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Identification and quantification of (polymeric) hindered-amine light stabilizers in polymers using pyrolysis–gas chromatography–mass spectrometry and liquid chromatography–ultraviolet absorbance detection–evaporative light scattering detection

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Abstract

Direct analysis of polymers containing polymeric hindered amine light stabilizers (HALS) by using pyrolysis coupled to GC–MS is applied successfully for fast and straightforward identification of these HALS additives. Each of the HALS additives shows different pyrolysis gas chromatograms containing characteristic pyrolysis products. As a result, HALS additives with very similar chemical structures, e.g. Chimassorb 944 and Chimassorb 2020, can be distinguished. A HPLC method with both ultraviolet (UV) and evaporative light scattering detection (ELSD) is developed to quantify the various HALS additives in extracts of polymers. The critical factor of the HPLC method is the use of a basic amine, like *n*-hexylamine, as a solvent additive to facilitate the elution of HALS additives. The various HALS additives can be distinguished according to retention time and peak shape and by using different detection methods. The suitability of the developed methods is demonstrated by the analytical performance of the HPLC method and the identification and determination of the actual content of HALS additives in polyolefines using pyrolysis GC–MS and HPLC. The HPLC method can also be used for the determination of the specific migration of HALS additives from food contact materials.

Keywords: Additives; HALS; Pyrolysis; GC–MS; HPLC; Migration

1. Introduction

Additives in polymers are used to protect polymers from degradation during processing or outdoor exposure as a result of reaction with, e.g. oxygen or UV light. There are several classes of additives, each with their own specific properties [1]. An important class of additives that protect polymers from UV radiation are the so-called hindered-amine light stabilizers (HALS). These additives are used for their radical scavenger ability. Some of these HALS additives have a polymeric structure. Due to their high molecular weight, these additives have the advantage of limited mobility in polymers and therefore loss of additive during processing or use is negligible. HALS additives are used in various amounts, depending on the type of polymer. For example, in polyolefines like LDPE or PP the amount of HALS additives may be as high as 3 wt% while in thermoplastics the amount of HALS rarely exceeds 0.5 wt% [2].

As a result of their complex chemical structure the analysis of HALS additives is not straightforward and, probably, did not receive as much attention as other classes of polymer additives, e.g. antioxidants, plasticizers.

One of the first techniques used to study HALS additives in polymers, was the application of pyrolysis coupled to gas chromatography (Py-GC) [3–5]. Due to their polymeric structure pyrolysis of these additives result in smaller

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degradation products that can be analyzed with gas chromatography. Some earlier studies have shown the capability of Py-GC to quantify HALS additives in polymers [3–5]. However, these authors did not have a specific detection method, e.g. mass spectrometry, in order to identify HALS additives unambiguously. Furthermore, prior to analysis the HALS additives were extracted from the polymer, instead of direct analysis of the polymer sample containing the HALS additives. However, simple and quick sample preparation is actually one of the major advantages of the use of Py-GC for the analysis of additives in polymers.

Other techniques that have been used to analyze HALS additives are UV-spectroscopy [6,7] and NMR [6] but these techniques are not able to differentiate between different HALS additives. Characterization of HALS additives has also been carried out with MALDI-TOF-MS [8] and pyrolysis GC–MS [9], although these techniques have not been used to identify and quantify HALS additives in polymers. However, MALDI-TOF-MS is certainly not a straightforward technique to directly identify and quantify HALS additives in polymers, while pyrolysis GC–MS has shown to be a very promising technique to achieve this, although some authors claim that this technique is not discriminative enough [10]. Wang [11] have already shown that pyrolysis GC–MS is able to identify various classes of additives using characteristic peaks and masses that discriminate between the various additives. Blazso [9] showed some promising results for HALS additives using pyrolysis GC–MS.

Interestingly, no report of a successful analysis of HALS additives with liquid chromatography has been made so far. Some attempts have been made, but the polymeric structure and the presence of secondary amine-groups are thought to be the major cause of the lack of liquid chromatography methods for HALS additives [12].

In this study it will be shown that pyrolysis GC–MS can be used for quick identification of HALS additives in polymers and that the various HALS additives can be distinguished from each other by using specific masses and pyrolysis products. Furthermore, a HPLC method using both UV and ELSD detection is developed to separate and quantify the various HALS additives as well as other additives like anti-oxidants, while often a mix of additives is present in polymers. The potential of the method is demonstrated for the determination of the amount of HALS additives in polymer samples and the specific migration of HALS additives from packaging materials into food simulants.

2. Experimental

2.1. Materials and chemicals

Additives were obtained from Ciba Specialty Chemicals Inc., Basel, Switzerland. Some characteristics of the various HALS additives studied are given in Table 1 while the chemical structures are shown in Fig. 1.

Standard solutions of HALS additives in THF were prepared for calibration and quantification purposes when using the HPLC methods.

The polymer samples used were commercially available polypropylene (PP) containing, aside from other types of additives, Tinuvin 770 and Chimassorb 944 and high density polyethylene (HDPE) containing, aside from other types of additives, Tinuvin 622 and Chimassorb 944.

The following chemicals were as solvent, eluent or additive: ethanol (Merck, p.a.), Iso-octane (Biosolve, HPLC grade), tetrahydrofuran (Biosolve, HPLC grade), isopropanol (J.T. Baker, p.a.), acetonitrile (Biosolve, HPLC grade), *n*-hexylamine (Aldrich), ammoniumacetate (J.T. Baker, p.a.), 25% ammonia (Merck, p.a.) and nanopure water.

2.2. Pyrolysis GC–MS

The pyrolysis GC–MS system consisted of an Agilent G1530A gas chromatograph (Agilent, Palo Alto, CA, USA) equipped with a Fisher GSG 1040 PSC Curie Point Pyrolyser (GSG GmbH, Bruchsal, Germany), an AS 24 Pyrolyser Carrousel (GSG GmbH, Bruchsal, Germany), an ATAS Optic II programmable injector (ATAS, Veldhoven, the Netherlands) and an Agilent 5973 mass selective detector (Agilent, Palo Alto, CA, USA).

