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

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### ► To cite this version:

Fleurine Akoueson, Chaza Chbib, Sébastien Monchy, Ika Paul-Pont, Périne Doyen, et al.. Identification and quantification of plastic additives using Pyrolysis-GC/MS: a review. *Science of the Total Environment*, 2021, 773, pp.145073. 10.1016/j.scitotenv.2021.145073 . anses-03137716

**HAL Id: anses-03137716**

**<https://anses.hal.science/anses-03137716v1>**

Submitted on 10 Feb 2021

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

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13 Published in *Science of The Total Environment* and available online at

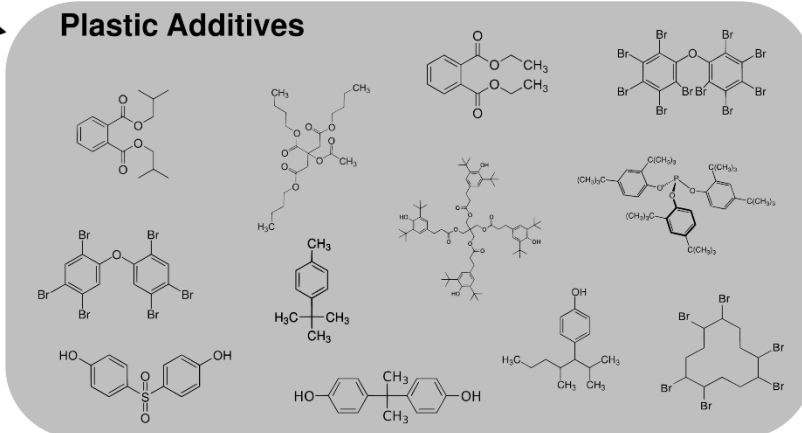
14 <https://doi.org/10.1016/j.scitotenv.2021.145073>

## Graphical Abstract

### Py-GC/MS



### Plastic Additives



## 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

15 **Abstract**

16

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

30 **Keywords**

31 Organic plastic additives (OPAs); plastic polymers; Py-GC/MS; multi-shot pyrolysis

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55

## 56 **1. Introduction**

57 Pyrolysis-gas chromatography coupled with mass spectrometry (Py-GC/MS) is used to characterize the  
58 chemical composition and the structure of volatile and non-volatile compounds (Riess et al., 2000). This  
59 characterization is performed under an inert atmosphere (usually using helium), by analysing the thermal  
60 degradation products of the compounds obtained after heating the sample to high temperatures, usually between  
61 250°C and 700°C (Fries et al., 2013; Herrera et al., 2003; Kleine-Benne and Rose, 2011; Tsuge et al., 2011;  
62 Wang, 2000b). Py-GC/MS is one of the oldest approaches to studying the structure of polymeric systems (Bart,  
63 2001), and has become established as a simple, quick and reliable analytical technique for a range of  
64 applications, including the analysis of various chemical aspects of polymeric materials including the  
65 characterization of organic plastic additives (OPAs). Various chemical additives are added to polymers during  
66 the manufacturing process to modify and improve their physical properties (Fries et al., 2013; Rios Mendoza et  
67 al., 2017; Rochman et al., 2019). There are several categories of additives, for instance pigments and dyestuffs  
68 to modify colour, antioxidants and UV stabilizers to maintain the inherent properties of the material by providing  
69 resistance to heat and aging or to improve resistance to light, and functional agents including flame retardants,  
70 anti-static additives, surfactants, and plasticizers. They can be small, volatile and semi-volatile molecules, or  
71 large and less or non-volatile compounds (Jansson et al., 2007).

