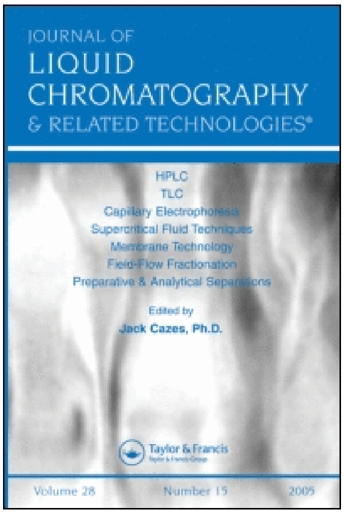

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Chromatographic Methods Used to Identify and Quantify Organic Polymer Additives

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Chromatographic Methods Used to Identify and Quantify Organic Polymer Additives[#]

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ABSTRACT

In this paper, methods for identification and quantitation of organic polymer additives are presented. Information is given in convenient tabular form and detailed references are provided.

Key Words: Polymer additives; Plastic materials; Chromatographic analysis; Polymer analysis; Polymer characterization; Chromatographic methods.

INTRODUCTION

Plastic materials are widely used in numerous industries. The physiochemical nature of these materials provides a multitude of diverse products

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with their necessary, desirable performance characteristics. Commercial plastics are very complex materials. In addition to the various base polymers, commercially viable plastics contain a number of compounding ingredients (additives) whose purpose is to give the material its desired physical and/or chemical properties. Table 1 provides a brief summary of the types of additives typically encountered in commercial polymer systems.

Polymers and polymer systems are characterized for many reasons, including the development of new materials or material sources, end use applications, life test studies, manufacturing control and troubleshooting, and material or vendor identification. As it is typically the additive package that establishes the performance and processing properties of the commercial polymer, characterization of a polymer system for its additive package is essential in terms of material development, manufacturing, use, re-use, and, ultimately, disposal. A complete polymer characterization includes both the identities of the additives and their levels in the product. The identification and quantification of additives in compounded polymers is generally a difficult task for the following reasons:

- There is a wide variety of chemically diverse additive types. Literally thousands of additives are commercially available, ranging from pure compounds, with molecular weights which vary from approximately 100 up to a few thousand mass units, to oligomers with up to 50 (or more) components.
- Many additives are labile and, thus, are difficult to analyze without decomposition.
- Complex mixtures of additives will normally be present in a commercial formulation.
- Separation of the base polymer and fillers from the organic additives is often required prior to additive analysis.
- The levels of the organic additives in a commercial polymer may be quite low (and variable) compared to the base polymer and its associated fillers.

It is for these reasons that chromatographic methods of analysis have been widely employed in polymer characterization. In this paper, a review is provided related to the chromatographic methods used to assess the identity and level of additives in polymer systems.

Table 1. Common additives and fillers.

Classification	Purpose	Examples
Antioxidants	Prevent thermal and/or oxidative degradation during processing, handling and use. Typically are radical scavengers which interrupt the chain propagation steps of polymer auto-oxidation	Irganox 1010, Irgafos 168, BHT
Light stabilizers	Absorb UV light to prevent photo-oxidation	Tinuvin 327, 328, 384, 440, etc. (derivatives of 2-hydroxy-benzophenone)
Heat stabilizers	Protect polymers during thermal processing	Metallic salts, especially of weak fatty acids (e.g., zinc stearate)
Plasticizers	Increase the workability, flexibility or distensibility of polymer	Derivatives of organic acids such as adipic, azelic, citric, phosphoric, phthalic, trimellitic acids.
Lubricants (slip agent)	Reduce polymer adhesion to metal surfaces during processing	Derivatives of fatty acids (esters, amides, metal salts, Erucamide, silicones)
Viscosity improvers	Control the flow and sagging of prepolymers	Ethoxylated fatty acids
Accelerators, activators	Compounds that control the rate or nature of cure of elastomers	Zinc oxide, stearic acid, 2-2′-dithiobis-benzothiazole, zinc dialkyldithio-carbamate
Mold release agents	Prevent adhesion between two surfaces (e.g., sticking of polymer and metal mold)	Derivatives of fatty acids, Montan wax, silicones, diethylene glycol monostearate, ethylene bis(stearamide)
Fillers (extenders)	Finely dissolved solids added to polymer systems to improve properties or reduce cost	Calcium carbonate, kaolin, talc, alumina trihydrate
Flame retardant	Decrease flammability	Alumina trihydrate, mixtures of halogenated organics, and antimony oxide

(continued)

Table 1. Continued.

Classification	Purpose	Examples
Antistatic agents	Dissipate electrostatic surface charge on polymer surfaces	Quaternary ammonium compounds, long chain derivatives of glycols and polyhydric compounds, Atmos 150, *N*,*N*-bis (2-hydroxy-ethyl)alkyl-amine
Colorants	Improve the appearance of polymers, mask discoloration due to processing	Carbon black, titanium dioxide, azo-type dyes
Antimicrobial agents (biocides)	Reduce growth of microbes on polymer surfaces	Copper 8-hydroxyquinolate, *n*-(trichloromethylthio) phthalate
Crosslinking agents	Molecules that have two or more groups capable of reacting with the functional groups of polymer chains, where such a reaction connects or links the chains	2-mercaptobenzothiazole, benzoyl peroxide, dicumyl peroxide, sulfur, toluene diisocyanate
Blowing agents	Gas forming agents that facilitate the expansion of the polymer during processing	Nitrogen, toluenesufonyl semicarbazide, 1,1′-azobis-foramide, phenyltetrazole

DISCUSSION

Given the variety of additives used in commercial polymers, the task of characterizing such multi-component systems for their additive packages can be a daunting one. While an analytical chemist has a multitude of chromatographic tools with which to perform an additives characterization, some guidance in terms of successfully applied strategies and methods can greatly facilitate the assessment. Thus, this paper contains a general compilation of published chromatographic methods and strategies that have been successfully applied to the identification and quantification of large numbers of the more commonly encountered packaging material additives (see Table 2 for a listing of additives which are considered in this paper's cited references). Examples are provided for each major separation strategy (e.g., HPLC, GC, TLC, SFC)

Table 2. Chemical names for the additives cited in this paper.

