Fast Analysis of Phenolic Antioxidants and Erucamide Slip Additives in Polypropylene Homopolymer Formulations Using 1200 Rapid Resolution Liquid Chromatography (RRLC) with Rapid Resolution High Throughput (RRHT) Columns and Method Translator

Application

Hydrocarbon Processing

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Abstract

Vitamin E (tocopherol), phenolic antioxidants and erucamide slip additives in polypropylene homopolymer formulations were resolved and detected using liquid chromatography with ultraviolet/visible detection, under guidelines suggested by ASTM Method D6042. Using the Agilent 1200 Rapid Resolution LC system with Agilent ZORBAX RRHT columns, the antioxidants could be rapidly separated with the same or improved resolution. The Agilent method translator was used to transfer the ASTM method into new methods based on the instrument parameters, column dimensions, and particle size in three modes: simple conversion and speed optimized and resolution optimized methods.

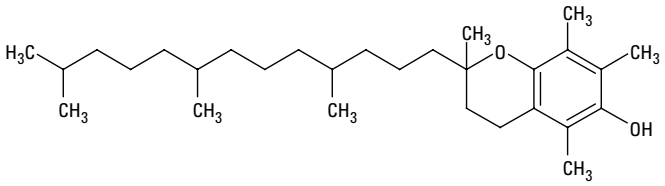
Introduction

Polymers are very popular all over the world owing to their unprecedented physical properties. Various additives are blended into polymeric materials to modify certain properties of the polymer formulation. Erucamide, Irganox 3114, Irganox 1010, Vitamin E (tocopherol), Irganox 1076, and Irgafos168 are often used as antioxidants to prevent the degradation of polypropylene homopolymer formulations by light, heat, and oxygen. In this work, with the goal to shorten the analysis time and reduce solvent consumption without losing separation quality, the existing ASTM method was recalculated for new operating conditions based on columns packed with smaller particle sizes. The chemical information of the antioxidants and Tinuvin P as internal standard is displayed in detail in Table 1.

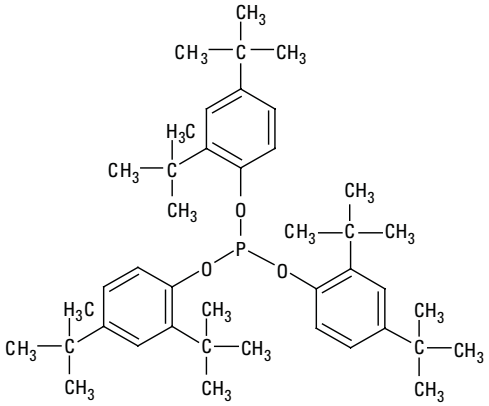
Specific additives and their concentrations in polymer formulations are critical to the properties of polymer, and careful analysis is required to ensure that the additives and levels are appropriate for the intended use. This application will compare two different stationary phases according to analyte retention characteristics and peak shape, show the influence of different injection volume of real sample on the peak shape, and then will focus on showing how to use the method translator. The latter is used to transfer the conventional method to new methods using smaller size columns to perform simple conversion and to extend the method to greater speed and higher resolution.

Table 1. Chemical Information of Antioxidants and Tinuvin P

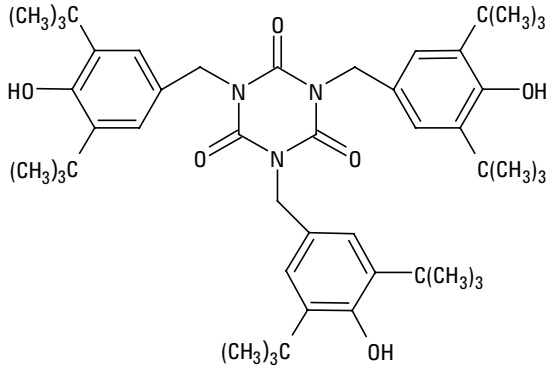
Name:	Vitamin E	DL-all-rac-α-Tocopherol
Formula:	$C_{29}H_{50}O_2$	
Molecular Weight:	430.71	
CAS No.:	10191-41-0	



Name:	Irgafos 168	Tris(2,4 di-tert-butylphenyl) phosphite
Formula:	$[[(CH_3)_3C]_2C_6H_3O]_3P$	
Molecular Weight:	646.92	
CAS No.:	31570-04-4	



Name:	Irganox 3114	Tris(3,5-di-tert-butyl-4-hydroxybenzyl) isocyanurate
Formula:	$C_{48}H_{69}N_3O_6$	
Molecular Weight:	784.08	
CAS No.:	27676-62-6	



Name:	Erucamide	cis-13-docosenamide
Formula:	$CH_3(CH_2)_7CH=CH(CH_2)_{11}CONH_2$	
Molecular Weight:	337.58	
CAS No.:	112-84-5	

