

Determination of polyolefin additives by reversed-phase liquid chromatography

Review Article

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Abstract: This article examines the contribution of liquid chromatography to the study of polyolefin additives commonly used to obtain improved environmental resistance (antioxidants, ultraviolet light stabilizers, antistatics, and so on) and appearance enhancements (e.g. colorants). Several reversed-phase liquid chromatographic methods are summarized, and a detailed description of different detectors is provided. In addition, ways of applying these methods to analyse food contact materials and plastic toys are emphasized. Finally, the potential use of these methods is addressed which complies with European health safety regulations.

Keywords: Polyolefins • Commercial additives • Natural extracts • Liquid chromatography • Sample treatment

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1. Introduction

Today, polyolefins consisting mostly of polyethylenes (PE) and polypropylenes (PP), are the main polymers manufactured by the plastics industry. Their properties facilitate the production of cheap, light and durable regular goods. In addition, they make the creation of innovative products possible. In this way, these polyolefins are key elements in various sectors of industry such as packaging, automotive, mechanical engineering or electronics [1-3]. The properties of polyolefins are defined by a simple molecular structure built from carbon and hydrogen. Initially, molecular weight, molecular weight distribution and the incorporation of comonomers are the major factors to define their properties [3,4]. Later, the physical and chemical properties of polyolefins are improved by the use of additives (nucleating agents, acid scavengers, stabilizers, mineral fillers, glass fibres, elastomers, flame retardants, pigments, carbon black, biocides, antistatics, and so on.) which let expand the number of final applications of these plastics. The commercial needs require not only to maintain the plastics properties but also to extend their service life [2,4,5].

Polyolefins typically come in the form of pellets which are processed (extruded, blow molded, injection molded, or rotomolded) and manufactured into the final products. It must also be considered that the need for differentiation in the market and the continuous evolution of polymers for new applications have steadily increased the demands during processing. Therefore, new additives or additive combinations to safeguard the original properties of the polymer under higher processing temperatures or higher shear forces are required [1,3-5].

When polyolefins are used for packaging food, these additives or their degradation products can migrate from plastics to foodstuffs during processing or storage. Therefore, food contact materials must be in compliance with specific legislation to ensure that packaged foods are safe for consumers according to the toxicity and the potential to migrate of the different substances [6,7]. Likewise, the use of toy materials is regulated by specific legislation [8] to avoid health risks.

Besides these specific regulations, Regulation 1907/2006 concerning the Registration, Evaluation, Authorisation and Restriction of Chemicals (REACH) [9] must be regarded for plastic articles.

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This subject has required the development of analytical procedures able to measure additive levels in polyolefins. In this context, the separation, identification and quantification of a wide range of analytes can be provided by LC.

Consequently, the goal of the herein work has been the review of analytical methodologies used for the determination of the polyolefin additives by LC. The manuscript is organized as follows: first section provides a short global view of different aspects of polyolefins (use, processing, properties, requirements, regulations, and so on); then LC separations and sample treatment methods for polyolefin additives are analyzed in more detail. Following these two sections, the action of each additive in the polymer and the additive chemical composition are also considered. Finally, the applicability of LC combined with sample treatment methodologies for plastic additives analysis is summarized.

2. Separation and detection of additives for polyolefins

2.1. Separation and detection of additives for environmental resistance

When plastic materials and articles are intended to come into food contact, only the additives authorised by the European regulation can be used in their manufacture. Potential health risk may occur from low molecular weight additives which can be transferred into food *via* migration from the plastic material. Therefore, these additives are subjected to established restrictions and specifications [7].

2.1.1. Antioxidants (AO)

In most cases, polyolefins need protection in every stage of their life cycle, both during processing and storage. Thus, hindered phenols are the most important antioxidants for polyolefins acting as long-term stabilizers (Fig. 1). Since they can act as H-donor, a hydrogen atom is donated from its OH group to deactivate free radicals (ROO•) stabilizing the material against photo and thermooxidation. The combination of high molecular mass phenolic antioxidants with phosphites or phosphonites antioxidants (Fig. 1) makes up an adequate processing stabilizer. Hydroperoxides can be reduced into more stable alcohol forms by phosphites or phosphonites, which act as hydroperoxide decomposers. Furthermore, this combination can be even further improved by using a benzofuranone derivative as a third component. As a radical scavenger, a hydrogen atom is directly donated to carbon-centered free radicals (R•).

That proves its efficiency at the increased processing temperatures [3,5,10,11].

The long-term stabilizers that have been the target of more studies are: Irganox 1076 (Ultranox 276), CAS 2082-79-3, and Irganox 1010 (AO-60, ADK Stab AO-60), CAS 6683-19-8 [2,12-14,17-22,24-27,28,30-34,37-46,48,50-52,54-55]. Furthermore, Irgafos 168 is the processing stabilizer that has been more studied (Hostanox PAR 24), CAS 31570-04-4 [16,18,21,27,28,30,32-33,37,40-46,50,51,54]. Initially, this last group of phosphite additives was distinguishable from its degradation products [18,23].

Different LC-methods developed to determine long-term and processing stabilizers are summarized in Table 1. Studies which focused on antioxidants degradation products are also included [12-17].

In most cases, reversed phase HPLC [2,12-27,28-51] was preferred over normal phase HPLC procedures [19,49,52-55]. Normal phase is usually recommended only for simple formulations [19,54]. As a general rule, UV and MS detectors were used for the analysis of antioxidants and their degradation products [2,12-33,35-46,48-52,54-55]. Many other detection methods were also tried in some particular cases: FL, RI, ELSD or FTIR [32-35,47].

Several natural extracts also contain a high amount of antioxidant chemical components. Their antioxidant efficiency for polyolefin films has also been studied. In most cases, polyphenolic extracts can be suitable as long-term antioxidants, while carotenoid extracts are effective as processing stabilizers [56-59].

α -tocopherol is the most studied natural antioxidant [38,47,48,60-69]. Anthocyanin, ascorbic acid, catechin and epicatechin have also been studied [70-72]. Different chromatographic methods were developed to study natural compounds used as antioxidant for plastic articles (Table 2). LC methods for determination of α -tocopherol were carried out by normal [60,61,64,67-69] or reversed [38,47,48,62,63,65,66] chromatographic phase under isocratic elution conditions and using UV/Vis [38,48,60,63,66,68,69] or FL [47,61,62,64,65,67] detectors.

Reversed phase LC methods were also developed to determine anthocyanin, ascorbic acid, catechin and epicatechin. UV/Vis detectors were used for anthocyanin and ascorbic acid, while UV/Vis and FL detectors coupled to LC proved to be the method of choice for catechin and epicatechin.

2.1.2 Ultraviolet Light Stabilizers (ULS)

Exposure of plastic articles to sunlight or fluorescent lighting can cause changes in color, chalking, cracking and deterioration in mechanical properties of plastic

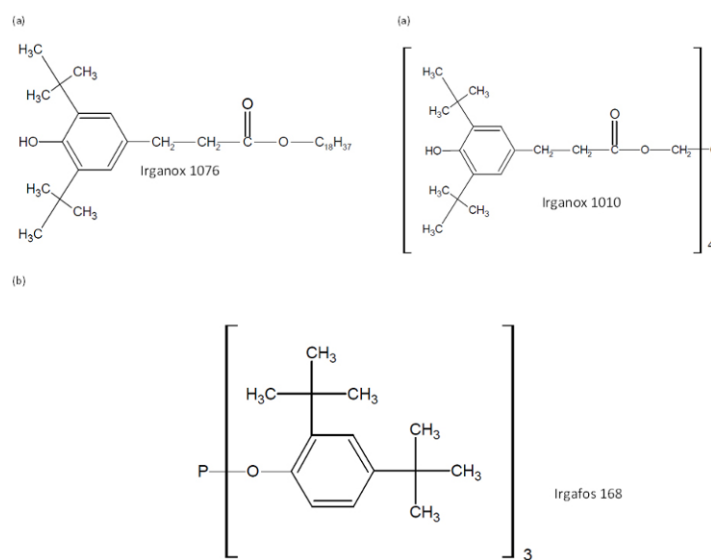


Figure 1. Structures of major polyolefin antioxidants (a) high mass phenolic antioxidants; (b) phosphite antioxidant.

articles [73,74]. Thus, Ultraviolet Light Stabilizers are added to polyolefins.

Hindered amine light stabilizers (HALS) are included in this group of additives. Initially, only low molecular mass HALS (HALS-1) were available. To avoid some disadvantages associated with low molecular mass stabilizers, polymeric HALS, highmolecular weight (HMW)-HALS (HALS-2 and HALS-3), were developed. Low-molecular mass HALS rapidly diffuse to the surface layers where the need for stabilizers is higher, whereas (HMW)-HALS resist to migration and extraction protecting polymers during longer periods [5,10,11,75]. Chromatographic studies are mainly focused on Tinuvin 770 [43,76-79] and Chimassorb 944, low and high molecular mass stabilizers, respectively [77-83]. They represent the most frequently used HALS in commercial articles. The LC- methods developed for the analysis of HALS and other ultraviolet light stabilizers are listed in Table 3.

LC separation and the determination of HALS were difficult during years because of their several amino groups that promoted the adsorption to silica-based column packing. So far, different authors have proposed the use of a deactivating agent in the mobile phase to achieve acceptable peak shapes. These agents were supposed to act blocking the residual active silanol groups of C₁₈ columns [78,82-85]. Chromatographic methods can be simplified if the addition of a deactivating agent in the mobile phase is saved. Therefore, the use of a column compatible with a buffered mobile phase adjusted to a pH value higher than pKa of HALS (pH>10) has been necessary in order to work with non-ionized forms of HALS [79]. Furthermore, chromatographic determination of (HMW)-HALS, as Chimassorb 944,

has been more problematic than that of the monomeric stabilizers [86].

LC coupled to UV/Vis proved to be, almost exclusively, the method of choice, in particular in the identification of these compounds. However, with the aim of having more knowledge about the polymeric distribution of HMW-HALS, they were also characterized by size-exclusion chromatography [82,83]. In addition, their characterization was also carried out by high-temperature LC with evaporative light-scattering [84] and MS [85] detection.