Trade name	Chemical name	CAS RN
AcraWax C	*N*,*N*′-Ethylene*bis*tearamide	110-30-5
Adkstab PEP-24G	Cyclinepentan tetrail bis(2,4-di-*tert*-butylphenyl) phosphite	29741-53-7
AM340		
ATBC	*o*-Acetyl-tri-*n*-butyl citrate (see Citroflex A-4)	—
Atmos 150	A mixture of glycerol mono- and distearate	11099-07-3
BAC-E	2,6-bis-[(Azidophenyl)methylene]-4-ethyl-cyclohexanone	
BBP	Benzyl *n*-butyl phthalate	85-68-7
Benzoflex-2860	A mixture of 19% di-(2-ethylhexyl)-adipate, 57% diethyleneglycol dibenzoate, 24% triethyleneglycol dibenzoate	400609-45-2
BEHB	Butylated hydroxyethylbenzene	
Behenamide	Docosanoic acid amide	3061-75-4
BHA	2-*tert*-Butyl-4-hydroxyanisole	25013-16-5
BHT	2,6-Di-*tert*-butyl-*p*-cresol	128-37-0
BHET	bis-(2-Hydroxyethyl)terephthalate	
Bis-A-bis azide	1,1′-(1-Methylethylidene)-bis[4-(4-axidophenoxybenzene]	
*bis*phenol A	2,2′-bis(4-Hydroxyphenyl)propane	80-05-7
Brominated *bis*phenol A		
Brominated phenol		
Butyl oleate	9-Octadecanoic acid, butyl ester	142-77-8
Butyl palmitate	Hexadecanoic acid, butyl ester	111-06-8
Butyl stearate	Octadecanoic acid, butyl ester	123-95-5
Calcium stearate	Stearic acid, calcium salt	1592-23-0
Caprolactam	2-Oxohexamethyleneimine	105-60-2
Chimasorb 81	2-Hydroxy-4-*n*-octyloxybenzophenone	1843-05-6
Chimassorb 119 FL		
Chimassorb 944	Poly-[[6-(1,1,3,3,-tetramethylbutyl)amino]-1,3,5-triazine-2,4-diyl][2.2.6.6-tetra-methyl-4-piperidinyl)imino]-1,6-hexanediyl[2,2,6,6-tetramethyl-4-piperidinyl)imino]]	71878-19-8
Citroflex A-4	2-Acetoxy-1,2,3-propanetricarboxylic acid tributyl ester	77-90-7
Cyanox 425	2,2′-Methylenebis-(6-*tert*-butyl-4-ethylphenol)	88-24-4

(continued)

Table 2. Continued.

Trade name	Chemical name	CAS RN
Cyanox 1790	1,3,5-*tris*(4-*tert*-Butyl-3-hydroxy-2,6-dimethylbenzyl)-1,3,5-triazine-(1H,3H,5H)trione	40601-76-1
Cyanox 2246	See Irganox 2246	—
Cyasorb UV9		
Cyasorb UV-24	2,2′-Dihydroxy-4-methoxybenzophenone	131-53-3
Cyasorb UV531	2-Hydroxy-4-(octyloxy) benzophenone	1843-05-6
Cyasorb UV 1084	2.2′-Thiobis(4-*tert*-octylphenoxy) (nibutylamine)nickel	14516-71-3
Cyasorb UV1164	2,4-bis(2,4-Dimethylphenyl)-6-(2-hydroxy-4-octyloxyphenyl)-1,3,5-triazine	2725-22-6
Cyasorb UV 2908	3,5-Di-*tert*-butyl-4-hydroxybenzoate	67845-93-6
Dechlorane plus	1,2,3,4,7,8,9,10,13,13,14,14-dodecachloro-1,4,4a,5,6,6a,7,10,10a,11,12,12a-dodecahydro-1,4,7,10-dimethanodibenzo [a,e] cyclooctene	13560-89-9
DEHA	Di-(2-ethylhexyl) adipate, dioctyl adipate	103-23-1
Di-Cup	Dicumyl peroxide	80-43-3
Dibutyl sebacate		109-43-3
DEG	Diethylene glycol	111-46-6
DBP	Di-*n*-butyl phthalate	84-74-2
DEHP, DOP	Di(2-ethylhexyl)phthalate	117-81-7
Dinonyl phthalate	1,2-Benzenedicarboxylic acid, dinonyl ester	84-76-4
DMTDP	3,3′-Thiodipropionic acid di-*n*-tetradecyl ester	16545-54-3
DSTDP	Dioctadecyl 3,3′-thiodipropionate	693-36-7
DLTDP	Dilauryl 3,3′-thiodipropionate	123-28-4
Docosane		629-97-0
Eicosane		112-95-8
Epoxol 9.5	Epoxidized linseed oil	8016-11-3
EG	Ethylene glycol	107-21-1
Erucamide	*cis*-13-docosenamide	112-84-5
Ethyl palmitate	Hexadecanoic acid ethyl ester	628-97-7
Ethyl linoleate	9,12-Octadecanoic acid ethyl ester	544-35-4
Ethyl oleate	9-Octadecanoic acid ethyl ester	111-62-6
Ethyl stearate	Octadecanoic acid ethyl ester	111-61-5
Ethanox 330	See Irganox 1330	—
Hexadecane		544-76-3
Hexacosane		630-01-3

(continued)

Table 2. Continued.

Trade name	Chemical name	CAS RN
Hostanox O 3	bis[3,3-bis(4-Hydroxy-3-*tert*-butylphenyl)-butanoic acid] ethylene glycol ester	32509-66-3
Hostavin TMN 20	2,2,4,4-Tetramethyl-21-oxo-7-oxa-3,20-diazadispiro[5.1.11.2]heneicosane	64338-16-5
Ionol 220	2,6-Di(*tert*-butyl)-4-methylphenol (see Topanol OC)	—
Ionox 100	4-Hydroxymethyl-2,6-di-*tert*-butylphenol	88-26-6
Ionox 129	2,2′-Ethylidenebis (4,6-di-*tert*-butylphenol)	35958-30-6
Ionox 220	4,4-Methylenebis (2,6-di-*tert*-butylphenol)	118-82-2
Irgafos 168	*tris*-(2,4-di-*tert*-butylphenyl)phosphite	31570-04-4
Irgafos P-EPQ	Tetrakis(2,4-di-*tert*-butylphenyl)-4,4′-biphenylene diphosphonite	38613-77-3
Irganox 245	Triethylene glycol bis-3-(3-*tert*-butyl-4-hydroxy-5-methyl)propionate	36443-68-2
Irganox 259	1,6-bis[3-(3,5-Di-*tert*-butyl-4-hydroxyphenyl)propionyloxy]hexane	35074-77-2
Irganox 565	2,4-bis(Octylthio)-6-(3,5-di-*tert*-butyl-4-hydroxyanilino)-1,3,5-triazine	991-84-4
Irganox 1010	Tetrakis-methylene-(3,5-di-*tert*-butyl-4-hydroxyhydrocinnamate)-methane	6683-19-8
Irganox 1035	2,2′-Thiodiethylene bis[3-(3,5-di-*tert*-butyl-4-hydroxyphenyl)propionate]	41484-35-9
Irganox 1076	Octadecyl-3-(3′,5′-di(*tert*-butyl)-4′-hydroxyphenyl)propionate	2082-79-3
Irganox 1098	*N*-*N*-bis[3-(3,5-di-*tert*-butyl-4-hydroxyphenyl)propionyl]hexamethylene-diamine	23128-74-7
Irganox 1222	Diethyl(3,5-di-*tert*-butyl-4-hydroxybenzyl)phosphonate	976-56-7
Irganox 1330	1,3,5-Trimethyl-2,4,6-*tris*-(3,5-di-*t*-butyl-4-hydroxy-benzyl)-benzene	1709-70-2
Irganox 1425	Calcium bis(ethyl 3,5-di-*tert*-butyl-4-hydroxybenzylphosphonate)	65140-91-2
Irganox 2246	2,2′-Methylene-bis-(4-methyl-6-*tert*-butylphenol)	119-47-1
Irganox 3052 FF	2,2′-Methylenebis(6-*tert*-butyl-4-methylphenol)monoacrylate	61167-58-6
Irganox 3114	1,3,5-*tris*-(3,5-Di-*t*-butyl-4-hydroxybenzyl)-s-triazine-2,4,6-(1H,3H,5H)trione	27676-62-6
Irganox MD1024	3,5-bis(1,1-dimethylethyl)-4-hydroxybenzenepropionic acid	32687-78-8

