Fast Analysis Method for Rubber Chemical Antidegradants Using 1200 Rapid Resolution Liquid Chromatography (RRLC) Systems with Rapid Resolution High Throughput (RRHT) Columns

Application

Hydrocarbon Processing

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Abstract

***p*-Phenylenediamine (PPD), a chemical antidegradant for rubber, and its analogs were found to be optimally determined using liquid chromatography with ultraviolet/visible detection according to the guidelines of ASTM Method D5666. Using the Agilent 1200 RRLC system with ZORBAX 1.8-µm columns, the PPDs could be separated in one run with a total analysis time up to 6.4 times faster than the conventional method based on a 5-µm column.**

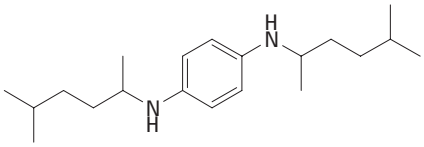
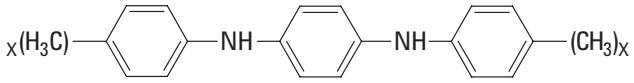
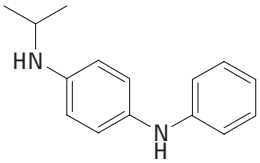
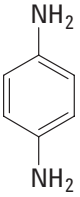
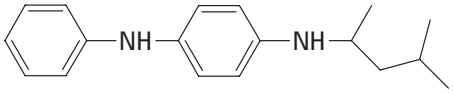
Introduction

Various additives are artificially incorporated into polymeric materials to modify certain properties of the polymer. Therefore, the additives and their concentration in the formulation are crucial to the properties of the end product. 77PD, DTPD, IPPD, PPD, and 6PPD (see Table 1) are often used as chemical antidegradants for rubber materials. The chemical information for five PPDs is displayed in detail in Table 1.

Liquid chromatography with ultraviolet\visible detection is a powerful approach to the qualitative and quantitative analysis of chemical antidegradants in rubber. The isocratic LC method for five PPDs is introduced by ASTM D5666. In this method, the five PPDs are divided into three groups and determined by three different methods (Table 1, ASTM Method D5666-95, 2004).

Agilent 1200 RRLC systems use conventional or sub-two-micron columns, in various lengths up to 300 mm, and can typically provide ultra-fast separations with the same or better resolution as the original method. This application will compare the retention capability and peak shape of the two different stationary phases and will focus on showing the separation of five PPDs in one run, within five minutes, using the 1200 RRLC system with Agilent RRHT reversed phase columns.

Table 1. Chemical Information of Five PPDs

Trade Name	CAS Number	Chemical Structure and Chemical Name
77PD	3081-14-9	N,N'-bis-(1,4-dimethylpentyl)-*p*-phenylenediamine 
DTPD	27417-40-9	N,N'-ditolyl-*p*-phenylenediamine 
IPPD	101-72-4	N-isopropyl-N'-phenyl-*p*-phenylenediamine 
PPD	106-50-3	*p*-phenylenediamine 
6PPD	793-24-8	N-(1,3 dimethylbutyl)-N'-phenyl-*p*-phenylenediamine 

Experimental

System

Agilent 1200 Series Rapid Resolution LC, 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

Mobile Phase Conditions

A: Water with 0.1 g/L ethanolamine
B: Acetonitrile (ACN) with 0.1 g/L ethanolamine

