Analysis of Phenolic Antioxidant and Erucamide Slip Additives in Polymer by Rapid-Resolution LC

Application

Hydrocarbon Processing

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Abstract

Liquid chromatography with ultraviolet/visible (UV/VIS) detection is a powerful approach for analyzing additives in polymer formulations. This application illustrates the use of the Agilent 1200 Series Rapid Resolution LC (RRLC) system for the separation of antioxidants and erucamide. The system can operate significantly faster than conventional HPLC without sacrificing resolution, precision, or sensitivity. The column chemistry and temperature influence on the separation and the sample preparation method are also discussed.

Introduction

Additives are incorporated into various polymeric materials to retard the degradation caused by ultraviolet light, heat, and oxygen or to modify processing characteristics. A rapid and accurate analytical method is required to ensure that the specified amount of an additive or combination of additives is incorporated into a polymer after the extrusion process. Conventional HPLC methods for additives [1,2] often require more then 30 minutes per analysis, while the application described here can achieve comparable results in as few as 3 minutes.

Agilent has developed an easy-to-use method conversion tool for transferring existing methods for higher speed and/or higher resolution. The tool was used for the method optimization in this application. [3]

This application examines additives mentioned in ASTM Methods D5815 and D1996. The chemical structures are shown in Table 1.

Table 1. Polymer Additives in ASTM Methods D5815 and D1996

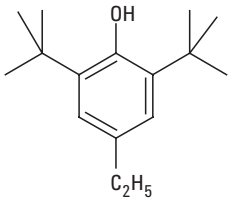
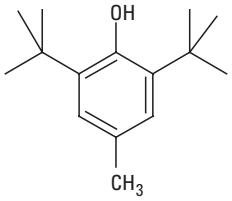
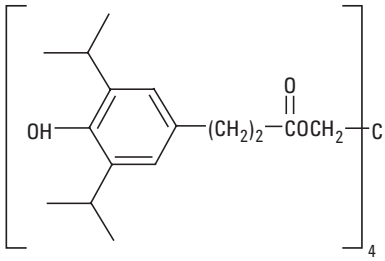
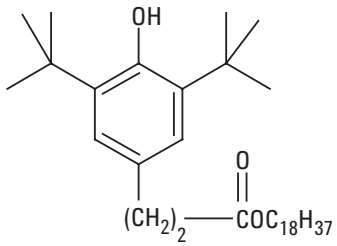
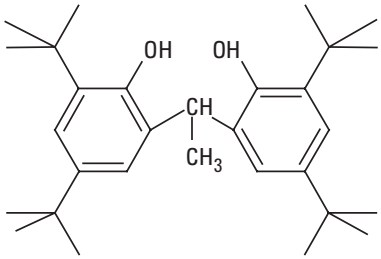
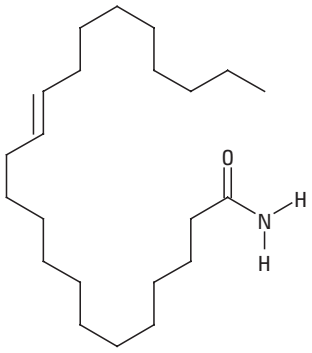
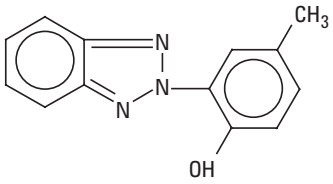
Registered trade name	CAS no.	Chemical name	Chemical structure
BHEB	4310-42-1	2,6-di-tert-butyl-4-ethyl-phenol or butylated hydroxyethyl benzene	
BHT	128-37-0	2,6-di-t-butyl-cresol or butylated hydroxy toluene	
Irganox 1010	6683-19-8	Tetrakis[methylene(3,5-di-t-butyl-4-hydroxy hydrocinnamate)] methane	
Irganox 1076	2082-79-3	Octadecyl-3,5-di-t-butyl-4-hydroxy hydrocinnamate	
Isonox 129	35958-30-6	2,2-ethylidene bis (4,6-di-t-butyl phenol)	

Table 1. Polymer Additives in ASTM Methods D5815 and D1996 (Continued)

Registered trade name	CAS no.	Chemical name	Chemical structure
Kemamide-E	112-84-5	Cis-13-docosenamide or Erucamide or Fatty acid amide ($C_{22}H_{43}NO$)	
Tinuvin P	2440-22-4	2(2'-hydroxy-5'-methyl phenyl) benzotriazole	