(continued)

Table 2. Continued.

Trade name	Chemical name	CAS RN
Irganox MD1025	*N*,*N*-bis[1-oxo-3(3,5-di-*tert*-butyl-4-hydroxyphenyl)propane]hydrazine	
Irganox PS800	Di-lauryl thio-dipropionate	123-28-4
Irganox PS802	Di-stearyl thio-dipropionate	693-36-7
Isonox 129	2,2′-Ethylidenebis[4,6-di-*tert*-butyl-phenol]	35958-30-6
Kemamide U	See Oleamide	—
Lauric acid	Dodecanoic acid	143-07-7
Lowinox 22M46	See Irganox 2246	—
MHET	Mono-(2-hydroxyethyl)terephthalate	155603-50-2
Myristic acid	Tetradecanoic acid	544-63-8
	N-*N*-bis(2-hydroxyethyl)alkyl-amine	
Naugard SP		94765-89-6
Naugard XL-1	2,2′-Oxamidobis[ethyl 3-(3,5-di-*tert*-butyl-4-hydroxyphenyl)propionate]	70331-94-1
Naugawhite	2-2′-Methylenebis (4-methyl-6-nonylphenol)	7786-17-6
NC-4	1-(2,6-Dimethylphenylimino)imidazolidine	4859-06-7
Nonflex CBP	2,2′-Methylenebis(6-(1-methylcyclohexyl)-*p*-cresol)	77-62-3
Noclizer M-17	2,6-di-*tert*-butyl-4-ethylphenol	4130-42-1
Octadecane		593-45-3
ODO	Octabromodiphenyl oxide	32536-52-0
Oleamide	9-Octadecenamide	301-02-0
Palmitic acid	Hexadecanoic acid	57-10-3
Palmitamide	Hexadecanoic acid amide	629-54-9
Permanax WSP	2,2′-Methylenebis[4-methyl-6-(1-methylcyclohexyl)phenol]	77-62-3
Sanol LS744		
Sanol LS770		
Santonox	See Yoshinox SR	—
Santowhite	4,4′-Butylidenebis-(3-methyl-6-*tert*-butylphenol)	85-60-9
Seesorb 101	2-Hydroxy-4-methylbenzophenone	131-57-7
Seesorb 202	4-*tert*-Butylphenylsalicylate	87-18-3
Seenox DM	3,3′-Thio-dipropionic acid dimyristyl ester	16545-54-3
Sodium benzoate	Benzoic acid, sodium salt	532-32-1
Stearamide	Octadecanamide	124-26-5
Stearic acid	Octadecanoic acid	57-11-4
Synprolam	Quaternary ammonium compounds, di-C13-C15-alkylmethyl, chlorides	308074-61-5

(continued)

Table 2. Continued.

Trade name	Chemical name	CAS RN
Terephthalic acid		100-21-0
TETO	Glyceryl tri-epoxyoleate	
Tetradecane		629-59-4
Tetracosane		646-31-1
Tinuvin 120	2′,4′-Di-*tert*-butylphenyl-3,5-di-*tert*-butyl-4-hydroxybenzoate	4221-80-1
Tinuvin 144	2-*tert*-butyl-2-(4-hydroxy-3,5-di-*tert*-butyl-benzyl)[bis(methyl,2,2,6,6-tetramethyl-4-piperidinyl)]dipropionate	63843-89-0
Tinuvin 234	2[2′-hydroxy-3,5-di91,1-dimethylbenzyl)-phenyl]-2H-benzotriazole	70321-86-7
Tinuvin 292	*bis*-(1-Methyl-2,2,6,6,tetramethylpiperidinyl)sebacate	41556-26-7
Tinuvin 312	*N*-(2-ethyoxyphenyl)-*N*′-(2-ethylphenyl)-ethanediamine	23949-66-8
Tinuvin 320	2-(2-Hydroxy-3,5-di-*tert*-butylphenyl)-2H-benzotriazole	3846-71-7
Tinuvin 326	2-(3-*tert*-Butyl-2-hydroxy-5-methyl-phenyl)-2H-5-chlorobenzotriazole	3896-11-5
Tinuvin 327	2-(2′-Hydroxy-3′,5′-di(*tert*butyl)phenyl)-2H-5-chlorobenzotriazole	3864-99-1
Tinuvin 328	2-(2′-Hydroxy-3′,5′-di(*tert*butyl)phenyl)-2H-chlorobenzotriazole	25973-55-1
Tinuvin 329	2-(2′-Hydroxy-5′-*tert*-octylphenyl)benzotriazole	3147-75-9
Tinuvin 350	2-(2H-benzotriazol-2-yl)-4-(1,1-dimethyl-ethyl)-6-(2-methylpropyl)phenol	134440-54-3
Tinuvin 384	Octyl 3-[3-(2H-benzotriazol-2-yl)-5-*tert*-butyl-4-hydroxyphenyl]propionate	84268-23-5
Tinuvin 662		
Tinuvin 770	(2-(2-Hydroxy-3,5-*bis*(1-methyl-1-phenyl-ether)phenyl)benzotriazole)	52829-07-9
Tinuvin 1130	α-[3-[2-(2H-benzotriazol-2-yl)-5-(1,1,-dimethylethyl)-4-hydroxyphenyl]-1-oxopropyl-hydroxy-poly(oxy-1,2-ethanediyl)	104810-48-2
Tinuvin P	2-(2-Hydroxy-5-methylphenyl)-2H-benzotriazole	2440-22-4
TNPP	*tris*(Nonylphenyl)phosphite	26523-78-4
Topanol CA	1,1,3-Tri(3-*tert*-butyl-4-hydroxy-6-methyl-phenyl)butane	1843-03-4

(continued)

Table 2. Continued.

