Journal of Analytical and Applied Pyrolysis
November 2022, Volume 168, Pages 105745 (10p.)
https://doi.org/10.1016/j.jaap.2022.105745
https://archimer.ifremer.fr/doc/00798/90965/

Identification of plastic additives: Py/TD-GC-HRMS method development and application on food containers

Akoueson Fleurine [1, 2], Chbib Chaza [3], Brémard Armance [1, 5], Monchy Sébastien [3], Paul-Pont Ika [4], Doyen Périne [2], Dehaut Alexandre [1], Duflos Guillaume [1, *]

[1] ANSES – LSAl, Boulevard du Bassin Napoléon, 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, F 62930 Wimereux, France
[4] Univ Brest, CNRS, IRD, Ifremer, LEMAR, F-29280 Plouzané, France
[5] Université Paris Saclay, Bât. 349, 91405 Orsay Cedex, France

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

---

Abstract :

The interest of studying organic plastic additives (OPAs) is growing since many of them are considered as toxic for human beings, marine organisms and have been found in the ecosystem. The impact and the extent of this pollution is not fully understood because of the lack of methods able to comprehensively analyze the wide diversity of OPAs. This study aims at offering a quick and efficient way to identify specific harmful plastic additives in polymer materials. For this purpose, a general method, for identifying 49 OPAs, has been successfully developed using pyrolyzer/thermal desorption-gas chromatography coupled to a high-resolution mass spectrometer (Py/TD-GC-HRMS). The retention indices were calculated for each compound and a high-resolution mass spectra database for plastic additives was implemented. This method was then applied to characterize the OPAs included in food containers that are frequently found in the environment. Four samples made of polypropylene (PP) and polylactic acid (PLA) coming from two distinct suppliers were then selected. A total of 10 additives, which were plasticizers (phthalates and adipates), antioxidants (bisphenol B) and phosphorous flames retardants, were found in these food packaging. Generally, higher peak signals were detected in the PP samples in comparison to PLA samples, except for tributyl phosphate and bisphenol B that were exclusively found in PLA samples. Moreover, the experimentations pointed out additives differences between suppliers, for products intended for the same use and made of the same polymer, for both PP and PLA samples highlighting the complexity of identifying and generalizing the additive content of plastic materials.

Highlights

► A single method for the analysis of OPAs using Py/TD-GC-HRMS has been implemented. ► The developed method allowed to create a plastic additive database. ► 49 additives molecules out of the selected 57 have been successfully identified. ► 10 plastic additives were found in PP and PLA food packaging.

Keywords : Phosphorous flame-retardants, Plasticizers, antioxidants, UV stabilizers, Py/TD-GC-HRMS, analytical method development

1. Introduction

Plastic pollution is a threat for the environment and marine organisms [1]. The presence of plastics is ubiquitous in the environment. In 2020, plastic production reached 307 million metric tons worldwide [2], of which 24% were used for food and beverages packaging [3]. These items are in the top ten of the most common plastic waste found in the environment [4].

A key concern of plastic pollution is linked to the risks to both ecosystem and human health. These adverse effects classified in several categories including the “physical” effects related to the inhalation and ingestion of plastic debris and the “chemical” effects related to the harmful chemicals associated with plastics such as the organic plastic additives (OPAs) included in the polymer [5,6]. While the “physical” impacts of plastics are well described in the literature, the “chemical” impacts, partly related to the presence of OPAs, is less documented and limited information is available for the majority of them. Several categories and families of OPAs exist, sorted by decreasing total amounts in polymers: plasticizers, flame retardants, colorants, antioxidants, heat stabilizers, UV stabilizers or bio-stabilizers (biocides), lubricants, foaming agents, and antistatic agents. These chemicals are added to polymers during their formulation, without being chemically bound to polymers [7], in order to confer them specific properties and advantages. However, there are increasing concerns about their impacts on marine organisms or human health since some of them were found to be toxic [7]. Indeed some phthalates, nonylphenols (NPs), Bisphenols, as well as some brominated flames retardants (BFRs) have been identified as carcinogens, mutagens and may have detrimental impacts on the reproduction being endocrine disrupting chemicals [1,8-11]. As most of the OPAs are not chemically bound to the polymeric matrix, they can leach into the surrounding environment or can be transferred to marine organisms or humans upon plastic debris uptake [5,12-14]. Additionally, OPAs may migrate from the packaging leading to contamination of the food packed [15-18]. As a result, the use of OPAs in plastics has become controversial and the assessment of their nature and toxicity is of utmost importance.

A considerable number (more than 5300) of polymer formulations are available on the market, and more than 4000 known chemicals are used in the formulation of plastic packaging, i.e. intentionally added substances (IAS). Additionally, plastic packaging may contain non-intentionally added substances (NIAS) [19,20]. That demonstrates the chemical complexity of plastic polymers. The identity of most IAS and NIAS are unknown making difficult to assess the safety of plastic materials, especially in regards with food contact materials (FCM). In order to broaden understanding of the chemical impact of these additives, it is necessary to have a more-detailed assessment of plastic packaging associated chemicals. This involves the development of robust analytical method to identify and quantify them. The analysis of OPAs in polymers is an analytical challenge because of the wide array of their chemical compositions and the diversity of the molecules mixed within a polymer. Also, the most frequently used processes, e.g. solvent extraction (SE), present constraints. These methods are time consuming for the sample preparation, generate wastes and involve the use of toxic solvents. Besides, there is no universal solvent able to dissolve all types of polymers [21-24]. Under such circumstances, the need of avoiding the complexity of analytical processes is of concern. Pyrolysis coupled to a gas chromatography and a mass spectrometry (Py-GC-MS) is an analytical tool that enables relatively quick and easy analyses [25]. Moreover, this technique minimizes the sample preparation steps, limiting the potential contamination prior to the analysis and does not require the use of toxic solvents [21,26-28]. Analytical pyrolysis also offers a major advantage. It permit to successively analyze both the OPAs and the polymer with a multi-step approach including an initial thermal desorption (TD) step at sub pyrolytic temperatures (i.e. approximately <500 °C) to characterize the additives regardless of the polymer, and a second pyrolysis step at higher temperatures (i.e. >500 °C) to analyze the polymeric matrix [29-31]. Py-GC-MS has already been reported as beneficial to thermally desorb and screen plastic additives in several studies using pyrolyzer/thermal desorption (Py/TD) GC-MS methods [32-34] and is a recognized method for the fast identification of OPAs. Akoueson et al., (2021) review, listed a wide array of OPAs studied using Py and Py/TD-GC-MS [25]. However all the developed methods focused on few analytes from a type of additives. No general method exists to analyze a wider diversity of additives. Thus, we aimed to develop a TD method able to identify diverse harmful, emergent, or widely used OPAs.

The objectives of the present study are: (i) set up a high-resolution Mass spectral library which includes a selection of OPAs used as plasticizers, flame retardants, antioxidants and stabilizers, (ii) implement a general analytical method using Py/TD-GC-HRMS to identify and detect the selected plastic additives, and (iii) apply the method to several items of food packaging materials in order to characterize their OPAs content.

2. Materials and methods

2.1. Implementation of a general GC-HRMS method for OPAs detection

2.1.1. Targeted additives, reagents and preparation of the samples

According to different criteria, detailed in part 3.1, 56 additives were selected. The additives and their corresponding suppliers are listed in Table 1. A standard mixed solution of C_3–C_{33} n-alkanes (Cat. No. 40147-U) was purchased from RESTEK (Lisses, France). Analytical GC grade solvents were used such as methanol, acetone, toluene or acetonitrile and were all purchased from Sigma-Aldrich Co. (Saint-Quentin-Fallavier, France).

Diluted solutions of each additives stock solutions were prepared in suitable solvents at concentrations ranging from 0.05 to 100 $mg.L^{-1}$. The diluted solutions were then transferred and conserved in 2 mL GC autosampler vials with a PTFE coated seal. An aliquot of 1 µL of each additive solution was injected in the GC-HRMS using a microliter syringe at increasing concentrations (0.12, 0.25, 0.5, 1, 2.5 and 5 $mg.L^{-1}$) until visualization of the limit of detection additives when the signal to noise (s/n) was > 3. For the mixed n-alkanes, 1 µL of the 10 $mg.L^{-1}$ solution was also injected.

2.1.2. GC-HRMS method and parameter settings

Samples were analysed using a GC Trace 1310-MS Orbitrap Q-exactive from ThermoFisher Scientific (Les Ulis, France) equipped with a TriPlus RSH auto-sampler. The compounds in standard solutions were separated on a 30 m × 0.25 mm × 0.25 µm RXi-5ms capillary column acquired from Restek (Lisses, France). The injection volume was 1 µL.

Based on the literature, several methods (Supplementary data S1) were compiled in order to propose a compromise, i.e. a general method suitable for the 56 selected additives, being aware of its limitations regarding the analysis sensitivity for each additive.

Analytical conditions are detailed in Table 2.

Chromatograms were analyzed using Thermo Scientific Xcalibur software (4.3.73.11) and with the help of an automated search for the markers by deconvolution using TraceFinder^{TM} software (5.0.889.0). The identity of the additives was confirmed using target and confirming ions obtained from the literature [35-40] and the National Institute of Standards and Technology (NIST) Database.