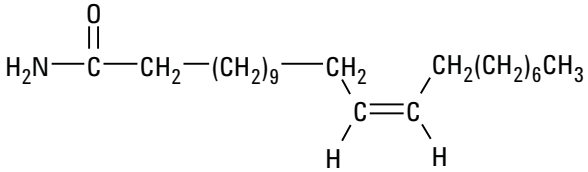
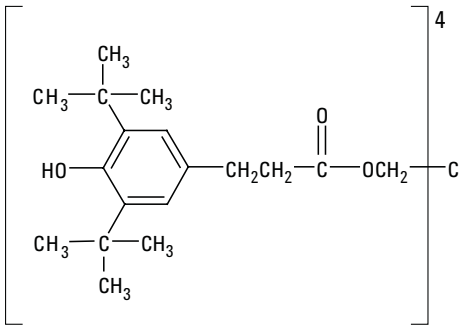
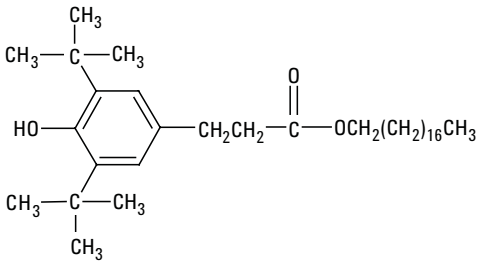
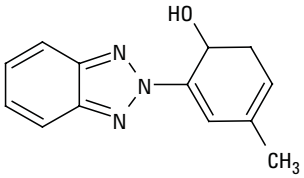


Table 1. Chemical Information of Antioxidants and Tinuvin P (Continued)

Name:	Irganox 1010	Pentaerythritol tetrakis (3,5-di-tert-butyl-4-hydroxyhydrocinnamate)
Formula:	$[HOC_6H_2[C(CH_3)_3]_2CH_2CH_2CO_2CH_2]_4C$	
Molecular Weight:	1177.63	
CAS No.:	6683-19-8	
Name:	Irganox 1076	Octadecyl 3-(3,5-di-tert-butyl-4-hydroxyphenyl) propionate
Formula:	$[(CH_3)_3C]_2C_6H_2(OH)CH_2CH_2CO_2(CH_2)_{17}CH_3$	
Molecular Weight:	530.86	
CAS No.:	2082-79-3	
Name:	Tinuvin P	2-(2-hydroxy-5-methylphenyl)benzotriazole
Formula:	$C_{13}H_{11}N_3O$	
Molecular Weight:	225.25	
CAS No.:	2440-22-4	

Experimental

System

Agilent 1200 Series Rapid Resolution LC (RRLC), consisting of:
G1379B micro vacuum degasser
G1312B binary pump SL
G1367C high-performance autosampler SL
G1316B thermostatted column compartment SL
G1315C UV/VIS diode array detector SL with 3 mm, 2 µL flow cell
ChemStation 32-bit version B.02.01-SR1

Columns

Agilent ZORBAX Eclipse XDB-C18, 4.6 mm × 150 mm, 5 µm
Agilent ZORBAX Eclipse XDB-C8, 4.6 mm × 150 mm, 5 µm
Agilent ZORBAX Eclipse XDB-C8, 4.6 mm × 100 mm, 3.5 µm
Agilent ZORBAX Eclipse XDB-C8, 4.6 mm × 50 mm, 1.8 µm
Agilent ZORBAX Eclipse XDB-C8, 3.0 mm × 100 mm, 3.5 µm
Agilent ZORBAX Eclipse XDB-C8, 3.0 mm × 50 mm, 1.8 µm

Mobile Phase

Gradients:	A: water B: acetonitrile (ACN)
Gradient conditions:	See individual chromatograms
Column temperature	See individual chromatograms

