Science of The Total Environment
June 2021, Volume 773, Pages 145073 (15p.)
https://doi.org/10.1016/j.scitotenv.2021.145073
https://archimer.ifremer.fr/doc/00678/78986/

Identification and quantification of plastic additives using Pyrolysis-GC/MS: a review

Akoueson Fleurine [1, 2], Chbib Chaza [3], Monchy Sébastien [3], Paul-Pont Ika [4], Doyen Périne [2], Dehaut Alexandre [1], Duflos Guillaume [1, *]

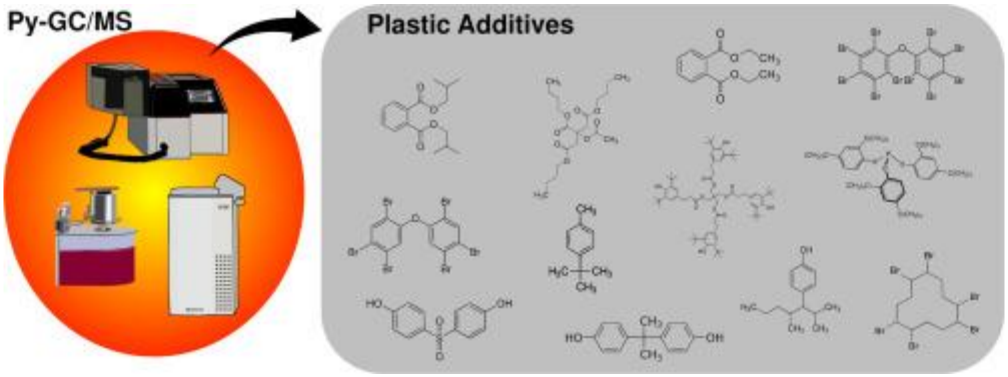
[1] ANSES – Laboratoire de Sécurité des Aliments, Boulevard du Bassin Napoléon, F-62200 Boulogne-sur-Mer, France
[2] Univ. Littoral Côte d'Opale, UMR 1158 BioEcoAgro, EA 7394, Institut Charles Viollette, USC ANSES, INRAe, Univ. Lille, Univ. Artois, Univ. Picardie Jules Verne, Uni. Liège, F-62200, Boulogne-sur-Mer, France
[3] Univ. Littoral Côte d'Opale, CNRS, Univ. Lille, UMR 8187, LOG, Laboratoire d'Océanologie et de Géosciences, F-62930 Wimereux, France
[4] Univ Brest, CNRS, IRD, IFREMER, LEMAR, F-29280 Plouzané, France

* Corresponding author : Guillaume Duflos, email address : guillaume.duflos@anses.fr

Abstract :

Analysis of organic plastic additives (OPAs) associated to plastic polymers is growing. The current review outlines the characteristics and the development of (multi-step) pyrolysis coupled with a gas chromatography mass spectrometer (Py-GC/MS) for the identification and semi-quantification of OPAs. Compared to traditional methods, Py-GC/MS offers advantages like suppressing extensive steps of preparation, limiting contamination due to solvents and the possibility to analyse minute particles. Its key advantage is the successive analysis of OPAs and the polymeric matrix of the same sample. Based on the studied articles, numerous methods have been described allowing identification and, in some case, semi-quantification of OPAs. There is nevertheless no gold standard method, especially given the huge diversity of OPAs and the risks of interferences with polymers or other additives, but, among other parameters, a consensus temperature seems to arise from studies. More broadly, this review also explores many aspects on the sample preparation like weight and size of particles and calibration strategies. After studying the various works, some development prospects emerge and it appears that methodological developments should focus on better characterizing the limits of the methods in order to consider which OPAs can be quantified and in which polymers this is feasible.

Graphical abstract



Highlights

► The analysis of OPAs in polymers is an analytical challenge ► Py-GC/MS allows an efficient thermal desorption to analyze OPAs ► Py-GC/MS allows the simultaneous analysis of OPAs & polymer in the same sample ► Pros and cons regarding the use of Py-GC/MS are thoroughly assessed ► Standardized and reliable quantitative methods for the analysis of OPAs is required

Keywords : Organic plastic additives (OPAs), plastic polymers, Py-GC/MS, multi-shot pyrolysis

1. Introduction

Pyrolysis-gas chromatography coupled with mass spectrometry (Py-GC/MS) is used to characterize the chemical composition and the structure of volatile and non-volatile compounds (Riess et al., 2000). This characterization is performed under an inert atmosphere (usually using helium), by analysing the thermal degradation products of the compounds obtained after heating the sample to high temperatures, usually between 250°C and 700°C (Fries et al., 2013; Herrera et al., 2003; Kleine-Benne and Rose, 2011; Tsuge et al., 2011; Wang, 2000b). Py-GC/MS is one of the oldest approaches to studying the structure of polymeric systems (Bart, 2001), and has become established as a simple, quick and reliable analytical technique for a range of applications, including the analysis of various chemical aspects of polymeric materials including the characterization of organic plastic additives (OPAs). Various chemical additives are added to polymers during the manufacturing process to modify and improve their physical properties (Fries et al., 2013; Rios Mendoza et al., 2017; Rochman et al., 2019). There are several categories of additives, for instance pigments and dyestuffs to modify colour, antioxidants and UV stabilizers to maintain the inherent properties of the material by providing resistance to heat and aging or to improve resistance to light, and functional agents including flame retardants, anti-static additives, surfactants, and plasticizers. They can be small, volatile and semi-volatile molecules, or large and less or non-volatile compounds (Jansson et al., 2007).

The use of a specific analytical tool such as Py-GC/MS enables to obtain information on the composition of the plastic material, for which there is no clear data on formulation. The molecular information on the polymer, additives, and the mixture additives-polymers will help to extend knowledge on the state of polymer degradation, to establish the link between formulation, properties and degradation (La Nasa et al., 2020), and to target toxic aspects. The analysis of OPAs has grown in importance over the past few decades since the use of certain additives has become a controversial issue as some of them were found to be toxic to human (Yanagisawa et al., 2018). Compared with other detection methods, such as liquid chromatography coupled with mass spectrometry (LC/MS) or GC/MS analysis with a solvent extraction (SE) step, Py-GC/MS has the advantage of having a relatively easy and fast sample preparation (Kim et al., 2016; Llana-Ruiz-Cabello et al., 2017; Maruyama et al., 2015; Odermatt et al., 2003; Yanagisawa et al., 2018). This technique has been applied to the qualitative and semi-quantitative analysis of a large variety of additives in polymers. In addition, for most compounds, analytical pyrolysis offers a major advantage when it comes to analysing a complex sample: it can identify mixed media and successively analyse both the polymer and the associated OPAs. This is called multi-shot Py-GC/MS, which includes an initial thermal extraction step to characterize the additives and a second flash pyrolysis step to analyse the polymeric matrix (Herrera et al., 2003; Jansson et al., 2007; Kleine-Benne and Rose, 2011).

This paper reviews the studies carried out on OPAs using the analytical Py-GC/MS technique. This literature review, based on 71 articles, identified in scientific databases and search engines (Scopus, Google Scholar, Science Direct). An extended bibliographic research was carried out on plastic additives, pyrolysis techniques, additive properties, the type of analysable molecules and the application of Py-GC/MS to plastic polymers and associated OPAs without targeting any specific additives. Then, a more targeted literature search was carried out by including the following key words: plastic additives, polymers, double- and multi-shot pyrolysis GC/MS and thermal desorption. The studies dated from 1983 up to August 2020. Articles were selected based on the title and the abstract and, often, on the references in those articles. The third step consisted in extracting, compiling, sorting and comparing the information given in the selected studies. This review presents the usefulness of the multi-shot Py-GC/MS technique for the analysis of OPAs and plastic polymers. It also explores the different criteria that need to be taken into account for successful analysis, from the knowledge of additives, polymers and their use, to the understanding of pyrolysis and its analytical parameters.

2. Pyrolysis-GC/MS and its contribution to the analysis of plastic additives

The analysis of the chemical compounds added to plastic formulations is complicated. The polymeric matrix is a mixture of molecules: oligomers, additives, and non intentionally added substances (NIAS) that must be identified using sensitive analytical techniques. Although various analytical techniques can be used to identify plastic additives in polymeric materials, most laboratories and studies use wet chemical techniques to extract additives from the polymers.

To date, many conventional methods for OPA analysis in polymer materials have been published. The majority of them use SE, such as Soxhlet extraction, coupled with GC/MS analysis (Kim et al., 2016; Kudo et al., 2019; Trimpin et al., 2009). SE allows for accurate qualitative and quantitative analysis, but requires complicated, costly, and time-consuming steps as well as large quantities of solvents. These steps are considered problematic because they can introduce errors in the analysis because of those manipulations. The various potential sources of errors (listed in Randle et al. (2013)) include (1) analysing a non-representative portion of the sample; (2) the risk of losing the targeted analytes during sample preparation; (3) reproducibility problems with the risk of deviations from the method's protocol; and (4) background contamination, coming from glassware, reagents or solvents, which increases with each additional step of the process. Moreover, another downside of SE is that some polymers, especially thermoplastic matrices such as polyethylene (PE) or polypropylene (PP), are insoluble or hardly soluble in some solvents (Bart, 2001; Okoffo et al., 2020; Wang, 2000b). For these reason, SE techniques do not always comprehensively isolate the additives from the polymeric matrix. Recalcitrant polymers usually require high temperatures and, either the final solution is too viscous to go through extraction procedures, or the solvent is very corrosive and presents safety hazards (Wang, 2000b).

Suppressing the extensive sample preparation steps prior to analysis can help to reduce the bias and the labour costs associated with each step. However, without prior separation of the additive from the macromolecular polymeric matrix using wet chemistry, the number of direct analytical methods that can be applied are limited (Bart, 2001). Methods such as Py-GC/MS that can easily analyse plastic additives have gained interest over the past several years. This thermal extraction method can be applied to solid samples when there is no simple way to extract the additive from the solid (Wang, 2000a).

2.1. Py-GC/MS for the identification of plastic additives and polymers

Over the last few years, flash pyrolysis has become the most common pyrolysis technique for the analysis of additives. With this method, additives are identified by determining their pyrolysis degradation products (Bart, 2001). One of the first experiments on additive analysis using flash Py-GC/MS was performed by Perlstein and Orme (1985). They identified and semi-quantified some UV-light stabilizers (Tinuvin® 144 (PubChem CID: 93348), Tinuvin® 622 (PubChem CID: 54328974), Tinuvin® 770 (PubChem CID: 164282) and Chimassorb® 944 (PubChem CID: 93418). They also identified an antioxidant, Irganox® 1010 (PubChem CID: 64819) embedded in low-density polyethylene (LDPE) and PP at 770°C, after a dissolution step by using sulfuric acid and methylene chloride. However, in addition to the complicated sample preparation (SE and pre-concentration steps) and the overlapping characteristic peaks, the low recovery rates (72–94%) limit the practicality of the method. Wang (2000b) used the same technique for the identification of some flame retardants and antioxidants at a pyrolysis temperature of 950°C. The flash pyrolysis technique is problematic for the direct analysis of OPAs in complex polymeric matrices because they are pyrolysed along with the polymer. On the pyrogram, the abundance of polymer fragments is greater than those of the additives. Furthermore, the proportion of additives is not equally distributed among polymer types. Some polymers require different amounts of additives according to their use, e.g. polyvinyl chloride (PVC): 73% w/w, PE and PP: 10% w/w and styrenics: 5% w/w (Rochman, 2015). Moreover, the proportion of the different additives within the polymers is also very disparate going from 0.005% to 70%. For example, plasticizers are found in the range of 10 to 70% w/w and most of brominated flame retardants (BFRs) in the range of 3-25% w/w. However, antioxidants or others flame retardants are present in low quantities, from approximately 0.005 to 7% w/w (ECHA, 2019; Hahladakis et al., 2018). For this reason, the pyrolysis products from OPAs during flash pyrolysis may be overshadowed by the products generated from the polymer, resulting in a complex mass spectrum analysis that hampers the identification of additive compounds. Thus, to be able to discriminate an additive from the decomposition products of the polymeric matrix, the spectra of the additive or its fragments must differ significantly from those of the polymer fragments.

