SHIMADZU

Application News

Gas Chromatography Mass Spectrometry No.M257

Analysis of Rubber by Pyrolysis-GC/MS -Introduction of Detector Splitting System-

■ Introduction

The Shimadzu GC/GCMS Advanced Flow Technologies (dual oven multi-dimensional, backflush, heartcut, detector splitting, detector switching) offer effective techniques for enhancing gas chromatographic analysis.
The detector splitting system introduced here is a system that can provide multiple chromatograms simultaneously by post-column splitting of the column effluent to multiple detectors. Due to the large amounts of information that can be obtained in a single analysis, improved analytical productivity and identification accuracy can be anticipated.
A specialized detector splitting device is connected at the outlet of the analytical column, and the column outlet pressure is controlled using an Advanced Pressure Controller (APC). A restrictor tube (capillary column) connects the flow lines to the detectors.
The detector splitting system diagram is shown in Fig. 1, and a picture of the detector splitting device is shown in Fig. 2. In addition to the hardware, integrated software is provided to enable simple setting of multiple sets of analytical conditions, allowing simple method development in GCsolution and GCMS solution software. (See Fig. 3)
Here we introduce an example of analysis focusing on sulfur compounds in rubber by pyrolysis-GC/MS using a system in which a mass spectrometer (MS) is connected as detector 1, and the high sensitivity sulfur detector, FPD (S-mode), is connected as detector 2.

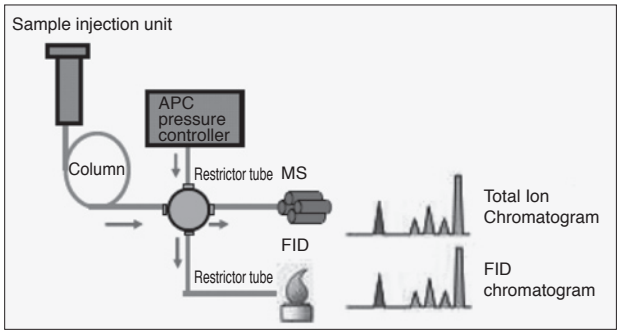

Fig. 1 Detector Splitting System

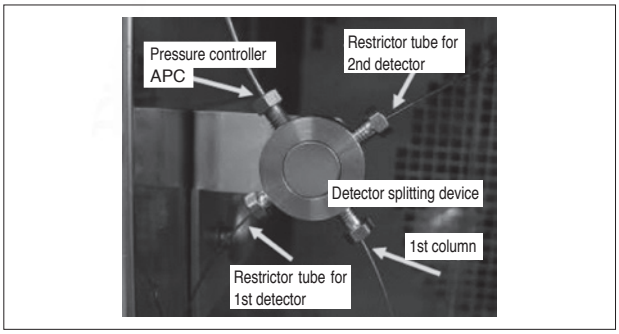

Fig. 2 Detector Splitting Device

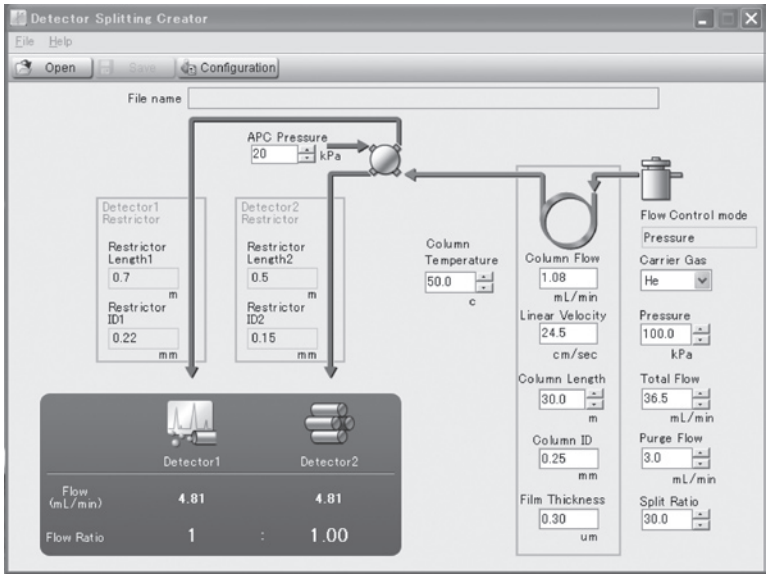

Fig. 3 Detector Splitting Software

■ Analysis

The vulcanizing agents and vulcanizing accelerators used in rubber products decompose and react within the rubber during the vulcanization reaction, making it impossible to identify the chemical structure of the initial raw material. Therefore, pyrolysis-GC/MS, a technique that can detect thermal decomposition products, is used for these types of qualitative analyses.

Although this method provides for easy analysis without sample pretreatment, detection of the sulfur compounds becomes difficult due to the appearance of a large quantity of hydrocarbon-derived substances that are the principal ingredients of rubber. On the other hand, the FPD (S-mode) detector can selectively detect sulfur compounds with high sensitivity. Here we report an example of qualitative analysis of sulfur compounds using an FPD and MS simultaneously.

