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Preparative HPLC followed by GPC-MS to investigate the potential leachable compounds produced by the degradation of pentaerythritol tetrakis (3-(3,5-di-tert-butyl-4-hydroxyphenyl) propionate)

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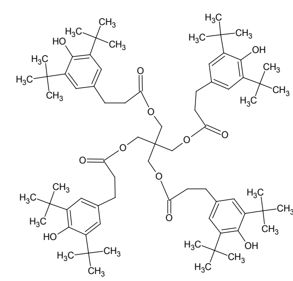
Abstract

Pentaerythritol tetrakis(3-(3,5-di-tert-butyl-4-hydroxyphenyl) propionate) is a highly effective sterically hindered primary phenolic additive which protects polymers against thermo-oxidative degradation.

This antioxidant, with the CAS number 6683-19-8, is commercialized under different trade names as Irganox® 1010, ADK STAB® AO 60, STAB AO® 1010, Songnox® 1010, and have the following chemical structure:



Introduction

At a concentration of about 1000 ppm in a polymer matrix, this additive provides excellent processing and long term thermal stability for a wide variety of materials such as plastics, synthetic fibers, elastomers, adhesives, waxes, oils and fats, and several analytical methods exist for its identification and quantification.

However, few studies deal with the possible non-intentionally added substances (NIAS) generated in the final plastic material by this additive. One of the first papers [1] investigating the organic compounds migrating from polyethylene pipelines into drinking water identified ten substances by GC, known today as Arvin fragments (Table 1).

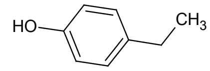
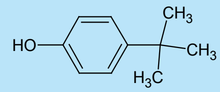
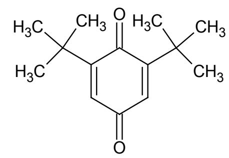
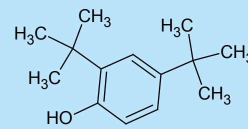
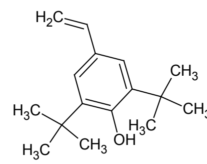
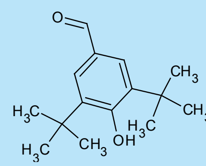
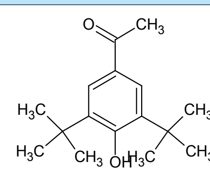
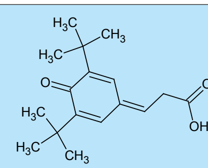
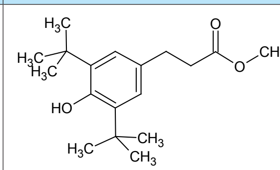
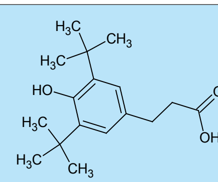
Code	Systematic name	CAS no	Formula	Structure
Arvin I	4-ethyl phenol	123-07-9	$C_8H_{10}O$	
Arvin II	4-tert-butyl phenol	98-54-4	$C_{10}H_{14}O$	
Arvin III	2,6-di-tert-butyl-p-benzoquinone	719-22-2	$C_{14}H_{20}O_2$	
Arvin IV	2,4-di-tert-butyl phenol	96-76-4	$C_{14}H_{22}O$	
Arvin V	3,5-di-tert-butyl-4-hydroxy styrene; 3,5-di-tert-butyl-4-vinyl phenol	19263-36-6	$C_{16}H_{24}O$	
Arvin VI	3,5-di-tert-butyl-4-hydroxy benzaldehyde	1620-98-0	$C_{15}H_{22}O_2$	
Arvin VII	3,5-di-tert-butyl-4-hydroxy acetophenone	14035-33-7	$C_{16}H_{24}O_2$	
Arvin VIII	Cyclohexa 1,4 dien, 1,5-bis(tert-butyl),6-on,4-(2-carboxy-ethylidene)	-	$C_{17}H_{24}O_3$	
Arvin IX	3-(3,5-di-tert-butyl-4-hydroxyphenyl) methyl propanoate	6386-38-5	$C_{18}H_{28}O_3$	
Arvin X	3-(3,5-di-tert-butyl-4-hydroxyphenyl) propanoic acid	20170-32-5	$C_{17}H_{26}O_3$	