2.1.3. Antistatics

Static electricity is created through a surplus or a deficiency of electrons on an isolated or ungrounded surface. Polymers are receptive to build-up static electricity due to their high superficial-specific resistance. This insufficient conductivity can result in processing difficulties presented as dust pick up and electrical discharges, which may give electrical shocks to employees or start a fire [3,74,87-89]. Therefore, amphiphilic molecules are incorporated into the polymer matrix as internal antistatics. The hydrophobic tail of these molecules is compatible with the polymer, whereas the hydrophilic head can migrate to the surface and interact with atmospheric moisture, reducing surface resistivity and setting up a conductive path to dissipate static charges [74,87,88-90].

Glycerol monostearate (fatty acid ester) and ethoxylated amines make up more than 50% of the total classic antistatic market. Both are the major types of non-ionic antistatic additives [87]. Span (sorbitan fatty acid esters) can also be used as antistatic additives in polymer matrix [91].

Table 1. Summary of liquid chromatography based methods for the determination of antioxidants in plastics.

Analytes (matrix)	Mobile phase (Solvents)	Flow	Column - Particle packing (Temperature)	Detection	LOQ	Reference
DBP, Irganox 1010, Irgafos 168, Ultrinox 626, oxidized Irgafos 168 (PP)	THF ACN MeOH water	1 mL min ⁻¹	LiChrospher RP-Select B, 250 x 4.6 mm, 5 μm	UV/Vis (280 nm), RI, MS	4.5 × 10 ⁻³ -5 × 10 ⁻³ mg mL ⁻¹ for UV/Vis	[18]
BHT, Irgafos 168, Irganox 1010, Irganox 1076, Irganox 1330, Irganox 3114, AM340 Ultrinox 626 (HDPE, LDPE, PP)	Reversed phase Water ACN Normal phase m-butyl chloride CH ₂ Cl ₂	Reversed phase 1.5 mL min ⁻¹ Normal phase: 0.75-2.5 mL min ⁻¹	Reversed phase: Nova Pack C18, 150 or 75 x 3.9 mm (40-55 °C) Normal phase: Resolve SiO ₂	UV/Vis (220-230 nm)	---	[19]
Irganox 1010 (PP)	MeOH:water 10:90 EtOAc:MeOH 57:43	0.7 mL min ⁻¹	Spherisorb ODS2, 100 x 4.6 mm Guard column: Spherisorb ODS2, 50 x 4.6 mm	UV/Vis (250-390 nm), MS	---	[12]
BHT, Irganox 1010, Irganox 1076, Santonox R, Ethyl 330, Goodrite 3114, Topanol CA	NH CH ₂ Cl ₂	2 mL min ⁻¹	μ-Porasil normal phase column, 300 x 3.9 mm Guard column: Corasil C18, 30 x 4 mm, 37 μm	UV/Vis (280 nm)	---	[52]
Irganox 1076, Naugard-XL (PP)	ACN water	0.4 mL min ⁻¹	Symmetry C8, 150 x 3.9 mm	UV/Vis (210 nm)-MS	1.3 × 10 ⁻⁵ -3 × 10 ⁻⁶ (LOD)	[20]
DBB, BHT, DBP, Irgafos 168, Irganox 1010, Irganox 1076	Antioxidants: ACN THF water Products derived from antioxidants: ACN water	1 mL min ⁻¹	Spherisorb ODS1, 250 x 4.6 mm, 5 μm Guard column: C18, 10 mm, 5 μm	UV/Vis (275 nm)	---	[21]
Irganox 1010 (PP)	MeOH	1 mL min ⁻¹	ODS2, 25 x 4.6 mm	UV/Vis (254 nm)	---	[22]
Ultrinox 626 and degradation products	Water ACN	1 mL min ⁻¹	Inertsil phenyl, 150 x 3 mm	UV/Vis (220, 230 nm)	---	[23]
BHT, Irganox 1076 (LDPE, PP)	MeOH Water THF	2 mL min ⁻¹	μBondapak C18, 600 x 3.9 mm	UV/Vis (254 nm)	---	[24]
BHT, Topanol CA, Goodrite 3114, Irganox 1010, Weston 618, Ethyl 330, Irganox 1076, (PP)	ACN THF HOAc	1.3 mL min ⁻¹	μBondapak C18	UV/Vis (280 nm), RI	---	[25]
Antioxidant MPJ, Ethanox 754, Irganox 1076, Irganox 1010, Irganox 1035, Irganox 1024 MD, Topanol CA, Vulkanox BKF, Vulkanox NKF, Irganox 3114, Irganox 245, Ethanox 702, Irgafos 168, Antioxidant TMB-6, Irganox PS-800	ACN water	---	LiChrosorb RP-18, 250 x 4 mm, 5 μm	UV/Vis (254, 280 nm)	---	[26]
Irganox 1010, Irgafos 168 (PE)	ACN	1 mL min ⁻¹	APEX, 150 x 4.6 mm	UV/Vis (245, 280 nm)	---	[27]

Continued Table 1. Summary of liquid chromatography based methods for the determination of antioxidants in plastics.

Analytes (matrix)	Mobile phase (Solvents)	Flow	Column - Particle packing (Temperature)	Detection	LOQ	Reference
BHT, BHBE, MD 1024, Isonox 129, Irgafos 168, Irganox 1010, Irganox 1076, AM 340 (HDPE)	ACN water	1.5 mL min ⁻¹	Nova Pack C18, 150 x 3.9 mm (50°C)	UV/Vis (225 nm)	---	[28]
Ethanox 330 (PE)	ACN MeOH THF	1 mL min ⁻¹	ODS Hypersil C18, 150 x 4.6 mm, 5.0 μm	UV/Vis (280 nm)	---	[29]
Irganox PS802, Irgafos 168, Irganox 1010, Irganox 1425	Irganox 1425 ACN 2-PrOH Others Water ACN 2-PrOH	Irganox 1425: 1 mL min ⁻¹ Others: 2 mL min ⁻¹	Irganox 1425: LiChroCart RP8, 250 x 4 mm, 5 μm (50°C) Others: LiChroCart RP18, 250 x 4 mm, 5 μm (50°C)	UV/Vis (282, 273 nm)	---	[30]
Irganox 1330 (PE)	NH:MeOH (99.8:0.2) % NH:MeOH (99.8:0.2) %	---	Normal phase silica gel column, 250 x 4 mm, 13 μm	UV/Vis	2.3 × 10 ⁻² mg mL ⁻¹ (LOD)	[53]
Irganox 1076 (LDPE)	ACN	5 μl min ⁻¹	Kromasil 100 ODS, 500 x 0.32 mm, 5 μm (7 to 90 °C, 3°C/min)	UV/Vis (280 nm)	3.3 × 10 ⁻⁵ mg mL ⁻¹ (LOD)	[31]
Irgafos P-EPQ, Irgafos 168, Sumilizer BHT, Irganox 1010, Irganox 1076, Irganox MD 1024, Irganox PS 802	ACN CHCl ₃ MeOH ACT CH ₂ Cl ₂ water	---	Spherisorb ODS, 3-μm Novapak C18, 200 x 0.32 mm, 4 μm Supelco LC18-DB, 250 x 4.6 mm, 5 μm Supelcosil-LC-NH2, 250 x 4.6 mm	UV/Vis; ELSD	---	[32]
Irganox 1076, Irganox 3114, Irganox 1010, Irgafos 168, Irgafos P-EPQ	ACN	5 μl min ⁻¹	Kromasil 100 ODS, 300 x 0.32 mm, 3.5 μm	UV/Vis, FTIR off-line	---	[33]
Irganox 1076 (LDPE)	ACN containing 10 mM TEA and FA	5 μl min ⁻¹ . Sample loading flow: 40 μl min ⁻¹	Kromasil C18, 27 x 0.25 mm, 3.5 μm and 250 x 0.25 mm, 3.5 μm (5 to 90°C)	ELSD	6 × 10 ⁻⁶ mg mL ⁻¹ (LOD)	[34]
Irganox 245, BHA, BHT, Topanol CA	Deuterated ACN water	1 mL min ⁻¹	Hypersil H5 ODS, 100 x 4.6 mm, 5 μm	UV/Vis, IR, NMR, MS	---	[35]
BHT, Irganox 2246, Irganox 1076, Irganox 1130, Irganox 1010, Irganox PS800, Irganox PS802, Irgafos 168	NH CH ₂ Cl ₂	1 mL min ⁻¹	Nucleosil 50 silica, 250 x 4.8 mm, 5 μm	UV/Vis	---	[54]
Phosphites	MeOH	1 mL min ⁻¹	ODS 2	UV/Vis (280 nm)	---	[36]
Irganox 1010, Irganox 1076, Irganox 1330	EtOAc MeOH water	0.7 mL min ⁻¹	Spherisorb S5 ODS1, 100 mm Guard column: Spherisorb S10 ODS1, 50 mm	UV/Vis	---	[13]
Irganox 1010, Irganox 1076 (PE, PP)	EtOAc MeOH water	2 mL min ⁻¹	Spherisorb ODS, 250 x 4.6 mm, 10 μm Guard column: Lichroprep RP-18 (25-40 pro), 50 x 4.6 mm (Room temperature)	UV/Vis (275 nm)	---	[14]

Continued **Table 1.** Summary of liquid chromatography based methods for the determination of antioxidants in plastics.

