Analysis of Low-Level Sulfur Compounds in Natural Gas and Propylene Using a Pulsed Flame Photometric Detector

Application Note

Hydrocarbon Processing

Authors

Chunxiao Wang
Agilent Technologies (Shanghai) Co Ltd.
412 YingLun Road
Waigaoqiao Free Trade Zone
Shanghai 200131
P.R. China

Mario Morales and Roger Firor
Agilent Technologies, Inc.
2850 Centerville Road
Wilmington DE 19808
USA

Abstract

Sulfur compounds in natural gas and propylene are analyzed based on an Agilent 7890A GC system equipped with an OI 5380 pulsed flame photometric detector (PFPD). Reliable routine detection of sulfur components in light hydrocarbon matrices including C3 streams to 50 ppbv is demonstrated.

Introduction

Sulfur compounds including hydrogen sulfide (H_2S), carbonyl sulfide (COS), and methyl mercaptan (CH_3SH) can be present in natural gas and olefin streams such as propylene. These sulfur compounds are odorous, corrosive to equipment, and can inhibit or destroy catalysts used in gas processing and petrochemical production. Analyzing sulfur compounds is essential to assure product quality and to control downstream processing.

Several methods have been developed based on SCD (Sulfur Chemiluminescence Detector), FPD (Flame Photometric Detector) and MSD [1], [2], [3] for the analysis of trace sulfur compounds in light hydrocarbons. This work reports on low level sulfur determinations using the PFPD. The PFPD is ideal for analyzing sulfur compounds at low ppm to 50 ppb in light hydrocarbon matrices like propylene and natural gas. The selectivity over carbon and very low quenching characteristics of the PFPD are investigated.

Selecting the best method based on many selective detector options for an application depends on many factors including sensitivity, selectivity, stability, ease of use, and sample characteristics. A comprehensive review of various sulfur selective detectors and applications has been previously discussed. [4]

Agilent Technologies

Experimental

An Agilent 7890A GC was equipped with the OI Analytical Model 5380 PFPD and volatiles interface (VI). The volatiles inlet was connected directly to a six-port gas-sampling valve (GSV). SilcoNert 2000-treated tubing including the sample loop was used for all lines that come in contact with the sample. It is extremely important that all lines in contact with the sample are deactivated for successful detection of sulfur compounds at the ppb level.

A dynamic blending system was used to prepare the low level sulfur compounds in different matrices. A four-port valve was used for selecting either the sample or standard mix. The valve was installed up-stream to the GSV. The configuration of the gas blending and GC-PFPD system is shown in Figure 1.

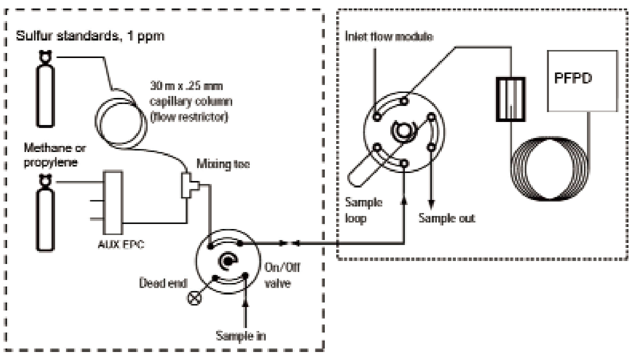


Figure1. The configuration of the gas blending and GC-PFPD system.

Sulfur standard No. 1 and Sulfur standard No. 2 at 1 ppm (V/V) per sulfur component are used for this study. Component details for these standards are listed in Table 1A and 1B.