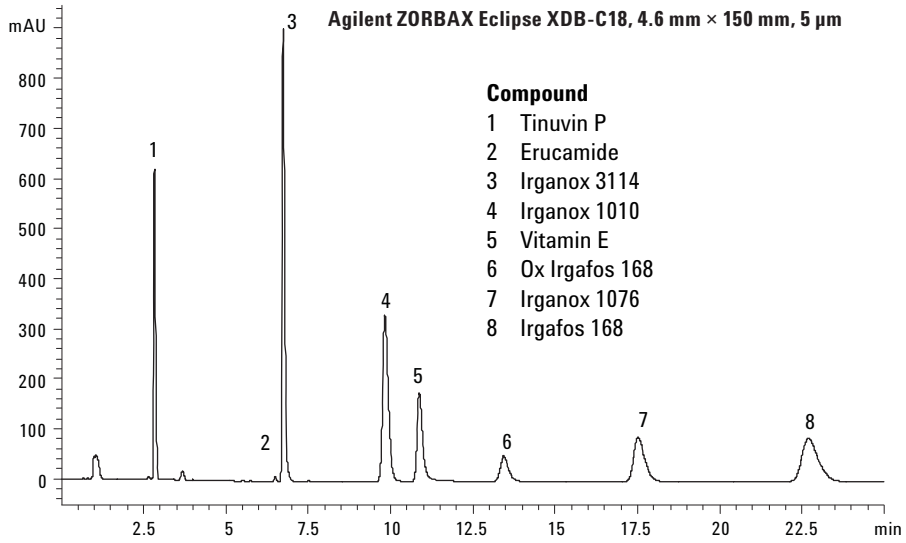
Samples

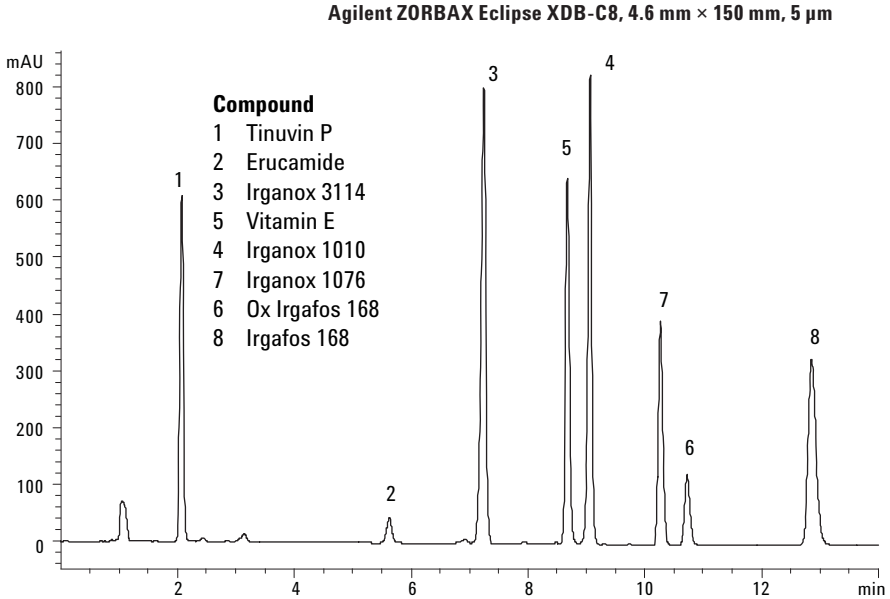
1. Standard mixture of Tinuvin P, Erucamide, Irganox 3114, Irganox 1010, Vitamin E, Irganox 1076, and Irgafos168, all 200 µg/mL in isopropanol
2. Polypropylene Homopolymer Formulation, from customer, extracted by ultrasonic according to the method ASTM D6042-04
3. Polypropylene extract spiked with 20 µg/mL standard mixture

Results and Discussion

Selection of Stationary Phase for the Separation of Antioxidants

It is desirable during method development to select a column that will provide the optimal analyte separation and shortest analysis time. Reversed phase C18 columns are recommended by ASTM D6042-04; however, in our application we determined that the retention characteristics of ZORBAX XDB-C18 columns were too strong for the specified solvents, resulting in broad peak shape and quantitation difficulties for late-eluting peaks. Compared with ZORBAX XDB-C18 columns, ZORBAX XDB-C8 columns showed better retention capability and peak shape. Therefore, we chose the ZORBAX XDB-C8 column for further method development. The different separations with ZORBAX XDB-C18 and ZORBAX XDB-C8 columns are shown in the Figure 1.





Conditions

Mobile phase:	A: water; B: ACN	ZORBAX chemistry:	Eclipse XDB-C18		Eclipse XDB-C8	
Flow rate:	1.5 mL/min	Gradient:	Min	%B	Min	%B
Wavelength:	200 nm		0.00	75	0.00	75
Injection volume:	10 µL		5.00	100	8.00	100
Column temperature:	50 °C		25.00	100	15.00	100
Column size:	4.6 mm × 150 mm, 5 µm		25.10	75	15.10	75
Sample:	Standard mixture, 200 µg/mL in isopropanol		30.00	75	20.00	75

