Microplastic and nanoplastic analysis: from Pyrolysis GC-MS to Pyrolysis GC×GC-MS – A critical review

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Abstract

The growing environmental and health concerns regarding micro- and nanoplastics have prompted the development of advanced analytical methods for accurate characterization and quantification. Pyrolysis-gas chromatography-mass spectrometry enables polymer identification by their thermal destruction into characteristic fragments. However, the small particle size and interferences originating from complex sample matrices complicate its analysis. Therefore, the integration of comprehensive two-dimensional gas chromatography would improve separation efficiency and sensitivity and provide a detailed composition of environmental and biological samples. This review documents (i) the evolution of pyrolysis-gas chromatography-mass spectrometry and (ii) the potential to resolve overlapping compounds, improving quantification accuracy, and detecting minor plastic compounds and degradation byproducts by comprehensive two-dimensional gas chromatography coupled to mass spectrometry as a crucial approach to measure micro- and nanoplastics. Despite the documented advancements, key challenges persist. The lack of standardized protocols for sample preparation and calibration, impeding the comparability of studies, is of prime concern. The massive presence of (in)organic interferences even further accentuates the absence of internal standards in terms of quantification. Therefore, to improve analytical reliability, future research should focus on developing standardized methodologies, improving detection sensitivity for nanoplastics, and incorporating complementary approaches. Additionally, coupling 2D GC with time-of-flight mass spectrometry further strengthens its capability to provide higher analytical resolution power and better chemical description of pyrolyzates. This review highlights the crucial role of advanced pyrolysis and chromatography-based techniques in supporting the analytical description of the extent of plastic pollution and to support evidence-based policymaking and successful mitigation efforts to protect ecosystems and public health.

Keywords

Pyrolysis-Gas Chromatography-Mass Spectrometry; Comprehensive Two-Dimensional Gas Chromatography; Environmental contaminants; Micro- and Nanoplastic Pollution; Polymer identification

1. Introduction

Due to global plastic pollution and its slow natural degradation process, plastics in all their forms, including microplastics (MPs) and nanoplastics (NPs), have become major pollutants in the environment. The most widely used plastic materials, accounting for about 90% of the global production, include polypropylene (PP), high- and low-density polyethylene (HDPE and LDPE), polyvinyl chloride (PVC), polyurethane (PUR), polyethylene terephthalate (PET), and polystyrene (PS) [1]. Micro- and nanoplastics (MNPs) are small plastic particles that differ in size but share similar origins and environmental concerns. This review focuses specifically on the analysis of MNPs, as analyzing these materials has become crucial for characterizing their composition and identifying their origins.

MPs are commonly defined as plastic particles with sizes ranging from 1 micrometer (µm) to 5 millimeters (mm) [2]. However, according to the ISO/TR 21960:2020, their size ranges between 1 µm and 1000 µm. The primary source of microplastics is their manufacturing. They are produced as microbeads used in cosmetics and personal care products, or pellets for industrial applications [3]. Moreover, (secondary) microplastics also result from the breakdown of larger plastic items due to environmental factors like UV irradiation and mechanical abrasion. Common sources include tire wear, synthetic textiles (through washing), plastic bottles, bags, fishing nets, and various plastic debris. MPs can be found in terrestrial and aquatic environments, including soils, sediments, oceans, lakes, rivers, groundwater, and even in the polar ice caps at both the northern and southern extremes of the Earth, mainly due to atmospheric deposition [3,4]. Since they are omnipresent, MPs can be ingested or inhaled by various organisms (see Figure 1), leading to physical and toxicological effects [5]. Both primary and secondary MPs contribute to environmental pollution, highlighting the need for their accurate identification and quantification to evaluate their abundance.

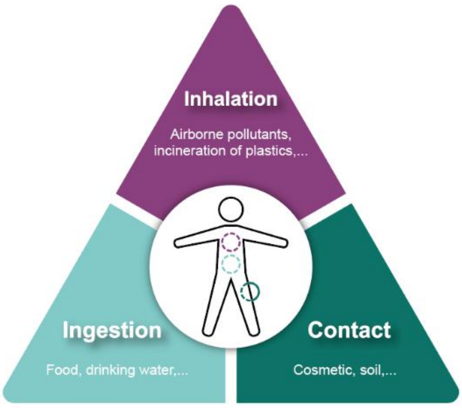

Figure 1: Examples of micro- and nanoplastic (MNP) exposure pathways in humans.

Concerns about MP pollution have recently expanded including NPs. NPs are defined by the ISO/TR 21960:2020 as plastic particles smaller than 1 µm, typically within the size range of 1 to 1000 nm [6]. Similarly to MPs, NPs are also classified into two groups. Primary NPs are intentionally manufactured for specific applications, including cosmetics, paint or textiles among others. On the other hand, secondary NPs can be generated through further degradation of microplastics by, for instance, mechanical abrasion or UV degradation. The latter type appears to be the most abundant in the environment, with major sources being tire wear, synthetic textiles and fishing nets. However, proper detection and quantification are still lacking to fully assess the scope of the NPs' ubiquity in the environment, their exposure pathways (Figure 1), and their impact on animal and human health [7].

Growing concerns are also emerging about the potential health impacts on wildlife and humans, particularly through the food chain and exposure through contaminated water and air. Understanding the characteristics, sources, and impacts of MNPs are crucial for developing strategies to mitigate their environmental presence and reduce potential harm to ecosystems and human health. Indeed, MNPs pose significant health risks as they accumulate in various tissues of organisms, including the intestines [8], liver [9], reproductive organs [10], and blood [11,12]. In the intestines, MPs can lead to inflammation, obstruction, and gut microbiota imbalance, potentially triggering immune responses [13]. A recent study highlighted that MNPs are increasingly being recognized as potential risk factors for cardiovascular disease in preclinical research [14]. Other studies on aquatic species and mammals have demonstrated MPs' ability to cause oxidative stress and intestinal dysbiosis [15–21]. Moreover, Shi *et al.*

observed metabolic function disruption in the mice liver, potentially leading to insulin resistance and diabetes. Mice exposed to polystyrene microspheres with a diameter of 1 µm exhibited high levels of fasting blood glucose and fasting insulin [22]. Exposure to MPs also negatively impacts reproductive health by interfering with endocrine functions and crossing the blood-placental barrier, causing developmental harm [23]. Additionally, MPs are linked to cancer risks in the lungs [24] and gastrointestinal tract [25], highlighting the widespread and severe health effects across different tissues [26–29]. Concerning NPs, due to their small size, they can penetrate biological membranes, potentially causing more severe biological and ecological effects compared to MPs. Indeed, they are more likely to be taken up by cells, potentially leading to toxicological impacts at cellular level [30]. More recently, a study reported the fact that MNPS may contribute to increased bacterial antimicrobial resistance, exacerbating environmental pressures [31]. These findings further underscore the need for accurate and comprehensive assessment of MNPs and their potential impacts.

