A Comparison of Sulfur Selective Detectors for Low Level Analysis in Gaseous Streams

Application

Gas Chromatography

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Abstract

A comparison of four selective detectors for analysis of single-digit ppb level sulfur is described. A dynamic blending system is used for point of use preparation of low level gaseous mixtures of eight sulfur compounds including H_2S, COS, CS_2 and selected mercaptans in helium, ethylene, propylene, and carbon dioxide. The criteria to consider for selecting the best detector for an application depends on many factors including, sensitivity, selectivity, stability, and ease of use. Guidelines for making the best detector choice are discussed. The Atomic Emission, Flame Photometric, Pulsed Flame Photometric, and Sulfur Chemiluminescent detectors are included in the study.

Introduction

The use of sulfur selective detectors in gas chromatography has grown in recent years with the increasing industrial demands for sulfur measurement. A major driving force has come from the hydrocarbon processing industry where the need for lower level more reliable sulfur measurements is intensifying. Regulations on sulfur levels in fuels continue to tighten. The need for low level sulfur measurements exists in nearly all segments of the chemical industry. Examples include the analysis of beverage grade CO_2 and the determination of ordorants in natural gas. In this paper, the characteristics and performance of four types of sulfur detectors will be compared with example applications used to demonstrate their operation under real-world conditions. The detectors include the AED (Atomic Emission Detector), SCD (Sulfur Chemiluminescent Detector), PFPD (Pulsed Flame Photometric Detector), and FPD (Flame Photometric Detector).

The Significance of Sulfur

Most sources of light hydrocarbons contain sulfur compounds that can be corrosive to pipes and equipment. The emission of undesirable odors caused by volatile sulfur compounds in intermediates and final products can have serious economic impact. Perhaps the most important consequence of sulfur is its' detrimental effect on a variety of catalysts used for processing and conversion of light hydrocarbon streams. Also, full compositional determinations of LPG (Liquefied Petroleum Gases) and propene mixes are required frequently where pricing of the end product is based on quality.

The presence of sulfur does not always come from natural sources. Sulfur is added to natural gas and LPG as a safety measure. In addition to the importance of monitoring concentration, some odorants tend to react over time forming compounds with different odor thresholds. Therefore, the need for measurement is important for a variety of reasons.

High purity ethylene and propylene are feedstocks for a wide variety of chemicals and end products. For example, ethylene is the base material for products such as styrene monomer, ethylene oxide/ethylene glycol, and low and high-density polyethylene. In polyolefin production, sulfur impurities commonly found include H_2S and COS. The removal of such impurities are required in order to prevent deactivation of polymerization catalysts, eliminate polymer with poor color or off-odor, enhance reaction rates, and provide consistent physical properties. The economic impact of any decrease in yield or catalyst life is quite high given the commodity nature of these processes. Strict quality control of hydrocarbon and sulfur impurities is, therefore, required. As measurement technologies advance, the acceptable levels decrease. However, the measurement methods must be reliable, stable, and easy to use before widespread acceptance is possible. The demand from the petrochemical industry is clearly growing.

Environmental concerns are also present. Allowable sulfur levels emitted into the atmosphere from both liquid and gaseous streams are constantly under scrutiny to reduce damage caused by precipitation of sulfuric acid in rain, for example.

Experimental

All detectors were interfaced to the Agilent 6890 gas chromatograph equipped with the volatiles interface (VI). The volatiles inlet was interfaced directly to a 6-port Hastelloy C automated gas-sampling valve (GSV). Additional insulation was used to cover the exposed length of line connecting the valve to the VI. Silcosteel tubing was used for all lines that had contact with sample. This tubing included use of Silcosteel treated sample loops. Sample loop size was typically 1.0 mL to maximize sensitivity. The use of 0.25 and 0.50 mL loops will result in better overall chromatography and peak shape for most applications where maximum sensitivities are not required. It is extremely important that all lines in contact with the sample are deactivated for successful detection of low level sulfur. All GC gas flows and pressures were controlled electronically. The Aux EPC module was plumbed so that Aux 5 was assigned as the diluent stream for the dynamic blending system described later in this section. The basic plumbing scheme employed for sample introduction is shown in Figure 1. A cross sectional view of the volatiles inlet is depicted in Figure 2. This inlet has an internal volume of only 35 µL and is also Silcosteel treated for inertness.