Analytes (matrix)	Mobile phase (Solvents)	Flow	Column - Particle packing (Temperature)	Detection	LOQ	Reference
Ethanox 330 (PP)	Ac MeOH water	0.7 mL min ⁻¹	Spherisorb S5 ODS1, 100 mm Guard column: Spherisorb S10 ODS1, 50 mm	UV/Vis, MS	---	[15]
Irganox 1010, Irganox 1076, Irgafos 168	MeOH	0.5 mL min ⁻¹	Zorbax Extend-C18, 100 × 2.1 mm, 3.5 μm (Room temperature)	UV/Vis (210, 280 nm)	---	[37]
Irganox 1010 (PP based)	Water ACN	0.31 mL min ⁻¹	Luna RP18, 150 x 2.1 mm, 5 μm (50°C)	UV/Vis (274, 282 nm)	---	[17]
Irganox 1010, Irganox 1076(PP)	ACN Water	1 mL min ⁻¹	Symmetry C18, 50 x 3.9 mm, 5 μm (40°C)	UV/Vis (220 nm)	---	[38]
BHA, Ionox 100, BHT, AO425, Irganox 1010, Irganox 1076, (PP)	ACN FA	0.3-0.5 mL min ⁻¹	Acquity UPLC BEH C18, 100 x 2.1mm, 1.7 μm (35°C)	UV/Vis (276 nm)	7 × 10 ⁻¹ -2 × 10 ⁻³ mg mL ⁻¹	[39]
ADK Stab AO-60, Kinox 30, Irganox 3114, Irganox 1076, and Cyanox 1790	ACN water	2 mL min ⁻¹ (HPLC-UV) 1 mL min ⁻¹ (HPLC-MS)	Zorbax Eclipse XDB- C18, 50 x 4.6, 1.8 μm (40°C)	UV/Vis (200 nm), MS	---	[2]
Irganox 1076, Irgafos 168, and Irganox 1010	ACN water	1.0 mL min ⁻¹	Symmetry C18, 50 x 3.9 mm, 5 μm (50°C)	UV/Vis (220 nm)	---	[40]
Irganox 1010, Irganox 1076, and Irgafos 168 (PE, PP)	Water ACN	1.9 mL min ⁻¹	Zorbax Eclipse XDB-C8, 50 x 4.6 mm, 3.5 mm Guard column : Zorbax Eclipse XDB-C8, 12.5 x 4.6 mm, 5 μm (50°C)	UV/Vis (210 nm)	1.2 × 10 ⁻² mg mL ⁻¹	[41]
BHA, Irganox MD 1024, Irgafos 126, HP 136, Irganox 3114, Irganox 1010, Irganox 1330, Irganox 1076, Irgafos 168 (PE)	Hex CH ₂ Cl ₂ ACN	1.5 mL min ⁻¹	Nucleosil 120-5 SIL, 250 x 4.6 mm, 5 μm Guard column: Nucleosil 120-5 SIL, 15 x 4.6 mm, 5 μm (30 °C)	UV/Vis (275 nm)	0.3 × 10 ⁻³ -1 × 10 ⁻³ mg mL ⁻¹	[55]
Irganox MD 1024, Irganox 1081, Irganox 1035, Irganox 3114, Irganox 1010, Irganox 1330, Irganox 1076, Chimassorb 81, Irgafos 126, Irgafos 38, Irgafos 168.	Water ACN	1 mL min ⁻¹	Zorbax Eclipse XDB- C18, 30 x 4.6 mm, 1.8 μm (40 °C)	MS	1 × 10 ⁻⁶ , 2.2 × 10 ⁻⁵ mg mL ⁻¹	[42]
BHEB, BHT, Irganox 1010, Irganox MD- 1024, Irganox 129, Irganox 1076 Irgafos 168, Oxidized Irgafos 168, Irganox 3114, Irganox PS-802, Irganox PS-800,	C8 - Water:ACN C18 - Water:MeOH	0.2 mL min ⁻¹	Zorbax Eclipse XDB-C8 Solvent Saver Plus, 100 x 3.0 mm, 3.5 μm (45°C) Zorbax Eclipse XDB-C18 Solvent Saver Plus, 150 x 3.0 mm, 3.5 μm (50 °C)	UV/Vis, MS	---	[43]

Continued Table 1. Summary of liquid chromatography based methods for the determination of antioxidants in plastics.

Analytes (matrix)	Mobile phase (Solvents)	Flow	Column – Particle packing (Temperature)	Detection	LOQ	Reference
Antioxidant 2246, BHEB, BHT, Chimassorb 81, Ethanox 330, Irganox 3114, Irganox 1330, Irganox 565, Irganox 1010, Irganox 1076, Irganox 3114, Irgafos 168, Irgafos 168 oxidised, Ultrinox 626, Irgafos 126, Weston 399, Weston 399 oxidised.	MeOH H ₂ O	1 mL min ⁻¹	Nova-Pak C18, 150 x 3.9, 4 μm Guard column: Nova-Pak Sentry C18, 20 x 3.9, 4 μm	UV/Vis (278 nm), MS	---	[44]
Irgafos 168, Irganox 1010 (PP)	ACN THF	1 mL min ⁻¹	Supelcosil LC18, 150 x 4.6 mm, 5 μm Hypersil ODS, 250 x 4.6 mm, 5 μm	UV/Vis (280 nm)	---	[45]
Hostanox PAR 24	2-ProOH ACN	1 mL min ⁻¹	Lichrospher 100 RP18, 250 x 4.6 mm, 5 μm (40 °C)	UV/Vis (230 nm), MS	---	[16]
Antioxidant 2246, BHT, Irganox 1010, Ethanox 330, Irgafos 168 oxidised, Irganox 1076.	Water MeOH	0.5 mL min ⁻¹	Acquity UPLC BEH C18, 50 x 2.1 mm, 1.7 μm (30 °C)	UV/Vis	8 × 10 ⁻⁵ -5 × 10 ⁻⁴ mg mL ⁻¹	[46]
BHA, BHT (LDPE)	MeOH	0.8 mL min ⁻¹	Omnispher C18, 150 x 4.6 mm (25 °C)	FL (λ _{exc} 292 nm; λ _{em} 310 nm for BHA) (λ _{exc} 282 nm; λ _{em} 308 nm for BHT)	5 × 10 ⁻² mg mL ⁻¹	[47]
Irganox 1076 (LDPE)	ACN water	1 mL min ⁻¹	Symmetry C18, 50 x 3.9 mm, 5 μm	UV-Vis (220 nm)	---	[48]
Santonox R (PE)	Reversed phase: ACN:water Normal phase: CHCl ₃	0.5 mL min ⁻¹	Reversed phase: Symmetry C18, 390 x 50 mm, 5 μm Normal-phase: Supelcosil, 150 x 4.5, 5 μm	Reversed Phase: UV/ Vis (220 nm) Normal Phase: UV/Vis (280 nm)	---	[49]
Irganox 1076, Irgafos 168 (LDPE)	MeOH water	0.5 mL min ⁻¹	Symmetry C18, 150 x 3.0 mm, 3.5 μm	UV/Vis (276 nm)	---	[50]
AO 2246, AO425, DBP, BHT, Ethanox 330, Irganox 1010, Irganox 1076, Irgafos 168 (PE, PP)	MeOH water	0.5 mL min ⁻¹	Symmetry C18, 150 x 3.0 mm, 3.5 μm	UV/Vis (276 nm)	---	[51]

Fatty acid esters appear in a complex mixture related to the distribution of the degree of esterification of polyol, the mixed composition of starting fatty acids of various chain lengths, the positional isomerism of the fatty acids esterified with the polyol hydroxyl groups and the different types of other linkage [92-95].

The composition of the commercial ethoxylated alkyl amines can change according to the supplier, and the information provided about them is usually not

very detailed. The correlation between structure and performance of these non-ionic antistatics cannot be easily determined due to their chemical complexity [96]. Although HPLC makes direct analysis of these compounds feasible without derivatization [32,43,96-98], these additives have been barely studied. The methods summarized in Table 4 employed a reversed-phase. The procedures are based on HPLC methods for compounds with an analogous structure.

Table 2. Summary of liquid chromatography based methods for the determination of natural antioxidants in plastics.

Analytes (matrix)	Mobile phase Initial – Final	Flow	Column – Particle packing (Temperature)	Detection	LOQ	Reference
α-tocopherol (LDPE)	Hex 1,4-dioxane	1 mL min ⁻¹	Zorbax SIL, 250 x 4.6 mm	UV-Vis (290 nm)	---	[60]
α-tocopherol (LDPE)	Hex 2-PrOH	0.5 mL min ⁻¹	LiChrosorb 5 silica, 250 x 2 mm	FL (λ _{exc.} : 292 nm; λ _{em.} : 324 nm)	---	[61]
α-tocopherol (LDPE)	MeOH water	1 mL min ⁻¹	Omnispher, (150 × 4.6mm, 5 μm) Microsorb, 100 x 4.6 mm, 5 μm)	FL (λ _{exc.} : 290 nm; λ _{em.} : 330 nm)	2.5 × 10 ⁻² mg mL ⁻¹	[62]
α-tocopherol (LDPE)	MeOH	1 mL min ⁻¹	Discovery C18, 250 x 4.6 mm, 5μm	UV-Vis (292 nm)	---	[63]
α-tocopherol (LDPE)	Hex 2-PrOH	1 mL min ⁻¹	Si60 Lichrosorb, 150 x 4.6 mm, 5 μm)	FL (λ _{exc.} : 294 nm; λ _{em.} : 330 nm)	24.2 μg g ⁻¹	[64]
α-tocopherol (LDPE)	MeOH	0.8 mL min ⁻¹	Omnispher C18, 150 x 4.6 mm	FL (λ _{exc.} : 292 nm; λ _{em.} : 310 nm)	0.5 μg g ⁻¹	[65]
α-tocopherol (LDPE)	MeOH	0.8 mL min ⁻¹	Omnispher C18, 150 x 4.6 mm (25°C)	FL (λ _{exc.} : 282 nm; λ _{em.} : 308 nm)	5 × 10 ⁻² mg mL ⁻¹	[47]
α-tocopherol (PE)	ACN water	1 mL min ⁻¹	Symmetry C18, 50 x 3.9 mm, 5 μm	UV-Vis (220 nm)	---	[66]
α-tocopherol (LDPE)	ACN water	1 mL min ⁻¹	Symmetry C18, 50 x 3.9 mm, 5 μm	UV-Vis (220 nm)	---	[48]
α-tocopherol (LDPE)	Hex 2-PrOH	0.5 mL min ⁻¹	LiChrosorb 5 silica, 250 x 2 mm	FL (λ _{exc.} : 292 nm; λ _{em.} : 324 nm)	---	[67]
α-tocopherol (PE and PP)	EtOH Hex	1.5 mL min ⁻¹	Zorbax IB-SIL-CN, 250 x 4.6 mm	UV-Vis (290 nm)	---	[68]
	Dioxane Hex	1 mL min ⁻¹	Zorbax SIL, 250 x 4.6 mm			
α-tocopherol (Polyolefins)	Hex: 1,4-dioxane	1 – 3.5 mL min ⁻¹	Zorbax SIL, 250 x 4.6 mm	UV-Vis (290, 275 nm)	---	[69]
α-tocopherol (PP)	ACN Water	1 mL min ⁻¹	Symmetry C18, 50 x 3.9 mm, 5 μm (40°C)	UV-Vis (220 nm)	---	[38]
Anthocyanin (PP, PVC)	MeOH FA water	1 mL min ⁻¹	Symmetry C18, 250 x 4.6 mm, 5 μm	UV-Vis (590 nm)	---	[70]
L-ascorbic acid (rosemary extract) (PP)	Aqueous Na ₂ HPO ₄ MeOH	1 mL min ⁻¹	Not specified	UV-vis (263 nm)	---	[71]
Catechin, epicatechin (PP)	MeOH water	0.5 mL min ⁻¹	SunFire C18, 150 x 3.0 mm, 3.5 μm	UV-Vis (277nm), FL (λ _{exc.} : 290 nm; λ _{em.} : 310 nm)	---	[72]