Experimental

System

Agilent 1200 Series rapid-resolution LC configured with
G1379B microvacuum degasser
G1312B binary pump SL
G1367B high-performance autosampler SL
G1316B thermostatted column compartment SL
G1315C UV/VIS diode array detector SL
ChemStation 32-bit version B.02.01

Column

ZORBAX Eclipse XDB-C18, 4.6 mm × 150 mm, 5 µm
ZORBAX Eclipse XDB-C18, 2.1 mm × 50 mm, 1.8 µm
ZORBAX SB-C18, 4.6 mm × 150 mm, 5 µm
ZORBAX SB-C18, 4.6 mm × 50 mm, 1.8 µm

Mobile phase

Gradients:	A: water B: acetonitrile (ACN)
Gradient slope:	See individual chromatograms for flow rate and gradient time
Column temperature:	See individual chromatograms

Samples

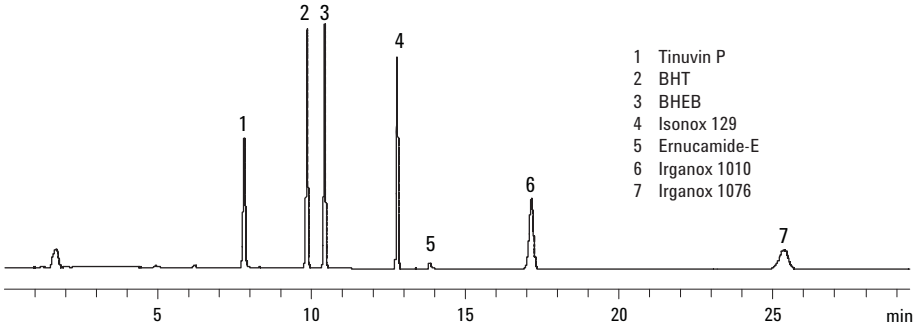
1. Standard mixture described in ASTM D5815 and D1996, 50 µg/mL, 200 µg/mL in isopropanol
2. Linear low-density polyethylene from customer, ground to 20 mesh, extracted by ultrasonic or reflux method

Results and Discussion

Fast Method Conversion

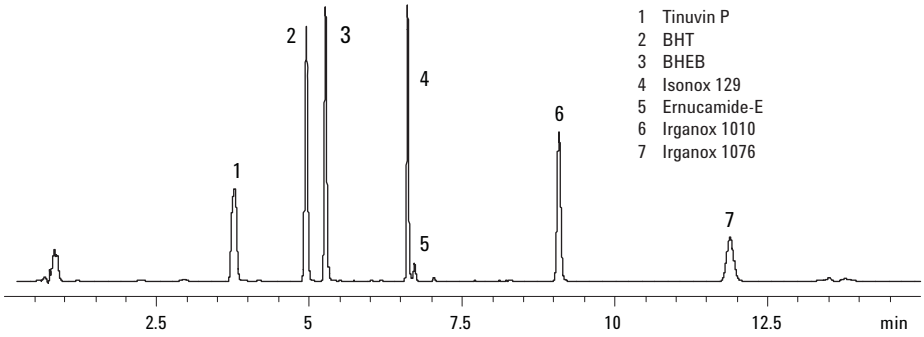
The separation was initially performed on a standard 4.6 mm × 150 mm, 5-µm ZORBAX Eclipse XDB-C18 column thermostatted to 60 °C (Figure 1) following the conditions in ASTM D5815 (or D1996). The method was then scaled in flow and time for exact translation to a 2.1 mm × 50 mm, 1.8-µm column (Figure 2). The analysis time was reduced from 25.5 to 12.5 minutes, and the solvent consumption was reduced from 25 to 2.5 mL.

The separation was then re-optimized for faster separation with the same gradient slope by increasing the flow rate from 0.21 to 0.9 mL/min and proportionately reducing the gradient time (Figure 3), achieving up to 10 times faster than conventional HPLC without sacrificing resolution, precision (showed in Table 2), or sensitivity. Figure 4 demonstrates that 1 ppm of additives can be determined with very good signal-to-noise response using the same condition in Figure 3, which exceeds the specification of 2 ppm of ASTM D5815 (or D1996). Peak 6, Irganox 1010, for example has a signal-to-noise response of 88 at 1 ppm.