Table 1
Characteristics of HALS additives used for analysis

Trade name	CAS. no.	M_w (Da)	Chemical name
Tinuvin 770	52829-07-9	481	Bis(2,2,6,6-tetramethyl-4-piperidinyl)sebacate
Tinuvin 622	65447-77-0	3100–4000	Poly-(*N*-b-hydroxyethyl-2,2,6,6-teramethyl-4hydroxy-piperdiyl succinate)
Chimassorb 119	106990-43-6	2286	*N*,*N*‴-[1,2-ethanediylbis[[[4,6-bis-[butyl(1,2,2,6,6-pentamethyl-4-piperidinyl)amino]-1,3,5-triazine-2-yl]imino]-1,3-propanediyl]]bis[*N*′,*N*″-dibutyl-*N*′,*N*″-bis(1,2,2,6,6-pentamethyl-4-piperidinyl)-1,3,5-triazine-2,4,6-triamine
Chimassorb 944	71878-19-8	2000–3100	Poly-{6-[1,1,3,3-tetramethylbutyl]-imino]-1,3,5-triazine-2,4-diyl}{2-(2,2,6,6-tetramethylpiperinyl)-imino}
Chimassorb 2020	192268-64-7	2600–3400	1,6-hexanediamine, *N*,*N*′-bis(2,2,6,6-tetramethyl-4-piperidinyl)-polymer, reaction products with *N*-butyl-1-butanamine and *N*-butyl-2,2,6,6-tetramethyl-4-piperidinamine

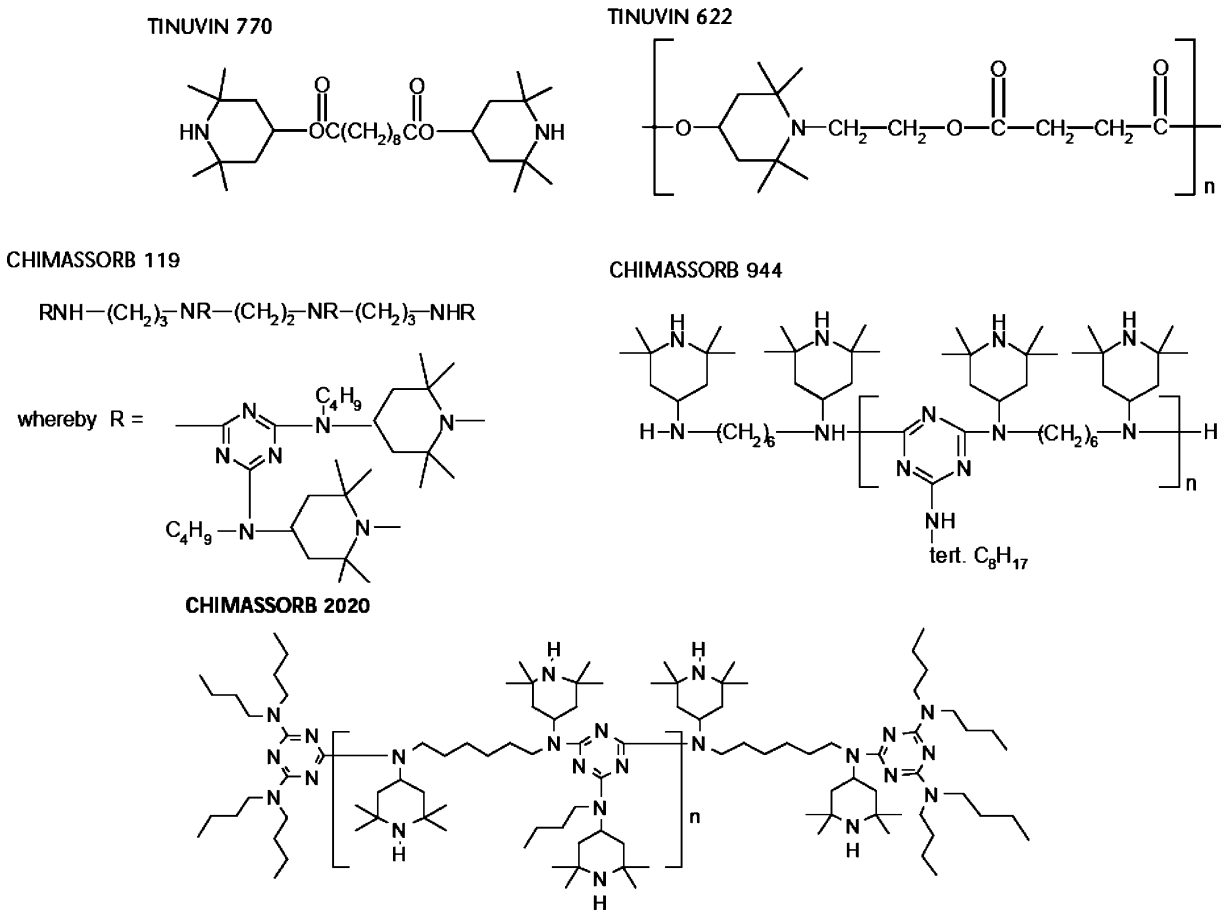

Fig. 1. Chemical structures of Tinuvin 770, Tinuvin 622, Chimassorb 119, Chimassorb 944 and Chimassorb 2020.

Sample holders of various Curie Point metal and alloys (GSG GmbH, Bruchsal, Germany) were used with a Curie point temperature in the range of 300–900 °C. A sample of about 125 μg was weighed into a pyrolysis sample holder and the sample holder was positioned in a glass liner. Next, the sample holder and glass liner were placed in the autosampler tray. Prior to analysis, the sample holder with glass liner were transferred automatically into the pyrolysis chamber, which was held at 200 °C.

Pyrolysis was carried out at 590 °C with a pyrolysis time of 15 s. A constant He flow of 10 ml/min was used to transfer the pyrolysis products from the pyrolysis chamber to the ATAS Optic II injector, which was permanently held at 250 °C. From the ATAS Optic II injector the pyrolysis products were transferred by the helium flow to the gas chromatograph using a split ratio of 1:20.

Separation of the pyrolysis products was carried out using a DB-5MS capillary column (30 m × 0.25 mm i.d.; film thickness 0.25 μm; J&W Scientific, Folsom, CA, USA). The GC oven was kept at 50 °C during pyrolysis and transfer of the pyrolysis products to the GC. After injection of the pyrolysis products the temperature was kept at 50 °C for 5 min followed by a linear increase to 320 °C with 15 °C/min and was held at 320 °C for 5 min.

2.3. HPLC-UV/ELSD

The LC system consisted of a Waters 2690 Separations Module (Waters, Milford, MA, USA), equipped with a vacuum degasser and a thermostatted column compartment. UV-detection was performed with a Waters PDA model 996 (Waters, Milford, MA, USA) with a wavelength range of λ = 200–450 nm. ELSD detection was performed with an Alltech ELSD detector (Alltech, Deerfield, IL, USA) using a nebulization temperature of 60 °C and a N_2 gas flow of 1.5 l/min.

Separation was achieved using an Xterra C8 column (150 mm × 3.0 mm; 5 μm particles; Waters, Milford, MA, USA) operated at 60 °C. The following linear solvent gradient was used:

Time (min)	Solvent A (%)	Solvent B (%)	Solvent C (%)
0	30	70	0
2	30	70	0
34	0	100	0
36	0	0	100
41	0	0	100

Solvent A: aqueous 10 mM NH_4Ac solution adjusted to pH 9.5 with 25% aqueous NH_4OH to which 500 μl/l *n*-hexylamine was added. Solvent B: acetonitrile to which 700 μl/l *n*-hexylamine was added. Solvent C: isopropanol to which 700 μl/l *n*-hexylamine was added.

The flow rate was 0.5 ml/min and the injection volume was 10 μl.

2.4. Extraction method

Prior to HPLC-UV/ELSD analysis the various HALS additives were extracted from the polymers by a dissolution/precipitation procedure. About 10 g of PP and HDPE samples was dissolved by refluxing in 100 ml toluene. Next, precipitation was carried out using 75 ml methanol. After filtration, the extract was evaporated and redissolved into 5 ml of THF. This procedure was carried out in duplicate.

