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# New method for extraction, identification, and quantification of non-intentionally added substances in polystyrene

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## Abstract

An efficient one-step extraction method was developed for the recovery of additives and non-intentionally added substances (NIAS) from polystyrene, performed at room temperature for 2.33 h, without grinding to avoid fostering the formation of NIAS unrelated to polymer processing. Solvent use (39.2 mL/g) was greatly reduced compared with extraction conditions previously reported. The study of NIAS is analytically challenging but with high importance since their presence is a potential threat to human health and to the environment while reducing plastic potential recyclability. For an understanding of NIAS formation and influence of processing parameters, a systematic approach was taken, using virgin polystyrene mixed with known quantities of standard additives as model materials (Irganox\_1076, Tinuvin\_326, Irgafos\_168). The degradation of one additive was identified by NMR and GC–MS. Precise multiple-point quantification with internal standard was performed by GC–MS, measuring a 5.1 wt% Irgafos\_168 degradation, with additives LOD ranging from 0.55–0.95 ppm. Evaluation of analytical challenges, such as matrix effects, was discussed and quantified. This method will help the quality control of virgin and recycled PS materials, including food contact ones, and improve the knowledge of PS processing impact on NIAS formation.

## KEYWORDS

extraction, GC–MS quantification, NIAS, polystyrene

## 1 | INTRODUCTION

In a context where the global plastic waste production might reach 1231 Mt/a in 2060 if no serious measures are implemented,<sup>1</sup> the treatment of end-of-life plastic material is paramount. So far, only 9%–10% of these wastes are being recycled globally. In Europe, this represents

26.9% of plastic wastes generated being recycled (2024),<sup>2</sup> whereas the objective is set at 50% by 2025 by the European authorities. Additives (from a few percents up to 20–30 wt%), also called IAS for Intentionally-Added-Substances, are usually added to virgin polymers to reach the specifications of the plastic objects: antioxidant, light stabilizer, flame retardant, and so forth. During the service

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life, the processing or the recycling of plastic materials, these additives can interact with the polymer matrix, with newly formed molecules (for example due to UV degradation) and/or degrade. Thus, the formation of non-intentionally added substances (NIAS) can result from the degradation of the polymer, of additives used, of contaminants, or from the interactions between these three categories. Aside from contaminants, additive degradation products are the major source of NIAS.<sup>3</sup> As an example, up to 100,000 NIAS could migrate from food contact materials (FCM) into food,<sup>4</sup> and some NIAS are still unidentified and thus unquantified.<sup>5</sup> The presence of these NIAS in recycled plastics raises several concerns such as environmental and human health threat<sup>4</sup> as they are estimated to amount 100 times more regarding migration from material to food compared with pesticides and environmental pollutants.<sup>6</sup> Their presence can also impact on the efficient recyclability of plastics by increasing the presence of undesired species and potentially impairing the properties of the material. Finally, their presence can hinder the efficiency of closed-loop recycling<sup>3</sup> for FCM for example, as materials recycled with other non-FCM will no longer meet the requirements for food application. Thus, to meet the recycling guidelines, the formation of NIAS needs to be better understood in order to minimize it by adjusting recycling parameters and reduce their presence and impact.

The analytical study of NIAS is usually performed by GC-MS or LC-MS (gas and liquid chromatography coupled with mass spectrometry) after standard solvent extraction or using dissolution/precipitation studies. Examples of headspace or thermal desorption of additives and NIAS have also been reported.<sup>7</sup> The advantages and limitation of each strategy and analytical method have been recently extensively described by Nern et al.<sup>7</sup> Concerning FCM, NIAS assessment is usually carried by migration tests using food simulants or real food followed by their identification using GC-MS or LC-MS.<sup>3,7</sup>

## 1.1 | IAS and NIAS extraction from polystyrene

Few examples of NIAS extraction from polystyrene have been reported in the literature, some are reported in Table 1, mainly focusing on the studied additives. Other extraction strategies have been investigated in the literature for the extraction or removal of flame retardant from styrenic materials<sup>8–10</sup> and will be discussed in later works. A standard extraction approach is the use of dissolution of the material followed by the precipitation of the polymer matrix. However, this method usually requires a lot of solvent: 100–200 mL/g of polystyrene (PS)<sup>11,12</sup> and resulted in poor yields for some of the additives such as Irganox\_1076 (22% in one extraction step<sup>12</sup>) or requiring many extraction and filtration steps (up to 8).<sup>11</sup> Smith et al. reported an improved extraction method using supercritical fluids (SFE with CO<sub>2</sub>) lowering the amount of solvent used for the extraction drastically (2 mL/g). However, a preliminary grinding was required, which could cause polymer or additive degradation into NIAS not related with the original material. Furthermore, cooling down to 4°C was required, increasing the energy use, on top of the more complex apparatus setup required for SFE. Furthermore, the use of cryomilling for thermoplastic particle size reduction was found to induce cracking<sup>13</sup> and impact molecular mass distribution and thermal properties of the materials.<sup>14</sup> Also, SFE processes were found to exhibit low extraction efficiency for higher polarity additives.<sup>15</sup> To this date, a simpler and more efficient extraction method for the additives studied is thus elusive. Concerning the extraction of PS intrinsic NIAS (monomer, and oligomers of styrene), the extraction method developed by Nagao et al.<sup>11</sup> was used by Gelbke et al.<sup>16,17</sup> or they were investigated within migration studies to mimic better the reality of FCM.<sup>18–21</sup>

TABLE 1 NIAS extraction methods reported in the literature.

Reference	Strategy	Total solvent amount (mL/g of PS)	Number of extraction steps	Total time <sup>a</sup> (h)	Temperature (°C)	Extraction yield (%)
Nagao et al. <sup>11</sup>	Repeated dissolution/precipitation in acetone/methanol	200	8	16 + 8 (filtrations)	40	Unknown
Smith et al. <sup>12</sup>	Dissolution (chloroform)/precipitation	100	1	2	Unknown	22 (Irganox_1076)
Smith et al. <sup>12</sup>	CO <sub>2</sub> SFE on grinded PS	2	2	2.33	4	100 (Irganox_1076)

Abbreviations: NIAS, non-intentionally added substances; SFE, supercritical fluid extraction.

<sup>a</sup>only includes extraction time and filtration steps and solvent evaporation as these were not specified.