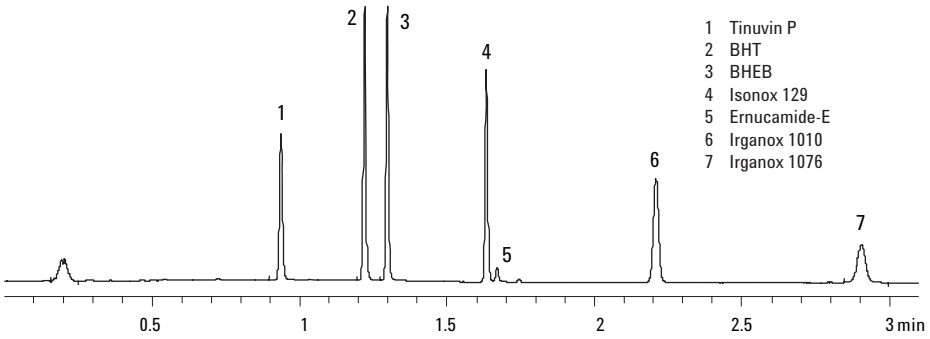
		Gradient	
Conventional method:	Follow ASTM D5815 (or D1996) method with		
	ZORBAX Eclipse XDB-C18,		%B
	4.6 mm × 150 mm, 5 µm	0	50
Sample:	Standard 50 µg/mL	11	100
Sample size:	10 µL	28	100
Detector:	UV 200 nm	28.1	50
Column temperature:	60 °C		
Mobile phase:	A: water		
	B: acetonitrile		
Flow rate:	1 mL/min		

Figure 1. Separation of additives standards on Eclipse XDB-C18, 4.6 mm × 150 mm, 5 µm.



		Gradient	
Simple-converted:	Translate the conventional method to a		
	ZORBAX Eclipse XDB-C18, 2.1 mm × 50 mm, 1.8 µm		%B
Sample:	Standard 50 µg/mL	0	50
Sample size:	2 µL	5.2	100
Detector:	UV 200 nm	12	100
Column temperature:	60 °C	12.1	50
Mobile phase:	A: water	15	50
	B: acetonitrile		
Flow rate:	0.21 mL/min (73 bar)		

Figure 2. Separation of additives standards on Eclipse XDB-C18, 2.1 mm × 50 mm, 1.8 µm.

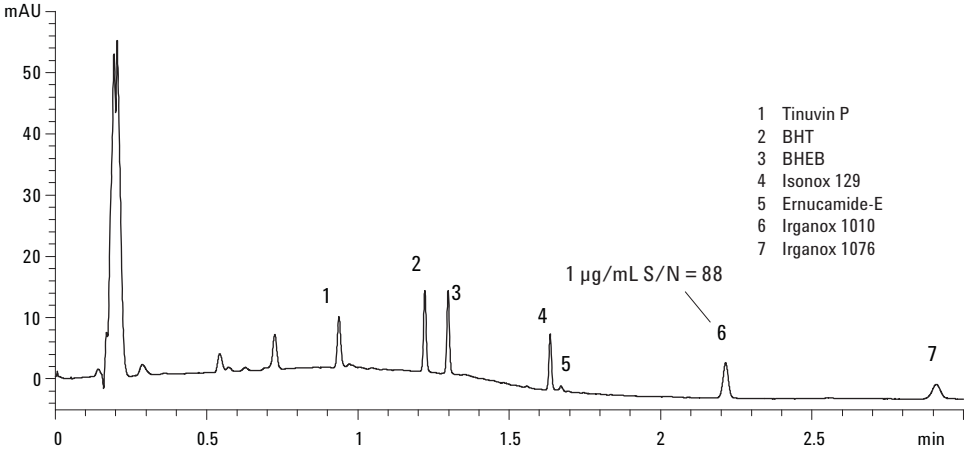


		Gradient	
Speed-optimized:	Optimize the conventional method for speed with ZORBAX Eclipse XDB-C18, 2.1 mm × 50 mm, 1.8 µm		%B
		0	50
Sample:	Standard 50 µg/mL	1.3	100
Sample size:	2 µL	3	100
Detector:	UV 200 nm	3.1	50
Column temperature:	60 °C	3.5	50
Mobile phase:	A: water B: acetonitrile		
Flow rate:	0.9 mL/min (357 bar)		

Figure 3. Fast separation of additives standards on Eclipse XDB-C18, 2.1 mm × 50 mm, 1.8 µm.

