Analysis of Thiophene in Benzene Using ASTM Methods and a Pulsed Flame Photometric Detector (PFPD)

Introduction

The ASTM International is a not-for-profit organization that provides a forum for the development and publication of voluntary consensus standards. The ASTM has established a specification of 1–ppm thiophene in refined benzene-535, and of 0.6–ppm thiophene in refined benzene-545. They have also published two standard test methods, ASTM methods D4735 [1] and D7011 [2], for the determination of trace levels of thiophene in refined benzene by gas chromatography with sulfur-selective detectors.

ASTM method D4735 specifies the use of either a flame photometric detector (FPD) or a pulsed flame photometric detector (PFPD), and ASTM method D7011 allows the use of any sulfur-selective detector provided that its performance meets the specified requirements and quality control (QC) criteria. The PFPD is the only sulfur-selective detector that is allowed for both methods.

This application note presents full instrument configuration and operating parameters for detection and quantitation of trace levels of thiophene in refined benzene using a PFPD and either ASTM method D4735 or D7011. Calibration curves, evaluations of precision, and analyses of thiophene in refined benzene using both methods are shown.

Instrumentation

Instrumentation used for this study included an OI Analytical Model 5380 PFPD (Figure 1) mounted on an Agilent 7890 GC.

Figure 1. Pulsed Flame Photometric Detector (PFPD) used for detection and quantitation of thiophene in benzene by ASTM methods D4735 and D7011.

PFPD Principle of Operation

Flame photometric detection has been used for many years to detect and quantify sulfur in petrochemical matrices, and although detector designs may vary, all flame photometric detectors have a common principle of operation. Sulfur compounds are combusted in a hydrogen-rich flame as they elute from the GC column. During combustion, the sulfur forms an excited-state sulfur dimer (S_2*) which emits a characteristic light energy as it relaxes to the ground state. The emissions from the S_2* range from very weak to very strong and encompass spectral wavelengths from about 300 to 500 nm. The emissions are detected by a photomultiplier tube (PMT) and the response of the PMT is quadratic and proportional to the amount of sulfur present. An optical filter is generally used to minimize interference from other emitting species and to optimize optical transmission.

In a conventional FPD, the flame remains static, and sulfur selectivity is achieved by using a narrow-band transmission filter that transmits a single band of light from the S_2* at 394 nm; all other sulfur emissions are blocked. An optical shield is sometimes used with the FPD to prevent hydrocarbon emissions from interfering and causing false positives or high background. By contrast, the PFPD uses a propagating flame that terminates within a quartz combustor. The kinetics of the gas phase reactions produced by the propagating flame result in light emissions with specific lifetimes; the S_2* emissions are chronologically separated from the hydrocarbon emissions. The time difference is responsible for the extreme sulfur-hydrocarbon selectivity of the PFPD, and eliminates the need for a narrow-band filter. Consequently, a broad-band transmission filter can be used with the PFPD, transmitting nearly all of the sulfur emissions between 300 and 500 nm and dramatically increasing sensitivity. Refer to Figure 2 for an illustration of PFPD operation.
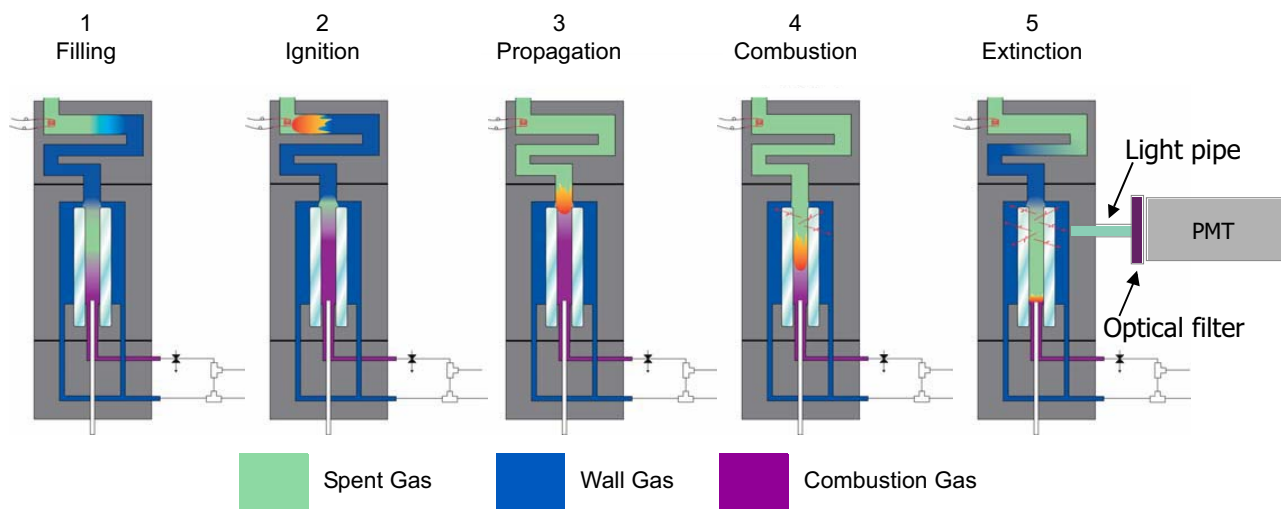