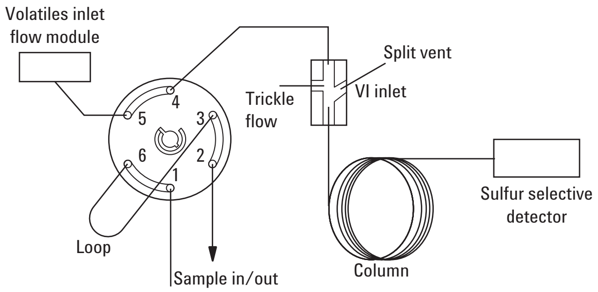


Figure 1. Silcosteel treated sample introduction system for ppb sulfur detection.

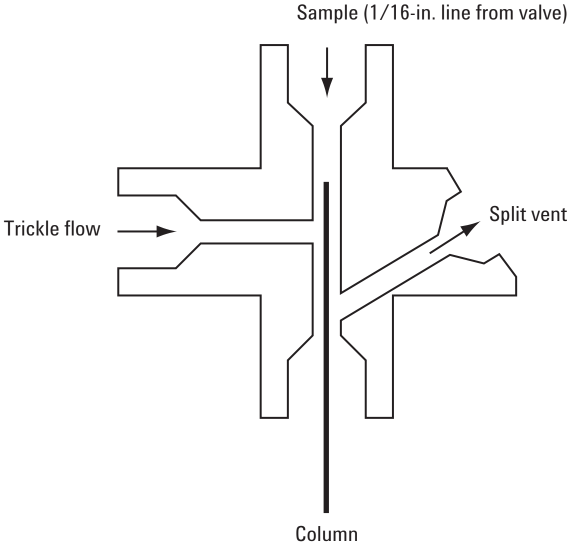
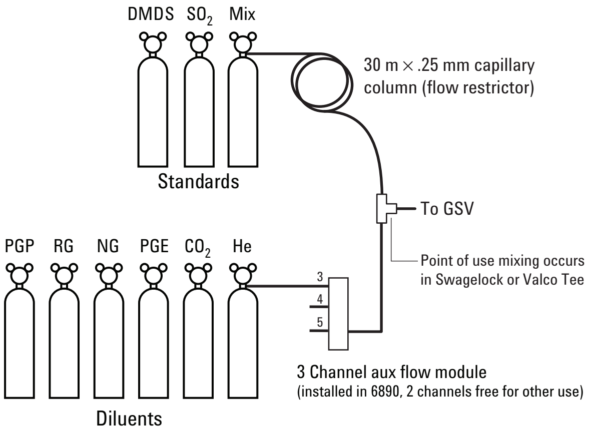


Figure 2. Cross-section of the Volatiles Inlet (not drawn to scale) depicting flow paths. All internal surfaces Silcosteel treated.

Calibration cylinders of light sulfur gases generally cannot be certified at levels below approximately 5 ppm per component due to the difficulty of preparation and the adsorption of sulfur species on the cylinder walls. As a result, calibration of sulfur selective detectors at ppb levels can be challenging. Point of use sample preparation is one relatively simple approach to the problem. This approach can be used for calibration by addition of a diluent to the high-level calibration standard. The diluent may be just helium or some other matrix such as ethylene or propylene. The ratio of total volumetric flow (diluent Aux 5 plus calibration mix) to the calibration mix flow will determine the dilution factor. When switching gas mixtures, take care to ensure that all lines are flushed to avoid carry over. In Figure 3, a simplified diagram of the point-of-use plumbing scheme is shown. The restrictor employed on the calibration mix flow path was a 30 m × 0.25 mm capillary column. The Agilent flow calculator program[1] is then used to determine flow rate at a given inlet pressure. Components in the sulfur mix used in this study are listed in Table 1. Peaks in the chromatograms (Figures 4 through 9) can be identified by number with reference to this table. The sulfur calibration mix was obtained from DCG Partnership I, LTD., Pearland, TX, 281-648-1894. Sulfur dioxide was used from a separate cylinder due to its reactivity.