Recovery experiments were carried out by adding known amounts of additives to the dissolved polymer solution. In this way the effectiveness of the extraction procedure could be controlled. Spiking of known amounts of additives to methanol followed by evaporation and redissolution in THF was carried out in order to be sure that no degradation or evaporation of the additives took place during evaporation. The redissolved THF extracts were analyzed with the HPLC method.

2.5. Migration experiments

Migration experiments were carried out in duplicate by total immersion of approximately 1.5 dm^2 of food contact material in 150 ml of 15% ethanol or iso-octane. After the appropriate storage conditions, i.e. 10 days at 40 °C for 15% ethanol and 2 days at 20 °C for iso-octane, the sample material was removed and the migration solution was slowly evaporated, redissolved in 5 ml THF and subsequently analyzed.

3. Results and discussion

3.1. Pyrolysis GC–MS of additives

Reference compounds of the various HALS additives of Table 1 were analyzed with pyrolysis GC–MS using various pyrolysis temperatures. The pyrolysis temperature has a strong influence on the amount and type of pyrolysis products formed. Not surprisingly, a high pyrolysis temperature leads to a relatively high amount of low molecular weight pyrolysis products. The advantage of these products is the relative straightforward identification using their mass spectra. For example, components comprising piperidin rings are very characteristic pyrolysis products of HALS additives [9]. However, most HALS additives contain these piperidin rings and hence these are not useful for distinguishing between the different HALS additives. For that reason, a relatively low pyrolysis temperature, e.g. 590 or 670 °C, was applied. Examples of pyrolysis chromatograms of four polymeric HALS additives are shown in Fig. 2. The pyrolysis GC–MS chromatogram of each HALS additive differs significantly from those of the other HALS additives (Fig. 2). However, pyrolysis of small amounts of additives in polymers will result in a chromatogram dominated by characteristic pyrolysis products of the polymer and as a result the pyrolysis products of additives are hardly visible (see Fig. 3). It is therefore necessary to select one or more characteristic pyrolysis products with high intensity that can be used to identify the HALS additives in polymers by selected ion extraction. Extensive studying of the chromatograms, shown in Fig. 2, made it possible to select these characteristic pyrolysis products for the various HALS additives (Table 2 and Fig. 4).

The most straightforward example is Tinuvin 770 (chromatogram not shown), a monomeric HALS additive, whose main 'pyrolysis product' is the intact molecule of Tinuvin 770 (M_w = 481 Da) with a retention time of 19.4 min. The mass spectrum of the peak of Tinuvin 770 is shown in Fig. 4A. The mass spectrum shows a relatively small mass peak for the molecular ion with *m*/*z* 456, but a very strong mass peak with *m*/*z* 124. The latter mass has been assigned by Blazso [9] as a characteristic MS fragment of the tetramethyl piperidinyl ring due to methyl loss. However, Tinuvin 770 has not a polymeric structure and was used in this study for reference only.

Tinuvin 622 is a polymeric HALS additive consisting of a distribution of components with a molecular weight (M_w) of 3100–4000 Da. The GC–MS chromatogram of Tinuvin 622 after pyrolysis at 590 °C is shown in Fig. 2A. In the pyrolysis GC–MS chromatogram some large peaks could be observed at the end of the chromatogram. These pyrolysis products were found to be characteristic of Tinuvin 622. One of these peaks, i.e. at a retention time of 14.8 min, could be positively identified as a monomer unit of Tinuvin 622, i.e. *N*-b-hydroxyethyl-2,2,6,6-tetramethyl-4-hydroxy-piperdinyl succinate, with a molecular weight of 297 Da. The mass spectrum of this peak is shown in Fig. 4B. The spectrum is identical to that published in [9] for this compound. One of the highest mass peaks in the mass spectrum, which also could be found in some of the other pyrolysis products of Tinuvin 622, was *m*/*z* 152. A possible assignment of this mass peak is a characteristic MS fragment of the *N*-ethyl-tetramethyl piperidinyl ring due to methyl loss, i.e. similar to Tinuvin 770, but now with an ethyl group attached to the nitrogen atom of the piperidinyl ring. This is a clear difference between Tinuvin 622 and Tinuvin 770, as in the latter additive the nitrogen in the piperidinyl ring is present as a secondary amine (see Fig. 1). The major peak in the pyrolysis GC–MS chromatogram of Tinuvin 622 at a retention time of 19.1 min was also considered characteristic for Tinuvin 622. The mass spectrum of this pyrolysis product is shown in Fig. 4C and the characteristic masses of the mass spectrum are given in Table 2. This peak could be tentatively identified as a monomer unit with an additional piperidinyl ring.

