

Simultaneous Analysis of 6PPD and Its Oxidation Product 6PPD-Quinone in Tire Rubber Using a High-Performance Liquid Chromatography System

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1. Introduction

Rubber products contain anti-degradant additives to prevent oxidation- and ozone-induced degradation and improve durability. 6PPD (N-(1,3-dimethylbutyl)-N'-phenyl-p-phenylenediamine) is a key additive for protecting tires from these effects. However, tire wear can release particles containing 6PPD into the environment. In the atmosphere, 6PPD reacts with ozone to form the highly toxic 6PPD-quinone (N-(1,3-dimethylbutyl)-N'-phenyl-p-phenylenediamine-quinone) (Fig. 1). 6PPD-quinone has been reported to be highly toxic to organisms and to cause acute mortality in salmonid fish, especially coho salmon¹. Currently, no commercial alternative can maintain tire stability and performance while minimizing environmental impact. This poster describes an example of analyzing 6PPD and 6PPD-quinone in tire rubber using an integrated HPLC system.

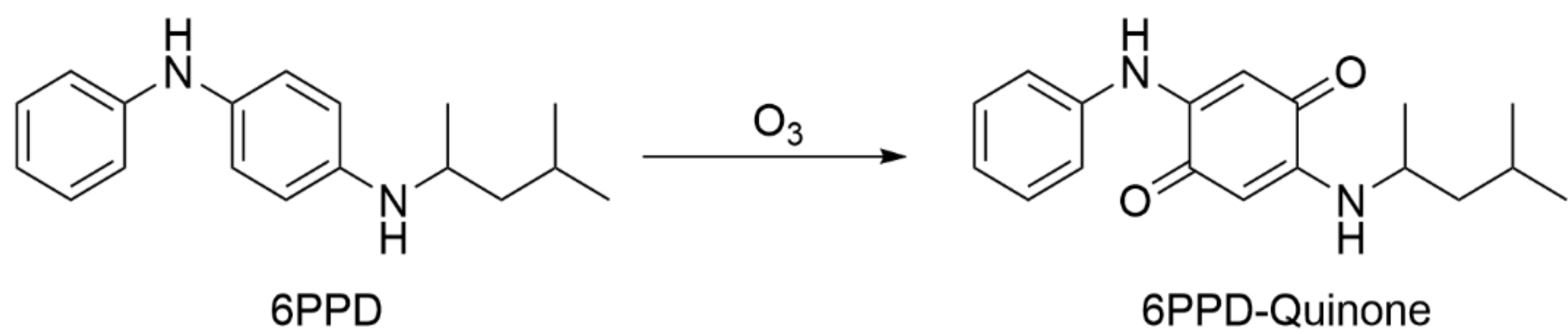


Fig. 1 6PPD Converted to 6PPD-Quinone by Oxidation

2. Sample Preparation and Pretreatment

- Samples were prepared in accordance with ISO 23075: 2021².
- 1) Dilution Solvent:**
Prepared by mixing a 1:1 (v/v) mixture of isopropanol (HPLC grade) and dichloromethane (HPLC grade).
- 2) Calibration Samples:**
Prepared by diluting standard solutions of commercially available 6PPD and 6PPD-quinone with the dilution solvent.
- 3) Analysis Samples:**
Rubber from commercial tires
- 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.

3. Analysis Conditions

Table 1 Analysis Conditions	
System	: LC-2070
Column	: Shim-pack™ GISS C18 (150 mm × 4.6 mm, 5μm)
Eluent A	: methanol / 0.01 mol/L ammonium acetate in water = 1:1
Eluent B	: methanol
Time program	: 30 % (0-25.00min)→100% (25.01- 30.00min) → 0% (30.01-35.00min)
Flow rate	: 1 mL/min
Column temp.	: 40 °C
Injection volume	: 10 μL
Detection	: UV Detector (Ch1: 290 nm for 6PPD, Ch2: 351 nm for 6PPD-quinone)

4. 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 2 Concentrations of 6PPD and 6PPD-Quinone in 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

