Use of GC/MSD for Determination of Volatile Sulfur: Application in Natural Gas Fuel Cell Systems and Other Gaseous Streams

Application

Fuel Cells, Petrochemicals

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Abstract

The mass selective detector is an ideal tool for the analysis of trace level volatile sulfur compounds. It is differentiated from other sulfur-selective detectors in that structural information is provided. When operated in the Selected Ion Monitoring mode, excellent sensitivity and selectivity is obtained. Eight volatile sulfur compounds are used to demonstrate low parts-per-billion analysis in a variety of hydrocarbon matrices. The system is well suited for fuel cell developers for characterization of fuel feedstocks and the analysis of impurities that can poison critical catalytic processes. Measurement of carbonyl sulfide in propylene is also demonstrated.

Introduction

Sulfur detectors are finding widespread use in a broad range of applications that cut across many industries. Demand for low-level sulfur detection will only increase in the future in response to more stringent quality control and regulation. The significance and need for low level sulfur measurements have been detailed in previous Agilent application literature [1, 2, 3, 4].

Emerging needs are found in alternative energy applications such as the fuel cell industry. Fuel processors serve a vital role in many fuel cell systems and are sensitive to feedstock composition and impurities. Potential fuels include hydrogen, natural gas, propane, methanol, gasoline and other hydrocarbon streams. Near-term development is concentrating on reformed hydrocarbon fuels creating a need to monitor composition and impurities. Fuel contaminants can adversely affect performance of the fuel cell system. This is especially true for Polymer Electrolyte Membrane (PEMFC) and Molten Carbonate (MCFC) types, although Phosphoric Acid (PAFC) and Solid Oxide (SOFC) technologies are also subject to sulfur poisoning. For example, natural gas feeds to external or internal catalytic reformers need to be desulfurized since low ppm sulfur levels can poison the reformer catalyst and fuel cell stack. Potential breakthrough of sulfur from the desulfurization beds needs to be closely monitored.

The mass selective detector (MSD) is usually not considered when the need for low-level volatile sulfur quantitation and speciation arises in the analytical laboratory or plant. Selective detectors such as the flame photometric (FPD), pulsed flame photometric (PFPD), and sulfur chemiluminescence (SCD) have traditionally dominated these applications [1]. The 6890N/5973N GC/MSD system is a very capable alternative to these detectors providing the added benefit of positive compound identification. Details on how to set up the system for optimum sensitivity and selectivity are discussed in this paper. The specific hardware configuration reviewed is applicable to a wide range of applications.

MSDs are now widely used in many routine applications including QA/QC environments. The 5973N is easy to use, compact in size, and stable over long time periods. Tuning is software controlled and automatic, a significantly easier task than what is needed for some sulfur-selective detectors.

A common problem with many sulfur-selective detectors is hydrocarbon interference, especially from chromatographic coelution [4]. The measurement challenge is acute when the interfering hydrocarbon comprises the majority of the sample, as in the analysis of impurities in ethylene and propylene. In most cases, an accurate determination of the sulfur compound is not possible. However, the use of the MSD and selected ion monitoring (SIM) can largely overcome the coelution problem for many applications.

Experimental

Networked versions of the 6890 and 5973, designated by the N following the product number were used in this work; replacing the previously HPIB-interfaced models. Well known benefits of LAN include reliability, lack of distance limitations and simple configuration.

The sulfur calibration mix consisted of the following components at 5 ppm each: Hydrogen sulfide, carbonyl sulfide, methyl mercaptan, ethyl mercaptan, dimethyl sulfide, carbonyl sulfide, t-butyl mercaptan, and tetrahydrothiophene. The blend in helium was purchased from DCG Partnership, Pearland, TX.

A 6-port gas-sampling valve was connected directly to the volatiles interface on the 6890N with Sulfinert 1/16-inch tubing. See the sample introduction diagram in Figure 1. The sample loop, tubing and inlet are either Sulfinert or Silcosteel treated for inertness. Table 1 contains the instrument conditions.

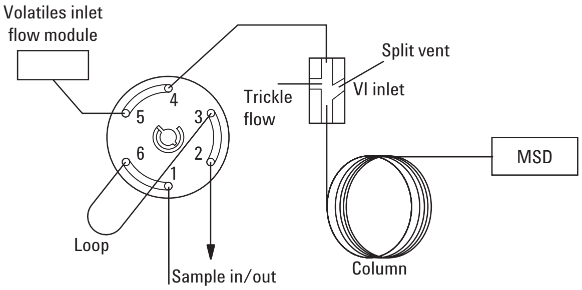


Figure 1. Sample introduction scheme.