2.1.3. Construction of the database

Following the acquisition, and after obtaining robust chromatograms signals for all the analytes, a database containing mass spectra for all the detected additives was implemented using TraceFinder software including quantitative and qualitative ions for each molecule, as specific as possible. The HRMS files are available on Zenodo [41].

Following the analysis of the standard additives solutions and the mixed *n*-alkane solution, the retention time (RT) of the additive analytes and the n-alkanes were used to calculate the Kováts retention indices (RI) following equation (1). Respective RI were calculated [42] and registered in the database. The RI were validated when the calculated values were in the range of RI values found in the literature.

$$RI = 100 \times (C_{n+1} - C_n) \times \left[\frac{(t_x - t_n)}{(t_{n+1} - t_n)}\right] + 100 \times C_n \qquad \textbf{(1)}$$

With the carbon numbers of *n*-alkanes eluted before (C_n) and after (C_{n+1}) the corresponding target molecule, retention time of the target molecule expressed in min (t_x) and retention times for C_n (t_n) and C_{n+1} (t_{n+1}) for the flanking n-alkanes expressed in min.

The RI and the specific qualitative and quantitative ions are gathered for each additive in Table 3.

2.2. Thermodesorption method development for the detection of OPAs using Py/TD-GC-HRMS

A TD step using a Pyrolyser, CDS Analytical Pyroprobe 6150 from Quad Service (Oxford, PA US), was added to the GC-HRMS developped method.

2.2.1. Sample preparation optimization

Four protocols of sample preparation (Supplementary data S2) were previously tested in order to ease the analytical process and to reduce the high volatility of several low molecular weight additives. Briefly, the analysis of the selected plastic additives have been done by introducing 1 µL of the additives stock solutions at concentrations ranging from 5 to 100 mg.L^{-1}. The solutions were either added in an empty pyrolysis quartz tube or in a pyrolysis quartz tube containing three types of different materials used as “solution trapping matrix” such as a piece of quartz filter, a piece of quartz wool or a small amount of diatomaceous earth (silicium dioxide). These media were selected for their documented chemically inert features and their thermal resistance [43,44]. In brief, considering the results (S2), the quartz filter was chosen as a suitable « trapping matrix » since it permit to stabilize the compounds despite the waiting time between the sample preparation and the analysis

2.2.2. Implementation of a general method using Py/TD-GC-HRMS device

The analyses were carried out using a Pyrolyser CDS Analytical Pyroprobe 6150 from Quad Service (Oxford, PA US) coupled to a GC-HRMS device (Trace 1310-MS Orbitrap Q-exactive, ThermoFisher Scientific) thanks to a heated transfer line with the method presented in part 2.1.2.

According to the preliminary results obtained following the sample preparation optimization tests presented part 2.2.1., 1 µL of the additives standard solutions was introduced in a pyrolysis quartz tube containing a piece of quartz filter. The pyrolysis quartz tube and the quartz filter were both heated beforehand at 1000 °C during 15 seconds to get rid of any residual compounds. Sample tubes were then placed in the pyrolyzer auto-sampler and analysis was performed. Selection of the thermal desorption temperature was carried out on the additives standard solutions by testing three desorption temperatures: 250 °C, 350 °C and 450 °C, with three replicates. The TD time was fixed at 60 seconds based on the litterature, beeing the most frequently used TD time (Table S1).

To ensure the reliability of the results and the absence of contamination in the analytical device two precautions were taken for each batch: (i) a 1000 °C auto-clean of the pyrolysis chamber during 15 seconds between each analysis; (ii) and five empty pyrolysis quartz tube without sample, hereafter referred as “blank”, were pyrolyzed at the beginning of each run.

2.3. Application: OPAs identification in food contact materials

2.3.1. Sample selection and preparation

Two types of food packaging items made of polypropylene (PP) and polylactic acid (PLA), coming from two different suppliers, tagged with either A or B, have been selected. The selection of PP was based on its high production and high presence in the marine environment [3,19]. The PLA was selected for being the most used bio-based alternative in order to compare its additive content to a petro-based polymer [45].

Punches, i.e. cylinders of 1 mm diameter, were cut in the food packaging items using biopsy punches from Farla-Medical (Antwerpen, Belgium), in order to have a homogeneous sample taking process. Thickness of the cylinders was measured using a binocular microscope (Olympus SZX16) and OLYMPYS cellSens Dimention 3.2 software (n=3). The volumes and the masses (µg) of each particle were calculated using the diameters and the thickness measurements. The cylinders were then introduced in pyrolysis sample cups. Sample tubes were placed in the pyrolyzer auto-sampler and analysis was performed (n=3).

2.3.2. Py/TD-GC-HRMS analyses

In order to thermally desorb the additives contained in the samples, each cylinder was successively analyzed three times at a thermal desorption temperature of 350 °C to maximize the extraction of the chemicals present in the samples. An approximation of the extraction efficiency percentage (%) was calculated dividing the area recorded at the first step by the total area over the three steps.

All analyses were carried out using the method previously developed and presented part 2.1.2.

The selected OPAs (Table 1) were identified on the basis of the RT, RI, quantitative and qualitative ions and ions ratios with the help of the previously implemented database. The obtained signals were corrected taking in account the procedural blanks, i.e., pyrolysis tubes without sample, the calculated mass of the samples and the extraction efficiency of the method.

2.4. Statistical analysis

All statistical analyses were performed using R-Studio software (1.4.1106) [46]. For all the analysis, the normality and the homoscedasticity of the distribution were verified before carrying out ANOVA follow by Tuckey post Hoc test (adding the car package (3.0-12) [47]). Assuming that one of the hypothesis was not verified, a non-parametric Kruskal-Wallis test was performed. Kruskal Wallis tests were followed by a Nemeyni's post hoc test. Post hoc tests were achieved using agricolae (1.3-5) [48] and PMCMR (4.4) [49] packages. Mean differences were considered as significant when p-value < 0.05.

3. Results and discussion

3.1. Preliminary work and implementation of a HR mass spectra database

A total of 56 additives were selected as relevant compounds. This selection was based on a bibliographic work including previous publications, the European Food Safety Authority's (EFSA) list containing their evaluation on substances for FCM and the European chemical agency's (ECHA) additives list containing 400 substances imported in the European Union that are used in plastic products with a trade volume higher than 100 ton/year (Table 1) [1,7,23,25,26,34,45,50-55]. This bibliographic work was performed based on different priority criteria such as: the use of additives in plastic and plastic packaging, a balance between their toxicity and their concentration in polymers, the environment and marine organisms, and finally, the feasibility of GC-MS analysis on these additives.

A standard solution containing all targeted compounds was prepared to set up a suitable GC–HRMS method for their simultaneous analysis. This preliminary work was carried out using GC-HRMS with the method presented part 2.1.2 and allowed the detection of all the selected additives (Figure 1). The spectra of each additives peaks in figure 1 permitted the implementation of our own plastic additives database [41].

The identification of the additives not already included in NIST database was confirmed by the presence of their respective quantitative and qualitative characteristic ions presented in table 3. An additional confirmation for this set of additives has been made using Kováts RI (Table 3).

In this work, as the analytes were partly selected on their amenability to GC-MS analysis, some additives known to be toxic and widely used in plastic materials (e.g. Tetrabromobisphenol A and the hexabromocyclododecane isomers (α, β and γ-HBCD)) were not targeted. Indeed, depending on their chemical nature, certain OPAs may be complex to analyze and are hard to mobilize [34]. These analytical limitations can be overcome with a derivatization step that will modify the sample and product more volatile derivative [56]. It was not employed in the present study, which consisted to implement a fast and easy method. However, using a derivatization approach or leading analysis using liquid extraction could be complementary to have a more complete analysis.

3.2. Optimization and characterization of a Py/TD-GC-HRMS method for the detection of OPAs

Three temperatures were tested at this step: 250 °C, 350 °C and 450 °C. The pyrolyzer thermal desorption temperature had a significant impact on the peaks area of several additives. Figure 2 illustrates the relevant temperature patterns for each additive families. The detailed results for each additive are presented in supplementary data S3.

The areas of most flame-retardants (9 out of 14) showed no significant difference between the three tested temperatures. Areas were significantly higher at 350 °C for three additives (TCEP, TCPP and TDCPP), whereas the area of the 2,4,6-TBP and BTBPE were significantly higher respectively at 250 °C and 450 °C. The analysis of the plasticizers additives indicates significantly higher areas at 350 °C for 13 additives (BBP, DBP, DCHP, DEHP, DEP, DHP, DIBP, DIDP, DIHP, DINCH, DNOP, DNP, DOA) out of 16, and at 450 °C for the ATBC. No significant difference has been detected for three additives between the three tested temperatures (DAP, DIHP and DMP). Concerning the antioxidants, areas were significantly higher at 450 °C for six additives (NPs, 4-NP, NP1OE, 4NP1OE and Irganox 1081®), at 350°C for the Lowinox TBM 8® and at 250 °C for the 4-t-OP. Five additives showed no significant difference between the tested temperatures. Finally, no significant difference was observed for the three UV stabilizers.