Pyrolysis analysis can help with this issue, by using a “multi-step” temperature approach that allows investigating the organic additives and the polymeric matrix separately and successively (Derenne and Quénéa, 2015; Fries et al., 2013; Okoffo et al., 2020; Wang, 2000b). This multi-step analysis, more commonly called multi-shot Py-GC/MS (Herrera et al., 2003) or sequential pyrolysis (Kleine-Benne and Rose, 2011), can lead two consecutive analyses of a single sample under different pyrolysis temperatures (Herrera et al., 2003; Kleine-Benne and Rose, 2011; Okoffo et al., 2020; Quénéa et al., 2006; Terán et al., 2009). The polymer sample is directly introduced into the pyrolyser device. The first shot is used to thermally desorb the organic compounds at the surface of the sample or the additives included in the polymers using a specified heating programme. It provides information on additives, regardless of the polymer, through rapid analysis of additives without degrading the polymeric matrix.

The second shot, also called fast or flash pyrolysis, thermally degrades the polymer matrix at higher temperatures (>500°C) and gives data on the polymer only (Herrera et al., 2003; Jansson et al., 2007; Okoffo et al., 2020).

Multi-shot Py-GC/MS has proven to be a good tool for the identification of OPAs and polymers, helping with the identification of additives and simplifying the interpretation of the polymer spectra by separating the additives detection from the polymers and thermally separating the different families of compounds at different temperature intervals (Dekiff et al., 2014; Fries et al., 2013; Herrera et al., 2003; Jansson et al., 2007; Odermatt et al., 2003). In 2019, Yanagisawa et al. (2019) developed and applied the first screening method for multiple additives, including plasticizers and various families of flame retardants: Tris(2-chloroethyl)phosphate (TCEP) (PubChem CID: 8295), decabromodiphenylether (decaBDE), Diisobutyl phthalate (DIBP) (PubChem CID: 6782), Di-n-butyl phthalate (DBP) (PubChem CID: 3026), Butyl benzyl phthalate (BBP) (PubChem CID: 2347), Di(2-etylhexyl)phthalate (DEHP) (PubChem CID: 8343) and Tetrabromobisphenol A (TBBPA) (PubChem CID: 6618).

The chemical nature of the additives needs to be taken into account. For instance, certain OPAs that are polar, unstable, or have high molecular weight and low volatility, such as some flame retardants or some antioxidants and light or UV stabilizers, are more complex to analyse than others (Riess et al., 2000; Yanagisawa et al., 2018). These additives, weakly detectable or even undetectable at a low pyrolysis temperature of 300°C, i.e. first-shot temperatures, need to be either derivatized to improve their volatility, or analysed at higher temperatures, i.e. approaching flash pyrolysis temperatures, with the risk of making the spectrum analysis difficult due to overlap with the peaks of the pyrolysed polymers (Yanagisawa et al., 2018).

There are a large number of pyrolysates produced during the pyrolysis of the polymeric matrix with complex additives; as a result, interpretation and identification of all components can be rather time consuming (Wang, 2000a). Another pyrolysis approach is evolved gas analysis-mass spectrometry (EGA-MS), which can give complementary information on the thermal features of the compound. EGA-MS provides thermal degradation profiles by thermally separating the materials of a sample, without chromatographic separation. Once the thermal zones of interest are obtained, appropriate pyrolysis temperature can be selected based on the EGA profile. Compounds can be identified according to the mass spectrum information and the ions present in a thermal region, (La Nasa et al., 2018; La Nasa et al., 2021).

Carefully examining specific ions for each additive is the key to achieve simultaneous screening. A good understanding of the pyrolytic behaviour of both the additives and the polymer can help select which fragments and specific ions to target and determine the presence of the molecules of interest (Jansson et al., 2007; Sitholé and Pimentel, 2009). By selecting appropriate quantifier and qualifier ions, all target analytes can be better visualized, identified, and measured without interfering with each other. The single ion monitoring (SIM) mode of the MS detector is also useful for checking and balancing interferences between the additives and the polymer matrix. These interference noise levels can result in lower abundance of the targeted molecules, due to ion suppression.

Py-GC/MS is now a recognized method for the fast identification and semi-quantification of organic contaminants, including OPAs (Table 1). It provides a well-known advantage: it does not require sample pre-treatment, such as SE (Llana-Ruiz-Cabello et al., 2017). Analysis can be carried out by simply placing a suitable amount of weighed out sample directly in a pyrolysis sample cup, thereby limiting background contamination (Dekiff et al., 2014; Fries et al., 2013; Kudo et al., 2019; Terán et al., 2009). Although cross-contamination coming from the sample preparation steps can be avoided, particular attention must be paid to the plastic additives already present in laboratory reagents and materials. In 2020, Hermabessiere et al. (2020) conducted a study on the presence of Irgafos® 168 (an antioxidant mainly incorporated in PP and PE) in various laboratory reagents and materials including plastic packaging, caps, bottles, containers, polymer powder, and deionized water and showed that this antioxidant was ubiquitous in the laboratory at high concentrations. To overcome this contamination, with the aim of conducting studies in realistic conditions and preventing certain additives, e.g. Irgafos® 168, from interfering with analytical studies, the source of plastic additives should be carefully considered.

Py-GC/MS has another substantial advantage: it can analyse tiny mass amounts of sample, of the order of microgram amounts, usually between 100 and 1000 µg depending on the study, Py-GC/MS has also been used on colloidal fractions presumably containing nanoplastics (<1 µm) (Ter Halle et al., 2017). This level of detection contrasts with other analytical techniques, such as SE methods, that are quite inaccurate at low concentrations and require a higher amounts of sample to surmount detection limits (Bart, 2001). In some cases, Py-GC/MS is the only characterization method that can be used when small amounts of material are available. It is also important to consider that, depending on the type of additive, only a low concentration of additives can be embedded in the polymeric matrix, as mentioned above. The low ranges of concentrations illustrates the critical need for a sensitive method, especially in the case of environmental sample analysis, where OPAs are more likely to be heterogeneous and present only in trace amounts (Fries et al., 2013).

2.2. Py-GC/MS for the quantitative analysis of plastic additives

The quantitative analysis of OPAs, with an initial thermal desorption (TD) step, is one of a wide diversity of applications of Py-GC/MS (Bart, 2001). More and more studies are showing interest for this application (Net et al., 2015). However, relatively few studies have managed to attain suitable quantification or semi-quantification of additives in polymers, with lacking information on the limits of detection or accuracy of the method for some studies (Table 2) and only on specific families of additives, mostly involving plasticizers especially phthalates (Fries et al., 2013; Kim et al., 2016; Kudo et al., 2019; La Nasa et al., 2021; Maruyama et al., 2015; Net et al., 2015; Yanagisawa et al., 2019) and BFRs (Rial-Otero et al., 2009; Yanagisawa et al., 2018).

The difficulty in acquiring quantitative data is a major drawback of pyrolysis. In the studies reporting Py-GC/MS quantitative determination of additives in polymeric matrices, a confounding factor is identified:

the matrix effects on pyrolysis. It has been shown that the polymeric matrix can have an effect on the thermal desorption and thus on the identification of the additive. This is one of the major issues for semi-quantitative analysis using Py-GC/MS, which is not considered as a routine analysis because this method requires (i) calibration standards with the same polymeric matrix as the sample; (ii) time-consuming multiple measurements; and (iii) taking into account divergent standard procedures (Bart, 2001). These limitations are discussed below.

To ensure the same pyrolysis efficiency and linearity of the signal intensity for a range of concentrations, calibration must be carried out using different concentrations of additive standards (Bart, 2001). With Py-GC/MS, quantitative additive analysis can be performed either with an external calibration (EC) method or with an internal calibration (IC) method, which is often preferable (Bart, 2001; Odermatt et al., 2003).

Across studies, various techniques have been used to establish standard samples for the calibration curves and they will be presented in Section 3.1.3. Regardless of the method employed, multi-shot Py-GC/MS shows good results and linearity for calibration with coefficients of determination (R^2) of > 0.98 and reported relative standard deviation (RSD) values of between 5% and 20% for most analyses (Table 2). The two available recovery rates reported for the verification of quantification using reference material (RMs) are satisfactory: greater than 70% in Yanagisawa et al. (2019) and 98.8–106.6% in Kim et al. (2017).

The accuracy of multi-shot pyrolysis must be compared with that of other extraction techniques (e.g. SE). In their study, Kim et al. (2017) found that for equivalent RSD values (i.e. <5%) between pyrolysis and SE techniques, wet chemical methods result in a lower extraction efficiency and recovery rates that can be attributed to losses during sample preparation. Other studies have shown that multi-shot Py-GC/MS performs better than SE analysis for the identification of phthalates (IEC, 2017; Kim et al., 2016; Randle et al., 2013). The International Electrotechnical Commission (IEC, 2017) study considered this technique suitable for the screening and the semi-quantitative analysis of seven phthalates: DIBP, DBP, (BBP), DEHP, di(n-octyl) phthalate (DNOP) (PubChem CID: 8346), di-isononyl phthalate (DINP) (PubChem CID: 590836), and di-isodecyl phthalate (DIDP) (PubChem CID: 33599) in polymers that are used in electro technical products in the range of 100 to 2000 mg/kg. In contrast, the SE technique followed by LC/MS analysis has shown limitations for the determination of phthalates: only five phthalates (BBP, DEHP, DNOP, DINP, and DIDP) were identified, due to low peak and spectral resolution quality. Several studies report equivalent and satisfactory results with multi-shot Py-GC/MS and with SE-GC/MS methods, regarding recovery and repeatability rates. For example, SE analysis of phthalates from different studies showed good recovery rates (97.6 to 104% (J.W.Kim et al., 2016; IEC et al., 2017)) and repeatability rates (%RSD), from 9 to 15% in the study of J.W.Kim et al (2016), 5.4% in the study of Kim et al (2017) and between 0.29 and 1.24% in the study of IEC (2017). In comparison, Py-GC/MS studies showed similar values with recovery rates of over 98% (La Nasa et al., 2021) and between 78 and 117% (J.W.Kim et al., 2016; Yanagisawa et al., 2019; Kudo et al., 2019) and high repeatabilities of 5% and 10% (Yanagisawa et al., 2018 and 2019 respectively) and between

7.7 to 20% (J.W.Kim et al., 2016). In this latter study, the high reproducibility of the Py-GC/MS method was also confirmed by six other international laboratories, and recommended by the IEC Technical Committee (TC) 111 Working Group 3 (WG3), which conducted the same studies. For TD followed by pyrolysis, the quantification recoveries were between 78.3–117.4% (Kim et al., 2016) and between 92-103%, for inter-lab studies (Kim et al., 2016). Finally, the comparison of studies for the quantification of plastic additives performed using either pyrolysis or SE methods showed comparable results, with most of the time a recovery rate for Py-GC/MS slightly lower than SE techniques (approximately 10% lower).

It is important to define precisely the limit of detection (LOD) and the limit of quantification (LOQ), considering the low concentrations of additives in environmental sample, ranging from sub ng/g to µg/g levels (Teuten et al., 2009), and of certain additives in polymeric matrix samples. The LOD and LOQ values of SE analysis are lower than pyrolysis values, indeed, solvent extraction has a pre-concentration step that makes it possible to reach lower LODs. In addition, regarding the LOD and LOQ values in the literature for pyrolysis analysis (Table 2), quantification can be complicated, especially because the amount of sample analysed in the pyrolyser is low too. Therefore, Py-GC/MS can usually only be considered as a semi-quantitative method. The quantitative potential of this technique still requires considerable development and control. This need for optimization certainly limits the acceptance of this technique for routine quantification in the industrial sector. Also, understanding and being aware of the artefacts generated during pyrolysis of environmental samples, which are complex samples, is crucial for reliable analysis (Terán et al., 2009). Thus, various preliminary experiments with clean matrix samples and pure standard mixtures must be performed.

2.3. Parameters influencing the analysis of plastic additives

The key to a successful analysis of plastic additives is to understand and have expertise on the properties of commercial additives, polymers and their applications, as well as the Py-GC/MS technique (Wang, 2000b). Several points are crucial for the correct identification of an additive. The detection of additives in polymers using Py-GC/MS can be influenced by (i) the fragmentation behaviour of the analytes — the degree of fragmentation depends on the temperature — ; (ii) the concentration; and (iii) the structure of the additive and polymer fragments (Bart, 2001).

Depending on the pyrolyser type, Py-GC/MS possesses a vast number of different instrumental configurations: Py-GC interface; presence of a cooled injection system (CIS); gas chromatographic characteristics such as column type, carrier flow rate, etc.; mass spectrometer characteristics including ionization mode; and operational variables such as pyrolysis temperatures, pyrolysis duration, vapor pressure, etc. Moreover, the composition of the pyrolysis products depends on specific conditions including temperature, duration, sample size, carrier gas flow rate, all of which make standardization difficult.

