SHIMADZU
Excellence in Science

Application News

No. G307A

Gas Chromatography

Analysis of Trace Thiophene in Benzene According to ASTM D7011 Using Nexis™ SCD-2030

Thiophene and other sulfur compounds are known for generating sulfur oxide upon combustion and also known as poisons in catalyst. For this reason, the quality control of petroleum products requires high-sensitivity analysis of sulfur compounds. In Application News No. G291, we introduced an analysis that employs gas chromatography using a Flame Photometric Detector (FPD).

ASTM D7011 introduces a method for analyzing trace thiophene in benzene by Sulfur Chemiluminescence Detector (SCD) at a level of approximately 0.03 mg/kg which is lower than what is conventionally analyzed with FPD.

The Nexis SCD-2030 next-generation sulfur chemiluminescence detection system (Fig. 1) with its best-in-class sensitivity and stability is capable of selectively detecting sulfur compound types with high sensitivity. This article shows an example of the analysis of thiophene in benzene at high sensitivity in conformance with ASTM D7011 and using the Nexis SCD-2030.

Y. Nagao

Fig. 1 Nexis™ SCD-2030

Instrument Configuration and Analysis Conditions

Table 1 lists the instrument configuration and analysis conditions. The GC analytical conditions according to ASTM D7011.

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
Detector	: SCD-2030
Injection Volume	: 1 µL
Injection Mode	: Split
Split Ratio	: 1 : 5
Injection Unit Temp.	: 125 °C
Carrier Gas	: He
Carrier Gas Control	: Constant Column Flow Mode (2.00 mL/min)
Column Temp.	: 40 °C (2 min) – 10 °C/min – 100 °C (1 min)
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

Analysis of Trace Thiophene

Standard solutions were prepared by diluting thiophene in thiophene-free benzene to concentrations between 10 and 1000 ppb (v/v) *1.

Fig. 2 shows four chromatograms comparing the thiophene elution positions of 10 ppb and 50 ppb thiophene, thiophene-free benzene and high purity benzene. As shown in Fig. 2, high purity benzene may contain several ppb of thiophene; consequently, and thiophene-free benzene is required in order to analyze thiophene in low ppb level.

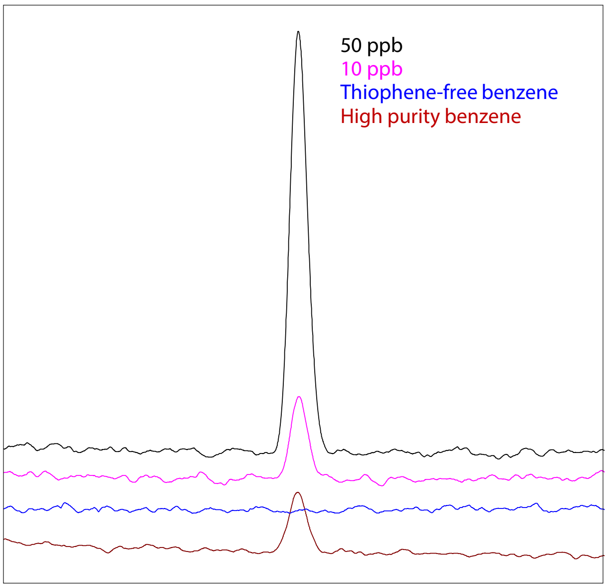

Fig. 2 Comparison of Thiophene Elution Positions of Trace Thiophene and Two Types of Benzenes
(Only high purity benzene was measured on a different day. The retention time was adjusted for comparison.)

