

Determination of Sulfur Species in Petrochemical Matrices by ASTM Methods Using a Pulsed Flame Photometric Detector

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INTRODUCTION

The ability to detect and measure sulfur contaminants in petrochemical products is essential for establishing proper operating conditions for desulfurization processes within the plant, quality control of finished products, and compliance with increasingly stringent regulatory requirements on total sulfur content.

ASTM International (ASTM) is a globally recognized, non-profit organization made up of committees that develop and publish international voluntary consensus standards. Several ASTM methods specify the Pulsed Flame Photometric Detector (PFPD) to quantify individual sulfur species in gas- and liquid-phase petrochemical products. The detector's equimolar response for sulfur allows simple and straightforward quantitation of the sulfur content in unknown peaks. Long-term calibration stability and minimum maintenance make the PFPD ideally suited to round-the-clock operation in petrochemical QC laboratories required to comply with ASTM method requirements.

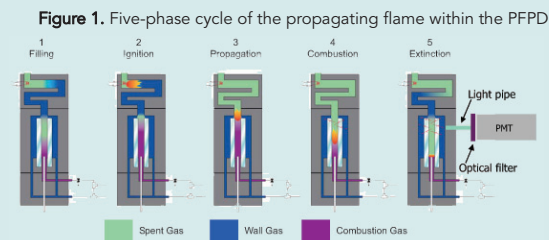
This poster includes discussion of the PFPD principle of operation, and includes experimental details from three ASTM methods using the PFPD to detect and quantify trace levels of sulfur species in petrochemical matrices.

PFPD PRINCIPLE OF OPERATION

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

In a conventional FPD, the flame is static and sulfur-hydrocarbon selectivity is achieved by using a narrow-band transmission filter that transmits a single band of light at 394 nm; all other emissions are blocked. An optical shield may be used with a FPD to prevent hydrocarbon emissions from interfering and causing false positives or a high background.

By contrast, the Pulsed FPD uses a propagating flame that terminates within a quartz combustor. The kinetics of the gas-phase reactions produced by the propagating flame results in light emissions with specific lifetimes; the S_2^* emissions are chronologically separated from the hydrocarbon emissions, resulting in nearly infinite sulfur-hydrocarbon selectivity. As a result of these design differences, the PFPD has several significant advantages over the conventional FPD, including a 10-fold increase in selectivity and 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 easier calibrations, and the acquisition of two simultaneous, mutually selective chromatograms. Figure 1 illustrates the 5-phase cycle of the propagating flame within the PFPD.



EXPERIMENTAL

Analyses of gas phase samples were performed on an OI Analytical SPRO-Select system, shown in Figure 2. Calibration curves were generated using permeation devices and the integrated permeation oven. A second instrument, configured with a split/splitless injector, a liquid autosampler, and a DB-WAX column, was used for analysis of thiophene in benzene. For both analytical systems, the PFPD was configured for sulfur analysis with a 2-mm quartz combustor, a BG-12 broadband optical filter, and a base temperature of 250 °C. The H_2 -to-air flow ratio was optimized to support maximum formation of the emitting species, S_2^* , within the propagating flame.

Figure 2. OI Analytical SPRO-Select system

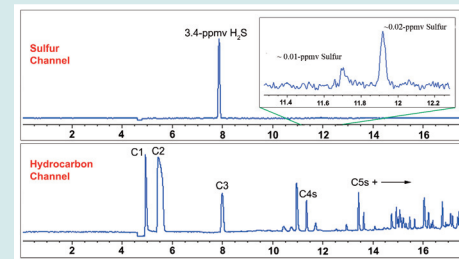


RESULTS & DISCUSSION

Sulfur in Natural Gas by ASTM Method D 6228-10

Natural gas and other gaseous fuels contain varying amounts and types of sulfur compounds, which can be corrosive to equipment and can inhibit or destroy catalysts used in gas processing. In addition, small amounts of sulfur odorants are added to natural gas and other liquefied petroleum gases for safety purposes. Accurate measurement of the levels of these sulfur species is essential to ensure proper processing and to monitor odorant levels for public safety. Determination of the sulfur content in gaseous fuels is done almost exclusively by GC with a sulfur-selective detector, and the PFPD is uniquely suited to this analysis because of its unambiguous sulfur recognition, increased sensitivity, and equimolar sulfur response. Figure 3 illustrates the simultaneous sulfur and hydrocarbon chromatograms of a natural gas sample analyzed by ASTM Method D 6228-10⁽¹⁾.