Py-GC/MS can be applied to analyse thermally labile and volatile additives, which result in extensive fragmentation. Derivatization can extend the applicability of the technique to certain molecules (Bart, 2001) (see Section 3.1.4.). If there is no derivatization treatment and the compounds cannot be extracted, flash pyrolysis of both the additive and the polymer must occur simultaneously. The SIM mode of MS detectors is an interesting approach and seems to be most informative, because it drastically simplifies the mass spectra and the identification process (Jansson et al., 2007). In addition, electron ionization (EI) allows the identification of the compounds considered too heavy to be identified using Py-GC/MS due to their high molecular weight (MW) which is above the limit of mass detection. Unlike soft ionization techniques, e.g. chemical ionization (CI), that allow conservation of more information on structure and molecular identity, EI at 70 eV causes extensive fragmentation (Bart, 2001). Thus, smaller characteristic fragments from the molecule are determined but not the exact MW of the compound. Sometimes the isolation of specific additive fragments for the identification of individual compounds is difficult when analysing a complex matrix. However, SIM mode detection, with a preliminary selection of specific ions, may help to isolate and identify co-existing additives in a polymer.

2.4. Advantages and limitations of Py-GC/MS

In the various analytical pyrolysis studies that we reviewed, the same assets and drawbacks were generally observed; they are summarized in Table 3.

First, contrary to the more “traditional” wet-chemistry techniques, Py-GC/MS does not require pre-treatment of the sample and extraction steps, limiting background contamination (Dekiff et al., 2014; Fries et al., 2013; Kudo et al., 2019; Terán et al., 2009). The possibility of conducting a multi-shot analysis is clearly the major advantage of Py-GC/MS, allowing the co-identification of OPAs and plastic polymeric matrices (Derenne and Quénéa, 2015; Fries et al., 2013; Okoffo et al., 2020; Wang, 2000b). Multi-shot pyrolysis is a suitable technique for extracting OPAs embedded into the polymeric matrix at lower temperatures before determining the polymers (Fries et al., 2013; Okoffo et al., 2020). Moreover, other additives, such as organic pigments, can be characterized by Py-GC/MS (La Nasa et al., 2019). Indeed, with this analytical technique, organic pigments generally do not interfere with the identification of the binding medium (Bart, 2001), a problem that has been mentioned for Raman analysis, which is only able to analyse the surface of a microplastic (MP) particle (Hermabessiere et al., 2018).

However, depending on the chemical nature of the additive, certain OPAs can be complex to analyse and can be hard to mobilize (Riess et al., 2000; Yanagisawa et al., 2018). To detect these additives, there are two solutions for improving their volatility: (1) a derivatization step, usually involving the use of TMAH, which is toxic for the environment and human health, (2) higher pyrolysis temperatures (>500°C), with the inconvenience of having a complicated chromatogram with overlapping peaks from the additives and the degraded polymeric matrix, especially since it has been shown that the polymeric matrix can have affect the thermal desorption and, thus, the identification of the additive (Bart, 2001).

Py-GC/MS analysis is nonetheless rapid, precise and sensitive, and can be used on various types of sample e.g. liquid or solid. Moreover, this is a powerful method for characterizing the complete composition of a polymeric material using a minimum amount of sample (10-100µg) allowing sampling without damaging the studied sample (La Nasa et al., 2020). These features make Py-GC/MS one of the only characterization methods that can be used for small amounts of material, especially in light of the fact that certain additives are present in low concentration in polymeric matrices. Quantifying the amount of additives included in a polymeric matrix sample turns out to be complicated. Few studies have managed to attain an adequate quantification or semi-quantification of additives, and excessive LOD and LOQ values prevent Py-GC/MS from being used for quantitative applications (Teuten et al., 2009).

3. Analytical methods for the analysis of plastic additives using multi-shot Py-GC/MS

Py-GC/MS has been used to identify and sometimes semi-quantify plastic additives in polymeric matrices. In this section, we discuss the different steps involved in sample preparation before analysis and the importance of the various parameters in a Py-GC/MS method for adequate identification of the additives according to their chemical family.

3.1. Sample preparation for the analysis of additives in plastics using pyrolysis

3.1.1. Sample weight and sizes

Depending on the studies, the mass of analysed sample vary. Most often, the amounts of polymers analysed in studies on plastic additives and polymer determination using Py-GC/MS range from 100 to 200 µg (Randle et al., 2013) or from 500 to 1000 µg (Fries et al., 2013; IEC, 2017; Kim et al., 2016; Yanagisawa et al., 2018; Yanagisawa et al., 2019; Yuzawa et al., 2003). Despite the limit of saturation of the analytical device, which depends on the targeted compound and the complexity of the matrix, there is no real minimum or maximum sample size limitation. The maximum size of plastic particles that can be analysed is determined by the diameter of the TD tubes (Fries et al., 2013) that vary from one device to another. Dekiff et al. (2014) estimated the minimum particle size required for pyrolysis at approximately 100 µm, because smaller particles are difficult to handle. However, Hermabessiere et al. (2018) proposed a lower size limit of 50µm for the analysis of plastic using Py-GC/MS. Moreover, although pyrolysis is able to analyse a small amount of sample, the detection of the whole additive content may be difficult due to the low proportion of certain additives in plastics.

Therefore, most of the time, a relatively large quantity of sample is required to identify the additives and detect a signal. In the study of Riess et al. (2000), the best results were obtained by pyrolysing 1.8 ± 0.1 mg of a sample in triplicate to test the reproducibility of the results. The RSD for the peak areas of the flame-retardants were between 2.1% for tribromobisphenol A and 20.6% for tetrabromobisphenol A (TBBPA). Even though a high RSD value of 20% is tolerated, this higher value was attributed to potential heterogeneities in the sample, due to small variations in the size or shape of the polymer. As mentioned above, this is one of the limitations in pyrolysis experiments (cf. Section 2.4) where the thermal desorption of plastic additives is influenced by the sample geometry (Bart, 2001).

3.1.2. Sample introduction methods

Prior the introduction into the pyrolysis device, the sample is cut, crushed and/or (cryo)-grind to improve its homogeneity. Then, the desired amount of sample is weighted using an analytical precision balance before analysis (Kim et al., 2016; Yuzawa et al., 2008). Two types of method have been distinguished in the literature and are described below:

(1) A "direct method", which is the analysis of a solid plastic sample that is weighed and directly introduced into the pyrolyser to thermally extract additives from the polymer (IEC, 2017; Randle et al., 2013). An approximate amount of deactivated quartz wool can be placed above the sample to avoid any loss of the sample. The sample can also be placed between two pieces of quartz wool to reduce the amount of material leaving the sampling tube during pyrolysis (Kudo et al., 2019; Tsuge et al., 2011).

(2) An "indirect method", which consists in analysing a dissolved sample. A certain amount of an appropriate solvent is added to the ground polymeric sample. After complete dissolution of the powder, a known volume, 10 or 20 µL, of the sample solution is added to a sample cup (Randle et al., 2013). However, the use of a solvent can add interference and cause contamination.

Randle et al. (2013) compared the analytical efficiency and precision of theses two methods. One of the advantages of the "indirect" method is the homogeneity of the aliquot, whereas the "direct" method is a random sampling of particles, which can cause sample-to-sample reproducibility problems. Considering that most additives are not chemically bound to the polymer, the concentration of additives may not be homogeneously distributed in the polymer matrix, resulting in potential high variability in additive concentration across matrices, e.g. the study on Irgafos® 168 analysis (Hermabessiere et al., 2020). Thus, the measurement accuracy depends on multiple factors: the homogeneity of the sample and the precision of the equipment (e.g. analytical balance, syringe) used to transfer the sample into the pyrolysis cups. Therefore, the analysis of a weighed amount of sample will not affect identification efficiency, but can cause some bias in precision, especially for quantification purposes (Riess et al., 2000).

3.1.3. Calibration curves

To ensure efficient pyrolysis for quantification purposes, calibration must be carried out with different concentrations of additive standards (Bart, 2001). According to various studies, several techniques have been employed to establish standard samples for the calibration curves in Py-GC/MS. They are presented below, by growing levels of implementation difficulty:

○ The "Pyrolysis cup spiking": the direct analysis of different concentrations of a liquid solution of additive standards directly injected in a pyrolysis sample cup. This method was used in two studies of Yanaguisawa et al., (2018; 2019) as the first step to develop a Py-GC/MS method. A standard solution mix containing all the targeted compounds (five phthalates and five flame retardants) was prepared at a concentration of 100 µg/mL in toluene and 5.0 µL of this standard solution was directly injected into a pyrolysis sample cup for the Py-GC/MS analysis. Then, different concentration levels (0, 250, 500, 750 and 1000 mg/kg) were prepared and analysed using this Py-GC/MS method. The obtained calibration curve was quite satisfactory, with an R^2 value greater than 0.996.

○ The "Quartz-wool spiking": introduction of some additive-free and inert quartz wool into the pyrolysis cup and spiking the wool with a liquid solution of additive standards. In an attempt to obtain a calibration curve using pyrolysis, some studies have spiked a 3mm diameter piece of quartz wool, pre-cleaned with hexane, with the additive(s) of interest or a mixture of a standard solution (Fries et al., 2013). The sample was then analysed using Py-GC/MS to extract and determine the standards spiked on the quartz wool.

The efficiency of these two techniques have not yet been compared in a single study; however, the presence of quartz wool likely increases the retention of the compounds to enhance their identification. These two methods do not include the polymeric matrix in the preparation of the samples for the calibration curves. If a few microliters of the standard solution is directly injected into a pyrolysis sample cup, the precision and the reproducibility for the additives may be poor, at least for the most volatile additive. Indeed, losses caused by evaporation can be significant, especially because they are spread out on the cup surface in a thin layer (Randle et al., 2013).

The application of a TD step with Py-GC/MS using these methods can be problematic for the accurate determination of some compounds. Semi-volatile compounds with high vapour pressure can evaporate during the sample preparation procedure and the waiting time before analysis (Hosaka et al., 2015; La Nasa et al., 2021). Hosaka et al. (2015) compared the TD analysis of a mixture of 10 phthalates in two conditions: immediate measurement after adding the phthalate stock solution to the pyrolysis sample cup, and the analysis of the solution after different waiting times (0, 50, 100, 150 and 200 min) at 25°C. As expected, peak areas of the most volatile phthalates (DMP and DEP) significantly decreased with increasing waiting time, to reach a reduction of 90 and 50%, respectively, at 200 min. On the other hand, the abundance of the eight other phthalates, less volatile with a lower vapour pressure, did not show any decrease. These results indicate that, using conventional sample cup spiking, it can be difficult to obtain a satisfactory calibration curve for the quantitative analysis of the most volatile compounds with high vapour pressure, due to their evaporation prior to analysis during the waiting time. Spiking the solution of additives on a polymeric matrix, using a pre-coated sample cup, i.e. coated with a thin layer of polymer, or polymeric certified reference materials (CRMs), can help prevent this evaporation.

Hosaka et al. (2015) was the first to use a pre-coated sample cup, in which a few microliters of the additive standards was added to the pyrolysis cup. The coating acts as a sorbent for the most volatile compounds and likely suppresses or at least reduces their rapid volatilization from the sample cup, especially for quantitative analysis (Hosaka et al., 2015; Kim et al., 2017). This reduction of emission was explained by the potential rapid diffusion of the additive mixture into the coated polymer film. In these two studies, the inner surface of a deactivated stainless steel cup was coated with a thin layer of PVC (10 to 20 µm with 0.5 and 1 mg of the polymer). In Hosaka et al. (2015) study, the results showed that the peak intensity for all the phthalates, even the one with high vapour pressure, are comparable for waiting times of 0 and 200 min. This result suggests that using a PVC-coated sample pyrolysis cup is an efficient way to reduce the volatilization of compounds. Moreover, this technique shows a great reproducibility with RSD values lower than 3%. Hosaka et al. (2015) also tested PS and poly(methyl methacrylate) (PMMA) as polymer coating that also showed great results in reducing the emission of semi-volatile phthalates. However, when heating polymers at high temperatures, is this case around 320°C, degradation products of the polymers may interfere with the measurement of the additives studied. Naphthalene, biphenyl and hydrogen chloride appeared in the chromatogram of PVC coated sample cup, styrene dimers and trimers peaks appeared in the PS coated cup and MMA dimers and trimers appeared in the PMMA coated sample cup. However, those peaks did not affect the analytical results because they were well separates from the additives peaks and the degradation product of PVC showed shorter retention times. Nonetheless, PVC is known to contain large amount of plasticizers, thus, people have to be careful of the amount of additives already included in the polymers, or, guarantee that the polymers used are additive free.

