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Application News

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Gas Chromatography

# Analysis of Thiophene in Benzene: Comparison of FPD(S) and SCD Analyses

The detectors chosen for trace analysis of sulfur compounds using gas chromatography are Flame Photometric Detector (FPD(S)) and Sulfur Chemiluminescence Detector (SCD) which offer highly sensitive and selective detection. These detectors have different detection characteristics for sulfur compounds because of their difference in the principles of detection. Therefore, looking at methods for analyzing thiophene in benzene, FPD is used in ASTM D4735 and SCD is used in D7011, but these methods analyze different concentration ranges of thiophene.

In this article, we measured results with FPD and SCD, and compared them to Flame Ionization Detector (FID), which is a general-purpose detector, through the analysis of thiophene in benzene as an example and described the differences between FPD and SCD.

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## Instrument Configuration and Analysis Conditions

Table 1 shows the instrument configuration and analysis conditions used in this analysis. FID and FPD employed hydrogen and air as the detector gases while SCD used hydrogen, nitrogen and oxygen.

Under the conditions for gas chromatography, SCD is a negative pressure system and FID/FPD are systems at atmospheric pressure. Therefore, the carrier gas linear velocity and column flow rate parameters will not match. In this analysis, the linear velocity was set to 37.7 cm/s for all the detectors.

## Comparison of Chromatograms with Each Detector

The results of analysis of a thiophene standard solution in benzene (10 ppm (v/v)) with each detector are shown in Fig. 1. In this figure, the chromatograms have been expanded and the baselines shifted to allow for easier comparison.

Benzene, the main compound of the mixture, was detected strongly with FID whereas it was obscured by both positive and negative peak shocks with FPD. With FPD, quenching by hydrocarbons may appear as a negative peak in the chromatogram, and depending on the state of separation of the analytes, this may adversely affect their peak shapes. Therefore, in analysis with FPD, it is important to confirm with FID in advance the elution positions of compounds other than the targets. On the other hand, benzene was hardly detected with SCD. This is because SCD has a higher selectivity than FPD for sulfur compounds.

**Table 1 Instrument Configuration and Analysis Conditions**

| | | |
|---|---|---|
| Main Unit | : | Nexis™ GC-2030/AOC-20i plus |
| Column | : | SH-WAX (30 m × 0.32 mm I.D., df = 1 µm) *1 |
| Injection Volume | : | 1 µL |
| Injection Mode | : | Split |
| Split Ratio | : | 1:15 |
| Injection Unit Temp. | : | 200 °C |
| Carrier Gas | : | He |
| Carrier Gas Control | : | Linear Velocity 37.7 cm/s |
| | | Column Flow |
| | | FID/FPD 2.20 mL/min |
| | | SCD 1.17 mL/min |
| Column Temp. | : | 75 °C |
| Detector | : | FID-2030 |
| Interface Temp. | : | 200 °C |
| Detector Gas | : | $H_2$ 32 mL/min, Air 200 mL/min |
| Makeup Gas | : | He 24 mL/min |
| Detector | : | FPD-2030 |
| Filter | : | S |
| Detector Temp. | : | 200 °C |
| Detector Gas | : | $H_2$ 40 mL/min, Air 60 mL/min |
| Detector | : | SCD-2030 |
| Interface Temp. | : | 200 °C |
| Furnace Temp. | : | 850 °C |
| Detector Gas | : | $H_2$ 100 mL/min, $N_2$ 10 mL/min, $O_2$ 12 mL/min, $O_3$ 25 mL/min |

*1 P/N: 221-75897-30

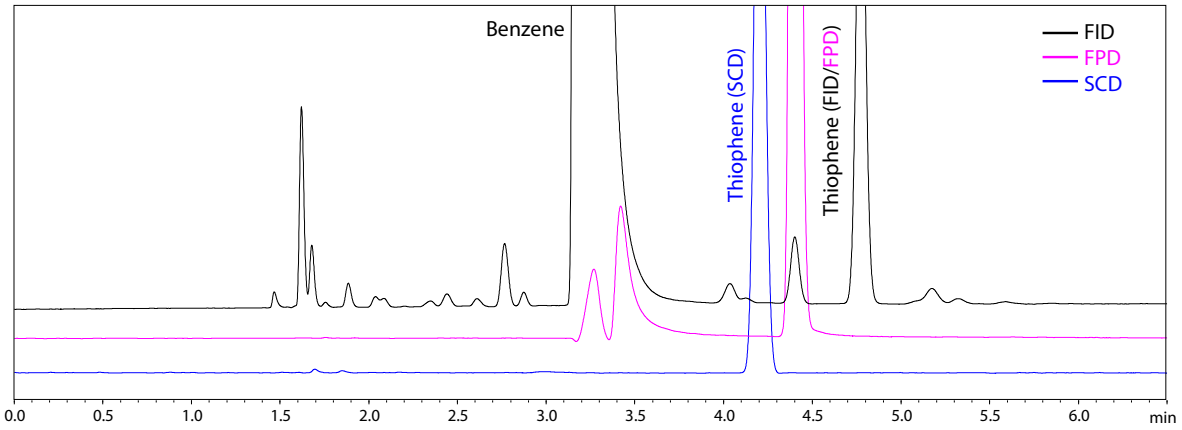


**Fig. 1 Comparison of Chromatograms of Thiophene in Benzene (10 ppm (v/v)) with Each Detector**
**The baseline is shifted for the purposes of the comparison, and expanded to give the noise levels for the FPD and SCD visual equivalence.**
**Also note that the FID, FPD and SCD were analyzed using different gas chromatographs, so the retention times are slightly different.**