## 1.2 | NIAS identification and quantification

The study of NIAS presence in polymers and recycled materials presents several challenges. Firstly, analytic limitations can hinder their identification and quantification as numerous chemical entities are present in the samples, sometimes in very small quantities. Thus, identification strategy might require the use of spectra libraries, and their quantification might require the use of standards, which are not always commercially available. Furthermore, NIAS study performed with different analytic strategies or analytic equipment might not give the same results, rendering relevant comparison difficult and showing the importance of a relevant and efficient extraction/identification/quantification plan.<sup>7</sup> Finally, when no information is available on the initial composition of the material, no quantitative conclusions can be drawn in terms of degradation pattern and mechanisms.

Few examples of the study of NIAS in polystyrene were reported, especially concerning the impact of the processing or recycling parameters on their formation or the interaction between PS matrix and impurities with the additives or their degradation products. Using the extraction procedure described by Nagao et al.<sup>11</sup> Gelbke et al. identified and quantified with precision the composition of the NIAS inherently present in polystyrene.<sup>17</sup> These NIAS were identified as residual oligomers of styrene: dimers and trimers accounting altogether for 980–12,620 mg/kg of PS. However, even if these oligomers of styrene could migrate into food for FCM, their presence was proven to have no endocrine activity after in vitro and in vivo study,<sup>16</sup> and no effect on reproductivity when assessing their impact on rats.<sup>11</sup> In another study, the analysis of the composition of the volatile organic compounds from virgin and recycled expanded polystyrene food containers allowed for the identification of 99 NIAS, helping to assess the quality of a recycled EPS compared with a virgin polymer. Despite meeting the threshold for EU regulation, these materials can be responsible for the leaching of many chemicals in food or the environment, including a high amount of styrene and styrene derivatives.<sup>22</sup> Tsochatzis et al. presented a fast GC–MS method for quantification of certain additives and NIAS after migration process using a food stimulant, followed by a liquid–liquid extraction. It was concluded that for some samples, the sum of styrene oligomers measured exceeded the limit of 10 µg/kg set by the European Food Safety Authority (EFSA).<sup>23</sup> Finally, several studies have investigated the migration of monomeric styrene, its oligomers or oxidation degradation products such as styrene oxide from FCM using food stimulants or real food, as well as covering

exposure and potential health risks for consumers.<sup>18,20,21,24–26</sup>

Overall, several studies have thus been conducted on NIAS identification, quantification and migration in PS, especially concerning PS intrinsic NIAS such as styrene monomer, oligomers or styrene oxide, using different strategies. However, to the best of the author's knowledge, none have reported a complete investigation of the proportion of degradation of additives or NIAS present in the original polymer with a known composition, especially for polystyrene. Indeed, a better understanding of the degradation products of the additives and their percentage of formation, linked to the recycling processing parameters would be of high interest to gain further insights on NIAS formation and relation with thermomechanical history. As the study of NIAS from polymers and recycled polymers is an analytical challenge, the work presented herein takes a systematic approach to obtain an in-depth understanding of the interactions between polymer, IAS and NIAS. The rigorous strategy adopted focused on model materials containing virgin polystyrene and known quantities of additives to evaluate their potential degradation and the interactions between the species present. Three common PS additives will be investigated in this first study: two antioxidants (Irganox\_1076 and Irgafos\_168) and one UV-stabilizer (Tinuvin\_326). Moreover, they will be introduced in the polymer matrix a higher quantity than their usual amount to over-express these chemical interactions.

An efficient extraction process to recover IAS and NIAS from the matrix without fostering their formation was developed, as a simpler alternative compared with existing protocols. The thermoplastic was processed using a small-scale polymer mixer, mimicking the recycling process. From the recovered material, IAS and NIAS were extracted, identified, and quantified using NMR and GC–MS. An in-depth study of the analytical influencing parameters was presented, such as matrix and co-matrix effects for GC–MS quantification. This allowed to identify and to quantify several of those substances, helping to understand their formation and adjust the recycling parameters to reduce or prevent their formation in the future. This extraction process could also be used to assess the quality of PS materials (virgin or recycled), including FCM.

## 2 | MATERIALS AND METHODS

### 2.1 | Chemicals

Chloroform (≥99.9%), *n*-hexane (≥99%), butylated hydroxytoluene (BHT): 2,6-Di-*tert*-butyl-4-methylphenol (≥99%) were purchased from Sigma-Aldrich (St. Louis,

MO, USA). Methanol ( $\geq 99.8\%$ ) was obtained from Alfa Aesar (Fair Lawn, NJ, USA). Styron™ 660 polystyrene was a gift from Trinseo (PA, USA). Irganox\_1076 ( $\geq 99\%$ ): Octadecyl 3-(3,5-di-tert-butyl-4-hydroxyphenyl)propionate was a gift from Barbier (France). Tinuvin\_326/UV\_326 ( $\geq 99\%$ ): 2-tert-Butyl-6-(5-chloro-2H-benzotriazol-2-yl)-4-methylphenol and Irgafos\_168/Alkanox\_240 ( $\geq 99\%$ ): Tris(2,4-di-tert-butylphenyl) phosphite were gifts from BASF (Germany).

## 2.2 | Polymer mixing

To mimic the recycling process of polystyrene, the polymers were mixed using a ThermoHaake PolyLab System–Rheomix 600p mixer equipped with Roller-Rotors R600. 5 wt% of each additive were added alongside polystyrene Styron\_660 (Table 2) to reach 50 g under the following conditions: 210°C, 10 min, 20 rpm screw speed. Data were gathered using the PolyLab Monitor. The polymer mixer was cleaned using a mix of polymer and cleaning agent Asaclean® (provided by IMCD), processed at 140°C for 10 min.