Table 1. Arvin fragments migrating from PE pipelines

Arvin fragments are low molecular weight and are easily investigated by GC, and their presence is explained by the hydrolysis of an ester group detaching an arm of the 1010 additive, or by splitting off the tertiary group. However, the analytical methods dealing with the remaining larger fragments are scarce. This is mainly because fragments with relatively high molecular weights of around 1000 g/mol are typically too high for analysis by GC. Therefore, in this Application Note we explore the chromatographic methods appropriate for this range of molecular weights.

Preparative HPLC

Instrumentation

Agilent Infinity II prep System equipped with a 1290 Infinity Binary pump, 1260 Infinity DAD and 1260 Infinity Fraction Collector.

Method for Analysis

Detector used	DAD@270nm
Mobile phase	Gradient water/methanol from 25/75 to 0/100 in 20 min
Columns	Zorbax SB C18 prep, 21.5 x 50 mm, 5 µm (P/N 870050-902)
Sample	Commercial “1010” additive powder
Concentration	10 mg/mL
Injection volume	500 µL
Flow Rate	20 mL/min
Software	OpenLab CDS Chemstation Edition Rev. C.01.07.SR4

Sample chromatograms

The reproducibility of the method was verified by injecting different solutions over several days, and the overlay of these chromatograms are shown in Figures 1a and 1b. Excellent reproducibility was obtained, proving the stability of the instrument and method.

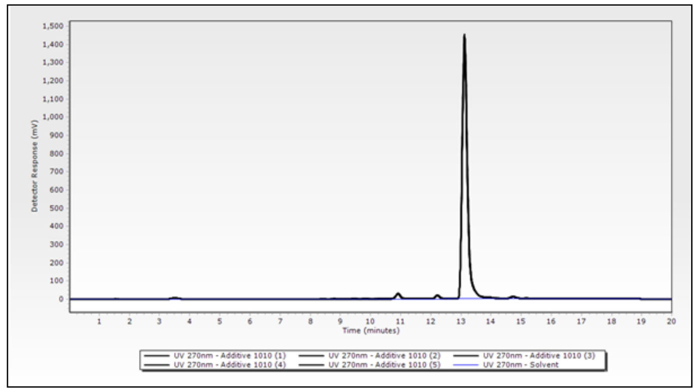


Figure 1a. Overlay of 5 injections showing excellent reproducibility.

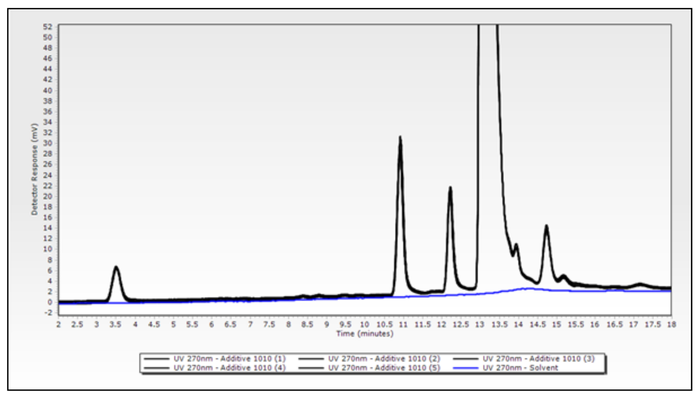


Figure 1b. Zoom of the overlay of 5 injections from Figure 1a.