Overall, based on these results, 350 °C seems to be the more relevant thermal desorption temperature for the analysis of the selected additives, either being significantly optimal or because no significant differences has been observed between the three temperatures. In line with our results, other studies generally used a thermal desorption temperature of 350 °C

[25,27,52]. Moreover, the temperature is one of the key factors for a successful extraction and subsequent detection [27]. Indeed, it affects the degree of fragmentation and the generated pyrolysis products, its selection must allow a suitable desorption of the additive without altering it. At too high temperatures, usually above 500 °C, the polymeric matrix begins to degrade and the excess of polymer fragments interfere with the identification of characteristic additive fragments, which make the analysis of the results complicated [21] and may lead to misinterpretation of the results.

The Py/TD-GC-HRMS method was used to analyze 56 additives at various concentration levels (1, 5, 10, 25, 50 and 100 mg.L^{-1}). Eight additives, marked with "*" in the Table 1, were not detected even when the highest concentration was injected in the pyrolyzer. Among them, three phosphorous flame-retardants (TCP, TCrP and TToP), two plasticizers (bisphenol S and TEHPA), two UV stabilizers (Uvinul 3049® and 3008®) and one antioxidant (NP2OE). The 49 additives identified have been detected at 5 ng except for the BDEs, the alkylphenols and the Irganox 1081® at 10 ng; for DIDP, DINP, DIHP and the BTBPE at 25 ng; for Lowinox TBM 6® at 50 ng; and for the Irganox 1076® with a detection threshold at 100 ng (Table 1).

A previous study [53] mentioned the complicated analysis of phosphorous flame-retardants. Indeed, some analytes are more difficult to analyze than others using Py/TD-GC-HRMS according to their physico-chemical properties [25]. For instance, TEHPA and Uvinul 3008® start to decompose at a temperature of 250°C and 350°C respectively, unlike BPS that has a low volatility and is more thermally stable than its bisphenol's analogs [57].

Increasing the thermal desorption temperature might help to volatilize the most stable additives, such as the BPS. Nonetheless, the temperatures selected in the study did not permit the desorption of the BPS. Other studies managed to analyze this molecule, for instance Becerra and Odermatt (2012) conducted their analysis with a temperature of 500 °C and added derivatizing agents using trimethyl ammonium hydroxide (TMAH), to increase the volatility of the additive [58]. However, in the present study, it was a thoughtful choice not to derivatize the samples, since the aim was to implement a quick method with minimal sample preparation steps. Some polymers, such as polystyrene (PS) or polyvinyl chloride (PVC), start to decompose at relatively low temperatures [21]. These limitations explain the selection of a method that does not permit the analysis of all additives.

3.3. Application of the method on plastic food packaging

3.3.1. Integration of samples mass variability

The masses (µg) of each sample cylinders were calculated using their diameter and thickness as well as the density of each polymer type. The average calculated mass of PP-B, i.e. 203 µg, is significantly different (p-value < 0.05) from the three other samples, i.e. 338 µg, 317 µg and 276 µg respectively for PP-A, PLA-B and PLA-A. Moreover, a high standard deviation (sd) is noticed especially for PLA-B sample and can be explain by thickness variations according to the location where the sample was cut out on the plastic container (supplementary data S4). In that respect, the respective masses of each analyzed food packaging cylinders were taken into account in order to normalize the additives signal measured in each sample.

3.3.2. Efficiency characterization

The method was developed on additives standard solutions. However, once additives are included in a polymeric matrix, some interactions can occur between the additives and the matrix [21]. Hence, the extraction efficiency of the method was directly calculated on the matrices of interest, i.e. following the analysis of PP and PLA food packaging samples, in order to take into account the potential interactions.

Each sample were submitted to three successive heating at a thermal desorption temperature of 350 °C. No additive was detected during the third analysis, indicating that the entirety of the additive included in the samples has been desorbed and analyzed during the first or second pyrolysis step (supplementary data S5). Consequently, the sum of the areas obtained during the two first analysis steps is considered as representing 100% of the additives amount included in each sample. The extraction efficiency percentage of each step was therefore calculated based on this assumption.

The results of the extraction efficiency after a first step of desorption were more than 80% for most compounds (Table 4, bold printed characters), with a few exceptions. Five additives required a total of two desorption steps to be fully extracted from the samples, e.g. DMP, DEP (for PP samples), DEHA (PP-A), TBP (PLA-A and PP-A) and TCPP, with average extraction efficiency percentages ranging from 50 to 80% or <50% upon the first desorption step (Table 4). Carrying out two desorption steps doubles the time of the analysis. For this reason, the developed method only includes one thermal desorption step at 350 °C. The average extraction efficiency percentages of each additive for each sample were taken into account in order to correct the additives signal recorded. However, care must be taken about the completeness of the extraction with this TD method. Although the punch is thin and the cross-section expose the core of the material. It can also be assumed that only the additives on the first layers of the punch could have been desorbed.

3.3.3. Identification of the selected OPAs in PP and PLA food packaging samples

The additives amounts detected in the food packaging samples are expresses in Area (Arbitrary unit (A.U)) per µg of plastic. The values were corrected with the extraction efficiency percentage and the calculated mass of each particle analyzed.

Ten OPAs of interest have been detected in the selected food packaging samples (Figure 3), mostly plasticizers (eight molecules) and flames retardants (two molecules). Two plasticizers, DEP and DIBP and a phosphorous flame retardant, TCPP, have been detected in all samples regardless of the supplier or polymer type. DMP and DBP plasticizers have been identified in all the samples except PLA-A, and DCHP was identified in all the samples except PP-B. Finally, the plasticizer DINP has only been detected in the two PP samples and Bisphenol B exclusively in the two PLA samples. TBP, a phosphorous flame retardant, has been identified both in PP-A and PLA-B only.

The area of DCHP is equivalent among all samples regardless of the supplier or polymer type. Overall, peaks areas for a majority of the OPAs are higher for the PP samples than for the PLA (six out of ten; Figure 3). DBP and DEP peak areas are significantly higher in PP-A samples than in PLA-A and B samples. The areas of DEHA, DIBP, DINP and TCPP in both PP samples are significantly higher than in PLA samples. On the other hand, the peak area of the phosphorous flame retardant TBP is significantly higher in the PLA-A than in both PP samples.

Looking at the differences between PLA-A and B (Figure 3), the PLA-B contains more additives than the PLA-A. Nine OPAs were identified in the PLA-B, including seven plasticizers (BPB, DBP, DCHP, DEHA, DEP, DIBP and DMP) and two flames retardants (TBP and TCPP), while only seven OPAs were identified in the PLA-A in which the DEHA and DMP have not been detected. In addition, a trend appears that the areas of the OPAs peaks found in PLA-B are mostly higher than those found in the PLA-A, except for the DCHP where the areas are identical. This trend is significant for the Bisphenol B (15 times higher in PLA-B) and the DEHA (absent in the PLA-A while detected in the PLA-B). The same pattern is observed when looking at the PP-A and B samples results (Figure 3). The PP-A contains two additives more than the PP-B. Nine OPAs have been detected in the PP-A, including seven plasticizers (DBP, DCHP, DEHA, DEP, DIBP, DINP and DMP) and two flames retardants (TBP and TCPP), while the PP-B sample only contains seven OPAs (DCHP and TBP missing). The peaks areas of the OPAs identified in the PP-A samples tends to be higher than in the PP-B. It is significant for the DBP (three times higher in PP-A), the DEHA (8x), the DIBP (x1.5), DMP (x2) and TCPP (x4).

However, regarding DEP and DIBP (respectively for PLA and PP, and for PLA only), it is difficult to draw conclusions. Indeed, a large spread in the data can be observed as these additives show a wide 95% confidence interval (IC 95 %). This dispersion can be explained by a lack of homogeneity in the distribution of additives within the same sample. This would then require the multiplication of replicates to be able to take these disparities into account.

These results lead to a few remarks:

First, a petro-based vs bio-based difference. For all analyzed sample, the majority of the OPAs identified were plasticizers. Indeed, during the formulation of plastic materials, OPAs are added at different proportions depending on the polymer and its usage. Most of the time, plasticizers are used extensively, reaching up 60% weight/weight (w/w) [59]. Here, the same number of additives detected in both PLA and PP materials (10 OPAs each) confirms that “bio-based” do not pledge “additives free”. Overall, lower amounts (Area (A.U)/mass (µg)) of additives were noticed in PLA samples (except BPB, DCHP and TBP), while, surprisingly, bisphenol B, a toxic endocrine disruptor analogue of the bisphenol A [10], has only been detected in PLA samples. Zimmerman et al., [19,60] tested the *in-vitro* toxicity and the chemical content of many bio-based materials (PLA items used as FCM). Their study detected priority concern compounds (such as additives, oligomers, along with non-intentional added substances (NIAS)) and highlighted that bio-based materials are not safer than conventional plastics regarding their chemicals content.