Currently, no unique method exists for the MNP identification and characterization in environmental samples as it is very dependent on the polymer type and size [2]. The plastic size and shape, and the polymer composition of plastic debris are important properties for determining its source and origin (primary or secondary waste) and assessing its potential to cause physical or physiological harm to exposed organisms [2].

Microplastic analysis typically involves spectroscopic techniques (i.e. µ-FTIR, µ-Raman). However, these techniques face limitations in terms of particle size and polymer type. For instance, the analysis of tire wear particles is not feasible due to the carbon black content [32]. Additionally, using these techniques, the detection of particles smaller than 10 µm is challenging [33].

Thermo-analytical techniques either or not coupled to chromatographic separation tools (i.e. Py-GC-MS, Thermal Extraction and Desorption (TED)-GC-MS [34], Thermal Desorption (TD)- Proton Transfer Reaction (PTR)-MS [35], and Thermogravimetric Analysis (TGA)-MS [36]) are more recently gaining increased attention as these techniques offer enhanced selectivity and quantitative capabilities, enabling more precise microplastic quantification [37]. A review of the actual literature reveals a substantial body of work on pyrolysis-GC-MS for microplastic and/or nanoplastic analysis, with 316 articles, 65 reviews, 12 book chapters and 2 books identified following the research methodology resumes on Figure 2 using Scopus. In the last ten years, Py-GC-MS has been applied for the analysis of MNPs starting with the analysis of polymers and additives in marine microplastic particles in 2013 [38] and since then, the number of articles published has steadily increased, with 94% papers published since 2020, as shown in Figure 2b. As of 2019 [39], papers published on the analysis of nanoplastics using Py-GC-MS account for 26% of documents on the subject (Figure 2b), highlighting the fact that nanoplastics, and in particular their analysis by Py-GC-MS, are a relatively new field. As a result, several loopholes are still present, and extensive research is highly recommended. As an example of a nanoplastic source, 1 L of bottled water contains approximately 24,000 plastic particles, with 90% being nanoplastics and 10% microplastics, representing a 100-fold increase from earlier estimates [40].

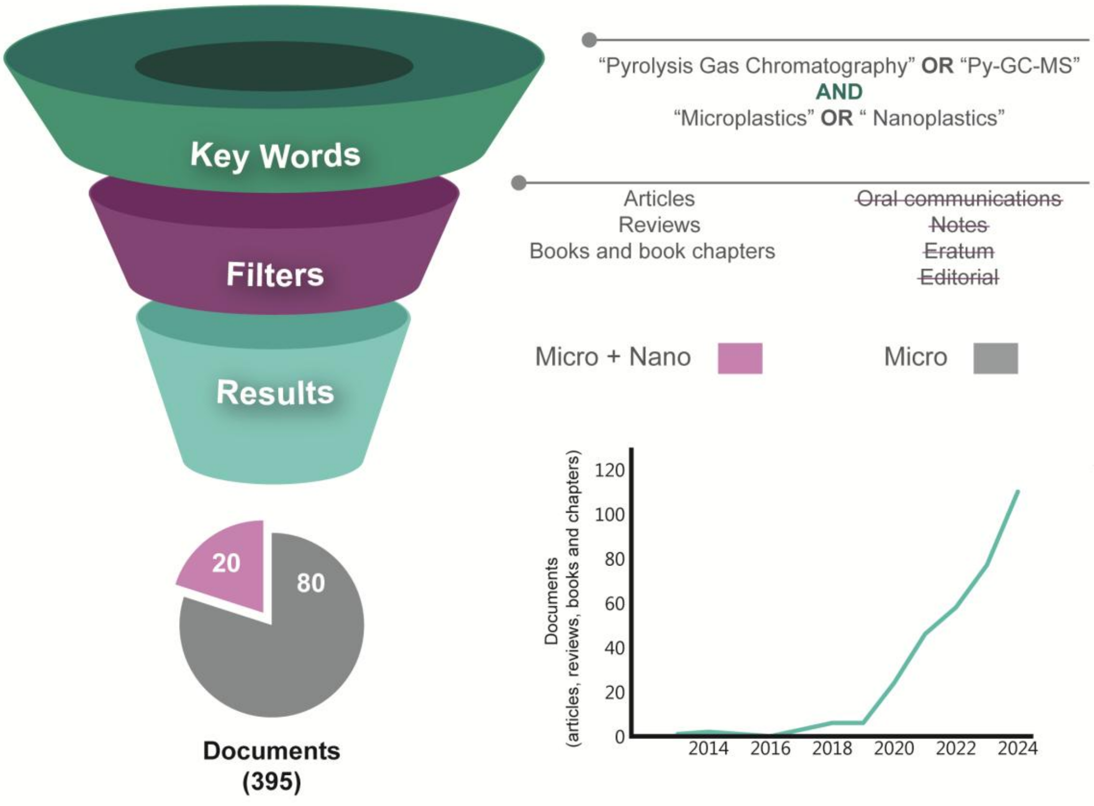

Figure 2: Research methodology followed using Scopus and the obtained results. Last update on April 23, 2025. Documents concerning the analysis of micro- and nanoplastics using Py-GC-MS published by year. Results obtained with Scopus using keywords "Py-GC-MS" OR "Pyrolysis gas chromatography mass spectrometry" AND "microplastics" OR "nanoplastics" limited to articles, reviews, books, and book chapters.

On the 65 reviews, 44 mentioned analysis of MPs and only 21 both MNPs. Table S1, in the supplementary materials, lists the 65 literature reviews found.

The primary aim of this review is to provide a concise summary of the basic principles of pyrolysis (Py). Next, an overview of the use of pyrolysis coupled with gas chromatography-mass spectrometry (Py-GC-MS) is presented as a tool to analyze MNPs in environmentally relevant samples. Then, we discuss the unique capabilities of comprehensive two-dimensional gas-chromatography (GC×GC) for the analysis of microplastics and nanoplastics. Finally, we present a series of proof of principle experiments on the future use of Py-GC×GC-ToFMS as a comprehensive analytical method for both micro- and nanoplastic analysis.

