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Pyrolysis gas chromatography-mass spectrometry in environmental analysis: focus on organic matter and microplastics

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Highlights

- Recent innovations in Py-GC-MS for environmental analysis are presented
- Advances in the design of currently used pyrolyzers are discussed
- Recently developed working modes within Py-GC-MS are described
- Py-GC-MS applications to organic matter and microplastics are highlighted
- Progresses and promising trends in Py-GC-MS analysis are pointed out
ABSTRACT

Pyrolysis gas chromatography-mass spectrometry (Py-GC-MS) has great potential within environmental analysis. This technique is mainly used for the chemical identification of macromolecules that cannot be characterized by either liquid or gas chromatography due to their big size. Through pyrolysis (controlled thermal degradation), these macromolecules are broken down into simpler molecules that can be separated by gas chromatography and detected by mass spectrometry. This technique has been traditionally used in environmental samples for the characterization of organic matter and humic substances, contaminants, lignins, etc. It attains the identification of the different types of chemical units that integrate the macromolecules. In addition, recently, this technique has experienced an important boom in the chemical characterization of microplastics present in environmental samples. This has triggered its use in this type of matrix. We describe the fundamentals and modalities of Py-GC-MS and outline some of the recent applications for the environmental analysis with special emphasis on humic substances and/or other types of organic matter components as well as microplastics, but reporting also other interesting application of environmental relevance.

Keywords: microfurnaces; filaments; Curie-point; Evolved gas analysis; Reactive pyrolysis.
1. Introduction

Pyrolysis gas chromatography-mass spectrometry (Py-GC-MS) is one of the essential and dynamic analytical tools available today to be able to analyze and characterize chemicals occurring in the environment. The International Union of Pure and Applied Chemistry (IUPAC) has classified Py-GC-MS as a type of reaction chromatography, in other words “a technique in which the identities of the sample components are intentionally changed between sample introduction and detection” [1]. In GC, these changes can occur before the column (the chemical compounds separated in the column differs of those of the original sample) or between the column and the detector (the original chemicals are separated in the column but their identity changes before reaching the detector). The IUPAC has also defined Pyrolysis (if used for analytical purposes) as “the characterization in an inert atmosphere, of a material or a chemical process by a chemical degradation reaction(s) induced by thermal energy”, and Py-GC as “a version of reaction chromatography in which a sample is thermally decomposed to simpler fragments before entering the column” [1]. This set of definitions gives a clear idea of the technique fundamentals also summarized in Figure 1. Nowadays, pyrolysis involves the thermal fragmentation of the analytical sample at a temperature between 500 -1400 °C. Under these conditions and in the presence of an inert gas, the original macromolecule is decomposed to characteristic units further separated chromatographically using fused silica capillary columns and, subsequently, identified by mass spectrometry mostly with the aid of mass spectral libraries or by the selection of characteristic ions of indicator compounds. This analytical technique can eliminate the need to pre-treat the sample as it is capable of performing the analysis directly on the macromolecules and/or polymers whether they are in a liquid or solid state but it is compatible with most of the pre-treatments applied to extract (macro)molecules from environmental samples.

Applications to identify substances of low volatility were first reported in 1961 for Py-GC [2-4] and in 1967 for Py-GC-MS [5, 6]. Since then, Py-GC-MS increases the range of tools applicable to the analysis of macromolecules including polymers, copolymers and additives, wheels, packaging materials, textile fibres, coatings, electronic intermediates, coals, paints, varnishes and lacquers, leather, paper or wood derivatives, bio-oils and biomass, fire retardants, food, drugs, surfactants, and fragrances. Surprisingly, a retrospective of the literature published since its origins shows that this technique has only been used when all other conventional methods of gas or liquid chromatography coupled to mass spectrometry have been exhausted. According to Web of Science (WoS) all databases (accessed by March 22, 2020), 6,849 peer-reviewed research articles based on the keyword “Py-GC-MS” as topic have been published since the technique’s begins, with a rate over the last ten years of near 500 publications yearly [7]. The applications of Py-GC-MS range from research, quality control and characterization of materials to forensic environmental analysis including the conservation and restoration of cultural heritage, as well as medicine, biology, biotechnology, geology, aeronautics, agriculture, energy fuels, etc. Reviews on Py-GC-MS are mostly focus on its applications, such as polymer characterization [8-10], lacquer [11], lignin [12], humic substances [13], soil organic matter [14], etc. Clearly, these reviews cover individual issues and none addresses global fields such as environmental analysis, a field in which it is recently becoming an indispensable tool.
To evidence this, it is sufficient to mention latest reviews on the identification of microplastics in the environment [15-19] or the study of environmental organic matter [14, 20]. Parallel, to find a review on the recent trends and developments within the technique is needed to back 12 years ago to 2008 [21]. This contrasts with the rapid technological evolution within Py-GC-MS in terms of devices design, inertness of their components, versatility of the working modes and reproducibility of the obtained data.

Within this review, key trends and recent evolutions in the area of Py-GC-MS are covered. In the past years, several important new developments have been made in the pyrolysis devices (microfurnace chambers, quartz liners for the sample, etc.) as well as in the GC-MS process itself (time-of-flight MS in the low- or high-resolution mode, comprehensive GCxGC, etc.). This review also presents some specific environmental applications within the environmental field that highlights the prospects achieved thanks to the implementation of these advances, based on the literature published in the last 5 years (2016-2020). Mostly microplastics and organic matter characterization but also other environmental applications of interest are included.

2. Fundamentals and instrumental advances of pyrolysis gas chromatography-mass spectrometry

As stated in the introduction, Py-GC-MS is a technique capable of analyzing macromolecules by gas chromatography breaking them into volatile fragments (schematized in Figure 2) [9, 10]. This hyphenated technique benefits from coupling as pyrolysis extends the scope of GC-MS to the analysis of non-volatile macromolecules in matrices such as, various types of new and ancient materials, biological and environmental samples. In turn, pyrolysis exploits the resolving power of gas chromatography and the identification capability of mass spectrometry. It involves an interesting symbiosis that provides a complex mixture of volatile fragments (pyrogram) of the original non-GC amenable sample (or macromolecule) that may be a very effective fingerprint [12, 13]. This is its most significant advantage.