To establish the fractionation parameters, the **Fraction Preview** tool was used in the control software of the fraction collector module, as shown in Figure 2:

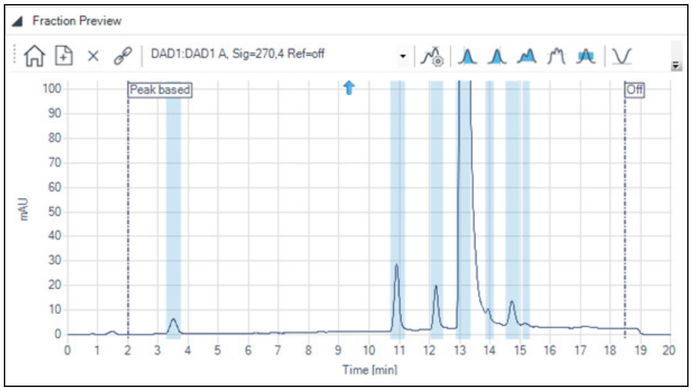


Figure 2. Fraction Preview

Due to excellent reproducibility of the instrument, and by running the method with the established parameters for collection, the expected fractions are obtained as presented in Figure 3:

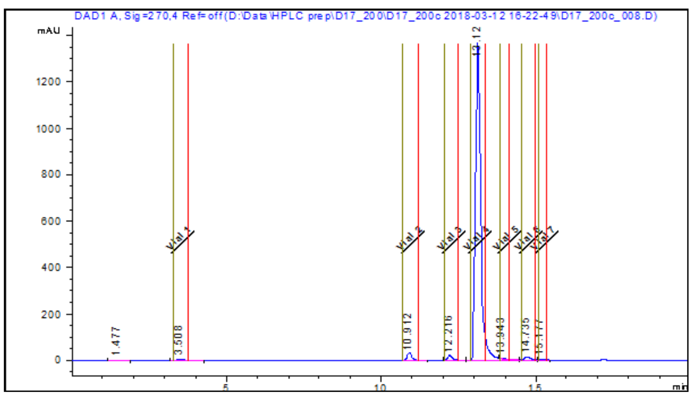


Figure 3. Seven Fractions obtained by fraction collection.

The fractions were then dried/concentrated under vacuum and dissolved in chloroform for GPC analysis.

GPC – MS Analysis

Instrumentation

Agilent Infinity 1260 System equipped with single quadrupole mass detector.

Method for Analysis

Mobile phase	Chloroform
Columns	2 x Agilent Resipore 4.6 x 250 mm
Standard	PS 580
Samples	7 fractions collected by HPLC prep
Injection volume	20 μL
Flow Rate	0.3 mL/min
Software	OpenLab CDS Chemstation Edition Rev. C.01.07

Separation on Agilent Resipore columns

When coupled with MS, the specific advantage of GPC over HPLC is that the separation is by molecular size as shown by a series of Polystyrene Standards in Figure 4.

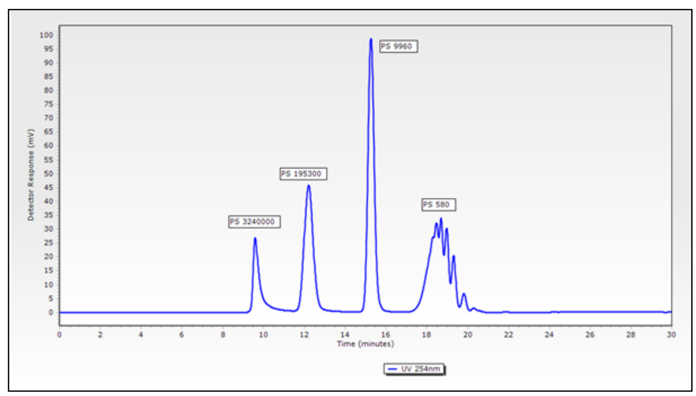


Figure 4. Separation of PS standards over a large MW range using Resipore columns

Since separation is by size we can protect the MS capillary from blockage by high molecular weight polymer fractions by diverting the flow to waste during the first 16 min. As shown in Figure 4, the Resipore columns provide particularly excellent resolution for low molecular weights, with seven oligomers in the PS 580 standard being clearly visible.

Analysis by GPC-MS of PS 580 standard

When coupling GPC with MS as a first step it is good practice to analyze the PS 580 standard in SCAN and SIM (single ion monitoring) modes as described in previous publications [2-5]. The total ion chromatogram (TIC) obtained for 2 Resipore columns is given in Figure 5.