2. Sample pre-treatment

Micro- and nanoplastics have already been identified and quantified in several matrices including soil [41], sea water [42], drinking water [43], seafood [44], table salt [45], and human blood [11] but some gaps still need to be covered to establish standardized identification and quantification procedures. Before reaching polymer identification and quantification, several steps must be performed, starting with the harmonized sample collection and preparation. Matrix effects remain an important factor due to their potential impact on microplastic identification and quantification. They can lead to an overestimation of the MNP content due to the presence of organic matter forming similar pyrolysis fragments. Rauert *et al.* highlighted the overestimation of PE in samples containing lipids as their pyrolysis products are similar [46]. Further, as mentioned by Wenzel *et al.*, the presence of organic matter is impacting the sensitivity of heavy pyrolysis fragments (e.g. 2,4,6-Triphenyl-1-hexene) [47]. Moreover, the presence of inorganic matrices can hamper the pyrolysis fragmentation of several polymers or can act as catalysts during the depolymerization reaction leading to biased results. Co-elution with organic matter pyrolysis products, originating from the initial matrix, may also cause MNP underestimation, as overlapping m/z values complicate accurate quantification [47]. Therefore, the sample pre-treatment step remains crucial in achieving reliable Py-GC-MS results but highly depends on the studied matrix. For instance, if the matrix of interest is air or drinking water, the sample preparation will be less extensive compared to sewage sludge or soil samples. Manual selection, based on the naked eye identification of plastic particles can be considered for bigger plastic particles. However, for nanometer size particles, alternative methods must be established [33]. Sample pre-treatment procedures have been extensively described and discussed in two recent literature reviews from Wenzel *et al.* and La Nasa *et al.*, published in 2020 and 2024 respectively, and are therefore out of scope in this review [47,48]. However, for the sake of completeness, the key findings are summarized in the paragraphs below.

Up to date, no standard procedures have been published, complicating the establishment of an exhaustive summary of the existing sample pre-treatment protocols. The different steps of sample pre-treatment include sieving, density separation, solvent extraction, filtration, and organic matter digestion. The establishment of the sample pre-treatment procedure is highly matrix dependent. The most common matrices include water, soil, sediment, and marine organisms [48]. As the matrix effect is an important factor to consider, the first step of the sample pre-treatment procedure is most commonly the removal of organic matter. In the case of soil and sediment, density separation is predominantly applied first, for which sodium chloride, sodium bromide and sodium iodide are mainly used [48]. However, the type of salt needs to be chosen based on the polymer of interest as well as the analytical method. Indeed, the compatibility of salt with Py-GC-MS has to be verified beforehand, and several steps concerning the salt removal need to be implemented in the procedure. To further remove the organic matter, a digestion can be performed using different reagents, including acids, bases, and oxidizing agents. It has been demonstrated that bases, like potassium hydroxide, damage the plastic particles and are therefore not recommended. The use of Fenton reagent and hydrogen peroxide appeared to exhibit essential properties by its common use [47,49]. Following the density separation or organic matter digestion, filtration is often the last step of the sample pre-treatment, prior to the instrumental analysis. However, also here several aspects need to be considered. First, the type of filters used should fulfill some criteria including resistance to heat, suitable pore size depending on the size fraction of interest and no polymeric materials similar to the sample composition can be present. Besides the physical and chemical properties, some practical properties can also be incorporated such as the diameter of the filter. This is of crucial importance as when the filter is too large (diameter > 15 mm), it cannot be directly transferred to the pyrolysis cup leading to an uncomplete injection of the sample. Even though the chemical properties should be evaluated before, it is recommended to bake the filter in a muffle furnace prior to its use as filter contaminations have already been reported [50]. After the filtration and depending on the type, the filter can be folded or crushed and directly introduced into the pyrolysis cup minimizing the sample loss and providing a complete overview of the sample composition [51,52]. If the folded filter cannot be introduced into the cup, extra steps, including cutting the filter, will have to be performed, increasing possibilities of sample loss, contamination or obtaining non-representative measurement. Different types of filters can be used, for instance the use of glass fiber filters has been reported the most in the literature [48]. The use of quartz filters with a diameter smaller than 15 mm is recommended by the International Organization for Standardization in the case of MPs analysis in water (ISO/CD 16094-3:2023 (E)). Moreover, the use of stainless-steel filters has also been reported in the literature [49]. The pore size of the filter is also an important parameter as this information cannot be obtained by Py-GC-MS analysis, cascade filtration can also be performed in order to analyze different size fractions. Nevertheless, prior to instrumental analysis, all residual chemicals have to be removed to avoid unwanted side-reaction hampering the polymer identification [47].

Moreover, among the sample pre-treatment procedures, pressurized liquid extraction (PLE), also called accelerated solvent extraction (ASE), has been documented in the literature. Okoffo *et al.* reported the use of PLE to reduce the organic content of the sample together with the use of double shot pyrolysis [41]. The use of microwave-assisted extraction (MAE) has also been reported in the literature by La Nasa *et al*. MAE can be used to quickly pre-treat the samples and combined with double shot pyrolysis to extract, identify, and quantify microplastics as well as additives in, for instance sand samples [53]. The first shot of double shot pyrolysis, the thermal desorption, can also be used as sample pre-treatment as this step is dedicated to the removal of non-polymeric materials present in the sample (i.e. additives and organic matter).

Subsequent to the offline sample preparation methods described, also an online approach (i.e. derivatization) is present for the detection of MNPs. Such derivatization process uses particular derivatization agents, like for instance tetramethylammonium hydroxide (TMAH), which aims to improve the detection of certain polymers, including polyamides (PA), polyethylene terephthalate (PET) and polyurethane (PU). The presence of TMAH enables the formation of volatile methylated compounds during pyrolysis, through a process called thermochemolysis. However, TMAH is classified as a dangerous reagent causing damage to the organs, severe skin burns and eyes damage and can be fatal in case of skin contact. Thus, this reagent needs to be handled cautiously, and both the advantages and drawbacks should be considered prior to its use [54].

3. Py-GC-MS and its contribution to microplastic analysis

3.1 Pyrolyzers

Pyrolysis, a thermochemical process, involves the cleavage of chemical bonds at high temperature under an inert atmosphere [55]. It has been widely applied for more than 60 years [56] across various industrial fields, such as energy production, industrial processes, waste management and recycling. Regarding energy production, biomass pyrolysis results in the production of bio-oil further used as biofuel. Through the pyrolysis process, chemicals, like for instance hydrocarbons, often used as starting material in the chemical industry, can also be produced. Further, it also plays a crucial role in waste management and recycling processes, including the treatment of wood, food, rubber, textiles, electronic and plastic waste. Pyrolyzing plastic waste can lead to the formation of pyrolysis oil, gas, and char. The latter can also be obtained by pyrolyzing biomass from agriculture and forest [57].