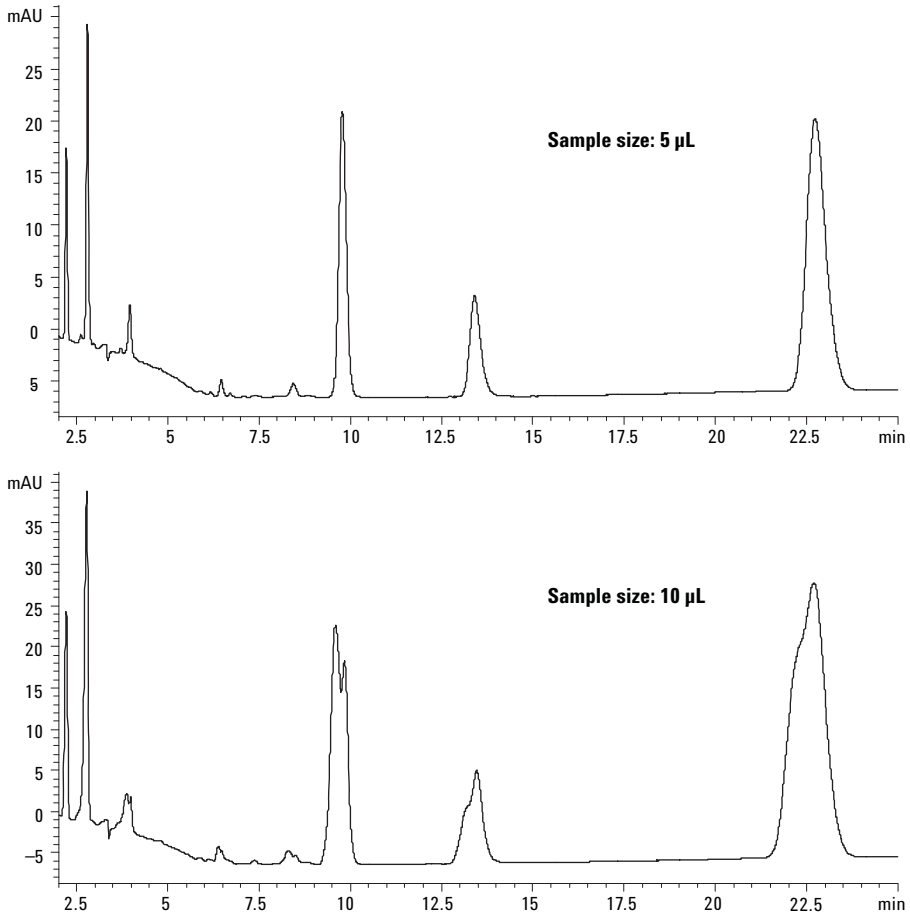
Figure 1. ZORBAX stationary phase comparison for antioxidants.

Injection Volume Influence of Real Sample Extraction Solution on the Peak Shape

According to ASTM D6042-04 [1], a solvent mixture of methylene chloride and cyclohexane (1/1 v/v) is used as the extraction solvent and, after filtration, the extracted solution is directly injected into the LC. Neither methylene chloride nor cyclohexane is miscible in the acetonitrile and water mobile phase. Peak splitting was observed when the injection volume was 10 µL. We decreased the sample size of real sample and found that the volume of 5 µL was suitable and free of solvent influence. The split and nonsplit peaks are shown in Figure 2. At the same time, the influence of injection volume was not found in the standard solution, which was dissolved in isopropanol per ASTM method guidance.

