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Application News

GC-MS GCMS-QP2020 NX and GCMS-QP2050

Analysis of Base Material and Additives in Tire Rubber
—Pyrolysis-GC-MS/FPD Detector Splitting—

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User Benefits

- With a split FPD(S) and MS detector system, sulfur compounds can be detected selectively and with high sensitivity by the FPD detector while being qualitatively analyzed simultaneously by the MS detector, which significantly reduces the time and effort required.
- The LabSolutions™ GCMS system makes it easy to configure settings for complex detector splitting.
- With evolved gas analysis, polymer materials can be inferred from thermogram average mass spectra.

■ Introduction

The rubber used in tires for automobiles, bicycles, and other types of tires needs to have high resistance to the weather, heat, and wear for long periods of use. But as the rubber wears, it mixes with mineral particles from the road to generate “tire and road wear particles” (TRWP). TRWP matter is known to be a type of microplastic that causes marine plastic pollution.

TRWP can contain a large variety of substances, such as vulcanizing accelerators, antioxidants (such as 6PPD), and plasticizers, and when released into the environment, TRWP substances can be harmful to ecosystems. Therefore, to reduce the quantity of TRWP matter released, it is important to increase the wear resistance of tires. To achieve this, an assessment of the base materials and additives in rubber is essential. Among additives, vulcanizing accelerators in particular improve the physical properties of tires by promoting sulfur vulcanization reactions.

This article analyzes the base materials in tire rubber and additives, such as vulcanizing accelerators and other sulfur components.

■ Analysis Process Flow

A pyrolysis gas chromatograph mass spectrometer (Py-GC-MS) system was used, as specified in the international standard ISO/TS 21396.[1)] Simply placing cut-up samples in a sample cup (Fig. 1) enables direct analysis of samples without pretreatment. The analytical process flow is indicated in Fig. 2.

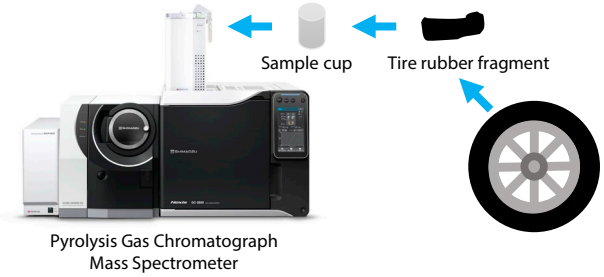

Fig. 1 Procedure for Loading Samples into the System

Analysis Method:	Evolved gas analysis by mass spectrometry (EGA-MS)
System Configuration:	Py-GC-MS
Purpose:	Qualitative analysis of polymer materials and determination of thermal desorption temperature

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Analysis Method:	Thermal desorption (TD)-GC/MS
System Configuration:	Py-GC-MS/FPD
Purpose:	Qualitative analysis of additives

Fig. 2 Process Flow of Analysis

■ Detector Splitting System

A Smart Micro Inert (SMI) detector splitting system (Fig. 3) was used to analyze the additives. The split ratio was determined based on the length and internal diameter of the respective restrictors used for splitting and by adjusting the AUX-APC (digital flow controller) pressure level.

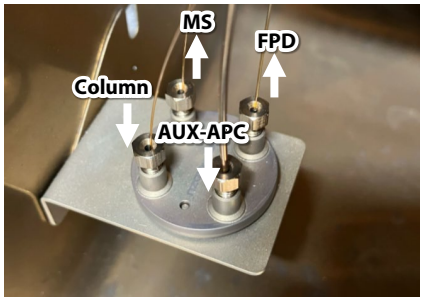

Fig. 3 SMI Detector Splitting System

Fig. 4 shows the data acquisition window in LabSolutions GCMS data analysis software. By using LabSolutions GCMS software, detailed settings can be specified for acquisition, data analysis, and detector splitting using a single program.

