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Application News

Analysis of Anti-Degradant Additive (6PPD) and its Transformation Product 6PPD-Quinone in Tire Rubber Using an Integrated HPLC System

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User Benefits

- The anti-degradant additive 6PPD and its transformation product 6PPD-quinone can be analyzed simultaneously using an integrated HPLC system.
- The detection limits for 6PPD and 6PPD-quinone with this method are sufficiently low, enabling high-sensitivity detection and quantitative analysis.
- The pretreatment is very simple, making this method suitable for screening samples.

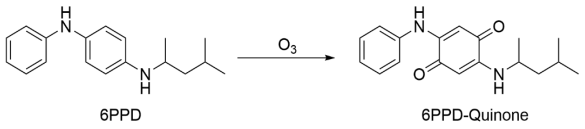
■ Introduction

Rubber products, especially tire rubber, contain various anti-degradant additives to prevent degradation by oxidation and ozone and to improve durability. 6PPD (N-(1,3-dimethylbutyl)-N′-phenyl-p-phenylenediamine) is one of the most important additives used to protect against oxidative and ozone-induced degradation. Tires readily develop cracks when exposed to oxygen and ozone, but 6PPD inhibits that degradation, helping to prolong tire lifespan.

However, when the tire wears, particles containing 6PPD may be emitted to the environment. 6PPD can react with ozone in the atmosphere to form a highly toxic substance called 6PPD-quinone (N-(1,3-dimethylbutyl)-N′-phenyl-p-phenylenediamine-quinone) (Fig. 1). 6PPD-quinone has been reported to be highly toxic to living organisms and has been shown to cause acute mortality in salmonid fish, specifically coho salmon.[1)]

Currently, there is no commercial alternative that can maintain tire stability and performance with minimal impact on the environment. Research into alternatives requires accurately assessing 6PPD levels in rubber products and objectively determining whether alternative compounds offer equivalent stability and performance while having a reduced impact on the environment.

This Application News article describes an example of analyzing the anti-degradant additive 6PPD and its transformation product 6PPD-quinone in tire rubber using an integrated HPLC system.



6PPD　　6PPD-Quinone

Fig. 1 6PPD Converted to 6PPD-Quinone by Oxidation

■ Sample Preparation and Pretreatment

In this experiment, samples were prepared and analyzed in accordance with ISO 23075: 2021.

1) **Dilution Solvent:** The dilution solvent was prepared by mixing a 1:1 (v/v) mixture of methanol (HPLC grade) and a 0.01 mol/L aqueous solution of ammonium acetate (AR grade).
2) **Calibration Samples:** Calibration samples were prepared by diluting standard solutions of commercially available 6PPD and 6PPD-quinone with the above dilution solvent.
3) **Analysis Samples:** Rubber from commercial tires was used.
4) **Pretreatment of Analysis Samples:** Approximately 1 g of the sample was cut into small pieces about 2 mm square. An approximately 200 mg portion of the small pieces was weighed and placed into a 20 mL flask. 10 mL of the dilution solvent was accurately added by pipette and the flask was stoppered. The 6PPD and 6PPD-quinone were extracted in an ultrasonic bath for 3 hours at a temperature not exceeding 30 °C. The extract solution was filtered through a PTFE filter prior to analysis.

■ Analysis Conditions

Analysis was performed using an i-Series integrated LC system (LC-2070). The picture of the instrument is shown in Fig. 2.

The analysis conditions are summarized in Table 1.

Table 1 Analysis Conditions

Column:	Shim-pack™ GISS C18 (150 mm × 4.6 mm, 5 µm)*1
Eluent A:	Methanol / 0.01 mol/L ammonium acetate = 1:1
Eluent B:	Methanol
Time Program (%B):	30 % (0.00 min) → 30 % (0.00-25.00 min) → 100 % (25.01 - 30.00 min) → 0 % (30.01 - 35.00 min)
Flowrate:	1 mL/min
Column Temp.:	40 °C
Injection Volume:	10 µL
Vials:	Shim-vial™ S Glass*2
Detection:	UV Detector Ch 1: 290 nm for 6PPD Ch 2: 351 nm for 6PPD-quinone

*1 P/N: 227-30061-06
*2 P/N: 227-34500-02

Fig. 2 i-Series LC-2070 HPLC System

■ Analysis of Calibration Samples and Detection Limits

The concentrations of 6PPD and 6PPD-quinone in respective calibration samples are indicated in Table 2. Fig. 3 and Fig. 4 indicate the respective calibration curves and correlation coefficient. All anions had excellent correlation coefficient exceeding 0.999.

Table 1 Concentrations of 6PPD and 6PPD-Quinonein Calibration Samples

Component (mg/L)	STD1	STD2	STD3	STD4	STD5
6PPD	0.5	1	5	10	50
6PPD-Quinone	0.1	0.2	1	2	10