Cylinder codes:
PGP - Polymer grade propylene
RG - Refinery gas
NG - Natural gas
PGE - Polymer grade ethylene
DMDS - Dimethyl disulfide

Figure 3. Plumbing scheme for dynamic blending.

Table 1. Sulfur Mix Components

Number	Compound
1	Hydrogen sulfide
2	Carbonyl sulfide
3	Methyl mercaptan
4	Ethyl mercaptan
5	Dimethyl sulfide
6	Carbon disulfide
7	t-Butyl mercaptan
8	Tetrahydrothiophene

Representative detector settings are given in Table 2.

Table 2 Detector Settings

Detector	Temperatures	Pressures and Flows
Agilent Flame Photometric	250 °C	H_2 50 mL/min Air 60 mL/min N_2 makeup 50 mL/min
Agilent G2350A Atomic Emission Carbon 193 nm, Sulfur 181nm	Cavity 245 °C Transfer line 245 °C	O_2 55 psi H_2 45 psi He makeup 100 mL/min
Antek 7090 Sulfur Chemiluminescent	950 °C Furnace	P1 38 detector P2 176 furnace H_2 200 mL/min O_2 8 mL/min O_3 25 mL/min
Sievers 355 Sulfur Chemiluminescent	803 °C Furnace	P1 5.4 detector P2 171 furnace H_2 100 mL/min O_2 8 mL/min O_3 5.6 psi
OI 5380 Pulsed Flame Photometric	250 °C	H_2 11.5 mL/min Air(1) 12.5 mL/min Air(2) 11.0 mL/min (makeup)

Unless otherwise stated, the following gas chromatographic conditions were used.

Gas Sampling Valve: 1 cc loop at 140 °C, Hastelloy C valve material

Column: 105 m × 0.53 mm × 5 µm DB-1

Oven: -20 °C (9.5 min), 10 °C/min to 250 °C, 80 °C/min to 255 °C

VI Inlet: 5 mL/min constant flow mode

Split ratio 0.1:1 typical

Temp 225 °C

Results and Discussion

Gas chromatographic sulfur selective detectors can be extremely powerful tools to characterize and quantify a wide range of low level sulfur species in gaseous streams. The FID, while sensitive, will not detect some sulfur gases such as H_2S, COS, CS_2, and SO_2. Thermal Conductivity Detectors have traditionally found application for sulfur analysis; however, ppb sensitivities required for many applications are not realistic.

Many factors must be considered when deciding on the best sulfur selective detector to employ for a given application. Attributes such as selectivity, response factor behavior, quenching, column compatibility, and sensitivity should be considered and matched to the application. All detectors studied in this work have at least three orders of magnitude dynamic range, making them suitable for a relatively wide concentration band. A summary of the detector characteristics used in this work is given in Table 3. The values for sensitivity, selectivity, and dynamic range are those claimed by the respective suppliers. In this study, instrumental conditions were generally optimized for maximum sensitivity. These conditions will not always lead to the best chromatography.

