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Application News

Using Deconvolution Analysis to Detect Vulcanizing Accelerator-Related Compounds in Tire Rubber

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User Benefits

- The deconvolution analysis feature in LabSolutions Insight Explore™ GCMS automatically detects and characterizes the peaks of trace amounts of compounds that are related to vulcanizing accelerators and other additives in tire rubber.
- The Polymer Additives Library Ver. 2 enables easy identification of the peaks of these additives.

■ Introduction

Vulcanizing accelerators are important additives used to improve wear resistance and other properties in tire rubber, so research and development of tire rubber requires analytical methods that provide detailed and accurate analysis of these compounds. Pyrolysis gas chromatograph mass spectrometer (Py-GC-MS), a commonly used technique that requires minimal sample pretreatment to analyze these vulcanizing accelerators, can detect and characterize both the vulcanizing accelerators and the compounds that are generated from the pyrolysis. (In this article, these compounds are referred to as "vulcanizing accelerator-related compounds.") However, the following two issues can prevent the detection and characterization of these compounds.

1. Py-GC-MS directly analyzes tire rubber samples with minimal pretreatment, and it produces a complex chromatogram due to the co-elution of a wide range of impurities, including various additives and other compounds generated by degradation of the base tire material.
2. Vulcanizing accelerators are altered chemically or consumed during tire rubber production due to the role they play in the vulcanization process. Any vulcanizing accelerator-related compounds that remain in the rubber after these chemical changes may only be present in very small amounts, making their detection difficult.

Deconvolution analysis is for detecting the peaks of trace-level components in chromatograms that also show numerous impurities.

This article describes using LabSolutions Insight Explore GCMS software, which offers simple tools for deconvolution analysis, and Py-GC-MS to determine vulcanizing accelerator-related compounds and other additives in tire rubber.

■ Analysis Methods

The analysis was performed using the GC-MS data that were presented in Application News No. 01-00901. About 0.5 mg of tire rubber was placed in a pyrolysis sample cup and additives in the sample were detected using a thermal desorption (TD)-GC/MS method (Fig. 1). The system used is equipped with a detector splitting system and a flame photometric detector (FPD(S)), so it can perform Py-GC-MS and Py-GC-FPD(S) simultaneously and detect sulfur compounds with a high degree of sensitivity and selectivity (Fig. 2). For more information about the equipment setup and conditions during analysis, please refer to the Application News article mentioned above.

Fig. 1 Adding the Tire Rubber Sample to the Analysis Equipment

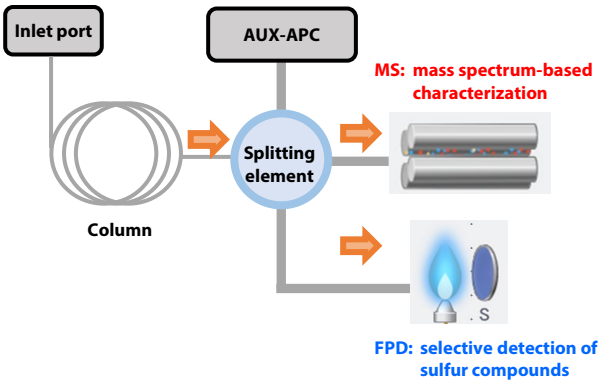


Fig. 2 Schematic Diagram of Simultaneous MS/FPD(S) Analysis with Detector Splitting System

The GC-MS data were subjected to deconvolution analysis by LabSolutions Insight Explore GCMS (Fig. 3) to detect and characterize vulcanizing accelerator-related compounds and other additives. Some of the compounds were characterized with the help of peaks detected by the FPD(S), which were recorded simultaneously with the GC-MS data. Detected compounds were characterized using a NIST mass spectral library (2023 version) and Shimadzu's Polymer Additives Library Ver. 2, which contains detailed information on a wide range of additives.