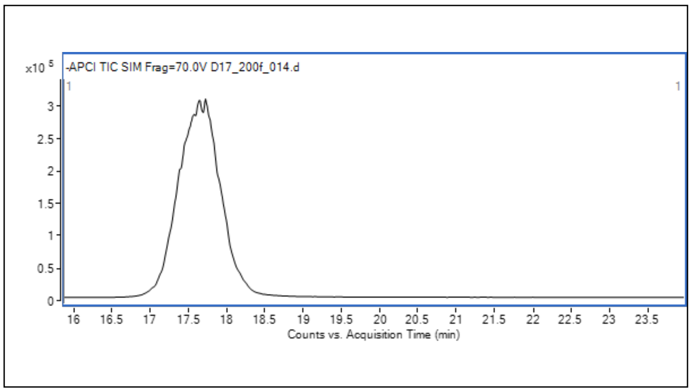


Figure 5. TIC for PS 580 standard using two Resipore columns.

With only one injection it is possible to extract the chromatogram of each PS oligomer with a polymerization degree between 4 and 18 as shown in Figure 6, confirming that the elution range of interest is between 16 and 19 min.

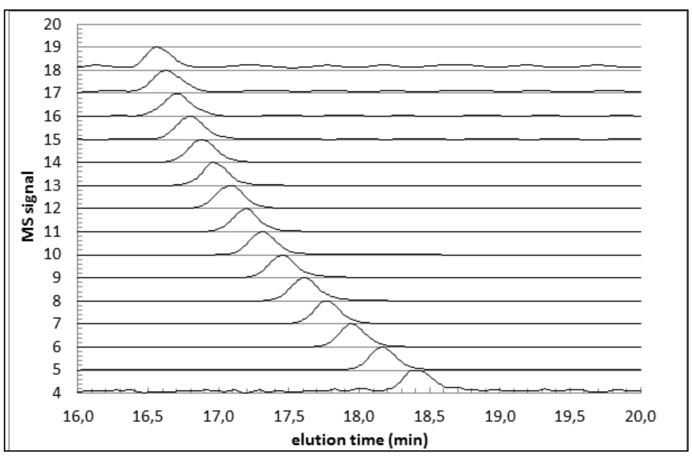


Figure 6. SIM chromatograms for each oligomer in PS 580; each chromatogram was scaled and its baseline shifted to the corresponding number of the degree of polymerization.

Analysis of additive "1010" fractions

Several fractions collected from the HPLC Prep stage were then analyzed by GPC-MS. First the fraction collected around 10.9 min in vial 2 was analyzed by GPC-MS, and the TIC is shown in Figure 7:

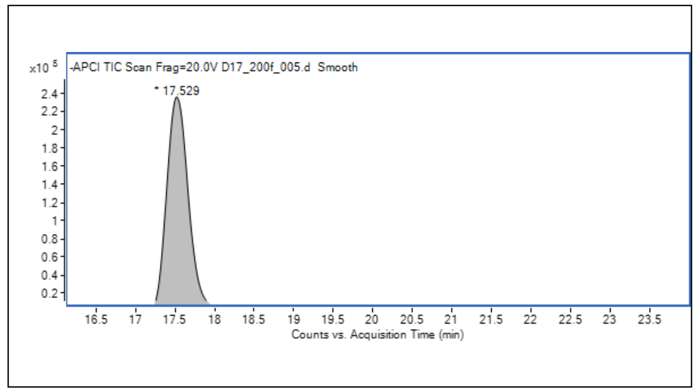


Figure 7. TIC for compounds collected in vial 2 (preparative HPLC peak around 10.9 min).

