





Determination of Trace Thiophene in Refined Benzene by Gas Chromatography and Sulfur Selective Detection according to ASTM D7011-15

-  **Fast Analysis in < 10 minutes**
-  **Excellent Sensitivity, Repeatability & Linearity**
-  **Robust Solution using PAC SeNse Detector**
-  **No matrix interference**

Keywords: SeNse, Sulfur, Thiophene, Benzene, ASTM D7011-15

INTRODUCTION

The test method covers the determination of thiophene in refined benzene using gas chromatography and sulfur selective detection. The test method is applicable to the determination of thiophene at levels of 0.03 to 2.11 mg/kg on the SCD. A reproducible volume of sample is injected. Quantitative results are obtained by the use of the external standard calibration technique.

Benzene is a natural constituent of crude oil, and is one of the most basic petrochemicals. Because it is a known carcinogen, its use as an additive in gasoline is now limited, but it is an important industrial solvent and precursor to basic industrial chemicals including drugs, plastics, synthetic rubber, and dyes. At room temperature, Thiophene is a colorless liquid with a mildly pleasant odor reminiscent of benzene, with which Thiophene shares some similarities. The separation of Thiophene from benzene is difficult by distillation due to their similar boiling points (4 °C difference at ambient pressure). The majority of Thiophene is removed from the benzene fraction by washing with sulfuric acid, however traces will remain. The analysis of low concentrations Thiophene in benzene is necessary as it is a building block for many other aromatic chemicals.

The various ASTM specifications for benzene are based mainly on end-use requirements. The ASTM D2359 Refined Benzene 535 Grade specification is the least stringent, D4734 Refined Benzene 545 is higher quality. ASTM D5871, (standard specification for Benzene for Cyclohexane Feedstock) is the highest quality specification.

INSTRUMENTAL

The thiophene concentration in refined benzene is determined at the sub-mg/kg to low mg/kg level using gas chromatography with the SeNse Sulfur selective detector. The application is configured with a S/SL inlet and a polyethylene glycol (wax type) capillary column to separate the trace Thiophene component from Benzene. A reproducible volume of sample is injected. Quantitative results are obtained by the use of the external standard calibration technique.



LINEARITY

Calibration blends covering the range of determination of thiophene in benzene have been prepared (0.025, 0.24, 0.57, 1.20 and 2.36 mg/kg). Each standard solution and blank benzene are analyzed in duplo conform ASTM D7011. A calibration curve is created to determine method linearity. An overlay of the different levels in duplo is pictured in figure 1. A correlation coefficient (r^2) > 0,999 has been obtained (figure 2).