Table 1A. Sulfur Standard No. 1

Compounds	Concentration ppm V/V	Compounds	Concentration ppm V
1 Hydrogen sulfide	1.05	9 1-propanethiol	1.05
2 Carbonyl sulfide	1.05	10 Methyl ethyl sulfide	1.05
3 Methyl mercaptan	1.05	11 2-Butanthiol	1.05
4 Ethyl mercaptan	1.05	12 Thiophene	1.05
5 Dimethyl sulfide	1.05	13 2-Methyl-1-propanethiol	1.05
6 Carbon disulfide (CS_2)	1.05	14 Diethyl sulfide	1.05
7 2-Propanethiol	1.05	15 1-Butanethiol	1.05
8 Tert-Butylmercaptan	1.05	16 Helium	Balance

Table 1B. Sulfur Standard No. 2

Compounds	Concentration ppm V/V	Compounds ppm V/V	Concentration % V/V
1 Hydrogen sulfide	1.05	14 Diethyl sulfide	1.05
2 Carbonyl sulfide	1.05	15 1-Butanethiol	1.05
3 Methyl mercaptan	1.05	16 Butane	3.02%
4 Ethyl mercaptan	1.05	17 Carbon dioxide	1.05%
5 Dimethyl sulfide	1.05	18 Ethane	9.02%
6 Carbon disulfide (CS_2)	1.05	19 Helium	0.499%
7 2-Propanethiol	1.05	20 Isobutane	2.99%
8 Tert-Butyl mercaptan	1.05	21 Isopentane	1.01%
9 1-propanethiol	1.05	22 Nitrogen	4.99%
10 Methyl ethyl sulfide	1.05	23 n-Pentane	1.00%
11 2-Butanthiol	1.05	24 Propane	6.05%
12 Thiophene	1	25 Methane	Balance
13 2-Methyl-1-propanethiol	1.05		

Typical GC conditions are listed in Table 2.

Table 2. Typical GC conditions

Oven temperature	40 °C (6 min), to 120 °C at 6 °C/min, to 180 °C (5 min) at 10 °C /min (for column 1)	
	30 °C (6 min), to 180 °C at 6 °C/min , post run 200 °C (2 min) (for column 2)	
Column 1	Select low sulfur column, 0.32 mm × 60 m, (CP8575)	
Column 2	HP-1, 0.32 mm × 60 m, 5.0 µm (19091Z-716)	
Inlet (VI)	200 °C, Split ratio: 3:1	
Carrier gas	Helium, constant flow, 2.0 mL/min	
Sample loop	1 mL	
PFPD Settings	Temperature	200 °C
	H_2 flow	12 mL/min
	Air (1) flow	13 mL/min
	Air (2) flow	12 mL/min
	CMT	610, tirgger level:500 mV

Results and Discussion

Two columns, HP-1 and Select Low Sulfur are used in this study. An HP-1 type column is recommended by ASTM 6228 [5] for the determination of sulfur compounds in natural gas and gaseous fuels. Figure 2 shows a chromatogram of sulfur compounds in methane with other light hydrocarbons (components details are listed in Table 1B for sulfur standard No. 2). Separation of sulfur compounds from light hydrocarbons is seen. Note that propane elutes after COS. However, a significant impact affecting the measurement of COS caused by a high concentration of propane is also observed. Therefore, in natural gas streams, analysis of low level COS in the presence of high propane concentration will be problematic using a non-polar methyl silicone phase.