The sulfur mix diluted with helium as per the point of use sample preparation scheme was used to access practical limits of detection. A methyl silicone column (105 m × 0.53 mm × 5 µm DB-1) was used for the comparison because very little adsorption of sulfur species occurs on the stationary phase, eliminating the potential for inaccurate MDL calculations. Adsorption of certain sulfur compounds is known to occur on Plot or silica columns, making their use somewhat more problematic. Chromatograms of the sulfur mix are shown in Figure 4 for each of the four detectors. Note that the time scales for the five GC traces do not line up, the chromatograms have been adjusted either right or left to make the figure easier to read. As is evident from the figure, the AED, PFPD, and SCD's are all capable of sulfur detection in the sub 10 ppb range with reasonable signal to noise ratios. Even the FPD can show good results at 50 ppb when the system is maximized for sensitivity.

The dynamic blending system provides a convenient means of looking at detector selectivity by mixing in real world samples (matrix) with the low-level sulfur calibration mix. It also allows looking at just the pure matrix once potential hydrocarbon or other gas interferences/coelutions are understood with any given column and temperature program

Table 3. Summary of Detector Characteristics

Detector characteristics

Detector	FPD	PFPD	SCD	AED
Supplier	Agilent	OI	Sievers/Antek	Agilent
MDL sulfur	20 pg/sec	1 pg/sec	0.5 pg/sec	2 pg/sec
Selectivity	10^5	10^6	10^6	10^5
Dynamic range	10^3	10^3	10^5, linear	10^4, linear
Quenching	Yes	Yes	No	No
Equimolar response	Approximate	Yes	Yes	Yes
Packed column compatible	Yes	No, 1 mL/min flow	Yes	Yes
Other elements	P, Sn	P	N	C,H,N,O,Cl, etc., total 26
Approximate relative cost	$	$$	$$$	$$$$

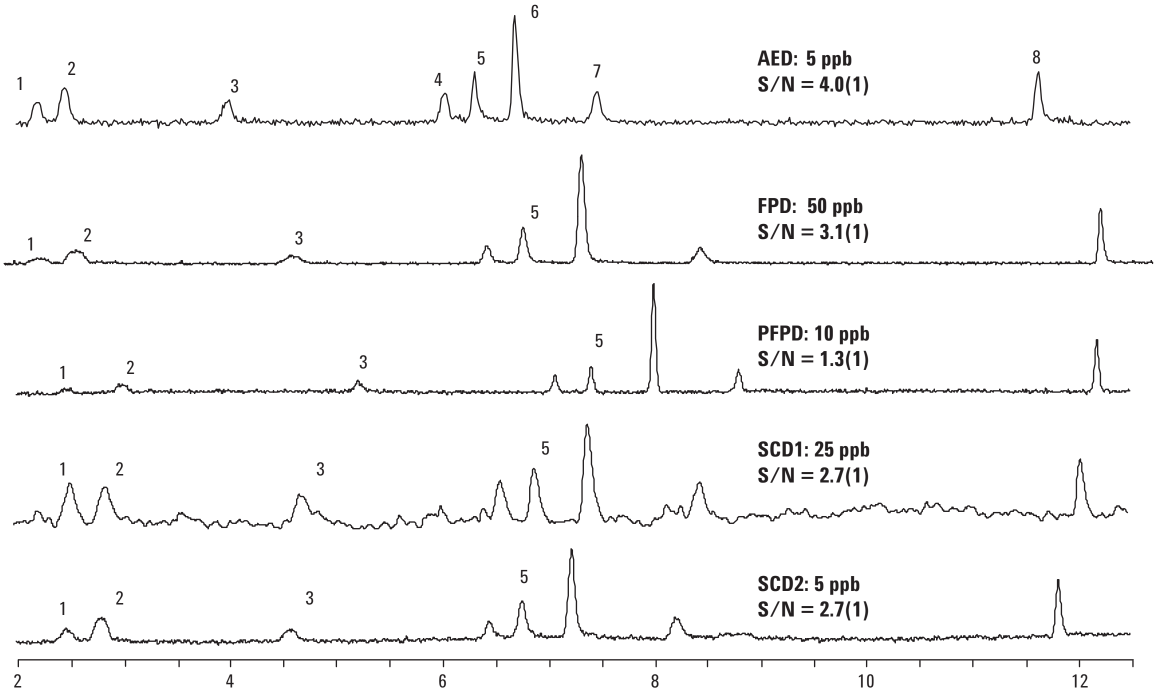


Figure 4. Detection limits for the four sulfur selective detectors using the eight component calibration mix.