Secondly, an inter-suppliers difference. This study underlined non-negligible differences on the identification of OPAs in two food-packaging products manufactured with the same polymer and that are intended to have the same use. That reflects the complexity to generalize and estimate the potentially dangerous additives in the studied material and thus the exposition of marine organisms and consumer, since the chemical composition of a material don’t seem to be related to the polymer type but to each individual product. This match the conclusion of Zimmermann, et al. [61] that investigated the toxicity and the chemical composition of several plastic leachates made of conventional in PLA sample including FCM. They ended up with that same conclusion being that the contaminant content and the toxicity cannot be generalized based on the polymer type and are product specific. Plastic products formulation is different depending on the manufacturers, and may explain this difference in additives types and additives abundances between products made with the same polymer. It underlines the need of identifying the chemical content and the chemical safety of each material rather than polymers types, which is not a straightforward task but is inevitable considering the disparity in plastic formulation of the commercially available products. Moreover, the formulation’s recipes remain unknown from the scientific community and hinder the evaluation of potential impacts and toxicity of plastic materials.

4. Conclusion

This study was conducted with the aim to set up a suitable Py/TD-GC–HRMS method for simultaneous identification of various selected organic additives and to set up a high-resolution spectral database. The developed method showed its ability to detect the majority of the targeted additives. Nevertheless, this method may be limiting for certain OPAs harder to mobilize using GC. In complement, a liquid extraction analysis would provide more comprehensive results. Ten additives were detected in PP and PLA food contact materials. The results indicate the presence of multiples additives, some of them being toxic, in both petro-based and bio-based food packaging samples (e.g. plasticizers, phosphorous flames retardants). Moreover, significant differences were pointed out depending on either the polymer type or the suppliers. The present study highlights the complexity to assess and generalize the additive content and their amount in plastic packaging items due the variety and differences in plastic formulation.

5. Declaration of competing interest

Authors do not declare any competing interest**.**

6. Funding

Fleurine Akoueson is very grateful to the Hauts-de-France Regional Council and ANSES (French Agency for Food, Environmental and Occupational Health & Safety) for financially supporting her 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 and IDEAL projects. The funding of CPER MARCO project consists in the acquisition of the Py-GC-HRMS device and consumables used for the experiments.

7. CRediT Roles

F.Akoueson: Conceptualization, Investigation, Methodology, Formal analysis, Software, Validation, Visualization, Writing - original draft, Writing - review & editing. **C. Chbib**: Methodology Investigation, Writing - review & editing. **A. Brémard**: Investigation, Formal analysis. **S. Monchy**: Writing - review & editing. **I. Paul-Pont**: Writing - review & editing. **P. Doyen**: Writing - review & editing. **A. Dehaut**: Conceptualization, Funding acquisition, Supervision, Project administration, Writing - review & editing. **G. Duflos**: Resources, Conceptualization, Funding acquisition, Supervision, Project administration, Writing - review & editing.

8. References

[1] K.J. Groh, T. Backhaus, B. Carney-Almroth, B. Geueke, P.A. Inostroza, A. Lennquist, H.A. Leslie, M. Maffini, D. Slunge, L. Trasande, A.M. Warhurst and J. Muncke,Overview of known plastic packaging-associated chemicals and their hazards, *Science of The Total Environment*, 651, (2019) 3253.https://doi.org/10.1016/j.scitotenv.2018.10.015

[2] PlasticEurope, Plastic Europe, the facts 2021, 2021, Plastic Europe, Available on: https://plasticseurope.org/wp-content/uploads/2021/12/Plastics-the-Facts-2021-web-final.pdf

[3] PlasticEurope, Plastic Europe, the facts 2020 2020, Plastic Europe, Available on: https://plasticseurope.org/knowledge-hub/plastics-the-facts-2020/

[4] O. Gerigny, M. Brun, C. Tomasino, M. Le Moigne, C. Lacroix, M. Kerambrun and F. Galgani, Évaluation du descripteur 10 « Déchets marins » en France métropolitaine. Rapport scientifique pour l'évaluation 2018 au titre de la DCSMM, 2018, Available on: https://sextant.ifremer.fr/documentation/dcsmm/documents/Evaluation_2018/Rapport_Evaluation_DCSMM_2018_D10_Ifremer_CEDRE.pdf

[5] M. Kumar, H. Chen, S. Sarsaiya, S. Qin, H. Liu, M.K. Awasthi, S. Kumar, L. Singh, Z. Zhang, N.S. Bolan, A. Pandey, S. Varjani and M.J. Taherzadeh,Current research trends on micro- and nano-plastics as an emerging threat to global environment: A review, *J Hazard Mater*, 409, (2021) 124967.https://doi.org/10.1016/j.jhazmat.2020.124967

[6] C. Campanale, C. Massarelli, I. Savino, V. Locaputo and V.F. Uricchio,A Detailed Review Study on Potential Effects of Microplastics and Additives of Concern on Human Health, *Int J Environ Res Public Health*, 17, (2020).https://doi.org/10.3390/ijerph17041212

[7] J.N. Hahladakis, C.A. Velis, R. Weber, E. Iacovidou and P. Purnell,An overview of chemical additives present in plastics: Migration, release, fate and environmental impact during their use, disposal and recycling, *J Hazard Mater*, 344, (2018) 179.https://doi.org/10.1016/j.jhazmat.2017.10.014

[8] I.A. Sheikh and M.A. Beg,Structural characterization of potential endocrine disrupting activity of alternate plasticizers di-(2-ethylhexyl) adipate (DEHA), acetyl tributyl citrate (ATBC) and 2,2,4-trimethyl 1,3-pentanediol diisobutyrate (TPIB) with human sex hormone-binding globulin, *Reprod Toxicol*, 83, (2019) 46.https://doi.org/10.1016/j.reprotox.2018.11.003

[9] D. Lithner, Å. Larsson and G. Dave,Environmental and health hazard ranking and assessment of plastic polymers based on chemical composition, *Science of The Total Environment*, 409, (2011) 3309.https://doi.org/10.1016/j.scitotenv.2011.04.038

[10] H. Serra, C. Beausoleil, R. Habert, C. Minier, N. Picard-Hagen and C. Michel,Evidence for Bisphenol B Endocrine Properties: Scientific and Regulatory Perspectives, *Environ Health Perspect*, 127, (2019) 106001.https://doi.org/10.1289/EHP5200

[11] S. Eladak, T. Grisin, D. Moison, M.J. Guerquin, T. N'Tumba-Byn, S. Pozzi-Gaudin, A. Benachi, G. Livera, V. Rouiller-Fabre and R. Habert,A new chapter in the bisphenol A story: bisphenol S and bisphenol F are not safe alternatives to this compound, *Fertil Steril*, 103, (2015) 11.https://doi.org/10.1016/j.fertnstert.2014.11.005

[12] J. Muncke, A.M. Andersson, T. Backhaus, J.M. Boucher, B. Carney Almroth, A. Castillo Castillo, J. Chevrier, B.A. Demeneix, J.A. Emmanuel, J.B. Fini, D. Gee, B.

Geueke, K. Groh, J.J. Heindel, J. Houlihan, C.D. Kassotis, C.F. Kwiatkowski, L.Y. Lefferts, M.V. Maffini, O.V. Martin, J.P. Myers, A. Nadal, C. Nerin, K.E. Pelch, S.R. Fernandez, R.M. Sargis, A.M. Soto, L. Trasande, L.N. Vandenberg, M. Wagner, C. Wu, R.T. Zoeller and M. Scheringer,Impacts of food contact chemicals on human health: a consensus statement, *Environ Health*, 19, (2020) 25.https://doi.org/10.1186/s12940-020-0572-5

[13] A.A. Koelmans, E. Besseling and E.M. Foekema,Leaching of plastic additives to marine organisms, *Environ Pollut*, 187, (2014) 49.http://dx.doi.org/10.1016/j.envpol.2013.12.013

[14] C.M. Rochman, E. Hoh, T. Kurobe and S.J. Teh,Ingested plastic transfers hazardous chemicals to fish and induces hepatic stress, *Sci Rep*, 3, (2013) 3263.https://doi.org/10.1038/srep03263

[15] E. Fasano, F. Bono-Blay, T. Cirillo, P. Montuori and S. Lacorte,Migration of phthalates, alkylphenols, bisphenol A and di(2-ethylhexyl)adipate from food packaging, *Food Control*, 27, (2012) 132.https://doi.org/10.1016/j.foodcont.2012.03.005

[16] P. Schmid and F. Welle,Chemical Migration from Beverage Packaging Materials—A Review, *Beverages*, 6, (2020).https://doi.org/10.3390/beverages6020037

[17] J.A. Garde, R. Catala and R. Gavara,Global and specific migration of antioxidants from polypropylene films into food simulants, *J Food Prot*, 61, (1998) 1000.https://doi.org/10.4315/0362-028X-61.8.1000

[18] Y. Tanaka, K. Takahashi, T. Sasao, T. Kirigaya, S. Hosoi, N. Nagaoka, T. Kawamura and H. Nakazawa,[Detection of tris(2,4-di-tert-butylphenyl)phosphite (Irgafos 168, antioxidant in plastics) and its oxide in commercial frozen vegetables], *Shokuhin Eiseigaku Zasshi*, 44, (2003) 181.https://doi.org/10.3358/shokueishi.44.181