Trade name	Chemical name	CAS RN
Topanol OC	2,4,6-Tri-*tert*-butylphenol	128-37-0
TPP	Triphenyl phosphate	115-86-6
Tributylacetylcitrate	See Citroflex A-4	—
Ultranox 626	bis-(2,4-Di-*t*-butylphenyl)-pentaerythritol-diphosphite	26741-53-7
Uvitex OB	2,5-bis(5′-*tert*-Butyl-2′-benzoazolyl) thiophene	7128-64-5
Vulkanox CS		94766-18-4
Wingstay T		12674-05-4
Yoshinox 425	2,2′-Methylenebis(4-ethyl-6-*tert*-butylphenol)	88-24-4
Yoshinox BB	See Santowhite	—
Yoshinox SR	4,4′-Thiobis[3-methyl-6-*tert*-butylphenol]	96-69-5
Zinc stearate	Stearic acid, zinc salt	557-05-1

and for most commonly employed detection methods (e.g., UV, MS, FID). While the compilations in Tables 3–10 are by no means exhaustive or comprehensive, they are sufficiently broad in scope to provide the investigator with a general overview of the ways in which chromatography has been applied to meet the objectives of a polymer's characterization.

Tables 3–10 provide general method details such as separation medium, elution, and detection conditions, and other operating conditions. The level of detail associated with each citation reflects the level of detail provided by the citation's author(s). The materials investigated, as well as the specific additives examined, are also indicated. General comments are provided in terms of sample preparation. Given the number of methods cited, it is not possible to provide chromatographic profiles, which are readily available in the cited references.

In generating this review, this author balanced two objectives. The first objective was to summarize the most current technologies being utilized for the task of polymer characterization, thus providing the researcher with the most relevant and state of the art tools for the task at hand. Thus, emerging automated and hyphenated techniques, which couple on-line sample preparation, high efficiency separations, and selective and sensitive detection (e.g., SFE/HPLC/MS) have a prominent place in this review. However, this author also notes that more historically relevant methods, such as GC and HPLC with UV detection, remain capable of providing a researcher with accurate, precise, and pertinent information. Thus, this review attempts to maintain a historical perspective as well.

Table 3. Examples of HPLC methods (UV detection) used to identify and/or quantify packaging system additives.

Material	Additive(s)	Sample preparation	Column	Mobile phase	λ (nm)	Others	Refs.
PE	Dicumyl peroxide, Santonox®	Extract with methanol, concentrate (evaporative)	Lichrosorb RP 18, 250 × 4.6 mm, 10 μm	Methanol/water, 80/20	254	1 mL min^{-1}	[1]
PVC	Di-(2-ethylhexyl) phthalate (DEHP), epoxidized linseed oil, *tris*(nonyphenyl) phosphite (TNPP)	Dissolve in THF, precipitate polymer with methanol, dry and dissolve residue	μPorasil C_{18}	Carbon tetrachloride-dichloromethane (65/35)	280	1 mL min^{-1}	[2]
LDPE, PP	BHT, Cyasorb 531, Tinuvin 327, Irganox 1076	Reflux with CCl_4 or THF, filter, concentrate	μBondapak C_{18}, 60 × 0.39 cm	Methanol/water/THF 63/7/30	254	2 mL min^{-1}	[3]
LDPE, HDPE	Tinuvin P, BHT, BEHB, Oleamide, Cyasorb UV 531, Isonox 129, AM340; Irganox 1010, 3114; Erucamide	Soxhlet, ultrasonic or microwave extraction with various solvent systems	Nova-Pak C_{18}, 150 × 3.9 mm, 4 μm	A = water, B = acetonitrile, 3/2 initial, linear gradient to 100% B in 5 min	200	1.5 mL min^{-1}, $T = 50°C$	[4]
PP	Irgafos 168, Irganox 1076, Irganox 3114, Irganox 1010, Tinuvin P, Irgafos PEP-Q	Microwave extraction with 98/2 methylene chloride/2-propanol	Nova-Pak silica (150 × 3.9 mm, 4 μm) or Resolve silica(150 × 3.9 mm, 5 μm)	70/30 *n*-butyl chloride/methylene chloride	225	1.5 mL min^{-1}, $T = 30°C$	[4]
Polyolefin	Irganox (245, 259, 565, 1010, 1035, 3114), Tinuvin (P, 234, 320, 326, 327, 328)	N/A[a]	Capcell Pak C_{18}, 250 × 4.6 mm	Methanol/water mixtures (95/5, 90/10, 88/12, 85/15)	Multiple	1 mL min^{-1}, $T = 45°C$, 20 μL	[5]

(continued)

Table 3. Continued.

Material	Additive(s)	Sample preparation	Column	Mobile phase	λ (nm)	Others	Refs.
Polyolefin	BHT, BHA, Irganox 1010, Irganox 565, Tinuvin 327, Tinuvin P	N/A[a]	Licrosphere 100 RP 18, 250 × 4.6 mm, 5 µm	Various binary and tertiary mixtures of methanol, water, and acetonitrile	Multiple	20 µL	[6]
General	BHT, Irganox anti-oxidants (245, 259, 565, 1010, 1035, 1076, 1098, 1222, 1330, and others), UV absorbers (Tinuvin P, 312, 320, 327, 328 and others)	N/A[a]	Ultrabase UB225, 250 × 4.6 mm, 5 µm; LiChrospher 100 RP 18e, 250 × 4.6 mm, 5 µm; Spheri 5-ODS, 250 × 4.6 mm, 5 µm	Quaternary gradient of THF, water, methanol, acetonitrile	Multiple wavelength UV and laser light scattering[b]	1 mL min^{-1}, 20 µL, ambient temperature	[7][c]
General	BHT, BHA	N/A[a]	Whatman Partisil PXS 10/25 ODS-2	0.05 M $LiClO_4$ in 85% methanol	UV-electrochemical-fluorescence	1 mL min^{-1}, 20 µL, $T = 40$°C	[8][d]
PP, ABS	Numerous[f]	Dissolve in $MeCl_2$, precipitate polymer with methanol	Spherisorb S30DS2, 150 × 4.6 mm, 3 µm	A = acetonitrile, B = water. Initial = 40% A, ramped to 100% A in 15 min, hold at 100% for 17 min	210, 280	1 mL min^{-1} (2 mL min^{-1} after 22 min) 10 µL	[12]
PE	Topanol OC, Cyasorb UV-531, Irganox 1010, 1076, 1330	SFE contrasted to Soxhlet extraction with dichloromethane	Kaseisorb ODS-5, 550 × 0.53 mm	Methanol	254 nm	Column pressure = 100 atm	[22]
PP	Irganox 1010, Irgafos 168	SFE	Licrosorb RP-18, 200 × 4.6 mm, 5 µm	Gradient from methanol/water (95/5) to 100% methanol in 17 min	280 nm	1.5 mL min^{-1}, 20 µL	[24]

