O·I·Analytical

ISO 9001

A Newly Approved ASTM Standard For Analysis of Thiophene in Benzene Using a Pulsed Flame Photometric Detector (PFPD)

Introduction

The ASTM Standard D4735-96, first approved in 1996 and reapproved in 2000, is a standard test method for the determination of trace levels of thiophene in benzene by gas chromatography with a flame photometric detector (FPD). The standard was recently reapproved in mid-2002 with modifications to include the use of the next generation of FPDs, the Pulsed Flame Photometric Detector (PFPD). Additionally, the method was upgraded to include the use of capillary columns. This application note presents data that were used to develop the new standard using the OI Analytical Model 5380 PFPD, including calibration range and linearity, precision and accuracy, intermediate repeatability, and ultimate sensitivity. All instrument configuration and operational parameters are included.

The detector specified in the original ASTM standard was "any flame photometric detector" that would meet the performance criteria outlined in the method. The PFPD, shown in Figure 1, is often referred to as the newest generation of flame photometric detectors and brings with it a 10-fold increase in both sensitivity and selectivity over the older FPDs. The PFPD has the added advantage of providing an equimolar response to sulfur, which the FPDs were not capable, and allows quantitation of unknown sulfur compounds that may also be present in the matrix. The PFPD also has the ability to achieve significantly lower analytical detection limits than the FPD. The PFPD's linearized square root function output permits the easy use of either linear or quadratic calibration curves. These features, along with its improved stability, reduced gas usage, and minimal maintenance requirements, make the PFPD the ideal and logical choice of detectors for this method.

The objective of this project was to establish instrument operating conditions using the PFPD that would meet or exceed performance criteria outlined in Standard D4735-96. Performance objectives to be demonstrated include the following:

- Calibration linearity
- Precision and accuracy
- Intermediate repeatability
- Ultimate sensitivity

Figure 1. The Model 5380 Pulsed Flame Photometric Detector (PFPD) is often referred to as the newest generation of flame photometric detectors.

Experimental

The PFPD was installed on an Agilent 6890N platform with a split/splitless injector. The PFPD was configured for selective sulfur detection and all injections were made with a liquid autosampler. Column selection is critical to ensure that the thiophene is sufficiently separated from the benzene matrix peak. The Carbowax®-type columns have been shown to perform best for this type of separation. Complete instrument configuration and operating conditions are listed in Table 1.

Table 1. Instrument Operating Conditions for ASTM Standard D4735-96

Parameter	Setting
Injection	Injector temperature 200°C; 1-µL injection; 50:1 split ratio
GC Column	DB-WAX, 30 m x 0.25 mm I.D. x 0.5-µm film; He carrier gas; constant flow mode
Oven Program	50°C for 1 minute; 10°C/minute to 200°C; hold for 1 minute
Detector Conditions	OI Analytical Model 5380 PFPD; 2-mm combustor; BG-12 broadband optical filter; 6–25 msec sulfur gate H_2/air gas ratio tuned for sulfur; 250°C; data acquired in both linear and quadratic mode