Figure 2. PFPD Principle of Operation

As a result of these design differences, the PFPD has several significant advantages over the conventional FPD including a 10-fold increase in sulfur-hydrocarbon selectivity, a 10-fold increase in sensitivity, and long-term flame stability with no flame outs. The gated electronics of the PFPD also enable a linear and equimolar sulfur signal for simplified calibrations, and the acquisition of two simultaneous, mutually selective chromatograms.

Experimental

An OI Analytical Model 5380 PFPD was mounted on an Agilent 7890 GC and configured for sulfur detection as described in Table 1. To demonstrate the proficiency of the PFPD as applied to the detection and quantitation of thiophene in benzene, a four-point calibration curve was generated covering the anticipated range of thiophene concentrations in the test samples. Two sets of "blind" samples of thiophene in benzene were acquired from a third party vendor, and each sample was analyzed in triplicate. Concentrations were calculated using the external calibration curve and compared to their expected concentrations.

Table 1. Instrument Configuration and Operating Conditions

PFPD Detector	OI Analytical Model 5380 PFPD
Detector	2-mm combustor, BG-12 broadband optical filter H_2/air ratio tuned for sulfur, 250 °C 6-24 msec sulfur gate, linear acquisition mode
Gas Chromatograph	**Agilent 7890 GC**
Injection Port	Split/Splitless operated in the split mode Temperature 200 °C Split ratio 12-to-1*
Column	DB-WAX, 30-m x 0.25-mm I.D. x 0.5-μm film Helium carrier gas, 1.5 mL/minute Constant Flow mode
Oven Program	50 °C for 1.0 minute 10 °C/minute to 100 °C, hold for 1.0 minute Total run time 7 minutes
***See Results and Discussion section**	

Results and Discussion

The calibration range spanned the anticipated concentration range for thiophene in benzene in the "blind" samples, as well as the specified concentrations of thiophene in refined benzene established by ASTM. Each of the four calibration standards were analyzed in triplicate. The percent Relative Standard Deviations (%RSD) were well below 1% for all four concentration levels, and the correlation coefficient (R^2) for the linear calibration curve was 0.9991. Calibration results are shown in Table 2 and Figure 3.

Table 2. Calibration Data for Thiophene in Benzene

Concentration	0.5 ppm	1.0 ppm	1.5 ppm	2.0 ppm
Rep 1 Response	681.5	1,648.4	2,679.5	3,772.3
Rep 2 Response	678.3	1,639.6	2,693.1	3,723.3
Rep 3 Response	684.2	1,633.2	2,657.5	3,777.6
Average Response	*681.3*	*1,640.4*	*2,676.7*	*3,757.7*
%RSD	*0.4*	*0.5*	*0.7*	*0.8*
R^2 for all 12 injections=0.9991				