In the pyrolyzer the sample is heated with GC carrier gas, typically an inert gas (helium is most commonly used) to a relatively low pressure. The high temperatures induce chemical changes in the macromolecules by a progressive bond breakage that goes from the weakest to the strongest according to the temperature. The main reactions involved are depolymerisation (resulting in decomposition to the basic units or, occasionally, oligomers), random excision (providing randomly smaller fragments as all C-C bonds are of equal energy) and the removal of side groups (side groups cleaved of the polymer bond). Other reactions such as, chard formation, cross-linking, cyclization, hydrogenation, isomerization, and oxidation are possible but minor. The molecular fragmentation caused by pyrolysis (and the formed products) depends on the relative strengths of the molecular bonds and the ability of the free radicals formed to give stable products [22, 23].

Nowadays, different working modes of the Py-GC-MS have been described depending on the purpose of the analysis [7, 23, 24]:

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Single-shot analysis (Py-GC-MS), in which, pyrolysis is performed at a single temperature, normally $>500^\circ$C (dependent on the material being examined). The sample temperature goes as rapid as possible from ambient to the pyrolysis temperature (in current instruments <20 ms). The macromolecules are almost instantly fragmented in the pyrolyzer and then, their pyrolyzate of their degradation products is separated in the chromatographic column.

Double-Shot analysis (TD/Py-GC-MS) provides information about both types of compounds, volatile (low molecular weight compounds analyzed at low temperature through a thermal desorption step) and non-volatile (analyzed at high pyrolysis temperatures that allow for the fragmentation of the macromolecules). Therefore, the analysis of the sample involves two stages: in the first one there is the thermal desorption of the volatile compounds then, analyzed by GC-MS and in the second one, the residual sample left after desorption (in which the non-volatile macromolecules remain) is pyrolyzed and the pyrolyzate is also analyzed by GC-MS.

Evolved gas analysis (EGA-MS) involves the separation of degradation products from macromolecules according to the temperature at which they are formed rather than according to their volatilization temperature. This is achieved through a sequential macromolecules degradation that takes place in the pyrolyzer using a slow temperature ramp (instead of reaching the pyrolyzation temperature as quickly as possible) and the replacement of the chromatographic column by a short and narrow (2.5 m, 0.15 mm i.d.) deactivated capillary tube without a stationary phase to connect directly GC-injector and MS-detector. This is very similar to the thermogravimetric analysis (TGA). The weight loss of the sample cannot be measured but the result shows the thermogram such as a differential thermogravimetric curve for a given sample. EGA-MS is done as previous step in order to identify the temperature range for the components and set-up Py-GC-MS for a more in-depth study of the identified compound.

Heart-cut analysis (Heart-cut EGA-GCMS), is the two-dimensional way of working in the combination of Py-GC. In this technique, EGA is used to obtain a thermogram and each temperature zone of interest is analyzed separately by heart cutting evaporated components and selectively introduce them to a GC column where they are temporarily trapped at the beginning of the column prior to analyze them by GC-MS. This technique allows examination of regions that may contain multiple components under a peak but are not obvious during Py-GC-MS analysis. This method could be incredibly useful to search both, for specific components in a highly complex matrix or the whole composition of a complex system.

Reactive Pyrolysis-GC-MS. The macromolecule undergoes a chemical derivatization reaction in the pyrolysis chamber. This may be instead of, or in addition to, heat-induced pyrolysis of the large polymer into smaller fragments. The most used derivatized agent is tetramethylammonium hydroxide (TMAH).

In addition to these modes, modern pyrolyzers can be also used only for thermal desorption of analytes (as in double-shot analysis).

Py-GC-MS can provide quantitative results with high accuracy and precision. As in any other analytical method compound quantification in the sample requires standards and
even isotopically labeled internal standard as well as the selection of proper ions[13, 25, 26].

Another advantage of this technique is the small sample amount (5–200 μg) without pre-treatment. However, samples must be dried and, as already mentioned, in the case of environmental samples, it is sometimes necessary to perform a previous extraction of the macromolecules. Py-GC-MS is compatible with most established method[11, 12, 27].

The most important disadvantage attributed to Py-GC-MS was poor reproducibility due to factors such as sample inhomogeneity, slow transfer of the pyrolyzate to the chromatographic column and catalytic events in the pyrolyzer, which may alter the chemical nature of the sample. Other disadvantages of the technique are its destructive character and the difficulty of interpreting the pyrograms obtained due to the large number of reactions that can take place and the density of peaks in the pyrograms [21].

Hence, developments have been focused on areas such as developing new approaches to improve the reproducibility of the pyrolyzer, to enhance separation of the compounds and to better identify the reactions products. Major instrumental developments in pyrolysis, chromatography and mass spectrometry are described in the following.

2.1. Pyrolyzer

The critical prerequisites for the apparatus in analytical pyrolysis affect pyrolysis temperature (its reproducibility, rapid rise, and accurate control are crucial to ensure proper results) and the connection of Py-GC that must be as direct as possible. Pyrolysis process as fast as possible is desirable to prevent pyrolyzates back into the injector. The pyrolyzer devices must be small and with little internal volume while the flow of carrier gas through them should be fast to ensure that all volatiles are swept into the column and do not remain in the pyrolyzer where they can undergo secondary pyrolysis. Small sample amount is needed to ensure that it is rapidly degraded and that the capacity of the column is not exceeded [5, 12].

Pyrolysis systems were classified according to the heating mechanisms into: continuous-mode pyrolyzers (furnace or microfurnace pyrolyzer) and pulse-mode (sample is introduced cold and receives a thermic pulse) pyrolyzers (heated filament and Curie-point) (schematized in Figure 3). The three types of pyrolyzers are able to carry out flash pyrolysis involving a very rapid temperature rate up to reach the pyrolysis temperature. Their ability to work in the different modes described in the previous section is summarized in Table 1.

Nowadays, filament pyrolysis (Figure 3a) uses as heating element a coil made a very thin wire of resistive metal (commonly platinum). A small quartz tube holds the sample inside is inserted into the coil. Recently, progress has been made in developing better and more effective sample holder designs that shorten the analyte diffusion path and reduce peak broadening. Poor temperature accuracy and reproducibility have been reported because of non-uniform heating (heat-transfer variations affect the temperature of the sample that is not directly measured). Considerable effort has been made in the
implementation of the technology ensuring accurate monitoring of the filament resistance and accurate temperature control. In addition to pulsed pyrolysis, recent instruments can also perform programmed heating to obtain sequential pyrolysis (multiple pyrolysis steps performed on a single sample at increasing temperatures) with temperature ramps that can be rapid or slow depending on the purpose. In the filament pyrolyzer, the sample preheating before analysis is essential to avoid condensation of high boiling point pyrolyzates. This preheating step causes evaporation of the volatile and semi-volatile compounds and denaturation, degradation or thermofixation of the samples. However, the last instruments can perform thermal desorption but using modular systems or complicated trapping sequences [23, 28, 29].