So, different methods based on RP have been reported for the separation of fatty acid derivatives [99,100]. Among them, the use of non aqueous RP has become one of the most used modes for the separation of these compounds [99].

The most used detection techniques are UV detection, evaporative light-scattering detection (ELSD) and MS detection. MS with several ionization techniques has been successfully used to determine the structure of these compounds. Among them, thermospray ionization, ESI and atmospheric pressure chemical ionization are used. Nevertheless, the performance of ESI with non-aqueous mobile phases is not optimum [99,101].

2.2. Separation and detection of additives for the enhancement of appearance

Colorants are not included in food contact material regulations and the European legislation restricts the use of these additives in toys [8].

Moreover, different colorants used as plastic additives, for example azo dyes, have been banned by the Registration, Evaluation, Authorisation and Restriction of Chemicals (REACH) [9], which covers restriction of chemicals in concentrations higher than 0.1% by mass of plasticized material.

Table 3. Summary of liquid chromatography based methods for the determination of ultraviolet light stabilizers in plastics.

Analytes (matrix)	Mobile phase Initial - Final	Flow	Column - Particle packing (Temperature)	Detection	LOQ	Reference
Tinuvin 770 and Hostavin TMN 20 (PP)	ACN water	2 mL min ⁻¹	Hibar 250-4 LiChrosorb-NH ₂ , 250 x 4 mm, 25-40 μm	UV/Vis (208 nm)	2 × 10 ⁻² mg mL ⁻¹	[76]
Chimassorb 944 (PP)	THF Water ACT MeOH + DEA	---	Nucleosil C18, 125 x 4.6 mm, 5 μm (Room temperature)	UV/Vis (240 nm)	---	[80]
Chimassorb 944 (PE)	TL + HHP	1 mL min ⁻¹	Ultraguard GPC 10 ² -10 ³ Å, 50 x 7.8 mm, 10 μm styrene-divinyl benzene copolymer	FID	2 × 10 ⁻² mg mL ⁻¹	[81]
Chimassorb 944 and Cyasorb UV 3346 (PP)	THF + DEA	1 mL min ⁻¹	Ultrastragel 1000 Å, 300 x 7.8 mm and Ultrastragel 500 Å, 300 x 7.8 mm connected in series.	UV/Vis (239 nm)	1 × 10 ⁻² mg mL ⁻¹ for Chimassorb 944 5 × 10 ⁻³ mg mL ⁻¹ for Cyasorb UV 3346	[82]
Chimassorb 944 (PP)	THF + DEA	1 mL min ⁻¹	LiChrogel PS4 and PS1 connected, 250 x 7 mm (Room temperature)	UV/Vis (244 nm)	---	[83]
Tinuvin 770 and Chimassorb 944 (HDPE)	CH ₂ Cl ₂	1 mL min ⁻¹	μ-Bondapak C18, 250 x 4.6 mm, 10 μm	UV/Vis (230 nm)	---	[77]
	CH ₂ Cl ₂	1 mL min ⁻¹	Zorbax-CN, 250 x 4.6 mm, 10 μm	UV/Vis (230 nm)	---	
	Hex	1 mL min ⁻¹	Silica 60, 250 x 4.6 mm, 10 μm	UV/Vis (230 nm)	---	
	ACN	1 mL min ⁻¹	NH ₂ μ-bondapak, 250 x 4.6 mm, 10 μm	UV/Vis (230 nm)	---	
	ACN water	1 mL min ⁻¹	NH ₂ Adsorbosphere, 250 x 4.6 mm, 10 μm	UV/Vis (230 nm)	---	
Chimassorb 944, Chimassorb 119, Chimassorb 2020, Tinuvin 622, Tinuvin 770, (PP and HDPE)	aqueous 10 mM NH ₄ Ac solution adjusted to pH 9.5 with 25 % aqueous NH ₄ OH to which 500 μL/L n-hexylamine ACN to which 700 μL/L n-hexylamine 2-PrOH I to which 700 μL/L n-hexylamine	0.5 mL min ⁻¹	Xterra C8, 150 x 30 mm; 5 μm (60 °C)	UV/Vis (240 nm), ELSD	5 × 10 ⁻² mg mL ⁻¹ for Chimassorb 944 622: 4 × 10 ⁻² mg mL ⁻¹ for Tinuvin	[78]
Tinuvin 328 (PE)	Hex CH ₂ Cl ₂ ACN	1.5 mL min ⁻¹	Nucleosil 120-5 SIL, 250 x 4.6 mm, 5 μm Guard column: Nucleosil 120-5 SIL, 15 x 4.6 mm, 5 μm (30 °C)	UV/Vis (275 nm)	3 × 10 ⁻⁴ - 1 × 10 ⁻³ mg mL ⁻¹	[55]
Chimassorb 81, Tinuvin 326, Tinuvin 327, Tinuvin 328.	MeOH water	1 mL min ⁻¹	Nova-Pak C18, 150 x 3.9 mm, 4 μm Guard column: Nova-Pak Sentry C18, 20 x 3.9 mm, 4 μm	UV/Vis (278 nm), MS	---	[44]
Tinuvin 328, Tinuvin 770.	Water ACN MeOH	0.2 mL min ⁻¹	Zorbax Eclipse XDB-C8 Solvent Saver Plus, 100 x 3.0 mm, 3.5 μm (50°C)	UV/Vis, MS	---	[43]
Chimassorb 81, Tinuvin 234, Tinuvin 326, Tinuvin 327, Tinuvin 328.	Water ACN	1 mL min ⁻¹	Zorbax Eclipse XDB-C18, 30 x 4.6 mm, 1.8 μm (40 °C)	MS	1 × 10 ⁻⁶ -2.2 × 10 ⁻⁵ mg mL ⁻¹	[42]

Continued Table 3. Summary of liquid chromatography based methods for the determination of ultraviolet light stabilizers in plastics.

Analytes (matrix)	Mobile phase Initial - Final	Flow	Column - Particle packing (Temperature)	Detection	LOQ	Reference
Tinuvin 770 and Chimassorb 944	UPLC-UV/Vis.- aqueous 10mM K ₂ HPO ₄ solution adjusted to pH 11.5 with 0.2% aqueous 2M KOH ACN	0.5 mL min ⁻¹	Acquity UPLC BEH C18, 50 x 2.1 mm, 1.7 μm (30 °C)	UV/Vis, LTQ FT Orbitrap MS	2.8 × 10 ⁻³ - 11.4 × 10 ⁻³ mg mL ⁻¹ for UV/Vis.	[79]
Tinuvin 326	THF ACN MeOH water	1 mL min ⁻¹	LiChrospher RP-Select B, 250 x 4.6 cm, 5 μm	UV/Vis (280 nm), RI, MS	4.5 · 10 ⁻³ - 5 · 10 ⁻³ mg mL ⁻¹ for UV/Vis	[18]

Table 4. Summary of liquid chromatography based methods for the determination of antistatics in plastics.

Analytes (matrix)	Mobile phase Initial - Final	Flow	Column - Particle packing (Temperature)	Detection	LOQ	Reference
Atmer 129	Water ACN MeOH	0.2 mL min ⁻¹	Zorbax Eclipse XDB-C8 Solvent Saver Plus, 100 x 3.0 mm, 3.5 μm (50 °C)	UV/Vis, MS	---	[43]
Span 20, Span 60, Span 65, Span 80, Span 85	2-PrOH water	0.4 mL min ⁻¹	SunFireTM C18, 15 x 3.0 mm, 3.5 μm (45 °C) for HPLC-UV/Vis Luna C18, 150 x 4.6 mm, 5 μm (30 °C) for HPLC-ESI-MS/MS	UV/Vis (220 nm), MS	1.1 × 10 ⁻¹ - 1.5 × 10 ⁻¹ mg mL ⁻¹ for UV/Vis	
Atmer 129	2-PrOH water	0.4 mL min ⁻¹	Luna C18, 150 x 4.6 mm, 5 μm particle (30 °C)	MS	---	[96]
	Water MeOH	0.5 mL min ⁻¹	Acquity UPLC BEH C18, 50 x 2.1 mm, 1.7 μm (30 °C)	ELSD	3 × 10 ⁻³ mg mL ⁻¹	
Atmer 163	aqueous 0.1% FA: ACN	0.2 mL min ⁻¹	Not specified	LTQFT Orbitrap mass spectrometer	1.2 × 10 ⁻⁴ mg mL ⁻¹	
Armostat 400, CAS 61791-31-9, amina	ACN CHCl ₃ MeOH ACT CH ₂ Cl ₂ water	---	Spherisorb ODS, 200 x 0.32 mm, 3 μm Novapak C18, 200 x 0.32 mm, 4 μm Supelco LC-18-DB, 250 x 4.6 mm, 5 μm Supelcosil-LC-NH ₂ , 250 x 4.6 mm	UV/Vis, ELSD	---	[32]
Armostat 1800, amina	C8 - Water:ACN C18 - Water:MeOH	0.2 mL min ⁻¹	Zorbax Eclipse XDB-C8 SolventSaver Plus, 100 x 3.0mm, 3.5 μm (45 °C) Zorbax Eclipse XDB-C18 Solvent Saver Plus, 150 x 3.0 mm, 3.5 μm (50 °C)	UV/Vis, MS	---	[43]
Pationic 909, Glycerol triestearate	C8 - Water:ACN C18 - Water:MeOH	0.2 mL min ⁻¹	Zorbax Eclipse XDB-C8 SolventSaver Plus, 100 x 3.0 mm, 3.5 μm (45 °C) Zorbax Eclipse XDB-C18 Solvent Saver Plus, 150 x 3.0 mm, 3.5 μm (50 °C)	UV/Vis, MS	---	[43]

Continued **Table 4.** Summary of liquid chromatography based methods for the determination of antistatics in plastics.