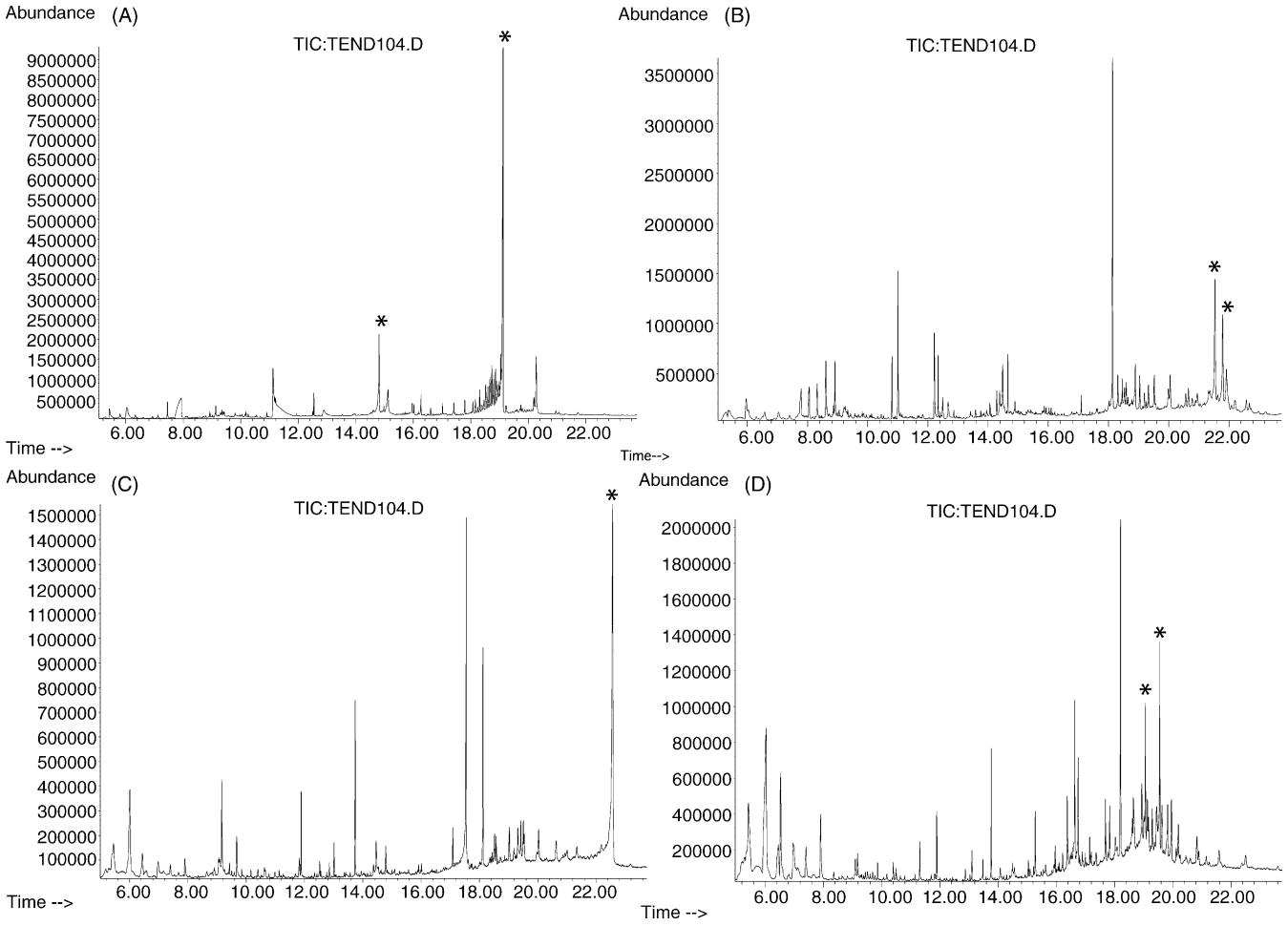

Fig. 2. Full scale pyrolysis GC–MS chromatograms of (A) Tinuvin 622, (B) Chimassorb 119, (C) Chimassorb 944 and (D) Chimassorb 2020 after pyrolysis at 590 °C. Indicated are the characteristic pyrolysis products.

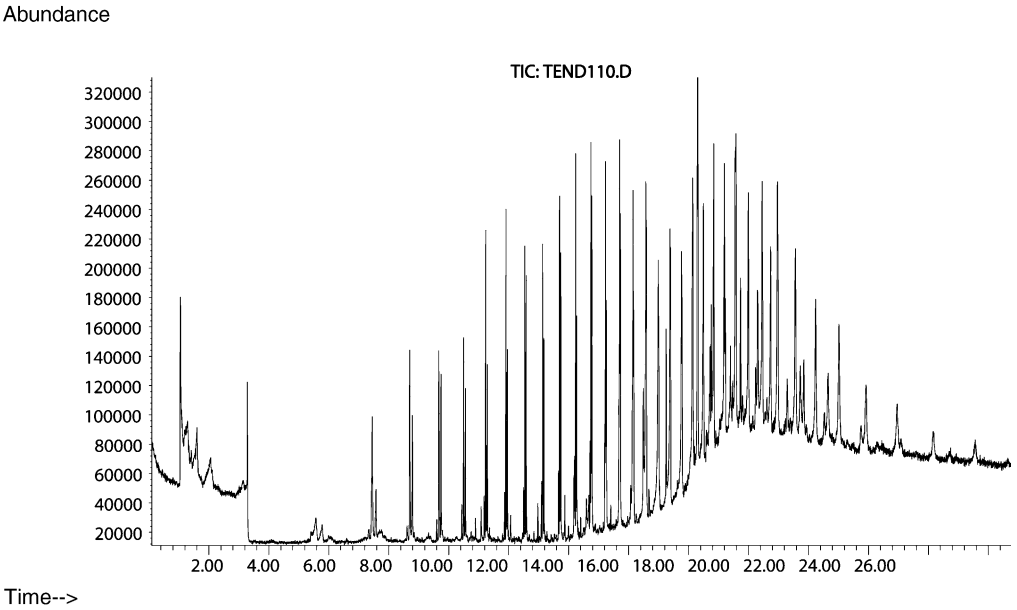

Fig. 3. Example of a pyrolysis GC–MS chromatogram of a HDPE polymer containing small amounts of additives.

