analytical approach was successfully exploited to investigate the spatial distribution of small potential MPs and their correlation with macroscopic/visible plastic debris in beach sediments (Germany) [8]. Data analyses demonstrated that the presence of macroscopic plastic debris was not significantly correlated with the occurrence of small plastic particles due to the fact that microplastics were distributed homogeneously. On the other hand, visible plastic debris primarily accumulated in the zone at the basis of the dune belt. Interestingly, fibres were not investigated due to their presence in procedural blanks (see Section 5). Besides enabling the simultaneous identification of polymer types and OPAs at a molecular level, these first studies highlighted the advantages of desorption-GC–MS of additives, without the use of solvents, compared to the analysis of additives based on solvent extraction.

Hendrickson et al. [42] exploited both Py-GC–MS and Fourier transform infrared spectroscopy (FTIR) to investigate the distribution of MP pollution in surface waters of the Western Lake Superior (Canada). Samples were subjected to an oxidation step with H_2O_2 and then to a density separation step with NaCl solution to isolate lighter plastic particles. Single plastic particles were selected for the analysis after microscopy morphological examination. The particles analysed by Py-GC–MS were identified as PVC, PE, PP, PET, CPE and PS. Incongruence between the two analytical techniques was found in some cases in the identification of CPE, PE and PVC, which the authors attributed to the heterogeneous chlorine content derived from the chlorination of PE and PVC and/or to the presence of copolymers.

It is to be underlined that the significant markers useful for the identification of specific polymers are generally minor products in polymer pyrolysates. In addition their yield is strongly influenced by the sample/matrix composition, due to the fact that matrix effects on the pyrolysis mechanisms are not negligible (see Section 5.4). Despite these limitations, the resolving power achieved by GC–MS makes pyrolysis more effective than vibrational spectroscopies in analysing mixtures of different polymers, in identifying specific monomers and co-monomers, and in investigating the presence of minor components of the plastic materials, such as additives and degradation products. An algorithm for the Py-GC/MS data processing and the automated identification of eleven types of synthetic polymers in MP samples containing plastic mixtures has been recently proposed [50].

Peters et al. [42] characterised single MP particles ingested by 1381 marine fish from six different species by washing their stomach contents with distilled deionized water through four filters, adapting a procedure previously developed for the analysis of the stomach content of sunfish in 2016 [87]. The composition of the MP particles analysed resulted to be: 44.1% PVC and PET, 2.3% epoxy resin, 2.3% silicone, 9.3% nylon and, interestingly, 42% of the examined particles were classified as unknown, due to a low pyrolytic abundance or to the lack of any clear polymer match. A large fraction of the unknown particles showed different morphologies, however, similar pyrograms (which included the presence of diethylphthalate among the pyrolysis products) suggesting a shared compositional origin. The authors hypothesized that this group of particles with a pyrolytic profile that was difficult to interpret could have been contaminated by - or originated from - petroleum waste or coal tar. This observation highlights how additional research is needed to investigate the potential of the polymers to absorb environmental pollutants, and the possible influence on the pyrolysis products.

Ter Halle et al. [49] recently performed analysis of the nanoplastic (< 1 µm) colloidal fraction of marine water selected by ultrafiltration through a 1.2 µm poly(ether sulfone) membrane and characterised by dynamic light scattering before Py-GC–MS analysis. The ultrafiltered colloidal fraction obtained was freeze-dried prior to Py-GC–MS analysis in different conditions: pyrolysis at 700 °C, thermodesorption at 300 °C, and thermochemolysis at 400 °C with tetramethylammonium hydroxide (TMAH). No pretreatment was applied to eliminate the organic matrix contribution. The authors used principal component analysis (PCA) of the hydrocarbons and aromatic pyrolysis profiles of the samples to obtain the composition of the mixture of polymers present in the nanocolloidal fraction. The study allowed the comparison of the pyrolysis response of hydrocarbons and aromatic compounds of different size fractions of plastic debris collected in the North Atlantic subtropical gyre: meso- (5–200 mm range), large micro- (1–5 mm range), small micro- (< 1 mm) and nanoplastics (1 – 999 nm), as shown in Fig. 4. The pyrolytic signals of PE were observed to change with decreasing debris size, which could be related to ageing and weathering effects.

The identification of polymer markers in complex pyrograms can be enhanced by high-resolution mass spectrometry which has seldom been applied to the analysis of MPs. The potential of Py-GC interfaced with an Exactive® Orbitrap MS (Resolution 60,000 at *m/z* 200) to detect methyl methacrylate (*m/z* 99.0441) and styrene (*m/z* 104.0621) for the quantitation of PMMA and PS in a spiked fishmeal alkaline digestate