The Curie-point pyrolyzer (Figure 3b) is similar to the filament pyrolyzer but the sample is inserted on an appropriate ferromagnetic alloy wire having the desired Curie-point; that is the exact reproducible temperature at which the ferromagnetic material loses its magnetism. The temperature ceases to rise when the Curie-point of the metal has been reached. The most important disadvantage of these pyrolyzers is that different temperature steps cannot be programmed, then, the evolved gas analysis (EGA) is impossible. The pre-heating of the sample is necessary, similar to the filament pyrolyzer [23, 28, 29].

The heating-furnace pyrolyzer mostly used in recent years is a vertical microfurnace-type (Figure 3c). This microfurnace is simply a hollow quartz tube covered by a heater device for rapid heating and cooling. State-of-art microfurnaces are equipped with hollow ceramic heater and powerful cooling fans achieve rapid heating and cooling across a wide temperature range as well as temperature sensors that measure the temperature in the sample. The sample is placed in an inert deactivated cup held at the ambient temperature in helium even through at the same time that the microfurnace is preheated to the pyrolysis temperature. Special thermal insulation achieves excellent thermal stability maintaining the sample at ambient temperature at the stand-by position when the furnace temperature is at a 600 °C and reaching 60 °C if the furnace is at 1000 °C. In the recent years, also evolutions in the sample cup materials such as chemically-bonded quartz thin layer on cup surface for inertness or directly quartz cups has been reported. In the moment of the analysis, the cup is dropped by free fall, due to gravity, into the center of the vertical furnace. Thus, in this case, the problems caused by the preheating for the filament and the Curie-point pyrolyzers of evaporation, degradation, or thermosetting before the analysis can be avoided. In addition, the sample is purged of oxygen before heated so that there are no oxidation reactions [22, 30, 31].

The pyrolysis unit (pyrolyzer) is connected directly to the injector port of the GC. Heavy and polar compounds are directly placed on-column and light compounds are never lost. The main concern is to transfer the analytes to the GC in a tight ‘plug’ so that the peaks are not broad and the column can separate them. At its most basic, this means heating the sample as quickly as possible so that the resulting volatiles are produced in a very short time and the resulting peaks are narrow and well separated. Cryotrapping capabilities are available for the Pyrolysis GC-MS in both pulse mode and continuous pyrolyzers. Prior to introduction into the GC-MS, the pyrolyzates are cryotrapped using liquid nitrogen. This is done to narrow the chromatographic band and improve the
2.2. Gas chromatography

Once the polymer/copolymer sample has been pyrolyzed, volatile fragments are swept from the heated pyrolysis unit by the carrier gas (helium) into the gas chromatograph. The volatile pyrolysis products (pyrolyzate) are chromatographically separated by using a fused silica capillary column, according to the boiling points and the affinity of analytes to the stationary phase (internal capillary column wall coating) [34].

Although GC-MS Pyrolysis has mostly been combined with conventional chromatographic separation, i.e. using a capillary column with a 5% phenylmethyl siloxane phase 30 x 0.25 mm and 0.25 um film thickness, there is no limitation in terms of possible GC separation modes. There are undoubtedly two major trends within separations in gas chromatography —fast chromatography and comprehensive two-dimensional GC (GCxGC) [3].

Fast GC involves reducing analysis time by using multiple combinations of narrower and shorter columns, with less phase thickness and/or higher carrier gas flow. There is no reason why this type of chromatography cannot be combined with Py-GC-MS. However and probably because pyrolyzates are very complex samples, to our knowledge, this combination has not been reported yet [26, 35].

GCxGC provides higher peak capacity and better resolution power by adding a second GC column of a different polarity, connected through a modulator (commonly a cryomodulator) that traps the eluting fractions of the first column and injects them into the second column to achieve true two-dimensional separation. Since one of the premises of Py-GC-MS is the separation of complex mixtures of molecules (the pyrolyzates), GCxGC has been combined with pyrolysis in several studies showing its great capacity to facilitate identification [36, 37]. In the future, this technique could gain a third dimension of separation if it is combined with Heart-cut EGA. However, it should be noted that the unquestionable improvement in separation implied by these techniques is sometimes slowed down by the great amount of information obtained and time required to interpret it.

2.3. Mass spectrometry

The detection technique of the separated compounds is typically mass spectrometry (MS). The analysis of the samples fingerprint pattern is often accomplished by single quadrupole mass analyzer, the most used system, due to its robustness and capacity to identify the molecules. The substances detected by the mass spectrometry are subsequently identified by the interpretation of the obtained mass spectra, by using mass spectra libraries (e.g., NIST/EPA/NIH, Wiley, MPW, Norman Mass Bank, m/z Cloud), or by using reference substances [23].

Triple quadrupole instruments (QqQ) were introduced more recently and today are the most recommended systems for the analysis of target compounds, mainly due to the higher sensitivity and specificity of the application of tandem MS (MS/MS). However,
this instrument is little used in combination with Py-GC-MS, since in this case the compounds that are formed in the pyrolysis are mostly unknown a priori, so the QqQ has less application. [27]

Contrarily, high resolution mass spectrometry (HRMS), mostly (quadrupole)time-of-flight (TOF or QqTOF), has become essential tools in Py-GC-MS. The use of these detectors provide information on the most probable empirical formula of both, the analyzed molecule and its characteristic fragment. This is a very structural useful information especially in the case of pyrolysis were the ultimate objective is to identify all the compounds responsible of the fingerprint pattern of the pyrogram. Although the application focus on using selected ion monitoring (SIM), the analysis of the scan spectra in the method development is essential. [13, 26]

3. Environmental applications of Py-GC-MS

Two of the most interesting applications of Py-GC-MS in environmental samples are (i) the evaluation of natural organic matter (NOM) and (ii) the identification and characterization of microplastics and nanoplastics.