72 The use of a specific analytical tool such as Py-GC/MS enables to obtain information on the composition  
73 of the plastic material, for which there is no clear data on formulation. The molecular information on the  
74 polymer, additives, and the mixture additives-polymers will help to extend knowledge on the state of polymer  
75 degradation, to establish the link between formulation, properties and degradation (La Nasa et al., 2020), and to  
76 target toxic aspects. The analysis of OPAs has grown in importance over the past few decades since the use of  
77 certain additives has become a controversial issue as some of them were found to be toxic to human  
78 (Yanagisawa et al., 2018). Compared with other detection methods, such as liquid chromatography coupled  
79 with mass spectrometry (LC/MS) or GC/MS analysis with a solvent extraction (SE) step, Py-GC/MS has the  
80 advantage of having a relatively easy and fast sample preparation (Kim et al., 2016; Llana-Ruiz-Cabello et al.,  
81 2017; Maruyama et al., 2015; Odermatt et al., 2003; Yanagisawa et al., 2018). This technique has been applied  
82 to the qualitative and semi-quantitative analysis of a large variety of additives in polymers. In addition, for most  
83 compounds, analytical pyrolysis offers a major advantage when it comes to analysing a complex sample: it can  
84 identify mixed media and successively analyse both the polymer and the associated OPAs. This is called multi-  
85 shot Py-GC/MS, which includes an initial thermal extraction step to characterize the additives and a second  
86 flash pyrolysis step to analyse the polymeric matrix (Herrera et al., 2003; Jansson et al., 2007; Kleine-Benne  
87 and Rose, 2011).

88 This paper reviews the studies carried out on OPAs using the analytical Py-GC/MS technique. This  
89 literature review, based on 71 articles, identified in scientific databases and search engines (Scopus, Google  
90 Scholar, Science Direct). An extended bibliographic research was carried out on plastic additives, pyrolysis

91 techniques, additive properties, the type of analysable molecules and the application of Py-GC/MS to plastic  
92 polymers and associated OPAs without targeting any specific additives. Then, a more targeted literature search  
93 was carried out by including the following key words: plastic additives, polymers, double- and multi-shot  
94 pyrolysis GC/MS and thermal desorption. The studies dated from 1983 up to August 2020. Articles were  
95 selected based on the title and the abstract and, often, on the references in those articles. The third step consisted  
96 in extracting, compiling, sorting and comparing the information given in the selected studies. This review  
97 presents the usefulness of the multi-shot Py-GC/MS technique for the analysis of OPAs and plastic polymers.  
98 It also explores the different criteria that need to be taken into account for successful analysis, from the  
99 knowledge of additives, polymers and their use, to the understanding of pyrolysis and its analytical parameters.

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

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

106 To date, many conventional methods for OPA analysis in polymer materials have been published. The  
107 majority of them use SE, such as Soxhlet extraction, coupled with GC/MS analysis (Kim et al., 2016; Kudo et  
108 al., 2019; Trimpin et al., 2009). SE allows for accurate qualitative and quantitative analysis, but requires  
109 complicated, costly, and time-consuming steps as well as large quantities of solvents. These steps are considered  
110 problematic because they can introduce errors in the analysis because of those manipulations. The various  
111 potential sources of errors (listed in Randle et al. (2013)) include (1) analysing a non-representative portion of  
112 the sample; (2) the risk of losing the targeted analytes during sample preparation; (3) reproducibility problems  
113 with the risk of deviations from the method's protocol; and (4) background contamination, coming from  
114 glassware, reagents or solvents, which increases with each additional step of the process. Moreover, another  
115 downside of SE is that some polymers, especially thermoplastic matrices such as polyethylene (PE) or  
116 polypropylene (PP), are insoluble or hardly soluble in some solvents (Bart, 2001; Okoffo et al., 2020; Wang,  
117 2000b). For these reason, SE techniques do not always comprehensively isolate the additives from the polymeric  
118 matrix. Recalcitrant polymers usually require high temperatures and, either the final solution is too viscous to  
119 go through extraction procedures, or the solvent is very corrosive and presents safety hazards (Wang, 2000b).

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

## 126 **2.1. Py-GC/MS for the identification of plastic additives and polymers**

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

151 Pyrolysis analysis can help with this issue, by using a “multi-step” temperature approach that allows  
152 investigating the organic additives and the polymeric matrix separately and successively (Derenne and Quénéa,  
153 2015; Fries et al., 2013; Okoffo et al., 2020; Wang, 2000b). This multi-step analysis, more commonly called  
154 multi-shot Py-GC/MS (Herrera et al., 2003) or sequential pyrolysis (Kleine-Benne and Rose, 2011), can lead  
155 two consecutive analyses of a single sample under different pyrolysis temperatures (Herrera et al., 2003; Kleine-  
156 Benne and Rose, 2011; Okoffo et al., 2020; Quénéa et al., 2006; Terán et al., 2009). The polymer sample is  
157 directly introduced into the pyrolyser device. The first shot is used to thermally desorb the organic compounds  
158 at the surface of the sample or the additives included in the polymers using a specified heating programme. It  
159 provides information on additives, regardless of the polymer, through rapid analysis of additives without  
160 degrading the polymeric matrix.