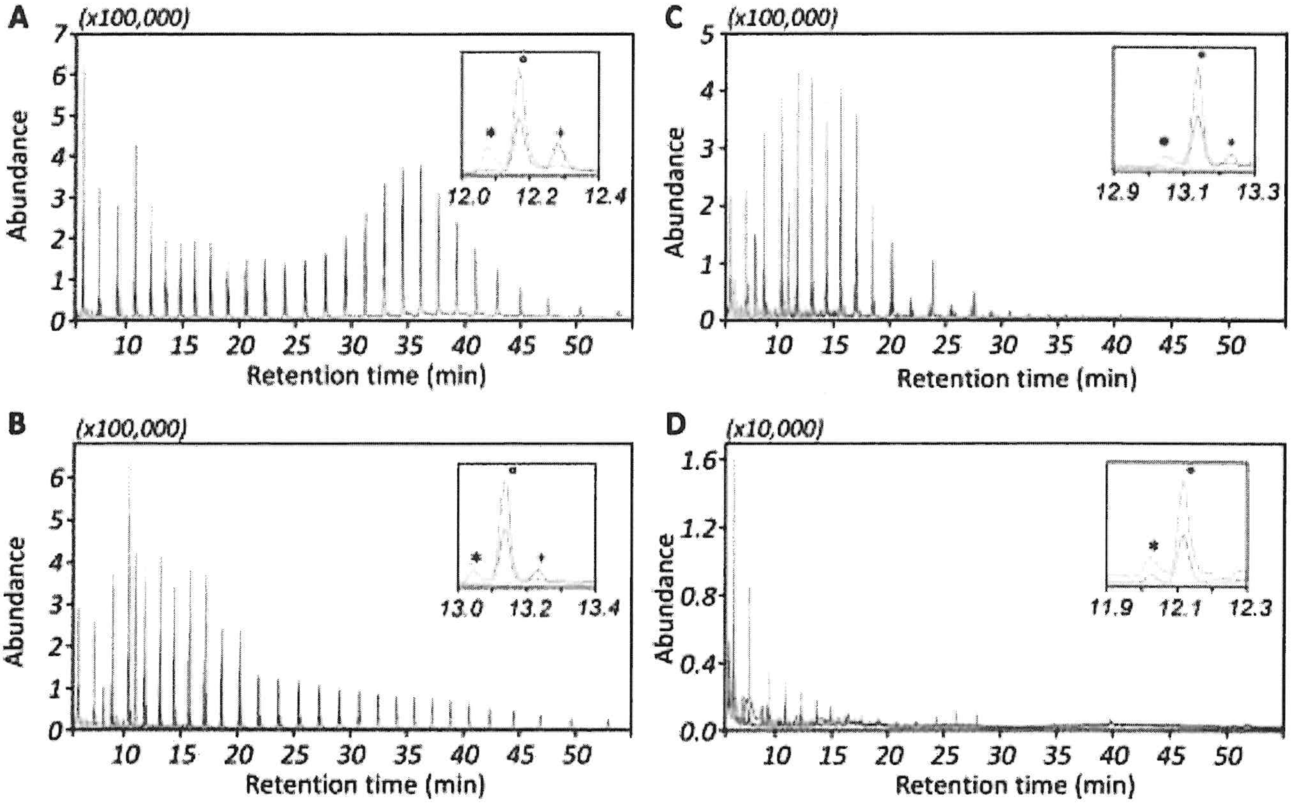

Fig. 4. From Ter Halle et al. [49] Single ion chromatograms (m/z = 55 in red and m/z = 57 in blue) of standard PE and A: plastic debris; B: microplastics (0.3–5 mm); C: small microplastic (25–300 µm); and D: the seawater colloidal fraction. The magnified portion of each plot (in the box) highlights the triplet n-alkadiene *, n-alkene and n-alkane + triplet with 11 C atoms.

was illustrated in a technical report [88]. The performance of the Exactive® Orbitrap MS was described for the analyses of relevant plastics (e.g. digested PP, cosmetic PE scrubs) and environmental samples (particles collected in lake waters by means of a manta trawl) [89].

Recently Py-GC coupled with atmospheric pressure chemical ionization-time-of-flight mass spectrometry (Py-GC-APCI-TOF-MS) was applied to the identification of PE, PP, PVC, PS and PET [90]. The APCI ionization/fragmentation process and the high mass resolution of TOF-MS were exploited to identify specific fragment ions in the pyrolyzates formed from model plastic mixtures, showing that the technique is a promising tool to characterize environmental MPs.

Thermally-desorbed additives and pyrolysis products of polymers were detected by DART-MS (Direct Analysis in Real Time-MS) on samples heated at 600 °C. The complexity of the mass spectra of real samples required a data analysis and statistical approach typical of petroleomics [91]. Py-GC-QTOF was used to identify the presence of PP, PS and PVC in river waters, and its potential for quantitation was also investigated [92]. Mintenig et al. used Py-GC–MS to identify PS in size fraction from the Asymmetrical Flow Field Flow Fractionation (A4F) of water samples spiked with nano and microplastic of the polymer. Samples were pyrolysed at 560 °C [93].

5. Quantitative analysis

5.1. From qualitative analysis to developments in the quantification of polymers in MP fractions

Quantitative analysis is defined by IUPAC as the analysis in which the amount or concentration of an analyte may be determined (estimated) and expressed as a numerical value in appropriate units. When quantitative analysis is the target in analytical pyrolysis, the intensity of the instrumental signals associated to specific pyrolysis products of a polymer is used to determine the amount (mass) of that polymer in the sample by means of calibration protocols under specified conditions. A critical evaluation of the use of Py-GC–MS to quantify PS in sediment samples was described in [65]. The experiments involved the quantification of PS in sediment samples without preliminary separation treatment and revealed the presence of PS at mg/g levels in the superficial layers of sediments in the Ravenna Lagoon (Italy). Quantification was based on calibration curves built on peak areas of styrene obtained through SIM of the styrene molecular ion m/z 104.

Even if the use of only the styrene peaks could lead to misleading results, this limitation can be partially overcome in those cases where the precise and univocal origin of the styrene peak can be highlighted. In some cases this is possible on the basis of the styrene/toluene peak area ratio: e.g. the styrene/toluene ratio is reported to be in the range of 0.1–0.4 for the pyrolysis products from the most abundant natural organic materials in soil and sediments [94], while the ratio is generally higher than 1 when the styrene derives from synthetic polymers [24]. The presence or absence of butadiene marker peaks (butadiene, butadiene dimer, butadiene trimers and styrene-butadiene) – and their relative abundance in comparison with the intensity of the styrene peak – can be used to evaluate the contribution of styrene-butadiene rubbers to the plastic components. The yield of styrene is influenced by the molecular weight of PS. The use of styrene-dimer or trimer as identification and quantification markers for PS is thus currently seen as a preferable solution.

Examples of the ability of analytical pyrolysis to obtain mass-based concentrations of MPs separated from samples of environmental importance are reported in Table 1. A list of pyrolysis products and indicator ions used for the calibration and quantification in published studies is reported in Table 2.

Since 2017 Fischer and Scholz-Böttcher [46,47,54] have been exploring the potential of Py-GC–MS to go beyond a qualitative identification by quantifying synthetic polymers present as MP mixtures in environmental samples at trace levels. In their first experiments, they

Table 1

Identification and concentration of total MPs obtained by pyrolysis quantification in samples of environmental importance.