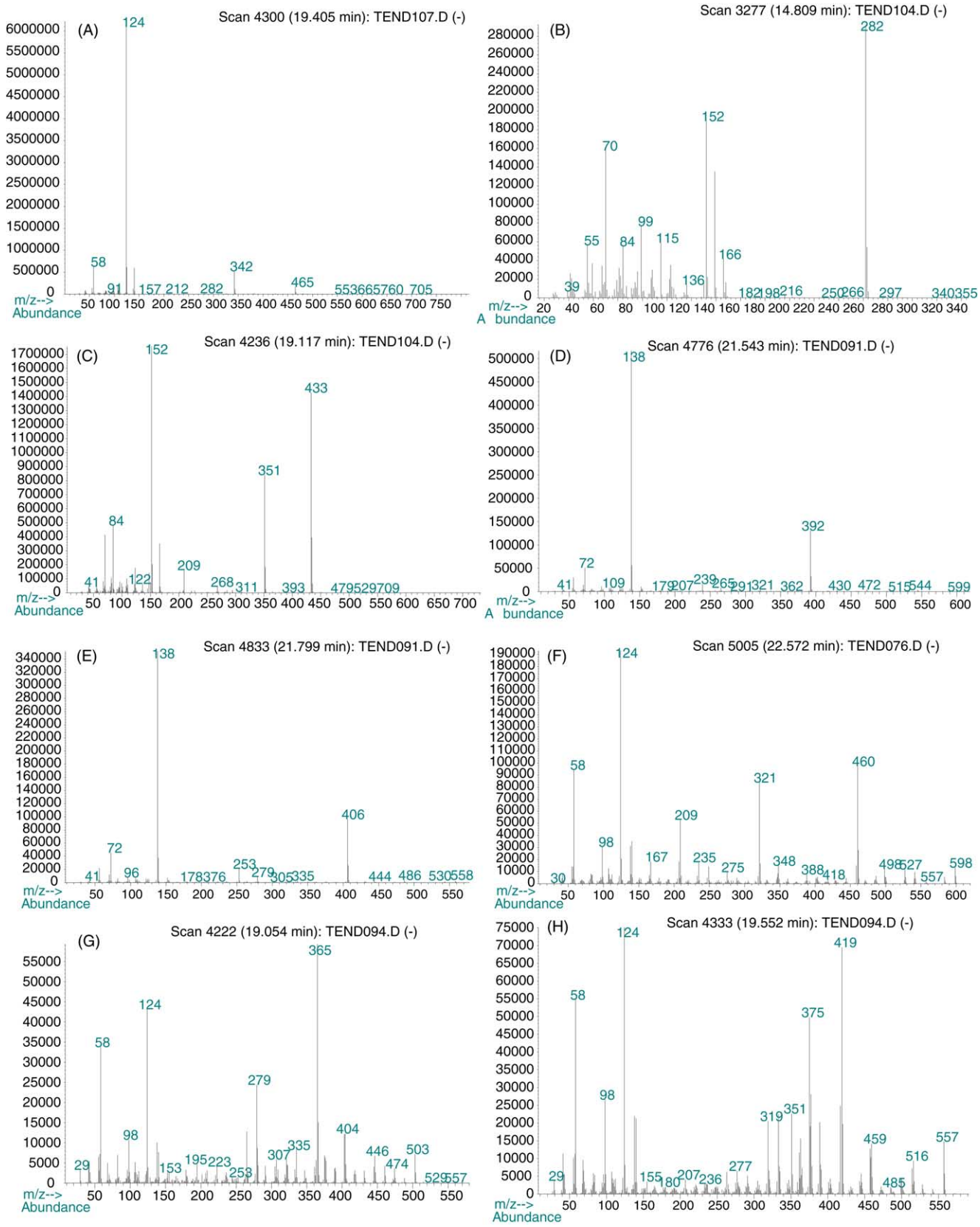

Fig. 4. Mass spectra of characteristic pyrolysis products of HALS additives and their corresponding retention times (t_r), see also Table 3. (A) Tinuvin 770, t_r = 19.4 min, (B) Tinuvin 622, t_r = 14.8 min, (C) Tinuvin 622, t_r = 19.1 min, (D) Chimassorb 119, t_r = 21.5 min, (E) Chimassorb 119, t_r = 21.8 min, (F) Chimassorb 944, t_r = 22.6 min, (G) Chimassorb 2020, t_r = 19.0 min and (H) Chimassorb 2020, t_r = 19.6 min.

Table 2
Characteristic mass peaks and pyrolysis products of various HALS additives obtained from pyrolysis GC–MS experiments

Additive	Characteristic mass peak (*m*/*z*)	Characteristic pyrolysis product		
		t_r (min)	*m*/*z*	Component
Tinuvin 770	124	19.4	342, 481	Molecular ion
Tinuvin 622	152	14.8	282, 297	Monomer-unit
		19.1	351, 433	Monomer + piperidinyl ring
Chimassorb 119	138	21.5	392, 544	Side group attached to N(H)
		21.8	406, 558	Side group attached to N(H)CH_2
Chimassorb 944	124	22.6	321, 460, 598	Monomer-unit
Chimassorb 2020	124	19.0	365, 503	?
		19.6	419, 557	End group

Chimassorb 119, 944 and 2020 are polymeric HALS additives consisting of piperidinyl rings, comparable with Tinuvin additives, and triazines. While Chimassorb 944 and Chimassorb 2020 consist of a distribution of compounds, Chimassorb 119 consists of a single compound with a molecular weight of 2286 Da (see Table 1 and Fig. 1). GC–MS chromatograms of these additives obtained after pyrolysis at 590 °C are shown in Fig. 2B–D.

There is one significant difference in chemical structure between Chimassorb 119 on the one hand and Chimassorb 944 and Chimassorb 2020 on the other hand. The N-atom in the piperidinyl ring of Chimassorb 119 is attached to a methyl group, while in Chimassorb 944 and Chimassorb 2020 the N-atom in the piperidinyl ring is present as a secondary amine (Fig. 1). This difference in chemical structure is reflected in the pyrolysis products. The mass spectra of several pyrolysis products of Chimassorb 119 contain a strong mass peak of *m*/*z* 138 while for Chimassorb 944 and Chimassorb 2020 a strong mass peak of *m*/*z* 124 is observed for several pyrolysis products. This difference of *m*/*z* 14 between the two mass peaks can be explained by the difference in chemical structure as explained above. The mass peak of *m*/*z* 124 was also observed for Tinuvin 770 and was assigned to a trimethyl piperidinyl ring. The mass peak of *m*/*z* 138 for Chimassorb 119 was also found by Blazso [9] and was identified as a characteristic MS fragment of the *N*-methyl-tetramethyl piperidinyl ring due to methyl loss. The mass peak of *m*/*z* 138 was considered characteristic for Chimassorb 119.

Furthermore, for Chimassorb 119 two characteristic pyrolysis products could be found, both containing the mass peak of *m*/*z* 138. The mass spectra of these two compounds are shown in Fig. 4D and E. The highest mass peaks that were found for these two compounds are *m*/*z* 544 and 558, respectively. Tentative identification of these two compounds suggested the presence of *N*′,*N*″-dibutyl-*N*′,*N*″-bis(1,2,2,6,6-pentamethyl-4-piperidinyl)-1,3,5-triazine-2,4,6-triamine groups, i.e. ‘side group’ of Chimassorb 119, attached to a N–H group of the backbone for the pyrolysis product with retention time of 21.5 min and attached to a N(H)–CH_2 group of the backbone for the pyrolysis product with retention time of 21.8 min.

Chimassorb 944 and Chimassorb 2020 have very similar chemical structures (see Fig. 1). The pyrolysis GC–MS chromatogram of Chimassorb 944 is shown in Fig. 2C. The pyrolysis products at retention times of 17.6 and 22.6 min are characteristic for Chimassorb 944. The mass spectrum of the latter peak is shown in Fig. 4F. This peak could be assigned to a monomer unit of Chimassorb 944, i.e. 6-[1,1,3,3-tetramethylbutyl]-imino]-1,3,5-triazine-2,4-diyl}{2-(2,2,6,6-tetramethylpiperinyl)-imino, with a molecular weight of 598 Da. The mass spectrum of the pyrolysis product with a retention time of 17.6 min showed mainly a mass peak of *m*/*z* 124. Some higher masses but with much lower intensity could be observed which made it difficult to identify this peak. Other HALS additives also showed pyrolysis products with a main mass peak of *m*/*z* 124, hence this pyrolysis product was not considered to be characteristic for Chimassorb 944.

The pyrolysis GC–MS chromatogram of Chimassorb 2020 showed two characteristic pyrolysis products at a retention time of 19.0 and 19.6 min. The mass spectra of these pyrolysis products are shown in Fig. 4G and H. The pyrolysis product with a retention time of 19.6 min could be tentatively identified as one of the end groups of Chimassorb 2020. The other pyrolysis product could not be clearly identified yet. However, both pyrolysis products were considered characteristic Chimassorb 2020 due to the great similarity of their mass spectra.

From the results described above, it could be concluded that each (polymeric) HALS additive showed one or more characteristic pyrolysis products and in some cases characteristic mass peaks were found. These mass peaks were found characteristic because it was a main mass peak in the mass spectra of various pyrolysis products and the *m*/*z* value of the mass peak could be related to the specific chemical structure of the various HALS additives. This characteristic mass peak can be used for a first screening for the presence of HALS additives. As a next step the characteristic pyrolysis products can be used to verify which specific HALS additive is present. An overview of the characteristic mass peaks and pyrolysis products are shown in Table 2.