Table 2. Repeatability for the Methods of Conventional, Simple-Converted, and Speed-Optimized Methods (n = 5)

	Area, RSD%		
Compounds (50 ppm)	**Conventional**	**Simple-converted**	**Speed-optimized**
Tinuvin P	0.37	0.39	0.09
Erucamide	0.40	0.57	0.13
Irganox 3114	0.44	0.49	0.22
Irganox 1010	0.38	0.39	0.26
Vitamin E	0.58	0.80	0.68
Irganox 1076	0.58	1.49	0.17
Irgafos 168	0.53	0.77	0.32



Speed-optimized method for analysis of additives standards with concentration of 1 µg/mL LC conditions is identical to that in Figure 3

Figure 4. Fast separation of 1 µg/mL additives standards on Eclipse XDB-C18, 2.1 mm × 50 mm, 1.8 µm.

Optimized Column Temperature

Increasing column temperature can lower both solvent viscosity and nonspecific column/analyte interactions. The new ZORBAX StableBond RRHT columns can operate at temperatures up to 90 °C. We tested operating temperatures at 60, 75, 85, and 90 °C with a ZORBAX SB-C8 4.6 mm × 150 mm, 5-µm column. The results (Figure 5) show that the analysis time obtained from 60 °C to 85 °C is reduced from 23.5 minutes to 17 minutes; at 90 °C, only an additional 0.5 minute is saved. Based on the combined speed reduction and optimized resolution of peaks 4 and 5, 85 °C is chosen as a suitable column temperature.

The method was then scaled in flow and time for exact translation to a 4.6 mm × 50 mm, 1.8-µm column (Figure 6). Finally, the separation was optimized for faster separation by increasing the flow rate from 1 mL/min to 3.5 mL/min, with only a 1.7-minute analysis time (Figure 7). This is really an excellent procedure for high-throughput screening and quantitation of a large number of samples. Figure 8, the separation of an extract of linear low-density polyethylene (LLDPE) spiked with 20 µg/mL of standard solution, shows excellent separation with real sample matrix.