## 2.3 | Extraction of IAS and NIAS from PS

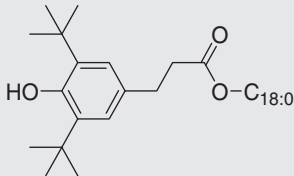
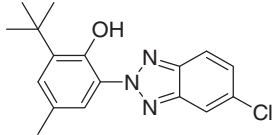
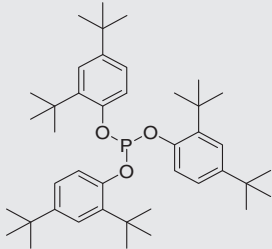
5 g of processed polystyrene was dissolved in 25 mL of  $\text{CHCl}_3$  (200 g/L) and stirred magnetically at room

temperature until complete dissolution (90–120 min depending on chunk size). 150 mL of MeOH/*n*-hexane (1:1, v:v) was added at room temperature to precipitate the polymer and recover the impurities, left under stirring (1000 rpm) for 10 min, followed by 10 minutes under sonication. The solvent mixture was recovered, then the swelled polystyrene was pressed to recover the liquid trapped inside and rinsed with 10 mL of the solvent mixture. The mixture was dried under reduced pressure at 40°C using a rotary evaporator. The recovered extract was solubilized in chloroform (1 mL) and precipitated in the solvent mixture (10 mL) as described above. The new mixture is filtrated with a 0.45  $\mu\text{m}$  PTFE syringe filter to remove the traces of polystyrene that could remain. The extracts were then characterized by NMR and GC–MS.

## 2.4 | Nuclear Magnetic Resonance (NMR) analysis

$^1\text{H}$  NMR,  $^{31}\text{P}$  NMR spectra were recorded on a Bruker® Avance™ 400 or 500 MHz spectrometer in  $\text{CDCl}_3$  solution with the internal solvent signal as a reference. NMR data are reported as follows using Topspin software: chemical shift (ppm), multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, quint = quintet, dd = doublet of doublets, m = multiplet or broad singlet), coupling constants (Hz), the number of protons (for  $^1\text{H}$  NMR) and assignment.

TABLE 2 Theoretical composition of each sample alongside additive description and structure.

Sample	Theoretical PS/additive amount (%)	Additive	Additive function	Additive structure
1	100/0	-	-	-
2	95/5	Irganox_1076	Primary antioxidant	
3	95/5	Tinuvin_326	UV-stabilizer	
4	95/5	Irgafos_168	Secondary antioxidant	



## 2.5 | GC–MS analysis

Analytes were weighed in 1.5 mL GC–MS vials and diluted in GC-grade chloroform using micropipettes. GC–MS analyses were performed using a Shimadzu GC-2010 with a ZB-5MS column (20 m × 0.18 mm × 0.18 μm, 100 mL/min) using helium as carrier gas (0.64 mL/min flow rate) and a GCMS-QP2010S detector (electron impact at 200°C). Column heating profile was from 80 to 315°C at a rate of 10°C/min with an injection at 250°C (split mode, 150 ratio).

## 2.6 | GC–MS calibration

The quantification was performed by means of GC–MS using a multiple point internal standard strategy. For optimal significance of the calibration curves, both area and height intensities (GC) were used to draw the respective curve for each additive. The intensity in area was found to exhibit lower standard deviation and variation coefficient as well as higher coefficient of determination  $R^2$  of the regression model. BHT (di-butyl-hydroxy toluene) was chosen as internal standard (IS), being structurally similar to the studied additives without interfering with the signals of these additives. A GC–MS of the BHT standard was performed to verify its purity and acquire the retention time (8.426 min) and fragmentation pattern (220, 205, 189, 177, 145, 57) as a reference. The possible concentrations of additives in the samples can range from 0.2–0.67 g/L depending on the number of additive present. Thus, the calibration should cover at least this range of concentration for each additive. The multiple point internal standard calibration was performed with 5 points (0.1, 0.3, 0.5, 0.7, 0.9 g/L) for each additive, each replicated 5 times, as presented in Table S5. The obtained calibration curves were tested with fake unknowns to verify their reliability. Variation (absolute value, compared with initial concentration) from sample concentration of the fake unknown to the calculated concentration were found to be up to 0.68% for Irganox\_1076, 0.56% for Tinuvin\_326 and 0.6% for Irgafos\_168.

## 2.7 | GC–MS quantification

### 2.7.1 | Preparation of samples

Around 1 mg (exact mass noted as  $m_{GC}$ ) of sample was diluted in 1.5 mL of  $\text{CHCl}_3$  alongside 1 mg of the internal standard. All quantification analyses were performed in 5 replicates.

### 2.7.2 | Calculations

The total mass of additive ( $m_{add}$ ) in the extraction product can be calculated based on the concentration of additive ( $C_A$ ) and mass of additive in the GC–MS sample ( $m_A$ ) (Equation 1).  $m_{extr}$  corresponds to the mass of extraction product obtained and  $m_{GC}$  the mass of this product used for this analysis, with a sample volume of 1.5 mL. The extraction percentage of the additive was calculated thanks to the quantification by GC (Equation 2), with the theoretical mass of additive extractable ( $m_{th}$ ) obtained by calculation of the exact composition of the mixed polymer thanks to NMR interpretation.

$$m_{add} = m_A \times \frac{m_{extr}}{m_{GC}} = C_A \times 1.5 \times \frac{m_{extr}}{m_{GC}}. \quad (1)$$

Equation (1) represents the calculation of the total mass of additive in the extraction product.

$$\%_{Extr} = \frac{m_{add}}{m_{th}} \times 100. \quad (2)$$

Equation (2) represents the calculation of the extraction percentage corresponding to each additive.

The degradation percentage, or percentage of NIAS formation, was calculated using the rest of the mass from the extraction product and the amount of impurities recovered from PS that is extracted ( $m_{impur-PS}$ ), with  $m_{tot}$  representing the mass of PS sample used for the extraction. From the extractions (7 replicates) carried on unprocessed and processed PS (Styron\_660), the middle value of PS intrinsic impurities extracted is equal to  $m\%_{impur-PS} = 7.3 \text{ mg/g}_{PS}$ .

$$m_{NIAS} = m_{extr} - m_{add} - m\%_{impur-PS} \times m_{tot}. \quad (3)$$

Equation (3) represents the calculation of the mass of NIAS formed.

$$\%_{degradation} = \frac{m_{NIAS}}{m_{add} + m_{NIAS}} \times 100. \quad (4)$$

Equation (4) represents the calculation of the degradation percentage of each additive.

Finally, this degradation percentage, or percentage of NIAS formation does not distinguish degradation products. If several products of degradation were to be observed, this method would only give the overall degradation percentage. A quantification using calibration curve for each degradation product would be necessary to have the individual degradation percentage in this case. The degradation product would have to be commercially available or easily synthesisable.