Table 1. Instrument Conditions

Injection port	**Volatiles interface**
Temperature	150 °C
Split ratios	1 : 1 up to 50 : 1
Carrier gas	Helium
Constant flow mode	1.9 mL/min
Injection source	**6-Port sampling valve**
Material	Hastelloy C
Temperature	150 °C
Loop	Sulfinert, 0.5 cc
Column	**60 m × 0.320 mm × 5.0 µm DB-1**
Initial temperature	40 °C
Initial time	5 min
Temperature ramp	25 °C/min
Final temperature	270 °C
Final time	2 min
5973 MSD	
Mass range	33 to 100 and 12 to 100
Scans	13.1/sec and 15.9/sec
Samples	2
Threshold	150
EM voltage	BFB.u tune voltage
Solvent delay	3 min
Source temperature	230 °C
Quad temperature	150 °C
Transfer line	280 °C

Gaseous blends of the sulfur standard in helium or other matrices such as natural gas, propylene, and refinery gas were prepared using dynamic blending at the point and time of use. Diluent (matrix) gases are mixed with the calibration standard using an Aux EPC module on the 6890N GC. This system and the hardware employed were described in detail previously [2].

Positioning of the column in the MSD must be carefully done to avoid loss of sulfur sensitivity. To position the column just inside the source, 2 to 3 millimeters of the column should be visible at the MSD end of the transfer line. See reference 5 for installation details.

Results and Discussion

System Calibration

First, the system was calibrated and checked for linearity by analyzing the sulfur mix at various concentrations. The dynamic blending system was used to prepare seven and five level calibrations using helium and natural gas as diluents, respectively. Table 2 lists the concentrations used. Calibrations were focused in the ppb range since this is where most analytical problems for sulfur analysis are found. SIM acquisition mode, discussed later in this section, was used.

Table 2. **Calibration levels for checking system linearity. Sulfur concentrations in ppbv.**

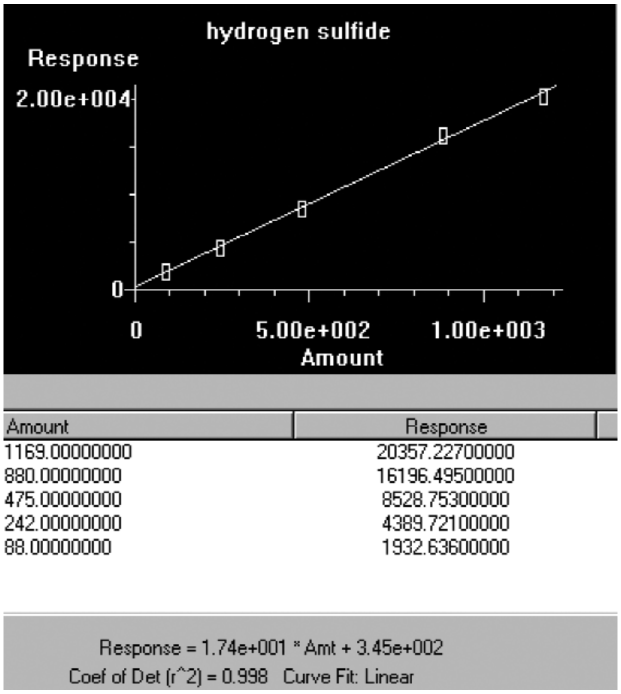
Cal Level	1	2	3	4	5	6	7
Conc. in helium	21	35	46	57	95	1600	3600
Conc. in nat gas	88	242	475	880	1170	--	--

Calibrations are linear in both matrices for all eight sulfur compounds. This is seen in Table 3 where the regression coefficient, r^2 values appear. This is an indication not only that the system response is linear but also that calculated concentrations from the blending system are accurate. Unlike some sulfur-selective detectors, the MSD does not show equimolar response. Each compound will have its own response characteristics, requiring each component's response factor to be determined.

Table 3. **Calibration Regression Coefficient r^2 Values**

Compound	Helium	Natural gas
H_2S	0.998	0.998
COS	0.998	0.999
CH_3SH	0.997	0.999
EtSH	0.996	0.998
DMS	0.998	0.998
CS_2	0.998	0.998
t-ButylSH	0.996	0.993
THT	0.996	0.992

One of the calibration plots as produced by the MSD Chemstation is shown in Figure 2 for the calibration of H_2S in natural gas.