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Polyolefin	Irganox PS802, 1010, 1076, 1425; calcium stearate, sodium benzoate	Microwave assisted solvent extraction	Various; ex., Microsper C_{18}, 250 × 4.6 mm, 5 μm	Water/acetonitrile/iso-propanol; Start = 12/88/0; 0.1 min = 5/65/30; 10 min = 0/65/30; 18 min = 0/65/30	273 nm, light scattering	2 mL min^{-1}, 10 μL, $T = 50°C$	[25]
PMMA	Irganox 1010, 1076; Irgafos 168	SFE	Nova Pack C18, 5 μm	Acetonitrile/water gradient; start at 80/20, change to 100/0 in 5 min	254 nm	50 μL	[33]
Dielectric resins	BAC-E, bis-A-bis-Azide	Dissolution in THF	Zorbax RX C8, 100 × 4.5 mm, 5 μm[e]	$A = 50/50$ acetonitrile/water, B = 90/10 mixture. Gradient was start ramp from 0% A to 100% B in 5 min, hold at 100% B for 5 min	254 nm (380 nm for internal standard)	3 mL min^{-1}	[34]

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[a] This reference examined the elution characteristics of the cited additives as a function of mobile phase and thus did not characterize actual polymers.

[b] These authors report that the UV response for the analytes is typically 5 to 50 times greater than the light-scattering response.

[c] Numerous other examples of separations provided.

[d] For BHA, the sensitivity was EC > UV (230 nm) > Fl. For BHT, the sensitivity was UV (280 nm) > EC > Fl.

[e] Pre-analytical column sample clean-up was achieved on-line by SEC. This pre-analytical processing was accomplished with a 25 cm × 250 μm I.D. fused silica capillary column (PL-Gel 50 Å, 5 μm) and a THF mobile phase at 1.3 μL min^{-1}.

[f] This study examined the elution characteristics, sensitivity, and analytical recoveries of over 25 additives.

Table 4. Examples of HPLC methods (IR Detection) used to identify and/or quantify packaging system additives.

Material	Additive(s)	Sample preparation	Column	Mobile phase	λ (nm)	Others	Refs.
Polyurethane	Irganox 1010	Extraction with *n*-hexane	μ-Porasil C_{18}	*n*-hexane/ dichloromethane (80/20)	254[a]	1 mL min^{-1}	[9]
PVC, PP, PE	Ionol 220, Irganox 1076, Tinuvin 327, Tinuvin 328, Cyasorb UV 531	Extraction with acetonitrile or methanol, evaporative concentration	RP: Spherisorb DDS-2, 100 × 1.0 mm, 3 μm; SEC: Plgel, 250 × 4.6 mm, 5 μm, 500 Å	RP = methanol/ water (95/5), SEC = Dimet-Dimethane	280[b]	0.1–0.2 mL min^{-1}	[10]
PP	Irganox 1010, 3114; Tinuvin 326, 327	N/A[c]	Zorbax ODS, 250 × 4.6 mm		N/A[d]	0.5 mL min^{-1}, 20 μL	[26]

PP, PE	Irganox 245, 259, 1010, 1076, 1098, 3114; Irgafos 168; Tinuvin 234, 327, 328, 350; Sanowhite, Ethanox 330; Lowinox 22M46; Kemamide U; Naugard; BHT; Ultranox 626; Cyasorb 2908; Cyasorb UV 531	N/A[c]	Sperisorb ODS-2, 250×4.6 mm, 5 μm	Several cited[e]	280 nm, and evaporative light scattering[f]	1 mL min^{-1}, 50 μL, ambient temperature	[32][g]

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[a] Peak collected on potassium bromide powder and an IR spectrum obtained off-line.

[b] On-line FTIR with spray-jet interface, deposition on a moving zinc selenide substrate. UV for quantitation, IR for identification.

[c] This reference examined the detection characteristics of the cited additives and thus did not characterize actual polymers.

[d] Used surface-enhanced infrared spectroscopy with effluent deposition on an Ag metal film (BaF_2 substrate). Reported a detection limit of 10 ng.

[e] Several separations are cited in this paper. A gradient using methanol and water was used for the separation of nine additives. Initial composition methanol/water (94/6), for 7 min, change immediately to 100% methanol, hold for 14 min.

[f] Portion of column effluent deposited on a rotating germanium disk via drying nebulization.

[g] Detection limits by IR were generally near 0.2 μg, with quantities needed for accurate identification being in the 0.5–1.0 μg range.

Table 5. Examples of HPLC methods (MS detection) used to identify and/or quantify packaging system additives.

Material	Additive(s)	Sample preparation	Column	Mobile phase	Detection	Other	Refs.
General (PP)	BHT, Irganox 1010, Irganox 1076, Irganox 1330, Santowhite	N/A[a]	ODS, 250 × 2.1 mm, 5 µm	A = acetonitrile/water (75/25), B = THF/acetonitrile (50/50), 0 min = 100% A, 10 min = 60% A, 20 min = 100% B, 30 min = 100% B, 32 min = 100% A	UV, 280 nm; Moving belt MS interface, CI and EI spectra obtained	0.2 mL min^{-1}, 10 µL	[11]
PVC	Mono-alkyl esters and di-alkyl phthalates	N/A[a]	Symmetry C-8, 150 × 3.9 mm, 5 µm	A = 0.1 M ammonium acetate in methanol/water (10/90), B = 0.1 M ammonium acetate in methanol 0–100% B over 25 min, hold for 5 min	UV, 277 nm; Thermospray MS + ions	1 mL min^{-1}	[13]
PP	NC-4, Naugard-XL, Irganox 1076	Extract with acetonitrile at 60°C for 72 hr	Symmetry C8, 150 × 3.9 mm, 3 µm	A = acetonitrile, B = water, 0 min = 30% A, 10 min = 100% A, 30 min = 30% A, 40 min = 30% A	Multiple λ UV, MS = EI and APCI (positive ion, SIM)		[14]
PP	Irganox 245, BHA, BHT, Bispenol A, Topanol CA	N/A	Hypersil H5ODS, 100 × 4.6 mm, 5 µm	deuterated acetonitile/water (80/20)	UV, IR, MS, NMR[b]	1 mL min^{-1}	[33]

[a] This reference examined the elution characteristics of the cited additives as a function of mobile phase and thus did not characterize actual polymers.

[b] The column effluent was split after the column (95/5) between the FTIR flowcell (ATR used) and the MS detector (single quad, positive ions). The effluent from the FTIR cell was directed through the UV and ultimately NMR detectors.