In addition to limiting the volatilization of additive compounds, adding the additive standards on the matrix also allows to be more representative of what happens during the thermal desorption process. Indeed, some interactions can occur between the different additives and the matrix there are included in. Including a "matrix effect" in the calibration process can help consider these potential interactions as well as the impact of the extraction procedure on the compounds. Bart (2001) advised the use of a mixture of polymers and additives, to compensate for the variations and normalize the signal. As explained in the review of Cuadros-Rodríguez et al. (2007), the matrix effect can be controlled by the "matrix-matched calibration" (MC) technique using a matrix CRM. Matrix CRMs contain different known concentrations of the analytes of interest and the compounds characterizing the polymeric matrix (Cuadros-Rodríguez et al., 2007; Kim et al., 2016; Maruyama et al., 2015). CRMs are recommended for calibration and sensitivity assessment of the instrument to ensure efficient analysis (Maruyama et al., 2015). RMs are also useful for comparing and verifying the recovery efficiency of the analytical method. Indeed, considering that an additive may react with degradation products or other additives present in the tested polymer, the quantitative method must also be verified before it can be accepted as a suitable approach and applied to unknown or environmental samples. Finding appropriate test samples is crucial for this verification procedure. Nonetheless, appropriate test samples are difficult to find. In addition, not all reference standards are commercially available for all polymers or plastic additives, nor for the simultaneous determination of multiple additives (Derenne and Quénéa, 2015). A few studies have mentioned this problem and propose using in-house RMs to overcome this issue. These RMs can be prepared in the laboratory as alternatives to CRMs by adding a pure or a mixed standard solution of additives to an additive-free polymeric matrix (Cuadros-Rodríguez et al., 2007; Kim et al., 2017) or polymer solution (Yanagisawa et al., 2019). They are called "in-house RMs". Two types of in-house RM approach have been differentiated:

(1) Spiking a virgin solid polymeric matrix with an additive standard solution (Randle et al., 2013). For this purpose, a weighed amount of additive-free polymer samples is placed in a pyrolysis sample cup and mixed with a known volume of the additive stock solution (Becerra and Odermatt, 2012; Odermatt et al., 2003). For example, Kim et al. (2017) added 0.1% of additives (according to the regulated concentration).

(2) Spiking a polymeric solution with an additive standard solution (IEC, 2017; Yanagisawa et al., 2019). To assure a homogeneous sample, the polymer particles are weighed and dissolved completely in an appropriate solvent to prevent precipitation. Then, a given volume, from 10 to 20 µL, of a known concentration (50 mg/mL) of the polymer solution and a few µL (ca. 5 µL) of a known concentration of additive standard mixture solution (100 µg/mL) are injected in a pyrolysis sample cup. This mixed solution is dried at room temperature in the sample cup before the TD analysis. Although this method allow a better homogeneity of the sample, using a solvent may introduce biases (i.e. contamination, toxicity for the technician, interference with the targeted molecule(s)) and some polymers are difficult to solubilise.

These matrix-matched calibrations requires a matrix free of target analyte(s). This is not always possible in the case of plastic polymers, as a matter of fact, some additives, e.g. BFRs such as TBBPA, are chemically bound to the polymer. For this reason, it is necessary to use the standard addition method. Standard addition allows quantifying the amount of analyte in any kind of sample, bacause this is the only method in which the results will not be affected by matrix effects (Cuadros-Rodríguez et al., 2007; IEC, 2017). However, this approach requires a lot of routine work analysis since a separate calibration must be made for each sample and each specific polymeric matrix. Standard addition can also integrate the interferences due to system contamination or to the matrix complexity.

3.1.4. Derivatization approach

Several drawbacks are associated with Py-GC/MS including the fact that certain compounds are difficult to analyse with Py-GC/MS. Only pyrolysis products that are GC-operable can be detected. Consequently, the pyrolysis compounds of the most polar or heavy MW products often show peak tailing, long elution times, poor reproducibility, or, in some cases, absence of peaks (Challinor, 1989; Derenne and Quénéa, 2015). The limitation of this analytical chromatographic system can be overcome with a derivatization step. The purpose of this derivatization reaction is to modify the sample to produce a more volatile derivate. It will enable to enhance chromatographic separation and detection results for the compounds that are not suitable for efficient detection, and will also improve the pyrolysis process for qualitative and quantitative analysis (González-Vila et al., 2001; Rial-Otero et al., 2009; Venema and Boom-Van Geest, 1995).

Applying derivatization during pyrolysis provides very beneficial and complementary information. The pyro-derivatization-GC/MS technique can be used to facilitate the detection and identification of small quantities of polar components of polymers and plastic additives. Derivatization allows the conversion of non-volatile or thermally sensitive compounds into relatively more volatile derivatives. The same technique has been adapted and is well established for polymer and additive analysis using Py-GC/MS, extending its capabilities by modifying the TD approach or enhancing the detectability of the molecules (Sobeih et al., 2008).

Challinor (1989) reported the first combined pyrolysis/derivatization of phenolic resins and polyester polymers, and polymer additives, with the addition of a derivative agent: tetramethylammonium hydroxide (TMAH). Different methods of derivatization have been reported such as hydrogenation, silylation, butylation, alkylation and methylation with addition of different derivative agents (Derenne and Quénéa, 2015; Rial-Otero et al., 2009; Sobeih et al., 2008). Methylation is the most common derivatization reaction which is mainly performed with TMAH (Becerra and Odermatt, 2012; Derenne and Quénéa, 2015; Jeknavorian et al., 1998; Manabe et al., 1999; Rial-Otero et al., 2009; Venema and Boom-Van Geest, 1995). However, this reagent needs to be handle with special care due to its potential hazard for the laboratory technician. In addition to its toxicity for the environment, TMAH is categorized as corrosive for the skin and eyes, and toxic for humans.

Derivatization is a simple procedure that consists in adding an excess of the derivatization agent to the sample pyrolysis cups, containing the sample, and to the calibration solution. The rationale behind this procedure lies in the fact that, when the analysis includes a derivatization step, the internal standard should also react in the same way as the analyte (Becerra and Odermatt, 2012). The derivatization process is time-consuming, and adding an exogenous solution runs the risk of adding other additives or impurities to the sample, emphasizing the importance of carrying out controls and blanks, but, in some situations, shows more sensitivity than the conventional technique (Challinor, 1989; Frederiksen et al., 2007). Derivatization has been applied in several studies to improve the analysis of some plastic additives using Py-GC/MS such as some anti-oxidants, e.g. Irganox® 1010 and 1076, Bisphenol A (BPA), Bisphenol S (BPS) (Becerra and Odermatt, 2012; FrontierLab; Manabe et al., 1999) and flame retardants such as PBDEs and TBBPA (Chokwe et al., 2017; Frederiksen et al., 2007). More recently, Fischer and Scholz-Bottcher (2017), demonstrated that thermochemolysis is an excellent analytical tool for identifying and quantifying MPs and their associated additives in environmental samples, at trace levels.

In several studies, some parameters influencing *in situ* methylation with TMAH during pyrolysis have been investigated. Both pyrolysis temperature and amount or concentration of the derivatizing agent, as well as pH value, can affect the chemical nature of the formed products.

The amount of TMAH determines the degree of methylation. After the addition of TMAH in excess, the pH can be adjusted by adding acetic acid for example. However, Venema and Boom-Van Geest (1995) demonstrated that pyrolysis temperature has a less pronounced effect than pH on derivatization efficiency. The role of the solvent is also subject to debate (Challinor, 2001; Venema and Boom-Van Geest, 1995). In general, the solvent of the derivatizing agents, i.e. methanol or water, does not affect the derivatization process and efficiency because the solvent added to the analyte is evaporated slowly before the introduction of the sample into the pyrolysis device. However, in the case of polycondensation polymers, such as polyamides (PA) or poly(ethylene terephthalate) (PET), the solvent effect is significant and strongly influences the methylation of the compounds, affecting the chemical nature of the product formed and, consequently, the pattern of the pyrogram. The use of water as a solvent for TMAH increases hydrolysis degradation mechanisms and creates different by-products, such as tetramethyl ammonium salt, which have to be pyrolysed at high inlet temperatures to form the corresponding methyl esters. However, in the case of methanol, TMAH behaves like a transesterification catalyst, resulting in the direct formation of methyl esters, even if the hydrolysis reaction is expected to be the most likely mechanism (Venema and Boom-Van Geest, 1995). Pyrolysis temperature may influence the success of the pyrolysis-derivatization process. Venema and Boom-Van Geest (1995) reported that there are more impurities, originating from the derivatizing reagent, i.e. TMAH, at temperatures above 500°C. The thermochemolysis process is very sensitive to the matrix effects of the studied polymer. Due to the complex chemistry related to different functional groups, and to the diverse parameters influencing detection and separation, the observed data need to be interpreted very carefully (Venema and Boom-Van Geest, 1995).

3.2. Multi-shot Py-GC/MS methods for the analysis of OPAs

Several pyrolysis methods have been developed for the identification and quantification of OPAs contained in a polymeric matrix (Table 4A and 4B). In the various studies on the analysis of plastic additives, two different approaches have been used. However, there is no established standard protocol to identify and quantify these compounds.

The majority of the first methods for the analysis of plastic additives were developed at high pyrolysis temperatures on different types of additives: antioxidants and light stabilizers at 770°C and 800°C respectively (Perlstein and Orme, 1985; Roberson and Patonay, 1990), BFRs at 950°C (Wang, 2000a), nonylphenols (NPs) and nonylphenol ethoxylates (NPEs) at 650°C (Sitholé and Pimentel, 2009). In these cases, the additives were identified by analysing the characteristic fragments that were produced during flash pyrolysis. Unfortunately, although these methods can successfully identify the targeted molecules in polymeric matrices, fragmentation at such high temperatures produces too many peaks for an easy and efficient detection in full scan detection mode. The polymer matrix is also broken down into monomers, oligomers, and other fragments. Thus, without preliminary work on finding indicator and specific ion(s) for the targeted molecule, it may be difficult to distinguish between fragments coming from the polymers or from the additive. Moreover, most of these studies did not directly analyse the sample, but included an SE step prior to pyrolysis.

These studies led to a second approach to identify plastic additives: multi-shot pyrolysis with a TD step during the first shot of pyrolysis. During this initial TD step, the polymer is heated at low temperatures (<500°C) to desorb the volatile compounds (e.g. OPAs) usually found in polymers, without degrading the plastics. Most of the time, a temperature around 300°C or 350°C is chosen (Table 4B). Heating the sample at low temperatures helps avoiding the breakdown of the polymeric matrix, leading exclusively to the desorption of the additives, making identification easier. Indeed, the additives are usually detected at temperatures below the decomposition temperature of the polymer (Bart, 2001). The various studies using this thermal extraction method have observed that, at such temperatures, the polymers do not decompose and no polymer markers are detected in the chromatogram. Moreover, no measurable effects have been reported on the accuracy of the further plastic identification and quantification (Okoffo et al., 2020). In their study of fast identification of polymer additives using Py-GC/MS, (Herrera et al., 2003), used SIM to monitor the appearance of certain ions of known m/z, such as m/z 149 and 205, which are characteristic of phthalate ester plasticizers and the antioxidant butylated hydroxytoluene (BHT) (PubChem CID: 31404). These two ions were found in the TD chromatogram after a heating at 300°C during the first thermal step, but not in the pyrogram after a heating at 500°C. This indicates that these ions arose from additives that were fully removed during the first step. Twenty years prior, the same observation was reported: a 1983 study (Lichtenstein and Quellmalz, 1983), on the analysis of the antioxidant BHT in butadiene/styrene copolymer using curie-point Py-GC/MS showed a better identification of the additive at a pyrolysis temperature of 300°C. At this temperature, the chromatogram revealed a unique peak with a high abundance, corresponding to BHT. In contrast, at 500°C the identification of the targeted molecule was complicated, abundance was low, and the peak was overshadowed with the multiple peaks of the polymer fragments. Furthermore, the complexity of pyrograms increases at higher pyrolysis temperatures (Terán et al., 2009).