Samples

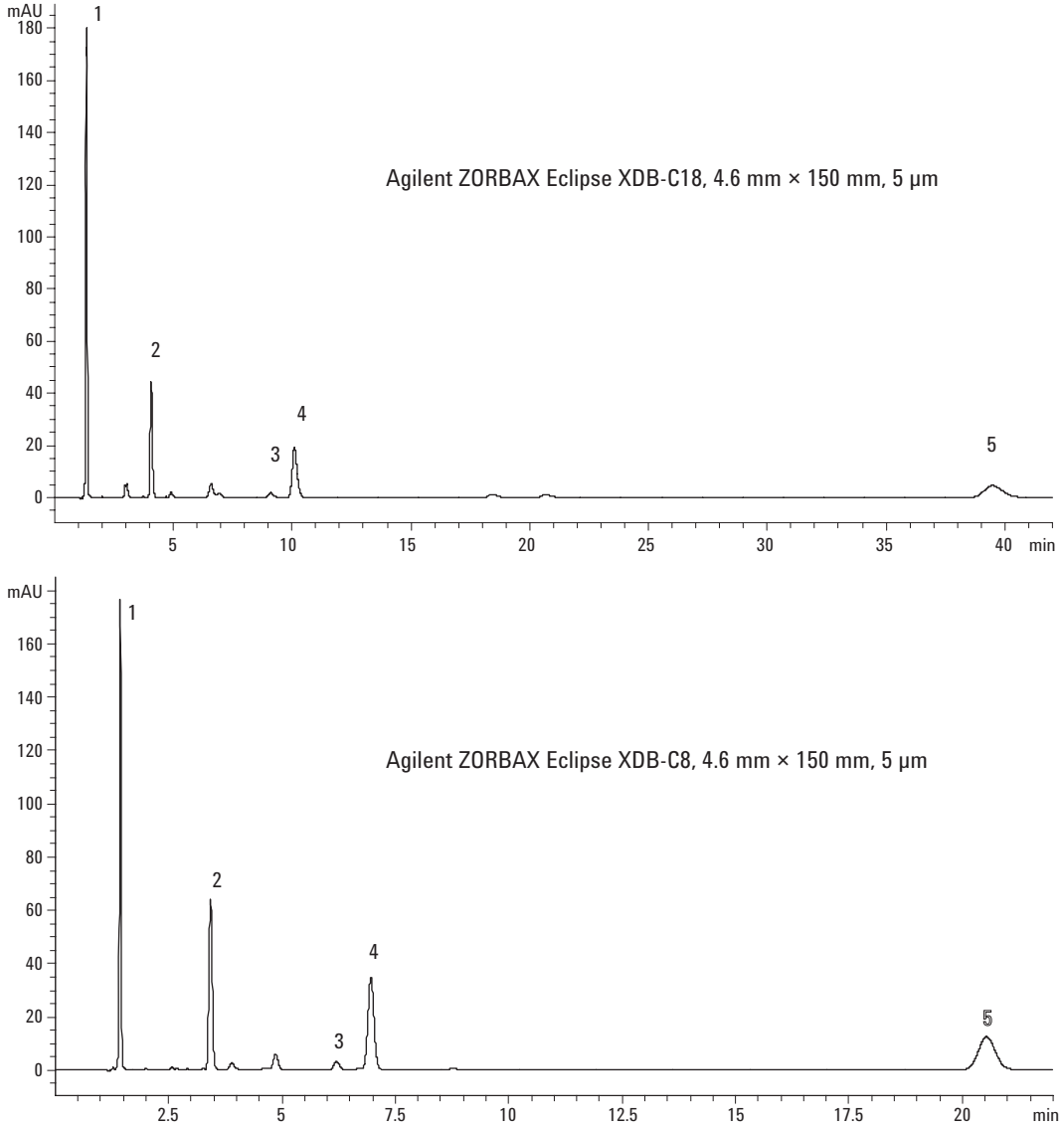
Mixture of 77PD, IPPD, PPD, DTPD, and 6PPD, all 50 µg/mL in acetonitrile. 77PD, IPPD, and PPD were standards from Sigma-Aldrich (St. Louis, Missouri, USA). DTPD and 6PPD were provided by a customer.

Results and Discussion

Selection of Stationary Phase for the Separation of Five PPDs

ASTM D5666-95 recommends a 10- to 15-cm long column packed with C18 grafted silica and 3- to 5-µm particle sizes. In our investigation, however, we observed that the retention characteristics of

ZORBAX Eclipse XDB-C18 were so strong that the total analysis time would be about 40 minutes or more. ZORBAX Eclipse XDB-C8 columns were found to have adequate resolution, and the retention time was only about half of the C18 column. Therefore, we chose the C8 column for further method development. The separations are shown in Figure 1.