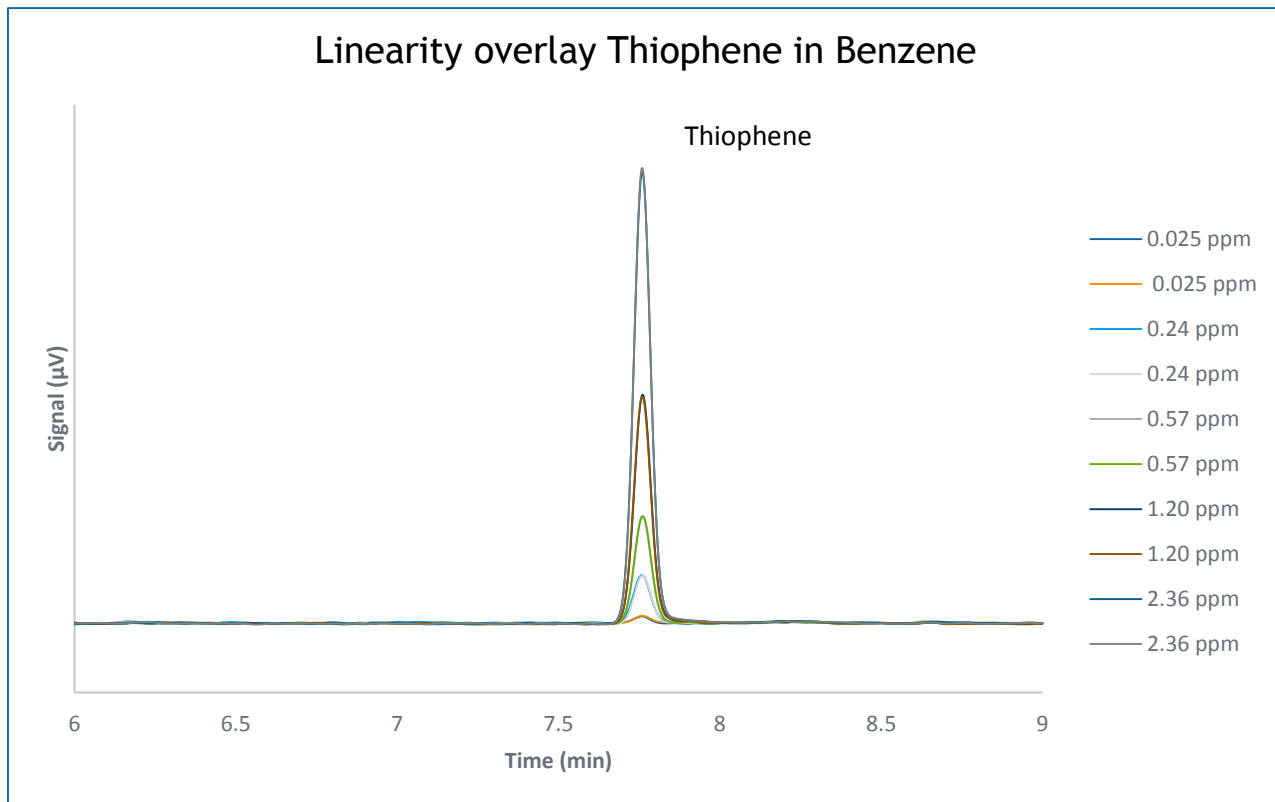


Figure 1: Overlay calibration solutions 0,025 – 2.36 mg/kg

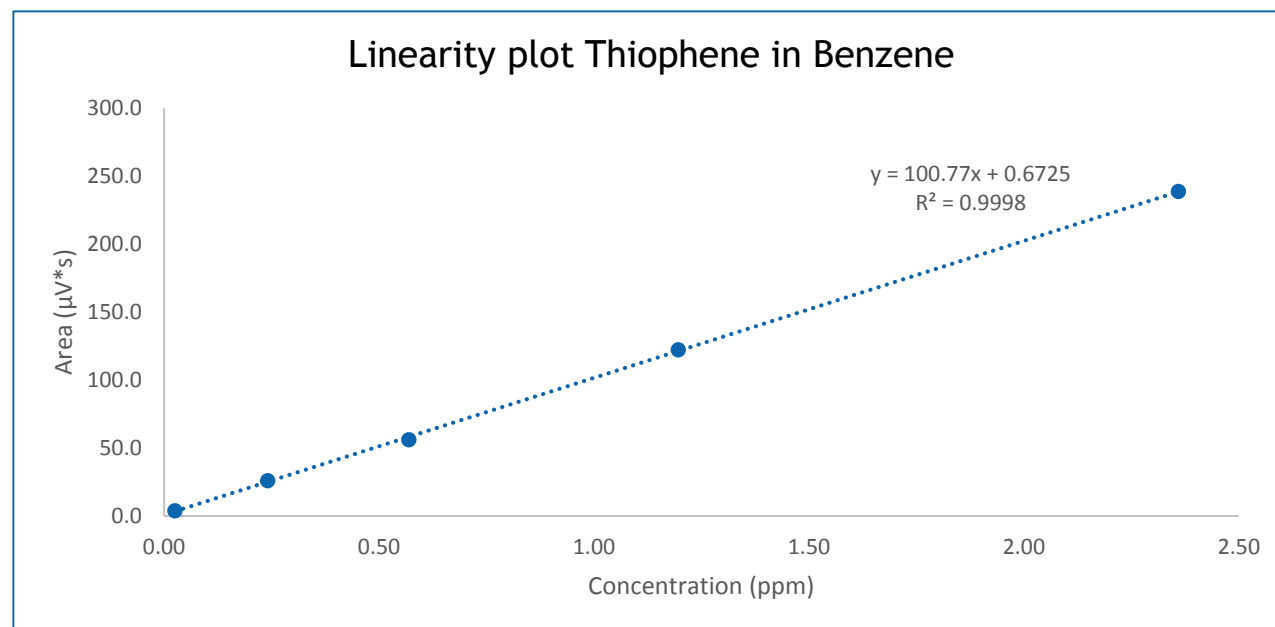


Figure 2: Linearity plot thiophene in benzene

MINIMUM DETECTABLE LEVEL

The application should meet a minimum detectable level (MDL) of less than 0.02 mg/kg thiophene in benzene. MDL can be calculated from the standard deviation (σ value in mg/kg) of repeated analyses close to the Quantification limit ($MDL = 6 \sigma$).