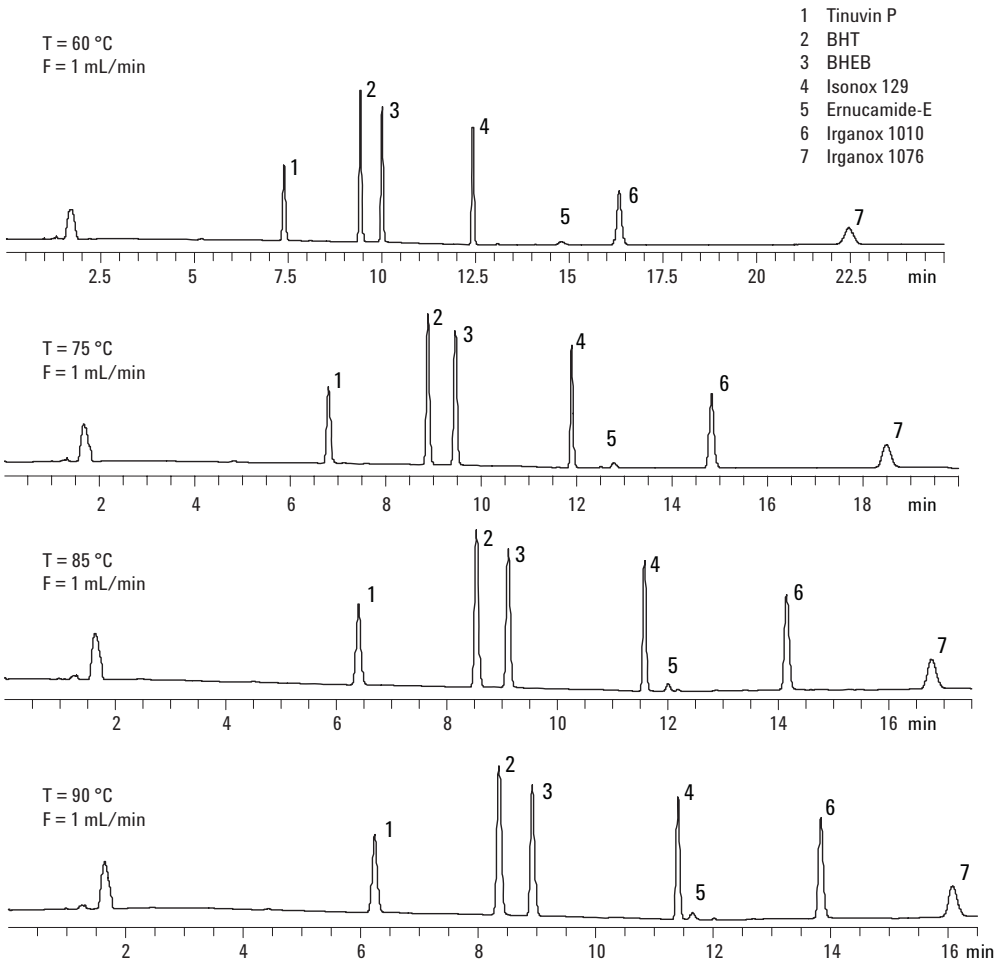
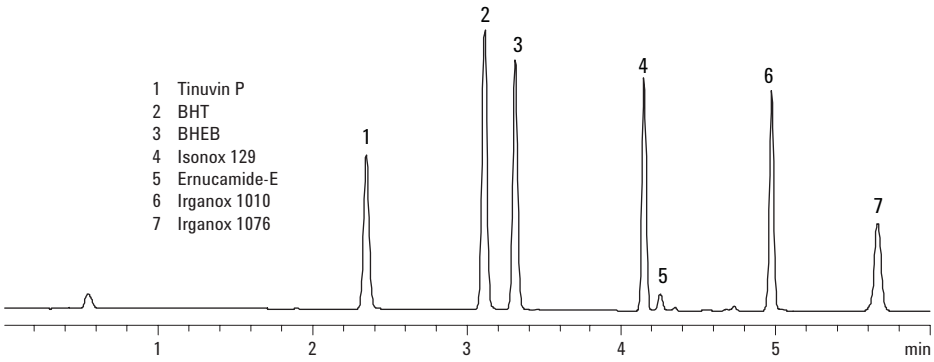
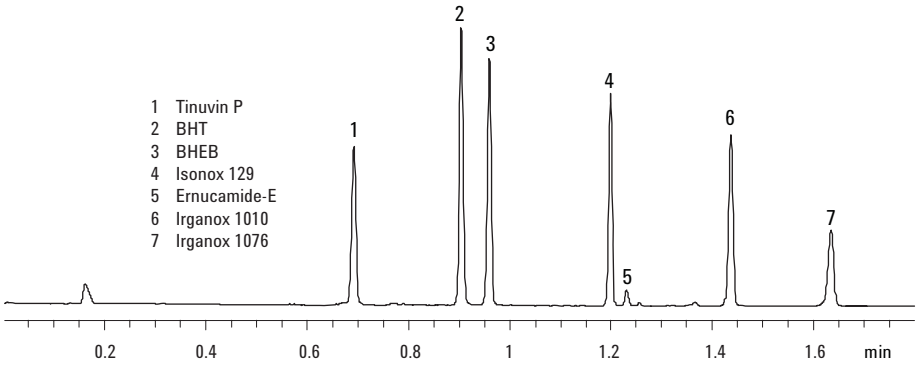


Figure 5. Separation of additives standards on ZORBAX StableBond RRHT SB-C18, 4.6 mm × 150 mm, 1.8 µm.



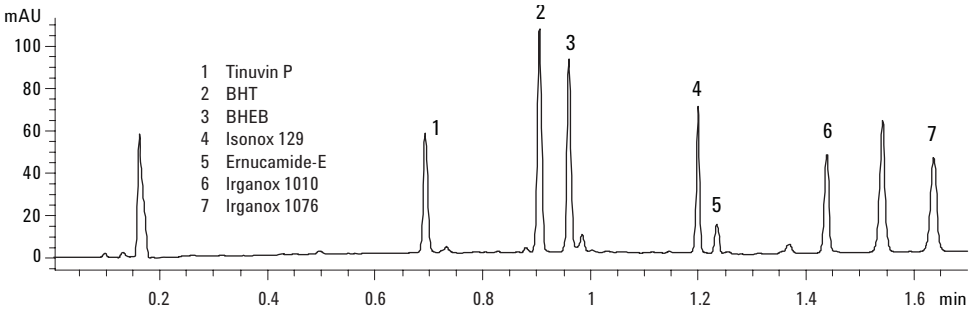
Sample:	Standard 200 mg/mL
Sample size:	2 µL
Detector:	UV 200 nm
Mobile phase:	A: water
	B: acetonitrile
Gradient slope:	6.8%
Flow rate:	1mL/min

