

Analysis of Sulfur Compound in Gasoline by GC-FPD

In GC analysis using the FPD, if hydrocarbons and other foreign components are eluted in large quantity, a phenomenon known as quenching can occur. When quenching occurs, the effect is seen in the chromatogram, in which the response of the co-eluting compound fluctuates and a normal response cannot be obtained. In analysis of samples containing large amounts of hydrocarbons with trace amounts of sulfur components, as in the case of gasoline, it has been

assumed that the analysis is difficult because the separation is difficult. We introduce here an application in which the FPD-2014, with its redesigned FPD nozzle to accommodate both packed and capillary columns, was used along with optimization of the flow ratio of the combustion gases to investigate the reduction of quenching in analysis of a trace amount of a sulfur compound in gasoline.

■ Change in Selectivity Depending on Flow Ratio of Detector Gases

We investigated the changes induced in the sensitivity ratio of the hydrocarbon and sulfur compounds by varying of the flow rates of the FPD detector gases (hydrogen, air). Using n-hexane as the hydrocarbon and dodecanethiol as the sulfur compound, the sensitivity ratio was obtained and used as an index of selectivity.

As shown in Fig.1, by changing the hydrogen and air flow ratio, the response of both n-hexane and dodecanethiol changed greatly, indicating the change in selectivity. It is believed that the quenching effect can be reduced by conducting analysis using flow rate conditions that provide high selectivity.

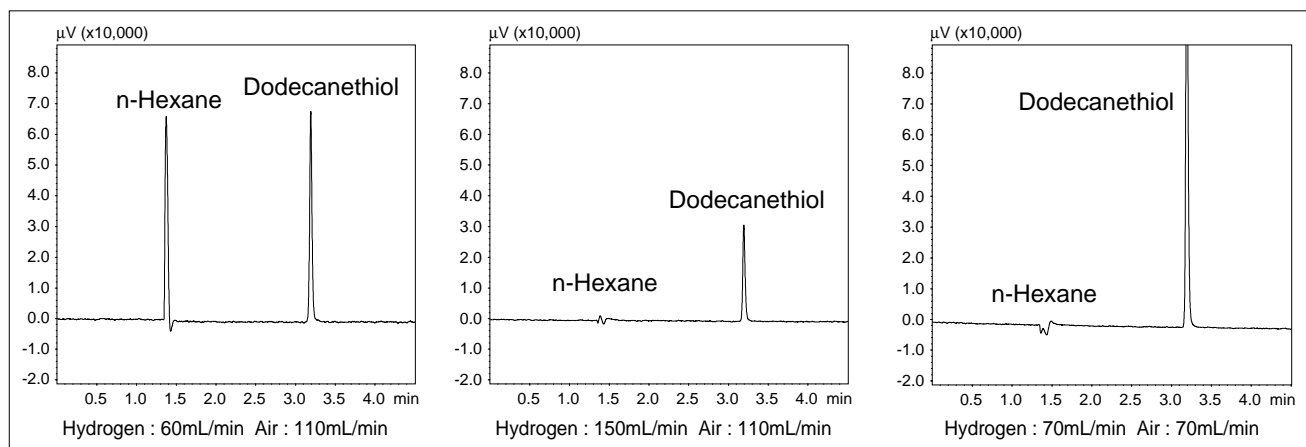


Fig.1 The Change of Selectivity Depending on the Ratio of Hydrogen-Air

Table 1 Analytical Conditions

Column	: Rtx-1 30m X 0.25mmI.D., df=0.25μm	Injection port	: 260°C	Split Ratio	: 1:20
Column Temp	: 180°C	Detector	: 260°C FPD S mode		
Carrier Gas	: He 150kPa(1.26mL/min, 35.3cm/sec)	Sample	: 10ppm Dodecanethiol / n-Hexane		

■ Analysis of Sulfur Compound in Gasoline

We investigated the applicability of selecting a hydrogen – air ratio to obtain a small hydrocarbon response without overly reducing the sulfur compound response in the analysis of the sulfur component in gasoline. To do this, the analytical column outlet for simultaneous detection by FID and FPD was bifurcated to enable comparison of the hydrocarbon component and sulfur component elution statuses.

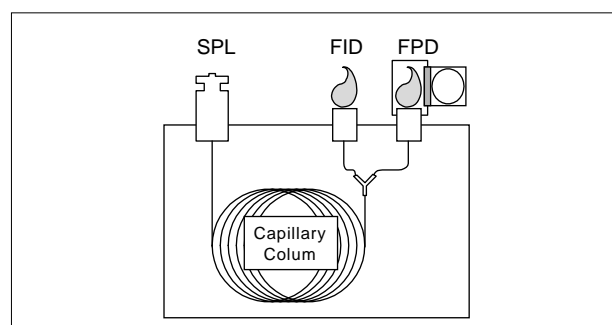


Fig.2 GC Configuration

Fig.3 shows chromatograms obtained from analysis of premium gasoline spiked with 10ppm thiophene, using simultaneous detection by FID and FPD in S mode. The analytical conditions are shown in Table 2. With a