Analytes (matrix)	Mobile phase Initial - Final		Flow	Column - Particle packing (Temperature)	Detection	LOQ	Reference
Sorbitan esters of palmitic, stearic, oleic, isostearic and sesquioleic acids from differentes sources (commercial names Span, Crills, Sorbac, Adochan, Hamorad) Span 40, span 60, span 65, span 80, span 85	2-PrOH water		---	Lichrosorb RP18, 10 μ m	UV/Vis (220 nm)	---	[97]
Span 20, span 60, span 80, arlancel 83	2-PrOH water	2-PrOH water	1 mL min ⁻¹	Nova-Pak C18, 100 x 8 mm, 5 μ m	UV/Vis (220 nm)	---	[94]
Span 80, span 85	2-PrOH water	2-PrOH water	0.3 mL min ⁻¹	Inertsil ODS, 250 x 4.6 mm (35 °C)	UV/Vis (210 nm)	---	[98]

2.2.1. Colorants

Product differentiation to make products more aesthetically pleasing and visual attention to make products more visually pleasing are perhaps the main reasons why polyolefins are frequently colored [3].

Colorants are divided into two classes taking into account their physical behavior. Pigments are practically insoluble, whereas dyes are soluble in the medium of application. Although the chemical structure of dyes and pigments is very similar, the solubility of dyes in the medium of application prevents the presence of visible particles and lets the medium remain unchanged [87]. Consequently, dyes supply a tint of colour that creates extra product differentiation for transparent polyolefin packagings, a market segment that constantly relies more and more on transparent plastics [3].

Among the several types of dyes, the azo derivatives have been extensively used mainly due to their colorfastness and low price. But their chromophoric azo group is related to toxicity risks due to the azo group. Under certain conditions it can be reduced to confirmed or suspected carcinogenic aromatic amines [102].

For example, the azo colorant DimethylYellow has been classified as a category 2B carcinogen to humans by the International Agency for Research on Cancer and its control in zones of wood, paper or textile of toys,

appears reflected in the normative EN 71-9 [103] with the sample treatment and the determination method signaled in the pr-EN 71-10 [104] and pr EN71-11 [105], respectively. These regulations were mandated by the European Commission (M/229). They addressed the risks presented by organic compounds in toys and took into account the potential exposure and toxicological effects of those substances which presented the greatest health risks.

The Sudan Black azo dye is one of the most used dyes in the toy industry and its reduction products are considered carcinogen aromatic amines classified as category 3 carcinogen by the International Agency for Research on Cancer [106].

According to the procedure for the estimation of probable toxicity of substances of Cramer and Ford [107], these azo dyes are seriously toxic class III substances several methods for the separation and determination of dyes by reversed phase HPLC are summarized in Table 5 [46,108,109]. UV/Vis detectors are used for the routine control of these compounds in different matrixes [46,108]. The MS detector seems more adequate when it needs to guarantee the compliance of the article with the regulation that bans the studied compounds, as the achieved detection limits are lower than those obtained with HPLC-UV/Vis [109].

Table 5. Summary of liquid chromatography based methods for the determination of colorants in plastics.

Analytes (matrix)	Mobile phase Initial – Final	Flow	Column – Particle packing (Temperature)	Detection	LOQ	Reference
Sudan I, Sudan IV and Disperse Red I (PVC)	MeOH	1 mL min ⁻¹	Trader Excel 120 ODSA, 250 x 4.6 mm, 5 μm	UV/Vis (230, 280 nm)	---	[108]
Fat Brown RR, Malachite Green Carbinol Base, Dimethyl Yellow, Sudan I, Antioxidant 2246, BHT, Irganox 1010, Sudan Orange G, Solvent Blue 35, Sudan II, Sudan Black, Sudan III, Sudan IV, Ethanox 330, Irgafos 168 oxidised, Irganox 1076.	Water MeOH	0.5 mL min ⁻¹	Acquity UPLC BEH C18, 50 x 2.1 mm, 1.7 μm (30 °C)	UV/Vis	8 × 10 ⁻⁵ - 5 × 10 ⁻⁴ mg mL ⁻¹	[46]
Fat Brown RR, Malachite Green Carbinol Base, Dimethyl Yellow, Sudan I, Sudan Orange G, Solvent Blue 35, Sudan II, Sudan Black, Sudan III, Sudan IV.	Water MeOH ACN	0.5 mL min ⁻¹	Luna C18, 150 × 4.6 mm, 5 μm (30 °C) for HPLC–ESI-MS/MS Symmetry C18, 150 × 3.0 mm, 3.5 μm (30 °C) for HPLC–UV/Vis	UV/Vis, MS	1 × 10 ⁻⁶ - 9 × 10 ⁻⁶ mg mL ⁻¹ for HPLC–ESI-MS/MS 2 × 10 ⁻⁴ - 6 × 10 ⁻⁴ mg mL ⁻¹ for HPLC–UV/Vis	[109]

Therefore, MS detection can be used in the validation step of HPLC–UV/Vis procedures which confirm the identity of each chromatographic peak.

In addition, chromatographic conditions from independent HPLC methods can be transferred to a single ultra performance liquid chromatography method, if different types of additives are required to be controlled in a short time period [46].

3. Sample treatment for concentration level measurements

Different extraction techniques were used to determine the level of additives in polymers [110].

Conventional extraction techniques namely dissolution and precipitation of the polymer, soxhlet

extraction, reflux and diffusion extraction are compiled in Table 6.

The extraction conditions employed usually depend on the type of additive, the polymeric matrix and its appearance (pellets, films, etc) [2, 12–15, 18, 20, 21, 23–26, 31, 36, 41, 45, 47, 49, 52, 60–65, 67, 68, 70, 73, 76, 78, 80, 81–83, 111–117]. Therefore, temperature and extraction time usually range between 25–160°C and 15 minutes - 72 hours, respectively. Additionally, chloroform [13–15, 26, 31, 49, 76, 77], toluene [36, 77, 78, 80, 83, 113] and dichloromethane [18, 21, 23, 25, 60, 68, 112] are the most frequently used solvents.

Other approaches to extraction techniques are shown in Table 7. New developments in extraction techniques applied to polymers, such as Microwave Assisted Extraction, Ultrasonic

Table 6. Extraction conditions of plastic additives by conventional extraction techniques (Dissolution or precipitation of the polymer, Soxhlet extraction, Heating under reflux...).

Polymer additives	Polymer matrix	Extraction conditions		HPLC method	Concentration range	Recovery (%)	Reference
		Type	Procedure				
DBP, Tinuvin 326, Irganox 1010, Irgafos 168, Ultrinox 626, oxidized Irgafos 168	PP	Soxhlet Dissolution+precipitation	Sample: 5 g Solvent: 250 mL of CH ₂ Cl ₂ Extraction conditions: 50 °C/6 h Dissolution: 100 mL of refluxing TL Precipitation: addition of 250 mL of MeOH Evaporation of the extract to dryness Dissolution of the residue in 2 mL of THF	HPLC-UV/Vis	40-900 mg Kg ⁻¹	---	[18]
Irganox 1010	PP	Heating under reflux	Sample: 0.5g Solvent: 10 mL of CHCl ₃ Extraction conditions: 4.5 h Filtration and evaporation to dryness Precipitation of oligomers by addition of EtOAc	HPLC-MS, UV/Vis	---	---	[12]
BHT, Irganox 1010, Irganox 1076, Santonox R, Ethyl 330, Goodrite 3114, Topanol CA	PE, PP	Dissolution+precipitation	Sample: 1-2 g Solvent: 50 mL of decalin Dissolution: heating and stirring 110 °C/30 min (or until complete dissolution) Precipitation: cooling to room temperature with stirring	HPLC-UV/Vis	≤ 0.1%	---	[55]
Irganox 1076, NC-4, Naurgard-XL	PP	Heating	Sample: 5 g Solvent: 10 mL of ACN Extraction conditions: 60 °C/72 h	HPLC-UV/Vis-MS	0.04-06%	---	[20]
DBB, BHT, DBP, Irgafos 168, Irganox 1010, Irganox 1076	PP based	US or Soxhlet	US: Sample: 3.7 g Solvent: 50 mL of CH ₂ Cl ₂ Soxhlet: Sample: 7.5 g Solvent: 100 mL of CH ₂ Cl ₂ Extraction conditions: up to 9h for both procedures	HPLC-UV/Vis	<150 mg Kg ⁻¹	---	[21]
Ultrinox 626 and degradation products	PP	Heating	Sample: 1 g Solvent: 20 mL of CH ₂ Cl ₂ Extraction conditions: 85°C/15 min	HPLC-UV/Vis	400-1000 mg Kg ⁻¹	90-100%	[23]
BHT, Irganox 1076	LDPE, PP	Heating under reflux	Sample: 2 g Solvent: 10 mL of CCl ₄ for LDPE and 10 mL of THF for PP Extraction conditions: 2 h Precipitation of LDPE by addition of 10 mL of ACT Filtration and evaporation to dryness	HPLC-UV/Vis	0.05%	≥98%	[24]
BHT, TNPP, Topanol CA, Goodrite 3114, Irganox 1010, Weston 618, Ethyl 330, DLTDP, Irganox 1076, DSTDP	PP	Soxhlet	Sample: 50 g Solvent: 250 mL of CH ₂ Cl ₂ Extraction conditions: 48 h for pellets, 2 h for film Evaporation to dryness and redissolution	HPLC-UV/Vis-IR	0.10-0.5%	10-120%	[25]

Continued Table 6. Extraction conditions of plastic additives by conventional extraction techniques (Dissolution or precipitation of the polymer, Soxhlet extraction, Heating under reflux...).