The present review focuses on analytical pyrolysis, which uses the same process on a smaller scale. It is generally coupled with a characterization method, such as gas chromatography-mass spectrometry (Py-GC-MS) or direct MS technology. GC-MS is the most suitable analytical technique for the characterization of volatile or semi-volatile non-polar molecules in a complex mixture. The compounds are first separated by gas chromatography and each compound is structurally identified by mass spectrometry [58]. To further extend the applicability of GC analysis, a pyrolysis unit can be used as an injector system, which expands the use of GC for non-volatile high molecular weight molecules by breaking them into smaller volatile fragments, providing a specific fingerprint for each analyte present in the sample [59]. Py-GC-MS is mainly used to analyze complex materials, especially polymers, such as micro- and nanoplastics, and other macromolecules [8,60]. However, due to its mass-based approach, information about the color, the density, the size or the shape cannot be obtained, by the pyrolysis process. During this process, the sample is exposed to high temperatures, ranging from 550°C to 1400°C, under an inert atmosphere. The produced pyrolyzed compounds, being characteristic fragments of each individual polymer, are called pyrolyzates, which are then transferred to a GC column by the carrier gas, separated, and analyzed by mass spectrometry. Even though pyrolysis is a radical reaction, the fragmentation can be predicted and is reproducible in fixed pyrolysis conditions [55]. Analytical pyrolysis is a destructive technique mainly used to determine polymeric and organic composition of various samples. The behavior of the molecules during the pyrolysis process or the pyrolysis fragments can be studied to determine the sample composition and concentration [61].

Based on the heating mechanism, two main pyrolysis approaches can be distinguished, the pulse mode and the continuous mode. On the one hand, during continuous mode pyrolysis the temperature is kept constant. On the other hand, during pulse mode, the sample is injected at a low temperature and subjected to a thermal pulse. For this pulse mode pyrolysis three different designs (i.e. laser pyrolyzer, heated-filament, and the Curie-point) are used [59]. The continuous mode pyrolysis is based on more commonly used vertical microfurnace [55]. In this system, the sample is placed in a stainless-steel cup and the temperature is precisely fixed allowing reproducible and accurate results [54]. Fischer and Scholtz-Böttcher highlighted the disadvantages of the Curie-Point pyrolyzer compared to the microfurnace, including sample loss during transfer and highly limited sample capacity [51]. The absence of a temperature program functionality of the Curie-point pyrolyzer has also been highlighted by Pico *et al*. [62]. Even though, the Curie-Point pyrolyzer has an excellent heat transfer and an accurate temperature control [51] the drawback of sample loss and the advantages of microfurnaces making the latter currently the most promising pyrolyzer for MNPs identification and mass characterization.

The microfurnace can be used with different temperature programs. First, the single shot mode heats the sample at a unique temperature ranging between 500°C and 750°C for short periods, typically between 10 and 20 seconds. This method provides a comprehensive overview of the entire organic composition. Nevertheless, the results can be difficult to interpret for complex samples, as the entire sample is pyrolyzed at once. Next, double-shot pyrolysis consists of a thermal desorption (TD) step prior to the pyrolysis. By performing this first step at a lower temperature (between 40°C and 310°C), volatile compounds are desorbed. It enables the analysis of non-covalently bond volatile molecules such as additives, residual solvents, monomers, and oligomers. With a more advanced system, these volatile molecules can be cryo-trapped before being injected into the column, increasing chromatographic resolution. Following the TD step, a rapid and reproducible flash pyrolysis allows fragmenting the remaining macromolecules [62]. The two-step process provides information about sample composition by discriminating small and large molecule fractions. The third mode available is the evolved gas analysis (EGA), which is similar to thermogravimetric analysis (TGA). Here, the sample is heated using a slow temperature ramp and the evolved gases are monitored, enabling the investigation of the thermal behavior of the sample. With this technique, the GC column is replaced with a deactivated capillary without any stationary phase, called EGA tube. This mode enables the identification of the degradation temperature range of each compound and helps to determine the pyrolysis temperature for further analysis [62–64]. The last mode is heart-cut analysis, which provides a more detailed chemical composition of the sample by selectively introducing each temperature range determined by EGA for sequential GC-MS analysis. Unique chromatograms are obtained for each temperature range selected, up to eight different temperature ranges can be measured [62,64,65].

After the pre-treatment, the sample can be transferred into the corresponding cups preceding its measurement. In case of commonly used continuous mode vertical microfurnace pyrolyzer, the sample cup is introduced into the furnace and volatile polymeric fragments are produced. A summary of different Py-GC-MS conditions is presented in Table S2-1 of the supplementary information. However, the mostly used pyrolysis conditions range from 500°C to 700°C for the temperature, while the sample is generally exposed to it for 10 to 60 seconds. The pyrolysis temperature plays an important role in the fragments' abundance and therefore needs to be chosen in accordance with the targeted polymers. An EGA-MS measurement can also be performed in order to determine the pyrolysis optimal conditions, as described by La Nasa *et al.* [53].

3.2 GC-MS conditions

Once pyrolyzed, the fragments are transferred into the gas chromatography column. The thermal degradation products of the different polymers produced include a wide range of compounds with different boiling points and different polarities. The most used column is a non-polar column containing 5% diphenyldimethyl polysiloxane, with the following dimensions, 30 m x 0.25 mm ID x 0.25 µm. The use of polysiloxane as stationary phase can be justified by its non-polar properties as the most produced fragments are non-polar, as well as its resistance to high temperatures. However, the use of other types of (polar) columns has not been reported in the literature yet, but might be of interest for more polar fragments (e.g. N-vinylpyrrolidone and pyrrolidone) of polymers like for instance polyvinylpyrrolidone [66].

Based on Table S2, the most applied GC oven temperature program starts at 40°C for 2 minutes and ramps until 320°C at a rate of 20°C per minute with a helium flow of 1 mL/min and a split ratio varying between 5 and 100. Nevertheless, the GC temperature program can be adapted to the polymers of interest by slowing the temperature ramp around the targeted markers' elution time to increase the peak separation.

In terms of mass analyzer, single quadrupole mass spectrometers (MS) using electron ionization (EI) are the most frequently used system. This MS can work in two different modes, in full scan, and in selected ion monitoring (SIM) mode. In the case of full scan mode, all ions within the set mass range passing through the quadrupole are detected, while in SIM mode, only a few selected ions are monitored, the main advantage being an increase of the time spent on a particular mass (dwell time) with consequent increase in sensitivity. The SIM mode is typically used when performing target measurements, while full scanning of masses is performed for non-target measurements, allowing for identification of all potential compounds of interest. In both cases, chromatographic traces are reconstructed based on the collected ions, either by summing all collected ions (total ion chromatogram – TIC) or by using only some of the selected ions (extraction ion chromatogram – EIC) [67].

The way ions are produced in the MS can impact the identification of the polymer. Electron ionization (EI) induces a strong fragmentation of the analyte in the ion source and the detection of some oxidized fragments can be hampered. The use of softer ionization modes (e.g. chemical ionization) might facilitate the identification of polymers by preserving larger molecular fragments or even parent ions than EI. A scheme of a microfurnace pyrolyzer coupled to a gas chromatography and a single quadrupole mass spectrometer is depicted at Figure 3.