MDL is tested by analyzing the lowest calibration level (0.025 mg/kg) 10 times (figure 3). Also a blank sample (thiophene free benzene) is analyzed to measure background contaminants (figure 4). The benzene blank should contain less than 0.02 mg/kg thiophene according method D7011.

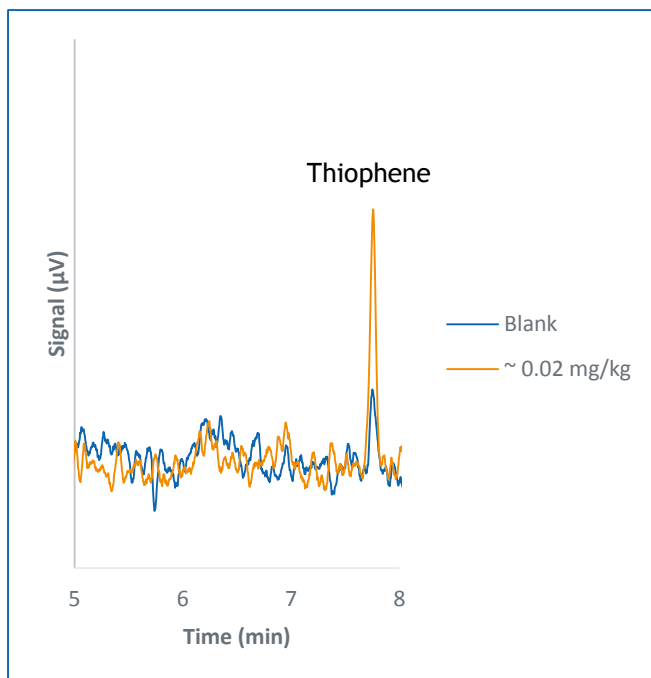
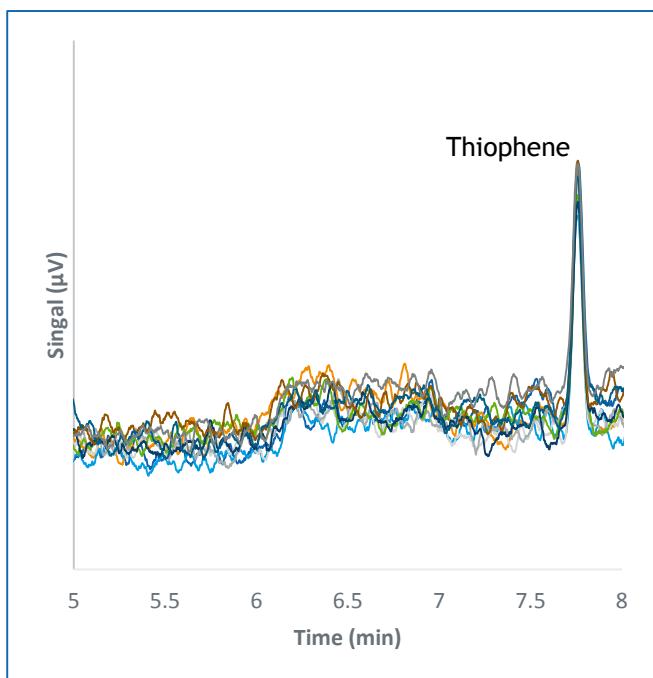