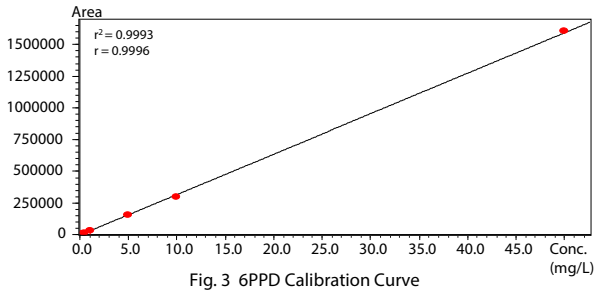


Fig. 3 6PPD Calibration Curve

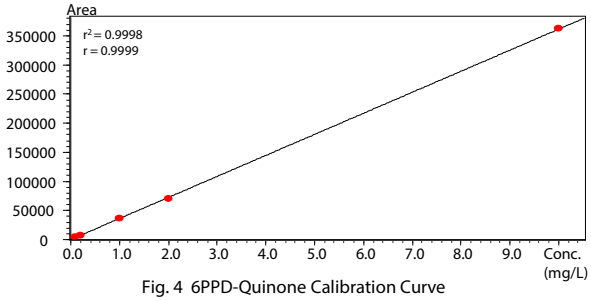


Fig. 4 6PPD-Quinone Calibration Curve

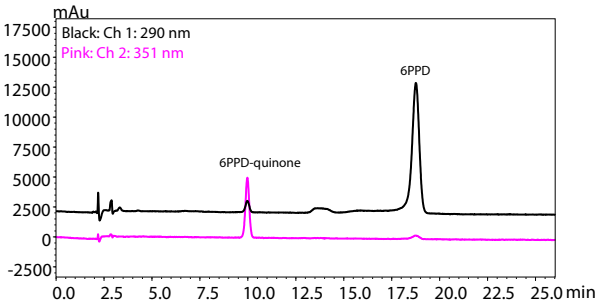


Fig. 5 Chromatograms of STD4

The detection limits (DLs) were determined using LabSolutions by finding the concentrations at which the signal-to-noise ratio (S/N) of each analyte peak reached 3. As a result, the detection limit for 6PPD in solution was 0.1 mg/L and for 6PPD-quinone in solution was 0.05 mg/L.

■ Sample Analysis and Spike Recovery Test

Sample pretreatment was performed according to the procedure specified in ISO 23075:2021. After pretreatment, each sample was analyzed in duplicate under identical conditions.

The accuracy was confirmed by spike recovery tests. Samples were evaluated by spiking a standard solution. Recoveries were calculated according to the formula shown in Table 3. The analysis was performed twice, with the two quantitative results obtained for each sample and the mean recovery rates calculated from each run summarized in Table 4.

Fig. 6 and Fig. 7 show chromatograms of the spiked and unspiked samples.

Table 3 Formula of Sample Recovery Rates

$$R=\frac{C_F-C}{F}\times 100$$

R = Percent recovered
C_F = Fortified sample concentration
C = Sample background concentration
F = Equivalent concentration added to sample

Table 4 Analysis Results of Spiked and Unspiked Samples (n = 2)

Component	Mean Conc. in Solution (mg/L)	Conc. in Solid Sample	Spike Conc. (mg/L)	Spike Recovery
6PPD	1.0	0.005 %	5	96 %
6PPD-Quinone	0.54	0.0027 %	1	92 %

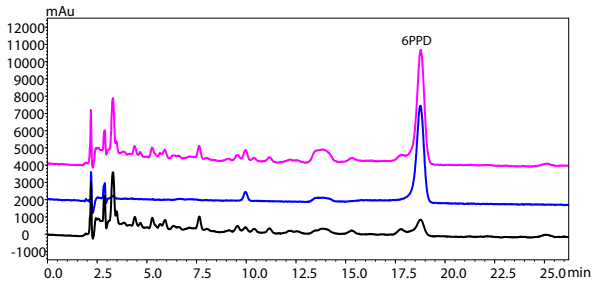


Fig. 6 Chromatograms of 6PPD in Spiked and Unspiked Samples (UV 290 nm)
(Pink: Spiked Sample, Blue: STD3-Spike Concentration, Black: Unspiked Sample)

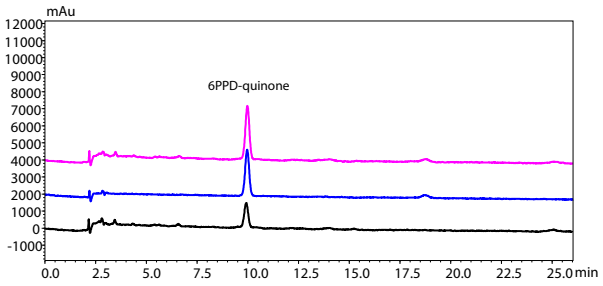


Fig. 7 Chromatograms of 6PPD-Quinone in Spiked and Unspiked Samples (UV 351 nm)
(Pink: Spiked Sample, Blue: STD3-Spike Concentration, Black: Unspiked Sample)

■ Conclusion

An i-Series (LC-2070) integrated HPLC system together with Shim-pack GISS series columns were used to establish a method for simultaneous quantitation of the anti-degradant 6PPD and its transformation product 6PPD-quinone in tire rubber.

Linearity of the calibration curves, detection limits, reproducibility of sample analysis, and recovery rates were all satisfactory, demonstrating that both components can be analyzed simultaneously in tire rubber with simple pretreatment.

References

1) Tian *et al.*, *Science, 371* (2021) 185-189
2) ISO 23075:2021 Vulcanized rubbers - Determination of antidegradants by high-performance liquid chromatography

Related Applications

1. Quantitative Analysis of Anti-Degradant Additive (6PPD) in Tire Rubber Using Pyrolysis-GC-MS, Application News No. 01-00952

01-01133-EN First Edition: Mar. 2026

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