Polymer additives	Extraction conditions			HPLC method	Concentration range	Recovery (%)	Reference
	Polymer matrix	Type	Procedure				
Irganox 1010, Irgafos 168	PE	Soxhlet	Sample: 10 g Solvent: 60 mL of CHCl ₃ Extraction conditions(x 3): 3h Evaporation of extract Precipitation of low molecular weight fractions by addition of ACN	HPLC-UV/Vis	200-900 mg Kg ⁻¹	---	[26]
Irganox 1330	PE	Dissolution+precipitation	Sample: 1 g Solvent: 100 mL of NH Dissolution: autoclave with magnetic stirrer, 160°C /15 min plus 45/160°C Precipitation: cooling into cold water for 40 min Filtration and injection of supernatant	HPLC-UV/Vis	>0.013 mg g ⁻¹	---	[111]
Irganox 1076	LDPE	Soxhlet or MAE	Soxhlet: Sample: 2.45 g Solvent: 125 mL of CHCl ₃ Extraction conditions: 40 °C/3 h MAE: Sample: 2.30 g Solvent: 50 mL of ACN Extraction conditions: 120 °C/30 min/2.5 bar/ cooling 30 min	HPLC-UV/Vis	0.57 mg Kg ⁻¹	≈ 90%	[31]
Phosphite derivatives	PP	Dissolution+precipitation	Sample: 10 g Solvent: 200 mL of TL Dissolution: heating to 110 °C Cooling 50 °C Precipitation: addition of 200 mL of MeOH	HPLC-UV/Vis	100 mg Kg ⁻¹	---	[36]
Irganox 1010, Irganox 1076, Irganox 1330	PP	Heating under reflux	Sample: 0.5 g Solvent: 10 mL of CHCl ₃ Extraction conditions: 4.5 h Precipitation of oligomers by addition of EtOAc	HPLC-UV/Vis-MS	0.1-0.25%	---	[13]
Irganox 1010, Irganox 1076	PE, PP	Heating under reflux	Sample: 500 mg Solvent: 10 mL of CHCl ₃ Extraction conditions: 3-4 h Filtration and evaporation	HPLC-UV/Vis	---	---	[14]
Irganox 1330	PP	Heating under reflux	Sample: 0.5 g Solvent: 10 mL of CHCl ₃ Extraction conditions: 4.5 h Precipitation of the oligomers by addition of EtOAc	HPLC-UV/Vis-MS	---	---	[15]
ADK Stab AO-60, Everfos 168, Kinox 30, Irganox 3114, Irganox 1076, and Cyanox 1790	PP	Heating under reflux	Sample: 500 mg Solvent: 50 mL of TL Extraction conditions: 1 h Cooling to room temperature Precipitation of PP by addition of 25-50 mL of MeOH Filtration, evaporation and redissolution	HPLC-UV/Vis HPLC-MS	---	---	[2]
Irganox 1010, Irganox 1076, and Irgafos 168	PE, PP	Dissolution+precipitation	Sample: 1g Solvent: 25 mL of TEP in OXYL Dissolution: heating and stirring 130°C/30 min Precipitation: stirring t>2 h	HPLC-UV/Vis	10-11350 mg Kg ⁻¹	74-126%	[41]

Continued Table 6. Extraction conditions of plastic additives by conventional extraction techniques (Dissolution or precipitation of the polymer, Soxhlet extraction, Heating under reflux...).

Polymer additives	Extraction conditions			HPLC method	Concentration range	Recovery (%)	Reference
	Polymer matrix	Type	Procedure				
BHT, Irganox 1330, Irganox 1076, Irganox PS800, Irganox 1520, Irganox 1035, Irganox 245, Irganox 3052	PE	Soxhlet	Sample: 10 g Solvent: 100 mL of CH ₂ Cl ₂ Extraction conditions: 40 °C/40 h Addition of 100µL L ⁻¹ of P(OEt) ₃ to prevent the degradation of additives and polymer chain scissions	HPLC-UV/Vis	150-2500 mg Kg ⁻¹	---	[112]
Irganox 1076	LDPE	Dissolution+precipitation	Sample: 0.1 g Solvent: 6 ml of TL Dissolution: heating to 70 °C Cooling at room temperature Precipitation: addition of 15 mL of MeOH. Centrifugation and separation Evaporation to dryness and reconstitution with 5 mL of MeOH.	HPLC-UV/Vis	1000-6000 mg Kg ⁻¹	---	[113]
Irgafos 168, Irganox 1010	PP based	Heating	Solvent: IOA:EtOH (90:10) Extraction conditions: 2 x (80 °C/24 h)	HPLC-UV/Vis	250-1100 mg Kg ⁻¹	---	[45]
BHA, BHT	LDPE	Heating under reflux	Sample: 1 g Solvent: 250 mL of ACN Extraction conditions: stirring under reflux and light protection 28 °C/24 h	HPLC-FL	1.5 %	> 69%	[47]
Santonox R	PE	Soxhlet or MAE	Soxhlet: Sample: 1.5 g Solvent: 100 ml of CHCl ₃ Extraction conditions: 5 h MAE: Sample: 100-130 mg Solvent: 10 ml of ACN Extraction conditions: 25 to 100 °C/40 min (total time)	HPLC-UV/Vis	---	---	[49]
Irganox 1010, Irgafos 168	PE, PP	Soxhlet, dissolution +precipitation, MAE, heating, ASE	Each participant selected their own experimental conditions.	HPLC	100-2000 mg Kg ⁻¹	70-98%	[114]
α-tocopherol	LDPE	Soxhlet	Sample: 10 g Solvent: CH ₂ Cl ₂ Extraction conditions: 6 h Evaporation of the extract to dryness Dissolution of the products in 10 mL of Hex	HPLC-UV/Vis	---	---	[60]
α-tocopherol	LDPE	Diffusion extraction	Sample: 1g Solvent: 40 mL of THF Extraction conditions: 24h Evaporation of the extracts to dryness in a Rotavapor at 30°C Dissolution in Hex to 20 mL	HPLC-FL	---	---	[61]
α-tocopherol	LDPE	Diffusion extraction	Sample: 0.1 g Solvent: 60 mL of THF Extraction conditions: 25 °C/24 h in darkness	HPLC-FL	0.13-1.74 %	82.9–86.0 %	[62]

Continued Table 6. Extraction conditions of plastic additives by conventional extraction techniques (Dissolution or precipitation of the polymer, Soxhlet extraction, Heating under reflux...).

Polymer additives	Extraction conditions			HPLC method	Concentration range	Recovery (%)	Reference
	Polymer matrix	Type	Procedure				
α-tocopherol	LDPE	Dissolution+precipitation	Sample: 1.0 g Solvent: 70 mL of TL Dissolution: heating and stirring 65 °C/15 min Precipitation: addition of 50 mL of cold MeOH Filtration and evaporation to dryness Dissolution of the residue in 5 mL of MeOH	HPLC-UV/Vis	1500-1621 mg Kg ⁻¹	95.8-106.0 %	[63]
α-tocopherol	LDPE	Heating under reflux	Sample: 1 g Solvent: 250 mL of ACN Extraction conditions: stirring under reflux and light protection 28 °C/24 h	HPLC-FL	19.1-30.2 mg Kg ⁻¹	86.3 %	[64]
α-tocopherol	LDPE	Diffusion extraction	Sample: 0.1 g Solvent: 60mL of THF Extraction conditions: 25 °C/24 h in darkness	HPLC-FL	----	90.5 %	[65]
α-tocopherol	LDPE	Heating under reflux	Sample: 1 g Solvent: 250 mL of ACN Extraction conditions: stirring under reflux and light protection 28 °C/24 h	HPLC-FL	11.8-30.7 mg g ⁻¹	90.5 %	[47]
α-tocopherol	LDPE	Diffusion extraction	Sample: 1 g Solvent: 40 ml of THF Extraction conditions: 24 h Evaporation to dryness Redissolution in Hex to 40-80 mL	HPLC- FL	---	90 %	[67]
α-tocopherol	PE and PP	Soxhlet	Soxhlet extraction: Solvent: CH ₂ Cl ₂ Extraction conditions: 8 h under nitrogen Evaporation under vacuum Redissolution of the products in Hex	HPLC-UV/Vis	---	---	[68]
α-tocopherol	LDPE	Diffusion extraction	Sample: 1.5 g Solvent: 80 mL of EtOH (96%) Extraction conditions: 25 and 3°C	HPLC-UV/Vis	---	---	[115]
α-tocopherol	PE and PP	Soxhlet	Not specified	HPLC-UV/Vis	---	---	[116]
α-tocopherol	PP	Extraction with solvent	Additives are dissolved in CH ₂ Cl ₂ or EtOH and delivered with the polymer feed by a high pressure liquid chromatography pump	HPLC-UV/Vis	---	---	[117]
Anthocyanin	PP, PVC	Diffusion extraction	Solvent: MeOH:water (50:50) containing 4% formic acid Preconcentration of extracts under nitrogen flow and load on a C18 Sep-Pak cartridge	HPLC-UV/Vis	---	---	[70]
Chimassorb 944	PE	Dissolution+precipitation	Sample: 0.5 g-2.0 g Solvent: 50 mL of decalin Dissolution: heating and stirring 120 °C/30 min Precipitation: cooling and stirring at room temperature	HPLC	>0.05 %	97-103 %	[81]
Tinuvin 770, Chimassorb 944	HDPE	Diffusion extraction	Sample: 10 g Solvent: 100 mL of CHCl ₃ Extraction conditions: 1 and 4 weeks at room temperature	HPLC-UV/Vis	---	---	[77]

Continued Table 6. Extraction conditions of plastic additives by conventional extraction techniques (Dissolution or precipitation of the polymer, Soxhlet extraction, Heating under reflux...).