3.1. Characterization of organic matter

The complex and variable composition of natural organic matter (NOM) (polysaccharides, amino sugars, proteins, polyhydroxy aromatics, lipids, lignin, etc) makes characterization of its components very challenging within environmental studies. Py-GC-MS has been applied to analyze the changes in the dissolved organic matter (DOM) in water [38, 39]. This technique has also demonstrated to be a potent tool for studying the molecular fingerprints of the natural organic matter (NOM) in soils and sediments, evaluating the changes in soil organic matter (SOM), identifying soil and sediment carbon storage [39]. Furthermore, other applications focus on characterization of humic acids because there is an urgent need to understand the structure and to improve definition of the function of humic substances in nature.

In water, separation and purification of DOM is important and often linked to further analysis. The first step is filtration through a glass filter to retain any other organic matter fraction. After filtration, the DOM in water is isolated and enriched by sorbent extraction methods, such as solid phase extraction SPE [39] and pre-HPLC [38]. In both techniques, DOM fraction is concentrated by reverse phase mechanisms. The characterization of soil and sediment organic matter does not require extraction, just to dry, sieve and pulverize the soil [30, 31, 40, 41]. However, there are many types of organic matter fractions, one of them commonly determined also in soils is DOM that can be extracted using a lysimeter-pump or by shaking soil with water [42]. Other fraction involves the humic substances, probably the most important one because soil fertility and stability depends on it. The extraction and purification humic acids (HA) and/or fulvic acids (FA) according to standard methods is compulsory to study them. These standard methods involved as a first step elimination of the free organic matter by flotation (using $H_3PO_4$) and demineralization (with $Na_2P_2O_7$ needed to remove Al associated with SOM and release the humic substances that are complexed with hydrous amorphous oxides). Then, HA and FA are extracted from soil using a basic solutions (NaOH), and separated by precipitation of the humic acids in the solution by
acidification (pH < 2). HA are further purified by washing with several acidic solutions [43] and/or dialyzed into cellophane bags [44, 45]. The acidified supernatant including FA was passed through a column of DAX-8, a nonfunctionalised polymethylmethacrylate resin with strong hydrophobic organic matter endorsed to humic and fulvic acids and through a strong cation-exchange resin column [46].

The three types of described pyrolyzers — micro furnace [30, 31, 34, 43, 47], platinum heated filament pyrolyzer [22, 41, 42, 44, 48, 49] and Curie point [38, 45] has been applied to characterize NOM in the environment. However, most of the studies only test the single shot [22, 30, 31, 34, 38, 41-45, 47, 49] at temperatures > 500 °C and < 800 °C. The reactive pyrolysis has also been applied in some studies [42, 46] because it provides less fragments simplifying the pyrogram. However, a study comparing the ability of both techniques to characterize soil-derived DOM across the Three Gorges Reservoir areas [48], concluded that Py-GC–MS fingerprinting is a more helpful tool able to quantify microbial DOM than reactive pyrolysis. Reactive Py-GC-MS is instead useful to determine the molecular features of the polyphenolic (cinnamic acids, lignin and tannin compositions) and aliphatic (identification of cutin and suberin) fractions. As an interesting alternative to palliate this problem, branched-chain fatty acids in HAs analyzed by Reactive py–GC-MS has been proposed as biomarkers (BMs) for determining the history of microbial activities that occurred during composting processes [46].

The double-shot pyrolysis that makes both, free volatiles and high molecular weight structures, accessible has been scarcely used in the studies involving NOM characterization, probably because the organic matter is formed by non-volatile compounds. In fact, Figure 4 illustrates that free evaporable molecular structures are barely present in terrestrial DOM. In contrast, a lot of components are accessible only in the pyrolysis step [39]. Hence, DOM mainly consists of large high molecular complex structures. Many of these are aromatic, especially phenolic compounds that are lignin degradation products.

In most of the covered studied, GC-MS is performed in practically all cases using the most conventional system, which involves 30 m capillary columns and a simple quadrupole working in scan mode. The detected pyrolysate compounds were assigned by comparing the obtained mass spectra with the NIST or any other of the mentioned mass spectral database. The identified compounds can be grouped according to their probable origin as: (i) aliphatic hydrocarbons (n-alkanes, n-alkenes and n-methyl ketones), (ii) aromatics and alkylbenzenes, (iii) polyaromatic hydrocarbons (PAHs) and benzo(furans, (iv) methyl esters, (v) lignin phenols, (vi) N-containing compounds, (vii) phenols and catechols, and (viii) polysaccharides. Commonly number of compounds identified in a pyrogram ranged from 100 to 400 compounds. The relative abundance of the pyrolysis products can be calculated by normalizing the peak areas of each individual compound to the total area for all the peaks of the detected products. Although powerful advances of GC and MS in last years, only one Py-GC-MS method reports the use two ionization systems EI and photon-ionization (PI) with different mass selective analyzers [quadrupole and a time-of-flight MS (ToFMS)] for the analysis of terrestrial DOM in water [39]. The PI—a soft ionization method—was performed by resonance-enhanced-multi-photon-ionization (REMPI) providing information on the
molecular weight and a high selectivity and sensitivity for aromatic hydrocarbons. Furthermore, the accurate mass of TOF-MS attains an additional confirmation. It enables the characterization of natural samples by a universal (electron ionization quadrupole MS) as well as an aromatic fingerprint (REMPI-TOF-MS). However, it is clear that new developments in the field of GC-MS have not been incorporated yet, perhaps because analysis using routine systems is enough complex and, especially, time-consuming and requires highly specialized personnel.

One of the main problems of the NOM characterization is, as stated in the previous paragraph, the complexity of the obtained pyrograms, all of them with a high number of compounds. If, in addition, the number of samples is very high, the amount of information to be processed increases exponentially making it very difficult for the analyst. Some studies have tried to find solutions to this problem, mostly using two different ways. The simplest way is to focus the study on a few good biomarkers of the processes that the organic matter undergoes. A study proposing the use of branched chain fatty acids as bioindicators has already been discussed [46]. The methoxyphenols (descriptors of organic matter composition) have also been proposed as indicators of the capacity of the soil C storage [34]. Methoxyphenols (12 major guaiacyl- and syringyl-type compounds) are released by Py-GC-MS from topsoil samples and are distinctive molecules supposedly advising on the occurrence and degree of alteration of lignin in soils as different statistical analysis (simple regression, partial least squares (PLS), statistical molecular design (SMD)) coincide in showing proper correlation between C storage in soil and the methoxyphenol complexity.