Origin	Concentration	MP type	Notes	Rif
Wadden Sea sediment	48–166 $\mu g\ kg_{dw}^{-1}$	PE, PVC > PP, PS, PET,PMMA	From replicates of a single sample (n = 4)	[54]
Boknaf Fjord (NO) sediments	41–495 $\mu g\ kg_{dw}^{-1}$	PE, PVC, PET > PP, PA66, PS, PMMA	Range from different samples	[53]
Fleur de Sel (Atlantic/Mediterranean)	138–1993 $\mu g\ kg^{-1}$	PE, PP, PS, PET, PVC, PC, PMMA, PA6, PUR	Range from different samples	[47]
Fleur de Sel	43 ± 12 μg/200g	As above	From replicates of a single sample (n = 5)	[47]
Sea salt (Atlantic/Mediterranean)	14–60 $\mu g\ kg^{-1}$	As above	Range from different samples	[47]
Atlantic Ocean water	0.12 $\mu g\ L^{-1}$	As above	Calculated from Fleur de Sel samples (mean value n = 7)	[47]
Mediterranean Sea water	0.20 $\mu g\ L^{-1}$	As above	Calculated from Fleur de Sel samples (mean value n = 5)	[47]
North Sea water	0.3 $\mu g\ L^{-1}$	PE, PP, PET, PVC, PMMA	One sample	[54]
Biosolids	2.8–6.6 $mg\ g^{-1}$	PE, PVC, PP, PS, PMMA	Range from 25 samples from single wastewater treatment plant	[68]
Soil	1–86 $\mu g\ g^{-1}$	PE, PP, PS	Validated on 2 samples	[45]
[illegible]	[illegible]	PE, PP, PS	RSD% below 10	[48]

used Curie Point Py-GC–MS combined with thermochemolysis using tetramethylammonium hydroxide (TMAH 25% in water) and selected characteristic pyrolysis fragments for the quantification. They quantified MPs in fish samples after a pretreatment consisting in enzymatic and chemical digestion in order to remove (or at least reduce) the biological matrix and to preconcentrate potential MPs. The aim was to obtain the simultaneous (Fig. 5), selective, and sensitive polymer specific identification and mass related quantification of MPs in environmental samples after the clean-up step [46]. In 2019 Fischer and Scholz-Böttcher [54] compared two different pyrolysis techniques, Curie-Point pyrolysis (CP-Py) along with thermochemolysis with TMAH and micro-furnace pyrolysis (MF-Py), for the simultaneous identification and quantification of MPs in environmental samples including sea salt, tidal flat sediments and North Sea surface water samples. All environmental samples need to be pretreated in order to reduce the organic components that are in the matrix and which could lead to interference. These authors quantified all the polymers previously analysed [46] along with methyl dimethyl diisocyanate-polyurethane (MDI-PUR) using MF-Py. The indicator ions used for calibration are reported in Table 2. In [47] Py-GC–MS along with thermochemolysis (TMAH), was applied to study MP contamination in different commercially available marine salt samples from the Atlantic Ocean and

Table 2

Examples of pyrolitic markers and peaks proposed for the identification and quantification of MPs. * Only after TMAH treatment. ^{f}n-$C_{16\text{-}26}$-alkadienes used for the quantification of PE.

Polymer	Identification		Quantification		
	Species	*m/z*	*Species*	*m/z*	*ref.*
PE	alkanes (e.g. C_{20})	85	alkanes (e.g. C_{20})	83 + 85?	[46]
	α-alkenes (e.g. C_{20})	83	1-tetradecene (C_{14})	83	[53]
	α,ω-alkenes (e.g. C_{20})	82	α,ω-alkenes (e.g. C_{20})^{f}	82	[47,54]
			1,14-pentadecadiene	81	[48]
			1-pentadecene	97	
PP	2,4-dimethyl-1-heptene	70, 126	2,4-dimethyl-1-heptene	70	[46,47,54]
			2,4-dimethyl-1-heptene	126	[48]
	2,4,6,8-tetramethylundecene (isotactic)	69, 111	2,4,6,8-tetramethylundecenes (three isomers)	69, 210	[46,53]
	2,4,6,8-tetramethylundecene (heterotactic)	69, 111			
	2,4,6,8-tetramethylundecene (syndiotactic)	69, 111			
PS	styrene	104	Styrene	104	[46,48]
	2,4-diphenyl-1-butene (styrene dimer)	91	2,4-diphenyl-1-butene (styrene dimer)	208	[53]
	2,4,6-triphenyl-1-hexene (styrene trimer)	91	2,4,6-triphenyl-1-hexene (styrene trimer)	91	[46,47,54]
PVC	benzene	78	Benzene	78	[46,47,54]
	chlorobenzene	112	1-methylnaphthalene	142	[53]
PA6	ε-caprolactam	113	ε-caprolactam	113	[46,47,54]
	N-methyl caprolactam*	113, 127	N-methyl caprolactam*	127	[46,47,54]
PA-66	Hexene	113, 84	hexaene	84	[53]
PMMA	methyl methacrylate	69, 100	methyl methacrylate	100	[46,47,53,54]
	methyl acrylate	55, 85, 86			
PET	dimethyl terephthalate*	163, 194	dimethyl terephthalate*	163	[46,47,53,54]
PC	*p*-methoxy-*tert*-butylbenzene*	149, 164	*p*-methoxy-*tert*-butylbenzene*	149	[53]
	2,2-bis(4′-methoxyphenyl)propane*	241, 256	2,2-bis(4′-methoxyphenyl)propane*	241	[46,47,54]
MDI-PUR	4,4′-methylenbis(N-methylaniline)*	226	4,4′-methylenbis(N,N-dimethylaniline)*	254	[47,54]
	N,N-dimethyl-4-(4-methylamino)benzylaniline*	240			
	4,4′-methylenbis(N,N-dimethylaniline)*	253, 254			
SBR, BR	vinylcyclohexene	54, 79, 93, 108	vinylcyclohexene	54	[55,81]
	butadiene	39, 54			
SBR	styrene	51, 78, 104			
	methylstyrene	78, 103, 118			
	cyclopenthylbenzene	115, 129, 144			
	cyclohexenylbenzene	104, 115, 129, 158			
	Phenyl-[4.4.0]bicyclodecene	91, 104, 156, 212			
BR	butadiene trimers and homologous	91, 148, 162, 176			
NR	dipentene	68, 93, 121, 136	Dipentene	68	
	isoprene trimers	119, 162, 189, 204			
	isoprene tetramers	93, 121, 134, 272			