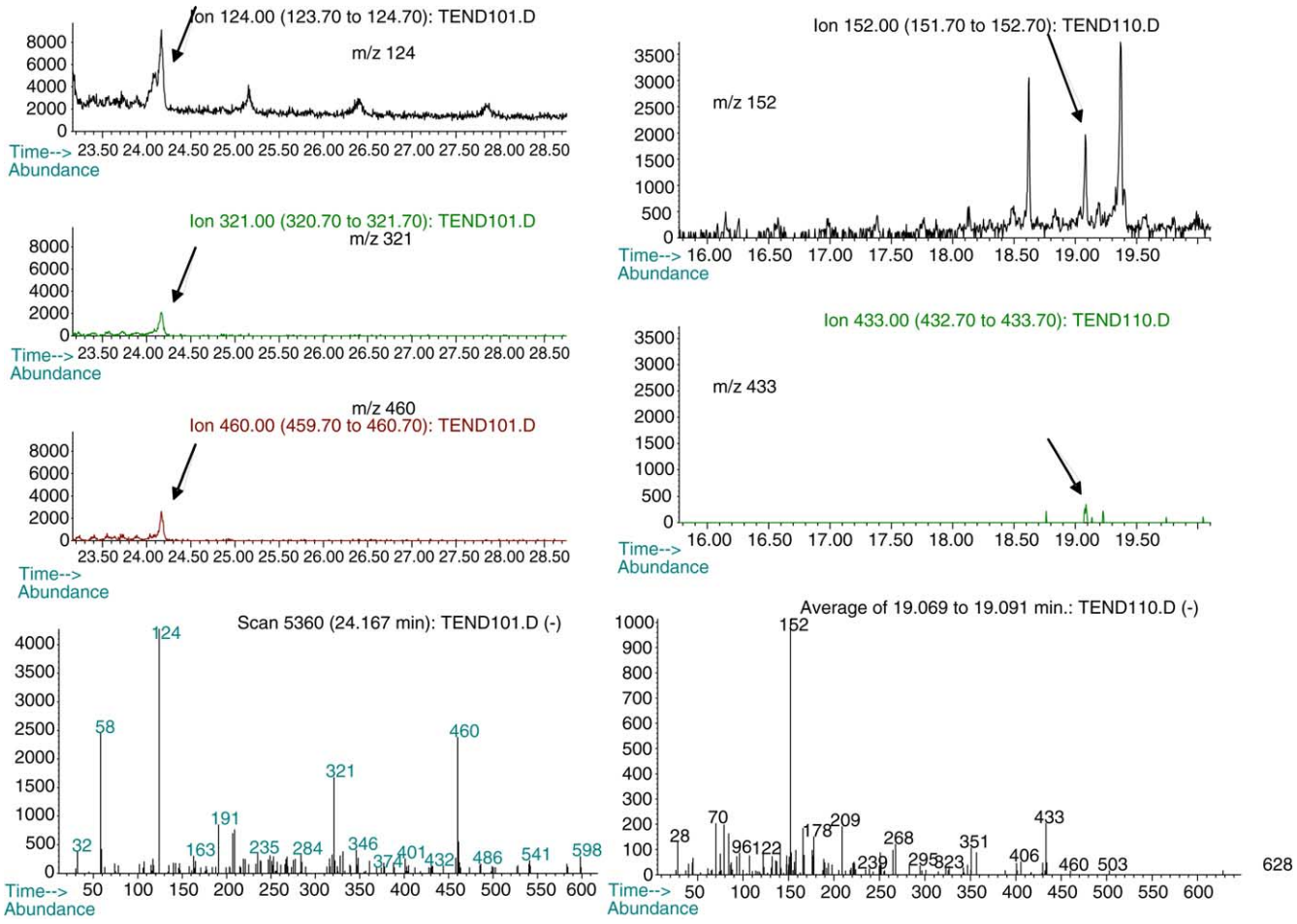

Fig. 5. Extracted ion chromatograms and corresponding mass spectra of characteristic pyrolysis products of (A) Chimassorb 944 (t_r = 22.6 min) in PP and (B) Tinuvin 622 (t_r = 19.1 min) in HDPE.

3.2. Identification of HALS additives in polymer samples with Py-GC–MS

In order to study the possibilities of the developed pyrolysis GC–MS method to identify HALS additives in polymers without any sample preparation, two types of polymers containing one or two HALS additives have been analyzed directly with pyrolysis GC–MS. The characteristic mass peaks and pyrolysis products from Table 2 have been used to identify the HALS additives.

An example is shown in Fig. 5 in which the extracted ion chromatograms are shown of *m/z* 124, 321 and 460 for a pyrolysis GC–MS analysis of a HDPE polymer sample. A peak at 22.6 min showed up for all three mass peaks. The corresponding mass spectrum of this peak is shown in Fig. 5A. The mass spectrum corresponds well with that in Fig. 4F, hence the peak could be identified as a pyrolysis product of Chimassorb 944. A similar example is shown in Fig. 5B for Tinuvin 622 in PP.

Note that in the same way other additives, like Chimassorb 81, Tinuvin 770, Irgafos 168 and Irganox 1076 could be identified in these polymer samples.

The limit of detection for identification of HALS additives in polymers depended strongly on the type of HALS additive and the polymer. In general the detection limit is in the order of 0.01–0.1 wt%.

3.3. HPLC-UV/ELSD of HALS additives

As already stated earlier, to our knowledge no suitable HPLC method has been reported to identify and quantify polymeric HALS additives. This is in contrast with other classes of additives, like anti-oxidants, for which several HPLC methods are available. In general, these HPLC methods are based on a reversed-phase mechanism using a C18 column and a solvent gradient from water to acetonitrile and using UV or MS detection, e.g. [13].

It was our aim to develop a HPLC method that can be applied for the analysis of anti-oxidants, UV absorbers and polymeric HALS additives in one measurement, as often a mix of these additives is present in polymers. Furthermore, the method should also be suitable to determine the specific migration of HALS additives from food contact materials into food simulants. Due to the absence of strong