## 3 | RESULTS AND DISCUSSION

### 3.1 | Extraction method

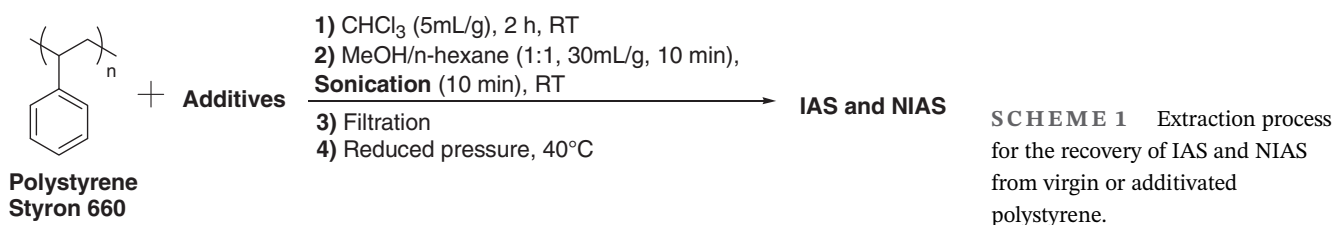
Virgin or additivated polystyrene PS\_Styron\_660 was processed using a polymer mixer to mimic recycling conditions. The final material was recovered as a hard plastic in big chunks. Using the extraction method developed, three common additives for PS were investigated: Irganox\_1076, a primary antioxidant, Tinuvin\_326, an UV absorber and Irgafos\_168, a secondary antioxidant (Table 2). Four materials were investigated within this study: non-additivated PS\_Styron\_660, and single-additivated PS containing each one of the additives described (5 wt%) (Table 2).

A robust extraction method allowing the study of a wide range of additives and their eventual degradation was developed as a simpler alternative to described extraction conditions (Scheme 1). 5 grams of processed polymer were dissolved in chloroform at room temperature (RT). Up to 2 h were necessary as the polymer was used as chunks as no grinding or other post-processing steps were performed after the polymer mixing. Chloroform proved to be an efficient solvent for the solubilization of the polymer as well as the common additives used for styrene. An equivolumetric mixture of two non-solvent of PS was used as precipitation solvent: methanol and *n*-hexane, and the mixture was stirred for 10 min at RT. This caused the precipitation of the polymer into a

swelled solid while the additives and NIAS stayed in solution. The mixture was then kept under sonication for 10 more minutes to promote ultrasonic assisted extraction. The swelled PS was rinsed, and the extract was dried using a rotary evaporator. The extraction product obtained was solubilized in chloroform again (1 mL) and precipitated using the mix of solvent (10 mL) and subsequently filtered upon 0.45  $\mu\text{m}$  PTFE syringe filter to eliminate the last traces of PS. The rest of the solvent was removed under reduced pressure, yielding the final extraction product.

Solubilization and precipitation solvent amounts were optimized as follows: as little chloroform as possible was added to fully solubilize polystyrene (5 mL/g). Precipitation solvent mixture quantity was minimized while keeping an efficient precipitation of polystyrene in a swelled solid that could be removed in one block (30 mL/g). This allowed to avoid potentially hour-long filtration step<sup>12</sup> by simply removing PS as a block, while extracting most of the additives of interest. A simple syringe filtration was performed (5 min) at the end of the process to eliminate the eventual traces of PS.

Several advantages can be outlined for this new extraction method (Table 3). First, the polystyrene does not require grinding, which can prove to be difficult. Indeed, even though PS is very brittle, its grinding induce rapid heating of the material leading to the expansion of PS that could degrade the polymer or the additives, introducing NIAS not related to the processing or recycling step. To prevent this, PS is often grinded under liquid



**TABLE 3** Comparison between extraction conditions for PS IAS and NIAS. D/P = dissolution followed by precipitation.

	D/P <sup>11,16</sup>	D/P <sup>12</sup>	SFE <sup>12</sup>	New method (D/P)
Grinding	No	No	Yes	No
Number of cycles	8	1	1–2	1
Extraction time (h)	16	1	1.17–2.33	2.33
Extraction temperature (°C)	40	Unknown	4	Room temperature
Filtration time (h)	8	1	-	0.08
Total solvent used (mL/g of PS)	200	100	2	39.2
Apparatus	Unknown	Unknown	Supercritical $\text{CO}_2$ extractor	Round-bottomed flask and syringe
Yields (Irganox_1076)	Unknown	22%	Up to 100%	96.6%

Abbreviations: NIAS, non-intentionally added substances; SFE, supercritical fluid extraction.

nitrogen cooling<sup>27</sup> to keep the material and apparatus at low temperature (cryomilling). However, cryomilling is known to alter material properties,<sup>13,14</sup> while adding an energy-intensive step. Second, the one-step extraction process is efficient with a total extraction time of 2.33 h (plus drying step), compared with the multiple steps<sup>11</sup> or hours-long extraction protocols reported so far.<sup>12</sup> Also, the process is carried out at room temperature eliminating the risk of polymer or additive degradation that would result in NIAS formation not related to the mixing process. The process does not require complicated apparatus like supercritical fluid extraction would and can be performed on a larger scale. Also, the proposed method allows for the exact determination of the extraction yield, knowing the initial composition of the material. Finally, the developed conditions should allow for the study of a wide range of additives and NIAS having various polarity and solubility profiles, using the simplest laboratory apparatus possible (round bottomed flask and syringe filter).