Table 6. Examples of SFC methods used to identify and/or quantify packaging system additives.

Material	Additive(s)	Sample preparation	Column	Mobile phase	Detection	Others	Refs.
General (PE)	Numerous[e]	N/A[a]; SFE	C_{18}, 250 × 4.6 mm	CO_2 with methanol modifier; 2% methanol for 1 min, linear to 10% after 10 min, hold for 5 min	APCI-MS (+ and − ionization), UV	2 mL min^{-1}, 10 μL	[16][b]
PE	BHT, Tinuvin 326	SFE with various traps	Fused silica capillary (10 m × 0.1 mm i.d.) with octyl phase, 0.5 μm film	CO_2, pressure program (100 atm for 10 min, increased at 5 atm^{-1} min^{-1} for 20 min)	FID	Column $T = 90°C$	[17]
Polyolefin (PP, PE)	BHT, Irganox PS800, PS802, 1010, 1076, 1330, 2246; Tinuvin P, 320, 326; Irgafos 168, Atmos 150	Soxhlet extraction with chloroform	Fused silica capillary (10 m × 0.05 mm i.d.) with 5% phenyl-polymethyl-siloxane, 0.4 μm film	Various pressure and temperature programs with CO_2 were reported	MS, EI	1 μL injection	[18, 19][c,d]

(continued)

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Table 6. Continued.

Material	Additive(s)	Sample preparation	Column	Mobile phase	Detection	Others	Refs.
PP	Numerous[f]	Soxhlet extraction with diethyl ether for 15 hr, precipitate polymer with ethanol	Fused silica capillary (15 m × 0.1 mm i.d.) with 5% phenyl-polymethyl-siloxane, 0.5 µm film	CO_2 at 140°C, pressure = 150 atm for 12 min, ramp to 350 atm at 3 $atm^{-1}min^{-1}$	FID, FTIR microscope	2 µL split injection, $T = 150°C$	[20]
PE	BHT, Irganox 1010, Irgafos 168	SFE (contrasted to Soxhlet extraction)	Fused silica capillary (15 m × 0.1 mm i.d.) with SB-biphenyl-30, 0.5 µm film	CO_2 at 140°C, pressure = 100 atm, ramp to 200 atm at 3 $atm^{-1}min^{-1}$, ramp at 10 atm/min to 400 atm	IR (flow through cell)	—	[21]
General	Tinuvin P, 326, 234, 770; Chimasorb 81, Irganox 1010, 1076, 1330; Irgafos 168, Irgafos P-EPQ, *N*-*N*-bis (2-hydroxyethyl) alkylamine	N/A[a]	Fused silica capillary (20 m × 0.1 mm i.d.) with DB-5, 0.4 µm film	CO_2, pressure = 10.6 MPa for 10 min, ramp to 15 MPa in 3.5 min, hold for 5 min. Ramp at 0.5 MPa min^{-1} to 35 MPa, hold for 10 min	FID and MS (EI, 70 eV)	2 mL min^{-1}, $T = 140°C$	[22]
LDPE	BHT, BHEB, Isonox 129, Irganox 1010, 1076	On-line SFE	Deltabond cyano, 100 × 1.0 mm i.d., 5 µm	100 atm for 3 min, 100–330 atm for 7 min, 330–450 atm for 1.5 min	FID	Column $T = 100°C$	[27][g]

Polyurethane	BHT; Irganox 1010; Irganox 1076; dinonyl phthalate[h]	On-line SFE	30% biphenyl polysiloxane, 10 m × 50 μm i.d., 0.25 μm film	CO_2, hold at 100 atm for 5 min, ramp at 5 atm min^{-1} to 300 atm, ramp at 20 atm min^{-1} to 400 atm	MS (EI)	Column $T = 100°C$	[36]
Nylon, polystyrene	Caprolactam and oligomers, stearic acid, Irganox 1076	One-line SFE	Deltabond cyano, 100 cm × 1 mm, 5 μm	CO_2, hold at 100 atm for 2 min, ramp at 15 atm min^{-1}	FT-IR	Column $T = 100°C$	[37]
PE, PP	BHT, Erucamide, Irgafos 168, Irganox 1010, 1076, Tinuvin 326, 770, Isonox 19, DLTDP	On-line SFE	Deltabond 300 Octyl, 250 cm × 1 mm	CO_2, hold at 1500 psi for 6 min, ramp at 200 psi min^{-1} to 6000 psi	FID	FID $T = 350°C$, Column $T = 150°C$	[56]

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[a] This reference examined the elution characteristics of the cited additives as a function of mobile phase and thus did not characterize actual polymers.

[b] This reference provides elution characteristics and relative intensities for specific positive and negative ions.

[c] The performance of the SFC method was compared to that of a isocratic RP-HPLC method (UV detection).

[d] GC/MS was also used for compound identification.

[e] Additives examined included: BHT, Irganox 245, 1010, 1035, 1076, 1330, 1425, PS802; Irgafos 168, Tinuvin 327, 328, 384, 440, 622, 770, 1130; Topanol CA, Cyasorb UV1164, Oleamide, Erucamide, Synprolam, Chimassorb 944.

[f] Additives included: Topanol OC, Tinuvin P, 292, 320, 326, 328, 770, 440, 144; Chimassorb 81, Erucamide, Irganox PS800, PS802, 245, 1010, 1035, MD1025, 1076, 1330, 3114.

[g] The SFE extraction was also coupled with HPLC separation and detection of the analytes.

[h] This method produced other additive peaks whose parent compound could not be identified.

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Table 7. Examples of SEC/GPC methods used to identify and/or quantify packaging system additives.

Material	Additive(s)	Sample preparation	Column	Mobile phase	Detection	Others	Refs.
PP	General[b]	Extraction with THF	Porogel A-1 (slurry packed)	THF	RI (collected fraction tested via IR for ID)	2 mL min^{-1}, Column $T = 30°C$	[28]
PS, PVC	Tinuvin P, TNPP, TETO	Solvent extraction	500, 100 and 50 Å PLgel (poly(styrene-divinylbenzene) 30 × 0.77 cm, 10 μm	THF	UV	2 mL min^{-1}, Column $T = 30°C$	[29]
Polyolefin (PP, PE)	BHT, Cyasorb UV 9, Cyasorb UV 1084, Tinuvin 326, 327, Irganox 1076	General[a]	SEC (PL-Gel, 50 Å, 300 × 7.5 mm) coupled with normal phase (Nucleosil 100-7 OH, 250 × 4.6 mm, 7 μm)	*n*-hexane/dichloromethane (73/27)	UV at 254 and 280 nm	0.9 mL min^{-1}, Column $T = 35°C$	[30]
Polyolefin co-polymers	Numerous[c]	Dissolution in THF	SEC (Uktrastyragel 10^4, 50 Å, 300 × 0.25 mm, 10 μm) coupled with GC (DB-1, 15 m × 0.32 mm i.d., 0.25 μm film)	SEC; THF mobile phase. GC; 100°C for 6 min, ramp at 16°C min^{-1} to 350°C	UV at 254 nm for SEC, MS (EI) for GC	For SEC: 3.0 μL min, 0.2 mL injected	[31]

[a] This reference examined the chromatographic characteristics of the cited additives as a function of mobile phase and thus did not characterize actual polymers.