Thiophene in Benzene Calibration Curve
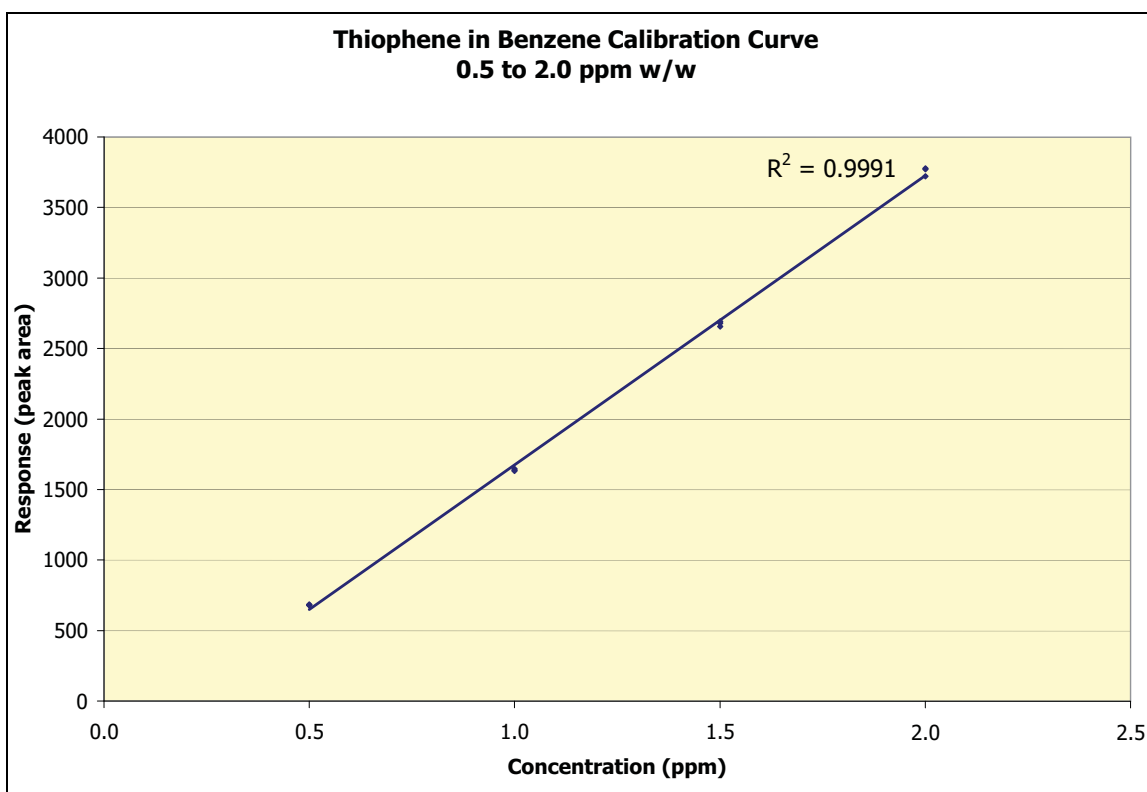**0.5 to 2.0 ppm w/w**

$R^2 = 0.9991$

Figure 3. Calibration curve for thiophene in refined benzene

One set of six "blind" test samples for method D4735 was acquired from a third party vendor. The six samples were analyzed in triplicate, with all RSDs well below 2%. After the analyses were completed, the calculated concentrations were compared to the expected concentrations. Recoveries ranged from 96.1% to 99.2% for five of the six samples; the sixth sample was pure benzene and had not been spiked with thiophene. Results are shown in Table 3.

Table 3. ASTM Method D4735 Test Sample Results

Sample ID	A	B	C	D	E	F
Expected Concentration	0.0 ppm	1.85 ppm	2.20 ppm	1.20 ppm	0.60 ppm	0.80 ppm
Rep 1 Conc (ppm)	0	1.80	2.18	1.15	0.58	0.78
Rep 2 Conc (ppm)	0	1.81	2.19	1.16	0.60	0.78
Rep 3 Conc (ppm)	0	1.79	2.18	1.15	0.59	0.79
Average Conc (ppm)	0	1.80	2.18	1.15	0.59	0.78
%RSD	*N/A*	*0.6*	*0.5*	*0.4*	*1.6*	*1.4*
%Recovery	*N/A*	*97.3%*	*99.2%*	*96.1%*	*98.3%*	*97.9%*

One set of seven "blind" test samples for method D7011 was also analyzed in triplicate. As with the first set of samples, one sample was blank benzene and had not been spiked. The seventh sample, Sample G, had been spiked with thiophene at a significantly lower concentration, 0.03 ppm (30 ppb), which could not be detected with the conditions listed in Table 1. The split ratio was reduced from 12-to-1 to 3-to-1, and the 30–ppb thiophene was easily detected and quantified using a separate calibration curve. Results for the D7011 test samples are shown in Table 4. One chromatogram of the 30–ppb thiophene test sample is shown in Figure 4.