regime. In Figure 5, FPD chromatograms are shown where polymer grade ethylene (PGE) was blended into the sulfur calibration mix. Sulfur levels of 50 ppb and 10 ppb per component are shown in the top and bottom traces, respectively. Because the sulfur compounds are well separated from the ethylene on the DB-1 column, most can still be quantified at 10 ppb. Only H_2S and SO_2, two of the more reactive; less well chromatographically behaved compounds disappear at 10 ppb. In Figures 6 through 9, chromatograms are shown for the AED, PFPD, SCD (Antek), and SCD (Sievers),

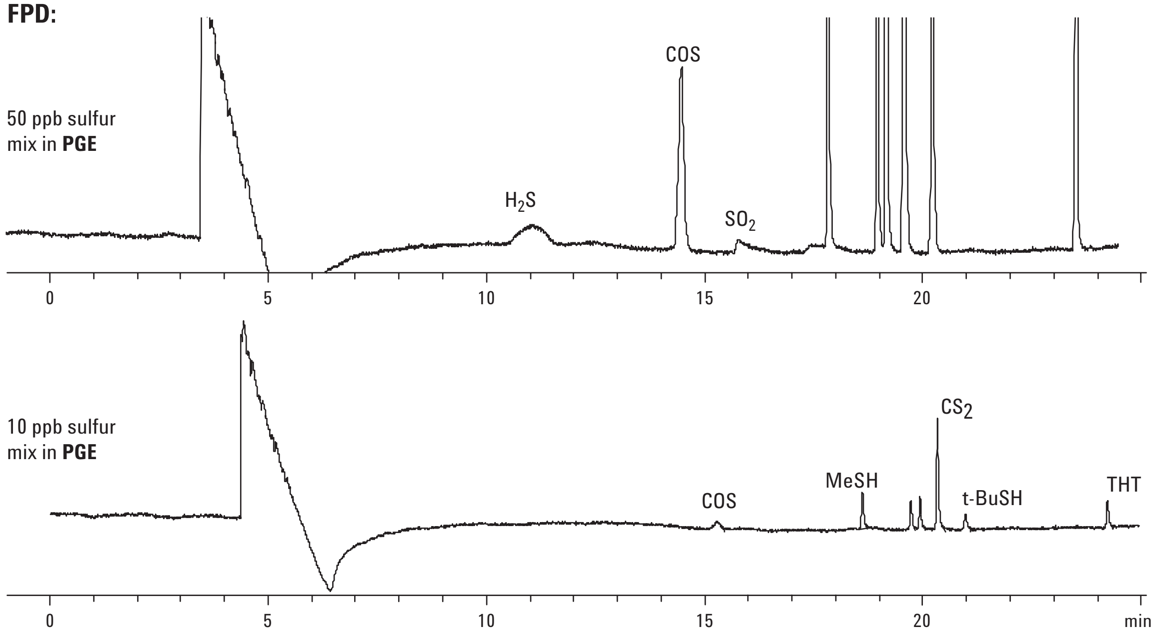


Figure 5. Agilent FPD, ppb level sulfur mix in polymer grade ethylene. Five cc sample loop.