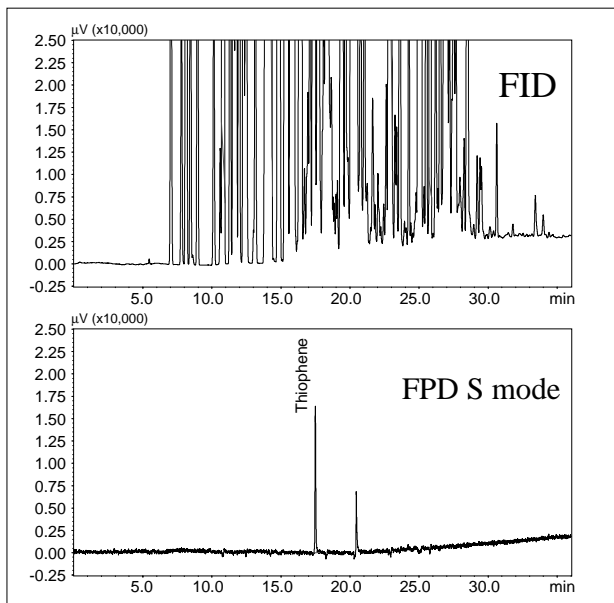


Fig.3 FPD and FID Chromatograms of Premium Gasoline with 10ppm Thiophene Added

Fig.4 shows chromatograms obtained from analysis of regular gasoline spiked with 1ppm thiophene, using simultaneous detection by FID and FPD in S Mode. With a split ratio of 1 : 10 and the two detectors in the branched configuration, it was clear that 1ppm thiophene could be adequately detected with almost no interference. However, when the split ratio is decreased, thereby increasing the quantity of

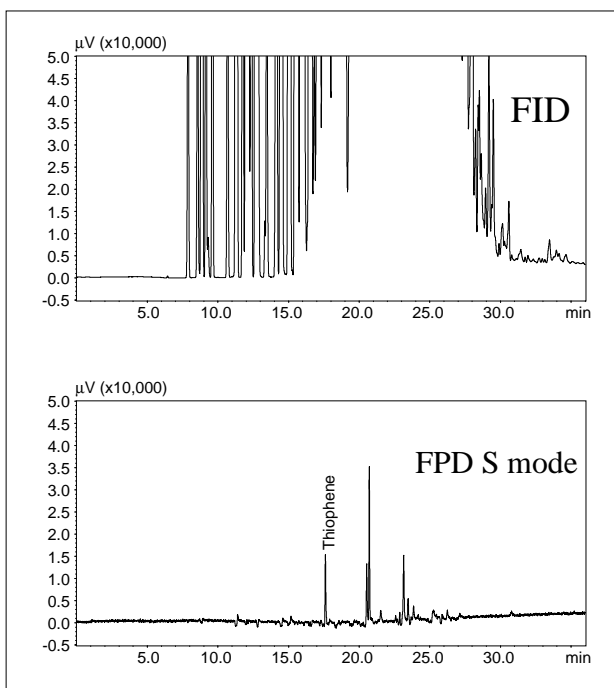


Fig.4 FPD and FID Chromatograms of Regular Gasoline with 1ppm Thiophene Added

split ratio of 1 : 30 and the two detectors in the branched configuration, it was clear that in the FPD S mode, analysis was possible without interference by the co-eluting hydrocarbons.

Table 2 Analytical Conditions

Column	: Rtx-1 60m × 0.32mm I.D., df=5.00μm
Column Temp	: 40°C(4min) - 10°C/min - 260°C(10min)
Carrier Gas	: He 23.7cm/sec Constant velocity mode (100kPa, 1.58mL/min)
Injection port	: 260°C
Detector	: FPD 260°C (S mode, Capillary nozzle)
	H ₂ : 90mL/min Air: 110mL/min
	FID 280°C
	H ₂ : 40mL/min Air: 400mL/min
	Make-up Gas: He 30mL/min
Sample	: Thiophene/Gasoline

hydrocarbon entering the detector, the quenching effect becomes large. To minimize the effect of quenching on the chromatogram, fine adjustment of the hydrogen – air flow ratio is necessary. For that reason, it is recommended to use an APC (electronic flow controller) for fine adjustment of the detector gas flow rates in order to optimize the analytical conditions.

Fig.5 shows the linearity of thiophene in premium gasoline when analysis was conducted using a 1 : 10 split ratio. When thiophene overlaps with a large hydrocarbon peak, the linearity deteriorates. To improve the linearity, either the separation must be improved or the split ratio must be increased to reduce the amount of hydrocarbon reaching the detector. The above demonstrates that when conducting high sensitivity analysis of a sulfur compound in a hydrocarbon sample, it is necessary to optimize the analytical conditions in consideration of quenching due to both sensitivity and foreign components, and it is also necessary to make fine adjustments to the instrument and the sample, as appropriate.

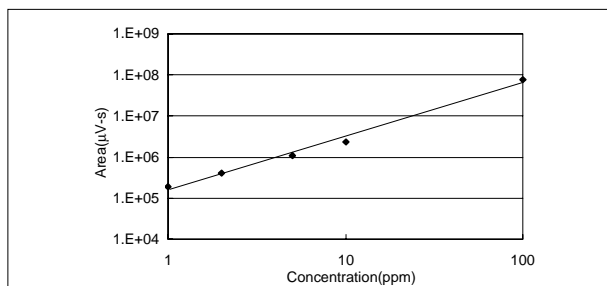


Fig.5 Calibration Curve of Thiophene in Premium Gasoline