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Application News

No. GC-007

Gas Chromatography

Trace Thiophene in Refined Benzene by GC with Nexis™ SCD-2030 Using Nitrogen Carrier Gas

■ Introduction

Determination of trace amounts of thiophene in refined benzene can be challenging due to the sensitivity required and potential detection of interference from the benzene matrix. Because of its sensitivity as well as selectivity, a gas chromatograph (GC) with sulfur chemiluminescence detector (SCD) allows trace amounts of thiophene to be accurately determined in a benzene matrix. Traditionally SCD requires using helium (He) carrier gas, which can be very costly due to a global supply shortage. In this application, we demonstrate that trace concentrations of thiophene can be successfully quantified in a benzene matrix using a Shimadzu Nexis™ SCD-2030 with nitrogen carrier gas.

■ Samples and Analytical Conditions/Experimental

An ASTM D7011 standard set was purchased from a chemical company, which contains the following standards: 0.02 mg/kg, 0.2 mg/kg, 0.5 mg/kg, 1.0 mg/kg and 2.0 mg/kg thiophene in benzene, as well as an unspiked benzene (blank). A Shimadzu GC-2030 equipped with a split/splitless injector and an SCD detector (Nexis™ SCD-2030) was used for this assay. The instrument settings are shown in Table 1.

Table 1: Instrument Configuration and Analysis Conditions

GC System	Shimadzu GC-2030 with SCD-2030 and AOC-20i Plus autosampler
Column	SH-Stabilwax, 30m x 0.32mm x 1.00µm
Injector Mode	Split at 1:5 ratio
Injection Volume	1µL
Carrier Gas	Nitrogen
Flow mode	Constant column flow at 2mL/min
Column Temp	40°C, 2 min – 10°C/min – 100°C, 1 min (total GC program 9min)
Interface Temp	150°C
SCD Furnace Temp	850°C
Detector Gases	H_2 100 mL/min, N_2 10 mL/min, O_2 12 mL/min, O_3 25 mL/min

■ Results and Discussion

The thiophene standards were assayed using nitrogen carrier gas per conditions described in ASTM D7011 method. Minimal interference was seen from benzene. However, a thiophene peak was observed in the purportedly thiophene-free, unspiked benzene blank. As shown in Figure 1, a significant thiophene peak is seen in the benzene blank (black trace). In contrast, no peak was seen in a hexane blank assayed after the highest calibration standard (pink trace).