Figure 3: Repeatability Overlay MDL (0.025 mg/kg) (n=10) **Figure 4: ASTM D7011 Blank specification & MDL**

Run	Area ($\mu V \cdot s$)	Concentration (mg/kg)
1	4.09	0.0286
2	4.69	0.0337
3	4.01	0.0279
4	4.25	0.0300
5	4.38	0.0311
6	4.19	0.0294
7	3.90	0.0270
8	3.98	0.0276
9	4.02	0.0280
10	4.32	0.0305
MIN		0.0270
MAX		0.0337
Average		0.03
stdev		0.0020
RSD		6.89%
MDL ($6 \cdot \sigma$)		0.012

Table 1: MDL calculation

MDL is calculated by determining the standard deviation ($n=10$) close to the quantification limit (see table 1). The MDL is determined at ~ 0.012 mg/kg which is lower than the required 0.02 mg/kg.

The benzene blank is analyzed to measure background contaminants. A small thiophene peak is visible (estimated at ~ 0.005 mg/kg), which is clearly lower than the required 0.02 mg/kg.

REPEATABILITY

Repeatability of the analyzer is tested by analyzing the 0.57 mg/kg calibration blend (figure 5). The repeatability values are compared with the repeatability limit as mentioned in the D7011 table. The repeatability result is in agreement with the method (table 2).

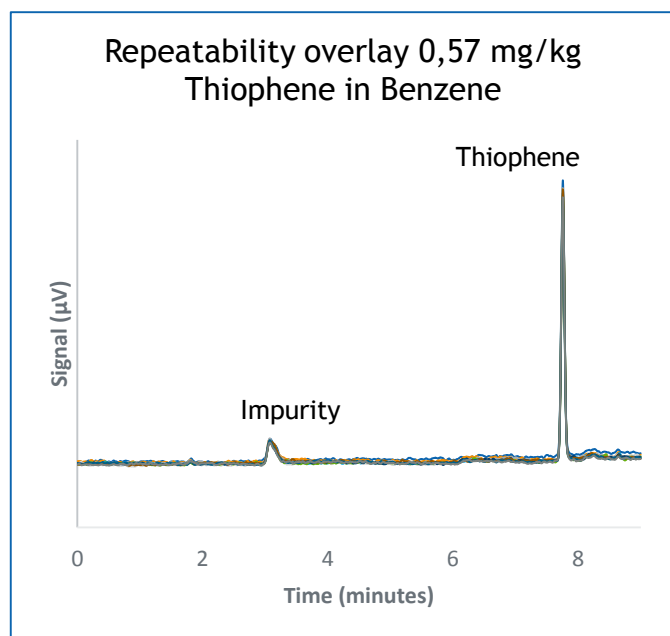


Figure 5: Repeatability Overlay 0.57 mg/kg (n=10)

Run	concentration (0.57 mg/kg)
1	0.59
2	0.57
3	0.56
4	0.56
5	0.57
6	0.55
7	0.55
8	0.56
9	0.55
10	0.55
Average	0.56
stdev measured	0.01
RSD	2.10%
r limit method	0.03
r measured (2.8 x stdev)	0.03

Table 2: Repeatability calculation

CONCLUSION

The AC D7011 analyzer is a dedicated solution for accurate determination of Thiophene in Benzene. Its performance not only meets but exceeds ASTM D7011 requirements, ensuring the best quality data that can be used to estimate effects of Thiophene in Benzene. The method complies with the various ASTM specification for benzene (ASTM D2359, D4734 and D5871)

The application with the novel AC SeNse detector, already well known for its stability and ruggedness, makes the AC D7011 system very robust and easy to use in routine environments. The AC D7011 analyzer provides low detection levels (down to < 20 mg/kg), excellent repeatability and recovery values every time.

AC Analytical Controls® has been the recognized leader in chromatography analyzers for gas, naphtha and gasoline streams in crude oil refining since 1981. AC also provides technology for residuals analysis for the hydrocarbon processing industry. Applications cover the entire spectrum of petroleum, petrochemical and refinery, gas and natural gas analysis; ACs Turn-Key Application solutions include the AC Reformulyzer®, DHA, SimDis, NGA, Hi-Speed RGA and Customized instruments.