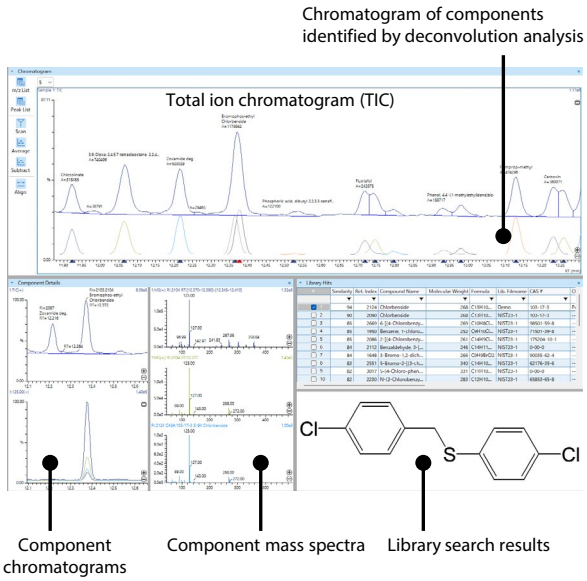


Fig. 3 Analysis Window in LabSolutions Insight Explore GCMS

■ Results

The vulcanizing accelerator-related compounds detected by the FPD(S) chromatogram, MS total ion chromatogram (TIC), and deconvolution analysis are shown in Fig. 4. FPD(S) is highly specific and sensitive for sulfur compounds, and the FPD(S) chromatogram shows the detection of multiple sulfur-containing compounds. All the major peaks (No. 1 to 6) detected were identified as sulfur-containing vulcanizing accelerator-related compounds, based on deconvolution analysis of the MS TIC. Application News No. 01-00901, which used the conventional method of confirming peak detection from TIC, was unable to detect and qualitatively identify compounds with particularly minute peaks No. 4 and 5.

Fig. 5 shows a magnified view of peak No. 4 in the TIC and the same peak after deconvolution analysis. This shows that deconvolution analysis enabled the automatic detection and characterization of very small peaks that were not readily discernible in the original TIC.

Fig. 6 shows the detailed analysis of peak No. 5. Although the library search listed 2-(p-fluorophenyl)-1-methylbenzimidazole as the top result (similarity: 76), the FPD(S) also detected peak No. 5, which suggests that the compound belonging to peak No. 5 probably contained sulfur. Checking the other library search results revealed that N-phenyl-2-benzothiazole, which contains sulfur, was listed second (similarity: 75), indicating that this is the compound detected as peak No. 5. As demonstrated here, peaks detected by the FPD(S) can be used as a reference to improve the accuracy of characterization by GC-MS.