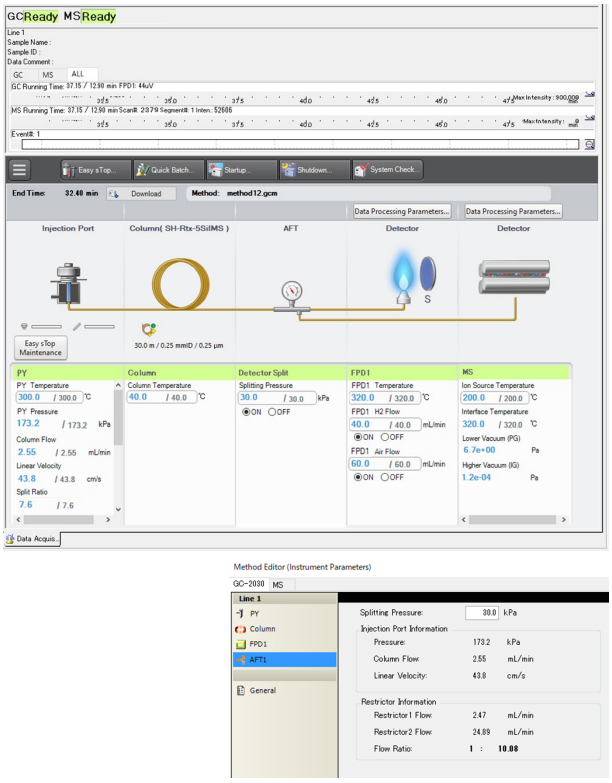

Fig. 4 LabSolutions GCMS Data Acquisition Window

■ Inferring Polymers

The evolved gas analysis (EGA-MS) method uses pyrolyzer (Py) and mass spectrometer (MS) units linked via a deactivated metal tube to heat samples to continuously increasing temperatures to generate gases from the samples, which are then detected by the MS.

Samples (0.2 mg) of tire rubber fragments were placed in sample cups, with fiberglass wool inserted to prevent them from dropping, and then analyzed. Analysis conditions are indicated in Table 1.

Thermograms obtained from that analysis are shown in Fig. 5. Originally, the horizontal axis of the thermogram is the time, but the heating temperature of the pyrolyzer can be calculated from the time. Peaks from polymer thermal decomposition products appear across the range of 370 to 500 °C. The average MS spectrum for that peak range and the results from inferring the polymer are shown in Fig. 6. Based on the F-Search EGA-MS Polymer Library (Frontier Laboratories Ltd.), the base material in the tire rubber was inferred to be styrene-butadiene rubber (SBR).

Enlarging the thermogram shows a shoulder peak between 240 and 370 °C. Assuming that the shoulder peak originated from an additive, a thermal desorption analysis was carried out with the temperature range from 60 to 370 °C.