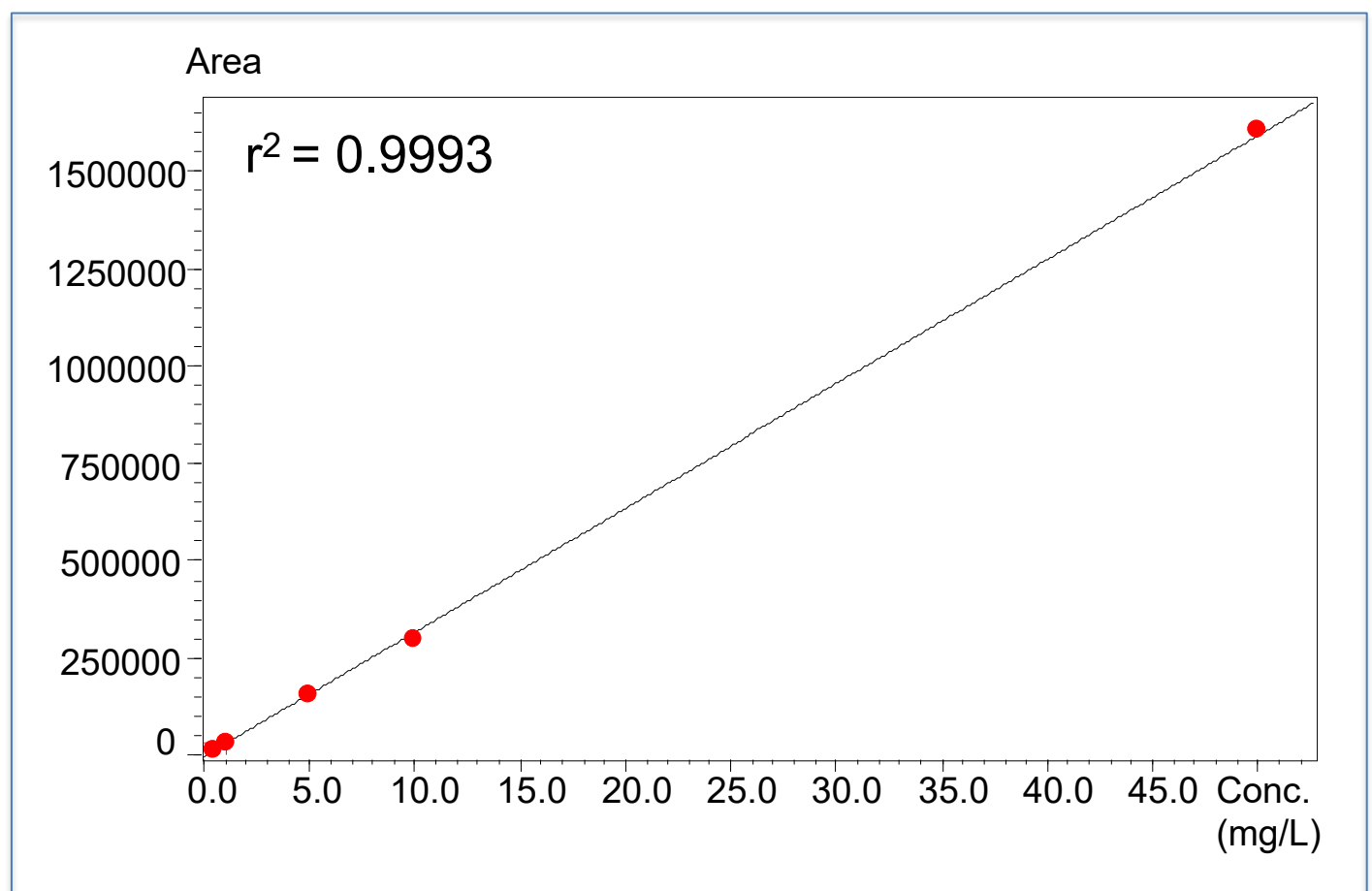


Fig. 3 6PPD Calibration Curve

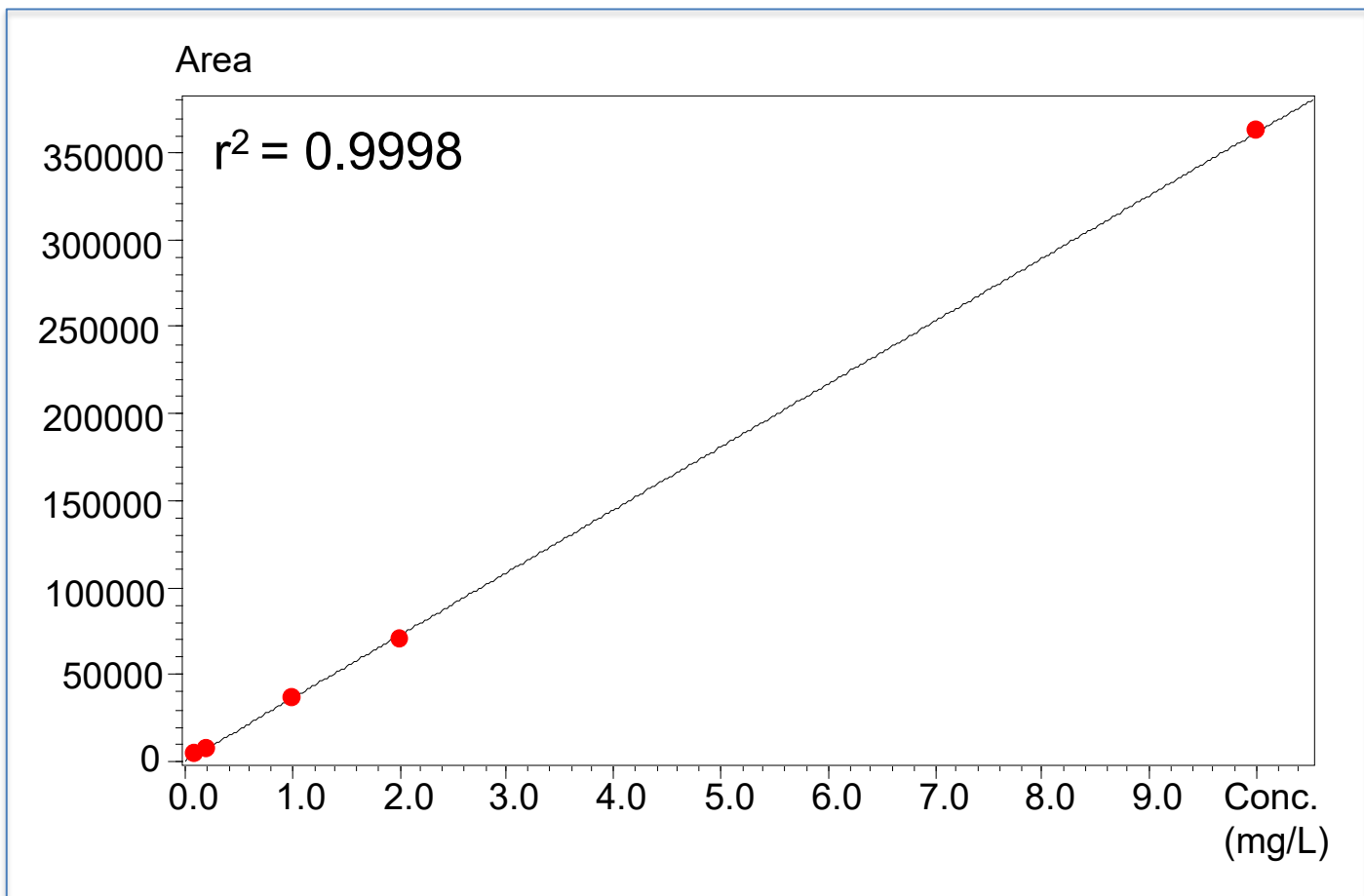


Fig. 4 6PPD-Quinone Calibration Curve

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. To reduce the influence of variability and measurement error in single measurements, the DL values from calibration samples STD1–STD5 were averaged. 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.