The other methods are based on the application of statistical tests that help to systematize or improve the visualization of the information obtained. Effort is devoted to develop automated identification and quantification software that helps to process mass chromatographs from Py-GC-MS and visualize the results [44, 50]. Moreover, pyrolyzates fluctuate significantly among samples in their presence and intensity. Statistical techniques can overcome the challenges of data interpretation. For example, analysis of variance (ANOVA) has been used to assess differences in functional groups among samples, whereas factor analysis has been reduce the dimension of pyrolyzates and separate the samples using the reduced variables, or factors. Fig. 5 exemplifies one systematic approach that has been proposed to obtain as much sample information as and overcome these limitations [50]. There are many more reported in the literature.

3.2. Determination of micro and nanoplastics

Environmental contamination by micro and nanoplastics is a globally recognized problem that has worldwide dimension. The large number of reviews on nano or micoplastics that have been published in recent years gives a proper picture of the raised concerns [15-19, 51-55]. Py-GC-MS has become one of the most promising techniques to identify micro and nanoplastics in environmental samples because it achieves detection of lower microplastics dimensions, is more sensitive than other methods and less affected by impurities and interferences of the samples. “Less” does not mean “absence”. Some samples present serious interferences due mainly to the organic matter. This is alleviated by the broad compatibility of Py-GC-MS with all
types of extraction and purification processes. Furthermore, this technique has open an interesting horizon to determine nanoplastics. The most difficult ones due to their low size.

Py-GC-MS has already been applied to determine microplastics in soil [56], soil amended with municipal solid waste compost [57], biosolids [58], salt [59, 60], river sediments, [30, 61], beach sediments [62], coastal sediments [63], tidal flat sediment [60], suspended particulate matter [30], wastewater, sea water [64], surface water [65], bivalves [66], fish and other types of biota. Furthermore, Py-GC-MS has been used to determine nanoplastics in water [67-69].

The determination of microplastics can be carried out directly in matrices, such as soil [57] but is usually performed by separating and concentrate them from the matrix by wet digestion (with acids, oxidants or enzymes [63, 70]) or density differences (using solutions of NaCl [62], NaI, ZnCl\textsubscript{2}, NaBr [59], sodium polytungstate [61]) and filtration. In the case, of wastewater analysis and due to its high organic matter content sequential filtration can help to isolate the microplastic without clogging filters [71]. As alternative technique, very recently pressurized liquid extraction (PLE) has been proposed since high temperature and pressure helps to solubilize microplastics in solvents, such as dichloromethane and tetrahydrofuran [58, 72]. In these extracts, not only microplastics but also NOM was extracted when analyzed sediment and soils, a pre-extraction with methanol, eliminates NOM without affecting the polymers.

Nanoplastics can be isolated by using filtration through common PTFE membranes (pore sizes 0.45 and 0.1 µm) to deposit MPs and NPs from aqueous samples working in the limit range of nanoscale (24 nm–52 nm) [68]. Ultrafiltration also retains altogether micro and nanoplastics from water but retains lower nanoplastics sizes than filter (5–50 nm) [67] Triton X-45 (TX-45)-based cloud-point extraction (CPE) has also been tested to preconcentrate nanoplastics [69]. This method provides enrichment factor of 500 without disturbing their original morphology and sizes. At present, nanoplastics can be analyzed using optical and spectroscopic techniques [73]. The optical methods can analyzed particles < 200 nm but cannot provide chemical identification, thus is prone of false positive [74]. By comparison, spectroscopy, such as Raman or Py-GC-MS can provide specific information about the polymer via its fingerprint spectra, but the small size of nanoplastics provides weak responses being prone of false negatives [73-75]. Imaging version of spectroscopies points as the solution to the determination of nanoplastics [73].

The determination by Py-GC-MS is also used in a very conventional format. The most commonly used pyrolyzer in the case of micro and nanoplastics is the micro furnace [58-63, 69]. Filament [56, 57, 68] and Curie point [56, 57, 68] pyrolyzers have also been reported in a much lesser extend. The advantage of the microfurnace is its higher sample capacity. In this case, the double-shot pyrolysis is the preferred mode because NOM compounds are a potential source of interfering during pyrolysis [30, 56, 58, 63, 69]. None of the natural materials compounds interfering with the selected indicators for polypropylene (PP), polyethylene terephthalate (PET), polycarbonate (PC), poly-(methyl methacrylate) (PMMA) and polystyrene (PS) when using thermal desorption (first-shot of the double-shot method) as a clean-up step. This is difficult to explain if
we take into account that in the previous section one of the conclusions drawn was that the NOM produced few compounds when thermo-desorbed. However, the great variability of composition of NOM and the wide range of different conditions used may well justify these apparently contradictory results. Residual organic matrix leads to a variety of non-volatile pyrolysis products, enhances the risk of interferences with specific indicator compounds, boosts the maintenance frequency and hampers reliable quantification. Regarding the preferred pyrolyzer, a comparison of Curie-Point and micro furnace pyrolyzers to determine microplastics in the environment [60]. showed that microfurnace Py-GC-MS can process more sample quantity because of the larger sample cups allowing the use of glass fibre filters for direct transfer of pre-concentrated microplastics. Besides simplification, this minimized sample losses during the transfer from the filter to the pyrolyzer.

The GC-MS is also very conventional with a quadrupole mass analyzer, even with a ToF (pulsed) analyzer was also reported with advantages over more common scanning mass spectrometers (quadrupole analyzers). In this study, ToF operated in nominal mass units (not accurate mass) similar to the quadrupole but offers substantial sensitivity because in a ToF, all the ions accumulated are transmitted to the detector [68]. Sensitivity is crucial to work in full scan mode because using quadrupolar detector. In most cases and unlike the analysis of NOM, selected ion monitoring (SIM) mode is the only working mode that attains sufficient sensitivity to detect microplastics still at much lower concentrations than organic matter.