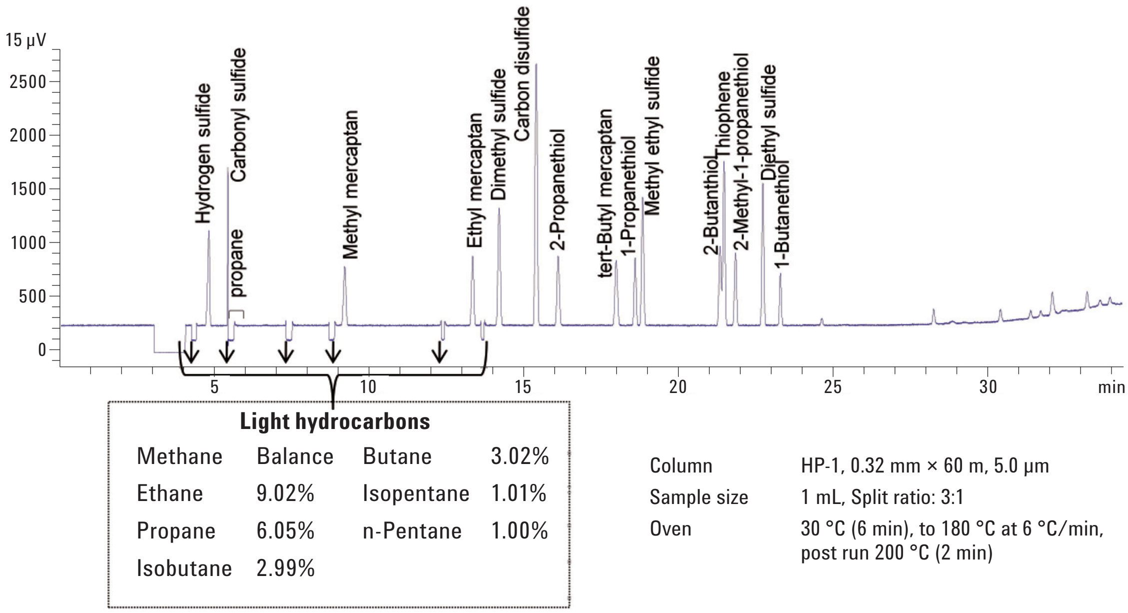


Figure 2. Chromatogram of sulfur compounds in methane with other light hydrocarbons as listed for sulfur standard No. 2.

For the analysis of sulfur in propylene, the co-elution of COS and propylene using the HP-1 column results in quenching. The Select Low Sulfur PLOT column provides good selectivity between H_2S, COS and CH_3SH in propylene streams [6] providing enough separation to avoid quenching. Figure 3 shows the complete separation of COS from propylene without matrix interference. CH_3SH shows peak broadening from column overloading by the large amount of propylene. Some column bleed is also observed at GC oven temperatures above 160 °C.

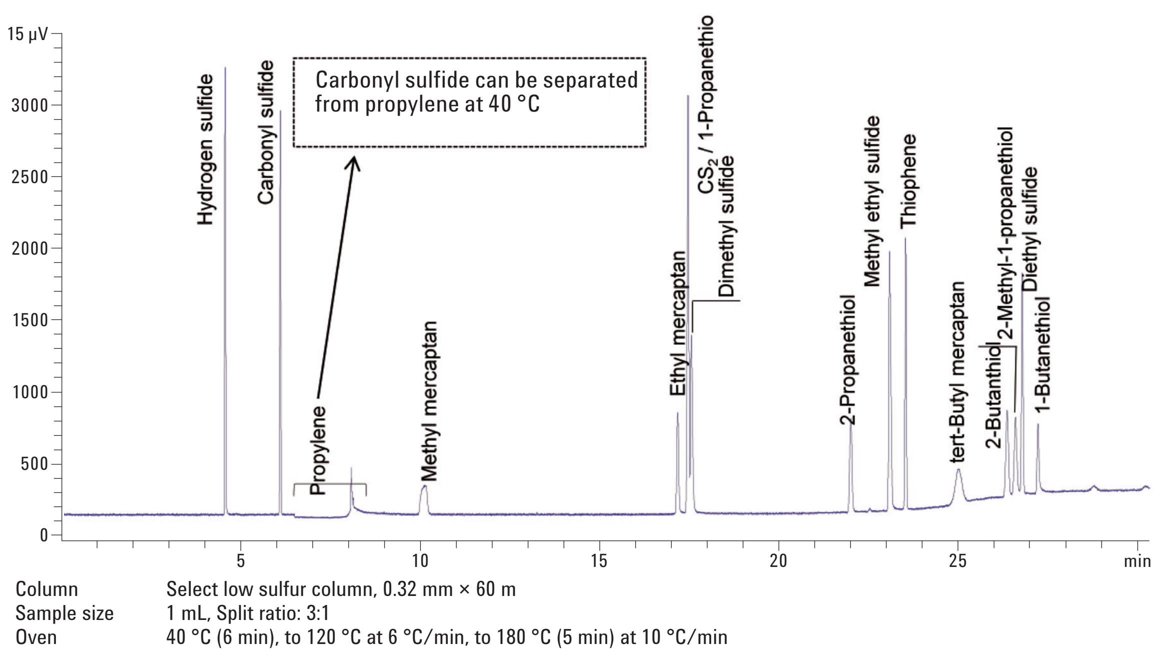
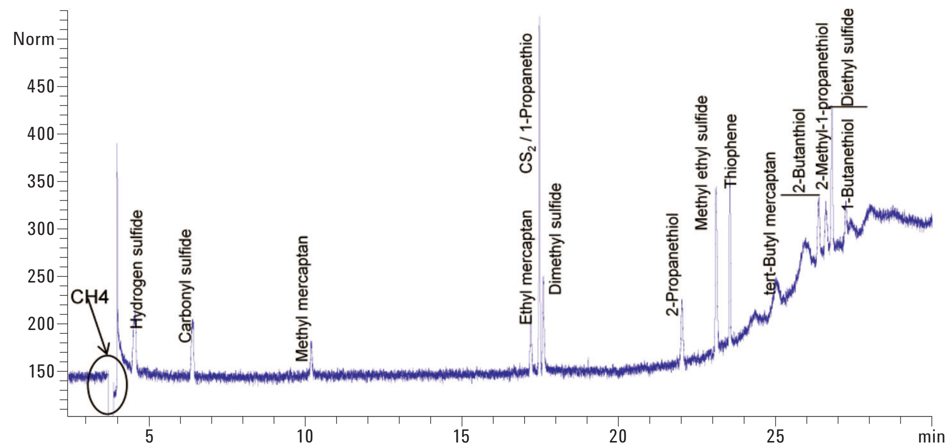