Although this technique shows variable efficiency and some limitations, according to the type of additive studied, multi-shot Py-GC/MS has been used — and is used — more and more frequently for the identification and even the semi-quantification of plastic additives (ASTM-7823:14, 2014; Fries et al., 2013; Hashimoto et al., 2001; Hermabessiere et al., 2020; Herrera et al., 2003; IEC, 2017; Kang et al., 2005; Kim et al., 2016; La Nasa et al., 2021; Liu et al., 2008; Okoffo et al., 2020; Terán et al., 2009; Yuzawa et al., 2009). As mentioned above, several parameters can be modified according to the type of compounds that need to be analysed and the polymer sample (e.g. pyrolysis temperature, pyrolysis duration, ion source temperature, injection temperature, transfer line temperature, oven GC temperature, CIS, split ratio, carrier gas, acquisition mode (full scan (FS) or SIM)).

3.2.1. The importance of pyrolysis temperature

The pyrolyser thermal program is one of the main factors for a successful extraction using Py-GC/MS (Kim et al., 2016). The pyrolysis temperature, along with other factors such as the type of additive, their molecular weight, their concentration and the type of polymer they are included in, affect the result of pyrolysis extraction and thus GC/MS detection. To select pyrolysis temperature, a compromise must be made between the mobilization of the undestroyed additive along with characteristic pyrolysis products and the ease of interpretation of pyrograms (Riess et al., 2000).

The level of fragmentation is crucial for the identification of an additive in a polymer. The degree of fragmentation depends on the temperature selected for pyrolysis (Bart, 2001). A distinction can be made between the volatile and semi-volatile compounds present in a polymer by adjusting the temperature of the analysis, or by applying two or several progressive temperature runs to the sample before flash pyrolysis. A mild pyrolysis temperature e.g. around 250°C, can desorb the most volatile constituents, for example the most volatile phthalates DMP and DEP, with MWs of 194 g/mol and 298 g/mol and vapour pressures of 2.63×10^{-1} and 6.48×10^{-2} Pa, respectively (Hosaka et al., 2015). In addition, minor fragmentation of the additives is expected and more structural information on the original molecule is acquired. At higher temperatures, but still below pyrolysis temperatures, e.g. between 300°C to 450°C, larger molecules, such as many antioxidants, larger plasticizers (DBP, BBP, DEHP, DNOP), and flame retardants are revealed (Jansson et al., 2007). However, at too high temperatures, many different decomposition products are formed, the polymer starts to degrade into oligomers, and the excess of such polymer fragments severely interfere with the identification of characteristic additive fragments and may complicate the interpretation of the results (Bart, 2001).

The concentration of the additive in the polymer affects its detection with Py-GC/MS. At a low temperature, only the component present at high concentrations will show a clear peak in the pyrogram, provided that it is volatile. For example, in Riess et al. (2000) study, at the lowest tested temperature (315°C), only octabromodiphenyl oxide, which is one of the main components present in the flame retardant commercial mixture, was identified. For compounds with low volatility or low concentration in the polymer, or, as mentioned above, with a relatively high molecular mass, no or only low concentrations are mobilized at low temperatures.

3.2.2. The influence of the type of molecule on the selection of an appropriate pyrolysis temperature

Certain additives, in general flame retardants, many antioxidants and light stabilizers show higher retention times than the other additives. This is related to their polarity, their high MW and relatively high thermal stability (Bart, 2001; Riess et al., 2000). Because these macromolecules are not or only slightly volatile, they must be pyrolysed at higher temperatures and, sometimes, according to the decomposition temperature of the polymer, along with the polymer matrix. Hosaka et al. (2005) study demonstrated the influence of pyrolysis temperature on additive extraction and on the signal intensity of a low volatile compound such as decaBDE. This study showed that this flame retardant is thermally stable at temperatures between 300°C and 370°C, the peak intensities are almost constant, but decompose at temperatures above 380°C. Therefore, they set the optimum temperature at 320°C. This mild temperature is suitable for various other additives. For example, the same temperature was chosen by Randle et al. (2013) for the analysis of plasticizers (phthalates, diisononyl hexahydrophthalate (DINCH) (PubChem CID: 11524680) and di-octyl adipate (DOA) (PubChem CID: 31271)) and prescribed by the American Society for Testing and Materials ASTM-7823:14 (2014) in their method for determination of low-level, regulated phthalates in PVC plastics using Py-GC/MS. Moreover, at 320ºC, the polymer is not decomposed nor analysed and remains in the sample cup. Yanagisawa et al. (2018) tested pyrolysis heating temperatures of up to 340°C on different materials, such as short-chain chlorinated paraffins (SCCPs), decaBDE, hexabromocyclododecane (HBCD) (PubChem CID: 15724678), and the plasticizer DEHP. They noted that temperatures between 300°C and 350°C were suitable to ensure a sufficient MS peak area for decaBDE, i.e. the less volatile compound, and did not create any adverse effect on the other analytes.

The 300-350°C temperature range seems to be the most relevant range, because the majority of studies use this range of temperature (Table 4A and 4B).

3.2.3. The influence of polymer type

It is important to consider the nature of the polymer in which the analyses are carried out. A pyrolysis temperature solely based on the nature of the additives may not be optimal. Some polymers are more thermally labile than others. Polystyrene (PS) and PVC start to decompose at relatively low temperatures, contrary to PE and PP (Bart, 2001). For example, for the analysis of decaBDE in PS, Yuzawa et al. (2008) showed that PS starts to pyrolyse around 300°C with maximum pyrolysis when the temperature reaches 340°C. At this temperature, the simultaneous pyrolysis of PS along with the desorption of the additive can cause contamination of the column with styrenic compounds, especially if repeated measurements for the same sample are done. Therefore, to avoid contamination, the highest pyrolysis temperature to analyse deBDE in a PS sample matrix, was set to 340˚C. This temperature allowed them to reach a TD recovery rate around 60% for decaBDE and the rest of the molecule remained in the residual PS in the pyrolysis sample cup.

Despite this knowledge and experimentation, it is still complicated to analyse plastic additives using a global and standardized method, especially for complex matrices like plastics. Analysing plastic additives using Py-GC/MS has certain limitations. In particular, the simultaneous screening of different additives is often performed using constant conditions that are not necessarily optimized for the quantification of each individual substance and all polymeric matrices. Several studies have published screening methods for certain restricted phthalates (Fries et al., 2013; IEC, 2017; Kim et al., 2016; Kudo et al., 2019; Maruyama et al., 2015; Yuzawa et al., 2009). However, to the best of our knowledge, for the diversity of plastic additives that are used in plastic goods, only one study (Yanagisawa et al., 2019) has implemented a screening technique using double-shot Py-GC/MS for various harmful additives, e.g. plasticizers and flame retardants, in different polymeric materials. Although this study made remarkable progress toward the use of Py-GC/MS for the screening of plastic additives, the efficiency of this polyvalent method is not equivalent for all analysed additives.

4. Conclusion

Pyrolysis-GC/MS is a good method with the major advantage of being able to rapidly analyse a single sample to determine the organic plastic additives and polymer type successively using different temperatures conditions: sub-pyrolysis for the thermal desorption of OPAs and higher pyrolysis temperatures for the characterization of polymers. Another advantage, in comparison with traditional chemical techniques, is that no extensive sample preparation is required, thereby minimizing sample preparation steps and limiting potential background contamination. Thus, multi-shot pyrolysis-GC/MS provides a fast and reliable procedure to characterize both volatile additives and polymers in the same sample. Due to the great variety of polymer types and additives, the identification can be complicated by the superimposed and overlapping characteristic peaks of the additives themselves or from the degraded polymer. All of which can interfere with the separation and the identification of the targeted compounds. Additionally, considering that more and more of these additives are regulated, developing a fast identification method for all compounds and extending the scope of screening has become a challenge.

The results from different studies suggest that major additives present in various polymeric materials can be determined simultaneously using Py-GC/MS. Depending on the purpose of the studies and the type of analysed additive, different types of devices can be set up. They include multi-step pyrolysis temperature separations, or the derivatization of certain products to overcome some limitations that can be encountered, especially for the detection of polar or high molecular weight molecules.

Qualitative and quantitative analysis require a rigorous approach to ensure instrumental and sampling repeatability. The majority of Py-GC/MS analyses on OPAs are qualitative. Although semi-quantitative analyses are possible, it remains difficult to obtain suitable quantitative data from pyrolysis studies, and this constitutes one of the major drawbacks of Py-GC/MS, particularly in light of the fact that polymer additives can be present in low concentrations. Mass detectors are sufficiently sensitive to detect plastic additive pyrolysate compounds and selecting ions with a SIM mode can simplify the identification of the compounds, thereby improving the sensitivity and lowering the limits of detection. It is recommended that each sample should be measured, if feasible, using the full-scan mode together with the SIM mode, especially for the analysis of trace additives. However, future work needs to focus on the improvement of this method for sensitive quantitative analysis that will lead to a robust, standardized analytical procedure for compounds present at low levels.

5. Acknowledgments

The authors are very grateful to the Hauts-de-France Regional Council and ANSES (French Agency for Food, Environmental and Occupational Health & Safety) for financially supporting Fleurine Akoueson's PhD scholarship. This work was also funded by the European Union (ERDF), the French government, the Hauts-de-France Regional Council and IFREMER, in the framework of the CPER MARCO project (2015-2020).

6. Authors contribution

Fleurine Akoueson: Conceptualization, data curation, investigation, methodology, writing - original draft, writing - review & editing**. Chaza Chbib:** Conceptualization, investigation, methodology, writing - review & editing**. Sébastien Monchy, Ika Paul-Pont & Périne Doyen:** Writing - review & editing**. Alexandre Dehaut & Guillaume Duflos:** Conceptualization, funding acquisition, methodology, project administration, supervision, writing - review & editing.

7. References

ASTM-7823:14. American society for testing material D7823:14, Standard Test Method for Determination of Low Level,Regulated Phthalates in Poly (Vinyl Chloride) Plastics by ThermalDesorption-Gas Chromatography/Mass Spectrometry. ASTM International, West Conshohocken, PA, 2014.

Bart JCJ. Polymer/additive analysis by flash pyrolysis techniques. Journal of Analytical and Applied Pyrolysis 2001; 58-59: 3-28.

Becerra V, Odermatt J. Detection and quantification of traces of bisphenol A and bisphenol S in paper samples using analytical pyrolysis-GC/MS. Analyst 2012; 137: 2250-9.

Challinor JM. A pyrolysis-derivatisation-gas chromatography technique for the structural elucidation of some synthetic polymers. Journal of Analytical and Applied Pyrolysis 1989; 16: 323-333.

Challinor JM. Review: the development and applications of thermally assisted hydrolysis and methylation reactions. Journal of Analytical and Applied Pyrolysis 2001; 61: 3-34.

Chokwe TB, Okonkwo JO, Nwamadi MS. Occurrence and distribution of tetrabromobisphenol A and its derivative in river sediments from Vaal River Catchment, South Africa. Emerging Contaminants 2017; 3: 121-126.

Cuadros-Rodríguez L, Bagur-González MG, Sánchez-Viñas M, González-Casado A, Gómez-Sáez AM. Principles of analytical calibration/quantification for the separation sciences. Journal of Chromatography A 2007; 1158: 33-46.

Dekiff JH, Remy D, Klasmeier J, Fries E. Occurrence and spatial distribution of microplastics in sediments from Norderney. Environ Pollut 2014; 186: 248-56.

Derenne S, Quénéa K. Analytical pyrolysis as a tool to probe soil organic matter. Journal of Analytical and Applied Pyrolysis 2015; 111: 108-120.

ECHA Eca-. Mapping exercise - Plastic additives initiative. 2020, 2019.

Fischer M, Scholz-Bottcher BM. Simultaneous Trace Identification and Quantification of Common Types of Microplastics in Environmental Samples by Pyrolysis-Gas Chromatography-Mass Spectrometry. Environ Sci Technol 2017; 51: 5052-5060.

Frederiksen M, Vorkamp K, Bossi R, Rigét F, Dam M, Svensmark B. Method development for simultaneous analysis of HBCD, TBBPA, and dimethyl-TBBPA in marine biota from Greenland and the Faroe Islands. International Journal of Environmental Analytical Chemistry 2007; 87: 1095-1109.

Fries E, Dekiff JH, Willmeyer J, Nuelle M-T, Ebert M, Remy D. Identification of polymer types and additives in marine microplastic particles using pyrolysis-GC/MS and scanning electron microscopy. Environmental Science. Processes & Impacts 2013; 15: 1949-1956.