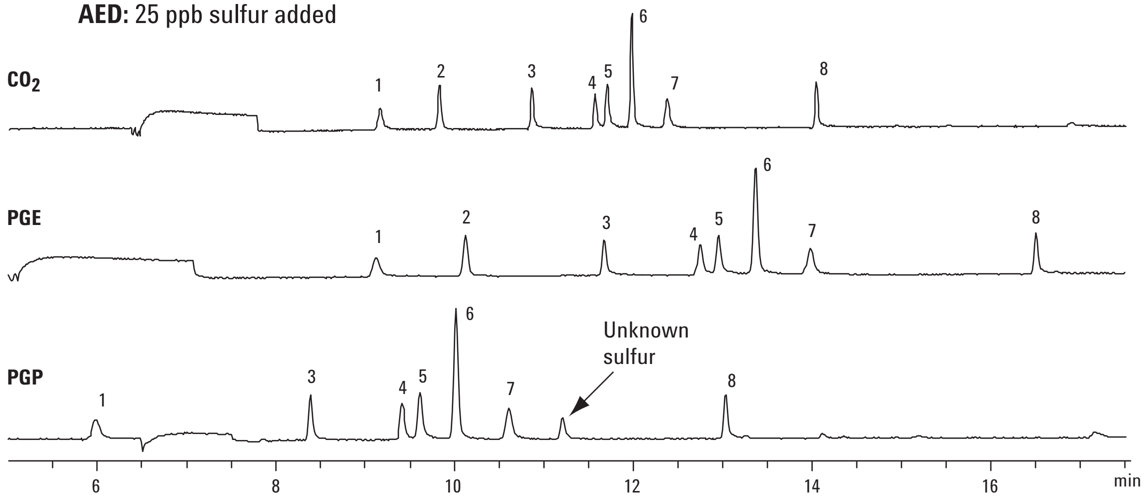


Figure 6. Agilent AED, ppb level sulfur mix in food grade CO_2, polymer grade ethylene, and polymer grade propylene.

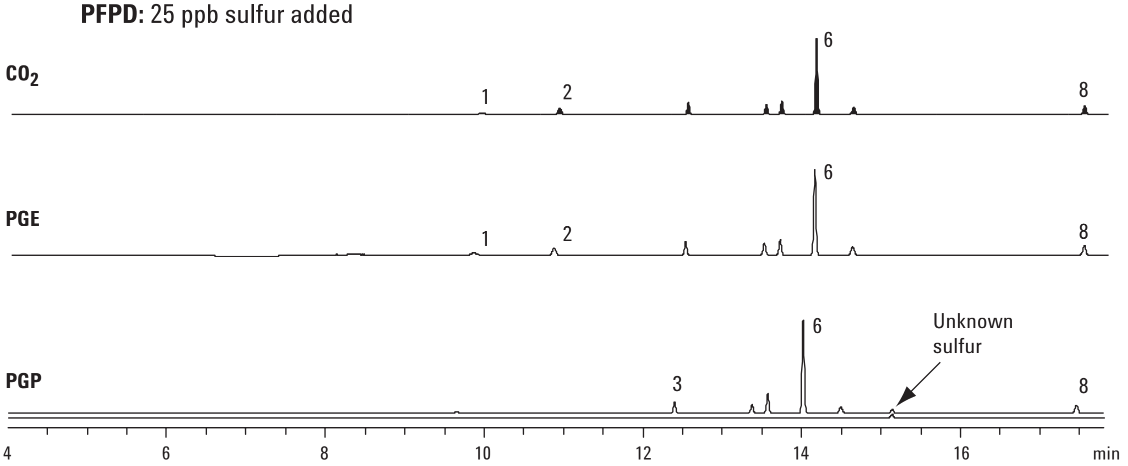


Figure 7. OI Analytical PFPD, ppb level sulfur mix in food grade CO_2, polymer grade ethylene, and polymer grade propylene.