Table 4. ASTM Method D7011 Test Sample Results

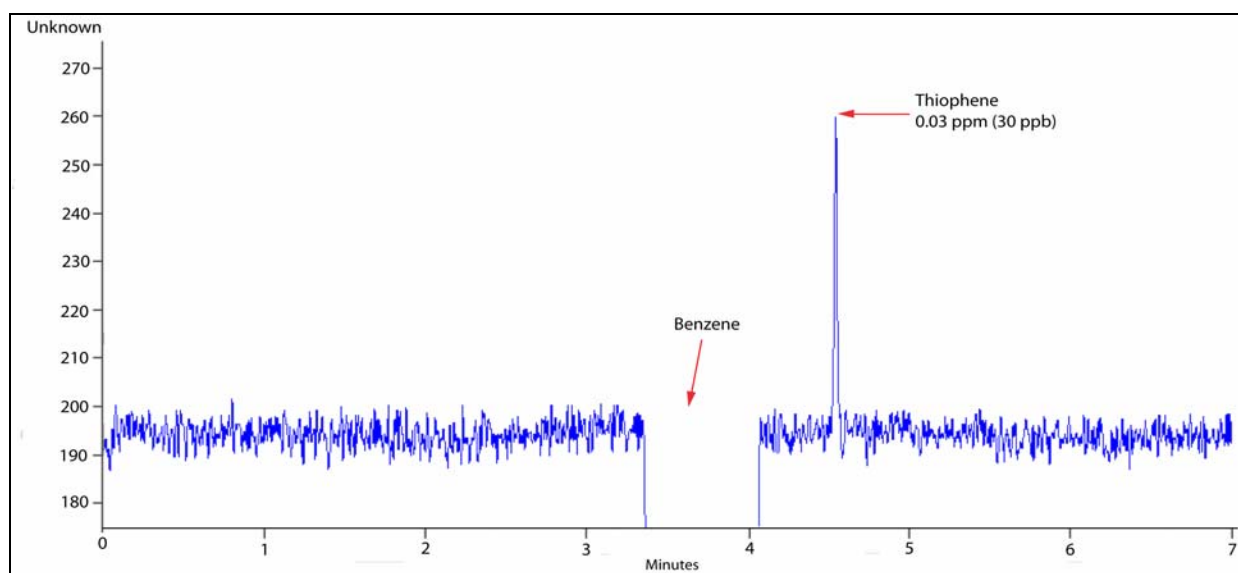| Sample ID	A	B	C	D	E	F	G*
Expected Concentration	0.80 ppm	1.00 ppm	1.85 ppm	1.20 ppm	0.0 ppm	0.60 ppm	0.03 ppm
Rep 1 Conc (ppm)	0.77	0.98	1.78	1.12	0	0.59	0.030
Rep 2 Conc (ppm)	0.77	0.96	1.84	1.12	0	0.58	0.027
Rep 3 Conc (ppm)	0.77	0.97	1.83	1.09	0	0.57	0.027
Average Conc (ppm)	0.77	0.97	1.82	1.11	0	0.58	0.028
%RSD	*0.3*	*1.3*	*1.9*	*1.5*	*N/A*	*1.2*	*1.1*
%Recovery	*96.3%*	*97.0%*	*98.2%*	*92.5%*	*N/A*	*96.7%*	*93.3%*
***See Results and Discussion section**							

Figure 4. PFPD chromatogram of thiophene in benzene at 0.03 ppm (30 ppb)

Conclusion

The Pulsed Flame Photometric Detector (PFPD) is ideally suited for analysis of thiophene in benzene using ASTM methods D4735 and D7011, and easily meets all requirements and QC criteria in both methods. The long-term stability of the PFPD and linear sulfur response provide the user with a detection system that is easy to use and requires little or no routine maintenance.

References

1. ASTM Standard D4735, 2002, "Standard Test Method for Determination of Trace Thiophene in Refined Benzene by Gas Chromatography," ASTM International, West Conshohocken, PA, www.astm.org

2. ASTM Standard D7011, 2004, "Standard Test Method for Determination of Trace Thiophene in Refined Benzene by Gas Chromatography and Sulfur Selective Detection," ASTM International, West Conshohocken, PA, www.astm.org

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