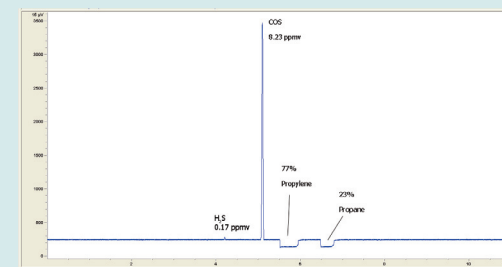
Figure 3. Simultaneous sulfur and hydrocarbon chromatograms of a natural gas sample analyzed by ASTM method D 6228-10. The sample contained 3.4 ppmv sulfur as H_2S and two unidentified sulfur compounds that were quantified at 0.01 and 0.02 ppmv sulfur using the PFPD equimolar response capability.



Sulfur in Propane/Propylene Feedstock by ASTM Method D 5303-92(2007)⁽²⁾

High grade ethylene and propylene feedstocks are used in production of a variety of fine chemicals, and determination of low-level sulfur impurities, such as H_2S and COS, in the feed is important because they can corrode equipment, poison catalysts during production, and affect polymer yield. Analysis of the volatile sulfur compounds in light hydrocarbon streams is traditionally done by ASTM methods for GC with sulfur-selective detectors and capillary columns. The column selected for this application (Agilent's Select Low-Sulfur column) was used because of its ability to provide complete baseline separation of the volatile sulfur impurities from the propane-propylene matrix, sharp symmetric peak shapes, and excellent response for the low-level sulfur compounds. Figure 4 is the PFPD sulfur chromatogram from a sample of 77% propylene and 23% propane acquired with a 1-mL gas sample loop and a 50-to-1 split ratio. The H_2S and COS were completely baseline resolved from the matrix. The estimated minimum detectable concentrations with a 10-to-1 split are approximately 0.02 to 0.03 ppmv.

Figure 4. H_2S (0.17 ppmv) and COS (8.23 ppmv) measured in a sample of 77% propylene and 23% propane using the PFPD and a specialized column developed specifically to baseline separate the analytes of interest from the C3 matrix injected using a 1-mL gas sample loop and a 50-to-1 split ratio

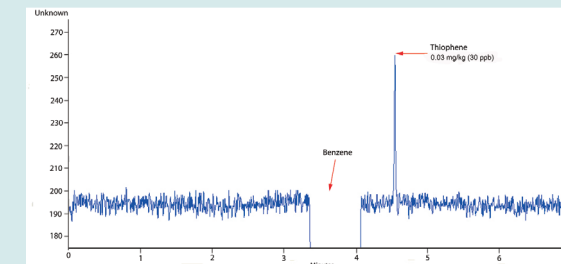


RESULTS & DISCUSSION

Thiophene in Benzene by ASTM Methods D 4735-09 and D 7011-10a

ASTM International has established a specification of 1 mg/kg thiophene in refined benzene-535 and 0.6 mg/kg thiophene in benzene-545. To verify that individual benzene stocks meet these specifications, ASTM has published two standard test methods for the determination of thiophene in refined benzene by GC with sulfur-selective detectors. ASTM Method D 4735-09⁽³⁾ was originally approved in 1996 and re-approved in 2000 and 2002, and ASTM Method D 7011-10a⁽⁴⁾ was published in 2010 and provides operating conditions for extending the analytical range to include trace levels of thiophene at 0.03 mg/kg. Figure 5 is a PFPD sulfur chromatogram of thiophene in benzene at 0.03 mg/kg acquired using ASTM Method D 7011-10a. The PFPD easily met all requirements and QC criteria for both methods.

Figure 5. PFPD sulfur chromatogram of thiophene in benzene at 0.03 mg/kg.



SUMMARY & CONCLUSIONS

The PFPD can be used to quantify individual sulfur species and calculate total sulfur content in gas-phase and liquid-phase petrochemical products over a wide range of concentrations. The detector's equimolar response for sulfur allows simple and straightforward quantitation of the sulfur content in unknown peaks. Long-term calibration stability and reduced maintenance make the PFPD ideally suited to round-the-clock operation in petrochemical QC laboratories required to comply with ASTM method requirements.

REFERENCES

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2. ASTM Method D 5303-92 (2007) Standard Test Method for Trace Carbonyl Sulfide in Propylene by Gas Chromatography, ASTM International, West Conshohocken, PA, www.astm.org.
3. ASTM Method D 4735-09 Standard Test Method for Determination of Trace Thiophene in Refined Benzene by Gas Chromatography, ASTM International, West Conshohocken, PA, www.astm.org.
4. ASTM Method D 7011-10a 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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