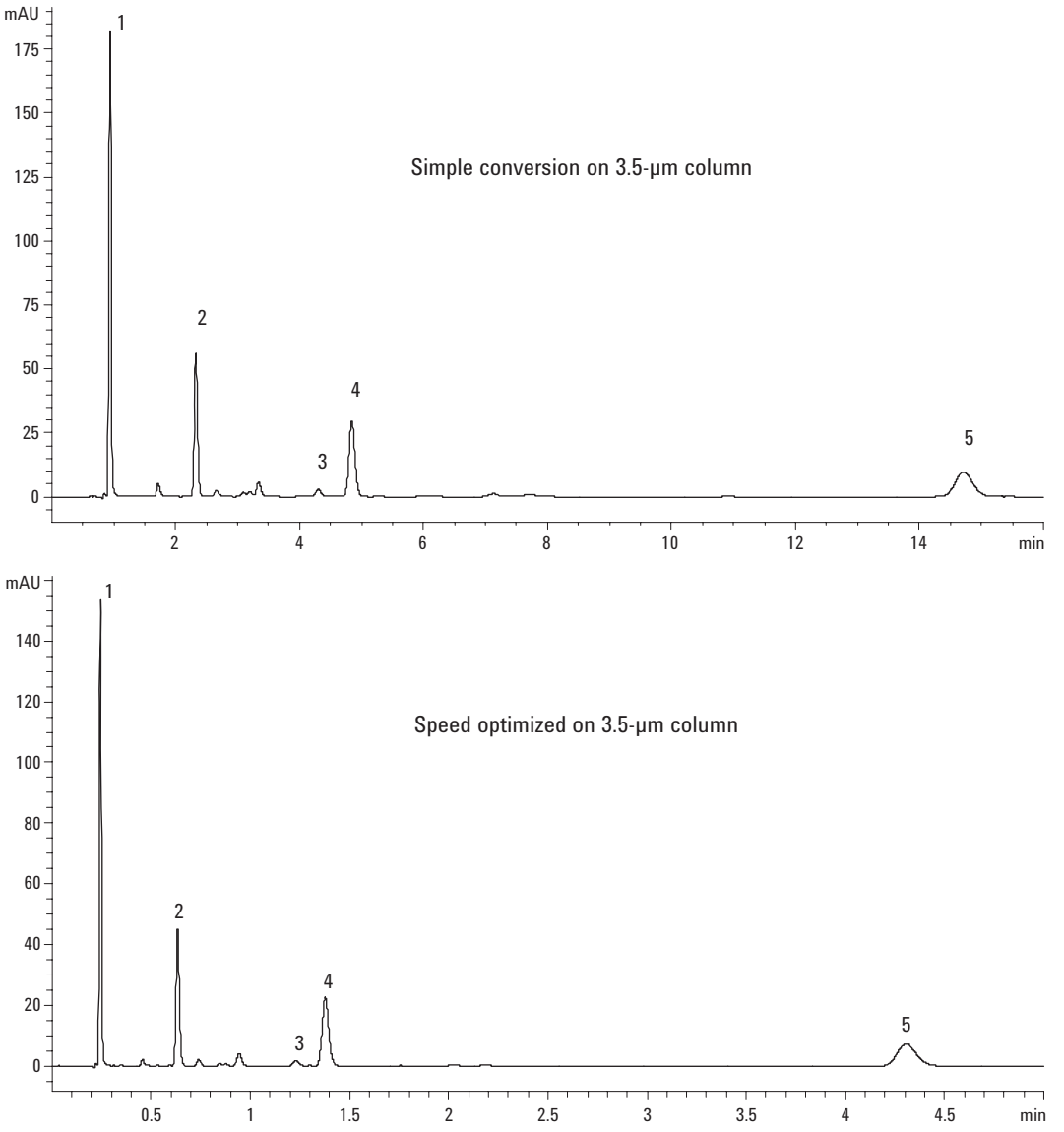
Compound	Conditions		
1 PPD	Mobile phase:	A: water with 0.1 g/L ethanolamine B: ACN with 0.1 g/L ethanolamine	
2 IPPD	Flow rate:	1.0 mL/min	
3 DTPD	Wavelength:	260 nm	
4 6PPD	Injection volume:	10 µL	
5 77PD	Column temperature:	35 °C	
	Sample:	Mixture, 50 µg/mL in ACN	
	Isocratic composition:	30% A, 70% B (v/v)	
	Column size:	4.6 mm × 150 mm, 5 µm	
	Stationary phase:	Agilent ZORBAX Eclipse XDB-C18	Agilent ZORBAX Eclipse XDB-C8
	Analysis time:	42 min	22.5 min