*1 1000 ppb (v/v) ≈ 1.2 mg/kg

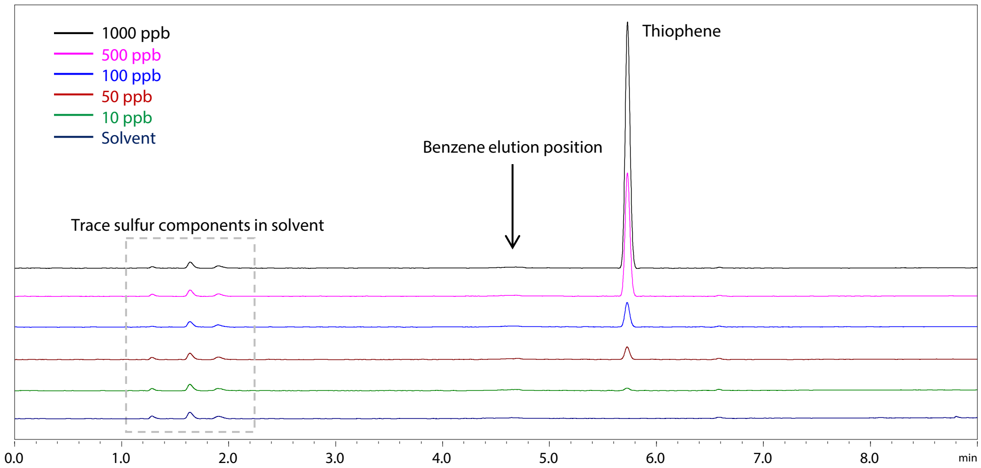

Fig. 3 Comparison of Chromatograms of Thiophene Standard Solutions (10 to 1000 ppb) and Solvent (Thiophene-Free Benzene)

Analysis of Standard Samples

Fig. 3 shows the results of analyzing the standard solutions. The baseline has been shifted in these results for comparing chromatograms. Note that the thiophene-free benzene used in this analysis contained trace sulfur components that were eluted one to two minutes into the retention time.

Table 2 lists the retention time and area repeatability (RSD%) and S/N average values obtained in analysis with n = 6. A sensitivity of S/N = 5.37 was observed for the 10 ppb thiophene. If we take the quantitative lower limit to be S/N = 10, the quantitative lower limit of this analysis can be calculated to be approximately 18 ppb. This demonstrates that this analysis system has a level of sensitivity capable of quantifying concentrations of thiophene lower than the 0.03 mg/kg (≈ 25 ppb (v/v)) specified in ASTM D7011.

Fig. 4 shows the calibration curve obtained from these standard samples. The R^2 value is higher than 0.9999, indicating good linearity. As with the GC-FPD method, introduced in Application News No. G291, due to its detection principle, a linear calibration curve must be created using the double logarithms of concentration and area for sulfur compounds. On the other hand, SCD allows the creation of a linear calibration curve based on the actual values of concentration and area of sulfur compounds.

Table 2 Retention Time and Area Repeatability and S/N Average with n=6

Concentration (ppb)	Retention time RSD (%)	Area RSD (%)	S/N Average
10	0.027	9.47	5.37
50	0.006	0.58	30.0
100	0.015	0.39	57.9
500	0.011	0.57	280
1000	0.013	0.51	544

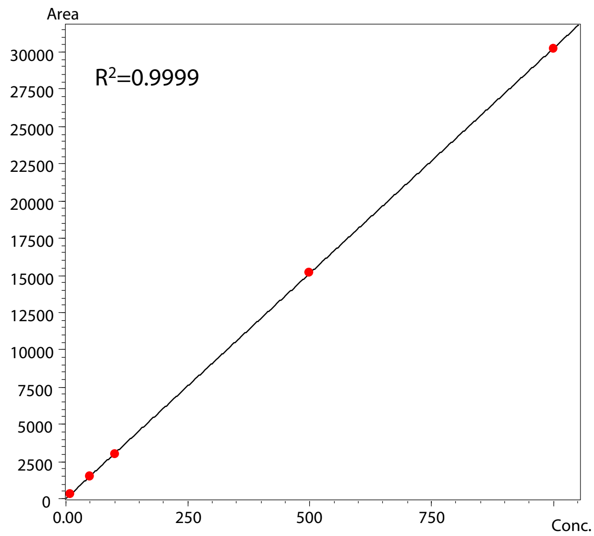

Fig. 4 Calibration Curve for Thiophene (10 to 1000 ppb)

Conclusion

We performed analysis of trace thiophene in benzene in conformance with ASTM D7011 using the Nexis SCD-2030 next-generation sulfur chemiluminescence detection system.

The Nexis SCD-2030 has best-in-class sensitivity and stability and demonstrated favorable sensitivity, repeatability, and linearity in this analysis. We determined that analyses according to ASTM D7011 are achievable by using this system.

SHIMADZU
Shimadzu Corporation
www.shimadzu.com/an/

First Edition: Jun. 2019
Revision A: Mar. 2023