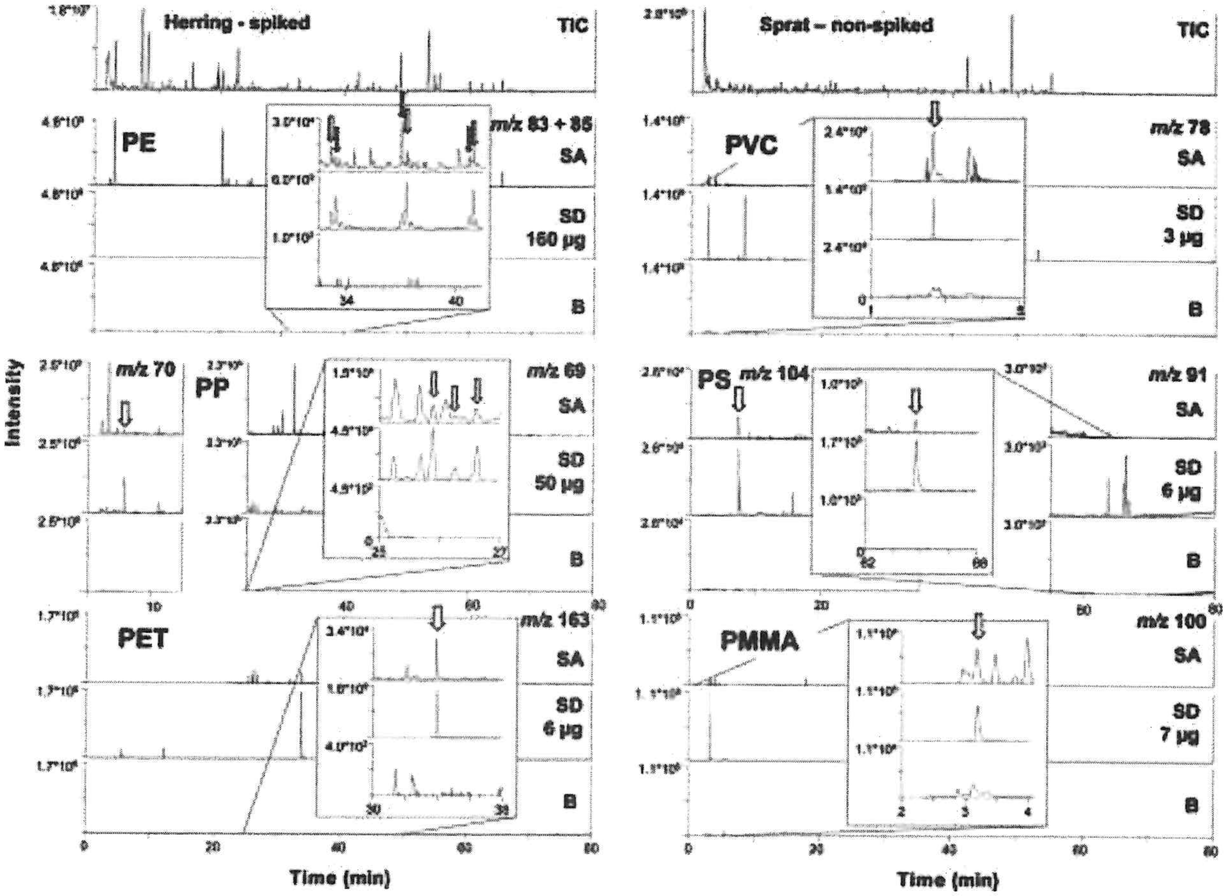

Fig. 5. Total ion chromatograms (TIC) of a spiked (left) and a non-spiked (right) MP fish sample. Left column: Herring sample, spiked with PE, PP, and PET; right column: Sprat sample (six stomachs pooled), nonspiked. Polymer indicator ion chromatograms and marker peaks (highlighted with arrows) of samples (SA) are compared with the respective standard mixtures chromatograms (SD) and procedural blanks (B). From Fisher et al. 2017 [46].

Mediterranean Sea. In particular, Fleur de Sel was analysed, which is an unprocessed natural product whose crystals are directly harvested from the sea surface and was proposed by the authors as an indicator substrate for the monitoring of the MP load of coastal waters. The qualitative MP composition of sea salts has shown very distinctive regional and supra-regional patterns, which are useful for assessing MP contamination levels on both temporal and spatial scales [53].

Ter Halle et al. [49] described a semi-quantitative approach to evaluate the relative amounts of different polymers in mixtures of MPs extracted from seawater, based on calculating the relative proportion of aromatic and aliphatic hydrocarbons in the colloidal fraction of seawater. The peak area of the selected m/z was integrated for each aromatic and aliphatic hydrocarbon and corrected by a mass spectra factor (MSF) calculated as the reciprocal of the proportion of the m/z (used for the integration) relating to the entire library mass spectra. They then determined the proportion of PVC, PS and PET in the aromatic fingerprint of nanoparticles using PCA.

An alternative thermoanalytical method "elemental analysis combined with the overdetermined equation method" (EA-OEM) was recently tested for the first time based on the calculation of combustion parameters of the determined materials. Although elemental analysis based on combustion is not a pyrolysis method, it is worth mention it here as an alternative approach aimed to determine the amount and composition of the MP content (PE and PP) in industrial effluent samples [95].

5.2. Selection of pyrolysis products for the identification and quantitation of MPs

Table 2 shows pyrolytic markers that have been used for the identification and quantification of MPs. The choice of indicator peaks and ions is a particularly delicate issue, especially for polyolefins where a wide of range of peaks can be used for the quantification. For example, the indicator ions for PE quantification proposed by Fischer et al. in [46] are m/z "83 + 85", while the same authors used m/z 82 – corresponding to α,ω-alkenes – in subsequent papers [47,54].

In the case of PS, styrene is the pyrolysis product that gives the highest yield, which is clearly beneficial for method sensitivity. However, styrene is not often selected as a quantitation marker because it is not a univocal pyrolysis product. Styrene is well known to be produced upon thermal degradation of various sources including humic substances [96], vegetables and fruit tannins, degraded lignins from wood and paper, plastic waste and diesel exhaust [48,81]. In addition, it is present among the pyrolysis products of several other synthetic polymers such as acrylonitrile-butadiene-styrene (ABS) and styrene-butadiene rubbers (SBR and SBS).