A stock solution of 100 ppm thiophene in benzene from Absolute Standards (part #92715) was diluted to prepare calibration and repeatability test standards. Benzene for preparation of standards was ACS Spectranalyzed® grade from Fisher Scientific and was certified to be "thiophene free." The benzene was demonstrated to be free of thiophene (i.e., below the detection limit with an injection volume five times the amount used for this method) prior to use by chromatographic analysis, as shown in Figure 2.
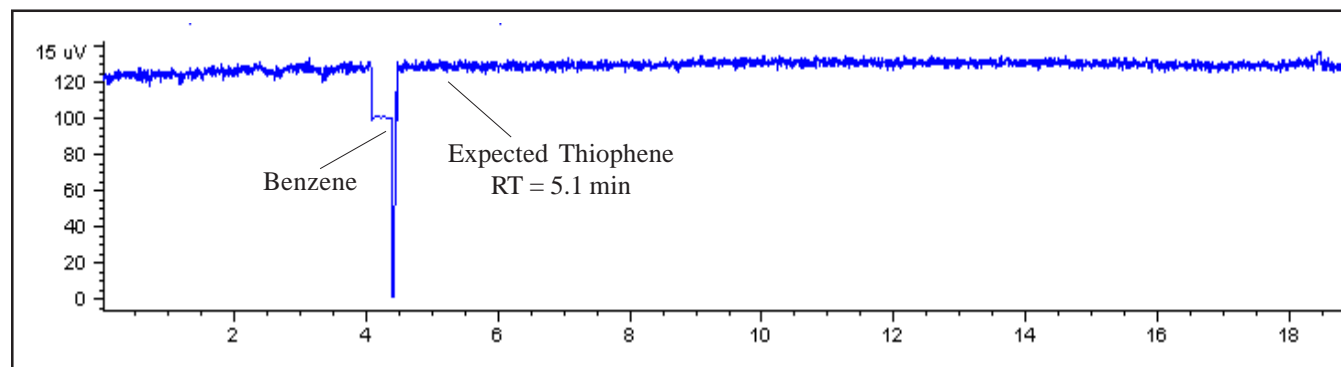

Figure 2. Chromatogram of "Thiophene-free" Benzene Used to Prepare Analytical Standards. Analysis was Performed Using a 1-µL Injection and a 10:1 Split Ratio (5x the Amount Used for the Method). No Thiophene was Detected at the Expected Retention Time.

Results and Discussion

Calibration

Six calibration standards spanning a range from 0.5–5.0 ppm thiophene were prepared and analyzed in triplicate using the conditions described above. The calibration curve was created using the average integrated peak areas at each concentration. Chromatograms of the 0.5 and 3.0 ppm standards are shown in Figure 3. Relative standard deviations over the 3 replicate injections for each concentration are shown in Table 2.
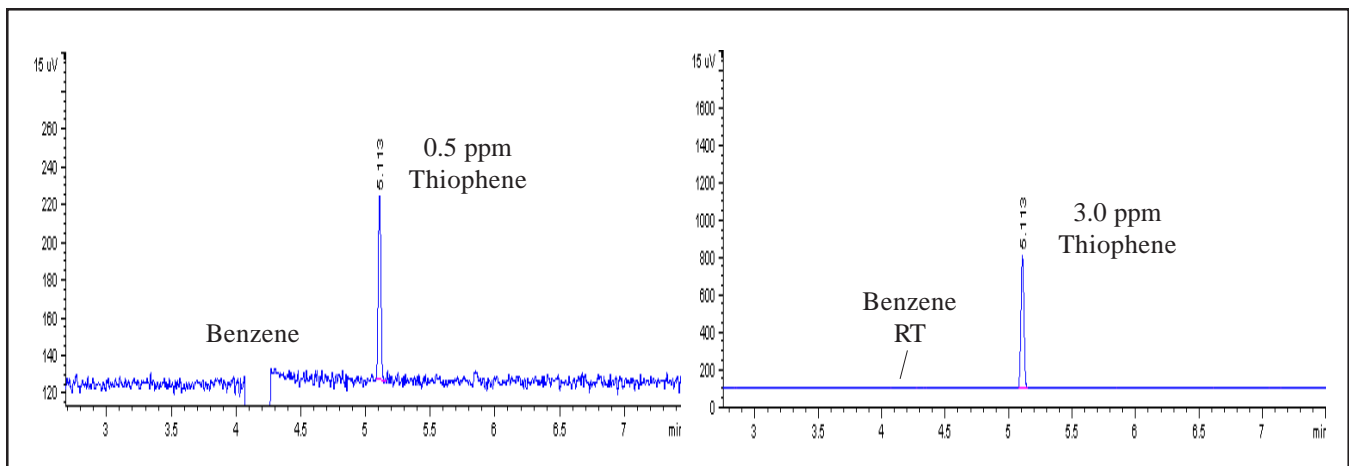
Figure 3. Chromatograms of the 0.5 ppm and 3.0 ppm Thiophene in Benzene Calibration Standards Acquired Using the PFPD. Data were Acquired Using the Conditions Listed in Table 1.