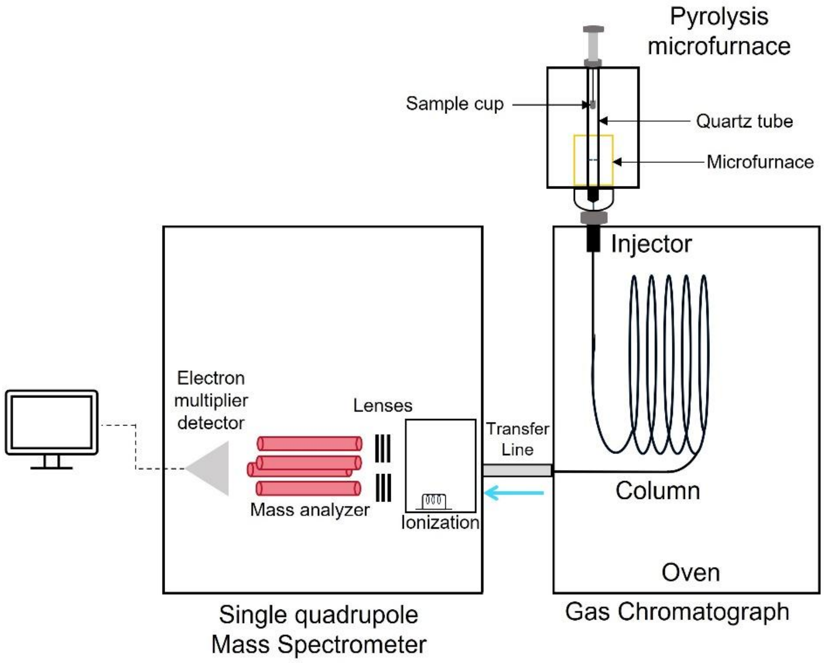

Figure 3: Instrument scheme of a microfurnace Py-GC-MS

The use of other MS types has been reported in literature. However, the choice of the mass analyzer format is mainly driven by its availability in laboratories. Albignac *et al.* [68,69] reported the use of a triple quadrupole instrument to perform tandem in space mass spectrometry to enhance MPs detection as well as reduce the sample pre-treatment procedure due to the enhanced selectivity of the tandem mode over background ions. This technique enables a step forward towards a reliable identification of polyethylene using transition ratios (production of daughter ions), as the pyrolysis of polyethylene produces similar fragments as organic matter [68]. When operated in multiple reaction monitoring (MRM) mode, both high selectivity and sensitivity are obtained as a limited number of ions/transitions are monitored [70].

In addition to these unit mass resolution spectrometers, so called high-resolution mass spectrometers are of interest when clear compound identification is mandatory. The time-of-flight mass spectrometer (ToFMS) is known for its fast acquisition time, and potential high mass resolution. Harata *et al.* reported the use of the pyrolysis-gas chromatography-atmospheric pressure chemical ionization-high resolution time of flight mass spectrometry (Py-GC-APCI-ToFMS) possessing different advantages. First, the soft ionization method provides extensive molecular ion information induced by a limited fragmentation in the ionization source. Moreover, the high mass resolution of the ToFMS helps to determine accurate masses enabling a reliable identification of different marker compounds. The advantages of this technique are particularly highlighted for the identification of polypropylene and polyethylene as these two polymers are abundant in the environment and as their marker compounds have difficulties to be distinguished using low mass resolution spectra [71]. However, the complexity of the obtained pyrogram might make untargeted analysis more complicated. The use of pyrolysis-gas chromatography-orbitrap-mass spectrometry has also been documented in the literature for target/untargeted analysis of MPs in air [50]. Torres-Agulo *et al.* developed a method using full scan and deconvolution in order to perform target and untargeted analysis [50]. The authors highlighted the advantage of the high mass resolution of an orbitrap among others by eliminating the need to choose between low-sensitivity full-scan acquisition and the potential loss of information associated with SIM or MRM modes. Instead, it enables comprehensive data collection with high selectivity and sensitivity through the use of narrow extracted ion chromatograms (EICs) afforded by high resolution, overpassing identification limitations encountered with other systems.

3.3 Polymer identification and quantification

To identify a polymer, different specific indicator compounds need to be selected, the most common marker compounds along with their corresponding qualifiers and quantifier ions have been reported several times in the literature. For the sake of completeness, a list of such markers, as well as their qualifier and quantifier ions, is also provided in Table S3 of the supplementary material. The different masses of the qualifier and quantifier ions are extracted, and the data are processed using extracted ions chromatograms (EIC). To quantify the identified polymers, a calibration curve is required. However, robust quantification remains challenging as no calibration method is standardized yet. Several methods to prepare calibration curves have been published in the literature. For instance, the use of accelerated solvent extraction (ASE) to prepare calibration standards, as well as the environmental samples analyzed, has been reported by Okoffo *et al.* [11,72,73]. Fischer and Scholtz-Böttcher described the preparation of calibration curves using Al_2O_3 as inert diluent and including the addition of TMAH [74]. Moreover, a workflow concerning the quantification of microplastics using the microplastics standard calibration mix commercialized by Frontier lab has also been documented. This solid mixture contains 12 different polymers including polyethylene, polypropylene, polystyrene, poly(methyl methacrylate), poly(vinyl chloride), polyethylene terephthalate, Nylon 6, Nylon 66, acrylonitrile butadiene styrene, styrene butadiene rubber, polycarbonate and polyurethane diluted in an inert diluent, calcium carbonate, and enables the quantification of the different polymers in a single run [75]. These different ways to prepare a calibration curve highlight the fact that to reliably quantify MNPs, the preparation of the calibration curve has to be in adequation with the targeted polymers and the matrix studied, especially in absence of internal standards. The use of an internal standard is of crucial importance in order to correct for matrix effects and pyrolysis efficiency [76,77]. Nonetheless, not all publications reporting Py-GC-MS quantification mention the use of such standards [43,78]. Deuterated internal standards are among the most common types of internal standards used in gas chromatography analyses. However, the use of deuterated polymers is not commonly documented in the case of MNP analysis except for polystyrene, which has been reported several times in the literature [41,79,80]. The use of deuterated polystyrene dissolved in DCM as well as a mixture of 9-Tetradecyl-1,2,3,4,5,6,7,8-octahydroanthracene (TOHA) and cholanic acid in n-hexane has been reported as internal standards by Coralli *et al* [81]. However, deuterated internal standards are employed, Lauschke *et al.* reported H-D exchange during the pyrolysis process and poly(4-fluorostyrene) was proposed as replacement [82]. Poly (4-fluorostyrene) has been used by Reis de Carvalho *et al.* as an internal standard to quantify polystyrene in soil and by Brits *et al.* to quantify polystyrene in blood [83]. The development of internal standards for each different polymer and their regular implementation are crucial to progress towards a reliable quantification of MNPs. As mentioned previously, the internal standard will help to correct the matrix effects. Moreover, the use of internal standards for each single polymer analyzed will also help to correct the co-pyrolysis interactions, leading to minimalized quantification errors. However, to date not all deuterated polymers are commercially available or, if so, very expensive, leading to their rare use.

