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Application News

Quantitative Analysis of Anti-Degradant Additive (6PPD) in Tire Rubber Using Pyrolysis-GC-MS

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User Benefits

- The simple analysis procedure required just cutting off a sample fragment and placing it in a sample cup without pretreatment.
- Utilizing a calibration standard that includes a resin solution allows for analysis under conditions that closely resemble those of samples, which improves the reliability of quantitative measurements.
- With Shimadzu's Polymer Additive Library, it is possible to acquire information on the additives of identified compounds.

■ Introduction

6PPD (*N*-(1,3-dimethylbutyl)-*N'*-phenyl-*p*-phenylenediamine) is an anti-degradant (anti-oxidant) additive that is used in many rubber products. Its chemical structure is shown in Fig. 1. It plays an important role in tires by preventing degradation and extending its lifespan. However, when 6PPD reacts with ozone in the atmosphere, it forms a highly toxic substance called 6PPD-quinone (6PPD-Q).

As an automotive tire wears, microscopic particles are released from the tire into the environment. These particles, tire road wear particles (TRWP), contain 6PPD-Q along with many other chemical substances. On rainy days, these particles are washed into rivers and other bodies of water, where they accumulate in the environment as microplastics.

There are serious concerns about the negative effects these microplastics have on ecosystems and the environment. 6PPD-Q has been shown to induce acute mortality in *Salmonidae* 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 article describes using a pyrolysis gas chromatograph mass spectrometer (Py-GC-MS) system to measure 6PPD levels in tire rubber.

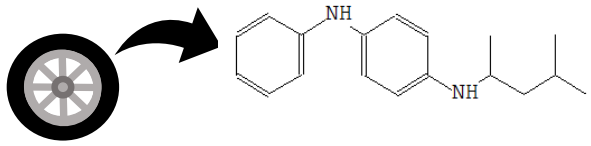

Fig. 1 Chemical Structure of 6PPD

■ Analysis Process

ISO/TS 21396[2)] describes a method for determining the mass concentration of TRWP in soil and sediment that uses Py-GC-MS. Similar to this method, Py-GC-MS was used for the analysis; however, this article employs optimized analytical conditions. A schematic diagram of the analysis process is shown in Fig. 2.

For more information on the analysis conditions and results from the evolved gas analysis (EGA-MS) method described in Fig. 2, please see Application News No. 01-00901.

The analysis conditions for the thermal desorption (TD)-GC/MS method used in this article are shown in Table 1. The thermal desorption temperature was chosen based on results obtained by the EGA-MS method.