Residual organic matrix present in the extract/sample leads to a variety of non-volatile pyrolysis products, enhances the risk of interferences with specific indicator compounds, boosts the maintenance frequency and hampers reliable quantification. Compounds in the pyrograms can be identified querying against any of the previous mentioned mass spectral database, custom database containing pre-acquired pyrograms with reference plastic samples or manually compared with the available literature [62, 76]. However, to identify and quantify plastics in environmental samples, specific indicator compounds are usually selected for each type of plastic. These indicator compounds, specific to each type of plastic, are selected either by using analytical standards of each type of plastic or by comparing the results of the pyrograms with the existing literature. Table 2 reports the most used indicator compounds for most reported type of plastics. These indicators are selected assessing their specificity against a number of natural materials: chitin, wood, pine needles, humic acid, cellulose, etc. [58]. Reactive pyrolysis [59, 61, 70] with TMAH as derivatization reagent has been used to reduce the organic matrix interferences and because this technique improve the detection sensitivity for PET and PC. If pyrolysis is performed after TMAH addition the pyrolytic behavior stayed unaffected for polyethylene (PE), PP, PS, and polyvinylchloride (PVC) while that of PET, PMMA, PC, and polyamide (PA6) changed. The determination PS is complicated, even though the microplastics derivatization because chitin, widely present in the natural environment, releases styrene (m/z 104) during pyrolysis, styrene is not indicative for PS identification and quantification in environmental samples, although it is an abundant PS pyrolysis product. In contrast, most of the studies used styrene trimer (m/z 312) because it is specific for PS [69].
The first international comparative study of commonly applied analytical methods for microplastic analysis served as a first attempt to assess the suitability of frequently used methods in microplastic research that also shows obstacles when conducting a comparative study for microplastics [77]. In this study, microscopy, Fourier-transform infrared microspectroscopy (μ-FTIR), Raman microspectroscopy (μ-Raman), thermal extraction and desorption or pyrolysis- combined with GC/MS, scanning electron microscopy and particle counter were compared regarding results on total particle number, polymer type, number of particles and/or particle mass for each polymer type. The quantification of polymer mass for identified polymer types was questionable for Py-GC-MS, whereas other methods failed to determine the correct polymer mass. For the identification of polymer type μ-Raman and Py-GC/MS performed best [77]. The other thermodegradation technique applied to microplastics, is thermogravimetric analysis (TGA), a thermal analysis technique that measures weight loss of a sample as it is heated at a programmed rate in a controlled gaseous environment and is coupled to several detectors, such as FTIR, MS or GC/MS [78, 79]. TGA has evolved to a new combination, thermo-extraction desorption gas chromatography mass spectrometry (TED-GC-MS) [80]. This approach is based on trapping the decomposition products from a TGA onto a solid-phase adsorber and then, analyzing the adsorber by thermal desorption gas chromatography mass spectrometry. Thus, the instrument remains cleaner and is more stable for extended time. Recently, an interlaboratory comparison of thermal procedures for the identification and quantification of polymers in freshwater suspended organic matter revealed an acceptable analyte recovery and reproducibility among participants performing Py-GC-MS, TGA-FTIR, and thermos extraction desorption gas chromatography mass spectrometry (TED-GC-MS) given the still relative novel character of this complex analyte/matrix combination [78].

In other studies, Py-GC-MS performance has been compared to that obtained by μ-FTIR and μ-Raman, as most successful complementary approaches in the identification of microplastics. The optimized Py-GC/MS method identified 40 particles already identified by μ-Raman. Py-GC-MS identified copolymer like PE-PP or PE-PP-PA6 which could be difficult to identify with μ-Raman without chemometrics approach leading to results with a finer identification [66]. In the case of μ-FTIR differentiated between plastic vs. non-plastic in the same way in 26 cases, with 19 particles and fibers (22 after re-evaluation) identified as the same polymer type. To illustrate the different information obtained by these different approaches and emphasize the complementarity of their information content, Fig. 5 shows the identification of the particles using μFTIR and py-GC-MS [61].

3.3. Others

The other application of Py-GC-MS are mostly focused on the determination of contaminants. The unintentional poisoning of off-target animals by bromadiolone, a second generation anticoagulant rodenticide has been determined through its analysis in liver and blood plasma by means of in-injector Py-GC-MS (heating the normal GC injector at 400 °C using with ion trap tandem mass analyzer with electron ionization
The pyrolysis products provided a very selective analysis without interferences of other rodenticides.

The analytical capabilities of double shot Py-GC–MS were applied to evaluate environmental samples of petroleum hydrocarbons from the Deepwater Horizon oil spill. EGA Py-GC–MS can quantify the overall degree of petroleum hydrocarbon weathering. Furthermore, Heart-cut Py-GC–MS can quantify specific compounds in the “thermal desorption zone” (50–370 °C), as well as characterize pyrolyzed fragments from non GC-amenable petroleum hydrocarbons (including oxygenated hydrocarbons) in the “cracking zone” (370–650 °C). This analysis not only elucidates weathering trends in Deepwater Horizon oil over several years, but also illustrates the analytical capacity of this method for future research on petroleum hydrocarbon, filling a void in research connecting Py-GC–MS and environmentally weathered oil samples [82]. As can be seen from the previously mentioned examples, the Py-GC-MS, although little exploited, can still have multiple applications in other environmental fields, especially in the determination of complex mixtures of contaminants.

4. Conclusions

Py-GC-MS has proven to be a valuable technique for environmental analysis, not widespread use but covering crucial environmental aspects. Characterization of NOM is essential for carbon sequestration and the maintenance of soil stability and fertility, evaluation of terrestrial inputs on oceans, etc. The evaluation of contamination by micro and nanoplastics has become an essential pillar. Py-GC-MS has demonstrated important advantages over other techniques such as µRaman and µFTIR to determine microplastics, and has been the only one able to detect nanoplastics. Something that until very recently was considered almost impossible.

However, either because of the difficulty in interpreting the results, or because the studies are more focused on the robustness of the pyrolyzer, the applications have not yet introduced the latest innovations in GC-MS.

Hopefully, in near future, Py-GC-MS will not only be applied in its conventional format but will also take advantage of the great separation power of GCxGC or the speed of rapid GC and will more frequently incorporate the incredible identification capability that HRMS and HRMS in tandem can provide. Furthermore, environmental analysis could also benefit from the application of other pyrolysis’ working modes, such as EGA or shot-cut-EGA, not applied yet in environmental analysis and could add a further dimension to multidimensional techniques. Therefore, there are still challenges to overcome in this aspect though we can be confident in that several of these new trends within Py-GC-MS will be applied soon to environmental analysis.

ACKNOWLEDGEMENTS

This work has been supported by the Spanish Ministry of Science, Innovation and Universities and the ERDF (European Regional Development Fund) through the project CICLIC -subproject WETANPACK (RTI2018-097158-B-C31), by the Generalitat
Valenciana through the project ANTROPOCEN@ (PROMETEO/ 2018/ 155) and the Generalitat de Catalunya (Consolidated Research Groups 2017 SGR 1404 - Water and Soil Quality Unit).