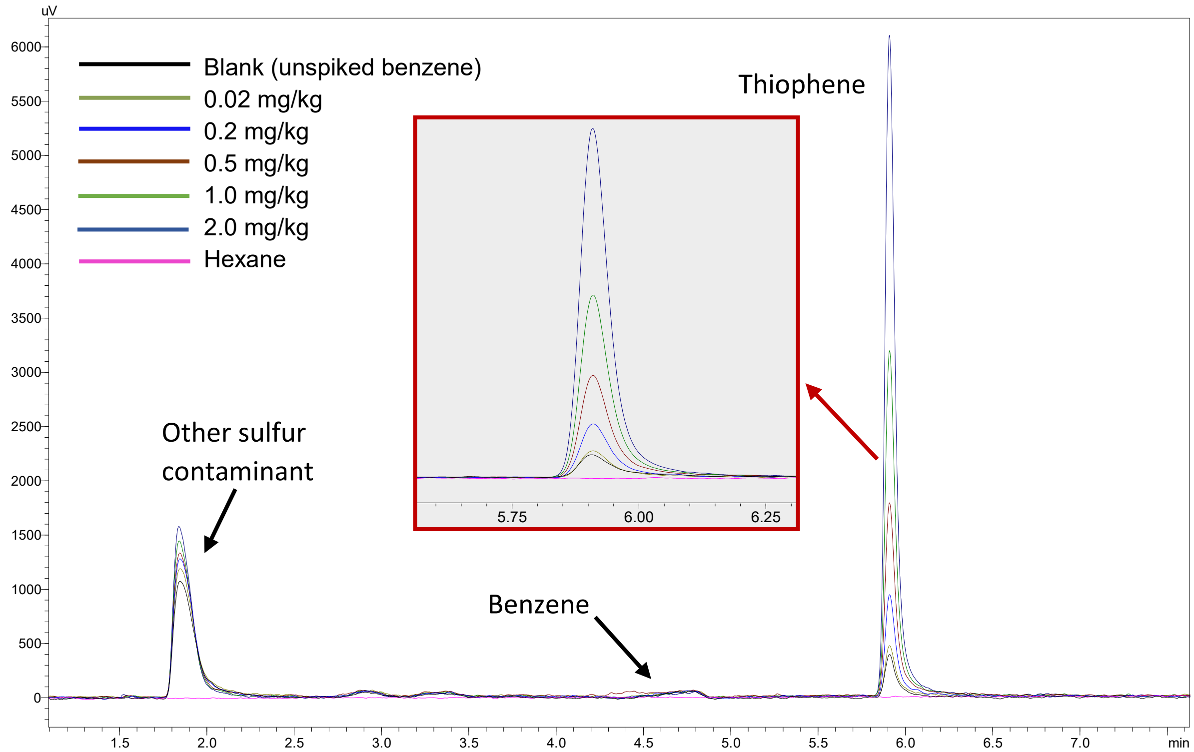

Figure 1: Example chromatograms of thiophene in benzene standards.

To investigate whether this was either an artifact of the system or the result of carryover, a sample of hexane was assayed before and after the benzene/thiophene samples. No thiophene peak was detected in the hexane injections before or after sample injections, indicating that the unspiked benzene blank contained a quantifiable amount of thiophene. This is not surprising, as it is very common for benzene to be contaminated with small amount of thiophene.

A five-point calibration curve was generated using the standards described above. The benzene blank still contains trace amount of thiophene. As a result, the calibration curve does not go through zero. Despite that, excellent linearity with $R^2 > 0.9999$ is obtained as can be seen in Figure 2.

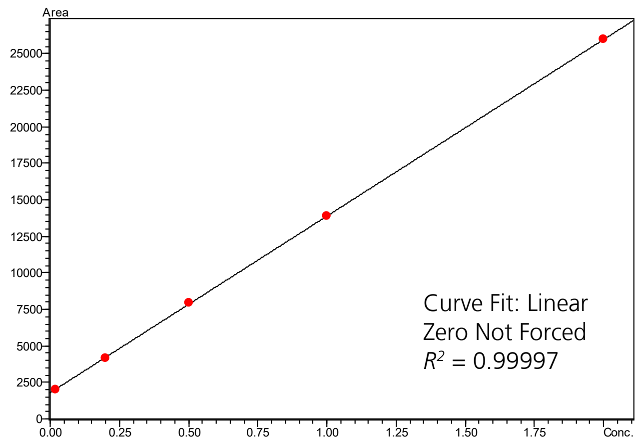

Figure 2: Five-point calibration curve of thiophene.

When using the standard addition calibration method, the concentration of thiophene in the benzene blank was determined to be 0.148 mg/kg. Unfortunately, this is above the amount allowed by the ASTM method (<0.02 mg/kg) to be considered thiophene-free benzene. Therefore, a future study using benzene of a higher purity grade will be needed.

Each standard and blank were analyzed four times and the results are shown in Table 2.

Table 2: Retention time and Area Repeatability and S/N for multiple injections (n=4).

Standard Sample	Retention Time % RSD	Area % RSD	Average S/N
0.02 mg/kg	0.0288	2.335	14.19
0.2 mg/kg	0.0123	2.732	33.85
0.5 mg/kg	0.0043	1.358	60.95
1.0 mg/kg	0.0138	0.665	107.89
2.0 mg/kg	0.0146	1.003	216.46
Blank (unspiked)	0.0302	1.982	13.07

The relative standard deviation (RSD) for multiple injections (n=4) are all under 3%, showing excellent repeatability. The % RSD for overall retention time for all 24 analyses in the table is 0.0207. Average signal to noise (S/N) for each sample is also shown.

■ Conclusion

Trace amounts of thiophene can easily be measured using Shimadzu GC with SCD-2030, due to the excellent sensitivity and selectivity. Furthermore, the Shimadzu SCD-2030 can work with nitrogen carrier gas in addition to traditional helium carrier gas, greatly reducing the cost of analysis. The SCD-2030 offers seamless integration with the GC system and software control, automatic start up, shutdown and conditioning, making operation of this detector streamlined and hassle-free.

■ References

- ASTM D7011-15, Standard Test Method for Determination of Trace Thiophene in Refined Benzene by Gas Chromatography and Sulfur Selective Detection, ASTM International, West Conshohocken, PA, 2015, www.astm.org
- Shimadzu application news No. G307, Analysis of Trace Thiophene in Benzene According to ASTM D7011 Using Nexis™ SCD-2030

■ Consumables

- 227-36252-01: SH-Stabilwax, 0.32mm x 1µm x 30m
- 227-35007-01: Deactivated split liners
- 036-11203-84: O-ring for liners
- 221-76650-01: Inlet septa
- 221-84141-41: SCD-2030 consumable kit

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