Polymer additives	Extraction conditions						
	Polymer matrix	Type	Procedure	HPLC method	Concentration range	Recovery (%)	Reference
Tinuvin 770, Chimassorb 944	HDPE	Heating	Sample: 10 g Solvent: TL Extraction conditions: under reflux 160 °C/2 to 4 h	HPLC-UV/Vis	---	95%	[77]
			Sample: 10 g Solvent: 100 mL of o-dichlorobenzene Extraction conditions: 160 °C/1 h. Precipitation of HDPE with 2-PrOH Filtration			65-70%	
			Sample: 5 g Soxtec extraction Solvent: 80 mL of CH ₂ Cl ₂			50%	
Chimassorb 944	PP	Dissolution+precipitation	Sample: 1 g Solvent: 30 mL of TL Dissolution: under reflux 130 °C/40 min Cooling to 60 °C Precipitation: addition of 75 mL of 1% TEA solution in MeOH Cooling to room temperature Filtration and evaporation to dryness Dissolution in 5 mL THF	HPLC-UV/Vis	0.02-1.0 %	---	[83]
Chimassorb 944	PP	Dissolution+precipitation	Sample: 0.9-1.1 g Solvent: 25 mL of TL Dissolution: stirring 40 min Cooling to 60 °C Precipitation: addition of 75 mL of MeOH Cooling to room temperature Filtration and evaporation to dryness of the combined filtrate Dissolution in 5 mL of THF	HPLC-UV/Vis	0.05-0.5 %	96%	[80]
Tinuvin 770, Hostavin TMN 20	PP	Dissolution+precipitation	Sample: 10 g Solvent: CHCl ₃ Dissolution: 16 h Concentration to 20 mL under flow of nitrogen. Precipitation: stirring with 80 mL of ACT Filtration and washed with hot ACT Concentration under flow of nitrogen with 10 mL of CHCl ₃	HPLC-UV/Vis	---	95.6-96.2%	[76]
Chimassorb 944, Cyasorb UV 3346	PP	Dissolution+precipitation	Sample: 2.5 g Solvent: 80 mL of OXYL Dissolution: under refluxing and stirring 30min Cooling to 100 °C Precipitation: addition of 160 mL of 2-PrOH Filtration and wash with OXYL: 2-PrOH (1:2) Evaporation to dryness Dissolution of the residue to 10 mL of THF	HPLC (GPC)-UV/Vis	---	90-100%	[82]

Continued Table 6. Extraction conditions of plastic additives by conventional extraction techniques (Dissolution or precipitation of the polymer, Soxhlet extraction, Heating under reflux...).

Polymer additives	Extraction conditions						
	Polymer matrix	Type	Procedure	HPLC method	Concentration range	Recovery (%)	Reference
Chimassorb 944	PP	Dissolution+precipitation	Sample: 1 g Solvent: 30 mL of TL Dissolution: under reflux 130 °C/40 min Cooling to 60 °C Precipitation: addition of 75 mL of 1% TEA solution in MeOH Cooling to room temperature Filtration Evaporation to dryness Dissolution in 5 mL THF	HPLC (GPC)-UV/Vis	0.02-1.0 %	82-98%	[83]
Chimassorb 944, Chimassorb 119, Chimassorb 2020, Tinuvin 622, Tinuvin 770.	PP and HDPE	Dissolution+precipitation	Sample: 10 g Solvent: 100 mL of TL Dissolution: under reflux Precipitation: addition of 75 mL of MeOH Filtration and evaporation Redissolution into 5 mL THF	HPLC-UV/Vis-ELSD	>0.05 %	---	[78]
Sudan I, Sudan IV, Disperse Red I	PVC	Soxhlet	Sample: 1 g Solvent: 70 mL of MeOH Extraction conditions: solvent boiling point temperature/7 h	HPLC-UV/Vis	---	95.3-22.6%	[108]

Table 7. New developments in additives extraction conditions from plastics (Microwave, Ultrasonic energy, Supercritical Fluid Extraction, Accelerated solvent extraction, Pressurized liquid extraction...).

Polymer additives	Polymer matrix	Type	Procedure	HPLC method	Concentration range	Recovery (%)	Reference
BHT, BHEB, Irgafos 168, Irganox 1010, Irganox 1076, Ultrinox 276, Irganox 1330, Goodrite 1330, Irganox 3114, AM340, Ultrinox 626	HDPE, LDPE, PP	MAE or US	Sample: 5 g MAE: Solvents: 50 mL of CYHA:2-PrOH (1:1) or CH ₂ Cl ₂ :2-PrOH (98:2) Extraction conditions: 20 min US: 50 mL of CYHA:2-PrOH (1:1) or CH ₂ Cl ₂ :CYHA (75:2) Extraction conditions: 30-60 min	HPLC-UV/Vis	500-1000 ppm	80-100%	[19]
DBB, BHT, DBP, Irgafos 168, Irganox 1010, Irganox 1076	PP based	US or Soxhlet	US: Sample: 3.7 g Solvent: 50 ml of CH ₂ Cl ₂ Soxhlet: Sample: 7.5 g Solvent: 100 ml of CH ₂ Cl ₂ Extraction conditions: up to 9h for both procedures	HPLC-UV/Vis	<150 µg g ⁻¹	---	[21]
Irgafos 168, Irganox 1010, Irganox 1076, Irganox PS800, Hostanox O3, Hostanox SE2	PP	SFE	Extraction conditions: 0.85 g L ⁻¹ CO ₂ /60 °C/ 2x 30 min (static with Hex and MeOH) plus 90 min (dynamic)	HPLC-UV/Vis	---	75%, except for Irganox 1010 and Hostanox O3	[118]

Continued Table 7. New developments in additives extraction conditions from plastics (Microwave, Ultrasonic energy, Supercritical Fluid Extraction, Accelerated solvent extraction, Pressurized liquid extraction...).

Polymer additives	Polymer matrix	Type	Procedure	HPLC method	Concentration range	Recovery (%)	Reference
Irganox 1010	PP	ASE	Sample: 0.2 g Solvent: 1.5-2.5 mL min ⁻¹ of 2-PrOH or ACT Extraction conditions: preheat 2 min and 150 °C/2 min (2-PrOH) or 140 °C/6 min (ACT)	HPLC-UV/Vis	---	90%	[22]
Irganox 1010, Irgafos 168	PE	US	Sample: 3 g Solvent: 15 mL of CHCl ₃ Extraction conditions: heating to 60 °C within 15 min and then keeping for 45 min Cooling and filtration	HPLC-UV/Vis	0.22-1.58 g Kg ⁻¹	≈ 100%	[27]
BHT, BHBE, MD 1024, Isonox 129, Irgafos 168, Irganox 1010, Irganox 1076, AM 340	HDPE	US	Sample: 5 g Solvent: 50 mL of CYHA:2-PrOH (50:50) or CH ₂ Cl ₂ :CYHA (75:25) Extraction conditions: 30-40 or 60 min Evaporation, redissolution and filtration	HPLC-UV/Vis	200-800 ppm	>80%	[28]
Ethanox 330	HDPE	SFE	Sample: 1 g Extraction conditions: 350 bar and 1 mL min ⁻¹ CO ₂ /110°C/MeOH 20% 20 min (static) plus 50 min (dynamic)	HPLC	500-1000 µg g ⁻¹	>90%	[29]
Irganox PS802, Irgafos 168, Irganox 1010, Irganox 1425	PP, PE	Microwave: One-step microwave assisted extraction (OSM) or two-step (TSM)	OSM (PP, PE): Sample: 2.5 g Solvent: 25 mL of EtOAc:1-Hex (75:25) Extraction conditions: 100-125°C/ 15 min/1000 W TSM (PP): Sample: 2 g Solvent: 25 mL mixtures with EtOAc, Hex, ACT, 2-PrOH or NH (depending on the sample) Extraction conditions: 125-140°C/30-40 min/1000 W	HPLC-UV/ELSD	1000 ppm	≥93%	[30]
Irganox 1076, Irgafos 168	PE	SFE	Sample: 0.5 g Extraction conditions: 450 bar and 2 mL min ⁻¹ CO ₂ /75 °C/MeOH 10% 5 min (static) plus 30 min(dynamic)	HPLC	200-1000 µg g ⁻¹	≥93% for recycled LDPE, 83% HDPE (2h)	[53]
Topanol OC, Irganox 1330, Irganox 1010, Irganox 1076	PE, PP	SFE	Sample: 3 mg Extraction conditions: 250 bar and 10-20 mL min ⁻¹ CO ₂ /35°C / 2 hours	HPLC-UV	≤1300 ppm	62-105% (relative to Soxhlet extraction)	[119]
Irganox 1076	LDPE	Soxhlet or MAE	Soxhlet: Sample: 2.45 g Solvent: 125 mL of CHCl ₃ Extraction conditions: 40 °C/3 h MAE: Sample: 2.30 g Solvent: 50 mL of ACN Extraction conditions: 120 °C/30 min/2.5 bar Cooling 30 min	HPLC-UV	0.57 ppm	≈ 90%	[31]

Continued Table 7. New developments in additives extraction conditions from plastics (Microwave, Ultrasonic energy, Supercritical Fluid Extraction, Accelerated solvent extraction, Pressurized liquid extraction...).