Dierkes et al. [48] monitored styrene (m/z 78) for the quantification of PS, and underlined that the results did not represent the PS concentration but a sum parameter of styrene containing polymers. These authors tested the selectivity of indicator compounds analysing organic matrixes that were not contaminated by plastics. They found that wood and engine oil interfered in the quantification of PS and PE, respectively. Also, fish filets can interfere in the quantification of PE because their high content of fatty acids release n-alkenes and n-alkanes during thermolysis. For these reasons, 2,4-diphenyl-1-butene (styrene dimer) and 2,4,6-triphenyl-1-hexene (styrene trimer) are recommended as quantification marker peaks of PS.

In the case of PE that yields several homologue pyrolysis products (see Fig. 1), different marker compounds have been used including summed alkadienes [51], 1-pentadecene (more sensitive) and 1,14-pentadecadiene (more selective) [48], or a single pyrolysis product (e.g. tetradec-1-ene [53]).

Relatively polar pyrolysis products, such as those produced by PET, give broad peaks with a non-polar GC stationary phase [21]. In order to improve GC performance and increase the range of MPs detectable by a single pyrolysis run, the advantages of using thermally-assisted hydrolysis and methylation (THM) with TMAH for condensation polymers and addition polymers with oxygenated side chains have been taken into consideration. The alkaline environment produced by TMAH plays a role in facilitating the chain-scission and methylation of the thermal degradation products of condensation polymers and polyesters such as polyvinyl, acryls, polycarbonated and polyamide resin. On the other hand the pyrolysis mechanisms of polyolefins are not altered by the presence of TMAH [46]. Table 2 reports the most abundant and/or polymer-specific compounds from THM-TMAH chromatograms chosen as markers for polymer specific qualitative and quantitative analyses which are indicated with an asterisk. Partial methylation may complicate quantitation [44,46]. For instance, both ε-caprolactam and its methylated derivative have been used to quantify PA6 by CP-Py [46].

Summarizing, for some polymers, the markers used for quantification are not the most abundant pyrolysis products as are derived from the qualitative identification. The choice of markers is crucial in quantification since the same pyrolysis products can derive from multiple origins.

5.3. *Calibration*

Calibration protocols have mainly been set up by weighing single polymer particles, for instance in the 0.5 – 50 µg range, and with few exceptions a satisfactory linearity (R^2 0.86 ÷ 0.99) has been shown by Py-GC–MS [46,53]. The calibration method is limited by the smallest particle that can be weighed by a proper balance and transferred into the sample holder of the pyrolysis apparatus. Under these circumstances, the limit of detection (LOD) by Py-GC–MS is below 0.1 µg and dependent on the polymer type (e.g. higher for the denser PVC, lower for PS [15]). Calibration solutions for soluble polymers can significantly reduce the LOD to 3 ng and the limit of quantitation (LOQ) as estimated for PS depending on the quantitation marker (e.g. LOQ 16 ng using styrene and 282 ng using a styrene trimer) [46], the use of calibration solutions for low polymer concentrations and weighed solid MP for higher concentrations is feasible within the same calibration curve [54].

Fischer and Scholz-Böttcher produced external calibration curves which were obtained by adding Al_2O_3 as an inert dilution matrix for the eight main common plastics PE, PP, PS, PET, PVC, PMMA, PC and polyamide 6 (PA6) [46]. The authors then demonstrated that internal calibration worked better than external calibration in particular for PET. Similarly, David et al. [23] found that internal calibration worked better than external calibration in the TG-MS analysis of PET in soil samples using the *m/z* 105 ion with LOD and LOQ of 0.07 and 1.7 wt% PET, respectively.

A major calibration problem is that the analytical measurement of pyrolysis products can be affected by such different factors such as experimental conditions, polymer properties and matrix composition. As far as the analytical parameters are concerned, pyrolysis temperature and split ratios affect the peak area and GC oven temperature peak temperature, especially for PE [43]. In the case of PS, thermal extraction conditions in TED-GC–MS can modify the proportion of the styrene monomer, dimer and trimer [21].

Matrix effects should be carefully evaluated. Pyrolysis of PS in the presence of sediment components (quartz, calcite, various clays) considerably influences the yield of pyrolysis products affecting the slope of the calibration curves [65]. Besides inorganic constituents, natural organic matter is critical specifically for the production of pyrolysis products that are identical to those of the target polymer, and more generally for the background contamination of the pyrolysis system which could reduce the number of samples that can be analysed sequentially [46]. Matrix effects can be mitigated by performing the calibration using the sample matrix or matrix-matching materials [65]. Dümichen et al. [51] prepared the calibration of PE in soil (0.15–5% range) for the TED-GC–MS.

Finally, the characteristics inherent in the polymer itself should be taken into consideration. For instance, styrene yields have been shown to be dependent on the molecular weight of the polymer [97]. Fortunately, at analytical concentrations, the molecular weight does not appear to influence the styrene peak area determined by Py-GC–MS [98]. The effect of ageing did not seem to significantly change the pyrolytic behaviour of the MPs [21].

Internal pyrolysis process standards ($ISTD_{py}$) have been proposed [47,54,99] to improve quantification by avoiding variabilities within the calibration curves due to variable organic loads. The proposed internal standards mimic the potential interactions of polymer specific indicator compounds with pyrolytic products of residual organic sample matrices during the pyrolysis process. The internal standards proposed by Fisher et al. include: an aliphatic compound (androstane), a planar aromatic compound (9-dodecyl-1,2,3,4,5,6,7,8-octahydro anthracene (DOHA) or 9-tetradecyl-1,2,3,4,5,6,7,8-octahydro anthracene (TOHA) and anthracene-d^{10}), and a polar compound (cholanic acid) whose acid group undergoes methylation during thermochemolysis. Individual calibration curves were created using the ratio of the area of the preselected indicator ions (Table 2) to the area of the matching $ISTD_{py}$ which was selected individually for each polymer, on the basis of the coefficient of determination, r^2, and the standard deviation, s_{xo}.