Fast Method Developed Based on New 1200 RRLC with Method Translator

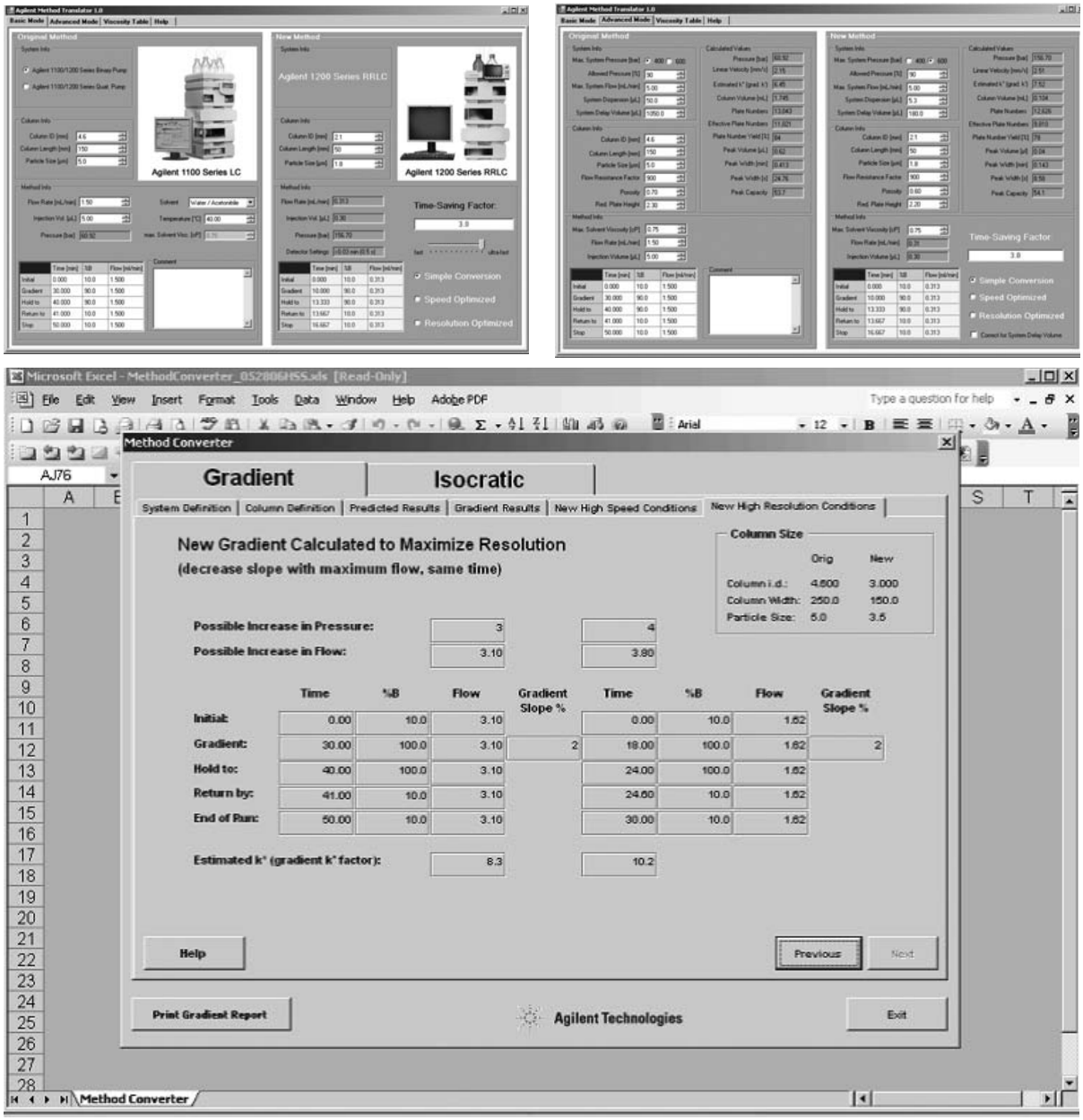
Due to the appearance of sub-two-micron columns and LC systems with higher pressure capabilities, the research of ultra-fast separation is more and more popular. Therefore, it is important to quickly and easily transfer conventional methods to fast or high-resolution methods. Agilent provides the users of RRLC systems with two versions of method translators; one is a Microsoft.net version, which requires that Net-Framework 2.0 be resident on the computer, the other is a Microsoft Excel version, which requires that Excel be resident on the PC. The interface of the two translators is displayed in Figure 3.



Conditions

Mobile phase:	A: water; B: ACN	**Gradient**:	
Flow rate:	1.5 mL/min	Min	%B
Wavelength:	200 nm	0.00	75
Injection volume:	5 or 10 µL	5.00	100
Column temperature:	50 °C	25.00	100
Column:	ZORBAX Eclipse XDB-C18 4.6 mm × 150 mm, 5 µm	25.10	75
Sample:	Polypropylene extraction solution	30.00	75

Figure 2. Injection volume influence of real sample extraction solution on the peak shape.



The upper one is the Microsoft.net version, the lower one is the Microsoft Excel version.

Figure 3. Two different method translators.

Sample Preparation

The two versions of method translators provide three modes of method conversion; the first is the simple conversion, which has the same gradient slope as the conventional method, and changes the flow rate according to equation 1:

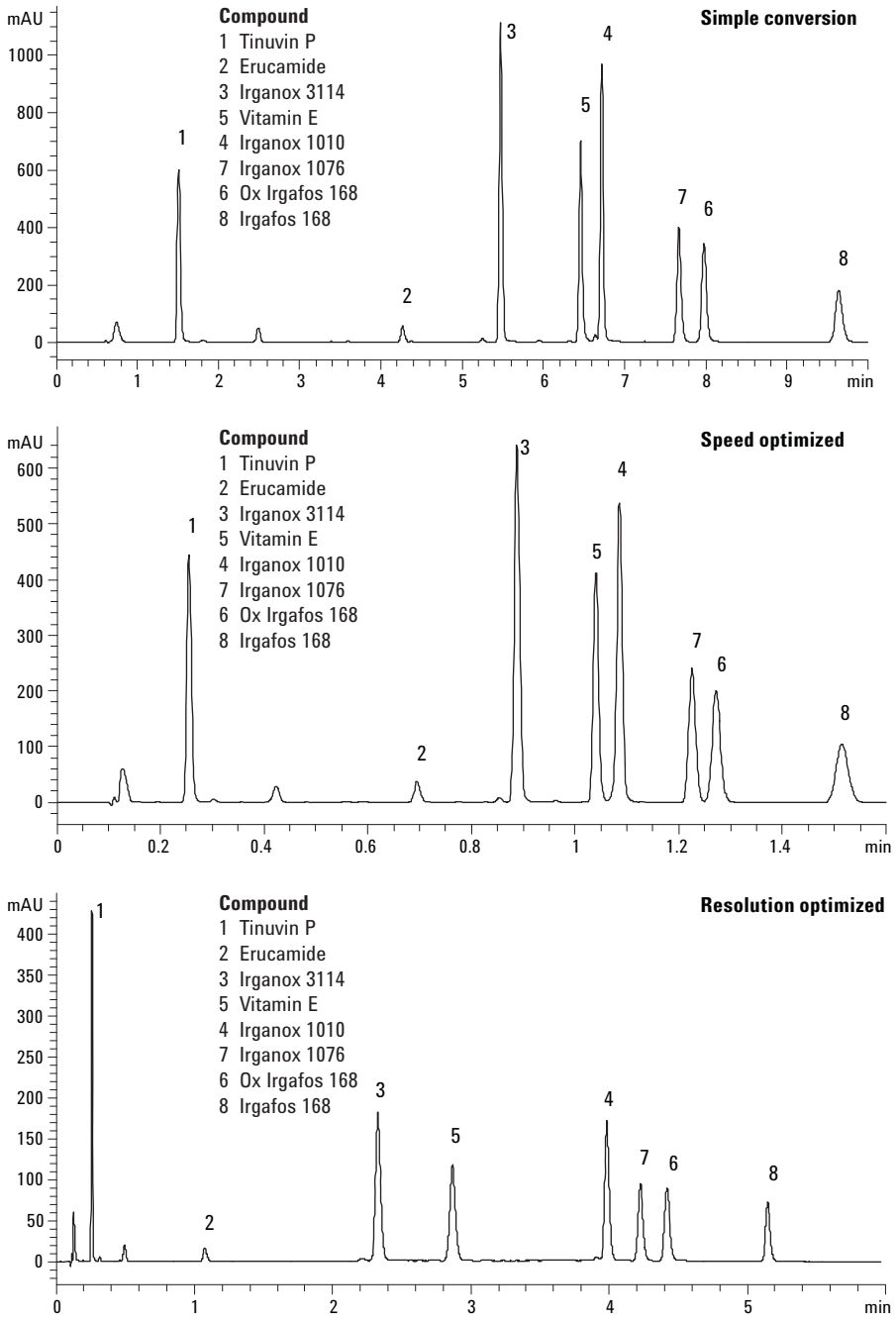
$$Flow_{Col.\,2} = \left[\frac{Diam_{Col.\,2}}{Diam_{Col.\,1}}\right]^2 \times Flow_{Col.\,1} \quad \text{(eq. 1)}$$

The second is the speed optimized conversion, which has the same gradient slope as the conventional method and maximizes the flow rate according the LC system pressure capability. The last is the resolution optimized conversion, which maximizes the flow rate according the LC system pressure capability and has the same gradient time as the simple converted mode, resulting in a reduced gradient slope that normally yields higher peak resolution. For the different columns, the injection volumes should be changed according to the relationship displayed in equation 2.

$$Inj.\ vol._{Col.\,2} = \left[\frac{Volume_{Col.\,2}}{Volume_{Col.\,1}}\right] \times Inj.\ vol._{Col.\,1} \quad \text{(eq. 2)}$$

As mentioned above, the method based on the ZORBAX Eclipse XDB-C8 4.6 mm x 150 mm, 5 µm, was selected as the initial method. Afterwards, the initial method was transferred with the method