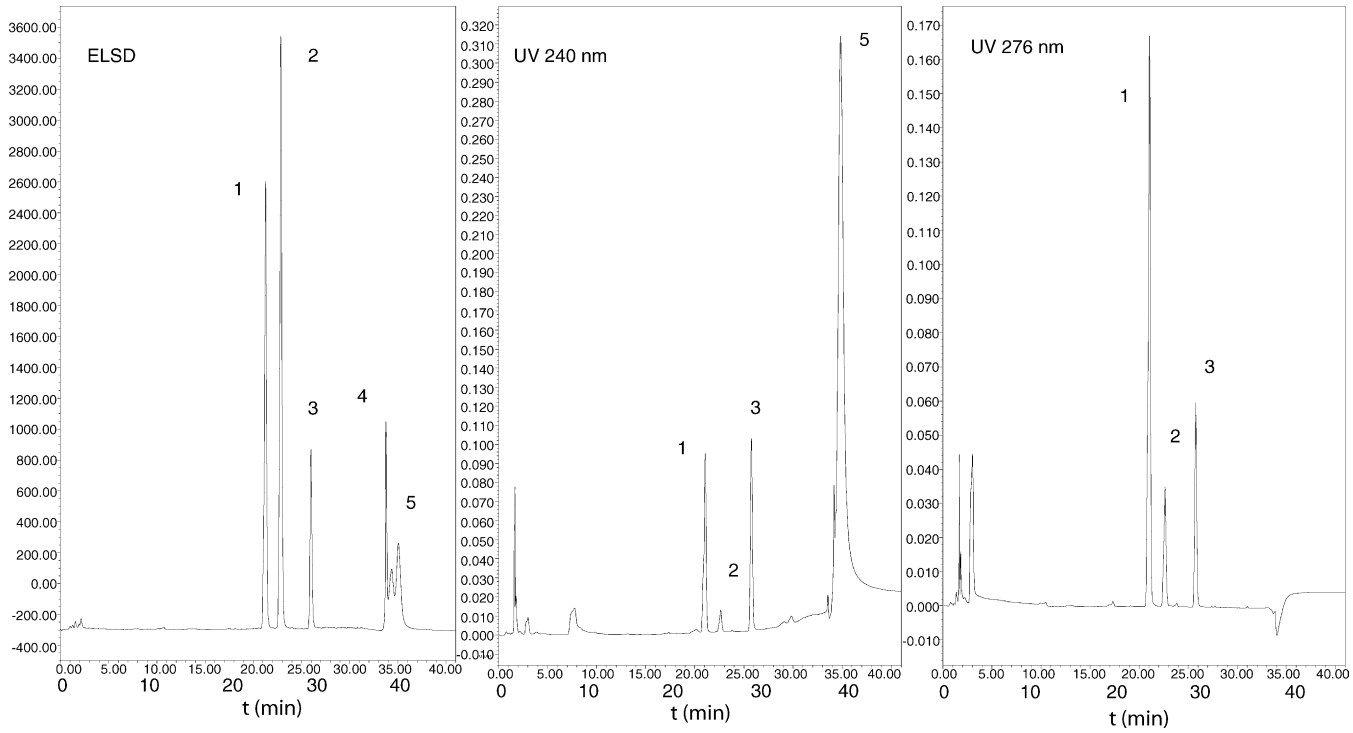

Fig. 6. HPLC chromatograms of a mixture of additives using ELSD detection and UV detection at 240 and 276 nm. The peaks indicated in the figure correspond to (1) Irganox 1010, (2) oxidized Irgafos 168, (3) Irgafos 168, (4) Tinuvin 622 and (5) Chimassorb 944.

UV absorbing groups in some of the HALS additives and the high molecular weight of the HALS additives, an on-line combination of UV and ELSD detection was considered most appropriate. MS detection was considered to be more specific but the relatively high molecular weight of the HALS additives, i.e. $M_w > 2000$ Da, makes it less straightforward to analyze these additives with standard LC–MS equipment. However, our first aim was to develop a suitable HPLC method to separate the various HALS using UV and ELSD detection. At a later stage MS may be applied as detection technique but this is considered as a future option.

The HALS additives are soluble in various organic solvents, like THF, chloroform, etc. Hence, separation by a precipitation/dissolution mechanism during HPLC was not thought to be a major problem in the elution of HALS additives. However, the secondary amine groups present are thought to be the major problem in the elution behaviour of these additives. First experiments using a gradient from water to acetonitrile did not give any elution for the polymeric HALS additives. As already stated by Carrot et al. [12], ion pairing may be the solution for this. *n*-Hexylamine was considered a good candidate as ion pair reagent. To this extent, a solvent gradient of 30% aqueous NH_4Ac (pH 9.5)/70% acetonitrile to 100% acetonitrile was tested to which small amounts of *n*-hexylamine (∼0.1%, v/v) were added to all solvents. With this method it was possible to elute antioxidants, like Irganox 1010 and Irgafos 168, and also some HALS additives, e.g. Tinuvin 770 and Tinuvin 622. However, Chimassorb-type additives did not elute with this method. To achieve elution of these additives an extra gradient step was applied in which the solvent was changed from 30% aqueous NH_4Ac (pH 9.5)/70% acetonitrile to 100% acetonitrile to 100% isopropanol, all containing 0.1% (v/v) *n*-hexylamine. With this gradient it was possible to elute all HALS additives completely. However, it should be noted that it is questionable whether *n*-hexylamine acts as an ion pair reagent in this case. It is unlikely that *n*-hexylamine and HALS additives containing amine groups form an ion pair. It more likely that *n*-hexylamine blocks the residual active groups on the C18 column preventing strong interaction of the HALS additives with the column and thus facilitating the elution of the HALS additives. An example of such an analysis is shown in Fig. 6, which shows LC–UV and LC–ELSD chromatograms of a mixture of several types of additives, i.e. Irganox 1010, Irgafos 168 (plus oxidized Irgafos 168), Tinuvin 622 and Chimassorb 944.

It can be seen from Fig. 6 that all additives showed up in the LC–ELSD chromatograms. With UV detection appropriate wavelengths have to be chosen to obtain maximum response, depending on the chemical structure. For example, at $\lambda = 276$ nm, neither Chimassorb 944 nor Tinuvin 622 are visible, while at $\lambda = 240$ nm Chimassorb 944 shows a very intense peak but Tinuvin 622 is nearly invisible. The presence of triazine-rings in Chimassorb-type additives explains the high response with UV detection at certain wavelengths. The absence of the triazine-rings in Tinuvin-type additives explains the low UV response for these type of additives, although some small UV intensity around 220 nm may be observed due to the presence of C=O groups.

Table 3
Characteristics of HALS additives obtained from HPLC-UV/ELSD measurements

Additive	t_r (min)	UV (240 nm)	ESLD	UV_{max} (nm)
Tinuvin 770	7	<	+	210
Tinuvin 622	33.9	<	+	210
Chimassorb 119	34.7	+	+	220
Chimassorb 944	34.9	+	+	226
Chimassorb 2020	34.6, 34.7	+	+	223

Tinuvin 770 and Tinuvin 622 can be distinguished by the present method based on a different retention time. Furthermore, Tinuvin-type additives can be distinguished from Chimassorb-type additives based on retention time and using a combination of UV/ELSD detection. This is summarized in Table 3.

To distinguish between the three Chimassorb-type additives is much more complex, as all three elute around the same time. Of course pyrolysis GC–MS can be used to identify which Chimassorb is present, as described earlier. Clear inspection of the chromatograms (see Fig. 7) reveals that there are some significant differences between the three Chimassorb-type additives, which can be used to distinguish between those additives. For example, Chimassorb 119 consists of a single compound instead of a distribution of compounds with different masses. As a result, Chimassorb 119 elutes as a relatively symmetrical and sharp peak, while Chimassorb 944 and Chimassorb 2020 elute as broad peaks with shoulders or multiple peaks. Moreover, close inspection of the chromatograms in Fig. 7 shows that the peak maximum of each additive occurs at a slightly different retention time.

In the case that both Chimassorb 944 and Chimassorb 2020 are present in a polymer, the present HPLC method is not suitable to distinguish between the two additives and hence quantification of the two additives will be very difficult. However, for most applications these two additives are considered to be alternatives and the chance that both additives are used in the same product can be considered small. No commercial additive packages exist to our knowledge that contain Chimassorb 944 and Chimassorb 2020.

To test the suitability of the developed method for the quantification of HALS additives in extracts of polymers, the analytical performance of the method was tested using calibration curves of the various HALS additives (see Table 4).