Figure 1. Column stationary phase comparison for five PPDs.

Fast Method Developed Based on New 1200 RRLC

The popular desire of chromatographers is to decrease the analysis time and increase the daily throughput with the same or similar resolution. Nowadays, the Agilent 1200 RRLC system with higher pressure capability and a higher temperature range can provide excellent chromatographic resolution with much shorter run times. Furthermore, a constant concern is how to quickly and easily transfer conventional methods to fast methods. Agilent provides two versions of method translators: one is a Microsoft.net version requiring that Net-Framework 2.0 be resident on the computer, and the other is a Microsoft Excel version requiring that Excel be resident on the PC. When the initial method is an isocratic method, the method translator can provide two modes of faster methods. One is simple conversion, with the scaled flow rate according to the column diameter; the other is speed optimized conversion, with the maximum flow rate and pressure. In gradient mode, an additional option is a resolution optimized conversion.

This application uses a set of Agilent ZORBAX Eclipse XDB-C8 columns, including 4.6 mm × 150 mm (5 µm), 4.6 mm × 100 mm (3.5 µm), and 4.6 mm × 50 mm (1.8 µm). The method translator is used to transfer the initial method on a 5-µm column to two fast methods on 3.5-µm and 1.8-µm columns, respectively. The resulting separation of five PPDs is depicted in Figure 2.