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Figure 4. Image plot (GC retention time vs. mass-to-charge-ratio vs. signal intensity) of At4 surface water (rich in tDOM) under TD (top) and Py (bottom) conditions resulting from the use of REMPI-ToFMS detection. Reprinted from ref. [39] Copyright (2016) royal society of chemistry.

Figure 5. Flowchart of the proposed systematic approach for unveiling the changes of chemical composition on pyrograms. ANOVA: analysis of variance; Tukey’s HSD: Tukey’s honest significant difference; and PCA: principal components analysis. Appropriate techniques can be used depending on whether or not the assumptions (such as independence of cases, normality, and homogeneity of variances for ANOVA) can be met. Reprinted from ref [50]. Copyright (2018) Elsevier.

Figure 6. ATR-FTIR spectra (left) and Py-GC-MS ion chromatograms (right) of the MP particles. a–d (black) each with a reference (red); C10–C38—alkadienes, alkenes, and alkanes with chain lengths; DiOP—diisoocetyl phthalate; DMP—dimethyl phthalate; FAME—fatty acid methyl ester; FADME—at 740 and 705 cm−1 (out-of-plane deformation of the aromatic ring). They originate presumably from phthalic acid fatty acid dimethyl ester; MB—methyl benzoate; P4ME—pentaerythritol tetramethyl ether, P3ME—pentaerythritol trimethyl ether, P2ME—pentaerythritol dimethyl ether, asterisk—thermochemolysis artifacts. Reprinted from ref. [61] Copyright (2018) Springer.
Table 1. Ability of working in different modes of the three types of pyrolyzers currently in use.

<table>
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<tr>
<th></th>
<th>Microfurnace</th>
<th>Filament</th>
<th>Curie-point</th>
</tr>
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<tbody>
<tr>
<td>Single-shot analysis (Py-GCMS)</td>
<td>Yes</td>
<td>Yes</td>
<td>Yes</td>
</tr>
<tr>
<td>Double-Shot analysis (TD/Py-GCMS)</td>
<td>Yes</td>
<td>Difficult</td>
<td>No</td>
</tr>
<tr>
<td>Evolved gas analysis (EGA-MS)</td>
<td>Yes</td>
<td>Yes</td>
<td>No</td>
</tr>
<tr>
<td>Heart-cut analysis (Heart-cut EGA-GCMS)</td>
<td>Yes</td>
<td>Yes</td>
<td>No</td>
</tr>
<tr>
<td>Reactive Pyrolysis-GC-MS:</td>
<td>Yes</td>
<td>Yes</td>
<td>Yes</td>
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Table 2. Plastic indicator compounds and ions monitored by MS in SIM

<table>
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<th>Plastic</th>
<th>Pyrolysis product</th>
<th>Indicator ions (m/z)</th>
<th>Reference</th>
</tr>
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<tbody>
<tr>
<td>PP</td>
<td>Dimethyl alkenes (2,4-Dimethyl-1-heptene, 2,4-Dimethyl-1-decene)</td>
<td>70, 83, <strong>126</strong> <strong>111, 97</strong></td>
<td>Okoffo et al., [58] Dierkes et al., [68] Fischer &amp; Scholz-Böttcher, [70] Steinmetz et al., [56] Dierkes et al., [68] Hermabessiere et al., [66]</td>
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<tr>
<td></td>
<td>Tertramethyl alkenes (2,4,6,8-tetramethyl-1-decene, 2,4,6,8-Tetramethyl-1-undecenes)</td>
<td>100, 69, 111, 97</td>
<td>Fischer &amp; Scholz-Böttcher, [70] Steinmetz et al., [56] Dierkes et al., [68]</td>
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<td></td>
<td>Methyl alkenes (7-methyl-decene, 7-methyl 1-undecene, 5 methyl undecene, 7 methyl-2-decene)</td>
<td>111, 97</td>
<td>Dierkes et al., [68]</td>
</tr>
<tr>
<td></td>
<td>3-Dodecene</td>
<td>111, 97</td>
<td>Dierkes et al., [68]</td>
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<tr>
<td></td>
<td>Trimethyl alkenes (2,4,8-trimethyl octane, 2,4,6-trimethyl nonene)</td>
<td>111, 97</td>
<td>Dierkes et al., [68]</td>
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<td>PS</td>
<td>5-Hexene-1,3,5-triyltribenzene (styrene trimer)</td>
<td><strong>91</strong>, 117, 194, 312, 207</td>
<td>Okoffo et al., [58], Zhou et al., [69] Steinmetz et al., [56] Mintening et al., [67]</td>
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<td></td>
<td>Styrene</td>
<td><strong>104</strong>, 78</td>
<td>Fischer &amp; Scholz-Böttcher, [70] Steinmetz et al., [56] Mintening et al., [67], Dierkes et al., [68]</td>
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<tr>
<td></td>
<td>2,4-Diphenyl-1-butene or 3-butene-1,3-diyl dibenzene (styrene dimer)</td>
<td><strong>91</strong>, 208</td>
<td>Fischer &amp; Scholz-Böttcher, [70], Hermabessiere et al., [66]</td>
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<td></td>
<td>α-Methylstyrene</td>
<td>103, 118</td>
<td>Steinmetz et al., [56]</td>
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<td></td>
<td>Toluene</td>
<td>91</td>
<td>Dierkes et al., [68]</td>
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<table>
<thead>
<tr>
<th>Plastic</th>
<th>Pyrolysis product</th>
<th>Indicator ions (m/z)</th>
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<tr>
<td></td>
<td>1-Ethyl-2-methylbenzene</td>
<td>117, 105</td>
<td>Dierkes et al.,[68]</td>
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<td>1,2,3-trimethylbenzene</td>
<td>120, 105</td>
<td>Dierkes et al.,[68]</td>
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<td>2-Propenyl-benzene</td>
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<td>3-Butenyl-benzene</td>
<td>132, 91</td>
<td>Dierkes et al.,[68]</td>
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<td>Bibenzyl</td>
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<td>1,1’-(1-Methyl-1,2-ethanediyl)bis-Benzene</td>
<td>105, 91</td>
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<td>Stilbene</td>
<td>180, 165</td>
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<td>1,2-Dihydro-3-phenylnaphthalene</td>
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<td>2,5-Diphenyl-1,5-hexadiene</td>
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<td>Methyl methacrylate</td>
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<td>Okoffo et al.,[58] Zhou et al.,[69] Hermabessiere et al.[66]</td>
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<td>Methylacrylate</td>
<td>55</td>
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<td>PET</td>
<td>Vinyl benzoate</td>
<td>105, 77, 148, 51</td>
<td>Okoffo et al.,[58] Hermabessiere et al.[66]</td>
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<td>Dimethyl terephthalate*</td>
<td>163</td>
<td>Fischer &amp; Scholz-Böttcher, [70] Hermabessiere et al.[66]</td>
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<td></td>
<td>Benzene</td>
<td>52, 78</td>
<td>Hermabessiere et al.[66]</td>
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<td>Indicator ions ((m/z))</td>
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<td>Acetophenone</td>
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<td>Benzoic acid</td>
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<td>77, 105, 122</td>
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<td>2,2-Bis(4’-methoxy-phenyl)propane*</td>
<td>256, 241</td>
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<td>p-Methoxy-tert-butylbenzene*</td>
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<td>Phenol</td>
<td>66, 94</td>
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<td>p-Cresol</td>
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<td>Hermabessiere et al.[66]</td>
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<td>Hermabessiere et al.[66]</td>
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<td>p-Vinylphenol</td>
<td>91, 120</td>
<td>Hermabessiere et al.[66]</td>
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<td>p-Isopropenylphenol</td>
<td>119, 134</td>
<td>Hermabessiere et al.[66]</td>
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<td>PE</td>
<td>1-Decene (C10:1), 1-Pentadecene (C15:1) Alkanes (e.g. C14, C15, C16, C17, C18), Alkenes (C9:1, C11:1, C12:1, C13:1 C14:1, C16:1, C17:1, C18:1), Alkanes (e.g. C20)</td>
<td>83, 97, 111, 140, 85, 55, 69</td>
<td>Okoff et al., [58] Fischer &amp; Scholz-Böttcher [70] Steinmetz et al.,[56] Hermabessiere et al.[66] Dierkes et al.,[68]</td>
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<td>α,ω-Alkenes (e.g. C20:2, C14:2, C16:2, C18:2)</td>
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<td>Fischer &amp; Scholz-Böttcher [83] Steinmetz et al.,[56]</td>
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<td>1,14-Pentadecadiene</td>
<td>81, 82, 95</td>
<td>Dierkes et al.,[68] Steinmetz et al.,[56]</td>
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<td>PVC</td>
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<td>78, 74, 52,</td>
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<td>Indicator ions ((m/z))</td>
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<td>91</td>
<td>Sullivan et al. [68] Hermabessiere et al.[66]</td>
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<td>116, 117</td>
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<td>1,4-dihydronaphthalene</td>
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<td>1-Methylnaphtalene or 2-methylnaphthalene</td>
<td>115, 142</td>
<td>Sullivan et al. [68] Hermabessiere et al.[66]</td>
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<td>Biphenyl</td>
<td>154</td>
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<td>Chlorobenzene</td>
<td>112</td>
<td>Fischer &amp; Scholz-Böttcher [60]</td>
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<td>78, 104</td>
<td>Sullivan et al. [68] Hermabessiere et al.[66]</td>
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<td>PA6</td>
<td>113</td>
<td>Fischer &amp; Scholz-Böttcher [60] Hermabessiere et al.[66]</td>
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<td>N-methyl caprolactam*</td>
<td>127</td>
<td>Fischer &amp; Scholz-Böttcher [60]</td>
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<td>MDI-PUR</td>
<td>N,N-Dimethyl-4-(4-methylamino)benzylanilin*</td>
<td>240</td>
<td>Fischer &amp; Scholz-Böttcher [60]</td>
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<td>4,4’-Methylenebis(N,N-dimethylaniline)*</td>
<td>253, 254</td>
<td>Fischer &amp; Scholz-Böttcher [60]</td>
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</table>