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

164 Multi-shot Py-GC/MS has proven to be a good tool for the identification of OPAs and polymers, helping  
165 with the identification of additives and simplifying the interpretation of the polymer spectra by separating the  
166 additives detection from the polymers and thermally separating the different families of compounds at different  
167 temperature intervals (Dekiff et al., 2014; Fries et al., 2013; Herrera et al., 2003; Jansson et al., 2007; Odermatt  
168 et al., 2003). In 2019, Yanagisawa et al. (2019) developed and applied the first screening method for multiple  
169 additives, including plasticizers and various families of flame retardants: Tris(2-chloroethyl)phosphate (TCEP)  
170 (PubChem CID: 8295), decabromodiphenylether (decaBDE), Diisobutyl phthalate (DIBP) (PubChem CID:  
171 6782), Di-n-butyl phthalate (DBP) (PubChem CID: 3026), Butyl benzyl phthalate (BBP) (PubChem CID:  
172 2347), Di(2-ethylhexyl)phthalate (DEHP) (PubChem CID: 8343) and Tetrabromobisphenol A (TBBPA)  
173 (PubChem CID: 6618).

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

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

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

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

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

## 220 **2.2. Py-GC/MS for the quantitative analysis of plastic additives**

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

228 The difficulty in acquiring quantitative data is a major drawback of pyrolysis. In the studies reporting Py-  
229 GC/MS quantitative determination of additives in polymeric matrices, a confounding factor is identified: the  
230 matrix effects on pyrolysis. It has been shown that the polymeric matrix can have an effect on the thermal  
231 desorption and thus on the identification of the additive. This is one of the major issues for semi-quantitative  
232 analysis using Py-GC/MS, which is not considered as a routine analysis because this method requires (i)

233 calibration standards with the same polymeric matrix as the sample; (ii) time-consuming multiple  
234 measurements; and (iii) taking into account divergent standard procedures (Bart, 2001). These limitations are  
235 discussed below.

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

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

246 The accuracy of multi-shot pyrolysis must be compared with that of other extraction techniques (e.g.  
247 SE). In their study, Kim et al. (2017) found that, for equivalent RSD values (i.e.  $<5\%$ ) between pyrolysis and  
248 SE techniques, wet chemical methods result in a lower extraction efficiency and recovery rates that can be  
249 attributed to losses during sample preparation. Other studies have shown that multi-shot Py-GC/MS performs  
250 better than SE analysis for the identification of phthalates (IEC, 2017; Kim et al., 2016; Randle et al., 2013).  
251 The International Electrotechnical Commission (IEC, 2017) study considered this technique suitable for the  
252 screening and the semi-quantitative analysis of seven phthalates: DIBP, DBP, (BBP), DEHP, di(n-octyl)  
253 phthalate (DNOP) (PubChem CID: 8346), di-isononyl phthalate (DINP) (PubChem CID: 590836), and di-  
254 isodecyl phthalate (DIDP) (PubChem CID: 33599) in polymers that are used in electro technical products in the  
255 range of 100 to 2000 mg/kg. In contrast, the SE technique followed by LC/MS analysis has shown limitations  
256 for the determination of phthalates: only five phthalates (BBP, DEHP, DNOP, DINP, and DIDP) were  
257 identified, due to low peak and spectral resolution quality. Several studies report equivalent and satisfactory  
258 results with multi-shot Py-GC/MS and with SE-GC/MS methods, regarding recovery and repeatability rates.  
259 For example, SE analysis of phthalates from different studies showed good recovery rates (97.6 to 104%  
260 (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  
261 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  
262 comparison, Py-GC/MS studies showed similar values with recovery rates of over 98% (La Nasa et al., 2021)  
263 and between 78 and 117% (J.W.Kim et al., 2016; Yanagisawa et al., 2019; Kudo et al., 2019) and high  
264 repeatabilities of 5% and 10% (Yanagisawa et al., 2018 and 2019 respectively) and between 7.7 to 20%  
265 (J.W.Kim et al., 2016). In this latter study, the high reproducibility of the Py-GC/MS method was also confirmed  
266 by six other international laboratories, and recommended by the IEC Technical Committee (TC) 111 Working  
267 Group 3 (WG3), which conducted the same studies. For TD followed by pyrolysis, the quantification recoveries  
268 were between 78.3–117.4% (Kim et al., 2016) and between 92–103%, for inter-lab studies (Kim et al., 2016).

