

Determination of Low-Level sulfur compounds in Natural gas and Petrochemicals by Gas Chromatography and Pulsed flamed photometric Detector

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RESEARCH ARTICLE

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ABSTRACT

The natural gas and petrochemical industries are just some areas in which the analysis of sulfur containing compounds in process streams is a critical quality control step. Not being able to right away detect and accurately assess or quantify these compounds can lead to contaminated products, damaged equipment, poisoned catalysts and process downtime. This article presents a fast, reliable and robust method for the determination of individual volatile sulfur containing compounds in gaseous fuels by gas chromatography coupled with pulsed flame photometric detection.

Keywords: Low-Level sulfur compounds, Natural gas, Petrochemicals, Gas Chromatography, Pulsed flamed photometric Detector.

1. Introduction

The determination of trace impurities by gas chromatography (GC) is a very common analysis in the petrochemical laboratory. Usually, these impurities, which can have a detrimental effect on catalytic deactivation or product quality (or both), consist of three types: hydrocarbons and sulfur- and oxygen-containing organo-molecules. Other impurities such as nitrogen- and heteroatoms- (arsenic, silicon, etc.) containing components may also have deleterious effects, but these are not addressed in this paper. The analysis of trace hydrocarbons can be accomplished very effectively using selective adsorbents such as silica, alumina, and carbon. However, the analyses of trace sulfur compound and oxygenates require a higher degree of inertness. For sulfur-containing compounds, a polydimethyl siloxane (PDMS) stationary phase for generic application or a silica-based stationary phase for special applications may be adequate. (1-4)

Natural and other petrochemical fuels contain various types of sulfur compounds which are odorous, corrosive, and poisonous to catalysts used in gaseous fuel processing. Natural gas

and other petrochemicals naturally contain varying quantities and classes of sulfur compounds, which can be corrosive, odorous to pipelines and equipment's, and inhibit or destroy catalysts used in gas processing. Even low amounts of sulfur can be destructive to processing. Typically, sulfur is also added in small amounts, 1 to 4 ppm, to natural gas and other petroleum products for safety purposes. Some sulfur compounds are more susceptible to reaction and may oxidize and form strong compounds

Accurate identification and measurement of sulfur compounds is critical in the Natural and petroleum industry; however, the analysis can be challenging due to the sensitivity, reactivity, and instability of sulfur compounds during sampling and analytical testing. The Pulsed Flame Photometric Detector (PFPD) has advantages over other sulfur detectors such as accurate sulfur detection and selectivity against hydrocarbon matrices, increased sensitivity, and equimolar sulfur response. Determination of sulfur compounds is essential to assure product quality and to control downstream processing. (4-7) This application note will describe the analysis of sulfur in different matrices using a Gas chromatography

6890/7890A with an OI Analytical Pulsed Flame Photometric Detector (PFPD). The highly selective and sensitive performance of the flame photometric detector (FPD) is well-known for the analysis of organosulfur (OS) and organophosphorus (OP) compounds in various sectors namely petrochemical, environmental, biological, industrial hygiene and food products applications. As compared to the other more complex and / or expensive

selective detectors for this purpose such as the pulsed flame photometric detector (PFPD), sulfur chemiluminescence detector (SCD), atomic emission detector (AED), and nitrogen chemiluminescence detector, the single-flame FPD does not require a high level of expertise for calibration, tuning, and maintenance to achieve adequate performance for trace level quantification in most analytical laboratories.

Table 1. List of Sulfur compounds can be determined by GC-PFPD

Hydrogen sulfide	N-propyl mercaptan
Methyl mercaptan	3- Methyl thiophene
Isobutyl mercaptan	2-Methyl thiophene
Ethyl mercaptan	2- Ethyl thiophene
Methyl sulfide	2,5 Dimethyl thiophene
Carbon sulfide	Diphenyl Sulfide
Dimethyl sulfide	Thiophene
Ethanethiol	5-Methyl Benzo(B)Thiophene
2-propanethiol	9-Methylbenzothiophene
1-propanethiol	Ethyl Methyl sulfide
t-butyl mercaptan	Isopropyl mercaptan