[b] This reference generated additive profiles for various test materials but did not specify the individual additives found.

[c] This reference documented chromatographic characteristics for many individual additives including plasticizers (phthalates, Citroflex A-4, TNPP), amides, Irganox and Irgafos antioxidants, UV absorbers (Tinuvin, Cyansorb), fatty acids (palmitic, stearic), Naugard XL-1 and others.

Table 8. Examples of TLC methods used to identify and/or quantify packaging system additives.

Material	Additive(s)	Sample preparation	Plate	Mobile phase	Detection	Other	Refs.
Rubber	Numerous[b]	N/A[a]	Silica Gel G, thickness of 250–300 μm	Numerous solvent systems examined vs. compound class	Various UV and visible developing reagents	Sample size: 3–5 μL	[38]
Polyolefin	Tinuvin 144, 770; Hostavin TMN 20	Extraction with chloroform, polymer precipitation, evaporative concentration	Alumina F254, 20 cm × 20 cm plate, 0.25 mm thickness	88/12 *n*-hexane/isopropanol	Chlorination with chlorine gas, sprayed with potassium iodide-starch solution	Sample size: 10 μL	[39]
Elastomers	BHT, Cyanox 2246, Cyanox 425, Permanax WSP, Naugawhite, Wingstay T, Naugard SP, Vulkanox CS	Soxhlet extraction with acetone, evaporative concentration	Merck 11845 silica gel	Benzene	Sprayed with 2.34% sodium tetraborate, 0.33% sodium hydroxide and 0.1% methanolic solution of *N*-chlorodichloro-2, 6-*p*-benzoquinone monoimine	Sample size: 20 μL	[40]
PP, PVC	Irganox 1010, Tinuvin 770, Chimassorb 119 FL, DEHP	N/A[a]	Silica gel 60 F254, 5 cm × 10 cm plate, 250 μm thickness	Toluene-diethyl ether (10/1) on first plate, acetone-formic acid (4/6) on second plate	UV for plate 1, plate 2 visualized by iodine vapor. Spots removed from plate 2 and analyzed by FT/IR.	Sample size: 2 μL	[41]

[a] This reference examined the chromatographic characteristics of the cited additives and thus did not characterize actual polymers.

[b] This reference documents the chromatographic properties of over 100 rubber-related amine and phenolic antioxidants, antiozonants, guanidines, accelerators, and amine hydrochlorides.

Table 9. Examples of GC methods used to identify and/or quantify packaging system additives.

Material	Additives	Sample preparation	Column	Oven program	Detection	Others	Refs.
PET	Diethylene glycol	High temperature and pressure extraction with water	Numerous[a]	Isothermal at 180°C	FID and TCD	Injector $T = 260°\text{C}$, Detector $T = 270°\text{C}$, He carrier at $50\,\text{mL min}^{-1}$	[42]
PET	BHET, EG, DEG, TA, MHET	N/A.[b] Samples TMS-dervatized with BSFTA (80°C for 10 min)	3% OV101 on 80–100 mesh Chromosorb W, 6 ft, 0.125 inch o.d., 0.05 inch i.d.	80°C for 3 min; ramp at $15°\text{C min}^{-1}$ to 265°C	FID	Injector $T = 270°\text{C}$, Detector $T = 280°\text{C}$, He carrier at $50\,\text{mL min}^{-1}$, 2 µL injection	[43]
Elastomers	Various antioxidants and additives	N/A[b]	3% SP2100 on 80–100 mesh Supelcoport	150°C for 2 min; ramp at $10°\text{C min}^{-1}$ to 250°C	MS	Injector $T = 270°\text{C}$, He carrier at $35\,\text{mL min}^{-1}$	[44]
Polyolefins	BHT, Irganox 1010,1076, 2246; Irgafos 168, Santowhite	Refluxed in acetone for 2–3 hour, evaporated to dryness and dissolved in chloroform	PS264, 15 m × 0.32 mm i.d., 0.15 µm film	90°C–280°C at $5°\text{C min}^{-1}$	FID	Detector $T = 300°\text{C}$, He carrier at inlet pressure of $0.5\,\text{kg cm}^{-2}$	[45]
PVC	Benzoflex 2860, ATBC, DEHA	SFE	SPB-5 fused silica capillary, 30 m × 0.25 mm i.d., 0.25 µm film	110–260°C at $10°\text{C min}^{-1}$	FID	Detector, Injector $T = 300°\text{C}$, he carrier at $50\,\text{cm sec}^{-1}$, 1 µL splitless	[46]

Polyolefins	Numerous[c]	Reflux with chloroform, evaporative concentration	HR-1701 (14% cyano-propylphenylmethyl-siloxane) fused silica capillary, 15 m × 0.53 mm i.d., 1.0 μm film	100°C for 2 min, 20°C min^{-1} to 210°C, 1.5°C min^{-1} to 222°C, 8°C min^{-1} to 350°C, hold for 10 min	FID	Injector and Detector $T = 350$°C, He carrier at 5 mL min^{-1}, 1 μL splitless injection	54
Pertoleum Resin	Numerous[c]	Dissolve in *n*-hexane, clean-up with silica column	DB-1701 (14% cyano-propylphenylmethyl-siloxane) fused silica capillary, 15 m × 0.53 mm i.d., 1.0 μm film	150°C for 2 min, 20°C min^{-1} to 210°C, 1.5°C min^{-1} to 222°C, 8°C min^{-1} to 350°C, hold for 10 min	FID	Injector and Detector $T = 300$°C, He carrier at 5 mL min^{-1}, 2 μL split injection (1 : 100 ratio)	54
PE	Numerous[d]	Dissolution	UA-1 HT (dimethylpoly-siloxane) fused silica capillary, 30 m × 0.25 mm i.d., 0.1 μm film	Start at 50°C, ramp at 20°C min^{-1} to 300°C, hold for 10 min	MS, EI, 70 eV, 40–700 m/z	Injector $T = 250$°C, He carrier at 1 psi, 1 μL split injection (1/2 ratio)	55

Note: BHET, *bis*-(2-hydroxyethyl)terephthalate; EG, ethylene glycol; DEG, diethylene glycol; TA, terephthalic acid; MHET, mono-(2-hydroxyethyl)terephthalate; ATBC, *o*-acetly-tri-*n*-butyl citrate; DEHA, di(ethylhexyl) adipate.