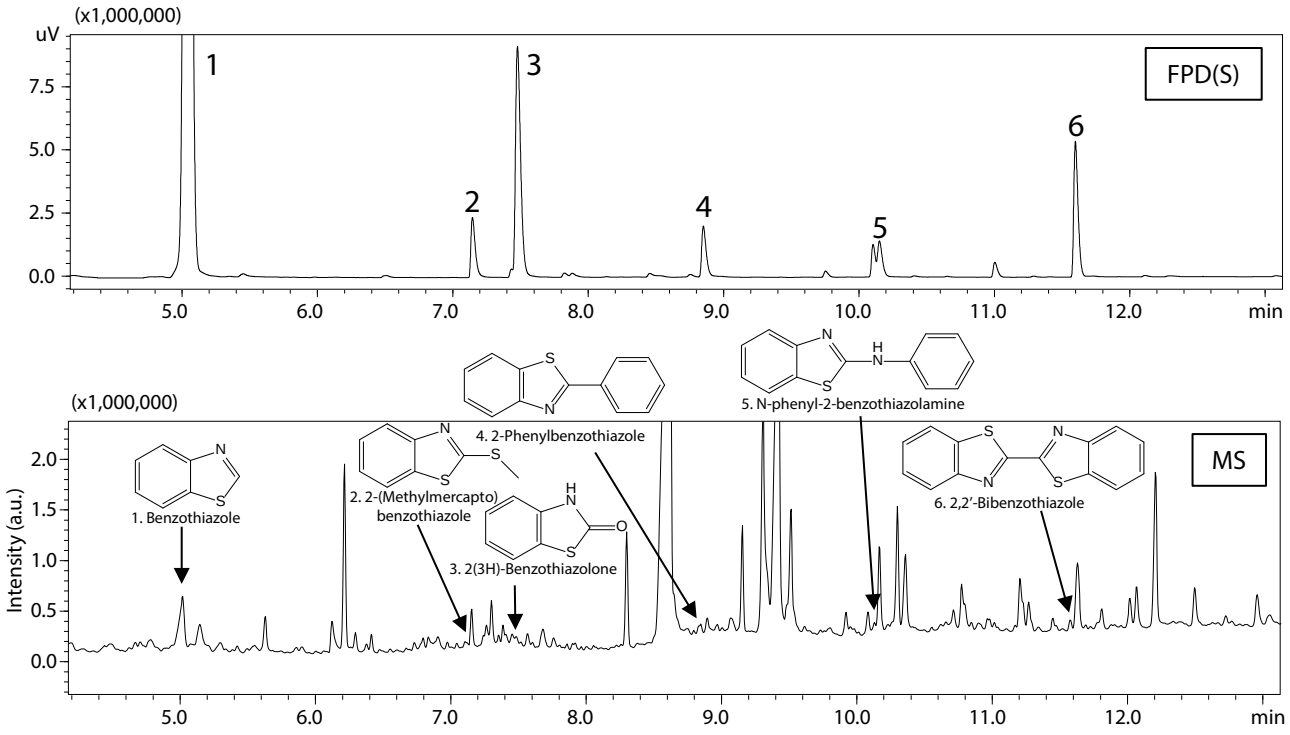


Fig. 4 Results Obtained Using Simultaneous Py-GC-MS/FPD(S) System

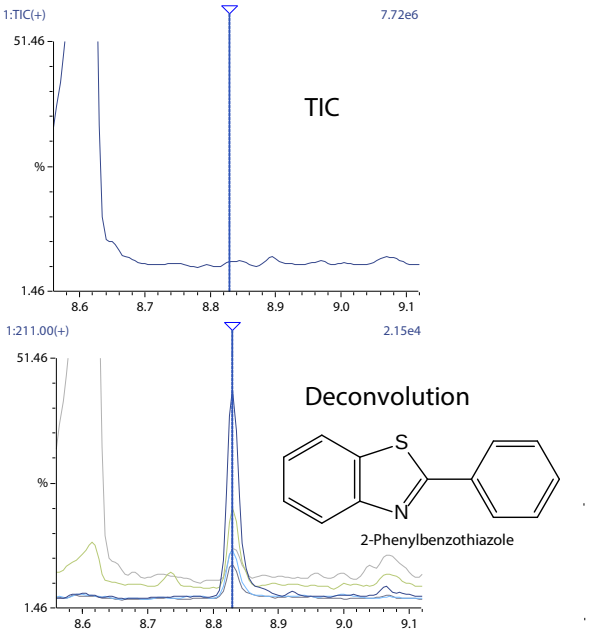


Fig. 5 Peak No. 4 Detection after Deconvolution Analysis

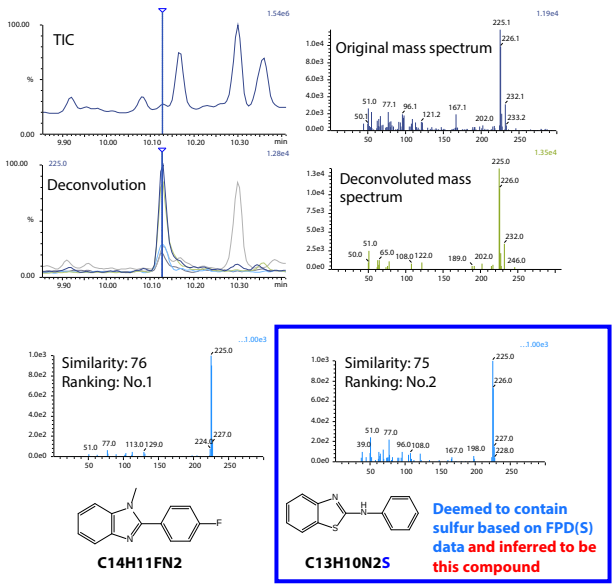


Fig. 6 Detailed Results of Peak No. 5 Analysis
(Characterization Accuracy Improved by FPD(S) Data)

The main compounds related with additives detected using deconvolution analysis are listed in Table 1. Compounds 1 to 6 are sulfur-containing compounds that were also detected by the FPD(S) and were estimated to be vulcanizing accelerator-related compounds, based on the classification data in Shimadzu's Polymer Additives Library Ver. 2. All six compounds contained a similar benzothiazole structure, which suggests that a benzothiazole-based vulcanizing accelerator was used in the tire rubber.

Compounds 7 to 9 were also derived from additives, but they were not from a vulcanizing accelerator. The Polymer Additives Library Ver. 2 identified that compound 7 was derived from the anti-degradant additive N-(1,3-dimethylbutyl)-N'-phenyl-p-phenylenediamine (6PPD), and compounds 8 and 9 were derived from the anti-degradant additive mono (or di or tri)(alpha-methylbenzyl) phenol. The classification data held on each additive in Polymer Additives Library Ver. 2 enabled detailed information to be obtained on the additives.

■ Conclusions

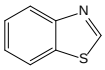
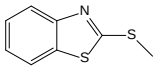
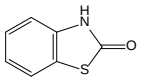
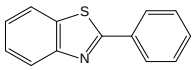
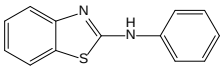
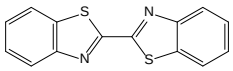
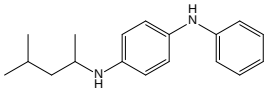