Figure 3. A complete separation of COS from propylene without matrix interference.

Initial setup of a PFPD method must be done carefully using WinPulse software to achieve the best performance. Once operational, sensitivity can be 3× to 5× better than the FPD, achieving at least a minimum detection limit of 50 ppbv in this work.

Figure 4 shows a chromatogram of selected common sulfur compounds in methane mix at 50 ppbv per component. Good signal to noise is seen even at this low sulfur level based on a 1-mL sample loop and split ratio of 3 to 1. Desired sample concentration is obtained by the dynamic blending system which dilutes the sulfur standard No. 1 as listed in Table 1A by 20× with methane.

Sulfur standard No. 1 which contains 15 sulfur compounds at about 1 ppmv in helium is systematically diluted with methane using the dynamic blending system to obtain concentrations from 0.1 to 1 ppmv. Linearity curves for two compounds, hydrogen sulfide and carbonyl sulfide are shown in Figure 5.



Compound	Signal/ noise
Hydrogen sulfide	3.8
Carbonyl sulfide	4.0
Methylmercaptan	2.2
Ethylmercaptan	3.8
Dimethyl sulfide	6.3
2-Propanethiol	4.3
Methyl ethyl sulfide	11
Thiophene	11
Tert-Butyl mercaptan	2.1
2-Butanthiol	4.5
2-Methyl-1 propanethiol	3.7
Diethylsulfide	9.8
1-Butanethiol	2.4

Column	Select low sulfur column, 0.32 mm × 60 m
Sample size	1 mL, Split ratio: 3:1
Oven	40 °C (6 min), to 120 °C at 6 °C/min, to 180 °C (5 min) at 10 °C/min

Figure 4. A chromatogram of sulfur compounds in methane mix at 50 ppbv per component.