### 3.2 | Polystyrene intrinsic NIAS

The described extraction protocol was applied on both virgin polystyrene and processed virgin PS to assess the impact of the mixing process on the stability of the polymer and its intrinsic impurities, as proof of concept. After drying, the extraction product of virgin PS sample was obtained:  $m\%_{\text{impur-PS}} = 7.3 \text{ mg/g of PS}$ , and was composed of styrene oligomers. This value is the result of 7 replicates with a variation coefficient equal to 0.18. This variance is induced by impurities that are gathered during the extraction process such as di-ethylhexyl-phthalate (DEHP, GC-MS: 18.437 min, fragmentation pattern: 279, 167, 149, 57 m/z) traces gathered during the syringe filtration. No difference in quantity or composition of PS NIAS was observed between the unprocessed and processed virgin PS, showing that the mixing process does not affect the PS NIAS. The  $m\%_{\text{impur-PS}}$  value obtained is in accordance with previous studies reporting a range of styrene

**TABLE 4** Composition of PS NIAS from non-additivated PS\_Styron\_660 (sample 1).

Identification	Number of isomers (number of different degradation patterns)	Sum of area percentage (GC-MS) in the extract (%)
Dimer of Styrene	10 (3)	75
Trimer of Styrene	3 (1)	17
Quadramer of Styrene	3 (1)	8

Abbreviation: NIAS, non-intentionally added substances.

oligomers equal to 0.98–12.62 mg/g of PS.<sup>17</sup> Three different dimers were observed according to GC-MS with different degradation patterns. Within these dimers, several isomers with the same fragmentation pattern but different retention times were obtained (Table 4). A total of 16 different styrene oligomers were observed in this particular PS sample and their analytic details are described in the supplementing information. The exact structure of each oligomer was not investigated as it was already detailed in other studies,<sup>17</sup> and the work presented herein focuses on the degradation of PS additives. The presence of such a large number of oligomers could prove to be detrimental for the thorough investigation of the NIAS formation pathways concerning their identification or quantification, showing the challenges around NIAS study in PS polymer matrixes.

### 3.3 | Study of standards

The reference analyses (NMR, GC-MS) of the internal standard, the three additives and the polystyrene were performed and are available in the supplementing information. The <sup>1</sup>H NMR of crude mixed PS (samples 2 to 4, Table 5) were performed to calculate the actual percentage of additive in each sample. A theoretical amount of 5 wt% of each additive were introduced but as some powders could stay on the walls of the flask (static effect), the real composition proved to be slightly different. A mean value of signals (<sup>1</sup>H NMR integration) without superimposition was used for this calculation (integration adjusted for 1 proton): 5 signals for sample 2 (Figure S3), one signal for sample 3 (Figure S5), 5 signals for sample 4 (Figure S7).

### 3.4 | Additives and NIAS

As described, PS impurities (styrene oligomers,  $n = 2-4$ ) remained unaltered by the mixing process and no

**TABLE 5** Theoretical and actual composition of polymer mixes.

Sample	Theoretical PS amount (%)	Additive	Theoretical amount of additive (wt%)	Calculated amount of additive (wt%) (NMR)
1	100	-	-	-
2	95	Irganox_1076	5	4.73
3	95	Tinuvin_326	5	4.66
4	95	Irgafos_168	5	4.7



interaction was observed between the PS intrinsic NIAS and the studied additives. Furthermore, no degradation of the additives Irganox\_1076 and Tinuvin\_326 was observed according to NMR and GC analyses, showing the stability of such additives and the absence of interaction with the PS matrix or its inherently present NIAS. The detailed GC-MS for samples 2 and 3 are available in the supplementing information.

On the other hand, the secondary antioxidant studied, Irgafos\_168 (sample 4), underwent partial degradation of its structure due to the mixing process. Without performing a detailed quantification by NMR, which is usually less sensitive than chromatographic quantifications (GC-MS, LC-MS), proton, and phosphorous NMR allowed to calculate the relative composition between species present. The first NIAS observed from the degradation of Irgafos\_168 was determined to be the result of its oxidation from a phosphite to the phosphate, represented by a new peak at  $-19.9$  ppm in  $^{31}\text{P}$  NMR (Figure 1). According to phosphorus NMR integration, the NIAS formed was present with a molar ratio of 97.0:3.0 (Irgafos\_168:phosphate). The second NIAS formed resulted from the fragmentation of the phosphate mentioned into 2,4-di-*tert*-butyl-phenol, or DTBP. It was observed in  $^1\text{H}$  NMR with a distinct set of peaks between 7.5–7.6 ppm (Figure S7, Figure S8). According to NMR integration, a molar ratio of 93.4:6.6 (Irgafos\_168:DTBP) was observed (Figure 1). The presence of DTBP was also confirmed thanks to the GC-MS of the extract: 8.447 min, fragmentation pattern: 206, 191, 57 m/z, area percentage = 0.41% (Figure 2). This NIAS observation follows the degradation pathway described in the literature<sup>28</sup> without

observing the intermediate degradation structures: mono and di-(2,4-di-*tert*-butylphenyl)-phosphate.

From the NMR integration obtained, it was possible, after normalization, to calculate the molar percentage of Irgafos\_168 degradation resulting from the mixing process applied, as well as the massic degradation percentage into NIAS (Table 6). The overall degradation of Irgafos\_168 was thus measured at 5.1 wt% according to NMR results.

However, this degradation calculation by NMR is only possible in the case where the degradation products are easily analyzed by NMR ( $^1\text{H}$  or  $^{31}\text{P}$ ): no overlapping peaks (proton NMR), presence of phosphorous atom. For this reason, a thorough quantification process was developed for the precise quantification of additives to obtain the extraction percentage relative to the extraction processes for each additive, as well as the degradation percentages, by means of GC-MS.

### 3.5 | GC-MS calibration curves and matrix effects

Before setting up the calibration analyses, the matrix effect (effect of the solvent on signal intensity) and potential co-matrix-effects (effect of the presence of other compounds) on additive signal intensity were investigated, as they can alter the intensity response obtained from the GC analysis.<sup>29</sup> Firstly, a kinetic study of the Irganox\_1076 was performed between 0 and 30 h after sample preparation (solubilization in chloroform). Figure 3 shows that the signal intensity stabilizes after 5–6 h to a plateau before