Table 2. Repeatability of Triplicate Injections at Each Calibration Concentration Level

Calibration Level	%RSD (n = 3)
0.5 ppm	3.7
1.0 ppm	6.1
2.0 ppm	1.9
3.0 ppm	0.6
4.0 ppm	0.2
5.0 ppm	0.6

The flame chemistry that occurs within the PFPD generates an excited sulfur species, S_2^*, that produces a quadratic response. This response can then be digitally processed at the operator's discretion to produce a linear output signal. The PFPD is capable of outputting two simultaneous chromatographic signals, thus, generating two simultaneous chromatograms. For the purpose of this experiment one signal was configured in the quadratic mode and the second signal used the PFPD's automatic square root function to produce a linear response output. In this manner, linear calibration data from the PFPD could be directly compared to the quadratic and log/log plots specified in the original versions of the ASTM standard. These three differ- ent treatments of the same data are illustrated in Figure 4. All three charting techniques result in excellent and equivalent calibration curves. The use of linearized data simplifies the calibration process, and allows for quantitation of other unknown sulfur peaks that may be detected using the equimolar response feature of the PFPD.
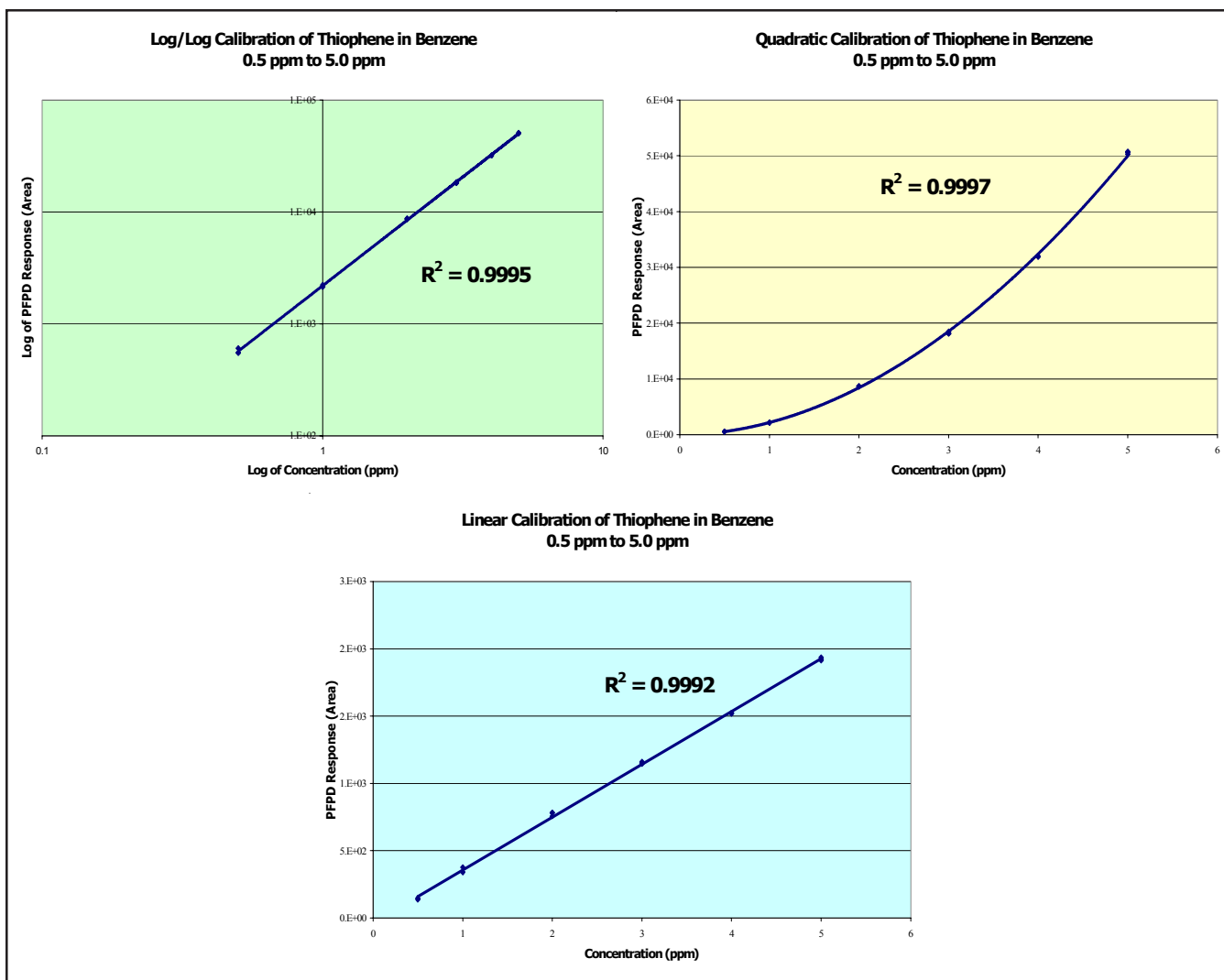
Figure 4. Three Different Graphical Treatments of the Same PFPD Calibration Data. Log/log Plots were Required in the Original Version of ASTM Standard D4735-96 Because the Older FPDs were not Capable of Producing a Linear Response. The OI Analytical Model 5380 PFPD Automatically Linearizes the Signal Using Digital Processing, Thus Greatly Simplifying the Calibration Process.