A completely different internal standardisation was used by Dierkes et al., where a polymeric internal standard, deuterated PS d5 – was used as the quantification internal standard. The method is based on the combination of pressurized liquid extraction and Py-GC–MS, and it led to low quantification limits for environmental samples. For the calibration curves they diluted different amounts of polymers in calcined sea sand. Gomiero et al. [53] used Py-GC–MS in combination with TMAH thermochemolysis to study sample sediments from an urban fjord in Norway after an enzymatic and peroxide treatment. In order to identify a possible trend in polymer space and size distribution, principal component analysis (PCA) was subsequently applied to the data obtained. PCA is very effective in interpreting Py-GC–MS data, differentiating between sites close to urban coastal areas and more open water sites.

The significant environmental impact of the pollution caused by tire and road wear particles (TRWP) was also explored by a quantitative Py-GC–MS approach [81]. Unice et al. proposed a calibration method including deuterated polymers (PS, polyisoprene and polyisobutadiene) as internal standards in order to quantify tire tread in environmental samples. In order to assess the content of tire wear-off, Eisentraut et al. [55] quantified the amount of SBR, which is found in most of car tire samples, in reference samples, and real samples from street runoff. Specific quantification marker compounds for SBR, BR and NR are listed in Table 2.

Optimizing sample pre-treatments entails quantifying MPs in environmental and fish/biota samples in order to avoid losses of analytes that could hamper or bias the obtained results. Controlled practices are needed for quantification in order to minimise the contamination with plastic and fibres from the sampling and laboratory environment, as described in the following section.

5.4. *Quality control and quality assurance in MP analysis*

Microplastic contamination from the sampling and laboratory environment is a major issue in the analysis of MPs in environmental samples, which can interfere with both qualitative and quantitative determination. Carrying out the entire treatment, digestion (in the analysis of animal or plant tissue), separation and drying steps in the same crucible or vial is advisable when possible, and in addition keeping it constantly covered e.g. protected with aluminium foil to prevent contamination from the laboratory environment [54].

Procedural blanks need to be analysed in parallel to monitor and estimate secondary contamination. To ensure the quality of the analysis the entire analytical procedure without the MP samples using the same system and reagents used for the environmental samples [67]. The blanks can also be evaluated by running the entire sample pretreatment procedure on analogous matrices to the cleaned environmental samples, such as calcined sea sand [48] or thermally pre-treated marine sediment [53]. Alternatively, commercial aquarium sand has been used by some authors to assess background contamination during extraction and flotation procedures [57].

Airborne contamination is another critical aspect during the entire sample treatment. The use of natural fibres clothes and protection is thus recommended for operators [100]. Fibrous fragments are in some cases excluded from the investigations to prevent the risk of overestimation related to substantial procedural contamination [58]. Doyen et al. used of four Petri dishes placed in strategic positions in the laboratory during the extraction and sample preparation in order to evaluate laboratory environmental contamination [101]. Finally, field blanks also need to be performed in order to ensure the absence of airborne contamination.

When an organic solvent extraction is used, the yield of the extraction is difficult to estimate, although crucial for quantification purposes. Extraction depends on the type of solvent, polymer and on its level of degradation. The most common approach to evaluating the yield of the organic solvent extraction of sediment is to extract the residue in order to assess the presence of residual plastic.

Another critical limitation that emerged in the first studies of environmental samples by Py-GC–MS is that the matrix-effect needs to be taken in consideration due to the fact that the composition of the affects heat-transmission influences the kinetic and thermal induced reaction, and thus the yield and distribution of the pyrolysis products. Eisentraut et al. [55] spiked the sample with standard polymers in order to take into account the matrix effects in the calibration curves.

Finally, as discussed in the previous section, the addition of an internal standard in the environmental samples is another good way of improving the performances of the analytical method. Deuterated polymers as internal standards have been used in several studies [48,81,99].

6. Concluding remarks and future perspectives

The analytical procedures for the identification of MPs based on analytical pyrolysis are summarised in Fig. 6.

Thermal analytical techniques are generally recognized as complementing spectroscopic approaches, such as Raman and infrared spectroscopies. Raman spectroscopy coupled with microscopy certainly has the advantage of using extremely low sample sizes and spatial resolutions (up to 1 µm) [102].

On the other hand, despite the good performance of the coupling with microscopy, the chemical information provided by Raman and FTIR spectra is limited compared to the GC—MS analysis of pyrolysis products. This is because the selectivity of vibrational spectroscopy is not sufficient to identify specific monomers and co-monomers, mixtures, additives, and degradation products. The second common limitation of Raman spectroscopy and ATR-FTIR is that the spectra are relative to the surface portion of the MP fragments [43,44].

Analytical pyrolysis overcomes these problems and characterizes MPs at a molecular level and identifies not only synthetic polymers, but also the possible presence of additives. The main advantage of Py-GC–MS over commonly applied FTIR spectroscopy is that both polymer types and organic plastic additives can be analysed in a single analytical run, and the monitoring of additives in MPs has attracted increasing attention due to their potential toxicity. The potential of double shot and multi-shot Py-GC–MS in the characterisation of volatile additives and polymers in the same sample, by exploiting their thermal separation, still needs to be evaluated in the MP analysis field.

Another possible instrumental set-up for the characterisation of polymer samples containing fractions with different thermal decomposition temperatures is evolved gas analysis coupled with mass-spectrometry (EGA-MS, set up in Fig. 7). EGA-MS also merits further research in MP analysis, in particular in degradation studies. The direct coupling of Pyrolysis with MS was also recently tested in a custom-made portable system as promising tool for in-field analysis of MPs, such as in ship-based marine surveys [103].

Sample handling in the analysis of MP particles is critical, in particular when the aim is to investigate the micro-and nanoparticles that cannot be managed and isolated manually. The analysis of MPs with sizes lower than 50 µm is complex when carried out manually. The review by Peñalver et al. [34] gave several recommendations for handling samples before Py-GC–MS measurements and providing possible solution to the particle size limitation.

The use of solvents for extraction from sediments or other matrices could partially overcome the limitations related to particle sizes. Although the organic solvent extraction approach is not able to characterize individual MPs, but it can be used to characterize mixtures by thermal separation (Multi-shot Py-GC/MS and EGA-MS), chromatographic separation, and mass spectrometric selectivity [67].

Despite the high efficiency of Py-GC–MS in identifying different types of polymers, as with vibrational spectroscopic approaches it has difficulties in discriminating between subtypes of plastics, i.e. differentiating LDPE from HDPE, or differentiating between PS, expanded PS, and crosslinked PS [63].