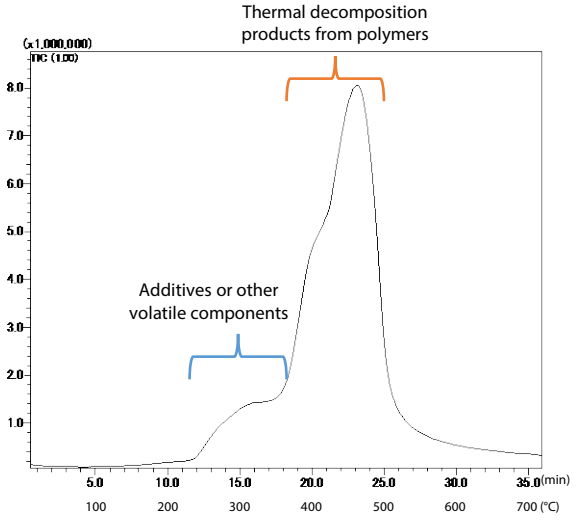

Fig. 5 Thermogram of Tire Rubber

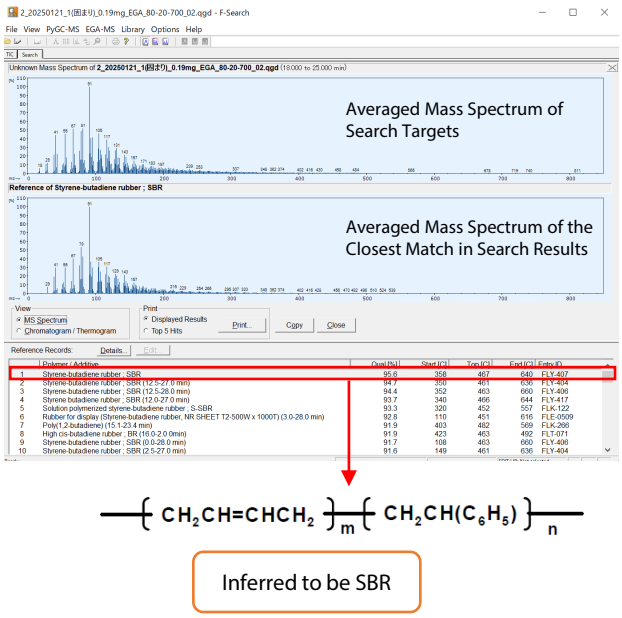

Fig. 6 Polymer Prediction Results (F-Search Window)

Table 1 EGA-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
EGA-MS	
Pyrolyzer	
Analysis Mode	: Direct EGA Analysis
Thermal Desorption Temp.	: 80 °C (4 min) - 20 °C/min-700 °C (1 min)
ITF Temp.	: 300 °C (Auto)
GC-MS Unit	
Column	: UA-DTM (2.5 m × 0.15 mm I.D.) (Frontier Laboratories Ltd.)
Oven Temp.	: 300 °C (36 min)
Sample Injection Unit	: 300 °C
Carrier Gas	: He
Control Mode	: Constant Pressure (100 kPa)
Injection Method	: Split
Split Ratio	: 50
ITF Temp.	: 300 °C
Ion Source Temp.	: 230 °C
Ionization Method	: EI
Measurement Mode	: Scan (*m/z* 10-1000)
Event Time	: 3.0 sec

■ Analyzing Additives

The sample (0.5 mg) of a tire rubber fragment was placed in sample cups, with fiberglass wool inserted to prevent them from dropping, and then analyzed.

Using the thermal desorption temperature determined by EGA-MS, a separation analysis of the sample was performed by thermal desorption (TD)-GC/MS/FPD analysis at the thermal desorption temperature determined by EGA-MS. Settings were configured to achieve an MS:FPD split ratio of about 1:10. Analysis conditions are indicated in Table 2.

Table 2 TD-GC/MS/FPD Analysis Conditions

Instruments	
Pyrolyzer Unit:	: EGA/PY-3030D Multi-Shot Pyrolyzer AS-1020E Auto-Shot Sampler (Frontier Laboratories Ltd.)
GC-MS:	: GCMS-QP2020 NX
Detector:	: FPD-2030
Detector Splitting:	: SMI FLOW DEVICE 2-Way Splitter with APC (P/N: 221-88100-43)
TD-GC-MS/FPD	
Pyrolyzer	
Analysis Mode	: Double-Short Analysis
Thermal Desorption Temp.	: 60 °C- 2 0 °C/min-370 °C (1 min)
ITF Temp.	: 300 °C (Auto)
GC	:
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 (0 min) - 15 °C/min - 310 °C (20 min)
Sample Injection Unit	: 300 °C
Carrier Gas	: He
Control Mode	: Constant linear velocity (43.8 cm/s)
Injection Method	: Split
Split Ratio	: 7.6
AFT	
Splitter Pressure	: 30 kPa (at 1:10.08 split ratio)
Restrictor 1	: Restrictor Tubing (1.2 m × 0.15 mm I.D.) (MS)
Restrictor 2	: Restrictor Tubing (1.0 m × 0.32 mm I.D.) (FPD)
FPD	
Temperature	: 320 °C
Interference Filter	: S
H2 Flowrate	: 40 mL/min
Air Flowrate	: 60 mL/min
MS	
ITF Temp.	: 320 °C
Ion Source Temp.	: 200 °C
Ionization Method	: EI
Measurement Mode	: Scan (*m/z* 44-500)
Event Time	: 0.3 sec
Detector Voltage	: +0.1 kV