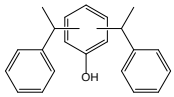
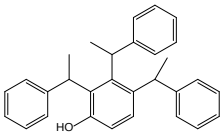
Using the deconvolution analysis feature in LabSolutions Insight Explore GCMS improved the accuracy for detecting very small peaks belonging to vulcanizing accelerator-related compounds that are difficult to discern in the TIC. Combining this analysis method with an FPD(S) that can detect sulfur compounds with excellent sensitivity and selectivity also improved the accuracy of compound characterization compared to MS alone. Furthermore, Shimadzu's Polymer Additives Library Ver. 2 was found to be an effective tool for characterizing compounds related to vulcanizing accelerators and other additives due to its extensive classification data on additives.

Acknowledgments
We are sincerely grateful to Yoshihiro Hatano of Hatano Automobile Industries for providing samples and other assistance in the preparation of this Application News.

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

Table 1 Major Additive-Related Compounds Detected Using Deconvolution Analysis

No.	Retention Time (min)		Structure	Compound Name	Classification
	MS	FPD(S)			
1	5.019	5.038		Benzothiazole	Vulcanizing accelerator-related compound
2	7.125	7.145		2-(Methylmercapto) benzothiazole	
3*	7.455	7.478		2(3H)-Benzothiazolone	
4*	8.829	8.85		2-Phenylbenzothiazole	
5	10.128	10.151		N-phenyl-2-benzothiazolamine	
6	11.575	11.599		2,2'-Bibenzothiazole	
7	10.300	-		N-(1,3-Dimethylbutyl)-N'-phenyl-p-phenylenediamine	Anti-degradant
8	10.897	-		Bis(alpha-methylbenzyl)phenol	Anti-degradant
9	13.323	-		2,3,4-Tris(1-phenylethyl)phenol	

* Identified using NIST23

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