By contrast, the PFPD uses a propagating flame that terminates within a fused silica combustor. The kinetics of the gas phase reactions produced by the propagating flame result in light emissions with specific lifetimes the S₂ emissions are chronologically separated from the hydrocarbon emissions. (7-10) This time difference is responsible for the extreme Sulphur-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 Sulphur emissions between 300 and 500 nm and dramatically increasing sensitivity. A combustible mixture of H₂ and air is introduced and fills the detector body and cap from the bottom up. The combustion mixture is ignited in the cap. The resulting flame propagates along the pathway consuming the H₂ /air mixture. Compounds eluting from the GC column are combusted within a quartz combustor and emit light at element-specific wavelengths. The flame is extinguished when it reaches the bottom of the detector and excited species continue to fluoresce for up to

25 milliseconds. Emissions from the excited species pass along a light pipe and selected emissions are transmitted through an

Several ASTM methods are available for the identification and quantitation of Sulphur in petrochemical matrices. Because of its selectivity for Sulphur versus hydrocarbon and excellent sensitivity, the PFPD has proven to be a suitable and reliable detector for these methods.

2. Material and method

Data for this study were acquired using the PerkinElmer Clarus 590 gas chromatograph with Total Chrom CDS, heated Hastelloy-C six-port gas sampling valve with passivated tubing and a 1ml loop, and an OI Analytical 5383 PFPD. Standards were prepared in four levels 0.5, 1.0, 10. And 50.0 respectively from 1000ppmv stock by diluting with nitrogen gas into dif and a KIN-TEK Flex Stream standard diluter. The PFPD was tuned for optimum sulfur response, and was configured for sulfur and hydrocarbon detection with the sulfur run in the linearized mode (i.e. with the square root function on). Simultaneous, mutually selective

sulfur and hydrocarbon chromatograms were produced from a single detector using the dual gate capability of the PFPD. Please see Figure 1 for the flow diagram of the PerkinElmer gas sampling system

3. Results and Discussion

The instrument was calibrated for H₂S, COS, MeSH, DMS, TP, and DMDS using permeation devices and a permeation oven held at a constant temperature of 40 °C. The concentrations of the compounds were varied by changing the nitrogen flow rate through the permeation oven using flows from 250 to 1500 ml/minute. In the modulation process, sulfur and phosphorus solutes were successfully trapped and remobilized to generate several pulses, with FPD peak width according to detector gas flow conditions. Figures below shows chromatogram of sulfur compounds in

methane with other light hydrocarbons. As we can see separation of sulfur is observed from light hydrocarbons. Using this instrument, a fast and reliable method to analyze sulfur compounds can be observed and this instrument is easy to operate compared to other instruments for sulfur detector.

GC is widely applied for trace impurity analysis in hydrocarbon streams. By selecting the optimal column, detectors, and system configuration, it is possible to determine trace levels of hydrocarbons, sulfur compounds, as well as oxygenated compounds. Gas Chromatography and Pulsed flamed photometric Detector combined together will allow to determine low level sulfur compounds more effectively and efficiently.