FrontierLab. Multi-functional Pyrolyzer® Technical Note PYA1-081E- Determination of antioxidants (Irganox 1076 and Irganox 1010) in polyethylene using thermal desorption and reactive pyrolysis. Frontier Lab, pp. 2.

González-Vila FJ, Amblès A, del Río JC, L G. Characterisation and differentiation of kerogens by pyrolytic and chemical degradation techniques. Journal of Analytical and Applied Pyrolysis 2001; 58-59: 315-328.

Hahladakis JN, Velis CA, Weber R, Iacovidou E, Purnell P. An overview of chemical additives present in plastics: Migration, release, fate and environmental impact during their use, disposal and recycling. J Hazard Mater 2018; 344: 179-199.

Hashimoto K, Urakami K, Fujiwara Y, Terada S, Watanabe C. Determination of residual solvents in pharmaceuticals by thermal desorption-GC/MS. Anal Sci 2001; 17: 645-8.

Hermabessiere L, Himber C, Boricaud B, Kazour M, Amara R, Cassone AL, et al. Optimization, performance, and application of a pyrolysis-GC/MS method for the identification of microplastics. Anal Bioanal Chem 2018; 410: 6663-6676.

Hermabessiere L, Receveur J, Himber C, Mazurais D, Huvet A, Lagarde F, et al. An Irgafos(R) 168 story: When the ubiquity of an additive prevents studying its leaching from plastics. Sci Total Environ 2020; 749: 141651.

Herrera M, Matuschek G, Kettrup A. Fast identification of polymer additives by pyrolysis-gas chromatography/mass spectrometry. Journal of Analytical and Applied Pyrolysis 2003; 70: 35-42.

Hosaka A, Watanabe A, Watanabe C, Teramae N, Ohtani H. Polymer-coated sample cup for quantitative analysis of semi-volatile phthalates in polymeric materials by thermal desorption-gas chromatography-mass spectrometry. J Chromatogr A 2015; 1391: 88-92.

Hosaka A, Watanabe C, Tsuge S. Rapid Determination of Decabromodiphenyl Ether in Polystyrene by Thermal Desorption-GC/MS. Analytical Sciences 2005; 21: 1145-1147.

IEC IEC-. IEC 62321-8 - Determination of certain substances in electrotechnical products - Part 8: Phthalates in polymers by gas chromatography-mass spectrometry (GC-MS), gas chromatographymass spectrometry using a pyrolyzer/thermal desorption accessory (Py/TD-GC-MS). 2017.

Jansson KD, Zawodny CP, Wampler TP. Determination of polymer additives using analytical pyrolysis. Journal of Analytical and Applied Pyrolysis 2007; 79: 353-361.

Jeknavorian AA, Mabud MA, Barry EF, Litzau JJ. Novel pyrolysis-gas chromatography/mass spectrometric techniques for the characterization of chemical additives in portland cement and concrete. Journal of Analytical and Applied Pyrolysis 1998; 46: 85-100.

Kang Y, Den W, Bai H, Ko F-H. Direct quantitative analysis of phthalate esters as micro-contaminants in cleanroom air and wafer surfaces by auto-thermal desorption–gas chromatography–mass spectrometry. Journal of Chromatography A 2005; 1070: 137-145.

Kim JW, Kim YM, Moon HM, Hosaka A, Watanabe C, Teramae N, et al. Comparative study of thermal desorption and solvent extraction-gas chromatography-mass spectrometric analysis for the quantification of phthalates in polymers. J Chromatogr A 2016; 1451: 33-40.

Kim YM, Kim JW, Moon HM, Lee MJ, Hosaka A, Watanabe A, et al. Rapid Quantification of N-Methyl-2-pyrrolidone in Polymer Matrices by Thermal Desorption-GC/MS. Anal Sci 2017; 33: 821-824.

Kleine-Benne E, Rose B. Versatile Automated Pyrolysis GC Combining a Filament Type Pyrolyzer with a Thermal Desorption Unit. Gerstel Application Note 4/2011. 2020. Gerstel Application Note, 2011, pp. 10.

Kudo Y, Obayashi K, Yanagisawa H, Maruyama F, Fujimaki S, Miyagawa H, et al. Development of a screening method for phthalate esters in polymers using a quantitative database in combination with pyrolyzer/thermal desorption gas chromatography mass spectrometry. Journal of Chromatography A 2019; 1602: 441-449.

La Nasa J, Biale G, Ferriani B, Colombini MP, Modugno F. A pyrolysis approach for characterizing and assessing degradation of polyurethane foam in cultural heritage objects. Journal of Analytical and Applied Pyrolysis 2018; 134: 562-572.

La Nasa J, Biale G, Ferriani B, Trevisan R, Colombini MP, Modugno F. Plastics in Heritage Science: Analytical Pyrolysis Techniques Applied to Objects of Design. Molecules 2020; 25.

La Nasa J, Biale G, Mattonai M, Modugno F. Microwave-assisted solvent extraction and double-shot analytical pyrolysis for the quali-quantitation of plasticizers and microplastics in beach sand samples. J Hazard Mater 2021; 401: 123287.
La Nasa J, Biale G, Sabatini F, Degano I, Colombini MP, Modugno F. Synthetic materials in art: a new comprehensive approach for the characterization of multi-material artworks by analytical pyrolysis. Heritage Science 2019; 7.
Lichtenstein N, Quellmalz K. Analyse von 2,6-Di-tert.butyl-p-kresol in Butadien/Styrol-Copolymeren durch Curie-Punkt-Pyrolyse/GC/MS. Fresenius' Zeitschrift für Analytische Chemie 1983; 316: 268-270.
Liu HC, Den W, Chan SF, Kin KT. Analysis of trace contamination of phthalate esters in ultrapure water using a modified solid-phase extraction procedure and automated thermal desorption-gas chromatography/mass spectrometry. J Chromatogr A 2008; 1188: 286-94.
Llana-Ruiz-Cabello M, Pichardo S, Jimenez-Morillo NT, Gonzalez-Vila FJ, Guillamon E, Bermudez JM, et al. Pyrolysis-gas chromatography-isotope ratio mass spectrometry for monitoring natural additives in polylactic acid active food packages. J Chromatogr A 2017; 1525: 145-151.
Manabe N, Toyoda T, Yokota Y. Determination of a hindered phenol-type antioxidant by pyrolysis-GC/MS in the presence of tetramethyl ammonium hydroxide. Bunseki kagaku 1999; 48: 449-456.
Maruyama F, Fujimaki S, Sakamoto Y, Kudo Y, Miyagawa H. Screening of phthalates in polymer materials by pyrolysis GC/MS. Anal Sci 2015; 31: 3-5.
Net S, Delmont A, Sempéré R, Paluselli A, Ouddane B. Reliable quantification of phthalates in environmental matrices (air, water, sludge, sediment and soil): A review. Science of The Total Environment 2015; 515-516: 162-180.
Odermatt J, Meier D, Leicht K, Meyer R, Runge T. Approaches to applying internal standards for the quantification of paper additives by Py-GC/MSD. Journal of Analytical and Applied Pyrolysis 2003; 68-69: 269-285.
Okoffo ED, Ribeiro F, O'Brien JW, O'Brien S, Tscharke BJ, Gallen M, et al. Identification and quantification of selected plastics in biosolids by pressurized liquid extraction combined with double-shot pyrolysis gas chromatography–mass spectrometry. Science of The Total Environment 2020; 715: 136924.
Perlstein P, Orme P. Determination of polymeric hindered-amine light stabilisers in plastics by pyrolysis—gas chromatography. Journal of Chromatography A 1985; 325: 87-93.
Quénéa K, Derenne S, González-Vila FJ, González-Pérez JA, Mariotti A, Largeau C. Double-shot pyrolysis of the non hydrolysable organic fraction isolated from a sandy forest soil (Landes de Gascogne, South-West France). Journal of Analytical and Applied Pyrolysis 2006; 76: 271-279.
Randle D, Freeman R, Hosaka A, Watanabe C. A fast, easy and “green” thermal desorption-GC/MS method for the analysis of phthalate esters in PVC. Gulf Coast Conference

October 16, 2013, Gulf Coast, 2013.
Rial-Otero R, Galesio M, Capelo J-L, Simal-Gándara J. A Review of Synthetic Polymer Characterization by Pyrolysis–GC–MS. Chromatographia 2009; 70: 339-348.
Riess M, Thoma H, Vierle O, van Eldik R. Identification of flame retardants in polymers using curie point pyrolysis-gas chromatography/mass spectrometry. J. Anal. Appl. Pyrolysis 2000: 14.
Rios Mendoza LM, Taniguchi S, Karapanagioti HK. Advanced Analytical Techniques for Assessing the Chemical Compounds Related to Microplastics. Comprehensive Analytical Chemistry 2017; 75: 209-240.
Roberson MA, Patonay G. <Robertson., 1990 - antiUVs - pyr GCMS - non directe.pdf>. Journal of Chromatography A 1990; 505: 375-384.

Rochman CM. The complex mixture, fate and toxicity of chemicals associated with plastic debris in the marine environment. In: Bergmann M., Gutow L., Klages M. (eds) Marine Anthropogenic Litter. Springer, Cham 2015: 117-140.

Rochman CM, Brookson C, Bikker J, Djuric N, Earn A, Bucci K, et al. Rethinking microplastics as a diverse contaminant suite. Environ Toxicol Chem 2019; 38: 703-711.

Sitholé B, Pimentel EJ. Determination of nonylphenol and nonylphenol ethoxylates in pulp samples by Py-GC/MS. Journal of Analytical and Applied Pyrolysis 2009; 85: 465-469.

Sobeih KL, Baron M, Gonzalez-Rodriguez J. Recent trends and developments in pyrolysis-gas chromatography. J Chromatogr A 2008; 1186: 51-66.

Ter Halle A, Jeanneau L, Martignac M, Jarde E, Pedrono B, Brach L, et al. Nanoplastic in the North Atlantic Subtropical Gyre. Environ Sci Technol 2017; 51: 13689-13697.

Terán A, Gonzalez-Vila FJ, Gonzalez-Perez JA. Detection of organic contamination in sediments by double-shoot pyrolysis–GC/MS. Environmental Chemistry Letters 2009; 7: 301-308.

Teuten EL, Saquing JM, Knappe DR, Barlaz MA, Jonsson S, Bjorn A, et al. Transport and release of chemicals from plastics to the environment and to wildlife. Philos Trans R Soc Lond B Biol Sci 2009; 364: 2027-45.

Trimpin S, Wijerathne K, McEwen CN. Rapid methods of polymer and polymer additives identification: multi-sample solvent-free MALDI, pyrolysis at atmospheric pressure, and atmospheric solids analysis probe mass spectrometry. Anal Chim Acta 2009; 654: 20-5.

Tsuge S, Ohtani H, Watanabe C. Pyrolysis-GC/MS data book of synthetic polymers: Elsevier B.V., Oxford, UK, 2011.

Venema A, Boom-Van Geest RCA. In-situ hydrolysis/methylation pyrolysis CGC for the characterization of polyaramides. Journal of Microcolumn Separations 1995; 7: 337-343.

Wang FC-Y. Polymer additive analysis by pyrolysis–gas chromatography- II. Flame retardants. Journal of Chromatography A 2000a; 886: 225-235.

Wang FC-Y. Polymer additive analysis by pyrolysis–gas chromatography I. Plasticizers. J. Chromatogr. A 2000b: 12.

Yanagisawa H, Kudo Y, Nakagawa K, Miyagawa H, Maruyama F, Fujimaki S. Simultaneous Screening of Major Flame Retardants and Plasticizers in Polymer Materials Using Pyrolyzer/Thermal Desorption Gas Chromatography Mass Spectrometry (Py/TD-GC-MS). Molecules 2018; 23.

Yanagisawa H, Maruyama F, Fujimaki S. Verification of simultaneous screening for major restricted additives in polymer materials using pyrolyzer/thermal desorption gas–chromatography mass spectrometry (Py/TD-GC-MS). Journal of Analytical and Applied Pyrolysis 2019; 137: 37-42.

Yuzawa T, Hosaka A, Watanabe C, Tsuge S. Evaluation of the Thermal Desorption-GC/MS Method for the Determination of Decabromodiphenyl Ether (DeBDE) in Order of a Few Hundred ppm Contained in a Certified Standard Polystyrene Sample. Analytical Sciences 2008; 24: 953-955.