It is worth noting that the particle size, particle number, and mass need to be determined in order to improve the understanding of the impact of MPs and to assess the associated environmental risks. However, to date MP mass data have been less investigated due to the lack of consolidated analytical methods to tackle this aspect.

Despite the limitations that have been highlighted in this review, thermoanalytical techniques currently have the best potential for the quantitative determination of MPs in the environment based on mass units. The awareness of these limitations is the main driver for finding solutions that lead to robust analytical procedures. The major potential for developments are intrinsic to the thermoanalytical techniques, i.e. sensitivity, hyphenation ability, data handling. The potential of trace analysis has been demonstrated at the nanogram level. New statistical approaches to tackle polymer variability and matrix interference are being developed, and combinations with highly selective separation systems (e.g. Py-GC/GC), detectors (e.g. HRMS) will soon be emerging.

While new methods are emerging, there is the need for standardisation and validation of methods and procedures, as highlighted in a recent study that compared different techniques including pyrolysis for the quali-quantitative analysis of MPs in water samples [104], and in an interlaboratory comparison specifically focused on thermal procedures [105]. This last study involved a number of laboratories, analysing a spiked sediment sample by Py-GC–MS, TGA-FTIR, TGA-MS, and TED-GC–MS. The reproducibility of the round-robin results was estimated 14% for PE and PS, and 40–50% for PP and PET, confirming a need for future harmonization of the currently wide range of procedural variants. The study highlighted limitations in TGA-MS, due to the dependence of this technique solely on mass fragments, without a retention time window as additional identifier.

Development of methods and validation procedures will require the production of reference materials by authorized organizations that should be made available to laboratories.

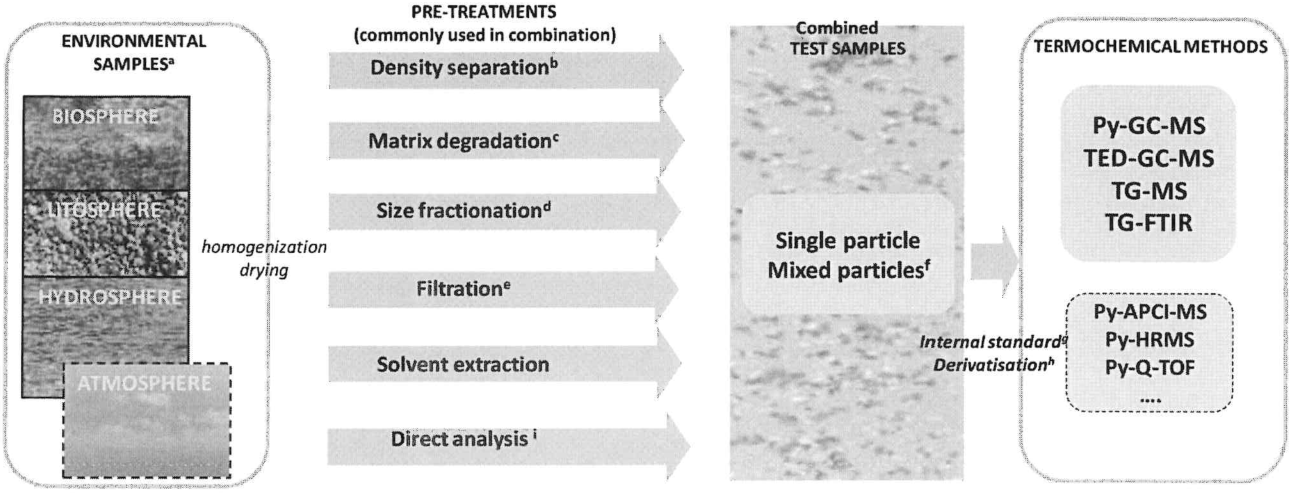

Fig. 6. The analytical procedures for MP analysis described in the literature to date and outlined in this review, with possible developments (dotted lines). [a]Samples from biosphere (mussel, fish); lithosphere (sand, river sediments); hydrosphere (seawater, river water, lake water, sea salt). [b]$3Na_2WO_4 9WO_3$; $ZnCl_2$; NaCl; NaBr; NaI. [c]KOH 10%; H_2O_2 30%; proteases. [d]Stainless sieve(> 0.25 mm, < 5 mm). [e]Glass microfiber filter (GF/F), Ø 15 mm, 0.2 µm. [f]Fragments picked up with tweezers, milled filter, etc. [g]Anthracene-d10 etc. [h]TMAH. [i]Or in alternative off-line pyrolysis.

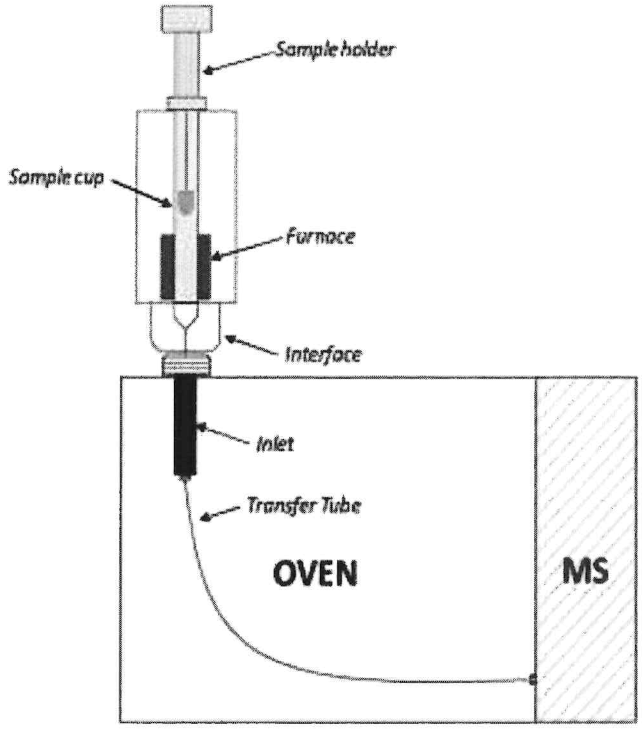

Fig. 7. Instrumental asset of a EGA-MS system based on a furnace pyrolyser (Frontier Lab, Japan). Reprinted with permission from [40].