To move forward towards data harmonization and especially comparison, Cowger *et al.* published a guidelines checklist. Concerning Py-GC-MS, the authors highlighted the importance of reporting the different experimental conditions including pyrolysis gas, temperature and time, the gas chromatography temperature program, carrier gas and column characteristics, and the mass spectrometry ionization voltage, temperature, mass range and scanning frequency. Concerning the reported data, the match threshold has to be mentioned as well as the linear retention and Kovats indices. Finally, the quantification technique has to be specified. Nevertheless, a quality assurance/quality control system has to be implemented in all procedures and measurements regardless of the sample type or the analytical technique used [84].

3.4 Gaps and needs for MNP identification and quantification by Py-GC-MS

As Py-GC-MS is a mass-based technique, the quantification does not rely on particle numbers or sizes, which allows a robust quantification of microplastics, especially for smaller size ranges. As a result, this mass-based technique's main advantage is the detection of plastic particles smaller than 10-20 µm, where particles number based techniques (i.e. µ-Raman and µ-FTIR) are facing problems. However, to quantify MNPs, the different polymers present need to be identified first. As mentioned previously, the polymer fragmentation is reproducible, and each polymer is forming characteristic fragments, in most cases, monomers and oligomers of the pyrolyzed polymer. The obtained pyrogram represents the fingerprint of the polymer without providing information about the shape, the density, or the color of the analyzed sample. If a full characterization of the sample, including structural information, is required, other complementary techniques should be employed, which are exhaustively described by Primpke *et al.* [33]. In the case of the analysis of particles smaller than 20 µm, including NPs, by Py-GC-MS, several challenges are rising. The first one is to reach a sufficient low limit of detection (LOD) and limit of quantification (LOQ). As the analyzed particles are small, enough particles have to be analyzed in order to reach a sufficient mass to be detected. This mass is typically smaller than 1 µg, depending on the polymer type [33]. The values of LOD and LOQ are also instrument and mode dependent as instruments with a higher sensitivity will allow them to reach lower LOD and LOQ values. Moreover, this size range is especially challenging as the particles cannot be seen with the naked eye and therefore their size must be determined during the sample pre-treatment, leading to an extensive procedure with possible particle loss and increased uncertainties.

During data analysis, targeted polymers are identified by extracting the corresponding masses of their qualifiers and quantifiers ions, as previously mentioned. Once the different ions are extracted, it is important to keep a critical overview of the results obtained. First, not all marker compounds can be used. Indeed, some fragments formed during the pyrolysis process can be common among different polymers or can originate from the sample matrix. For instance, the pyrolysis of polystyrene produces three main fragments including styrene,

styrene dimer and styrene trimer. To quantify PS in an unknown sample, it is recommended to use the styrene trimer as the styrene monomer, even though it is the most abundant fragment, can originate from other sources (e.g. organic matrix) [83,85]. Moreover, the identification and quantification of PVC encounter some challenges as most of the fragments produced during its pyrolysis (i.e. benzene, toluene, naphthalene) are aromatic compounds, which are also produced during the pyrolysis of organic matter. Furthermore, the selection of markers is delicate as their abundance is matrix dependent, different aspects including accuracy, specificity and sensitivity need to be considered [47]. The different peaks obtained represent pyrolysis fragments of polymers, which can originate from several sources, and not the polymer itself, leading to a non-straightforward conclusion of the sample composition. As highlighted by Dibke *et al.* and Coralli *et al.*, the reported results from environmental samples should be presented as polymer clusters including the pure polymer, copolymer, polymer-containing formulations, and related polymers that release the corresponding characteristic indicator ion(s) [42,81]. Furthermore, on the one hand, Lou *et al.*, reported co-pyrolysis interactions during the pyrolysis of a polymer mixture, complicating the accurate quantification of each polymer present in the mixture. For this study, pyrograms of single and mixed polymers, including PS, PP, PVC, poly(methyl methacrylate) (PMMA) and PE, have been compared and different marker compounds have been investigated. The authors reported variable yields of the different pyrolyzates concerning the pyrolysis of PS, PP and PE when pyrolyzed in a mixture and proposed new marker compounds, less affected by the occurrence of other polymers [86]. On the other hand, Coralli *et al.* reported co-pyrolysis interactions during the pyrolysis of PET and PVC simultaneously, as well as during the pyrolysis of polyamide 6 (PA6) and polyamide 66 (PA66) [87].

4. From GC to GC×GC

4.1 The contribution of comprehensive two-dimensional gas chromatography (GC×GC)

Comprehensive two-dimensional gas chromatography (GC×GC) is an advanced technique developed to overcome limitations of conventional one-dimensional 1D-GC systems and meet the increasing demand for complex sample analysis. GC×GC improves separation efficiency by enhancing peak capacity, dynamic range, and specificity. It involves subjecting the sample to two consecutive separation processes coupled online [88,89]. The first dimension (^{1}D) column is connected to a second dimension (^{2}D) column through a temperature-controlled interface known as the modulator [90]. A cryogenic modulator facilitates high sampling rates, transfers the sample to the ^{2}D column, and acts as a signal enhancer through zone compression [91]. During a short modulation period (few seconds [92]), the ^{1}D chromatographic peaks are divided into slices that are rapidly transferred into the ^{2}D column, potentially enabling the separation of ^{1}D co-eluting compounds based on their interaction with the ^{2}D stationary phase [93]. This approach increases separation power and sensitivity [94]. A unique detector, not necessarily a mass-selective detector, is placed at the end of the second column and operates like in traditional 1D-GC, continuously monitoring the chromatographic signal. Because of the modulation process, multiple high-speed secondary chromatograms, each lasting for a few seconds, are recorded and ^{2}D chromatographic signals corresponding to the same analyte can be combined to visualize the global elution pattern using contour plots in the chromatographic separation space [95]. Specialized softwares process the collected data to extract multidimensional information. GC×GC, often combined with fast acquisition time-of-flight mass spectrometry (ToFMS), is highly effective in analyzing complex samples, especially those made of volatile organic compounds (VOCs) of various chemical families [96,97]. Because of the non-scanning aspect of their data acquisition process, ToFMS analyzers offer the advantage of producing non-skewed spectral data that permit efficient mass deconvolution of signals issued from different chemical species. This can be seen as a back-up option to resolve chromatographic co-elutions that could still be present in the second dimension of the GC×GC system. Regarding applications, GC×GC has now proven to be of great utility in many different fields, such as health [98,99], drug discovery [100], food [101–103], petrochemistry [102,104], and environmental science [105].