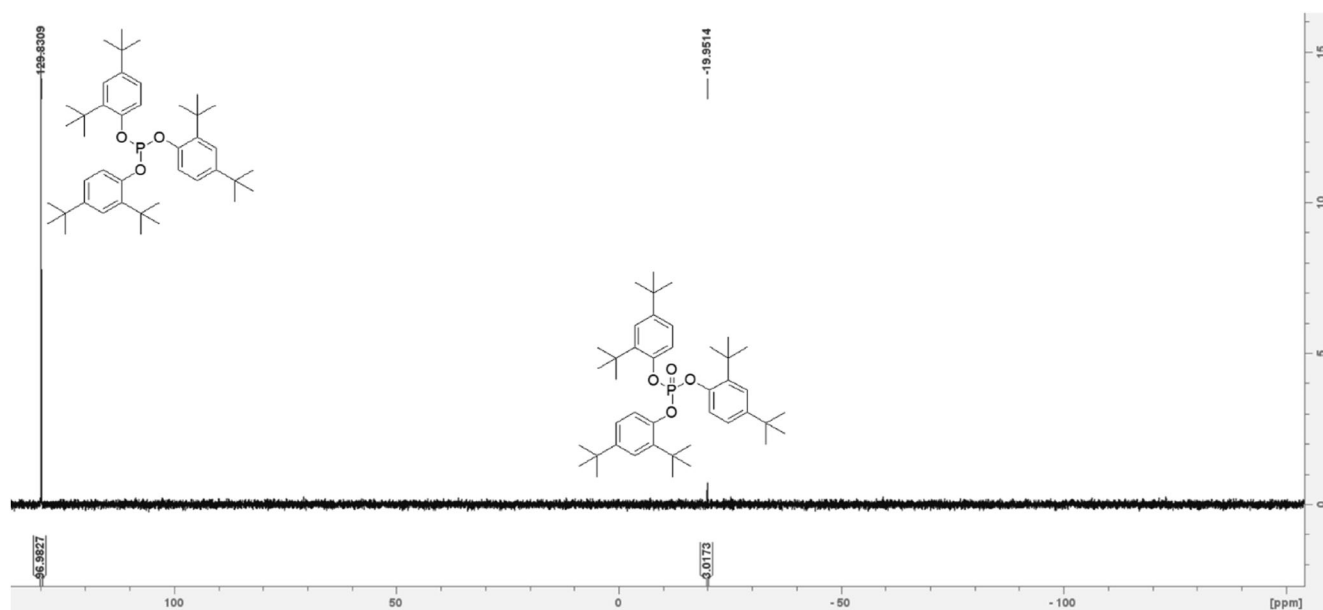


FIGURE 1  $^{31}\text{P}$  NMR of the extraction product of sample 4 containing the additive Irgafos\_168.

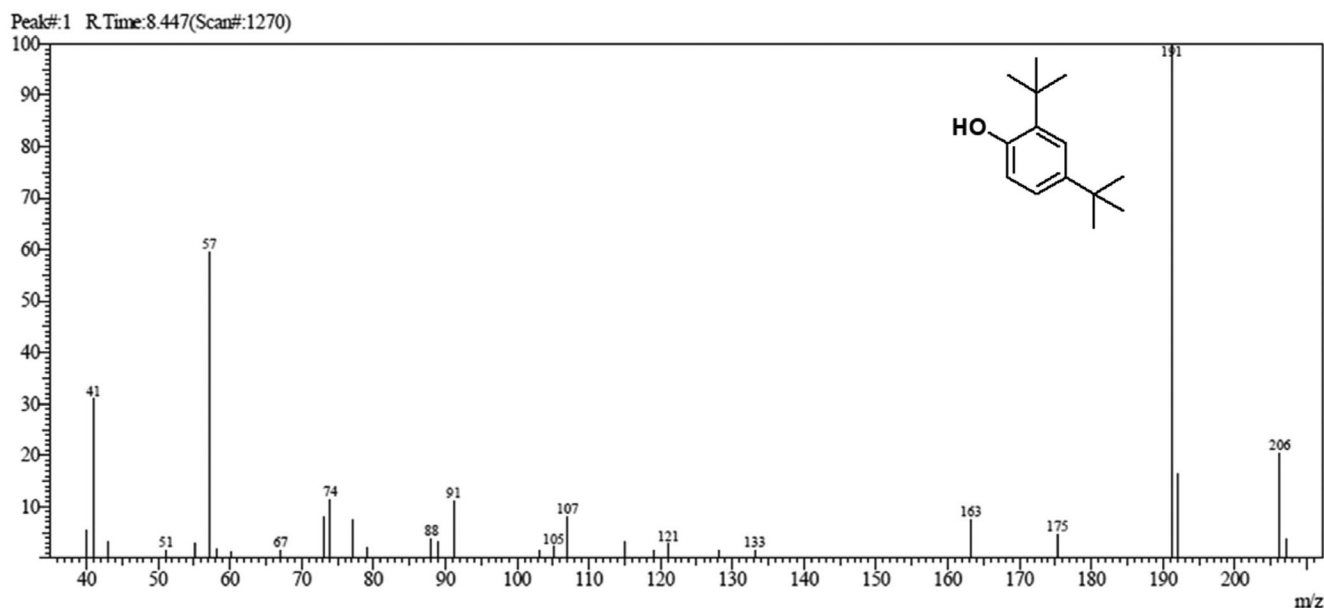


FIGURE 2 Mass spectrum of the degradation product of additive Irgafos\_168: di-*tert*-butylphenol.

TABLE 6 Percentage of degradation obtained from  $^1\text{H}$  and  $^{31}\text{P}$  NMR (normalized).