It can be seen from Table 4 that the calibration curves are linear with a correlation coefficient >0.996 with a L.O.Q. of ∼0.1 mg/ml for both additives. The values obtained were considered satisfactory and therefore it was concluded that the HPLC method was suitable to identify and quantify HALS additives in polymers.

3.4. Quantification of HALS additives in polymers using HPLC-UV/ELSD

Next, the HPLC method developed in the previous section was tested for the quantification of HALS additives in a PP polymer. The amount of HALS additives in the polymer were 2.2 ± 0.2 wt% Tinuvin 770 and 0.8% ± 0.1% Chimassorb 944. The recovery experiments showed that both the extraction and evaporation procedure were acceptable. With the current set-up of the sample preparation and the detection limits of the HPLC method, the limit of quantification of HALS additives in polymers is about 0.05 wt%. No significant interferences with other extractables, e.g. polymer/oligomers or other additives, were observed.

3.5. Specific migration of HALS additives into food simulants using HPLC-UV/ELSD

In the case that plastic materials are used for food contact applications, these materials should be in compliance with the regulations on food contact materials to guarantee no detrimental effects on the health of consumers. For example, food contact materials used in EU should be in compliance with EU directive 2002/72/EC. In the case of HALS additives in these materials, the specific migration of these HALS additives into food simulants should be tested. For example, the specific migration of Chimassorb 944 should not be higher than 3 mg/kg food, while for Tinuvin 622 the specific migration should not exceed 30 mg/kg food.

In order to verify whether the developed HPLC-UV/ELSD method was suitable to determine the specific migration of HALS additives, migration experiments were carried out with HDPE containing Chimassorb 944, Tinuvin 622, Irganox 1010 and Irgafos 168. The specific migration of the HALS additives was not detected above the detection limit of

Table 4
Statistical results of the HPLC-UV/ELSD method to determine HALS additives

Additive	Detection	Statistical evaluation ($n = 5$)[a]
Chimassorb 944	UV (240 nm)	$Y = 7529634X - 119407$ $R = 0.9984$ $R^2 = 0.9968$ L.O.D. = 0.05 mg/ml L.O.Q. = 0.1 mg/ml
Tinuvin 622	ELSD	$Y = 14356918X - 836608$ $R = 0.9994$ $R^2 = 0.9988$ L.O.D. = 0.04 mg/ml L.O.Q. = 0.08 mg/ml

[a] Calculations were carried out using a validated spreadsheet based Deutsche Norm DIN 32645, 'Nachweis-, Erfassungs- und Bestimmungsgrenze', May 1994.

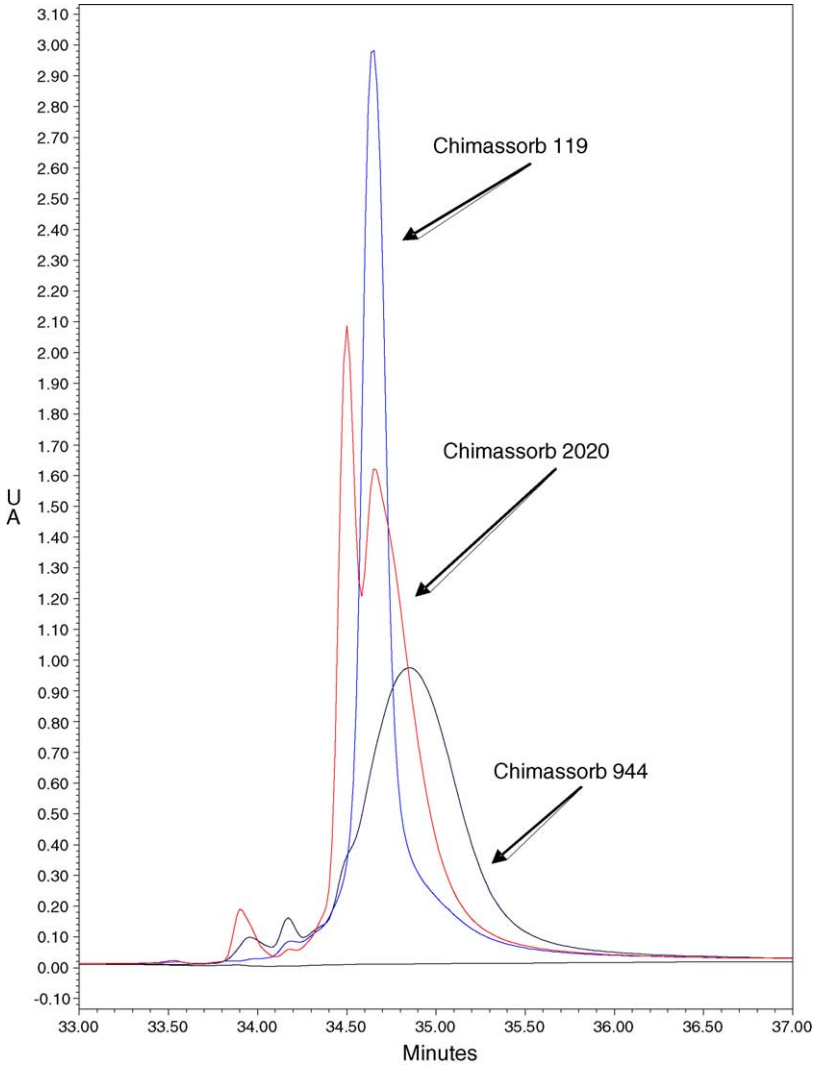

Fig. 7. Overlay of HPLC-UV chromatograms of Chimassorb 119, Chimassorb 944 and Chimassorb 2020.

0.1 mg/ml. This detection limit corresponds to a migration of 1.5 mg/kg food, which is significantly lower than the specific migration limit of Chimassorb 944 (SML 3 mg/kg) and Tinuvin 622 (SML 30 mg/kg). Hence it was concluded that the HPLC-UV/ELSD method could also be used to determine the specific migration of HALS additives from food contact materials.

4. Conclusions

Different analytical methods were developed and applied to identify and quantify polymeric hindered amine light stabilizers (HALS) in polymers. For fast and straightforward identification of HALS additives in polymers, without any significant sample preparation, a pyrolysis GC–MS method was developed and successfully applied. Each HALS additive showed characteristic pyrolysis products that could be used to identify the presence of these HALS additives unambiguously and to distinguish between the different HALS additives, even when they have very similar chemical structures.

For quantification of HALS additives in polymers, a HPLC method with both UV and ELSD detection was developed. In order to elute HALS additives from the column with satisfactory peak shapes, *n*-hexylamine was added to the eluents. With this method also other types of additives, like anti-oxidants, could be analyzed. Based on retention time, detection method and peak shape, the various HALS additives could be distinguished. The analytical performance, i.e. detection limit, linearity, was considered satisfactory. The applicability of the method was demonstrated by the identification and quantification of HALS additives in polyolefins and of the specific migration of HALS additives from food contact materials into food simulants. The detection limits achieved were satisfactory and the combination of UV and ELSD detection was successful to distinguish between the various HALS additives.

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