Instantaneous pyrolysis (600 °C) of a 0.5 mg rubber sample was conducted, followed by gas chromatographic separation using a capillary column, and simultaneous analysis by MS and FPD (S), using the detector splitting system. The total ion chromatogram obtained from the MS is shown in Fig. 4, and the FPD (S-mode) chromatogram is shown in Fig. 5. Benzothiazole (C_7H_5NS) is the only sulfur compound that was detected as a major peak in the total ion chromatogram obtained from the MS. On the other hand, many peaks (S compounds) were obtained in the FPD chromatogram: these sulfur compounds, although represented as minor peaks in the TIC, could be identified by library searching of their mass spectra.

Table 1 Analytical Conditions

Model	: GCMS-QP2010 Plus		
-PY-	: PY-2020iD (Frontier Laboratories,Ltd)		
Py.Temp.	: 600 °C		
-GC-			
Column	: Rtx-5MS (30 m × 0.25 mm I.D. df = 0.25 µm)		
Col.Temp.	: 40 °C (3 min)-8 °C/min-320 °C (4 min)		
Carrier Gas	: He, 47.6 cm/sec		
Carrier Gas Mode	: Constant Linear Velocity Mode		
Inj.Temp.	: 300 °C		
Injection Method	: Split Injection		
Split Ratio	: 20 : 1		
Sample Amount	: 0.5 mg		
-Det1:MS-		-Det2:FPD(S)-	
I.F. Temp.	: 300 °C	Det.Temp.	: 320 °C
I.S. Temp.	: 230 °C	H_2 Gas	: 60 mL/min
Ionization Method	: EI	Air Gas	: 70 mL/min
Scan Range	: *m/z* 20-500		
Scan Interval	: 0.2 sec		

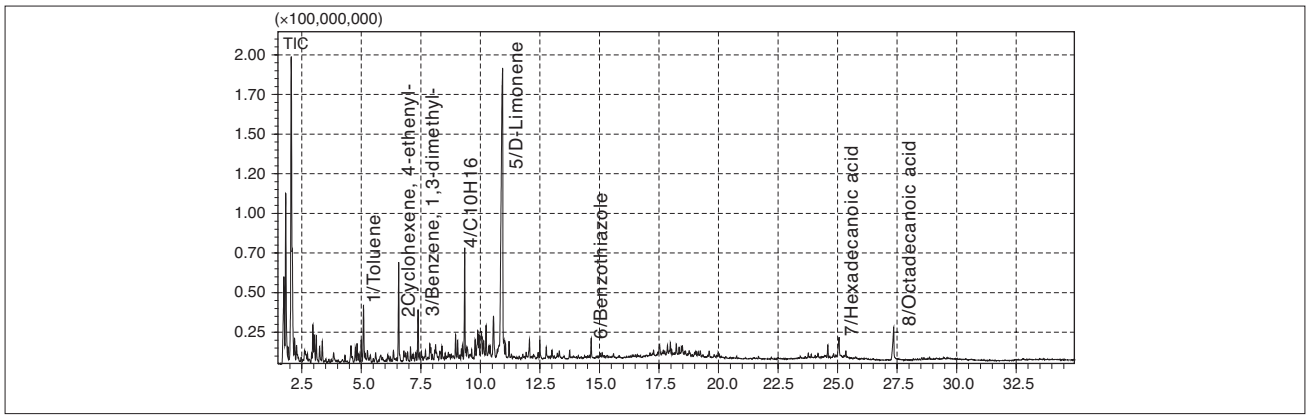

Fig. 4 Total Ion Chromatogram

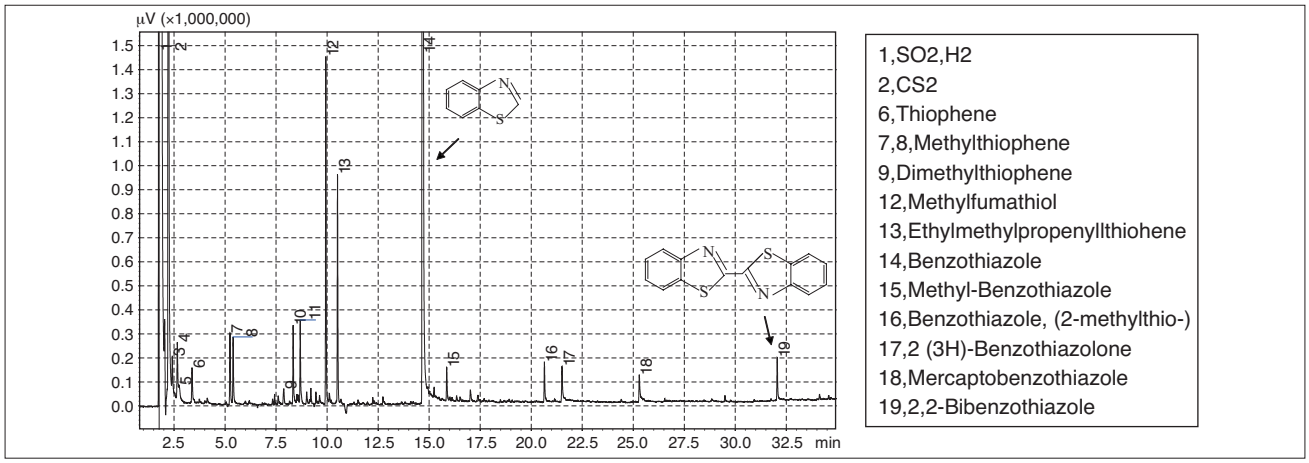

Fig. 5 FPD(S) Chromatogram

■ Conclusion

This system, which provides abundant information in a single analysis, not only cuts cost and time, but allows improved identification accuracy by using a selective detector.

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