GC×GC has become an important technique for characterizing complex samples of (semi-)volatile analytes. Compared to conventional 1D-GC, GC×GC offers much higher peak capacities [106]. It also produces structured chromatograms where analyte classes are grouped, and homologous series and isomers can be identified, resulting in detailed, interpretable fingerprints of complex products. While GC-MS remains the benchmark for identifying specific analytes and quantitatively analyzing limited numbers of targets, GC×GC offers distinct advantages for fingerprinting. GC×GC excels at separating numerous isomers and other isobaric compounds, providing reproducible and easily interpretable fingerprints. Consequently, GC×GC has become an established technique in many laboratories [107].

Another aspect that explains the success of GC×GC is the addition of a mass spectrometry (MS) detector, which enhances the ability to identify minor compounds, determine members of homologous series, and characterize ordered peak patterns of related compounds visible in the GC×GC chromatogram [108]. Indeed, a review of recent literature shows that the majority of the articles on GC×GC mention the use of MS as most of the systems can be coupled with MS [107]. Since MS instruments need a high acquisition rate to properly characterize ^{2}D peaks with a sufficient number of spectra, ToF-MS has been recognized as the best choice [109] even though other MS systems are increasingly being used in combination with GC×GC. This is the case for triple quadrupoles (QqQ) [110–112], hybrid quadrupole-time-of-flight (Q-ToF) [113,114], and orbitraps [115]. The benchmark method for ionization in MS is the -70 eV electron ionization (EI) but, advancements in MS systems for use in combination with GC×GC has also led to the use of other ionization techniques [116] such as chemical ionization (CI), which is more selective than EI, or photo ionization (PI) [117–119] and field ionization (FI) [120,121], being softer than EI, that can be both used in combination with high resolution (HR) MS techniques [122,123].

4.2 Advantages of Py-GC×GC-MS for the analysis of micro- and nanoplastics (MNPs)

As already demonstrated for the analysis of volatiles of pyrolysis bio-oil, the advantages of GC×GC compared to 1D-GC are considerable [124]. As mentioned previously, the addition of a second dimension provides a better chromatographic separation, higher peak capacity, and enhanced sensitivity. Depending on the type of column combinations, saturated and aromatic or saturated and polar-oxygenated compounds can be separated. As summarized in Table S3, different markers are produced during the pyrolysis of the polymers. In the literature, the separation potential GC×GC-ToF-MS has already been highlighted for different classes, leading to promising improved separations in the case of MNPs analysis.

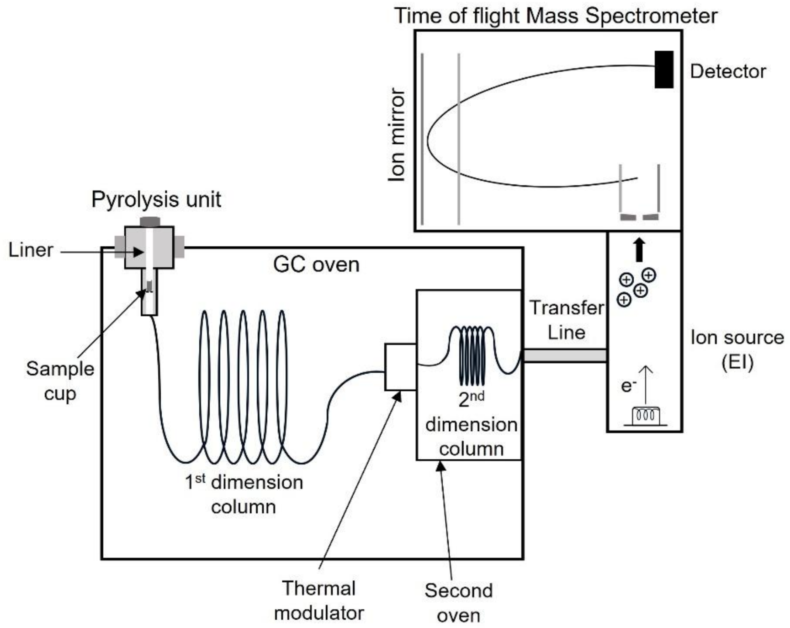

Figure 4: Instrument scheme of a Py-GC×GC-ToFMS, adapted from Hartner *et al.* (2022) [125].

The combination of Pyrolysis (Py) with comprehensive gas chromatography (GC×GC) and Time-of-Flight Mass Spectrometry (ToF-MS) (Figure 4 adapted from Hartner *et al*. [125]) can offer an effective alternative for analyzing microplastics in environmental samples [126]. This method might reduce extensive sample preparation while delivering superior chromatographic separation and high-quality deconvoluted mass spectral data. It enables the resolution, detection, and identification of MNP degradation products, additives, and other complex chemical mixtures present in the environment. As a concrete example, Jones *et al.* focused on the analysis of microplastics in environmental samples using pyrolysis (Py) and thermal desorption (TD) combined with comprehensive two-dimensional gas chromatography (GC×GC) and time-of-flight mass spectrometry (ToFMS) [126]. The paper discusses the use of polymer standards and environmental samples, specifically from aerosol filters collected in London and Augsburg [126]. Nine polymer types were analyzed, including common polymers such as PS and PE. Samples were analyzed both in 1D and 2D mode. The analysis focused on pyrolysis breakdown products and included comparisons with reference databases and chromatographic data. The method effectively identified various polymers and their degradation products in environmental samples. The two-step thermal desorption/pyrolysis process allowed for comprehensive analysis of volatile and semi-volatile compounds, enhancing the detection of microplastic markers. The study confirms that GC×GC-ToFMS, combined with the novel two-step thermal desorption/pyrolysis approach, is a promising method for the detection and analysis of microplastics in complex environmental matrices, paving the way for further optimization.