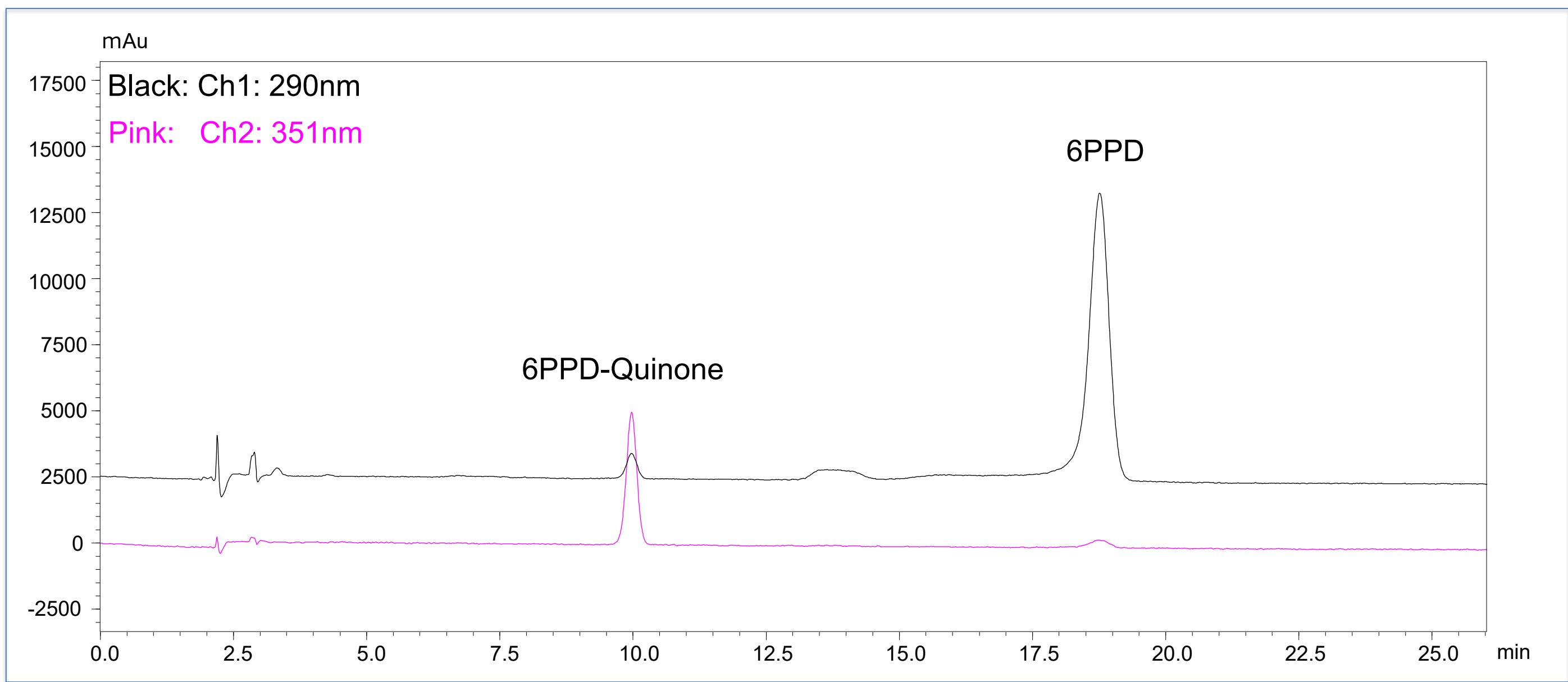


Fig. 5 Chromatograms of STD4

5. Sample Analysis and Spike Recovery Test

The accuracy was confirmed by spike recovery tests. Samples were evaluated by spiking a standard solution. 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 3. Fig. 6 and Fig. 7 show chromatograms of the spiked and unspiked samples.