[19] L. Zimmermann, G. Dierkes, T.A. Ternes, C. Volker and M. Wagner,Benchmarking the in Vitro Toxicity and Chemical Composition of Plastic Consumer Products, *Environ Sci Technol*, 53, (2019) 11467.https://doi.org/10.1021/acs.est.9b02293

[20] L.S. Kato and C.A. Conte-Junior,Safety of Plastic Food Packaging: The Challenges about Non-Intentionally Added Substances (NIAS) Discovery, Identification and Risk Assessment, *Polymers (Basel)*, 13, (2021).https://doi.org/10.3390/polym13132077

[21] J.C.J. Bart,Polymer/additive analysis by flash pyrolysis techniques, *Journal of Analytical and Applied Pyrolysis*, 58-59, (2001) 3.https://doi.org/10.1016/S0165-2370(00)00160-1

[22] Y. Kudo, K. Obayashi, H. Yanagisawa, F. Maruyama, S. Fujimaki, H. Miyagawa and K. Nakagawa,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*, 1602, (2019) 441.https://doi.org/10.1016/j.chroma.2019.06.014

[23] F.C.-Y. Wang,Polymer additive analysis by pyrolysis–gas chromatography I. Plasticizers, *J. Chromatogr. A*, (2000) 12.https://doi.org/10.1016/S0021-9673(00)00346-0

[24] L. Hermabessiere and C.M. Rochman,Microwave-Assisted Extraction for Quantification of Microplastics Using Pyrolysis-Gas Chromatography/Mass Spectrometry, *Environ Toxicol Chem*, 40, (2021) 2733.https://doi.org/10.1002/etc.5179

[25] F. Akoueson, C. Chbib, S. Monchy, I. Paul-Pont, P. Doyen, A. Dehaut and G. Duflos,Identification and quantification of plastic additives using pyrolysis-GC/MS: A review, *Sci Total Environ*, 773, (2021) 145073.https://doi.org/10.1016/j.scitotenv.2021.145073

[26] F. Maruyama, S. Fujimaki, Y. Sakamoto, Y. Kudo and H. Miyagawa,Screening of phthalates in polymer materials by pyrolysis GC/MS, *Anal Sci*, 31, (2015) 3.https://doi.org/10.2116/analsci.31.3

[27] J.W. Kim, Y.M. Kim, H.M. Moon, A. Hosaka, C. Watanabe, N. Teramae, E.K. Choe and S.W. Myung,Comparative study of thermal desorption and solvent extraction-gas chromatography-mass spectrometric analysis for the quantification of phthalates in polymers, *J Chromatogr A*, 1451, (2016) 33.https://doi.org/10.1016/j.chroma.2016.05.014

[28] M. Llana-Ruiz-Cabello, S. Pichardo, N.T. Jimenez-Morillo, F.J. Gonzalez-Vila, E. Guillamon, J.M. Bermudez, S. Aucejo, A.M. Camean and J.A. Gonzalez-Perez,Pyrolysis-gas chromatography-isotope ratio mass spectrometry for monitoring natural additives in polylactic acid active food packages, *J Chromatogr A*, 1525, (2017) 145.https://doi.org/10.1016/j.chroma.2017.10.023

[29] E.D. Okoffo, F. Ribeiro, J.W. O'Brien, S. O'Brien, B.J. Tscharke, M. Gallen, S. Samanipour, J.F. Mueller and K.V. Thomas,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*, 715, (2020) 136924.https://doi.org/10.1016/j.scitotenv.2020.136924

[30] K.D. Jansson, C.P. Zawodny and T.P. Wampler,Determination of polymer additives using analytical pyrolysis, *Journal of Analytical and Applied Pyrolysis*, 79, (2007) 353.https://doi.org/10.1016/j.jaap.2006.12.009

[31] M. Herrera, G. Matuschek and A. Kettrup,Fast identification of polymer additives by pyrolysis-gas chromatography/mass spectrometry, *Journal of Analytical and Applied Pyrolysis*, 70, (2003) 35.https://doi.org/10.1016/S0165-2370(02)00078-5

[32] International Electrotechnical Commission, 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, Available on: http://mapnamagz.yabesh.ir/std/handle/yse/233172

[33] Y.M. Kim, J.W. Kim, H.M. Moon, M.J. Lee, A. Hosaka, A. Watanabe, N. Teramae, Y.K. Park and S.W. Myung,Rapid Quantification of N-Methyl-2-pyrrolidone in Polymer Matrices by Thermal Desorption-GC/MS, *Anal Sci*, 33, (2017) 821.https://doi.org/10.2116/analsci.33.821

[34] H. Yanagisawa, Y. Kudo, K. Nakagawa, H. Miyagawa, F. Maruyama and S. Fujimaki,Simultaneous Screening of Major Flame Retardants and Plasticizers in Polymer Materials Using Pyrolyzer/Thermal Desorption Gas Chromatography Mass Spectrometry (Py/TD-GC-MS), *Molecules*, 23, (2018).https://doi.org/10.3390/molecules23040728

[35] P. Gimeno, S. Thomas, C. Bousquet, A.F. Maggio, C. Civade, C. Brenier and P.A. Bonnet,Identification and quantification of 14 phthalates and 5 non-phthalate plasticizers in PVC medical devices by GC-MS, *J Chromatogr B Analyt Technol Biomed Life Sci*, 949-950, (2014) 99.http://dx.doi.org/10.1016/j.jchromb.2013.12.037

[36] J. Zhang, Phtalathes Analysis With Method GB 5009.271-2016 Using the Agilent 8890 GC and MSD with Agilent JetClean, 2019, Agilent Technologies Application Notes, Available on: https://www.agilent.com/cs/library/applications/application-phthalates-8890-gc-jetclean-5994-0656en-agilent.pdf

[37] C. Chattelier and F. Lestremau, Considérations sur certains aspects metrologiques liés à la mesure du 4-nonylphénol - Etat de l’art et perspectives – Rapport AQUAREF 2014, 2014, Available on: https://professionnels.ofb.fr/sites/default/files/pdf/2014_109.pdf

[38] M. Bolgar, J. Hubball, J. Groeger and S. Meronek, *Handbook for the chemical analysis of plastic and polymer additives*, Taylor & Francis Group, 2016, p. https://doi.org/10.1201/9781420044881

[39] R. Espejo, K. Valter, M. Simona, Y. Janin and P. Arrizabalaga,Determination of nineteen 4-alkylphenol endocrine disrupters in Geneva municipal sewage wastewater, *Journal of Chromatography A*, 976, (2002) 335.https://doi.org/10.1016/S0021-9673(02)01229-3

[40] M. Frederiksen, K. Vorkamp, R. Bossi, F. Rigét, M. Dam and B. Svensmark,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*, 87, (2007) 1095.https://doi.org/10.1080/03067310701451178

[41] F. Akoueson, C. Chbib, A. Dehaut and G. Duflos, Organic Plastic Additives High-Resolution Mass Spectra., 2022, Zenodo, https://doi.org/10.5281/zenodo.6599058

[42] G. Castello, P. Moretti and S. Vezzani,Retention models for programmed gas chromatography, *J Chromatogr A*, 1216, (2009) 1607.https://doi.org/10.1016/j.chroma.2008.11.049

[43] P. Fields, S. Allen, Z. Korunic, A. McLaughlin and T. Stathers, *Standardised testing for diatomaceous earth*, at: 2003, 779.

[44] B. Kolahgar and E. Pfannkoch, The use of different PTV inlet liner types for trapping alkanes, aromatics and oxygenated compounds during thermal desorption; 2002; Available on: https://www.gerstelus.com/wp-content/uploads/2017/07/technote-2002-03_cis-liner-type.pdf; Accessed on: 22/08/2022;

[45] B. Geueke, C.C. Wagner and J. Muncke,Food contact substances and chemicals of concern: a comparison of inventories, *Food Addit Contam Part A Chem Anal Control Expo Risk Assess*, 31, (2014) 1438.https://doi.org/10.1080/19440049.2014.931600

[46] R Core Team, R: The R Project for Statistical Computing; Available on: https://www.r-project.org/; Accessed on: 2022-05-15;

[47] J. Fox, S. Weisberg, B. Price, D. Adler, D. Bates, G. Baud-Bovy, B. Bolker, S. Ellison, D. Firth, M. Friendly, A. Zeileis and R-Core,Companion to Applied Regression, *R package version*, (2022)

[48] F. De Mendiburu, Statistical Procedures for Agricultural Research, 2021, R package version, Available on: https://cran.r-project.org/web/packages/agricolae/index.html

[49] T. Pohlert, Calculate Pairwise Multiple Comparisons of Mean Rank Sums, 2021, R package version, Available on: https://cran.r-project.org/web/packages/PMCMR/PMCMR.pdf

[50] ECHA, Mapping exercise – Plastic additives initiative; 2019; Available on: https://echa.europa.eu/fr/mapping-exercise-plastic-additives-initiative; Accessed on: 2020/07/02;

[51] J.H. Bridson, E.C. Gaugler, D.A. Smith, G.L. Northcott and S. Gaw,Leaching and extraction of additives from plastic pollution to inform environmental risk: A multidisciplinary review of analytical approaches, *J Hazard Mater*, 414, (2021) 125571.https://doi.org/10.1016/j.jhazmat.2021.125571