Precision and Accuracy

Approximately eleven days after the initial calibration was completed, a fresh set of standards was made for the ASTM precision and accuracy studies. Seven replicate injections of four different concentrations across the calibration range were made over a period of about one week, and concentrations were calculated based on the original calibration curve. No additional tuning or optimization of the PFPD was necessary. Precision was measured as the percent relative standard deviation (%RSD) of the calculated concentrations from the seven injections. The %RSDs ranged from 1.4% for the 0.5 ppm standard to 0.6% for the 5.0 ppm standard. Complete data are reported in Table 3. Overlaid chromatograms of the replicate analyses are shown in Figure 5.

Table 3. Calculated Concentrations of Thiophene in Benzene in Standards with Prepared Concentrations of 0.5 ppm, 1.0 ppm, 3.0 ppm, and 5.0 ppm. Precision is Reported as %RSD.

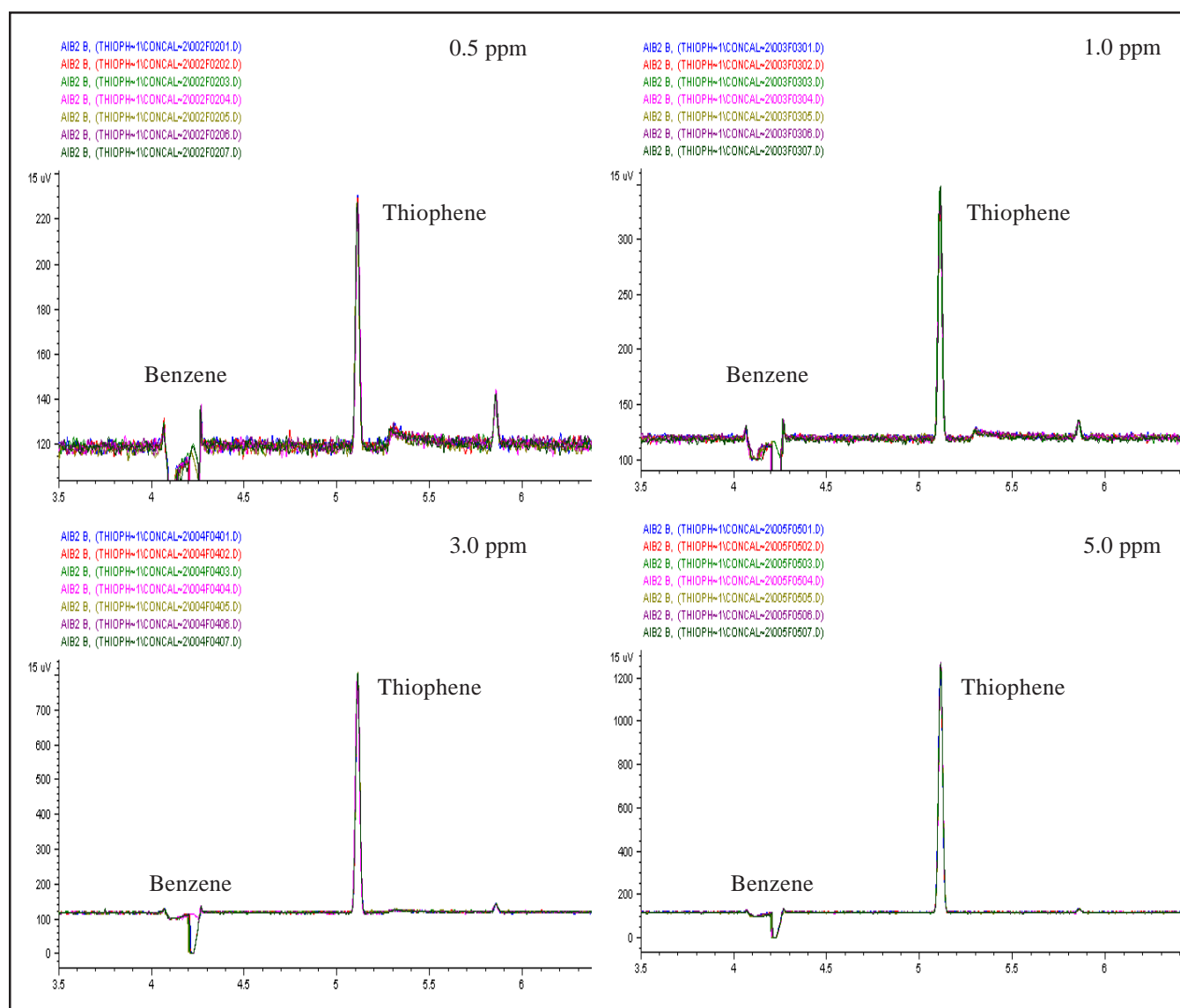| Run No.	Calculated Concentrations (ppm)			
Run 1	0.51	0.97	2.98	4.91
Run 2	0.49	0.96	2.92	4.96
Run 3	0.50	0.96	2.97	4.97
Run 4	0.49	0.98	2.98	5.01
Run 5	0.49	0.97	2.97	4.98
Run 6	0.49	0.97	2.96	4.99
Run 7	0.50	0.99	2.99	4.96
Average Conc.	0.50	0.97	2.97	4.97
%RSD	**1.4%**	**1.3%**	**0.8%**	**0.6%**

Figure 5. Overlaid PFPD Chromatograms from Seven Replicate Analyses of Thiophene in Benzene at Different Concentrations

Accuracy of the average calculated concentrations from the replicate injections is reported as percent recovery over the calibration range, and is tabulated in Table 4.

Table 4. Accuracy of Calculated Concentrations of Thiophene in Benzene Using the PFPD is Reported as Percent Recovery

Expected Concentration (ppm)	0.50	1.0	3.0	5.0
Average Calculated Concentration for n = 7 (ppm)	0.50	0.97	2.97	4.97
% Recovery	**99.1**	**97.2**	**98.9**	**99.3**

The ASTM Standard D4735-02 specifies method criteria for precision in terms of "intermediate precision" for single laboratory results and "reproducibility" for results from two or more laboratories following the same method. These criteria are represented as average measured concentrations with standard deviations reported on a mg/kg (ppm) basis. Table 5 compares the single laboratory "intermediate precision" data from the PFPD in D4735-02 to the data originally reported for D4735-96. The single lab data demonstrate that the PFPD is capable of analytical precision 3 to 4 times better than the FPD used in the original study.