As another example for the utilization of GC×GC for complex samples, Bridge *et al.* [127] demonstrated that Py-GC×GC–MS improved compound differentiation in the second dimension, reducing ambiguity during comparisons for the analysis of tire. Indeed, Py-GC–MS is the primary technique employed by forensic scientists for analyzing tire evidence chemically [128,129]. Pyrograms generated from rubber traces collected from tire impressions can then be compared to those from a suspect vehicle's tires. But tires are chemically intricate, often consisting of over 200 compounds such as natural and synthetic rubber, oils, plasticizers, antioxidants, antiozonants, accelerators, vulcanizing agents, and curing systems [130]. This complexity can lead to co-elution of compounds, making accurate matching difficult and increasing the risk of errors. In this study [127], a flash pyrolysis method was used to pyrolyze a small (~50 µg) sample of the main tread from a tire. The pyrolyzates were separated using multidimensional chromatography. Due to the complexity of tire samples, identifying individual compounds is challenging with one-dimensional Py-GC–MS alone. However, Py-GC×GC–MS improved compound differentiation in the second dimension, reducing ambiguity during comparisons. This enhanced accuracy is crucial for minimizing errors and improving match determinations in forensic investigations. The highlighted added value of the Py-GC×GC–MS in the forensic field could also be beneficial for environmental analysis. The use of Py-GC-MS to identify and quantify tire wear particles in the environment is steadily growing, and two ISO technical specifications have already been released concerning the determination of mass concentration of tire and road wear particles in soil and sediments (ISO/TS 21396:2017) and ambient air (ISO/TS 2093:2017) but refinement are still needed as mentioned by Rauert *et al.* [131].

Moreover, as mentioned previously, co-pyrolysis effect impacting the pyrolysis fragmentation has been reported in the literature. The presence of nitrogen-containing aromatic compounds as well as chlorinated benzoic acid derivatives have been noticed during the pyrolysis of PET with PA and PVC respectively [81]. Considering the increased sensitivity of GC×GC, an easier identification of these fragments would be expected. In addition, its high separation power could play an important role in reducing co-elution due to remaining organic matter. Moreover, once in the environment, plastic particles undergo several physical processes leading to degradation and aging. To date, very little is known about the impact of aging on the pyrolysis fragmentation and the obtained pyrolyzates. In this case, the addition of an extra separation step, either or not combined with soft ionization could help to fully characterize the pyrogram of aged or true-to-life plastic particles and determine specific markers. The advantage of GC×GC could also help to dive into biodegradable, bio-based and recycled polymer analysis in more detail. For instance, Courtene-Jones *et al.* used Py-GC×GC-ToFMS to determine the chemical composition of new teabags and those that had been exposed to the soil environment. It confirmed that some teabags were composed of cellulose fibers blended with PLA (polylactic acid) while others consist solely out of PLA. Pyrolysis products included lactide isomers from PLA and levoglucosan, anhydrosugars, furans, and carbonyl/aromatic compounds from cellulose degradation. The purpose of Py-GC×GC-ToFMS in this study was to characterize the chemical makeup of teabags before and after degradation in soil. It was also used to verify that no significant changes occurred in boiled teabags compared to unused ones. Additionally, it helped detect degradation markers and assessed whether PLA compounds underwent significant breakdown [132].

Nevertheless, it is important to note that while this technique significantly enhances separation, the vast amount of data generated can sometimes slow down the process due to the time needed for thorough interpretation [46]. Data interpretation in GC×GC-MS can be performed by applying advanced chemometric methods including signal pre-processing, data alignment, data curing, data pre-processing, supervised and non-supervised data analysis, feature selection, model building and validation to extract meaningful information from complex datasets and support reliable, large-scale screening. The continuous development of such chemometric tools helps to deal with the constantly increasing complexity of GC×GC-MS data sets [133]. Recent advances in artificial intelligence and easier access to such tools open the field to machine learning-based data processing workflows and decision-making strategies that will improve global analytical efficiency [134,135].

Finally, the knowledge gained concerning pyrolysis products thanks to the second dimension could eventually be transferred back to routine measurements using a targeted SIM method, avoiding the unnecessary use of Py-GC×GC–MS in routine analysis and therefore reducing the amount of produced data.

5. Summary and Outlook

This review addressing Py-GC-MS and its advanced applications, like for instance Py-GC×GC-MS, provides a critical overview of the current body of evidence for identifying and quantifying MPs and NPs in different matrices. The discussion underscores the increasing importance of these techniques in solving the environmental and biological challenges caused by plastic pollution.

Py-GC-MS is a strong analytical tool to analyze polymeric materials by its ability to break down these polymers consistently into characteristic fragments under controlled pyrolysis conditions. The technique strengths are enabling the identification and quantification of polymers and associated additives in complex environmental samples (e.g. water, soil, and air), and biological matrices (e.g. human tissues and marine organisms). Further, the integration of GC×GC into this framework will be the next step to enhance separation efficiencies. The latter added value is mainly found in the fact that GC×GC can significantly increase chromatographic resolution and sensitivity, especially for complex samples where traditional 1D-GC faces limitations. GC×GC improves the separation of co-eluting compounds, resulted from introducing an extra chromatographic dimension, providing unique chromatographic fingerprints. This advanced technique can become critical for analyzing mixtures with diverse polymer types, additives, contaminants and weathered particles. The resulting data offers a detailed insight into the chemical composition of MNPs, improving the understanding of their sources, degradation processes, and environmental impacts. For example, Py-GC×GC-ToFMS was used to analyze microplastics in aerosol filters, offering insights into urban pollution.

Despite the advancements offered by comprehensive 2D GC, this review also highlights several challenges that need to be addressed. First, the lack of standardized protocols for sample preparation and analysis is a recurring issue. In addition, varying matrix compositions, such as (in)organic content, can negatively impact data interpretation, emphasizing the need for rigorous pre-treatment (e.g. filtration, density separation, organic matter digestion and solvent extraction). Next, an urge towards standardized calibration techniques and the broader adoption of internal standards to improve quantification accuracy, is currently still present. The current body of literature also highlights the limitations of existing methods for analyzing NPs, which are considered also harmful due to their potential to cross biological barriers and cause severe ecological and health impacts. Compared to MPs, NPs are more challenging to measure due to their smaller size and greater interaction with environmental matrices this is why this review advocates for the increasing need of new developments of more sensitive instruments and methodologies, including enhancements to GC×GC. As a result, Py-GC-MS and Py-GC×GC-MS are not just analytical techniques but critical parts of a larger strategy to understand and mitigate plastic pollution in order to inform regulatory frameworks and environmental policies aimed at reducing plastic waste and its associated risks to ecosystems and human health.

In conclusion, this review identified Py-GC-MS and Py-GC×GC-MS as promising techniques for analyzing micro- and nanoplastics. Their versatility across various sample types combined with their analytical precision makes them essential in tackling the growing plastic pollution crisis. However, further innovations are required to address existing loopholes, including the development of universal standards, more robust quantification methods and integrated approaches that combine multiple analytical techniques. Tackling these challenges will strengthen the role of Py-GC×GC-MS in deepening the understanding of micro- and nanoplastic contamination, contributing to global initiatives to protect both environmental and public health.

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Conflict of interest

The authors declare no conflict of interest.

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