[52] E. Fries, J.H. Dekiff, J. Willmeyer, M.-T. Nuelle, M. Ebert and D. Remy,Identification of polymer types and additives in marine microplastic particles using pyrolysis-GC/MS and scanning electron microscopy, *Environmental Science. Processes & Impacts*, 15, (2013) 1949.https://doi.org/10.1039/c3em00214d

[53] F.C.-Y. Wang,Polymer additive analysis by pyrolysis–gas chromatography- II. Flame retardants, *Journal of Chromatography A*, 886, (2000) 225.https://doi.org/10.1016/S0021-9673(00)00538-0

[54] F.C.-Y. Wang,Polymer additive analysis by pyrolysis–gas chromatography - IV. Antioxydants, *Journal of Chromatography A*, 891, (2000) 325.https://doi.org/10.1016/S0021-9673(00)00647-6

[55] EFSA, Scientific Opinion of the Panel on food contact materials, enzymes, flavourings and processing aids (CEF) on 25th list of substances for food contact materials, in *EFSA Journal*, EFSA Journal edn., 2009, Chapter 1-20, p. 1196.https://doi.org/10.2903/j.efsa.2009.1196

[56] A. Venema and R.C. Boom-Van Geest,In-situ hydrolysis/methylation pyrolysis CGC for the characterization of polyaramides, *Journal of Microcolumn Separations*, 7, (1995) 337. https://doi.org/10.1002/mcs.1220070406

[57] I. IyIgUndoGdu, G.A. UstUnda and Y. Duydu,Toxicological Evaluation of Bisphenol A and Its Analogues, *Turk J Pharm Sci*, 17, (2020) 457.https://doi.org/10.4274/tjps.galenos.2019.58219

[58] V. Becerra and J. Odermatt,Detection and quantification of traces of bisphenol A and bisphenol S in paper samples using analytical pyrolysis-GC/MS, *Analyst*, 137, (2012) 2250.https://doi.org/10.1039/C2AN15961A

[59] E.L. Teuten, J.M. Saquing, D.R. Knappe, M.A. Barlaz, S. Jonsson, A. Bjorn, S.J. Rowland, R.C. Thompson, T.S. Galloway, R. Yamashita, D. Ochi, Y. Watanuki, C. Moore, P.H. Viet, T.S. Tana, M. Prudente, R. Boonyatumanond, M.P. Zakaria, K. Akkhavong, Y. Ogata, H. Hirai, S. Iwasa, K. Mizukawa, Y. Hagino, A. Imamura, M. Saha and H. Takada,Transport and release of chemicals from plastics to the environment and to wildlife, *Philos Trans R Soc Lond B Biol Sci*, 364, (2009) 2027.https://doi.org/10.1098/rstb.2008.0284

[60] L. Zimmermann, A. Dombrowski, C. Volker and M. Wagner,Are bioplastics and plant-based materials safer than conventional plastics? In vitro toxicity and chemical composition, *Environ Int*, 145, (2020) 106066.https://doi.org/10.1016/j.envint.2020.106066

[61] L. Zimmermann, Z. Bartosova, K. Braun, J. Oehlmann, C. Volker and M. Wagner,Plastic Products Leach Chemicals That Induce In Vitro Toxicity under Realistic Use Conditions, *Environ Sci Technol*, 55, (2021) 11814.https://doi.org/10.1021/acs.est.1c01103

Figure captions

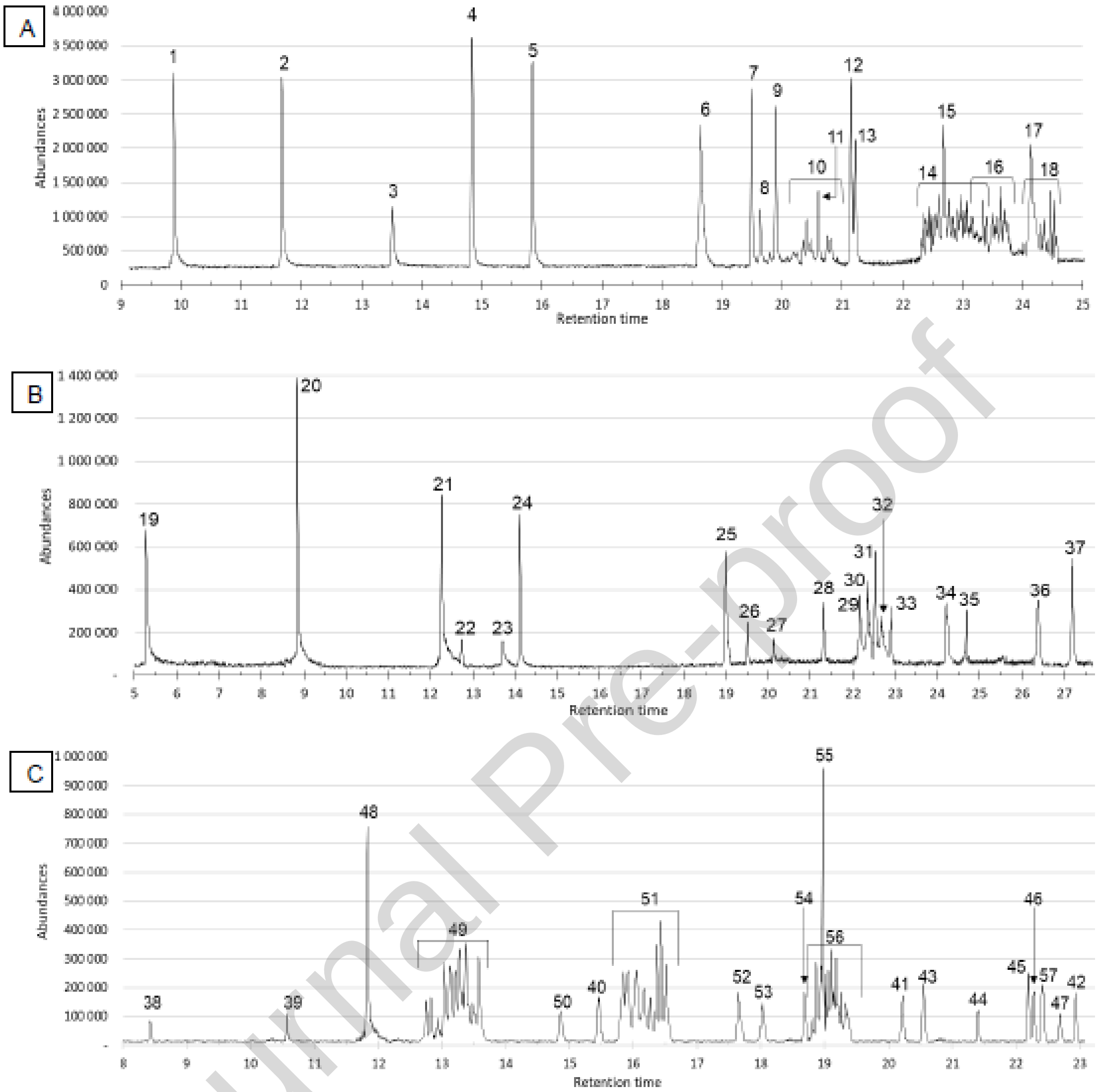

Figure 1: Chromatograms of the targeted plastic additives analyzed using GC-HRMS. (A) plasticizers additives; (B) flames retardants additives; and (C) antioxidants, UV stabilizers and plasticizers additives. The numbers refer to the name of the molecules mentioned in Table 1.