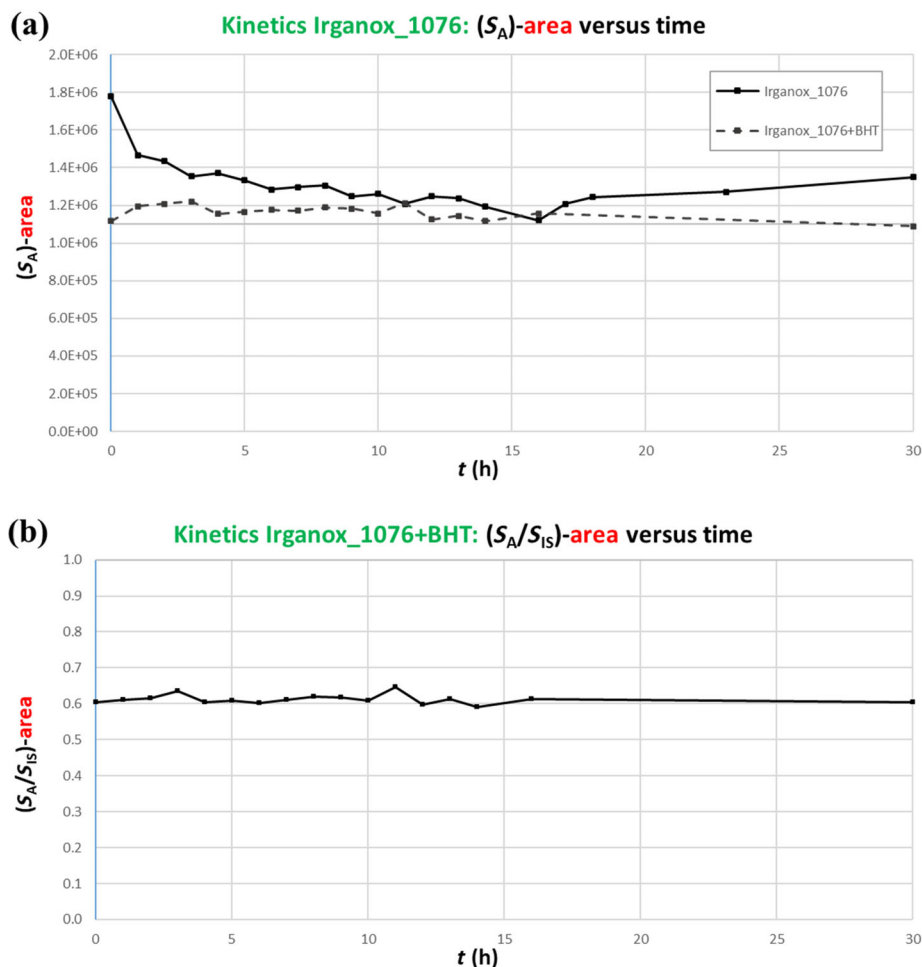
Compound	mol% ( $^1\text{H}$ and $^{31}\text{P}$ NMR)	$M_w$ (g/mol)	wt%
Irgafos_168	90.8	647	94.9
Degradation product 1 (phosphate)	2.8	663	3.0
Degradation product 2 (DTBP)	6.4	206	2.1

increasing again after 15 h due to solvent evaporation after multiple perforation of the membrane of the vial's cap. The solvent matrix effect was quantified by a decrease of the signal intensity of  $-29\%$  from the initial signal compared with the plateau. An internal standard (IS) was added to improve the calibration and quantification accuracy. BHT was chosen as standard due to its similarity in chemical structure compared with the additives, without interfering with the studied additives signals. The addition of BHT helped to limit the solvent matrix effect with a stable intensity signal obtained after approximately 2 h (Figure 3, dashed line). Furthermore, the variation coefficient of the values in the plateau range (5–15 h) was reduced from 4.2 to 2.4% (Table S6, Figure 3A). However, the introduction of BHT within analysis samples induced a co-matrix effect, lowering the plateau by  $-8.5\%$  (Figure 3A, Table S6), which is not detrimental for analysis accuracy if the IS is always present. Finally, when plotting the intensity ratio between the additive and the IS ( $S_A/S_{IS}$ ) versus their respective

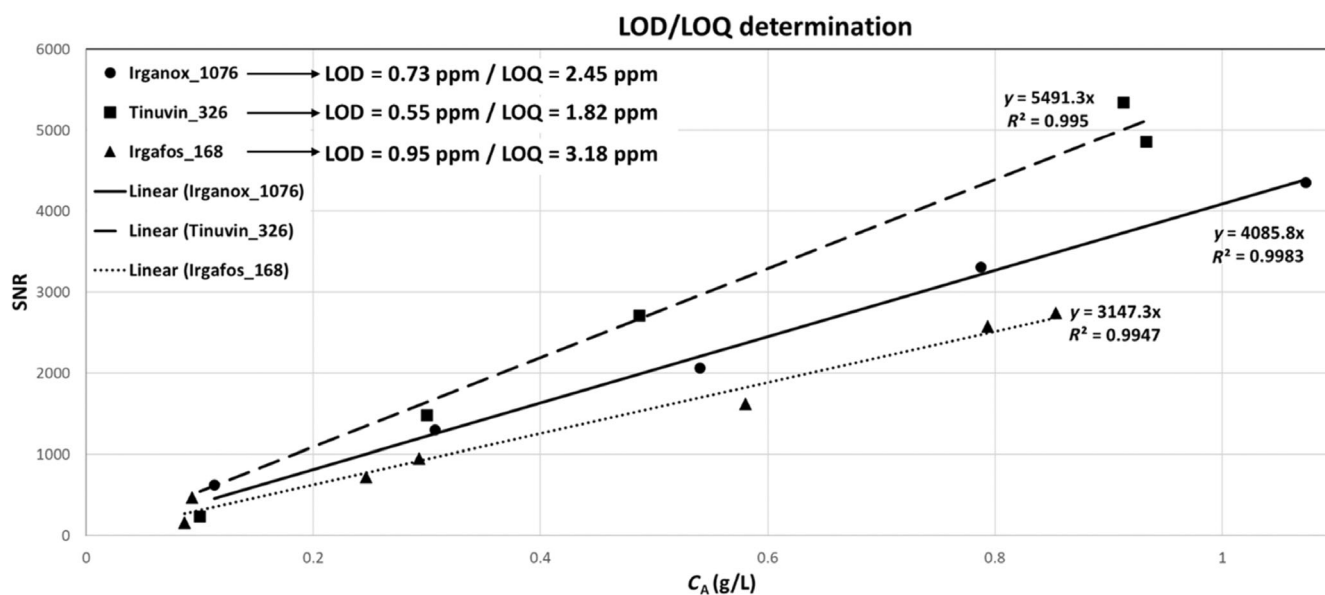
concentration ratio, the signal was found to reach the plateau immediately ( $t = 0$  h) and stayed stable up to 30 h (Figure 3B). The stability after 15 h despite partial solvent evaporation is explained by the fact that the increase in concentration is the same for both the analyte and the standard, leaving their intensity ratio unchanged. This shows the positive impact of the addition of the IS for the calibration and quantification of additives and NIAS by GC–MS. Finally, co-matrix effect between additives were observed, meaning that the presence of other additives, similarly to the presence of the IS, can influence the intensity signal of other analytes. These poly-additivated materials will not be covered in this study.

Using the multiple point calibration with internal standard (BHT) strategy, calibration curves were drawn thanks to GC–MS analyses for the 3 additives studied in the presence of BHT. The obtained calibration curves proved to be highly precise with coefficients of determination  $R^2$  up to 0.998 (Figure S9, Figure S10, Figure S11, Table S7), yielding reliable calibration equations in the range of sample concentration desired, tested with fake unknowns as described above.