Yuzawa T, Watanabe C, Freeman RR, Tsuge S. Rapid determination of phtalates in plastic toys by a thermal desorption-GC/MS method. Anal Sci 2009; 25: 1057-8.

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.

☐The authors declare the following financial interests/personal relationships which may be considered as potential competing interests:

Table 1: List of plastic additives studied with pyrolysis-GC/MS

Compound	Abbreviation/Other Names	PubChem CID	Polymer studied [a; b]	Ref. [c]
Plasticizers				
Diethyl phthalate	DEP	7282	PE, PS, PP, PA	[1] [3]*
			HDPE, PP, PS	[31]*
			PVA	[32]
Dimethyl phthalate	DMP	8554	PET, PVC, PE, PS, PA	[4]
			HDPE, PP, PS	[31]*
Di(2-etylhexyl)phthalate	DEHP	8343	PE, PS, PP, PA	[1]
			n.a	[2]*
			PE	[3]*
			PET, PVC, PE, PS, PA	[4]
			ABS	[5]
			PE, PVC	[6]*
			PVC	[7]* [8]* [9]
			PS, PVC, ABS, modified PS, cellulose propionate	[10]
			PE, PS, PP, PVC	[11]*
			PET, ABS, PVC, PS	[12]*
			HDPE, PP, PS	[31]*
Butyl benzyl phthalate	BBP	2347	PE, PVC	[6]* [2]*
			PVC	[9]
			PET, ABS, PVC, PS	[7]* [8]* [12]*
			HDPE, PP, PS	[31]*
Diisobutyl phthalate	DIBP	6782	PE, PS, PP, PA	[1]
			n.a	[2]*
			PE	[3]*
			PET, ABS, PVC, PS	[12]*
			PVA	[32]
Di-n-butyl phthalate	DBP	3026	PE, PS, PP, PA	[1]
			n.a	[2]*
			PE	[3]*
			PET, PVC, PE, PS, PA	[4]
			PET, ABS, PVC, PS	[12]*
			HDPE, PP, PS	[31]*
			PVA	[32]
Di(n-octyl) phthalate	DNOP	8346	PVC, PE	[2]*
			PVC	[7]* [8]* [9]
Di-isononyl phthalate	DINP	590836	PVC, PE	[2]*
			PVC	[7]* [8]* [9]

Compound	Abbreviation/Other Names	PubChem CID	Polymer studied [a; b]	Ref. [c]
			HDPE, PP, PS	[31]*
Di-isodecyl phthalate	DIDP	33599	PVC, PE	[2]*
			PVC	[7]* [8]* [9]
			HDPE, PP, PS	[31]*
Hexahydrophtalate de diisononyle	DINCH	11524680	PVC	[8]* [9]
Di-octyl adipate	DOA	31271	PVC	[8]*
			PS, PVC, ABS, modified PS, cellulose propionate	[10]
Acetyl Tributylcitrate	ATBC	6505	PS, PVC, ABS, modified PS, cellulose propionate	[10]
Nonylphenols and nonylphenols ethoxylates	NPs and NPEs	-	ABS	[1] [5] [29]
benzaldehyde	-	-	PE, PS, PP, PA	[1]
Triphenyl phosphate	TPP	8289	PE	[10]
Flames retardants				
Octabromobiphenyl	-	3032840	n.a	[9]
Octabromodipheyl ether	-	6537506	n.a	[9]
Decabromodiphenyl oxide	-	14410	n.a	[9]
gama-Hexabromocyclododecane	γ-HBCD	11377211	n.a	[11]*
Poly bromo diphenyl ethers	PBDEs	-	PE, PS, PP, PVC	[11]*
			PET, ABS, PVC, PS	[12]*
			PS	[13] [14]
tris(2-chloroethyl)phosphate	TCEP	8295	PET, ABS, PVC, PS	[12]*
short chain chlorinated paraffins	SCCPs	-	PET, ABS, PVC, PS	[12]*
Tetrabromobisphenol A	TBBPA	6618	PVC, epoxy coated material	[9] [15]*
			PET, ABS, PVC, PS	[12]*
Flames retardants	-	-	PVC, PC, ABS	[16]
Antioxidants				
Pentaerythritol tetrakis(3-(3,5-di-tert-butyl-4-hydroxyphenyl)propionate	Irganox 1010	64819	PP; PBT	[17]
			gum base (blend of polymers)	[18]
			PE	[19]
			PE, PBT	[22]
Octadecyl 3-(3,5-di-tert-butyl-4-hydroxyphenyl)propionate	Irganox 1076	16386	PE	[19]
			PP, LDPE	[20]*
			PE, PBT	[22]
2-(1,1-dimethylethyl)-6-3-(1,1-dimethylethyl)-2-hydroxy-5-methylphenylmethyl-4-methylphenyl acrylate	Irganox 3052FF	109058	PP	[21]*
1,3,5-tris[(3,5-ditert-butyl-4-hydroxyphenyl)methyl]-1,3,5-triazinane-	Irganox 3114	93115	PP	[21]*

Compound	Abbreviation/Other Names	PubChem CID	Polymer studied $^{a; b}$	Ref. ^{c}
2,4,6-trione			PE, PBT	[22]
3,5-Bis(1,1-dimethylethyl)-4-hydroxybenzenepropanoic acid thiodi-2,1-ethanediyl ester	Irganox 1035	64883	PE, PBT	[22]
Tris(2,4-di-tert-butylphenyl)phosphite	Irgafos 168 = Alkanox 240	91601	PE, PP	[23]*
			gum base (blend of polymers)	[18]
1,2-bis(3,5-di-tert-butyl-4-hydroxyhydrocinnamoyl)hydrazine	Irganox MD1024	61916	PE, PBT	[22]
Hexamethylene bis[3-(3,5-di-tert-butyl-4-hydroxyphenyl)propionate]	Irganox 259	64870	PE, PBT	[22]
Calcium bis(ethyl 3,5-di-tert-butyl-4-hydroxybenzylphosphonate)	Irganox 1425	103255	PE, PBT	[22]
2-(2′-hydroxy-3′,5′-di-t-butyl-phenyl)benzotriazole	Tinuvin 320	77455	polyamide-6	[24]*
			PP	[21]*
bis(1,2,2,6,6-pentamethylpiperidin-4-yl) 2-butyl-2-[(3,5-ditert-butyl-4-hydroxyphenyl)methyl]propanedioate	Tinuvin 144	93348	PP, LDPE	[20]*
Tinuvin 571	Tinuvin 571	135332164	PP	[21]*
4-[2-(4-hydroxy-2,2,6,6-tetramethylpiperidin-1-yl)ethoxy]-4-oxobutanoic acid	Tinuvin 622	54328974	gum base (blend of polymers)	[18]
			PP, LDPE	[20]*
			PP	[25]
bis(2,2,6,6-tetramethylpiperidin-4-yl) decanedioate	Tinuvin 770	164282	PP, LDPE	[20]*
2,2,4,4-tetramethyl-7-oxa-3,20-diazadispiro[5.1.118.26]henicosan-21-one	Hostavin N20	631596	PP, LDPE	[20]*
			PP	[21]*
7-Oxa-3,20-Diazadispiro[5.1.11.2]Heneicosan-21-One,2,2,4,4-Tetramethyl-, Hydrochloride	Hostavin N30	348885796	PP	[21]*
2-[3,3-bis(3-tert-butyl-4-hydroxyphenyl)butanoyloxy]ethyl 3,3-bis(3-tert-butyl-4-hydroxyphenyl)butanoate	Hostanox O3	122891	PP	[21]*
N,N-dioctadecylhydroxylamine	Irgastab FS 042	3507778	Gum base (blend of polymers)	[18]
Butylated hydroxytoluene	BHT	31404	ABS	[5]
			Gum base (blend of polymers)	[18]
			Butadiene/styrene copolymer	[28]
4-tert-butyltoluene	TBT	7390	ABS	[5]
4-tert-octylphenol	4-t-OP	8814	ABS	
2.4-Di-tert-butylphenol	-	7311	PE, PS, PP, PA	[1] [4]
2,6-di-tert-butyl-p-cresol	-	31404	ABS	[26]
propyl benzene	-	7668	ABS	[5]
1,3,5-trimethylbenzene	-	7947	ABS	[5]
N,N'-bis(2,2,6,6-tetramethylpiperidin-4-yl)hexane-1,6-diamine;2,4,6-trichloro-1,3,5-triazine;2,4,4-trimethylpentan-2-amine	Chimassorb 944	83418	PP, LDPE; n.a	[20]* [24]*

Compound	Abbreviation/Other Names	PubChem CID	Polymer studied [a; b]	Ref. [c]
Monomer or intermediate				
Bisphenol A	BPA	6623	n.a	[16] [27]*
Bisphenol S	BPS	6626	n.a	[27]*
Other				
N-methyl-2-pyrrolidone	NMP	13387	PS, PMMA, PVC	[33]

[a] PE: Polyethylene, LDPE: Low density polyethylene, PS: polystyrene, PP polypropylene, PC: polycarbonate; PVC: polyvinyl chloride, PVA: polyvinyl acetate, PA: Polyacrylamide, ABS: Acrylonitrile butadiene styrene, PET: Polyethylene terephthalate, PBT: poly(butylene terephthalate)

[b] n.a: not available

[c] absence of sign = qualitative study; * = semi-quantitative study

[1]: Fries et al. (2013) ; [2]*: IEC (2017) ; [3]*: Kudo et al. (2019); [4]: Dekiff et al. (2014); [5]: Herrera et al. (2003); [6]*:Kim et al. (2016); [7]*: Maruyama et al. (2015); [8]*: Randle et al. (2013); [9] Riess et al. (2000); [10]: Wang (2000c) ; [11]*:Yanagisawa et al. (2018) ; [12]*: Yanagisawa et al. (2019) ; [13]: Hosaka et al. (2005) ; [14] : Yuzawa et al. (2008) ; [15]*: Rial-Otero et al. (2009) ; [16]: Wang (2000a) ; [17]: Manabe et al. (1999) ; [18]: Jansson et al. (2007) ; [19]: FrontierLab - Technote – Irganox ; [20]*: Perlstein and Orme (1985) ; [21]*: Meyer-Dulheuer et al., 1998 (seen in Bart., 2001) ; [22] : Wang (2000b) ; [23]* : Hermabessiere et al. (2020) ; [24]* : Kuch., 1990 - unpublished results ; [25]: Roberson and Patonay (1990) ; [26]*: Lichtenstein et al., 1986 (seen in Bart., 2001) ; [27]*: Becerra and Odermatt (2012) ; [28] : Lichtenstein and Quellmalz (1983) ; [29]: Sitholé et Pimentel (2009) ; [30] : Kleine-Benne and rose (2011) ; [31]* : La Nasa et al.,2021 ; [32] : La Nasa et al., 2019 ; [33] : Kim et al. 2017

Table 2: Data about quantitative analysis of organic plastic additives with multi-shot Py-GC/MS