[a] Columns used included: Carbowax 20M, Chromosorb W-HMDS, Aeropak Number 30, 10 foot × 1/8-inch × 0.055 inch i.d.

[b] This reference examined the chromatographic characteristics of the cited additives and thus did not characterize actual polymers.

[c] Additives chromatographed including antioxidants (BHT, Irganox 1076, 1330; Yoshinow BB, SR, 2246 R; Irgafos 168, Ultranox 626, Topanol CA, DLTDP, DMTDP, DSTDP), light stabilizers (Sanol LS744, LS770; Tinuvin 120, 326, 327; UV 531), and slip agents (palmitic acid amide, oleic amide, stearic acid amide, erucic amide).

[d] This reference included the separation of 53 polymer additives including antioxidants, UV stabilizers, lubricants, and plasticizers. Performance details are provided.

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Table 10. Examples of pyrolysis/GC methods used to identify and/or quantify packaging system additives.

Material	Additives	Pyrolysis conditions	Column	Oven program	Detection	Others	Refs.
Polyolefin, PMMA	Hostanox O3, Hostavin N 20, Irganox 3052 FF, Irganox 3114, Tinuvin 320, 329, 350	100 μg sample at 550°C	RTX-5 fused silica capillary, 60 m × 0.32 mm i.d., 0.5 μm film	60°–300°C at 7°C min^{-1}	MS (EI, 45–700 mass range)	Injector $T = 260°C$, Detector $T = 270°C$, He carrier at 50 mL min^{-1}	[47]
PVC	DEHP	0.5 mg sample at 700°C	DB-5 fused silica capillary, 30 m × 0.25 mm i.d., 1.0 μm film	40°C for 4 min; ramp at 10°C min^{-1} to 320°C, hold for 18 min	MS (EI, 15–650 mass range)	Injector $T = 300°C$, Detector $T = 300°C$, 30/1 injection split	[48][c,d]
Cellulose	Dioctyl adipate						
Copolymer[a]	Dibutyl sebacate, tributyl acetylcitrate						
PS/PC blend	TPP						
PU	Mixture of didecyl phthalate esters						
Epoxy resin[b]	Brominated *bis*phenol A	0.5 mg sample at 950°C	DB-5 fused silica capillary, 30 m × 0.25 mm i.d., 1.0 μm film	40°C for 4 min; ramp at 10°C min^{-1} to 320°C, hold for 18 min	MS (EI, 15–650 mass range)	Injector $T = 300°C$, Detector $T = 300°C$, 30/1 injection split	[49][c,e]
Poly-(diallyl-phthalate)	Dechlorane plus						

ABS	Octabromo-diphenyl oxide						
PC-ABS blend	Brominated phenol, triphenyl phosphate						
General	Various waxes, stearic acid, butyl stearate, zinc stearate, butyl oleate, butyl palmitate, stearamide, AcraWax C	0.5 mg sample at 950°C	DB-5 fused silica capillary, 30 m × 0.25 mm i.d., 1.0 μm film	40°C for 4 min; ramp at 10°C min^{-1} to 320°C, hold for 18 min	MS (EI, 15–650 mass range)	Injector $T = 300°\mathrm{C}$, Detector $T = 300°\mathrm{C}$, 30/1 injection split	[50][c,f]
General	Irganox 565, 1010, MD1024, 1035, 1076, 1425, 3114; Irgafos 168	0.5 mg sample at 950°C	DB-5 fused silica capillary, 30 m × 0.25 mm i.d., 1.0 μm film	40°C for 4 min; ramp at 10°C min^{-1} to 320°C, hold for 18 min	MS (EI, 15–650 mass range)	Injector $T = 300°\mathrm{C}$, Detector $T = 300°\mathrm{C}$, 30/1 injection split	[51][c,g]

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[a] Vinyl-chloride–vinylidene chloride copolymer.

[b] Crosslinked epoxy resin (thermoset of bisphenol-A diglycidyl ether).

[c] A more rapid oven program was also used to produce pyrograms via FID detection.

[d] This paper deals with plasticizers as a class of additives.

[e] This paper deals with flame retardants as a class of additives.

[f] This paper deals with lubricants as a class of additives.

[g] This paper deals with antioxidants as a class of additives.

Finally, while it is not a chromatographic issue per se, pre-injection sample preparation, nevertheless, is an important consideration in the successful application of a complete analytical process. This fact is borne out in the observation that recent technological advances in polymer characterization focus not only on the analytical characterization of a test sample, but also on the method of generation of that sample. Innovation in sample preparation is driven by both scientific considerations [the difficulty, but necessity, of isolating the analytes of interest (additives) from the sample matrix (bulk polymer) in such a way that the additives are not impacted by the process (e.g., see Ref.[52]), and by practical considerations associated with all analytical chemistry (e.g., time and cost efficiency). While it is beyond the scope of this paper to exhaustively discuss sample preparation strategies for polymer

Table 11. Solubility of polymers.

Polymer	Soluble in
Alkyd resin	Chlorinated hydrocarbons, lower alcohols, esters
Acrylonitrile-butadiene-styrene terepolymer	Methylene chloride
Polyacrylamide	Water
Polyamides	Phenols, *m*-cresol, concentrated mineral acids, formic acid
Polycarbonate	Ethanolamine, dioxane, chlorinated hydrocarbons, cyclohexanone
Polyethylene	Dichlorobenzene, pentachloroethylene, dichloroethylene, tetralin
Poly(ethylene terephthalate)	Cresol, concentrated sulfuric acid, chlorophenol, trichloroacetic acid
Polyformaldehyde	Dichlorobenzene, DMF, chlorophenol, benzyl alcohol
Polystyrene	Aromatic and chlorinated hydrocarbons, pyridine, ethyl acetate, dioxane, chloroform, acetone
Polytetrafluoroethylene	Fluorocarbon oil
Polyurethanes	Dioxane, THF, DMF, DMSO, *m*-cresol, formic acid, 60% sulfuric acid
Poly(vinyl chloride)	Cyclohexanone, THF, DMF, ethylene dichloride
Poly(vinylidene chloride)	THF, ketones, DMF, chlorobenzene
Vinyl chloride–vinyl acetate copolymers	Methylene chloride, THF, cyclohexanone

characterization, the following general information is provided to facilitate this important step of the overall analytical process. In terms of specific sample preparation methods, Nerin et al.[53] have recently provided a review of sample treatment techniques applicable to polymer extract analysis, including headspace methods, supercritical fluid extraction, and solid phase micro-extraction. In terms of general knowledge, Table 11 provides solubility information relevant to polymer dissolution.

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