269 Finally, the comparison of studies for the quantification of plastic additives performed using either pyrolysis or  
270 SE methods showed comparable results, with most of the time a recovery rate for Py-GC/MS slightly lower  
271 than SE techniques (approximately 10% lower).

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

### 284 **2.3. Parameters influencing the analysis of plastic additives**

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

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

297 Py-GC/MS can be applied to analyse thermally labile and volatile additives, which result in extensive  
298 fragmentation. Derivatization can extend the applicability of the technique to certain molecules (Bart, 2001)  
299 (see Section 3.1.4.). If there is no derivatization treatment and the compounds cannot be extracted, flash  
300 pyrolysis of both the additive and the polymer must occur simultaneously. The SIM mode of MS detectors is  
301 an interesting approach and seems to be most informative, because it drastically simplifies the mass spectra and  
302 the identification process (Jansson et al., 2007). In addition, electron ionization (EI) allows the identification of  
303 the compounds considered too heavy to be identified using Py-GC/MS due to their high molecular weight (MW)

304 which is above the limit of mass detection. Unlike soft ionization techniques, e.g. chemical ionization (CI), that  
305 allow conservation of more information on structure and molecular identity, EI at 70 eV causes extensive  
306 fragmentation (Bart, 2001). Thus, smaller characteristic fragments from the molecule are determined but not  
307 the exact MW of the compound. Sometimes the isolation of specific additive fragments for the identification of  
308 individual compounds is difficult when analysing a complex matrix. However, SIM mode detection, with a  
309 preliminary selection of specific ions, may help to isolate and identify co-existing additives in a polymer.

#### 310 **2.4. Advantages and limitations of Py-GC/MS**

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

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

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

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

338 quantification of additives, and excessive LOD and LOQ values prevent Py-GC/MS from being used for  
339 quantitative applications (Teuten et al., 2009).

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

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

#### 345 **3.1. Sample preparation for the analysis of additives in plastics using pyrolysis**

##### 346 **3.1.1. Sample weight and sizes**

347 Depending on the studies, the mass of analysed sample vary. Most often, the amounts of polymers  
348 analysed in studies on plastic additives and polymer determination using Py-GC/MS range from 100 to 200 µg  
349 (Randle et al., 2013) or from 500 to 1000 µg (Fries et al., 2013; IEC, 2017; Kim et al., 2016; Yanagisawa et al.,  
350 2018; Yanagisawa et al., 2019; Yuzawa et al., 2008). Despite the limit of saturation of the analytical device,  
351 which depends on the targeted compound and the complexity of the matrix, there is no real minimum or  
352 maximum sample size limitation. The maximum size of plastic particles that can be analysed is determined by  
353 the diameter of the TD tubes (Fries et al., 2013) that vary from one device to another. Dekiff et al. (2014)  
354 estimated the minimum particle size required for pyrolysis at approximately 100 µm, because smaller particles  
355 are difficult to handle. However, Hermabessiere et al. (2018) proposed a lower size limit of 50µm for the  
356 analysis of plastic using Py-GC/MS. Moreover, although pyrolysis is able to analyse a small amount of sample,  
357 the detection of the whole additive content may be difficult due to the low proportion of certain additives in  
358 plastics.