The limits of detection (LOD) and quantification (LOQ) were determined using the surface/noise ratio (SNR) for each additive at different concentrations with a SNR of 3 and 10 for LOD and LOQ respectively. Obtained values ranged from 0.55 to 0.95 ppm for LOD and 1.82 to 3.18 ppm for LOQ (Figure 4). These LOD and LOQ are deemed to be satisfying compared with LOD reported in the literature for the study of plastic additives that could range from 0.001 to 100 ppm.<sup>30–32</sup>



**FIGURE 3** Kinetics of the intensity (area) curve over time without internal standard (Irganox\_1076) and with IS (Irganox\_1076 + BHT) (A), and of the intensity ratio (area) curve between analyte (Irganox\_1076) and the IS (BHT) over time (B).



**FIGURE 4** Surface/Noise Ratio (SNR) versus additive concentration ( $C_A$ ) allowing the determination of limits of detection (LOD) and quantification (LOQ).

### 3.6 | Quantification

Using the calibration data obtained, the mass of additive and percentage of additive extraction were obtained,

alongside the extrapolated mass of NIAS, using the mass of PS impurities present in processed PS ( $m\%_{\text{impur-PS}}$ ) and finally the percentage of additive degradation, or NIAS formation. Table 7 gathers the results of GC-MS

**TABLE 7** GC–MS quantification calculation results using BHT as IS. For each sample analyzed, 5 replicate analyses were performed.

Sample	Number of samples analyzed	% <sub>Extr</sub> of additive	Mass of NIAS $m_{\text{NIAS}}$ (mg)	% <sub>Degrad</sub> of additive
2 (5% Irganox_1076)	3	96.6	1.8	0.8
3 (5% Tinuvin_326)	3	82.9	−0.1	0.0
4 (5% Irgafos_168)	4	76.7	3.4	5.1

Abbreviations: BHT, butylated hydroxytoluene; NIAS, non-intentionally added substances.

quantification being the means of 3 or 4 samples analyzed with 5 analytical replicates each, for polymer samples 1 (PS + 5 wt% Irganox\_1076), 2 (PS + 5 wt% Tinuvin\_326) and 3 (PS + 5 wt% Irgafos\_168).

The extraction of the primary antioxidant (Irganox\_1076) proved to be the most efficient with a 96.6 wt% recovery of the additive present in the mixed polymer. Tinuvin\_326-containing material extraction yielded 82.9 wt% of the extractable additive due to a lower solubility profile in the precipitation solvent mixture. 76.7 wt% of Irgafos\_168 was recovered, due to the partial degradation of the additive, forming new NIAS. However, regarding the simplicity of the proposed extraction method (Table 3), good extraction yields are obtained ranging from 81.8 to 96.6 wt% when including additive degradation products, particularly when comparing with other one-step extraction strategies yielding as low as 22 wt% Irganox\_1076 for example.<sup>12</sup> The first two additives (Sample 1 and Sample 2) do not display a significant NIAS formation, in accordance with the absence of new NIAS observed in <sup>1</sup>H, <sup>31</sup>P. However, a small variation (0.8%) is observed after the calculation for Sample 1. This is due to the mass of PS intrinsic NIAS and process impurities gathered during each extraction protocol ( $m_{\text{impur-PS}}$ ) which can vary depending on the amount of pollutants gathered during the process (mainly phthalates from syringe, filter, GC vial) and could shift the result of the calculation slightly. For the quantification of the degradation of Irgafos\_168, 5.1 wt% of NIAS formation are obtained, which corresponds to the calculated amount obtained from phosphorous and proton NMR composition: 3 wt% of phosphate and 2.1 wt% of di-*tert*-butyl-phenol. This proves that both GC–MS quantification and NMR composition methods are concordant.

## 4 | CONCLUSIONS

The results presented in this study underline the challenges associated with the investigation of NIAS formation in polymer matrices. A systematic approach

was used by introducing known amounts of common additives in polystyrene to evaluate their extraction, identification, and quantification. The new simple alternative extraction protocol described was performed on unground material at room temperature, in a short time (2.33 h total) to prevent NIAS formation not related to the mixing process and required simple equipment. As proof of concept, the extraction by solubilization followed by precipitation allowed to recover up to 96.6 wt% of the studied additives, while considerably reducing solvent use in the simplest laboratory apparatus available.

The virgin PS matrix contained intrinsic NIAS (7.3 mg/g of PS) composed of styrene oligomers, mainly dimers, that were unaffected by the mixing process. Additives Irganox\_1076 and Tinuvin\_326 did not show any sign of degradation or NIAS formation under the PS mixing conditions. However, two NIAS formed by the degradation of the secondary antioxidant Irgafos\_168 were identified: tris(2,4-di-*tert*-butylphenyl)phosphate, the oxidized version of the additive, and 2,4-di-*tert*-butyl-phenol (DTBP). This confirms the degradation pattern of this additive by oxidation followed by the fragmentation into DTBP units. These NIAS were quantified by means of GC–MS by multiple point internal standard quantification, yielding 3 wt% of the phosphate and 2.1 wt% of DTBP, with the help of NMR composition calculation. In addition to the analytical challenges encountered in previous works, such as solubility of IAS and NIAS, limits of detection or quantification (LOD and LOQ), this work also shows the impact of solvent and internal standard presence on sample response in GC–MS analyses, linked to matrix and co-matrix effects.

Further work is required to enlarge the spectrum of PS additives studied, the impact of the presence of other additives within the polymer matrix in terms of NIAS formation as well as the impact of the mixing or recycling parameters variation and number of cycles, and the evaluation of other analytical methods such as LC–MS. This work is a new step towards the improvement of the recycling processes to help understand the mechanisms of

NIAS formation in plastics that would eventually allow the tuning of processing or recycling parameters to obtain safer and more performant recycled plastic materials. The proposed simple extraction method could also be used to control the quality of PS/recycled PS by extracting, identifying and quantifying the species present in a PS material, in particular for FCM.

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## DATA AVAILABILITY STATEMENT

The data that support the findings of this study are available from the corresponding author upon reasonable request.

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## SUPPORTING INFORMATION

Additional supporting information can be found online in the Supporting Information section at the end of this article.

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