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 %

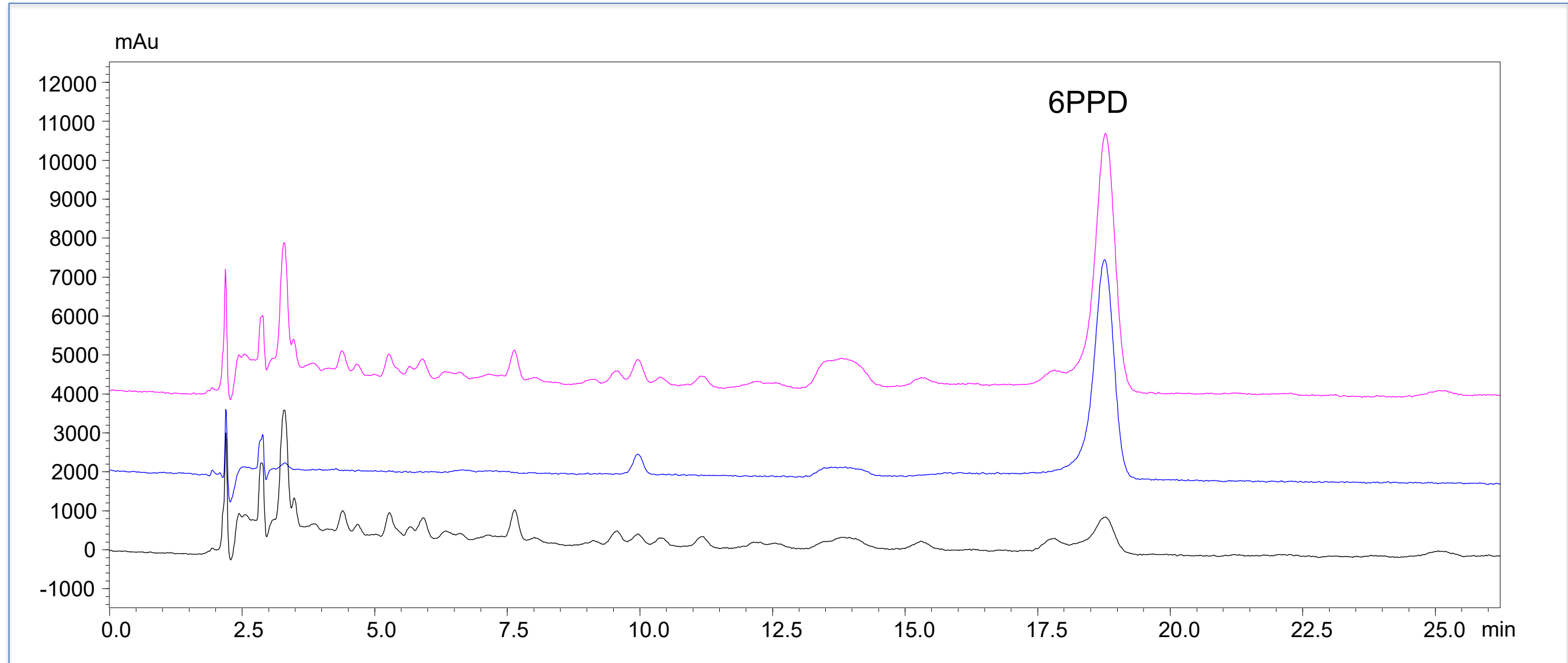


Fig. 6 6PPD in Spiked and Unspiked Samples (UV 290 nm)
(Pink: Spiked Sample, Blue: STD3-Spike Concentration, Black: Unspiked Sample)

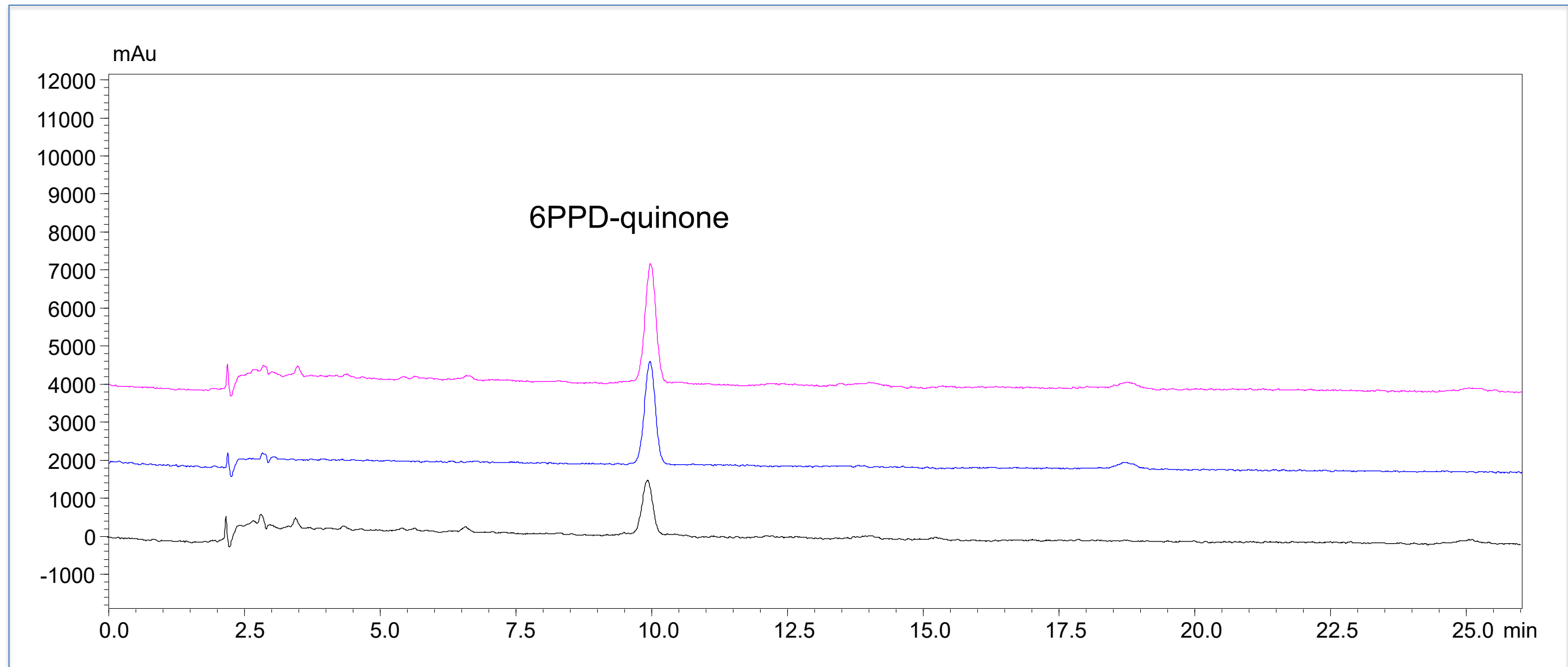


Fig. 7 6PPD-Quinone in Spiked and Unspiked Samples (UV 351 nm)
(Pink: Spiked Sample, Blue: STD3-Spike Concentration, Black: Unspiked Sample)

6. 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

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