*1 P/N: 221-76127-30

The FPD(S) chromatogram is shown in Fig. 7, and the TIC chromatogram from the MS is shown in Fig. 8. The main peaks detected by the FPD(S) unit were confirmed by the MS. Library searches were conducted using NIST-23.
It was inferred that peak No. 1 was from Benzothiazole, peak No. 2 from 2-(Methylmercapto) benzothiazole, peak No. 3 from 2-Benzothiazolinone, and peak No. 4 from 2,2'-Bibenzothiazole.

Peak No. 2 could not be automatically detected as a sulfur component based on the TIC chromatogram alone. Therefore, the MS chromatogram near the RT of No. 2 detected in FPD (S) in Fig. 7 was examined (within the red frame in Fig. 8). By examining the mass chromatogram of *m/z* 181 (Fig. 9), 2-(Methylmercapto) benzothiazole, which is a sulfur component, was successfully identified.

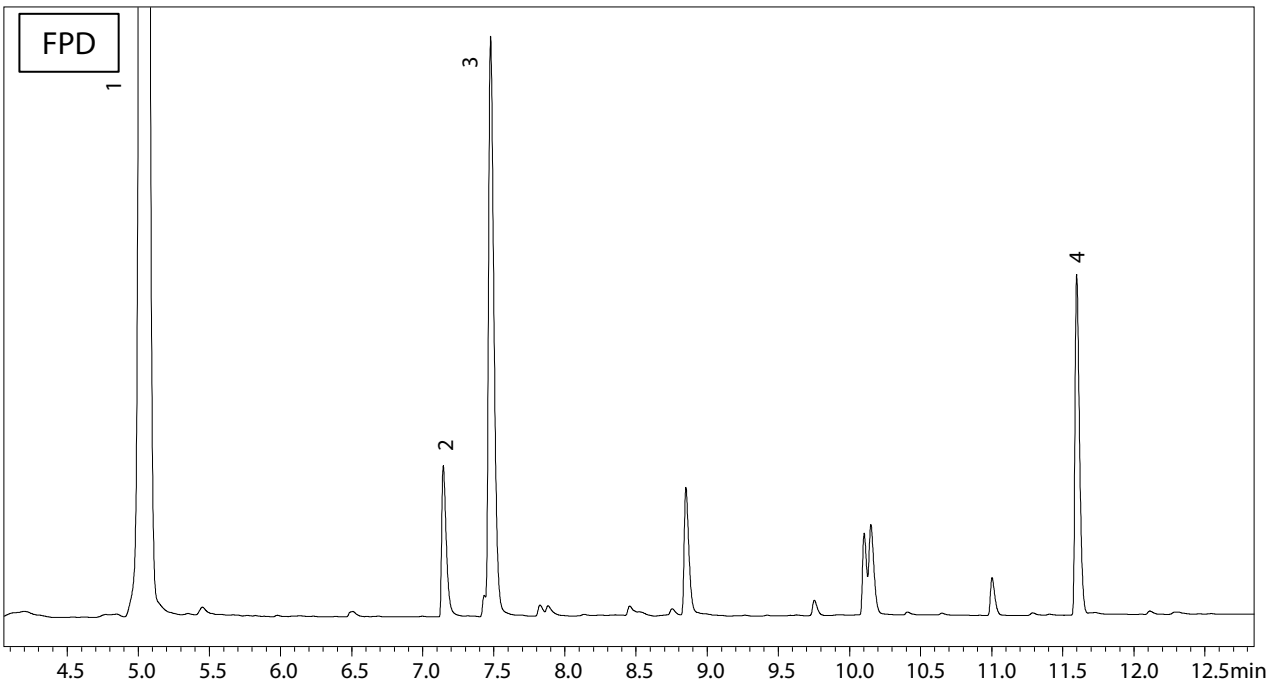

Fig. 7 FPD(S) Chromatogram

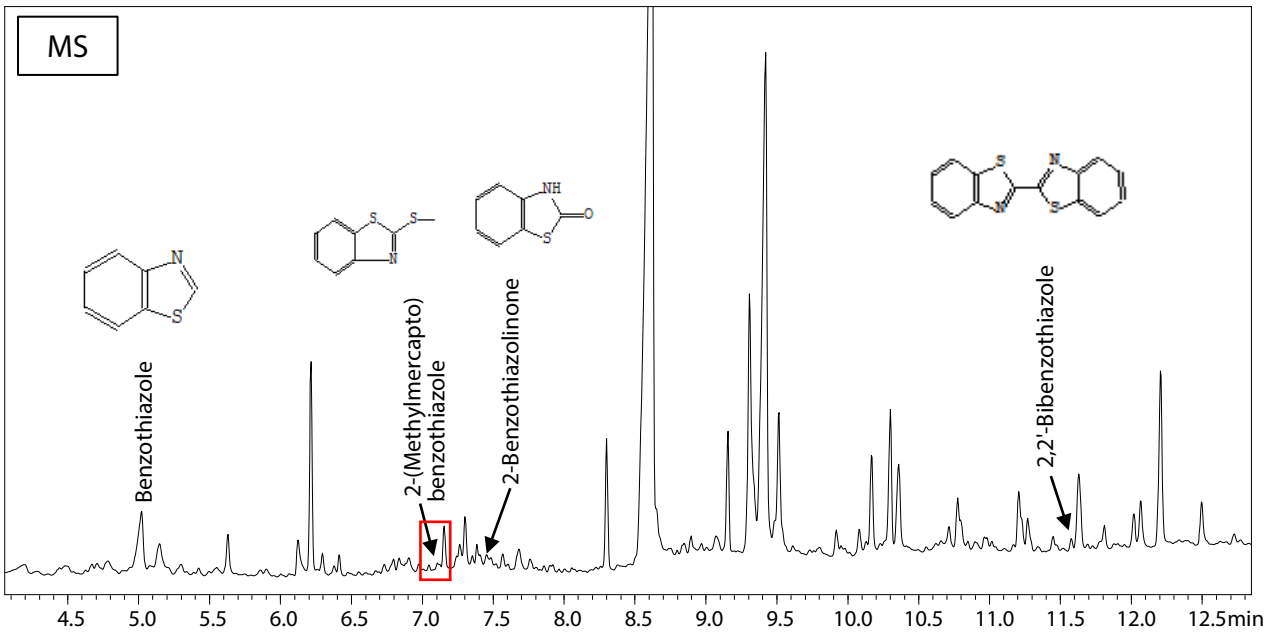

Fig. 8 TIC Chromatogram from MS

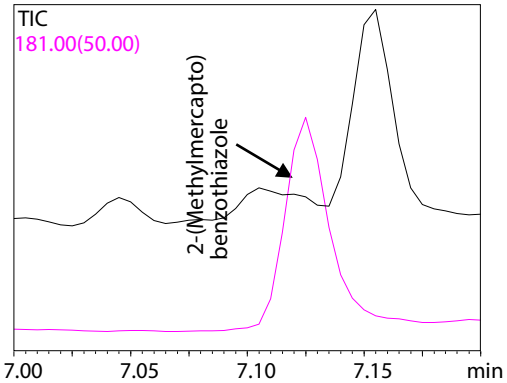

Fig. 9 Chromatogram Enlargement (7.0 to 7.2 min)