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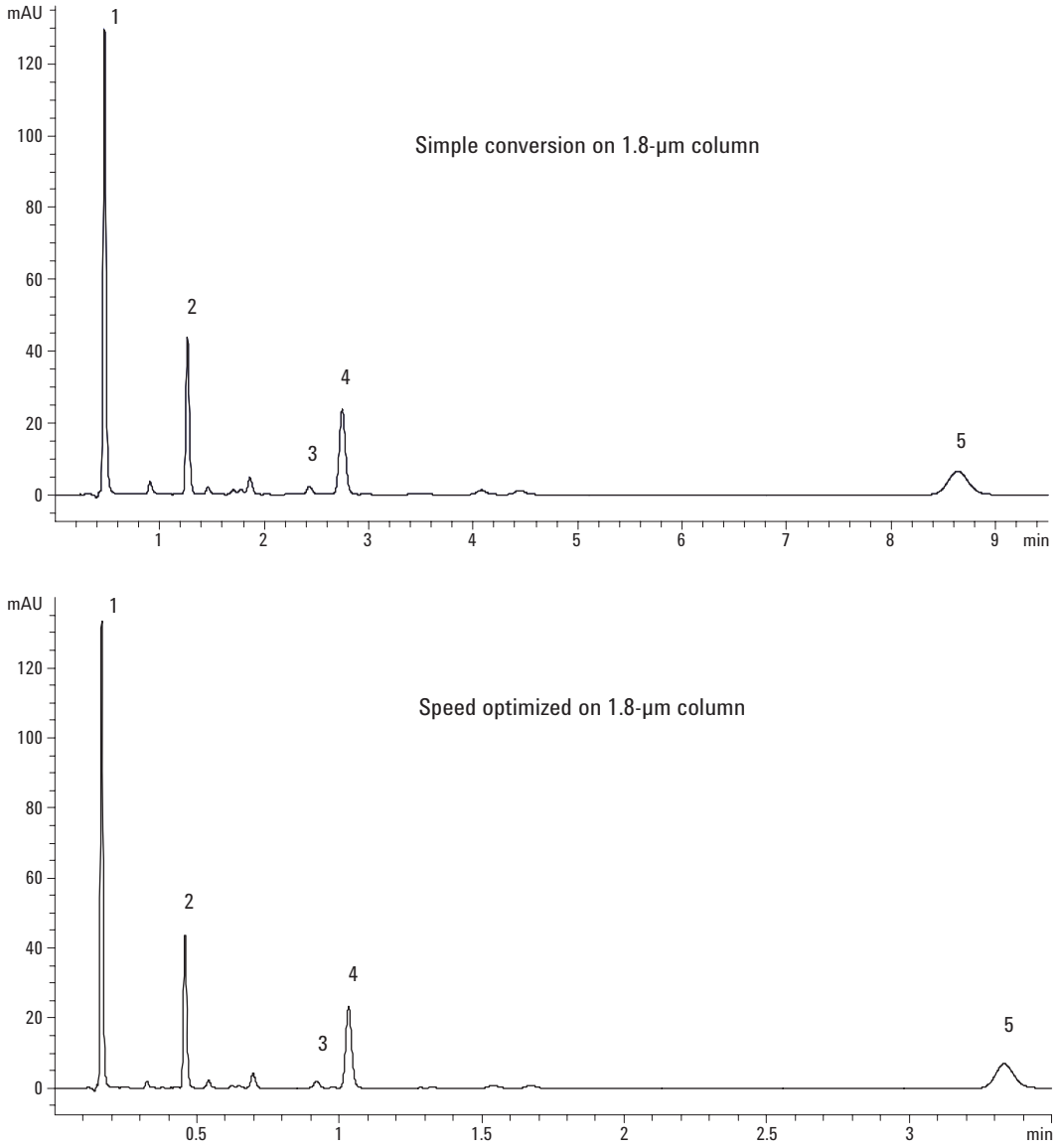

Compound	Conditions				
1 PPD	Stationary phase:	Agilent ZORBAX Eclipse XDB-C8			
2 IPPD	Mobile phase:	A: water with 0.1 g/L ethanolamine			
3 DTPD		B: ACN with 0.1 g/L ethanolamine			
4 6PPD	Isocratic composition:	30% A, 70% B (v/v)			
5 77PD	Column temperature:	35 °C			
	Wavelength:	260 nm			
	Column size	4.6 mm × 100 mm, 3.5 µm		4.6 mm × 50 mm, 1.8 µm	
	Conversion mode:	Simple	Speed optimized	Simple	Speed optimized
	Flow rate:	1.0 mL/min	4.0 mL/min	1.0 mL/min	3.0 mL/min
	Injection volume:	6.7 µL	6.7 µL	3.3 µL	3.3 µL
	Analysis time:	15 min	5 min	10 min	3.5 min

Figure 2. Separation of five PPDs on a smaller particle size column using the transferred methods.

Conclusions

As a powerful approach, liquid chromatography with ultraviolet\visible detection is often used to determine the chemical antidegradants in rubber. Agilent 1200 RRLC systems typically provide the customer with a rapid separation having the same or similar resolution. The method translator can convert any isocratic or gradient method to fast method according to customer requirements. This application details the selection of stationary phases for the separation of five PPDs, separates five PPDs with the RRLC system in one run, and applies the method translator to develop fast methods based on smaller particle size columns. With 1.8-µm column, the total analysis time of five PPDs in one run is about 6.4 times faster than the original 5-µm column method.

References

1. ASTM D5666-95 (Reapproved 2004) "Standard Test Method for Rubber Chemical Antidegradants - Purity of *p*-Phenylenediamine (PPD) Antidegradants by High Performance Liquid Chromatography"
2. Michael Woodman, "Improving the Effectiveness of Method Translation for Fast and High Resolution Separations," Agilent Technologies publication 5989-5177EN, 2006.

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