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

##### 367 **3.1.2. Sample introduction methods**

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

- 372 (1) A “direct method”, which is the analysis of a solid plastic sample that is weighed and directly introduced  
373 into the pyrolyser to thermally extract additives from the polymer (IEC, 2017; Randle et al., 2013). An  
374 approximate amount of deactivated quartz wool can be placed above the sample to avoid any loss of the  
375 sample. The sample can also be placed between two pieces of quartz wool to reduce the amount of  
376 material leaving the sampling tube during pyrolysis (Kudo et al., 2019; Tsuge et al., 2011).  
377
- 378 (2) An “indirect method”, which consists in analysing a dissolved sample. A certain amount of an appropriate  
379 solvent is added to the ground polymeric sample. After complete dissolution of the powder, a known  
380 volume, 10 or 20  $\mu\text{L}$ , of the sample solution is added to a sample cup (Randle et al., 2013). However, the  
381 use of a solvent can add interference and cause contamination.

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

### 392 **3.1.3. Calibration curves**

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

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

405 ○ The “Quartz-wool spiking”: introduction of some additive-free and inert quartz wool into the  
406 pyrolysis cup and spiking the wool with a liquid solution of additive standards. In an attempt to obtain a  
407 calibration curve using pyrolysis, some studies have spiked a 3mm diameter piece of quartz wool, pre-cleaned

408 with hexane, with the additive(s) of interest or a mixture of a standard solution (Fries et al., 2013). The sample  
409 was then analysed using Py-GC/MS to extract and determine the standards spiked on the quartz wool.

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

417 The application of a TD step with Py-GC/MS using these methods can be problematic for the accurate  
418 determination of some compounds. Semi-volatile compounds with high vapour pressure can evaporate during  
419 the sample preparation procedure and the waiting time before analysis (Hosaka et al., 2015; La Nasa et al.,  
420 2021). Hosaka et al. (2015) compared the TD analysis of a mixture of 10 phthalates in two conditions: immediate  
421 measurement after adding the phthalate stock solution to the pyrolysis sample cup, and the analysis of the  
422 solution after different waiting times (0, 50, 100, 150 and 200 min) at 25°C. As expected, peak areas of the most  
423 volatile phthalates (DMP and DEP) significantly decreased with increasing waiting time, to reach a reduction  
424 of 90 and 50%, respectively, at 200 min. On the other hand, the abundance of the eight other phthalates, less  
425 volatile with a lower vapour pressure, did not show any decrease. These results indicate that, using conventional  
426 sample cup spiking, it can be difficult to obtain a satisfactory calibration curve for the quantitative analysis of  
427 the most volatile compounds with high vapour pressure, due to their evaporation prior to analysis during the  
428 waiting time. Spiking the solution of additives on a polymeric matrix, using a pre-coated sample cup, i.e. coated  
429 with a thin layer of polymer, or polymeric certified reference materials (CRMs), can help prevent this  
430 evaporation.

431 Hosaka et al. (2015) was the first to use a pre-coated sample cup, in which a few microliters of the  
432 additive standards was added to the pyrolysis cup. The coating acts as a sorbent for the most volatile compounds  
433 and likely suppresses or at least reduces their rapid volatilization from the sample cup, especially for quantitative  
434 analysis (Hosaka et al., 2015; Kim et al., 2017). This reduction of emission was explained by the potential rapid  
435 diffusion of the additive mixture into the coated polymer film. In these two studies, the inner surface of a  
436 deactivated stainless steel cup was coated with a thin layer of PVC (10 to 20 µm with 0.5 and 1 mg of the  
437 polymer). In Hosaka et al. (2015) study, the results showed that the peak intensity for all the phthalates, even  
438 the one with high vapour pressure, are comparable for waiting times of 0 and 200 min. This result suggests that  
439 using a PVC-coated sample pyrolysis cup is an efficient way to reduce the volatilization of compounds.  
440 Moreover, this technique shows a great reproducibility with RSD values lower than 3%. Hosaka et al. (2015)  
441 also tested PS and poly(methyl methacrylate) (PMMA) as polymer coating that also showed great results in  
442 reducing the emission of semi-volatile phthalates. However, when heating polymers at high temperatures, in  
443 this case around 320°C, degradation products of the polymers may interfere with the measurement of the



444 additives studied. Naphthalene, biphenyl and hydrogen chloride appeared in the chromatogram of PVC coated  
445 sample cup, styrene dimers and trimers peaks appeared in the PS coated cup and MMA dimers and trimers  
446 appeared in the PMMA coated sample cup. However, those peaks did not affect the analytical results because  
447 they were well separates from the additives peaks and the degradation product of PVC showed shorter retention  
448 times. Nonetheless, PVC is known to contain large amount of plasticizers, thus, people have to be careful of the  
449 amount of additives already included in the polymers, or, guarantee that the polymers used are additive free.