Compounds ^{a}	**Type of analysis**	**Method**	**Matrices**	**RSD (%)**	**R²**	**Recovery (%)**	**LOD (mg/kg)**	**LOQ (mg/kg)**	**Concentration ranges (mg/kg)**	**Ref.**
Phthtalates										
DIBP, DBP, BBP, DEHP	recovery test	in house RMs solution	PS, ABS, PET, PVC	10	n.a	> 70	n.a	n.a	100 – 1000	[1]
Phthtalates	Semi-quant	RMs	PE	< 15	n.a	79 - 113	n.a	n.a	110 – 110x10^3	[2]
DEHP	Calibration	pyolysis cup spiking	PP, PVC, PS	5	>0.98	n.a	14 - 46	n.a	0 – 2000	[3]
DIBP, DBP, BBP, DEHP, DNOP, DINP, DIDP	Calibration	RMs	n.a	< 9	0.99	n.a	< 28	n.a	80 – 965	[4]
	Semi-quant	indirect method	n.a	< 7.4 < 20	0.99	78 - 117.4 92 - 103	n.a	n.a	2.03 – 957	[4]
Phthtalates	Calibration	RMs	PVC	n.a	n.a	n.a	< 100	n.a	n.a	[5]
	Semi-quant	indirect method	PVC	n.a	n.a	n.a	12.0 - 17	n.a	n.a	[5]
DMP, DBP, BBP, DEHP, DINP and DIDP	Calibration	pyrolysis cup spiking	n.a	n.a	0.99	96 – 100%	< 1	< 3.5	0.003 – 3.67	[6]
Flames retardants										
TBBPA	recovery test	in house RMs solution	PS, ABS, PET, PVC	10	n.a	> 70	n.a	n.a	100 – 1000	[1]
TCEP, decaBDE	recovery test	in house RMs solution	PS, ABS, PET, PVC	10	n.a	> 70	n.a	n.a	100 – 1000	[1]
BFRs, SCCPS	Calibration	pyolysis cup spiking w/ stock solution	PP, PVC, PS	5	>0.98	n.a	14 - 46	n.a	0 – 2000	[3]
TBBPA	Semi-quant	Direct method	epoxy coates	n.a	n.a	n.a	n.a	n.a	n.a	[7]
Antioxidants										
Tinuvin 622 Chimasorb	Calibration	SE step prior to pyrolysis	PP	n.a	n.a	86 - 99.4	< 50	n.a	210 – 8790 46 – 7947	[8]
Monomer or intermediates										
BPA	Calibration	in-house solid RMs	paper	4; 19; 56	0.99	n.a	0.35 - 0.61	0.99 - 1.83	0 – 100	[9]
BPS	Calibration	in-house solid RMs	paper	2.6 ; 4.4	0.99	n.a	0.4 - 0.97	1.29 - 1.56	0 – 100	[9]
Other										

solvent (NMP)	Calibration	precoated sample cups spiked with stock solution	PS, PMMA, PVC	< 5.3	0.99	n.a	0.016	0.05	0.1 – 1	[10]
solvent (NMP)	recovery test	in-house solid RMs in precoated sample cup	PS, PMMA, PVC	< 5	0.99	98.8 - 106.6	n.a	n.a	600	[10]

[a] NMP = N-Methyl-2-pyrrolidone

n.a: not available

[1]: Yanagisawa et al. (2019) ; [2]: Kudo et al. (2019) ; [3]: Yanagisawa et al. (2018) ; [4]: Kim et al. (2016) ; [5]: Maruyama et al. (2015) ; [6]: La Nasa et al., 2021 ; [7] : Rial-Otero et al. (2009) ; [8]: Roberson and Patonay (1990) ; [9]: Becerra and Odermatt (2012) ; [10]: Kim et al. (2017)

Table 3: Summary of the main advantages and drawbacks of analytical pyrolysis devices for plastic additives and polymer analysis.

Advantages	**Drawbacks and limitations**
- Minimal and short sample preparation time - Wide application range – applicable to various polymers and various organic additives - Simultaneous identification and semi-quantitation of various additives in one experimental run without prior separation - Direct analysis of complex mixtures - Successive and rapid identification of plastic additive and plastic polymer, with multistep method - Analysis solid or liquid samples (solid polymers dissolved in an adequate solvent) - Small samples quantities (<1mg) and sizes - Automation and short analysis time; rapid screening - High sensitivity (detection at a concentration <50 mg OPA/kg of polymers). Trace analysis - High information content: Molecular structural information from the mass spectral fragmentation pattern and elemental compositions of mass signals from high resolution mass spectrometry - Fewer interferences between polymers and additives (such as pigments) - Automated solvent venting removes unwanted solvent prior to pyrolysis (it potentially eliminate manual sample preparation steps and permits the accurate analysis introduction of small amounts of polymer in solution)	- Destructive analysis - Lack of detection for polar, high molecular weight and low volatile products (without any prior sample treatment such as derivatization). - Quantitative analysis is not easy to perform. - Complex mixtures produce many pyrolysis products and fragments (electron-impact fragmentation), which makes a mass spectrum difficult to interpret - The TD of plastic additives is influenced by the geometrical surface of the particle => Sampling problems for heterogenic materials. - Difficult interlaboratory reproducibility of Py-GC/MS caused by various factors, including the materials and the different methods of pyrolysis and GC analysis. - Strict standardization is required of all experimental conditions.

Table 4: Py-GC/MS method parameters for the analysis of plastic additives in various studies. Cf. Table 1 for the corresponding compounds analyzed.

Ref.	Pyrolysis T° (°C)	Pyrolysis time (sec)	Thermochemoanalysis	GC-MS oven program	Ion source T° (°C)	Transfer line T° (°C)	Injection T° (°C)	Split	Scan Range (amu)	Vent flow (mL/min)	CIS	Column
[1]; [23]	350	60	-	40°C → 10°C/min → 350°C (10min)	n.a	350	n.a	splitless	10-600	60	-50	HP-5MS 30m x 250µm x 0.25µm
[2]	340	60	-	80°C → (20°C /min) → 300°C (5 min)	230	300	300	50	50 - 1000	1.5	non	Type of column : n.a 30m x 0.25 mm x 0.25µm
[3]	340	60	-	80°C → 20°C/min → 300°C (5min)	230	300	300	50	50 - 1000	52.1 cm/s	non	Ultra ALLOY-PBDE 15m x 0.25mm x 0.05 µm
[5]	300	150	-	60°C → 5°C/min → 90°C (1,5min) → 10°C/min → 300°C (10min)	n.a	300	280	n.a	SIM	1.5	-196	UA5-30M-0.25F Frontier Lab 30 m, 0.25 mm, 0.25 µm
[6]	340	60	-	40°C (1 min) → (50°C/min) → 200°C → (15°C/min) → 300°C (5 min)	230	300	300	50	50 - 500	1	non	Ultra ALLOY-PBDE 15m × 0.25mm × 0.05µm
[7]	340	60	-	80°C → (20°C /min) → 300°C (5min)	230	n.a	320	50	50 - 500	52.1 cm/s	non	Ultra ALLOY-PBDE 15m x 0.25mm x 0.05µm
[8]	320	n.a	-	(1) 80°C(1min)→ 50°C/min →200°C→15°C/min→ 350°C(2min) (2) 40°C → 40°C/min → 200°C →5°C/min → 300°C(1min) → 20ºC/min → 320°C(2.5min)	230	300	300	20	29 - 600	1.3	non	Ultra ALLOY-5 30m x 0.25mm x 0.25µm
[9]	445	10	-	100°C → 20°C/min → 130°C → 5°C/min → 290°C → 20°C/min → 340°C (15 min)	n.a	n.a	280	splitless	n.a	n.a	non	SGE BPX 5 30m x 250µm x 0.25µm
[9]	350	n.a	-	80 °C → (10°C/min) →320°C	n.a	300	n.a	50	50 - 500	50	non	Ultra Alloy Phthalate (FrontLab): 30m x 0.25mm x 0.05µm
[10]	375	20	-	40°C(4 min) → 10°C/min → 320°C (18 min)	n.a	n.a	300	30	15 - 650	n.a	non	J & W Scientific DB-5 30m x 0.25mm x 1µm
[11]	340	60	-	80°C → (20°C/min) → 300°C (5min)	230	300	320	50	50 - 1000	52.1 cm/s	non	Ultra ALLOY-PBDE 15m x 0.25 mm x 0.05µm
[12]	340	60	-	80°C → (20°C/min) → 300°C (5min)	230	300	320	50	50 - 1000	52.1 cm/s	non	Ultra ALLOY-PBDE 15m x 0.25 mm x 0.05µm
[13]	320	60	-	40°C → (20°C/min) →320 °C	300	300	300	20	n.a	1	non	Ultra ALLOY-PBDE 15m x 0.25 mm x 0.05µm
[14]	340	60	-	80°C → (20°C /min) → 320°C (3min)	300	300	300	20	n.a	1	non	Ultra ALLOY-PBDE 15m x 0.25 mm x 0.05µm

Ref.	Pyrolysis T° (°C)	Pyrolysis time (sec)	Thermochemoanalysis	GC-MS oven program	Ion source T° (°C)	Transfer line T° (°C)	Injection T° (°C)	Split	Scan Range (amu)	Vent flow (mL/min)	CIS	Column
[15]	315; 423; 500; 590	10	-	-20°C → 20°C/min → 300°C (5min)	230	n.a	270	n.a	10 - 760	180	-20	DB-5HT 15m x 0.25mm x 0.1µm
[16]	950	20	-	40°C(4 min) → 10°C/min → 320°C (18 min)	n.a	n.a	300	30	15 - 650	n.a	non	J & W Scientific DB-5 30m x 0.25mm x 1µm
[17]	250	n.a	TMAH + sulfuric acid	n.a	n.a	n.a	n.a	n.a	n.a	n.a	non	n.a
[18]	100&350	15	-	40°C → 10°C/min → 300°C	n.a	n.a	n.a	50	30 - 550	n.a	non	Type of column : n.a 30 m x 0.25 mm
[19]	320	n.a	TMAH	40°C → 10°C /min → 150°C → 20°C/min → 320°C (3min)	n.a	n.a	n.a	30	n.a	n.a	non	Ultra ALLOY-PBDE 15m x 0.25mm x 0.05µm
[20]	770	n.a	SE - dissolution	120°C → 12°C /min → 250°C	250	n.a	125	n.a	n.a	30	non	Porapak QS 1.6m x 0.4mm
[22]	950	20	-	40°C(4 min) → 10°C/min → 320°C (18 min)	n.a	n.a	300	30	15 - 650	n.a	non	J & W Scientific DB-5 30m x 0.25mm x 1µm
[25]	800	n.a	SE	70°C → 5°C/min → 130°C	n.a	n.a	n.a	splitless	n.a	2.43	non	Quadrex capillary aluminum clad 25 m x 1.7 mm I.D.
[27]	500	0.5	TMAH	100°C → 10°C /min → 250°C → 5°C/min → 275°C → 15°C/min → 320°C (5min)	230	280	300	30	35 - 400 + SIM	1	non	DB5 fused-silica 30m × 0.25 mm × 0.25µm
[28]	300 &500	5	-	50°C → (20°C/min) → 250°C	250	n.a	n.a	100	n.a	1.5	non	Type of column : n.a 50 m
[29]	650	20	SE	50°C (2min) → 8°C/min → 310°C (0.5min)	250	300	300	25	50 - 650	1.6	non	DB5-HAT 30m x 0.25mmx0.10µm
[30]	275	90	-	30°C (4min) → 10°C/min → 320°C (7min)	n.a	n.a	n.a	splitless	n.a	1	-50	HP-5MS (Agilent) 30m x 0.25 mm x 0.25µm
[31]	350	125	Microwave assisted SE	40°C (5min) → 10°C/min → 310°C (20min)	n.a	280	280	10	35-700	n.a	non	HP-5MS (Agilent) 30m x 0.25 mmx 0.25 µm
[32]	260	n.a	-	40°C (5min) → 10°C/min → 310°C (20min)	230	280	280	10	35-700	1.2	non	HP-5MS (Agilent) 30m x 0.25 mmx 0.25 µm
[33]	260	n.a	-	50°C (1min) → (20°C/min) → 270°C (5min)	n.a	n.a	n.a	20	25 - 500	20	non	HP-INNOWAX 30m × 0.25 mm × 0.25 µm

n.a: not available

[1]: Fries et al. (2013) ; [2]: IEC (2017) ; [3]: Kudo et al. (2019); [5]: Herrera et al. (2003); [6]: Kim et al. (2016); [7]: Maruyama et al. (2015); [8]: Randle et al. (2013); [9] Riess et al. (2000); [10]: Wang (2000c) ; [11]: Yanagisawa et al. (2018) ; [12]: Yanagisawa et al. (2019); [13]: Hosaka et al. (2005) ; [14] : Yuzawa et al. (2008) ; [15]: Rial-Otero et al. (2009) ; [16]: Wang (2000a) ; [17]: Manabe et al. (1999) ; [18]: Jansson et al. (2007); [19]: FrontierLab - Tech note – Irganox ; [20]: Perlstein and Orme (1985); [22] : Wang (2000b) ; [23] : Hermabessiere et al. (2020) ; [25]: Roberson and Patonay (1990) ; [27]: Becerra and Odermatt (2012) ; [28] : Lichtenstein and Quellmalz (1983); [29]: Sitholé et Pimentel (2009) ; [30] : Kleine-Benne and rose (2011) ; [31] : La Nasa et al.,2021 ; [32] : La Nasa et al., 2019 ; [33] : Kim et al. 2017.

Graphical abstract

Highlights

- The analysis of OPAs in polymers is an analytical challenge
- Py-GC/MS allows an efficient thermal desorption to analyze OPAs
- Py-GC/MS allows the simultaneous analysis of OPAs & polymer in the same sample
- Pros and cons regarding the use of Py-GC/MS are thoroughly assessed
- Standardized and reliable quantitative methods for the analysis of OPAs is required