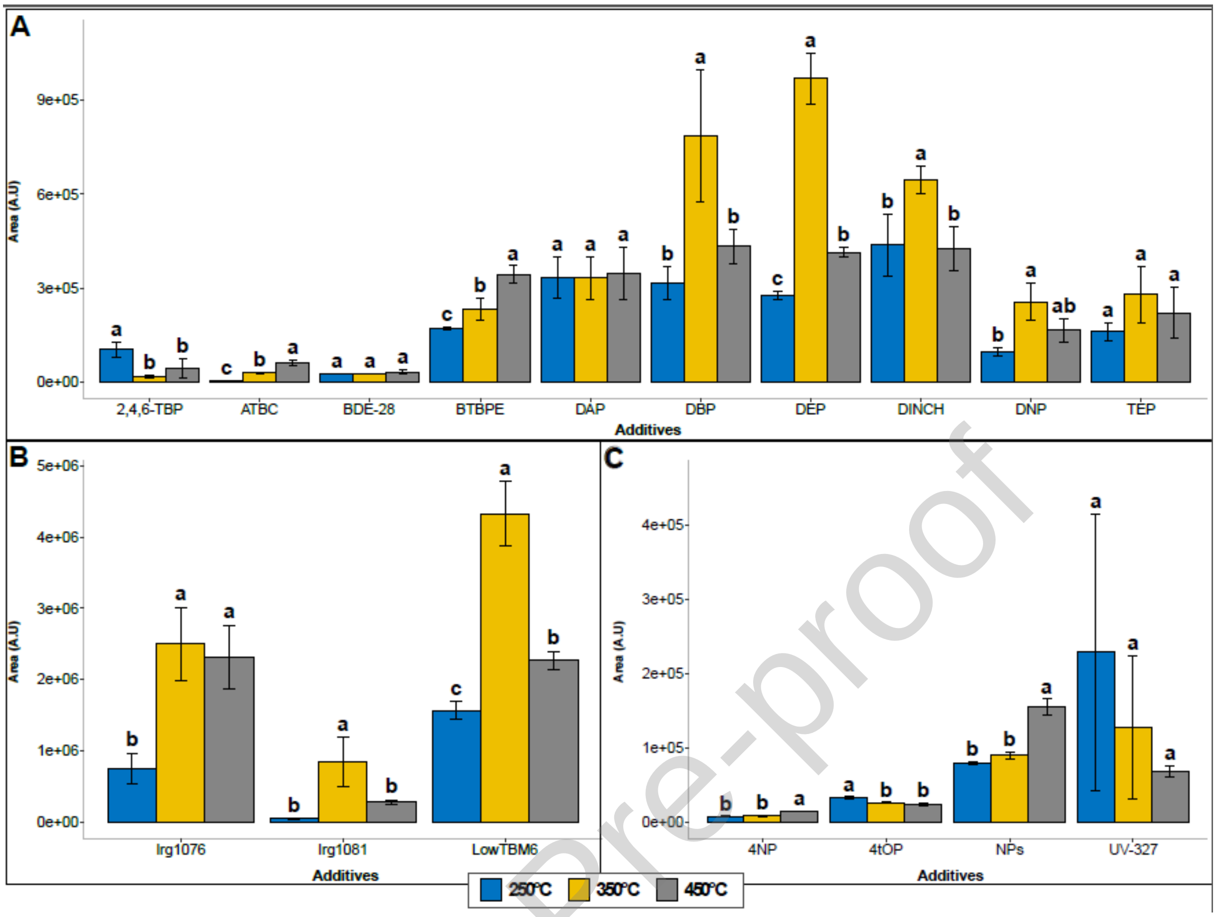

Figure 2: Peak areas of some selected OPAs depending on the thermal desorption temperature (250 °C, 350 °C and 450 °C, respectively in blue, yellow and grey). (A) plasticizers and flame-retardants; (B) antioxidants; and (C) antioxidants and UV-stabilizers. Values are expresses as mean± 95% confidence interval. Homogeneous groups are indicated by the same letter.(n=3).

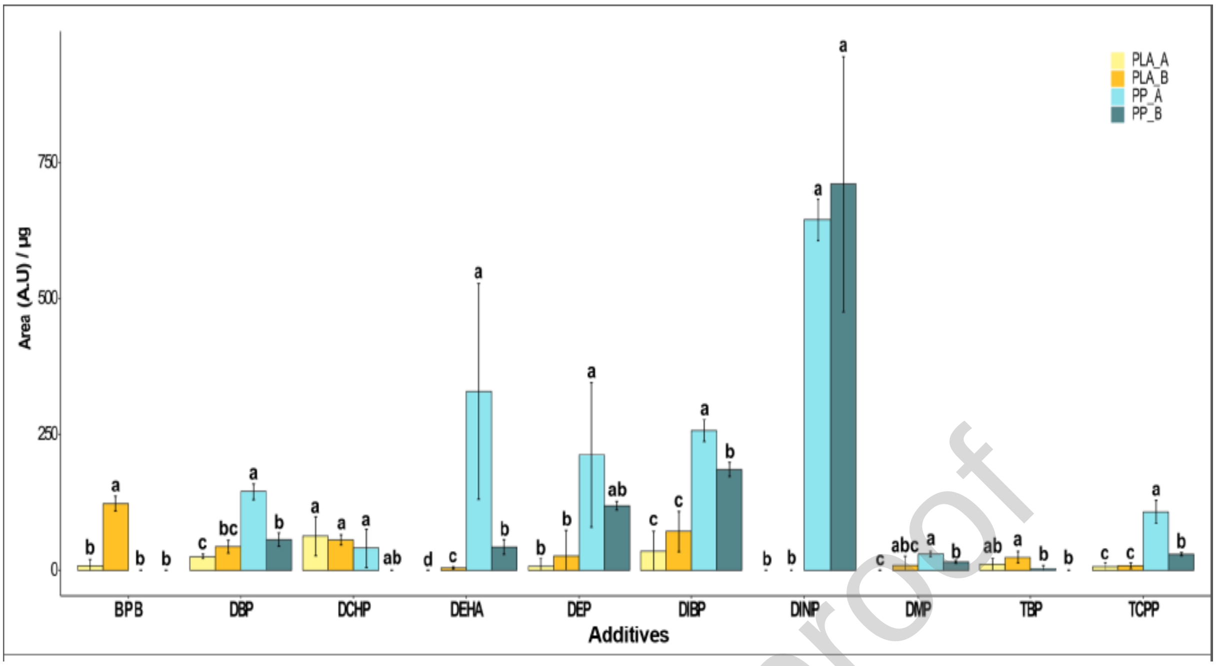

Figure 3: Corrected peak areas of the OPAs found in the 4 food plastic packaging samples in polypropylene (PP) and polylactic acid (PLA). The letters A and B referred to the suppliers. Homogeneous groups are indicated by the same letter. (n=3).

Table 1: selected organic plastic additives (OPAs) with their corresponding suppliers and the quantity that allowed peaks detection using Py-GC-HRMS analysis. The molecules tagged with "*" represent the OPAs not detected (n.d) at the highest concentration available.

Function	**N°**	**Additive**	**Abbreviation**	**CAS**	**Suppliers**	**Limit of detection (ng) (split 5)**
Plasticizers	1	Dimethyl phthalate	**DMP**	**131-11-3**	Restek	5
	2	Diethyl phthalate	**DEP**	**84-66-2**		
	3	Di-allyl phthalate	**DAIP**	**131-17-9**		
	4	Diisobutyl phthalate	**DIBP**	**84-69-5**		
	5	Di-n-butyl phthalate	**DBP**	**84-74-2**		
	6	Tributyl Acetyl Citrate	**ATBC**	**77-90-7**	Accustandard	
	7	Di-n-hexyl phthalate	**DHP**	**84-75-3**	Restek	
	8	Benzyl butyl phthalate	**BBP**	**85-68-7**		
	9	Bis-2-Ethylhexyl Adipate	**DEHA**	**103-23-1**	Accustandard	
	1	Diisoheptyl phthalate	**DIHP**	**71888-**	Accustand	25

Function	N°	Additive	Abbreviation	CAS	Suppliers	Limit of detection (ng) (split 5)
	0			**89-6**	ard	
	11	Tri(2-ethylhexyl) phosphate	**TEHPA ***	**78-42-2**	Accustandard	n.d (at 100)
	12	Dicylcohexyl phthalate	**DCHP**	**84-61-7**	Restek	5
	13	Bis(2-Ethylhexyl) phthalate	**DEHP**	**117-81-7**		
	14	Diisononyl hexahydrophthalate	**DINCH**	**166412-78-8**	Accustandard	
	15	Di-n-octyl phthalate	**DIOP**	**117-84-0**	Restek	
	16	Diisononyl phthalate	**DINP**	**68515-48-0**	Accustandard	25
	17	Di-nonyl phthalate	**DNP**	**84-76-4**	Restek	5
	18	Diisodecyl phthalate	**DIDP**	**68515-49-1**	Accustandard	25
Flames retardants	19	Triethyl Phosphate	**TEP**	**78-40-0**	LGC standard	5
	20	Tripropyl Phosphate	**TPP**	**115-86-6**		
	21	Tributyl Phosphate	**TBP**	**126-73-8**		
	22	2,4,6-Tribromophenol	**2,4,6,TBP**	**118-79-6**	LGC standard	
	23	Tris(2-Chloroethyl)Phosphate	**TCEP**	**115-96-8**	LGC standard	
	24	Tris(2-Chloroisopropyl)Phosphate	**TCPP**	**13674-84-5**	LGC standard	
	25	2,4,4’-Tribromodiphenyl ether	**BDE-28**	**41318-75-6**	Accustandard	10
	26	Tris(1,3-Dichloro-2-Propyl)Phosphate	**TDCPP**	**13674-87-8**	LGC standard	5
	27	Triphenyl Phosphate	**TPhP**	**513-08-6**		
	28	2,2’,4,4’-Tetrabromodiphenyl ether	**BDE-47**	**5436-43-1**	Accustandard	10
	29	Tricresyl Phosphate	**TCP ***	**1330-78-5**	Accustandard	n.d (at 100)
	30	Tricresyl Phosphate - isomer	**TCrP ***	**78-30-8**		n.d (at 100)
	31	2,2’,4,4’,6-Pentabromodiphenyl ether	**BDE-100**	**60348-60-9**	Accustandard	5
	32	Tri-o-tolyl phosphate	**TToP ***	**78-30-8**	Accustandard	n.d (at 100)
	33	2,2’,4,4’,5-Pentabromodiphenyl ether	**BDE-99**	**189084-64-8**	Accustandard	10
	34	2,2’,4,4’,5,5’-Hexabromodiphenyl ether	**BDE-153**	**68631-49-2**		
	35	2,2’,4,4’,5,6’-Hexabromodiphenyl ether	**BDE-154**	**207122-15-4**		
	36	2,2’,3,4,4’,5’,6-Heptabromodiphenyl ether	**BDE-183**	**207122-16-5**		