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

471  
472 (1) Spiking a virgin solid polymeric matrix with an additive standard solution (Randle et al., 2013).  
473 For this purpose, a weighed amount of additive-free polymer samples is placed in a pyrolysis sample cup and  
474 mixed with a known volume of the additive stock solution (Becerra and Odermatt, 2012; Odermatt et al., 2003).  
475 For example, Kim et al. (2017) added 0.1% of additives (according to the regulated concentration).

476  
477 (2) Spiking a polymeric solution with an additive standard solution (IEC, 2017; Yanagisawa et al.,  
478 2019). To assure a homogeneous sample, the polymer particles are weighed and dissolved completely in an  
479 appropriate solvent to prevent precipitation. Then, a given volume, from 10 to 20  $\mu\text{L}$ , of a known concentration

480 (50 mg/mL) of the polymer solution and a few  $\mu\text{L}$  (ca. 5  $\mu\text{L}$ ) of a known concentration of additive standard  
481 mixture solution (100  $\mu\text{g}/\text{mL}$ ) are injected in a pyrolysis sample cup. This mixed solution is dried at room  
482 temperature in the sample cup before the TD analysis. Although this method allow a better homogeneity of the  
483 sample, using a solvent may introduce biases (i.e. contamination, toxicity for the technician, interference with  
484 the targeted molecule(s)) and some polymers are difficult to solubilise.

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

#### 493 **3.1.4. Derivatization approach**

494 Several drawbacks are associated with Py-GC/MS including the fact that certain compounds are  
495 difficult to analyse with Py-GC/MS. Only pyrolysis products that are GC-operable can be detected.  
496 Consequently, the pyrolysis compounds of the most polar or heavy MW products often show peak tailing, long  
497 elution times, poor reproducibility, or, in some cases, absence of peaks (Challinor, 1989; Derenne and Quénéa,  
498 2015). The limitation of this analytical chromatographic system can be overcome with a derivatization step. The  
499 purpose of this derivatization reaction is to modify the sample to produce a more volatile derivate. It will enable  
500 to enhance chromatographic separation and detection results for the compounds that are not suitable for efficient  
501 detection, and will also improve the pyrolysis process for qualitative and quantitative analysis (González-Vila  
502 et al., 2001; Rial-Otero et al., 2009; Venema and Boom-Van Geest, 1995).

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

509 Challinor (1989) reported the first combined pyrolysis/derivatization of phenolic resins and polyester  
510 polymers, and polymer additives, with the addition of a derivative agent: tetramethylammonium hydroxide  
511 (TMAH). Different methods of derivatization have been reported such as hydrogenation, silylation, butylation,  
512 alkylation and methylation with addition of different derivative agents (Derenne and Quénéa, 2015; Rial-Otero  
513 et al., 2009; Sobeih et al., 2008). Methylation is the most common derivatization reaction which is mainly  
514 performed with TMAH (Becerra and Odermatt, 2012; Derenne and Quénéa, 2015; Jeknavorian et al., 1998;

515 Manabe et al., 1999; Rial-Otero et al., 2009; Venema and Boom-Van Geest, 1995). However, this reagent needs  
516 to be handle with special care due to its potential hazard for the laboratory technician. In addition to its toxicity  
517 for the environment, TMAH is categorized as corrosive for the skin and eyes, and toxic for humans.