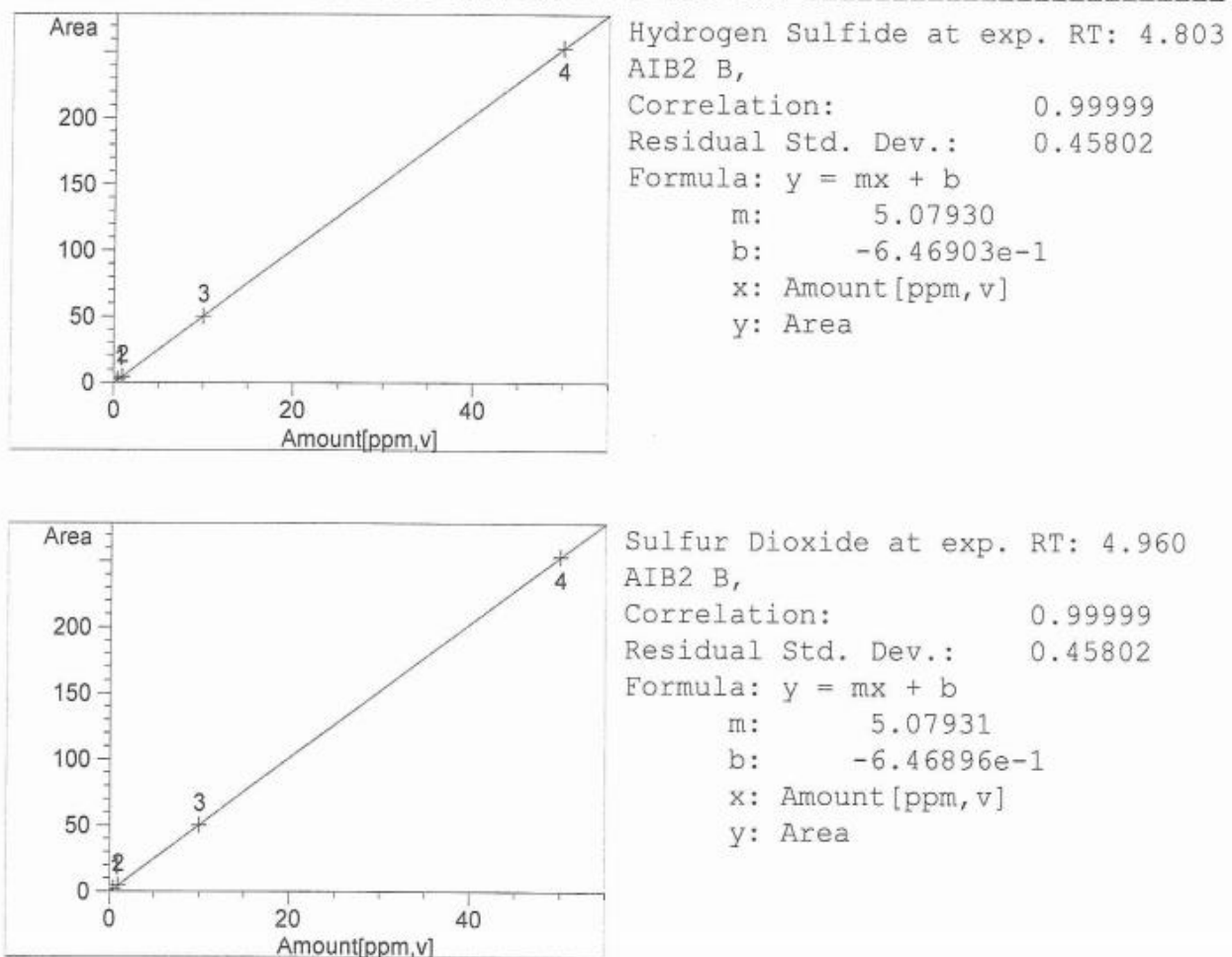


Figure 1. Calibration curves of hydrogen sulfide and Sulfur Dioxide

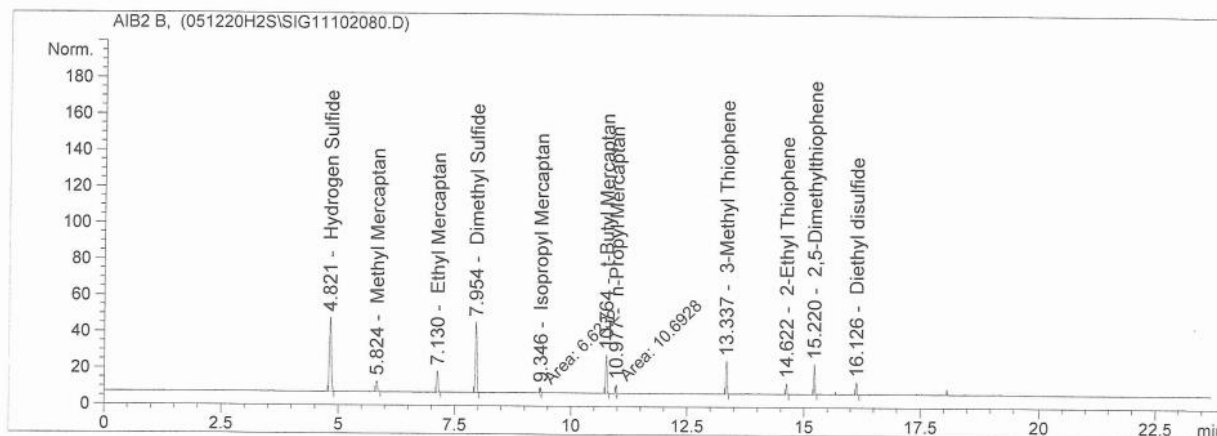


Figure 2. A chromatogram of some sulfur compounds of laboratory standard marker mixture

4. Conclusion

The instrumentation (GC-PFPD) used provides a fast, reliable method for analyzing sulfur compounds in a variety of matrices. Other compounds or matrices can also be analyzed with this system without having to make significant changes to the method. Ultimately, the matrix concentration can be balanced with the required sulfur sensitivity and GC split ratios or sample dilution to optimize performance for various analyses.

Acknowledgement

NA

Conflicts of Interest

The author declares that there are no conflicts of interest.

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