Table 5. Single Laboratory "Intermediate Precision" Data for the OI Analytical Model 5380 PFPD Compared to the Original FPD Data

Intermediate Precision Data From D4735-96	
Thiophene Concentration (mg/kg)	**Intermediate Precision (mg/kg)**
0.80	0.040
1.80	0.078
Intermediate Precision Data From D4735-02	
Thiophene Concentration (mg/kg)	**Intermediate Precision (mg/kg)**
0.50	0.010
1.00	0.010
3.00	0.023
5.00	0.031

Ultimate Sensitivity
Since the analytical conditions used to validate the new standard included a split ratio of 50:1, there was significant capacity to improve the ultimate sensitivity of the method by simply reducing the split ratio. Although lower concentration ranges are beyond the scope of the official method, the ability of the PFPD to determine low-level ppb ranges was investigated. The lowest calibration test standard with concentration of 0.5 ppm was diluted by a factor of 10 to produce a sensitivity check standard at 0.05 ppm (50 ppb) thiophene. A 1-μL injection of this sensitivity check standard was made using a 10:1 split ratio and produced the chromatogram shown in Figure 6. The chromatographic peak in Figure 6 represents 50 ppb thiophene or approximately 1.9 pg sulfur on column, and it has a signal-to-noise ratio of about 3:1. Thus, the range of Standard D4735-02 can be easily expanded to include thiophene concentrations as low as 50 ppb or less simply by modifying the split ratio.
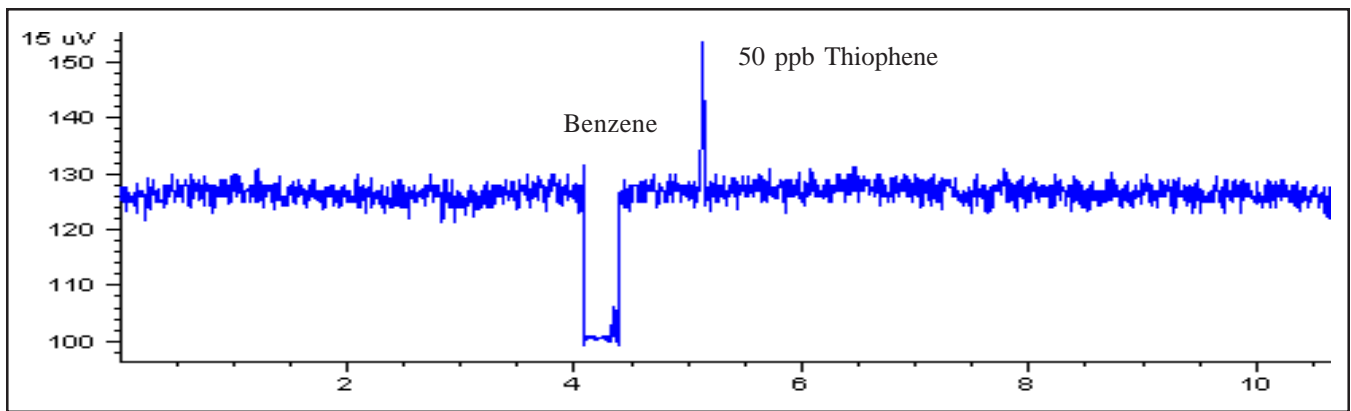
Figure 6. Chromatogram of 50 ppb Thiophene Acquired Using a 1-μL Injection and a 10:1 Split Ratio. Lower Split Ratios or Larger Injection Volumes Could Facilitate Analysis of Thiophene in the 15–20 ppb Range.

Conclusions

The PFPD, the newest generation of flame photometric detectors, has been shown to meet all the performance criteria specified in ASTM Standard D4735-02, and the new modifications were officially approved in 2002. Calibration is simplified by digital processing of the PFPD signal to produce a linear output, and thus, a linear calibration curve, which is equivalent to the more complex log/log plots required by the original standard. Ultimate sensitivity of the method can be lowered by one order of magnitude or more simply by reducing the split ratio. The PFPD's superior stability allows data to be acquired over a period of days or even weeks with no additional detector tuning or optimization required. The PFPD's equimolar response provides a means to measure the concentration of any other unknown sulfur species that may also be present in the matrix.

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