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

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

534 The amount of TMAH determines the degree of methylation. After the addition of TMAH in excess,  
535 the pH can be adjusted by adding acetic acid for example. However, Venema and Boom-Van Geest (1995)  
536 demonstrated that pyrolysis temperature has a less pronounced effect than pH on derivatization efficiency. The  
537 role of the solvent is also subject to debate (Challinor, 2001; Venema and Boom-Van Geest, 1995). In general,  
538 the solvent of the derivatizing agents, i.e. methanol or water, does not affect the derivatization process and  
539 efficiency because the solvent added to the analyte is evaporated slowly before the introduction of the sample  
540 into the pyrolysis device. However, in the case of polycondensation polymers, such as polyamides (PA) or  
541 poly(ethylene terephthalate) (PET), the solvent effect is significant and strongly influences the methylation of  
542 the compounds, affecting the chemical nature of the product formed and, consequently, the pattern of the  
543 pyrogram. The use of water as a solvent for TMAH increases hydrolysis degradation mechanisms and creates  
544 different by-products, such as tetramethyl ammonium salt, which have to be pyrolysed at high inlet temperatures  
545 to form the corresponding methyl esters. However, in the case of methanol, TMAH behaves like a  
546 transesterification catalyst, resulting in the direct formation of methyl esters, even if the hydrolysis reaction is  
547 expected to be the most likely mechanism (Venema and Boom-Van Geest, 1995). Pyrolysis temperature may  
548 influence the success of the pyrolysis-derivatization process. Venema and Boom-Van Geest (1995) reported  
549 that there are more impurities, originating from the derivatizing reagent, i.e. TMAH, at temperatures above  
550 500°C. The thermochemolysis process is very sensitive to the matrix effects of the studied polymer. Due to the

551 complex chemistry related to different functional groups, and to the diverse parameters influencing detection  
552 and separation, the observed data need to be interpreted very carefully (Venema and Boom-Van Geest, 1995).

### 553 **3.2. Multi-shot Py-GC/MS methods for the analysis of OPAs**

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

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

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

587 abundance, corresponding to BHT. In contrast, at 500°C the identification of the targeted molecule was  
588 complicated, abundance was low, and the peak was overshadowed with the multiple peaks of the polymer  
589 fragments. Furthermore, the complexity of pyrograms increases at higher pyrolysis temperatures (Terán et al.,  
590 2009).

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

### 600 **3.2.1. The importance of pyrolysis temperature**

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

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

620 The concentration of the additive in the polymer affects its detection with Py-GC/MS. At a low  
621 temperature, only the component present at high concentrations will show a clear peak in the pyrogram,  
622 provided that it is volatile. For example, in Riess et al. (2000) study, at the lowest tested temperature (315°C),

623 only octabromodiphenyl oxide, which is one of the main components present in the flame retardant commercial  
624 mixture, was identified. For compounds with low volatility or low concentration in the polymer, or, as  
625 mentioned above, with a relatively high molecular mass, no or only low concentrations are mobilized at low  
626 temperatures.

### 627 **3.2.2. The influence of the type of molecule on the selection of an appropriate pyrolysis temperature**

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

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

### 648 **3.2.3. The influence of polymer type**

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

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

#### 670 **4. Conclusion**

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

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

688 Qualitative and quantitative analysis require a rigorous approach to ensure instrumental and sampling  
689 repeatability. The majority of Py-GC/MS analyses on OPAs are qualitative. Although semi-quantitative  
690 analyses are possible, it remains difficult to obtain suitable quantitative data from pyrolysis studies, and this  
691 constitutes one of the major drawbacks of Py-GC/MS, particularly in light of the fact that polymer additives can  
692 be present in low concentrations. Mass detectors are sufficiently sensitive to detect plastic additive pyrolysate  
693 compounds and selecting ions with a SIM mode can simplify the identification of the compounds, thereby

694 improving the sensitivity and lowering the limits of detection. It is recommended that each sample should be  
695 measured, if feasible, using the full-scan mode together with the SIM mode, especially for the analysis of trace  
696 additives. However, future work needs to focus on the improvement of this method for sensitive quantitative  
697 analysis that will lead to a robust, standardized analytical procedure for compounds present at low levels.