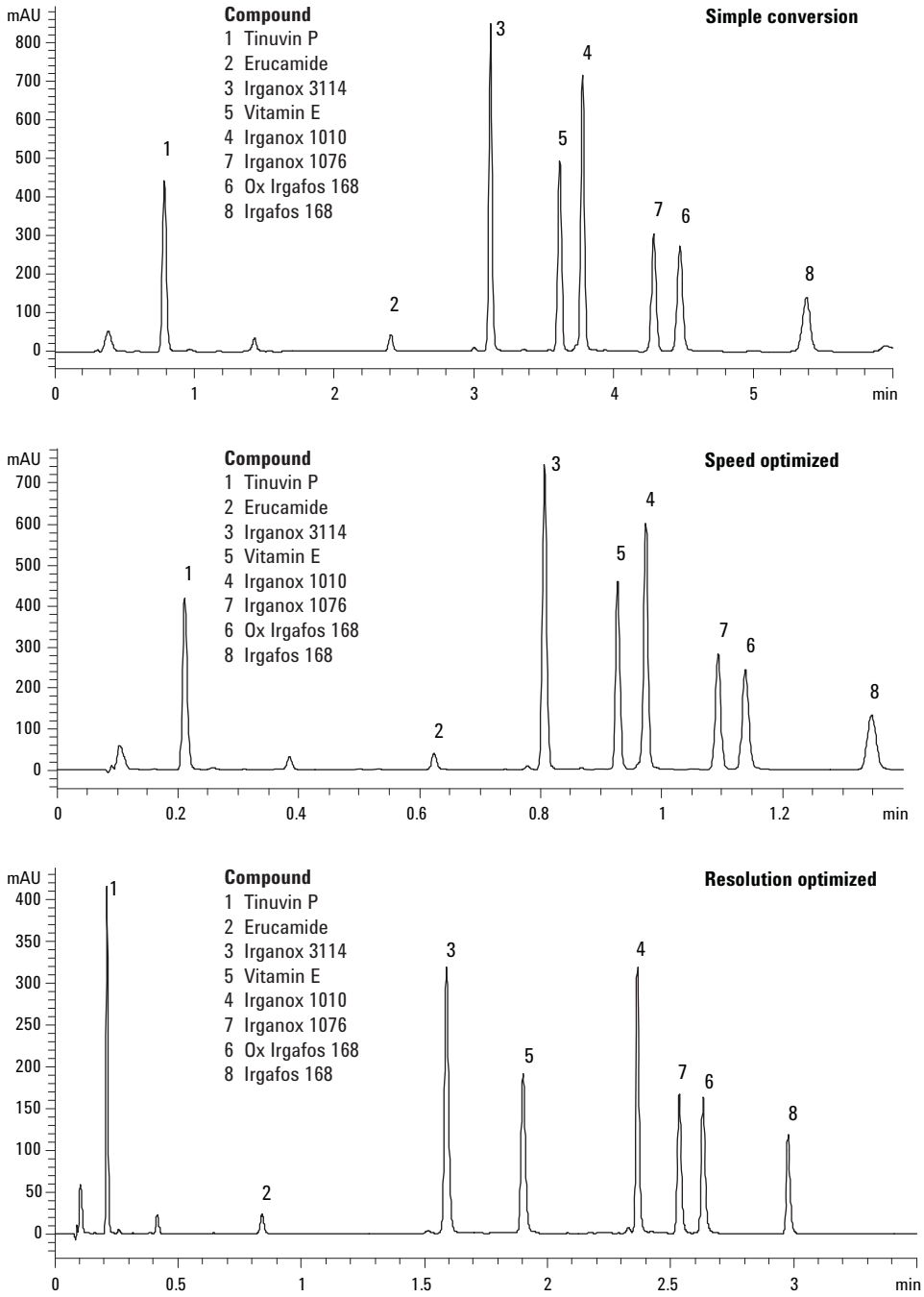
translator into three modes on different column lengths (100, 50 mm) and particle sizes (3.5, 1.8 µm), respectively. Figures 4 and 5 show the separation of antioxidants in smaller particle size columns with the recalculated methods.



Conditions

Sample:	Standard mixture, 200 µg/mL in isopropanol			
Mobile phase:	A: water; B: ACN			
Temperature:	50 °C			
Wavelength:	200 nm			
Injection volume:	6.7 µL			
Column:	ZORBAX Eclipse XDB-C8 3.0 mm × 100 mm, 3.5 µm			
Mode:	Simple converted	Speed optimized	Resolution optimized	
Flow rate:	0.64 mL/min	4.00 mL/min	4.00 mL/min	
	Pressure:	110 bar	460 bar	460 bar
	Gradient slope:	3.1%	3.1%	0.5%
	Analysis time:	10 min	1.6 min	5.5 min

Figure 4. Separation of antioxidants on ZORBAX Eclipse XDB-C8 3.0 mm × 100 mm, 3.5 µm.