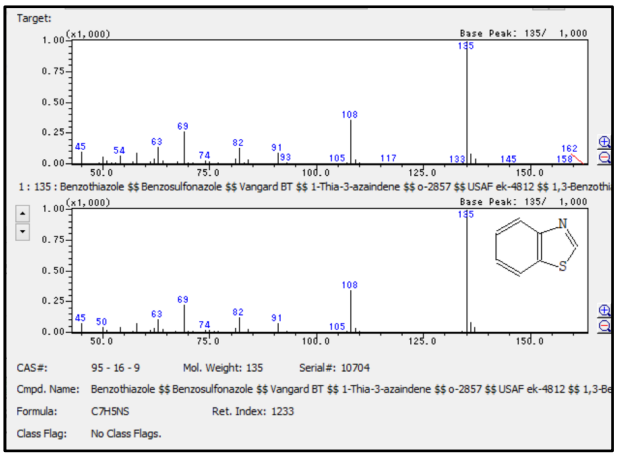

Fig. 10 Library Search Results for Peak No. 1

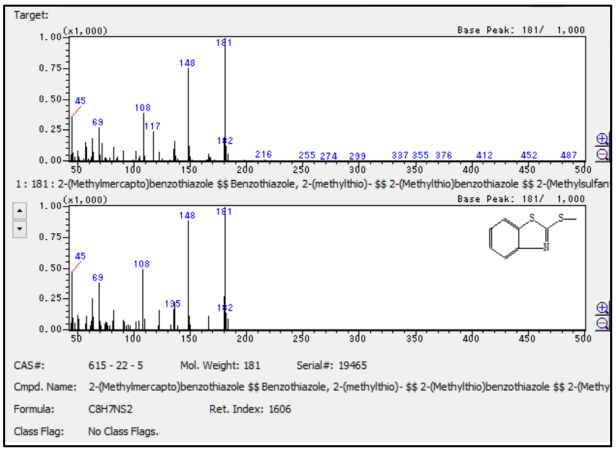

Fig. 11 Library Search Results for Peak No. 2

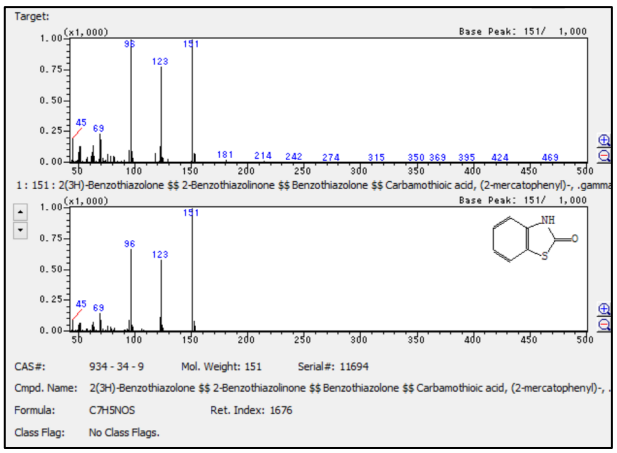

Fig. 12 Library Search Results for Peak No. 3

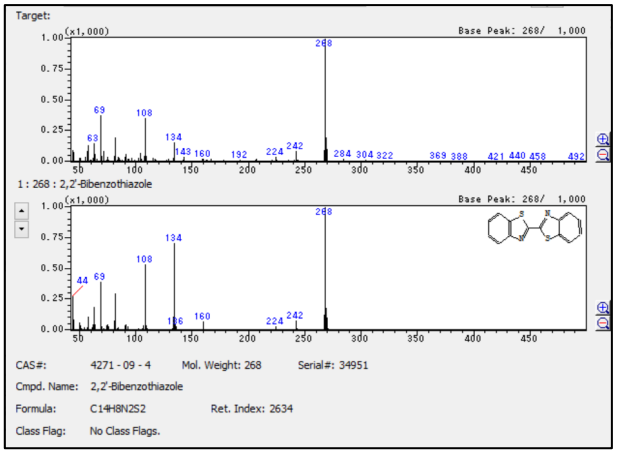

Fig. 13 Library Search Results for Peak No. 4

Library search results for Peaks No. 1 to 4 are shown in Figs. 10 to 13. All four had a similarity score of at least 80. Most of the peaks detected are assumed to be compounds derived from vulcanization accelerators.

■ Conclusion

By combining FPD (S) that selectively and sensitively detects sulfur compounds, with Py-GC-MS, sulfur compounds in tire rubber were easily detected and simultaneously analyzed qualitatively by the MS.

Acknowledgments

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References

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

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