## 698 **5. Acknowledgments**

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



703 **6. Authors contribution**

704

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

710 **7. References**

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

Compound	Abbreviation/Other Names	PubChem CID	Polymer studied <sup>a; b</sup>	Ref. <sup>c</sup>
<b>Plasticizers</b>				
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-ethylhexyl)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]*
Butyl benzyl phthalate	BBP	2347	HDPE, PP, PS	[31]*
			PE, PVC	[6]* [2]*
			PVC	[9]
			PET, ABS, PVC, PS	[7]* [8]* [12]*
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]*
Di(n-octyl) phthalate	DNOP	8346	PVA	[32]
			PVC, PE	[2]*
Di-isononyl phthalate	DINP	590836	PVC	[7]* [8]* [9]
			PVC, PE	[2]*
			HDPE, PP, PS	[31]*
Di-isodecyl phthalate	DIDP	33599	PVC	[7]* [8]* [9]
			PVC, PE	[2]*
			HDPE, PP, PS	[31]*
Hexahydrophthalate 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]
<b>Flames retardants</b>				
Octabromobiphenyl	-	3032840	n.a	[9]
Octabromodipheyl ether	-	6537506	n.a	[9]
Decabromodiphenyl oxide	-	14410	n.a	[9]
gama-Hexabromocyclododecane	$\gamma$ -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]
<b>Antioxidants</b>				
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-2,4,6-trione	Irganox 3114	93115	PP	[21]*
			PE, PBT	[22]
3,5-Bis(1,1-dimethylethyl)-4-hydroxybenzenepropanoic acid thiodi-2,1-ethanediy 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	135332164
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]heneicosan-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-diocetadecylhydroxylamine	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]*
<b>Monomer or intermediate</b>				
Bisphenol A	BPA	6623	n.a	[16] [27]*
Bisphenol S	BPS	6626	n.a	[27]*
<b>Other</b>				
N-methyl-2-pyrrolidone	NMP	13387	PS, PMMA, PVC	[33]
<p><sup>a</sup> 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)</p> <p><sup>b</sup> n.a: not available</p> <p><sup>c</sup> absence of sign = qualitative study; * = semi-quantitative study</p> <p>[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 - Tech note – 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., 1999 - 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</p>				

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

Compounds <sup>a</sup>	Type of analysis	Method	Matrices	RSD (%)	R <sup>2</sup>	Recovery (%)	LOD (mg/kg)	LOQ (mg/kg)	Concentration ranges (mg/kg)	Ref.
<b>Phthalates</b>										
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]
Phthalates	Semi-quant	RMs	PE	< 15	n.a	79 - 113	n.a	n.a	110 – 110x10 <sup>3</sup>	[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]
Phthalates	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]
<b>Flames retardants</b>										
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]
<b>Antioxidants</b>										
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]
<b>Monomer or intermediates</b>										
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]
<b>Other</b>										
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]
<sup>a</sup> 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
<ul style="list-style-type: none"> <li>- Minimal and short sample preparation time</li> <li>- Wide application range – applicable to various polymers and various organic additives</li> <li>- Simultaneous identification and semi-quantitation of various additives in one experimental run without prior separation</li> <li>- Direct analysis of complex mixtures</li> <li>- Successive and rapid identification of plastic additive and plastic polymer, with multistep method</li> <li>- Analysis solid or liquid samples (solid polymers dissolved in an adequate solvent)</li> <li>- Small samples quantities (&lt;1mg) and sizes</li> <li>- Automation and short analysis time; rapid screening</li> <li>- High sensitivity (detection at a concentration &lt;50 mg OPA/kg of polymers). Trace analysis</li> <li>- High information content: Molecular structural information from the mass spectral fragmentation pattern and elemental compositions of mass signals from high resolution mass spectrometry</li> <li>- Fewer interferences between polymers and additives (such as pigments)</li> <li>- 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)</li> </ul>	<ul style="list-style-type: none"> <li>- Destructive analysis</li> <li>- Lack of detection for polar, high molecular weight and low volatile products (without any prior sample treatment such as derivatization).</li> <li>- Quantitative analysis is not easy to perform.</li> <li>- Complex mixtures produce many pyrolysis products and fragments (electron-impact fragmentation), which makes a mass spectrum difficult to interpret</li> <li>- The TD of plastic additives is influenced by the geometrical surface of the particle =&gt; Sampling problems for heterogenic materials.</li> <li>- Difficult interlaboratory reproducibility of Py-GC/MS caused by various factors, including the materials and the different methods of pyrolysis and GC analysis.</li> <li>- Strict standardization is required of all experimental conditions.</li> </ul>

**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)	Thermoche moanalysis	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 x 0.25mm x 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) → 20°C/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 → 180°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
[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

Ref.	Pyrolysis T° (°C)	Pyrolysis time (sec)	Thermoche moanalysis	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
[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 x 0.25 mm x 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 x 0.25 mm x 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.