Polymer additives	Polymer matrix	Type	Procedure	HPLC method	Concentration range	Recovery (%)	Reference
Irganox 1010, Irgafos 168	PE (LDPE, HDPE), PP	MAE	Sample: 1 g Solvent: 30 mL of ACT:NH (1:1) or TCA Extraction conditions: 2-6 min (ACT:NH (1:1)) or 3 min (TCA)/70% power (420W)	HPLC	0.1 %	91-97%	[120]
Irganox 1010, Irganox 1076	PP	MAE	Sample: 0.4 g Solvent: 5 mL of 2-PROH + 5 mL 0.04 mg mL ⁻¹ of internal standard in 2-PROH Extraction conditions: up to 80 °C/75% power/6 min, 80-110 °C/100% power and 110 °C/100% power/30 min)	HPLC-UV/Vis	0.1 %	---	[38]
Irgafos 126, Irgafos 168, BHT, BMP, MD1024, HP136, Irganox 3114, Irganox 1330	PE	PLE	Sample: 1.5 g Solvent: 2-PROH:CYHA (92.5:7.5) Extraction conditions: 105°C/15 min/103 bar	HPLC-UV-Vis	30-350 µg g ⁻¹	---	[121]
Irgafos 168, Irganox 1076	LDPE, HDPE	SFE	Sample: 4 g Extraction conditions: 450 bar and 5 mL min ⁻¹ CO ₂ /80°C/0.1 mL min ⁻¹ MeOH	HPLC-UV-Vis	333-666 mg Kg ⁻¹	>94%	[122]
BPA, BHA, Ionox 100, BHT, AO425, Irganox 1010, Irganox 1076 UV-0, UV-9, UV-P, UV-24, UV-234, UV-326, UV-327, and UV-531	PE	US	Sample: 1.0 g Solvent: 15 mL of ACN Extraction conditions: 20 min Centrifugation: 4000 rpm/5 min Evaporation of the extract to dryness and redissolution	UPLC-UV-Vis	5 µg g ⁻¹ spiked sample	65-94%	[39]
Irganox 1076, Irgafos 168, and Irganox 1010	PP	SFE, ESE	SFE: Extraction conditions: 680 bar CO ₂ /100°C/MeOH 10% 70 min ESE: Extraction conditions: 100°C/5 mL min ⁻¹ /2-PROH:CYHA (75:25) 90 min(static)	HPLC-UV/Vis	---	>95% except for Irganox 1010 with 62% by SFE and 86% by ESE	[40]
BHA, Irganox MD 1024, BMP, Irgafos 126, HP 136, Irganox 3114, Irganox 1010, Irganox 1330, Irganox 1076, Irgafos 168	PE	PLE	Solvent: 2-PROH + 7.5 % of CYHA Extraction conditions: 105 °C/15 min/103 bar	NP-HPLC-UV/Vis	--	97-105 %	[55]
Irganox 1076	LDPE	MAE	Sample: 0.3-0.5 g Solvent: 15 mL of ACN or 22 mL of CHCl ₃ :2-PROH Extraction conditions: 80-100 °C/X min (depending on the sample)	HPLC-UV/Vis	----	----	[48]

Continued Table 7. New developments in additives extraction conditions from plastics (Microwave, Ultrasonic energy, Supercritical Fluid Extraction, Accelerated solvent extraction, Pressurized liquid extraction...).

Polymer additives	Polymer matrix	Type	Procedure	HPLC method	Concentration range	Recovery (%)	Reference
Santonox R	PE	Soxhlet or MAE	Soxhlet: Sample: 1.5 g Solvent: 100 mL of CHCl ₃ Extraction conditions: 5 h MAE: Sample: 100-130 mg Solvent: 10 ml of ACN Extraction conditions: 25-100 °C/40 min (total time)	HPLC-UV/Vis	---	---	[49]
Irganox 1010, Irgafos 168	PE, PP	Soxhlet, solution and precipitation, MAE, heating, ASE	Each participant selected their own experimental conditions.	HPLC	100-2000 mg Kg ⁻¹	70-98%	[114]
Irganox 1076, Irgafos 168	LDPE	MAE	Sample: 2 g Solvent: 30mL of CH ₂ Cl ₂ Extraction conditions: 55 °C/2 min and 1 min of extraction time	HPLC	500-1000 µg g ⁻¹	---	[50]
α-tocopherol	PE	MAE	Sample: 0.5 g Solvent: 15 mL of ACN Extraction conditions: up to 80 °C/6 min/75% power, 80 to 100 °C/4 min/100% power and 100 °C/30 min/90% power	HPLC-UV-Vis	---	---	[66]
α-tocopherol	LDPE	MAE	Sample: 0.5 g Solvent. 15 mL of ACN	HPLC-UV-Vis	---	---	[48]
α-tocopherol	PP	MAE	Sample: 0.4 g Solvent: 5 mL of 2-PrOH + 5 mL of 0.04 mg mL ⁻¹ of internal standard in 2-PrOH Extraction conditions: up to 80 °C/6 min/75%, 80 to 110 °C/100% power and 110 °C/30 min/100% power	HPLC-UV/Vis	---	---	[38]
Tinuvin 770, Chimassorb 944	HDPE	US	Sample: 10 g Solvent: 100 mL of CYHA:CH ₂ Cl ₂ (50:50) and CYHA:2-PrOH (50:50) Extraction conditions: 1-4 h at room temperature	HPLC-UV/Vis	---	---	[77]
Tinuvin 328	PE	PLE	Solvent: 2-PrOH + 7.5 % CYHA Extraction conditions: 105 °C/15 min/103 bar	NP-HPLC-UV/Vis	---	97-105 %	[55]
Sudan I, Sudan IV, Disperse Red I	PVC	MAE	Sample. 0.5 g Solvent: 15 mL of MeOH Extraction conditions: 120° C/20 min	HPLC-UV/Vis	---	99.8-59.5%	[108]
Sudan I, Sudan IV, Disperse Red I	PVC	SFE	Sample. 0.4 g Solvent: 8 mL of MeOH Extraction conditions: 552 bar CO ₂ /120° C/30 min (static + dynamic)	HPLC-UV/Vis	---	95.2-41.1%	[108]

Energy, Supercritical Fluid Extraction or Accelerated Solvent Extraction [19,21,22,27,28-31,38-40,48-50,53,55,66,77,108,114,118-122] are summarized in Table 7. Pure solvents or mixtures of ACN, chloroform, isopropanol, cyclohexane and dichloromethane represent the most commonly used solvents in these studies [19,21,27,28,30,31,38,48-50,55,77,121]. The use of alcohols in phosphate antioxidant extraction is related to the degradation process of this type of additive [28]. Concerning extraction time, the quickest methodologies have been achieved using either MAE (3-40 minutes) or ASE (10-40 minutes), and 30 minutes is the average extraction time reported. In most cases, extraction temperatures ranged between 25 and 150°C.

Studies also included the effects of different variables (temperature, time, etc.) on the extraction efficiency. Different authors have emphasized the importance of thickness regarding recovery improvement [27,53,120]. Likewise, different applications of experimental design to optimize extraction variables were also reported [50,55].

Several extraction techniques, such as Soxhlet, solution/precipitation, MAE, heating and ASE have been compared in an interlaboratory study, remarking MAE and solution/precipitation techniques as providing the best results [114]. References of standard methods to determine antioxidants in polyolefins are also included [114].

These methodologies have been applied in most instances to the analysis of PE, LDPE, HDPE, PP as the most common polymers used in food contact materials and toys. Occasionally, they have been applied to analyze PVC as well. Accordingly, the performance of antioxidants in polyolefins can be estimated during polyolefin processing [36,115] and for polyolefin articles [38,47,63,65].

4. Conclusion

The applicability of HPLC methods for the analysis of additives such as antioxidants, ultraviolet light stabilizers, colorants, etc. in commercial polyolefinic samples was demonstrated in many publications over the past few years, as outlined in this review. Nevertheless, more research is required for the evaluation of strategies that focus on improving the determination of some other polyolefin additives such as antistatics.

The tendency of polyolefins to be oxidized during processing and their service life makes antioxidants the most common and studied polyolefin additives. Overall, reversed phase LC and UV or MS detectors were used for the analysis of both antioxidants and their degradation products.

Furthermore, the structural information provided by the MS detectors which allowed the proper identification of each compound, made these detectors adequate for control of banned colorants.

Recently, simple chromatographic methods for determining HALS have been reported using columns compatible with the buffered mobile phase adjusted to a pH value higher than pKa of HALS (pH>10). This condition works with the non-ionized forms of HALS which avoids the addition of a deactivating agent to the mobile phase.

Moreover, few HPLC methodologies using UV, ELSD or MS detection have been reported that analyse non-ionic antistatic additives and which shows the complexity of these mixtures.

In addition, varied techniques have been applied to the extraction of additives from polyolefin before chromatographic analysis. These techniques cover conventional polymer dissolution and precipitation as well as the most innovative MW or ASE, the latter being the most rapid methodologies.

Therefore, the combination of extraction and HPLC methods allows knowledge on the performance of additives; for example the behaviour of antioxidants during processing and plastics shelf life.

Today, the number of additives used in the polyolefin industry is far higher than those addressed in this paper and so, optimized methods are still required. On the one hand, methods that provide detailed information about each additive are necessary. On the other hand, protocols for quality control capable to determine multiple additives are required.

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Abbreviations

1-Hex: 1-hexane;
2-PrOH: isopropanol;
Ac: acetate;
ACN: acetonitrile;
ACT: acetone;
ASE: accelerated solvent extraction;
CYHA: cyclohexane;
DEA: diethanolamine;
ESE: enhanced fluid extraction;
EtOAc: ethyl acetate;
FA: formic acid;
HDPE: high density polyethylene;
Hex: n-hexane;
HHP: piperidine;
HOAc: acetic acid;
IOA: isooctane;
LDPE: low density polyethylene;
MAE: microwave assisted extraction MeOH: methanol;
NH: n-heptane;
NH₄Ac: ammonium acetate;
OXYL: o-xylene;
P(OEt)₃: triethylphosphite;
PE: polyethylene;
PLE: pressurized liquid extraction;
PP: polypropylene;
PVC: polyvinyl chloride;
SFE: supercritical fluid extraction;
TCA: 1,1,1-trichloroethane;
TEA: triethylamine;
TEP: triethylphosphate;
THF: tetrahydrofurane;
TL: toluene;
US: ultrasonic extraction.

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