Declaration of competing interest

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

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as floating marine litter. The degradation of plastic debris under the effect of UV-light and moisture is responsible for the fragmentation into small particles (secondary MPs) [12].

There is increasing scientific concern regarding the effects of MPs on aquatic life [4] as they persist in the marine environment and have been reported to retain contaminants as persistent organic pollutants [13]. In fact, MPs are considered a vector for introducing bacteria and hazardous chemicals into organisms through ingestion [14], such as organic additives [15] or residual monomers [16], with potential toxic effects for the aquatic biota. These aspects are fundamental for human health since MPs ingested by fish and shellfish have recently been suspected to contaminate the human food chain [13,17].

Environmental scientists, regulators and other interested parties have highlighted the urgent need for quantitative and qualitative data on the amount and types of MPs, in order to evaluate their sources and distribution in environmental matrices [18], organisms, and in commodities for human use [13,17,19], and to perform scale spatial and temporal comparisons.

This need has fostered intense research to develop, optimize, evaluate and apply analytical methods for the characterisation of MPs in aquatic, terrestrial or biological samples.

An additional crucial issue is the lack of standardisation in the sampling and analysis of MPs, and focused research actions are now tackling this fundamental task (see for instance [20]), activating massive scientific efforts in developing, optimizing and evaluating methods. Instrumental analytical techniques based on analytical pyrolysis and thermal analysis in the last years have become candidates to become of general use in the analysis of MP, as an integration to spectroscopic methods. Most of the data on MP contamination have been obtained by microscopic visualizations, which are based on the particle number and size. Although quantitation based on particle counts is important especially in ecotoxicological studies, data cannot be converted into mass by calculating the shape and density without strong approximations due to the highly variable morphology of MPs. Unlike spectroscopic methods (FTIR, Raman) which are essentially applied for polymer identification, thermochemical methods provide both qualitative and mass based quantitative information.

Thermal analysis [21–23] and analytical pyrolysis [24,25] methods are based on the thermal decomposition of polymers or polymer mixtures and on their characterisation through the analysis of the pyrolysates (Fig. 1). These approaches are recognized crucial and powerful tools for the molecular and thermal/physical characterisation of polymeric materials, thus their application to the analysis of MPs has been a natural step.

In particular, analytical pyrolysis coupled with gas chromatography and mass spectrometry has been recently considered with great attention as a means to provide molecular and mass spectral information on MP composition and degradation in the environment.

Although several reviews [26–33] have been published on the chemical analysis of MPs in various environmental matrices that mention thermochemical methods, including a specific overview on the subject [34], a detailed and comprehensive critical examination focused on a quantitative analysis integrated within a historical perspective is lacking.

This paper reviews the research carried out to date in the analysis of MPs by analytical thermal and pyrolysis techniques. This could then provide a basis for monitoring the rapid ongoing development of this sector of analytical chemistry, and also the activities aimed at evaluating, comparing and standardising analytical techniques and analytical data in MP research.

2. Pyrolysis of plastic polymers

The main pyrolysis products of common plastics are reported in Fig. 1. Thermal analyses proposed for the determination of MPs, but which do not involve the pyrolysis process were not considered in this review (e.g. TGA-DSC exploiting the endothermic solid-liquid transition of polymers [35]).

Where applicable the abbreviations used in this review are consistent with the IUPAC nomenclature for polymers (see Fig. 1) [36], analytical pyrolysis [37], and thermal analysis [38]. For analytical pyrolysis coupled with gas chromatography and mass spectrometry, the abbreviation Py-GC–MS is recommended and herein used. Fig. 2 reports the scheme of the set-up for a typical furnace Py-GC–MS system. The majority of common plastic polymers are reported to undergo full volatilisation during pyrolysis (PE, PS, PMMA, PP), while a certain amount of charred residue is reported for PC, PET and PVC (for example 23%, 9% and 6% of the starting mass for the three polymers respectively) [39].

The abbreviation TED-GC–MS is used for TGA combined with solid phase extraction (SPE and thermal desorption TDS-GC–MS) [21]. Fig. 3 reports the scheme of a TED-GC–MS system.

3. Sample pre-treatments and isolation of MPs for thermochemical analysis

3.1. General aspects

An opportune treatment of the sample is crucial in order to produce a suitable portion of material to introduce into the Py-GC–MS system. Plastic particles can be collected by visual inspection – using a microscope and tweezers – for particles with a minimum size suitable for handling, that can be approximatively estimated as > 0.1 mm in size or > 0.1 mg in weight [42].

A lower size or weight may be possible depending on the type of fragment (e.g. microfiber vs. microsphere) and polymer (e.g. high vs. low density) [43]. Plastic particles can be directly picked up from the sample and transferred into the pyrolysis holder, as reported for the sand surface [43] or stomach content of marine fish [42]. However, even when plastic particles are manually selected, a concentration/separation step from the samples is often necessary. For instance, in one study particles from surface lake water tow were sieved, treated with Fe^{2+}/30%H_2O_2 to degrade labile organic matter, separated by density with NaCl, and transferred into a Nylon filter from which selected items were manually selected and transferred to Py-GC–MS for identification [42].

The sample treatments described in the literature strongly depend on the features of the environmental matrix under investigation. The main types of matrices that have been analysed by thermoanalytical methods for MP fragment analysis include water [21,42,43], sediments [44], soil [45], and marine organisms [43,46]. Marine organisms can be sampled as whole individuals, or animal tissue, or as the content of fish stomachs. Investigating the presence of MPs in commercial food products is gaining increasing importance due to the implications for human exposure. The category of commercial food products often overlaps with marine organisms/animal tissue because it is most seafood and fish products for human consumption. Other types of food supplies derived from the marine environment, such as algae or sea salt, are also of interest [47].

Single-particle analysis is not the only application of thermochemical methods. Due to the selectivity achieved by the coupling with GC–MS, analytical pyrolysis techniques are suitable for the analysis of mixtures of different micro- and nanoplastics obtained by extraction or filtration [21,41,46,48–50], and can also be potentially exploited for the analysis of solid microportions of homogenized ground mixtures of particles of different polymers. Cryo-milling is recommended in the homogenisation of solid plastic samples in order to facilitate milling and to avoid heating and alterations in the polymers. However the effects of these types of sample pretreatment on the polymer analytical response need to be investigated further [51].