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Application Note

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Analysis of Sulfur Compounds in Light Petroleum Liquids Using ASTM Method D5623, Gas Chromatography and Pulsed Flame Photometric Detector (PFPD)

PETROCHEMICAL SERIES

Introduction

ASTM D5623 is a method primarily for the determination of volatile sulfur-containing compounds in light petroleum liquids with a final boiling point of 230 °C or lower at atmospheric pressure, such as petroleum distillates and gasoline. Many sulfur compounds in light petroleum liquids are odorous, can cause corrosion to equipment, inhibit or destroy catalysts, and ultimately have a negative impact on product costs and quality. Sulfur in fuels also causes air pollution. The ability to speciate sulfur compounds is useful in controlling them in finished products and is often more important than determining total sulfur content alone. Gas chromatography combined with a Pulsed Flame Photometric Detector (PFPD) can provide a reliable means to identify and quantify sulfur compounds in petroleum liquids. Other sulfur selective detectors may be used for ASTM D5623, but the PFPD offers several advantages. The PFPD has improved sulfur selectivity from hydrocarbon matrices, increased sensitivity, and equimolar sulfur response vs. standard Flame Photometric Detectors (FPDs).

Figure 1. OI Analytical 5383 Pulsed Flame Photometric Detector

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The equimolar response allows quantitation of unknown sulfur compounds that may be present in samples. This study will demonstrate the use of a new generation PFPD for the analysis of light petroleum liquids following the current ASTM D5623. A robust, yet sensitive, method is needed for both total and speciated sulfur, especially in light of the rapid approach of United States Environmental Protection Agency (USEPA) Tier 3 requirements in 2017. This rule sets new vehicle emissions standards and lowers the sulfur content in gasoline to 10 ppm. We present here the instrument configuration and operating parameters for the detection and quantification of sulfur compounds in light petroleum liquids using ASTM Method D5623 and a PFPD.

Experimentation

Instrumentation for this study included an OI Analytical Model 5383 PFPD (Figure 1) mounted on an Agilent 7890A GC system with split/splitless injection port.

Instrument operation conditions are shown in Table 1. The PFPD was tuned for optimum sulfur response. It was configured for simultaneous sulfur and hydrocarbon detection with sulfur run in the linearized mode (i.e., with the square root turned on).

A stock standard containing varying amounts (100 ppm, 75 ppm, 50 ppm, and 20 ppm) of sulfur in 90% isooctane and 10% toluene was obtained from DCG Partnership. Working calibration standards were diluted in 90% isooctane and 10% toluene. The instrument was calibrated by manually injecting 1µl of the standards. The method system test mixture and matrix blank were also analyzed.

Table 1. Instrument Configuration & Operating Conditions

Agilent 7890A GC & OIA 5383 PFPD	
Inlet	250 ˚C Split mode Split ratio 10:1 Sulfinert®-coated 4 mm precision liner
GC Column	Restek Rxi – 1 ms 30-m x 0.32-mm ID x 4.0 µm df Helium carrier gas, 1.0 mL / min
Oven Program (Agilent 7890A)	40 ˚C for 2 minutes 10 ˚C / minute to 100 ˚C Hold for 8 minutes 30 ˚C / minute to 300 ˚C Hold for 2 minutes* Total run time 24.7 minutes
Sulfur Detection	Pulsed Flame Photometric Detector (PFPD) 2-mm combustor, BG-12 filter, R1924 PMT Detector base temperature 250 ˚C H_2 / air ratio tuned for optimum sulfur emission 6-24 milliseconds sulfur gate (linear mode; square root on) 1-2 milliseconds hydrocarbon gate

* Final hold may need to be adjusted according to the matrix.

Calibration

An eight-point calibration was performed which included the range of 0.1 ppm to 10 ppm for most compounds. The Agilent GC Chemstation OpenLab Data System was used to generate the calibration curve using linear regression. See Table 2. Great care must be taken with standards because of volatility and instability.