Italics and bold values used for calibration and quantification. *Only after TMAH treatment

MDI-PUR= MDIPolyurethane, PA6=Polyamide, PC= Polycarbonate, PE=polyethylene, PET= Polyethylene terephthalate, PMMA= Poly-
<table>
<thead>
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<th>Pyrolysis product</th>
<th>Indicator ions (m/z)</th>
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<tr>
<td>(methyl methacrylate), PP= polypropylene, PS= polystyrene, PVC= polyvinylchloride</td>
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REFERENCES


[29] Z. Zhang, G. Xu, Q. Wang, Z. Cui, L. Wang, Pyrolysis characteristics, kinetics, and evolved gas determination of chrome-tanned sludge by thermogravimetry-Fourier-transform infrared spectroscopy and pyrolysis gas chromatography-mass spectrometry, Waste Management, 93 (2019) 130-137


[46] M. Fukushima, X. Tu, A. Aneksampant, A. Tanaka, Analysis of branched-chain fatty acids in humic substances as indices for compost maturity by pyrolysis-gas chromatography/mass spectrometry with tetramethylammonium hydroxide


[60] M. Fischer, B.M. Scholz-Boettcher, Microplastics analysis in environmental samples - recent pyrolysis-gas chromatography-mass spectrometry method improvements to increase the reliability of mass-related data, Analytical Methods, 11 (2019) 2489-2497


[76] E. Hendrickson, E.C. Minor, K. Schreiner, Microplastic Abundance and Composition in Western Lake Superior As Determined via Microscopy, Pyr-GC/MS, and FTIR, Environmental Science and Technology, 52 (2018) 1787-1796


M3 / At4 (surface) – TD (250 °C) – GC/REMPI-ToFMS

- Less complex spectrum
- Low signal intensities

M3 / A4 (surface) – Pyrolysis (500 °C) – GC/REMPI-ToFMS

- Broad substance spectrum
- High signal intensity
→ More high molecular compounds
Step 1: Differences in chemical classes

- Analysis of chemical class
  - ANOVA
  - Kruskal-Wallis
  - t test
  - ...

Is the effect significant?

Yes

- Samples have different % in chemical class(es)

No

- Samples have similar % in chemical class(es)

Step 2: Differences in pyrolysates

- Analysis on pyrolysates
  - Factor analysis
  - PCA

Are samples in groups?

Yes

- Using the structure of pyrolysates in F1-F2 loading projection to explain the difference among sample groups

No

Ecological applications

Proposed systematic approach
Highlights

- In the environmental sciences, Py-GC-MS is becoming more and more relevant
- Advances in the design of currently used pyrolyzers are discussed
- Recently developed working modes within Py-GC-MS are described
- Py-GC-MS application to organic matter and microplastics is highlighted.
- Progresses and promising trends in Py-GC;S analysis are pointed out.
Declaration of interests

☒ 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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