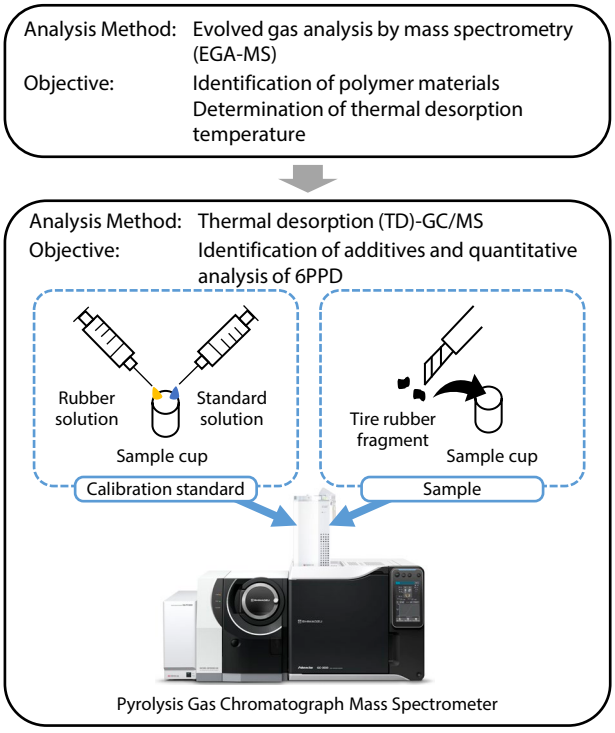

Fig. 2 Analysis Process

Table 1 TD-GC/MS Analysis Conditions

Instruments	
Pyrolyzer Unit	: EGA/PY-3030D Multi-Shot Pyrolyzer AS-1020E Auto-Shot Sampler (Frontier Laboratories Ltd.)
GC-MS	: GCMS-QP2020 NX
TD-GC-MS	
Pyrolyzer	
Analysis Mode	: Double-Short Analysis
Thermal Desorption Temp.	: 60 °C-20 °C/min-370 °C (1min)
ITF Temp.	: 300 °C (Auto)
Gas Chromatograph	
Column	: SH-5Sil MS (30 m × 0.25 mm I.D., df = 0.25 µm) *1
Oven Temp.	: 40 °C (0 min)→25 °C/min→250 °C (0min) →15 °C/min→310 °C (20 min)
Sample Injection Unit	: 300 °C
Carrier Gas	: He
Control Mode	: Constant linear velocity (40.0 cm/s)
Injection Method	: Split
Split Ratio	: 15
Mass Spectrometer	
ITF Temp.	: 320 °C
Ion Source Temp.	: 200 °C
Ionization Method	: EI
Measurement Mode	: Scan (*m/z* 44-500)
Event Time	: 0.3 sec

*1 P/N: 221-76127-30

■ Sample Preparation

Calibration standards were prepared by combining a standard solution of the target compound (6PPD) and a resin solution. A solution of styrene-butadiene rubber (SBR), the rubber used in the sample, was used as the calibration standard to ensure that the calibration standards and the sample had the same thermal desorption rate.

The 6PPD standard solution was prepared by diluting 6PPD in toluene. Calibration standards with prescribed amounts of 6PPD were prepared by adding 1 µL of 6PPD standard solution and 20 µL of the resin solution to a sample cup. The mixture was then dried at room temperature and analyzed by TD-GC/MS (Fig. 3).

A fragment of tire rubber was used as a sample. A knife was used to cut off approx. 0.5 mg of tire rubber and glass wool was added to prevent the sample from falling. This sample was analyzed by TD-GC/MS.

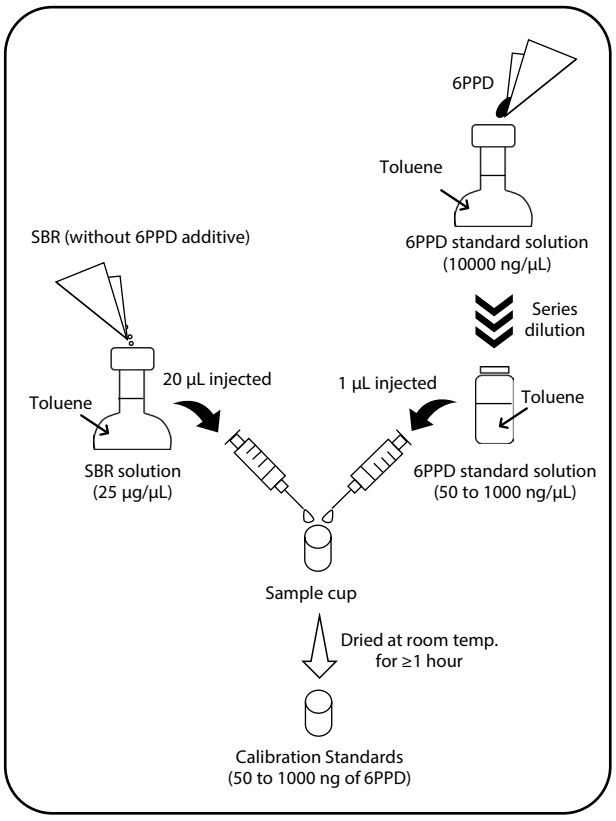

Fig. 3 Preparation of Calibration Standards

■ Qualitative Analysis of Additive

The total ion current (TIC) chromatogram obtained from analyzing the tire rubber is shown in Fig. 4. A spectral library search was also performed using NIST-23 and Shimadzu's Polymer Additives Library. The library search results for the peak that eluted at around 10.43 minutes are shown in Fig. 5. Based on the results from Shimadzu's Polymer Additives Library, the peak was estimated to be the anti-degradant Nocrac 6C (a trade name for the chemical 6PPD).