Function	N°	Additive	Abbreviation	CAS	Suppliers	Limit of detection (ng) (split 5)
	37	1,2-Bis (2,4,6 Tribromophenoxy) ethane	**BTBPE**	**37853-59-1**	LGC Standard	25
Antioxidants	38	6,6'-di-tert-butyl-2,2'-thiodi-p-cresol	**Irganox® 1081**	**90-66-4**	Accustandard	10
	39	Butylated hydroxytoluene	**BHT**	**128-37-0**	Accustandard	5
	40	3,5-di-tert-butyl-4-hydroxyhydrocinnamic acid, octadecyl ester	**Irganox® 1076**	**2082-79-3**	Accustandard	100
	41	6,6'-ditert-butyl-4,4'-thiodin-m-cresol	**Lowinox® TBM-6**	**96-69-5**		50
UV stabilizers	42	2,2-dihydroxy-4,4-dimethoxybenzophenone	**Uvinul® 3049 ***	**131-54-4**	Accustandard	n.d. (at 100)
	43	2-t-Butyl-6(5-chloro-2H-benzotriazol-2-yl)-4-methylphenol	**UV-326**	**3896-11-5-**		5
	44	2-(2H-Benzotriazol-2-yl)-4,6-di-tert-pentylphenol	**UV-328**	**25973-55-1**		
	45	2,4-Di-tert-butyl-6-(5-chloro-2H-benzotriazol-2-yl)phenol	**UV-327**	**3864-99-1**		
	46	2-hydroxy-4-octyloxybenzophenone	**Uvinul 3008 ***	**1843-05-6**		n.d. (at 100)
Antioxidants – plasticizers - stabilizers	47	4-Tert-Octylphenol	**4-t-OP**	**140-66-9**	Accustandard	5
	48	Nonylphenol	**NPs**	**84852-15-3**	Accustandard	10
	49	4-nonylphenol	**4-NP**	**104-40-5**	Accustandard	
	50	Nonylphenol Monoethoxylate	**NP1EO**	**27986-36-3**	Accustandard	
	51	Bisphenol F	**BPF**	**620-92-8**	Accustandard	5
	52	4-Nonylphenol Monoethoxylate	**4-NP1EO**	**104-35-8**	Accustandard	10
	53	Bisphenol A	**BPA**	**80-05-7**	Accustandard	5
	54	Bisphenol B	**BPB**	**77-40-7**		
	55	Nonylphenol diethoxylate	**NP2EO ***	**N/A**	Accustandard	n.d. (at 10)
	56	Bisphenol S	**BPS ***	**80-09-1**	Accustandard	n.d (at 100)

Table 2: GC-HRMS analytical conditions

Parameters	**Settings**
GC	
Injection port temperature	300°C
Column temperature (°C)	80°C (0.5 min) → 10°C/min → 330°C (3 min)
Injection mode	Split (split ratio 1:5)
Carrier gas	Helium
Carrier Gas flow	1 mL.min^{-1}
Transfer line temperature	300°C
MS	
Ion source temperature	300°C
Ionization method	Electron Ionization (EI), 70 eV.
Analytical mode	Full Scan mode (FS)
Scan Range	30.00000 – 750.00000 m/z
Solvent Delay	5 min

Table 3: Kováts retention indices (RI) values and quantitative and qualitative ions for the selected plastic additives molecules. n.d. = not detected.

Function	Molecules	RI	Quantitative ions	Qualitative ions
Plasticizers	**DMP**	1469	163.03888	133.02846
	DEP	1608	149.02333	177.05455
	DAlP	1756	149.0231	189.05432
	DIBP	1872	149.02333	161.05917
	DBP	1972	149.02333	160.08830
	ATBC	2160	129.01845	259.15451 ; 137.99502
	DHP	2374	149.02333	234.12006
	BBP	2401	149.02333	206.09376
	DEHA	2404	111.04393	101.05960 ; 129.05444
	DIHP	2380 - 2509	149.02333	265.14313 ; 99.11672
	TEHPA	2477	98.98428	113.13261
	DCHP	2558	149.02333	249.11210
	DEHP	2570	149.02333	279.15909
	DINCH	2630 – 2870	155.07002	109.06474 ; 127.07529
	DIOP	2756	149.02333	261.14876
	DINP	2731 – 2867	149.02323	71.08553
	DNP	2936	149.02333	293.17474
	DIDP	2876 - 3010	149.02332	n.d.
Flames retardants	**TEP**	1124	98.98432	127.01567 ; 109.00512
	TPP	1383	98.98432	141.03133
	TBP	1650	98.98432	211.10963
	2,4,6,TBP	1656	331.76931	222.85798
	TCEP	1769	142.96611	222.96906 ; 248.98479
	TCPP	1808	125.00023	201.00710 ; 156.98178
	BDE-28	2283	245.96733	139.05414
	TDCPP	2354	98.98432	190.94284 ; 154.96611
	TPhP	2421	325.06296	233.03670 ; 215.02596
	BDE-47	2550	325.87582	323.87792
	TCP	2676	165.07015	243.05746 ; 368.11771
	TCrP	2707		
	BDE-100	2763	403.78613	563.62171
	TToP	2738	165.07015	243.05746 ; 368.11771
	BDE-99	2823	405.78452	563.62171
	BDE-153	3000	483.69452	242.84599 ; 643.53162
	BDE-154	3092		
	BDE-183	3375	563.60352	281.80109
	BTBPE	3453	356.79514	277.87637
Antioxidants	**Irganox® 1081**	1366	149.09674	164.12027
	BHT	1520	205.158752	206.16206
	Irganox® 1076	3611	147.08102	263.16534 ; 217.15947
	Lowinox® TBM-6	2795	358.19647	259.07922
UV stabilizers	**Uvinul® 3049**	2503	151.03903	257.08099 ; 124.05204
	UV-326	2575	300.08972	272.05853
	UV-328	2681	322.19113	351.23003
	UV-327	2692	342.13678	357.16034 ; 286.07428
	Uvinul 3008	2790	213.05461	325.17978 ; 137.02342
Antioxidants; Plasticizers; Stabilizers	**4-t-OP**	1611	135.08041	206.16644
	NPs	1700 – 1770	135.08041	197.13233 ; 212.15582
	4-NP	1873	107.04916	221.18555
	NP1EO	1969 - 2030	179.10652	193.12220
	BPF	2104	200.08276	n.d
	4-NP1EO	2146	107.04916	151.07530 ; 264.20834
	BPA	2221	213.09113	228.11452
	BPB	2321	213.09065	227.10631

Function	Molecules	RI	Quantitative ions	Qualitative ions
	NP2EO	2027 - 2321	107.04916	151.07530 ; 264.20834
	BPS	2765.2777	141.00046	110.03627

Table 4: average extraction efficiency percentages and, in parenthesis, standard deviations of the method following the 1st pyrolysis step, after analyzing the additive content of PLA and PP samples (n=3). Each sample was successively analyzed 3 times at 350 °C. Bold printed characters represent average extraction efficiencies >80%. n.d = not detected.

	PLA-A	**PLA-B**	**PP-A**	**PP-B**
DMP	n.d	33 (56)	79 (10)	48 (9)
DEP	**90 (17)**	**95 (9)**	70 (4)	65 (9)
DBP	**94 (10)**	**99 (3)**	**100 (0)**	**100 (0)**
DIBP	**98 (3)**	**98 (3)**	**100 (0)**	**100 (0)**
DCHP	**100 (0)**	**100 (0)**	**100 (0)**	n.d
DINP	n.d	n.d	**87 (2)**	**88 (4)**
DEHA	n.d	**90 (18)**	59 (36)	**93 (2)**
TBP	59 (51)	**93 (6)**	23 (40)	n.d
TCPP	62 (54)	76 (9)	65 (5)	79 (11)
BPB	**100 (0)**	**93 (2)**	n.d	n.d

CRediT authorship contribution statement

F.Akoueson: Conceptualization, Investigation, Methodology, Formal analysis, Software, Validation, Visualization, Writing - original draft, Writing - review & editing. **C. Chbib**: Methodology Investigation, Writing - review & editing. **A. Brémard**: Investigation, Formal analysis. **S. Monchy**: Writing - review & editing. **I. Paul-Pont**: Writing - review & editing. **P. Doyen**: Writing - review & editing. **A. Dehaut**: Conceptualization, Funding acquisition, Supervision, Project administration, Writing - review & editing. **G. Duflos**: Resources, Conceptualization, Funding acquisition, Supervision, Project administration, Writing - review & editing.

Declaration of Competing Interest

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

Highlights

- A single method for the analysis of OPAs using Py/TD-GC-HRMS has been implemented
- The developed method allowed to create a plastic additive database
- 49 additives molecules out of the selected 57 have been successfully identified
- 10 plastic additives were found in PP and PLA food packaging