## Sensitivity Comparison of FPD and SCD

Using the analysis conditions in Table 1, the standard solution of thiophene (0.1, 10 ppm (v/v)) was analyzed five times in a row, and the S/N ratios of the resulting thiophene peaks with each detector were compared (Table 2). At 0.1 ppm, a S/N ratio higher than that with FPD was obtained with SCD. On the other hand, at 10 ppm, the S/N ratio obtained with FPD was higher than that with SCD. These are because, SCD has better sensitivity for sulfur compounds than FPD, and detects down to lower concentrations, and the FPD obtains an area value proportional to roughly the square of the concentration due to its principle of detection.

**Table 2 S/N Ratio for Each Concentration of Thiophene with Each Detector (Average of n = 5)**

| Detector | Concentration, ppm (v/v) | |
|---|---|---|
| | 0.1 | 10 |
| FID | – | 92 |
| FPD(S) | 7.2 | 6085 |
| SCD | 13.6 | 1305 |

## FPD and SCD Calibration Curves

The standard solution of thiophene (0.05 to 10 ppm (v/v)) was analyzed, and the calibration curve obtained with FPD is shown in Fig. 2 while that obtained with SCD is shown in Fig. 3.

With FPD, a linear calibration curve was drawn with logarithms of both the area values and the concentrations, as its area value proportion to roughtly the square of the concentration. Note that its linear range is about $10^3$, so a calibration curve is usually created only in the vicinity of the concentration targeted in the analysis. In Fig. 2, a linear calibration curve was drawn for the range of 0.05 to 1 ppm or 0.5 to 10 ppm with $R^2$ of greater than 0.99.

With SCD, on the other hand, a linear calibration curve will be drawn with the actually measured concentrations and area values. The linear range is broader than with FPD at over $10^4$. As shown in Fig. 3, good linearity was obtained over the wide concentration range of 0.05 to 10 ppm.

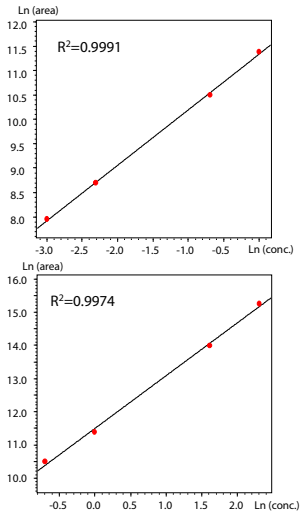


**Fig. 2 Calibration Curve for Thiophene Using FPD (Top: 0.05 – 1 ppm, bottom: 0.5 – 10 ppm)**

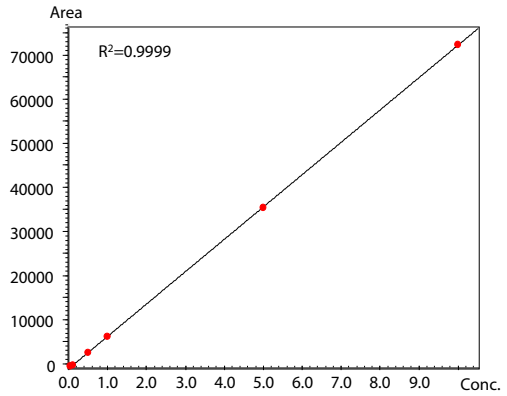


**Fig. 3 Calibration Curve for Thiophene Using SCD (0.05 – 10 ppm)**

## Comparison of Repeatability

Repeatability was examined with FPD and with SCD (Table 3) for the standard solution (0.05 to 10 ppm (v/v)) used to create the calibration curve. Though repeatability was acceptable with either detector, SCD proved to be the better of the two. The better repeatabillity by SCD was due to FPD's susceptibility to a peak shape distortion by coeluting hydrocarbons(e.g. benzene).

**Table 3 Area Repeatability of Thiophene with Each Detector (n=5)**

| Concentration ppm (v/v) | FPD | | SCD | |
|---|---|---|---|---|
| | Area Average Value µVs | Repeatability RSD% | Area Average Value µVs | Repeatability RSD% |
| 0.05 | 2852 | 7.21 | 325 | 5.37 |
| 0.1 | 5990 | 3.61 | 711 | 4.69 |
| 0.5 | 36022 | 1.78 | 3540 | 0.74 |
| 1 | 87598 | 1.77 | 7076 | 0.83 |
| 5 | 1176572 | 1.24 | 36318 | 0.21 |
| 10 | 4189355 | 0.54 | 73249 | 0.22 |

## Conclusion

We compared analyses of thiophene in benzene using Flame Photometric Detector (FPD(S)) and Sulfur Chemiluminescence Detector (SCD) which both offer highly sensitive and selective detection of sulfur compounds.

Although both detectors provide sufficient sensitivity and repeatability for the analysis of thiophene in benzene, more consideration needs to be given to the separation of sulfur compound subject to analysis from the other compounds in the case of FPD when compared to SCD.

In the gas chromatography analysis of sulfur compounds, SCD is a superior detector because it has higher selectivity and sensitivity than FPD, and provides good linearity over a wide concentration range. On the other hand, FPD can selectively detect compounds containing P or Sn when the optical filters are replaced. Select the appropriate detector for the equipment used and the purpose of the analysis.



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