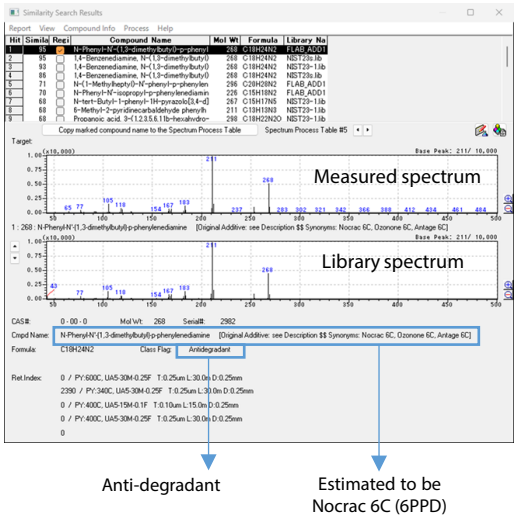

Fig. 5 Qualitative Analysis with Polymer Additives Library

■ Investigation of Quantifier Ions

Fig. 6 shows the TIC and mass chromatogram for the 1000 ng 6PPD calibration standard. The ions at *m/z* 211 and *m/z* 268 were selected as the quantifier ion and the reference ion, respectively, based on their high signal intensity and the absence of interference from resin components.

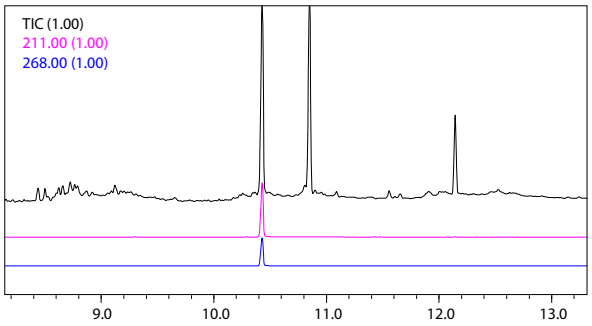

Fig. 6 TIC and Mass Chromatogram of Calibration Standard (1000 ng)