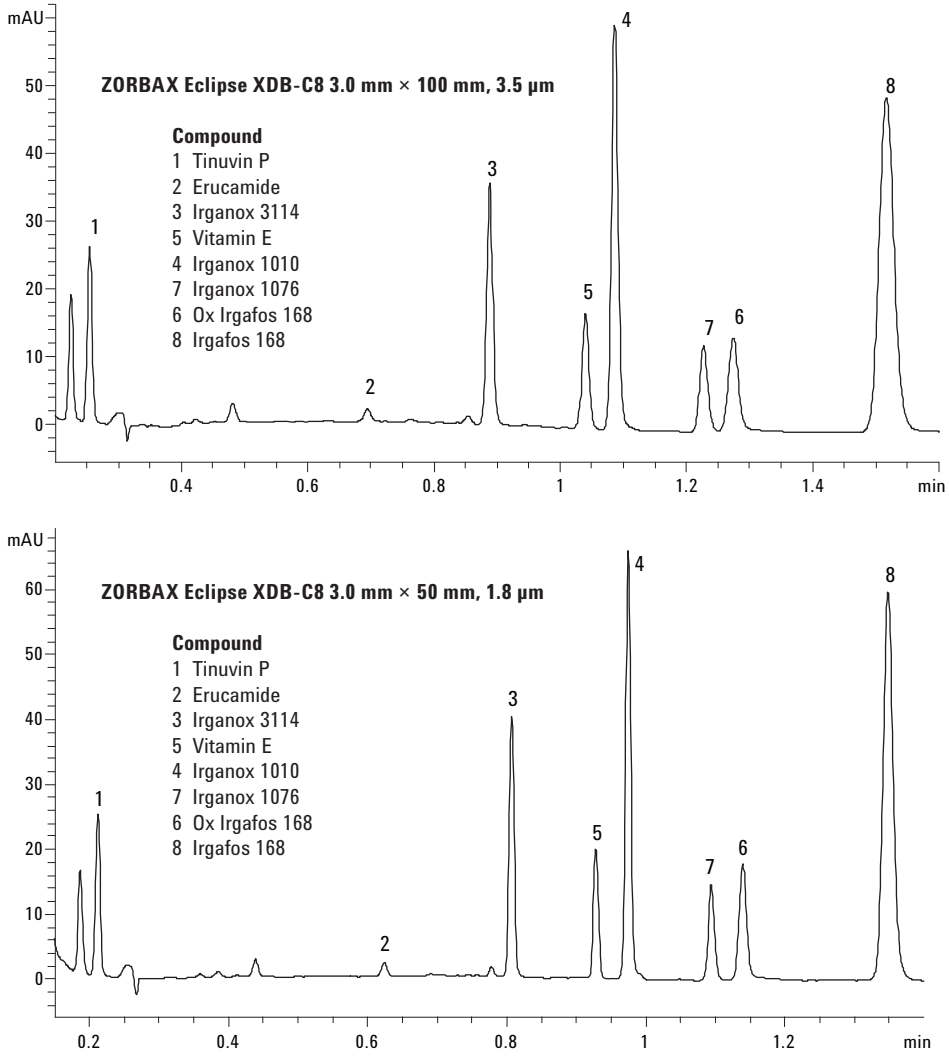


Conditions

Sample:	Standard mixture, 200 µg/mL in isopropanol		
Mobile phase:	A: water; B: ACN		
Temperature:	50 °C		
Wavelength:	200 nm		
Injection volume:	3.3 µL		
Column:	ZORBAX Eclipse XDB-C8 3.0 mm × 50 mm, 1.8 µm		
Mode:	Simple converted	Speed optimized	Resolution optimized
Flow rate:	0.64 mL/min	2.50 mL/min	2.50 mL/min
Pressure:	160 bar	460 bar	460 bar
Gradient slope:	3.1%	3.1%	0.8%
Analysis time:	6 min	1.4 min	3 min

Figure 5. Separation of antioxidants on ZORBAX Eclipse XDB-C8 3.0 mm × 50 mm, 1.8 µm.

To identify the matrix influence on the separation, the polypropylene extract was spiked with 20 µg/mL standard mixture and injected into the LC system. Figure 6 depicts the separation of spiked sample with the speed optimized method, which shows a sufficient separation of antioxidant in polymer matrix with about 10 times faster speed than the conventional method mentioned above.



Conditions

Sample:	Polypropylene extract spiked with 20 µg/mL standard mixture	
Mobile phase:	A: water; B: ACN	
Temperature:	50 °C	
Wavelength:	200 nm	
Stationary phase:	ZORBAX Eclipse XDB-C8	
Column size:	3.0 mm × 100 mm, 3.5 µm	3.0 mm × 50 mm, 1.8 µm
Injection volume:	3 µL	1 µL
Mode:	Speed optimized	Speed optimized
Flow rate:	4.00 mL/min	2.50 mL/min
Pressure:	460 bar	460 bar
Gradient slope:	3.1%	3.1%
Analysis time:	1.6 min	1.4 min

Figure 6. Separation of spiked polypropylene extract by the speed optimized method.

Conclusions

As an important innovation in the advancement of liquid chromatography, the Agilent 1200 Rapid Resolution LC system provides the customer not only a rapid separation with the same or similar resolution, but also includes a method translator to convert any initial conventional method to a fast or high-resolution method according to the requirements of the user. This note applies the method translation tool in the separation of polymer additives and demonstrates the ease-of-use and power of the method translator using separations of a standard mixture and spiked real sample.

References

1. ASTM D6042-04, “Standard Test Method for Determination of Phenolic Antioxidants and Erucamide Slip Additives in Polypropylene Homopolymer Formulations Using Liquid Chromatography (LC)”
2. Michael Woodman, “Improving the Effectiveness of Method Translation for Fast and High Resolution Separations”
3. Michael Woodman, “Screening and Qualitative Identification of Antioxidant Polymer Additives by HPLC with UV/VIS and APCI-MS Detection”

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