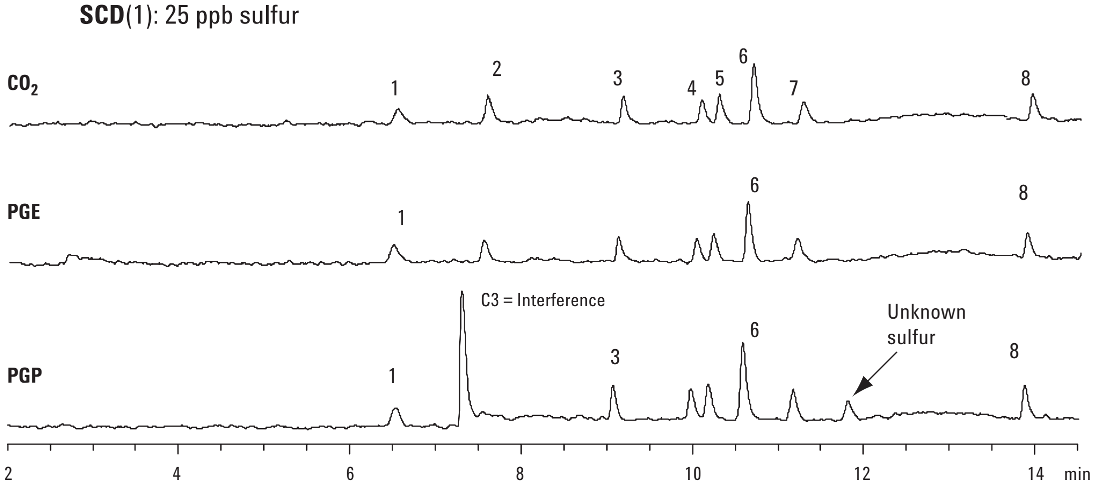


Figure 8. Antek SCD, ppb level sulfur mix in food grade CO_2, polymer grade ethylene, and polymer grade propylene.

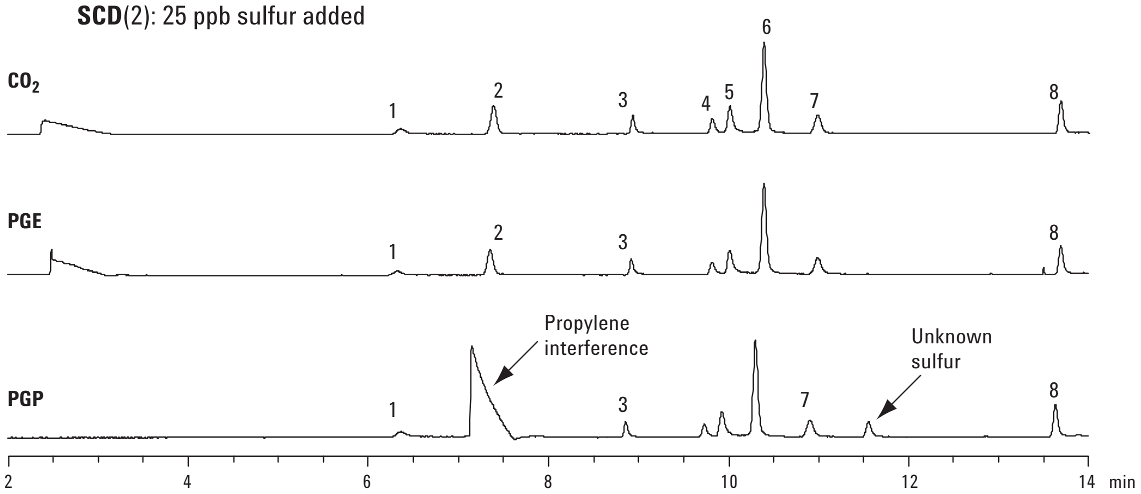


Figure 9. Sievers SCD, ppb level sulfur mix in food grade CO_2, polymer grade ethylene, and polymer grade propylene.

respectively, with 25 ppb per sulfur component added into matrices of CO_2, polymer grade ethylene (PGE), and polymer grade propylene (PGP). Note that with all four detectors, COS cannot be analyzed in propylene on the methyl silicone column due to hydrocarbon coelution. The method developer should consider use of the J&W GasPro column for situations where COS must be quantified.