Figure 6. Separation of additives standards on ZORBAX SB-C18, 4.6 mm × 50 mm, 1.8 µm, at 85 °C.



Sample:	Standard_200 mg/mL
Sample size:	2 µL
Detector:	UV 200 nm
Mobile phase:	A: water
	B: acetonitrile
Gradient slope:	6.8%
Flow rate:	3.5 mL/min

Figure 7. Fast separation of additives standards on ZORBAX SB-C18, 4.6 mm × 50 mm, 1.8 µm, at 85 °C.



LC conditions are identical with those in Figure 7.

Figure 8. Fast separation of spiked real sample-LLDPE (20 µg/mL) on ZORBAX SB-C18, 4.6 mm × 50 mm, 1.8 µm, at 85 °C.

Sample Preparation

ASTM D5815 (or D1996) method recommends using a reflux apparatus for extracting additives in polymer. This requires periodic operator intervention over the 1.5-hour-long extraction period. To find a time-saving sample-preparation method, ultrasonic extraction was also tested, producing comparable results in 30 minutes. In terms of extraction efficiency, there is not much difference between these two methods. Figure 9 shows very good overlays of extractions by reflux and ultrasonic extraction methods for a LLDPE. Conditions are identical to those in Figure 1.

Conclusions

Liquid chromatography with ultraviolet/visible detection is an effective tool for analyzing additives in polymer formulations. The Agilent 1200 Series RRLC system equipped with RRHT 1.8-µm columns was used to achieve up to 10 times faster than the conventional HPLC method. The ultrasonic extraction method allowed fast extraction without user intervention for a significant reduction in overall analysis time. Total time saved was more than 80 minutes per sample when compared to the conventional analysis and extraction methods.

References

1. ASTM D5815-95, “Standard Test Method for Determination of Phenolic Antioxidants and Erucamide Slip Additives in Linear Low-Density Polyethylene Using Liquid Chromatography (LC).”
2. ASTM D1996-97, “Standard Test Method for Determination of Phenolic Antioxidants and Erucamide Slip Additives in Low-Density Polyethylene Using Liquid Chromatography (LC).”
3. Agilent Application Compendium CD, 5989-5130EN, June 2006.
4. Michael Woodman, “Improving the Effectiveness of Method Translation for Fast and High Resolution Separations,” Agilent Technologies, publication 5989-5177EN.

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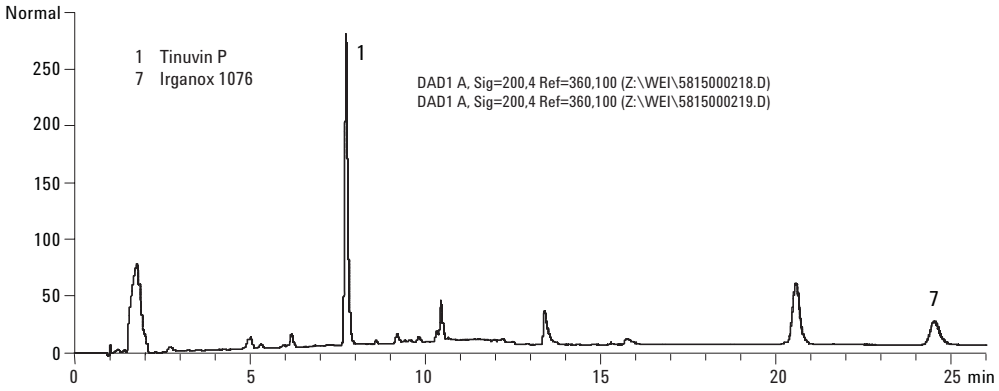

Figure 9. Chromatogram Overlays of extractions by reflux and ultrasonic extraction methods for LLDPE.

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