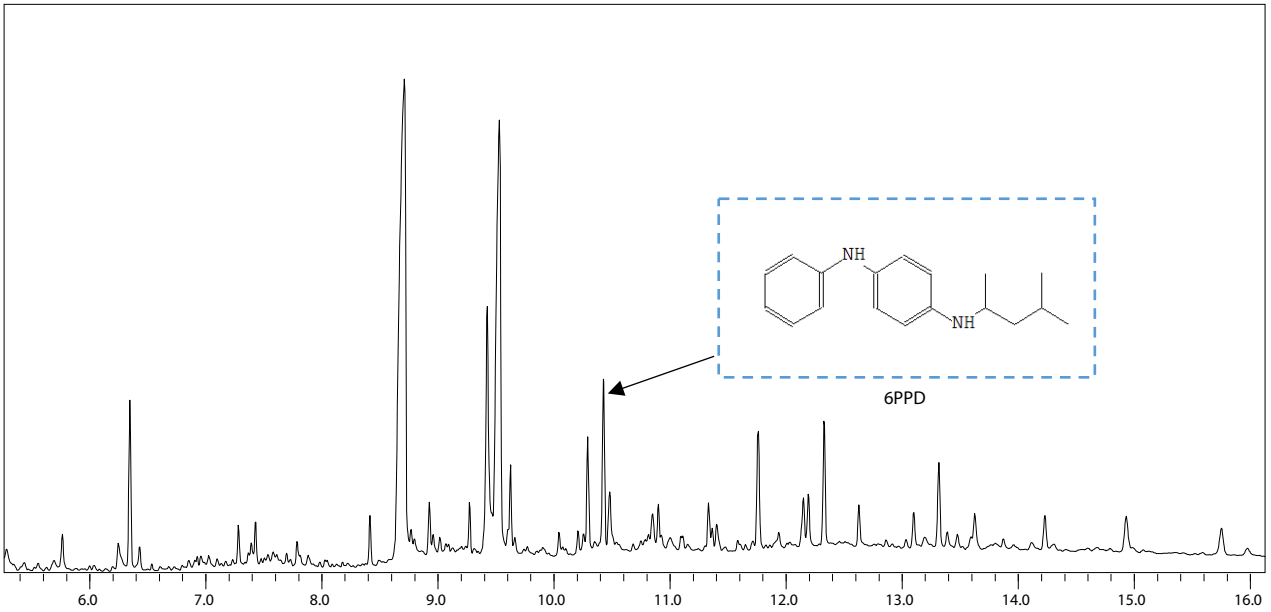

Fig. 4 TIC Chromatogram of Tire Rubber Fragment

■ Calibration Curve

A calibration curve for external standard method was prepared by analyzing calibration standards of 0, 50, 250, 500, and 1000 ng of 6PPD. The linearity of the calibration curve was good, with an R^2 above 0.999 (Fig. 7).

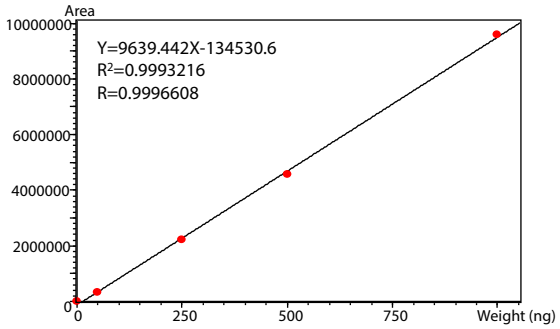

Fig. 7 6PPD Calibration Curve

■ Checking Repeatability, Limit of Quantification, and Limit of Detection

The 50 ng 6PPD calibration standard was analyzed seven times in succession to examine repeatability based on %RSD. The limit of quantitation (LOQ) and limit of detection (LOD) were calculated by the methods shown below. The repeatability of the method was good, with a %RSD below 5.0 %. The method was also sensitive enough for practical use with an LOD of 3.0 ng (Table 2).

LOQ and LOD Calculation Methods

LOQ = 10σ/slope	slope: calibration curve slope
LOD = 3σ/slope	σ: standard deviation at 50 ng

Table 2 Repeatability, LOQ, and LOD

%RSD at 50 ng	LOQ (ng)	LOD (ng)
3.3	10.2	3.0

■ Analysis of the Sample

The amount of 6PPD measured in tire rubber is shown in Table 3. The analysis showed the tire rubber contained 1200 mg/kg of 6PPD.

Table 3 Quantitative Results for 6PPD

Sample Analyzed (mg)	6PPD Weight (ng)	6PPD Conc. (mg/kg)
0.53	620	1200

■ Conclusion

This article presents an analysis of the additive 6PPD in tire rubber utilizing Py-GC-MS. Good results were obtained for calibration curve linearity, calibration standard repeatability, limit of quantification, and limit of detection.

Shimadzu's Polymer Additives Library was used to identify the additive.

Acknowledgments

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<References>

1) Tian *et al.*, *Science, 371* (2021) 185-189

2) ISO/TS 21396:2017 Rubber — Determination of mass concentration of tire and road wear particles (TRWP) in soil and sediments — Pyrolysis-GC/MS method

<Related Application News Articles>

1. Analysis of Base Material and Additives in Tire Rubber — Pyrolysis-GC-MS/FPD Detector Splitting—Application News No. 01-00901

2. Analysis of 6-PPD-Quinone in River Water and Local Stream Matrix using LCMS-8060 Triple Quadrupole Mass Spectrometer Application News No. SSI-LCMS-133

3. Detailed Analysis of an Unknown Polymer Using the Py-GC/MS System with Polymer Additives and F-Search Polymer Libraries Technical Report

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