Detector Considerations

FPD

A good over-all choice for sulfur levels above approximately 100 ppb when using the configuration described here. Sulfur response is determined by a square root relationship since the flame reaction converts sulfur atoms to an S_2 complex. The FPD has ease-of-use equivalent to a FID and compatibility with many column types. However, quenching can be an issue; hence the need for complete separation of the sulfur analytes from the matrix for ppb analyses. Maximum sensitivity is obtained by running a hydrogen rich flame. Cost is also the lowest of all detectors in this comparison.

SCD

A good detector for low-level sulfur, reaching 5 to 10 ppb in ideal cases. Quenching is not a problem with this detector, however, response factors can drift over a period of just a few days. Coking in the reaction chamber can also occur and care must be taken to avoid overload. When well tuned 10^6 selectivity is possible.

PFPD

Setup can be time consuming to achieve best performance. Once operational, sensitivity can be 5X to 7X better than the FPD. Very good specificity and equimolar sulfur response are among the detector's strong points. Quenching problems may be somewhat less severe than the FPD if ideally tuned. The column flow is limited to approximately 1 mL/min with a margin of only ±10%, thus column choices are very limited.

AED

The AED is the ultimate sulfur detector with low ppb sensitivity, no quenching, equimolar response and compatibility with many column types. Reliability, stability and ease of use are all proven attributes of the AED. The ability to perform compound independent calibration and determine molecular formulas empirically are useful features.[2] For many hydrocarbon streams, the ability to simultaneously collect carbon chromatograms (C 179 nm for high levels and C 193 nm for low levels) and sulfur is extremely useful. For example, quantitation of hydrocarbons, CO, CO_2, and sulfur in propylene is possible in one run, followed by a second run to obtain trace arsine and phosphine. These features come at the expense of a higher price point than other sulfur selective detectors. However, versatility with detection of 26 elements can make the AED a very cost-effective solution for many petrochemical applications.

Conclusions and Application Guidelines

When choosing a chromatographic system for trace sulfur detection, first look at your sensitivity requirements; this may eliminate some choices. Always employ Silcosteel or Sulfinert tubing and fitting where possible in the sample path. The low volume inert volatiles interface is a real asset for trace work providing a convenient low volume valve/column interface. If the matrix is reasonably simple and sulfur levels are in the low ppm to 50 ppb range then the FPD will usually be a good choice. In fact, with careful attention paid to sample introduction hardware and column choice, the FPD is surprisingly sensitive (sub 50 ppb sensitivity). For samples where it is not feasible to completely separate sulfur components from the hydrocarbon matrix and low ppb sensitivities are required, the SCD can be considered if experienced users are available. The PFPD also is capable of excellent sensitivity to low ppb levels. Because of quenching, it is best suited for light sulfur and hydrocarbon streams where good separation is achievable. Dynamic range must be considered as well. The AED and SCD can handle the widest concentration range from low ppb to high ppm levels. In terms of over all performance, the AED will handle the widest range of applications obtaining carbon and sulfur chromatograms simultaneously without time consuming “tuning” for optimal operation. Analysis down to 5 ppb in complex matrices is easily accomplished.

References

1. Agilent's FlowCalc 2.0 software (available free from the Agilent Technologies Web site, http://www.chem.agilent.com/cag/servsup/usersoft/main.html
2. M .J. Szelewski, *Empirical Formula Determinations and Compound-Independent Calibration Using a GC-AED System*, Application Note 228-382, Publication Number 5965-8144E, May 1997 (Downloadable from agilent.com).

Statement Concerning Use of Third Party Detectors

The information presented here for non-Agilent sulfur selective detectors is based on one detector of each model number. The SCD's and PFPD were setup and operated per the manufacturers' written documentation. Agilent does not claim to be an expert in the operation of these detectors.

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