Table 2. Calibration Data

Peak	Compound	Stock Concentration (ppm wt)	Linear Regression (R^2)
1	*Sulfur dioxide	100	0.9998
2	*Carbonyl sulfide	100	0.9998
3	Methyl mercaptan	100	0.9991
4	Ethyl mercaptan	100	0.9993
5	Dimethyl sulfide	100	0.9995
6	Carbon disulfide	20	0.9990
7	Isopropyl mercaptan	100	0.9994
8	tert-Butyl mercaptan	50	0.9992
9	n-Propyl mercaptan	100	0.9994
10	Ethyl methyl sulfide	50	0.9993
11	sec-Butyl mercaptan	50	0.9988
12	Thiophene	100	0.9990
13	Isobutyl mercaptan	100	0.9982
14	Diethyl sulfide	75	0.9994
15	n-Butyl mercaptan	50	0.9996
16	Dimethyl disulfide	20	0.9996
17	2-Methylthiophene	75	0.9994
18	3-Methylthiophene	100	0.9980
19	Diethyl disulfide	20	0.9995
20	Benzothiophene	75	0.9998
21	3-Methylbenzothiophene	100	0.9998

* These compounds co-elute.

Figure 2. Mid-Level Standard

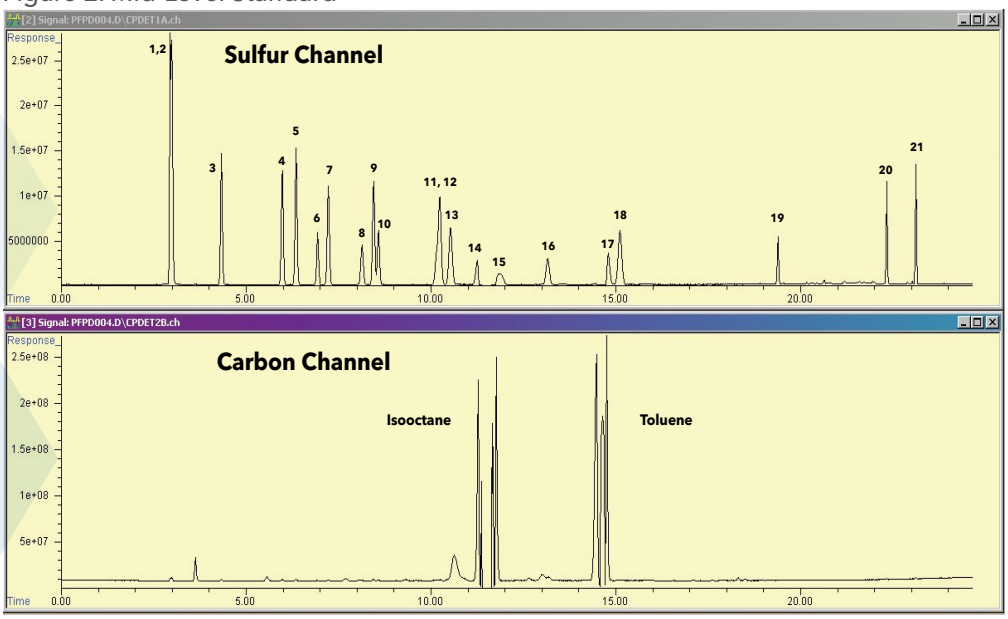


Figure 3. Gasoline #1

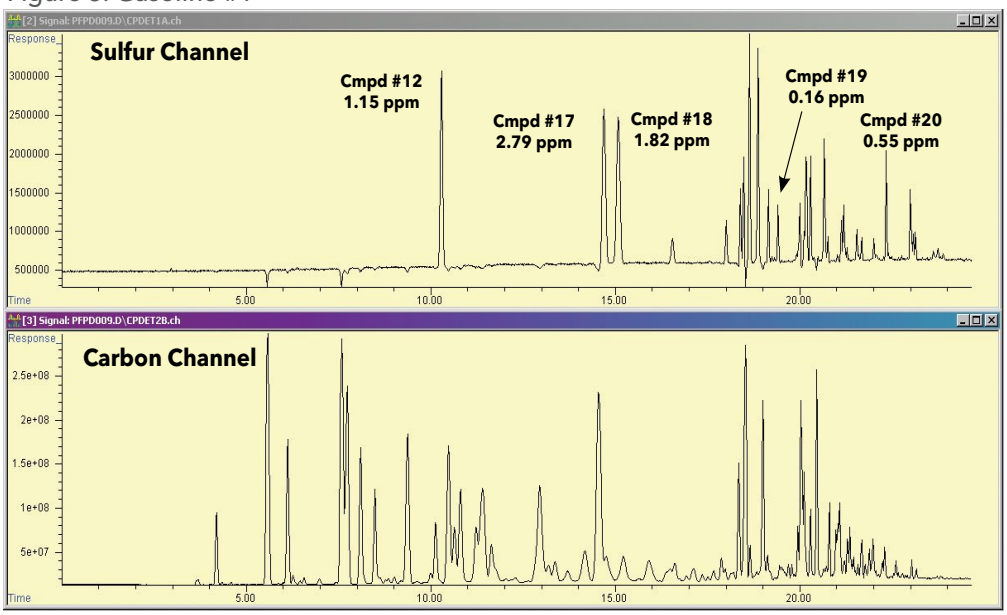
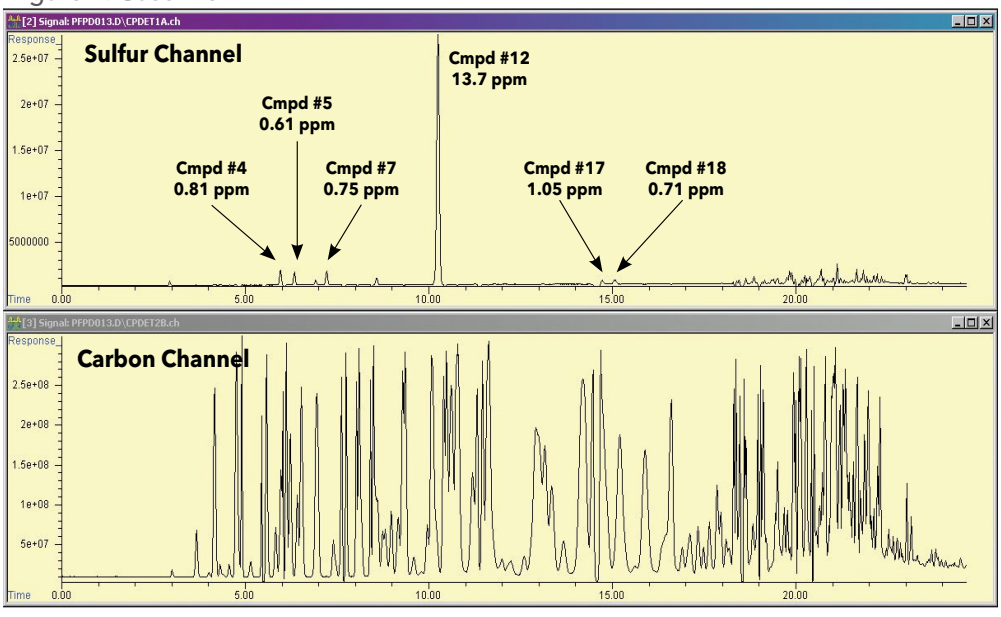


Figure 4. Gasoline #2



Conclusion

This ASTM method provides a good framework for determining sulfur compounds in light petroleum hydrocarbons. The PFPD provides the sensitivity demanded of the method and selectivity needed for hydrocarbon analysis.

Reference

ASTM D5623-94 (2014), Standard Test Method for Sulfur Compounds in Light Petroleum Liquids by Gas Chromatography and Sulfur Selective Detection, ASTM International, West Conshohocken, PA, 2014, www.astm.org

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