The mass spectra extracted from the GPC peak revealed the existence of a compound having the m/z of the base ion with chlorine ionization of $[M+Cl]^-$ of 951.6. The other ions with m/z around 916.5 correponds to the same compound negative ionized $[M]^-$:

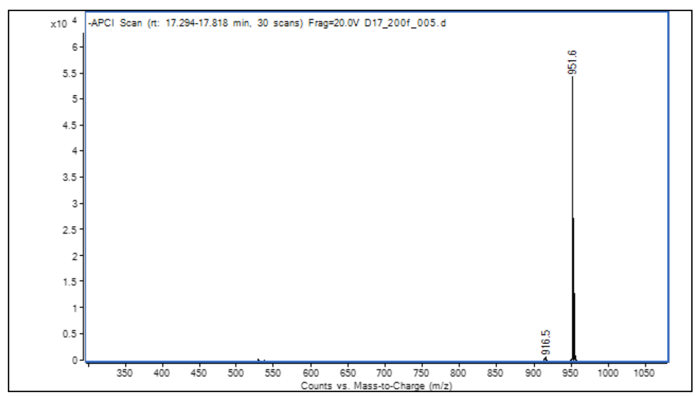
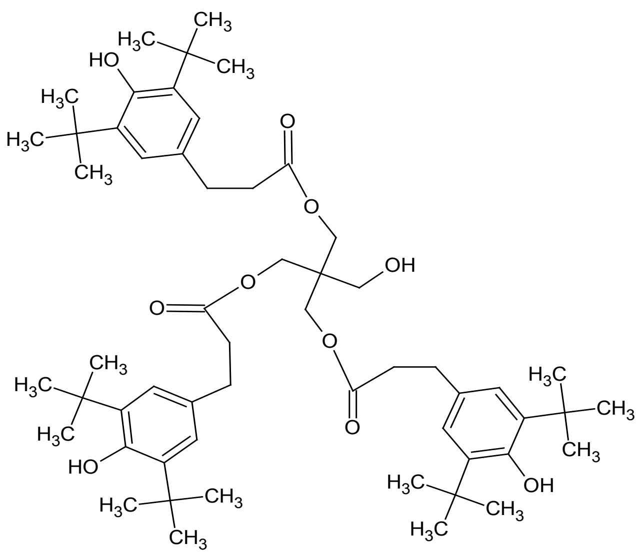


Figure 8. MS corresponding to GPC peak in Figure 7.

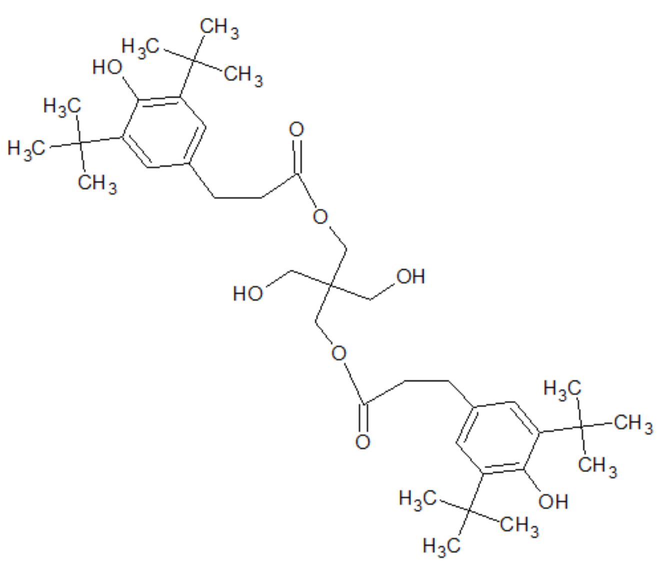
Based on the isotope distribution, the following chemical structure was proposed, in which (3,5-di-tert-butyl-4 hydroxyphenyl) propionate moiety of 1010 additive is missing:

Structure 1010-I, $C_{56}H_{84}O_{10}$ (CAS No. 84633-54-5)



Further investigation revealed the presence also of the fragment in which two (3,5-di-tert-butyl-4 hydroxyphenyl) propionate moieties of additive “1010” are missing:

Structure 1010-II, $C_{39}H_{60}O_8$ (CAS No. 36913-60-7)



The second fraction to be analysed by GPC-MS is from the HPLC peak collected around 12.2 min in vial 3, and the TIC is given in Figure 9:

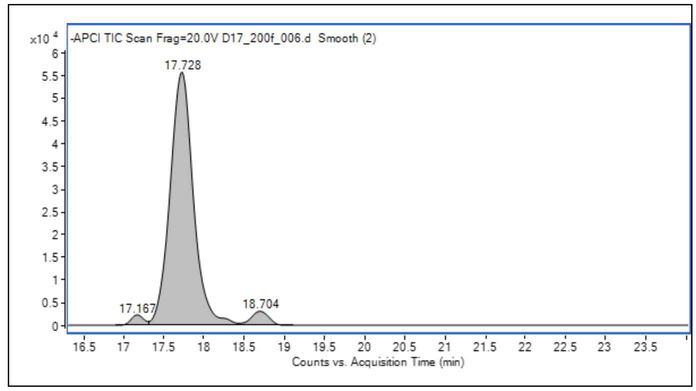


Figure 9. TIC for compounds collected in vial 3 (preparative HPLC peak around 12.2 min).

The mass spectra extracted from the major GPC peak revealed the existence of a compound having the m/z of the base ion with chlorine ionization of $[M+Cl]^-$ of 1155.7. The other ions with m/z around 1120.7 corresponds to the same compound negative ionized $[M]^-$:

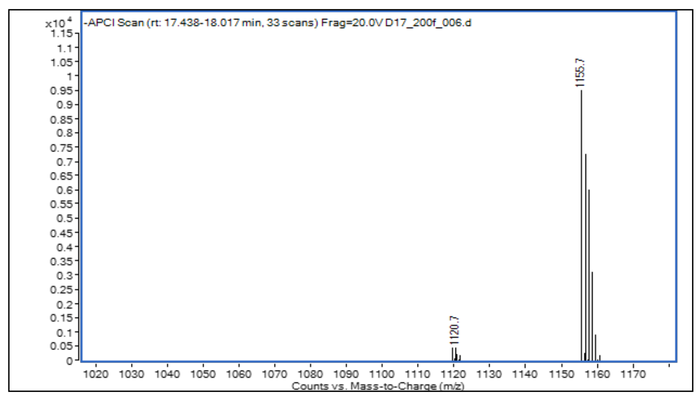
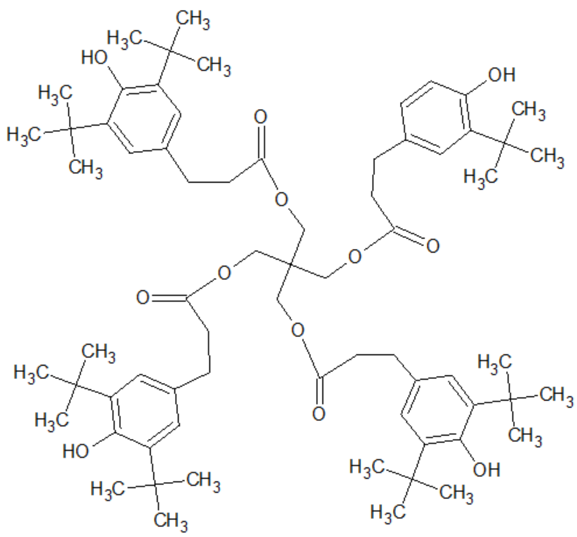


Figure 10. MS corresponding to major GPC peak in Figure 9.

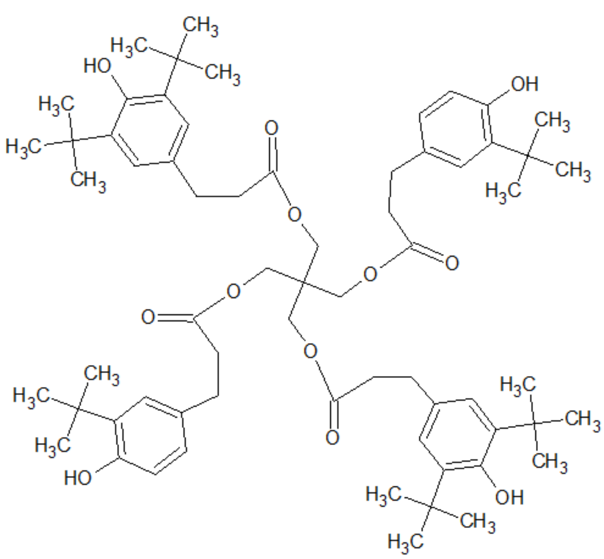
Based on the isotope distribution, the following chemical structure was proposed, in which a tertiary group is absent from the structure of the 1010 additive:

Structure 1010-III, $C_{69}H_{100}O_{12}$:



Further investigation revealed the presence of an additional fragment in which two tertiary groups are absent from the structure of the additive "1010":

Structure 1010-IV, $C_{65}H_{92}O_{12}$:



Finally the mass spectra extracted from the GPC peak at 18.7 min revealed the existence of a compound having the m/z of the base ion with chlorine ionization of $[M+Cl]^-$ of 895.5:

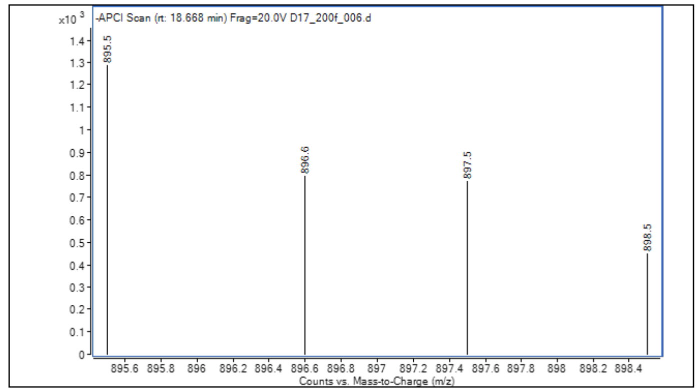
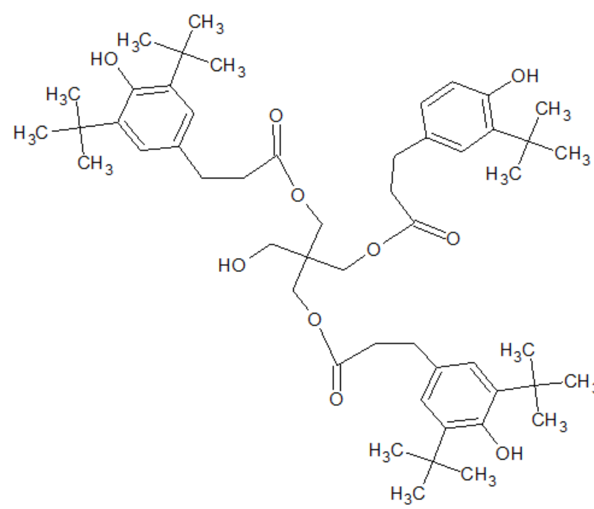


Figure 11. MS corresponding to GPC peak at 18.7 in Figure 9.

This corresponds to the fragment in which an arm and a butyl group are not present as compared with the structure of additive “1010”:

Structure 1010-V, $C_{52}H_{76}O_{10}$:



Conclusion

Preparative HPLC followed by GPC-MS was shown to be a powerful analytical technique for investigation of the chemical structures of fragments leaching from the additive. The concentration of these fragments is very low compared to the parent chemical so preparative fractionation of these components and subsequent concentration by evaporation is needed for further analysis.

Although in the polymer matrix the presence of these fragments can be explained by additive degradation, it is also possible that these fragments are produced by side reactions during the synthesis of the additive [6].

This additive itself has a molecular weight higher than 1000 g/mol, so following the criteria of Scientific Committee for Food (SCF) there is little absorption in the gastrointestinal tract, and in principle, no toxicological data are required for the substance itself. However, the fragments investigated have molecular weights lower than 1000, so they could be of interest for safety evaluation [7].

In this respect, the method could be beneficial to isolate enough quantities of these compounds for further toxicological studies.

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Printed in Europe, April 19, 2018
5991-9326EN