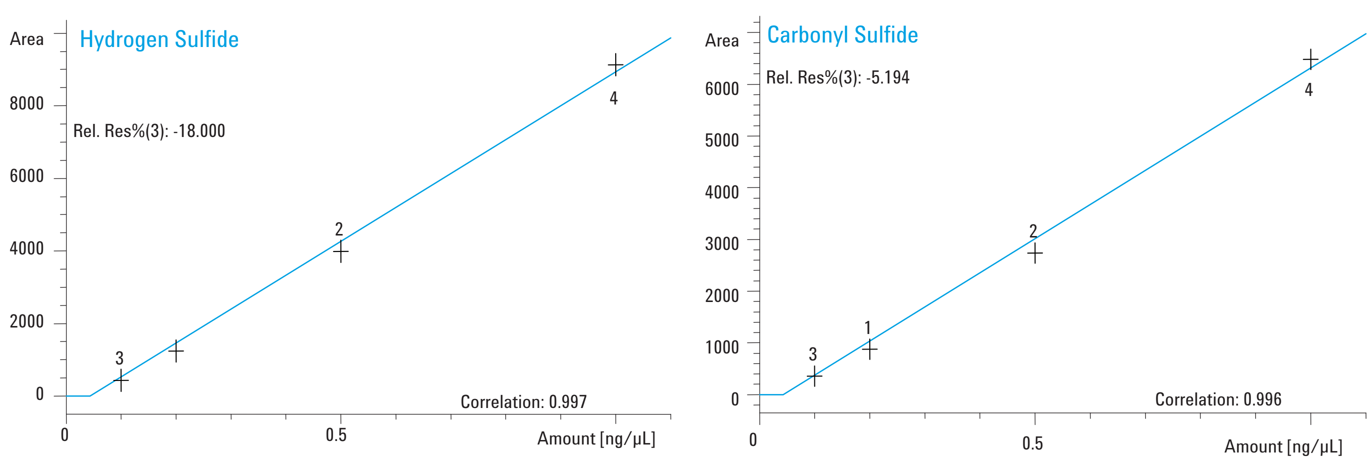


Figure 5. Calibration curves for hydrogen sulfide and carbonyl sulfide.

Conclusions

The PFPD is complimentary to other selective sulfur detectors such as the FPD and SCD. It provides better sensitivity with less quenching than an FPD at somewhat higher cost and complexity. The SCD will give the highest sensitivity without quenching of all popular sulfur selective detectors.

The setup of a PFPD method must be done carefully to achieve best performance. WinPulse interface software is used for gate optimization and reprocessing of chromatograms for method development. Once tuned, sensitivity can be up to 5× better than the FPD. Reliable routine detection of sulfur components in light hydrocarbon matrices under 50 ppbv can be achieved.

The Select Low Sulfur Column, with a novel stationary phase provides complete separation of H_2S, COS and CH_3SH in C3 streams without matrix interference. This avoids possible quenching effects caused by co-eluting of high concentration hydrocarbons. This column offers a high level of inertness, capacity, and efficiency for volatile sulfur analysis.

SP1 Ordering Information

SP1 7890-0560	Hardware only (no checkout), PFPD installed on 7890 GC. Option G3440A (AIB board) required
SP1 7890-0560	OI Analytical PFPDView software on CD-ROM (must be ordered with hardware SP1)

References

1. Wenmin Liu and Mario Morales,"Detection of Sulfur Compounds in Natural Gas According to ASTM D5504 with Agilent's Dual Plasma Sulfur Chemiluminescence Detector (G6603A) on the 7890A Gas Chromatograph," Agilent Technologies publication 5989-9234EN
2. Roger L. Firor, "Volatile Sulfur in Natural Gas,Refinery Gas, and Liquified Petroleum Gas," Agilent Technologies publication 5988-2791EN
3. Roger L. Firor, "Use of GC/MSD for Determination of Volatile Sulfur: Application in Natural Gas Fuel Cell Systems and Other Gaseous Streams," Agilent Technologies publication 5988-4453EN
4. Roger L. Firor and Bruce D. Quimby, "A Comparison of Sulfur Selective Detectors for Low Level Analysis in Gaseous Streams," Agilent Technologies publication 5988-2426EN
5. ASTM D 6228, Standard Test Method for Determination of Sulfur Compounds in Natural Gas and Gaseous Fuels by Gas Chromatography and Flame Photometric Detection
6. Helena Jacobse, "GC Analysis of Sulfur Components in Propylene using a Pulsed Flame Photometric Detector," Agilent Technologies publication 5990-6990EN

For More Information

For more information on our products and services, visit our Web site at www.agilent.com/chem.

www.agilent.com/chem

Printed in the USA
October 20, 2011
5990-9215EN

Agilent Technologies