Amount	Response
1169.00000000	20357.22700000
880.00000000	16196.49500000
475.00000000	8528.75300000
242.00000000	4389.72100000
88.00000000	1932.63600000

Response = 1.74e+001 * Amt + 3.45e+002
Coef of Det (r^2) = 0.998 Curve Fit: Linear

Figure 2. **Five level calibration plot of H_2S using natural gas as the diluent. Calibration range is from 88 to 1170 ppb.**

Scan Results

The total ion chromatogram (TIC) of the eight-component sulfur mix at 1.3 ppm in helium is shown in Figure 3 using a split ratio of 0.5 to 1. As is evident in the figure, H_2S is close to the minimum detectable limit (MDL) for this particular set of operating conditions. While operating in scan mode is useful for initial method development, unknown identification and retention time determinations, use of extracted ions from a scan and/or SIM are required to improve overall sensitivity and selectivity.

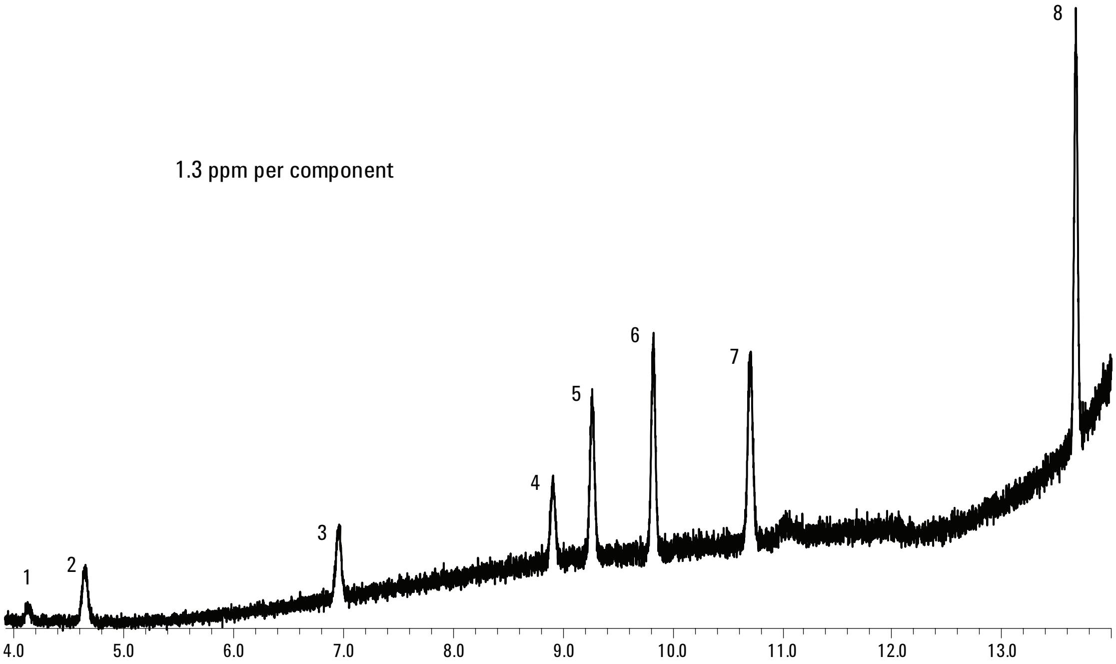


Figure 3. **Total ion chromatogram of the eight-component sulfur mix at 1.3 ppm per component. Scan 33-100 amu. Peak labels: 1. hydrogen sulfide, 2. carbonyl sulfide, 3. methyl mercaptan, 4. ethyl mercaptan, 5. dimethyl sulfide, 6. carbon disulfide, 7. t-butyl sulfide, 8. tetrahydrothiophene.**

Extracted Ion Results

In Figure 4, extracted ion chromatograms are shown for ions 60 and 62. Three of the eight sulfur compounds are found with these target ions. Ion 60 is present in COS and tetrahydrothiophene, and ion 62 is found in ethyl mercaptan and dimethyl sulfide. The concentration of the sample was 86 ppb per component in helium. Extracted ion chromatograms for the other sulfur compounds show similar signal to noise ratios at the concentration level. A considerable improvement in sensitivity is achieved by using extracted ions. In cases where this does not provide sufficient sensitivity, the next step should be SIM.

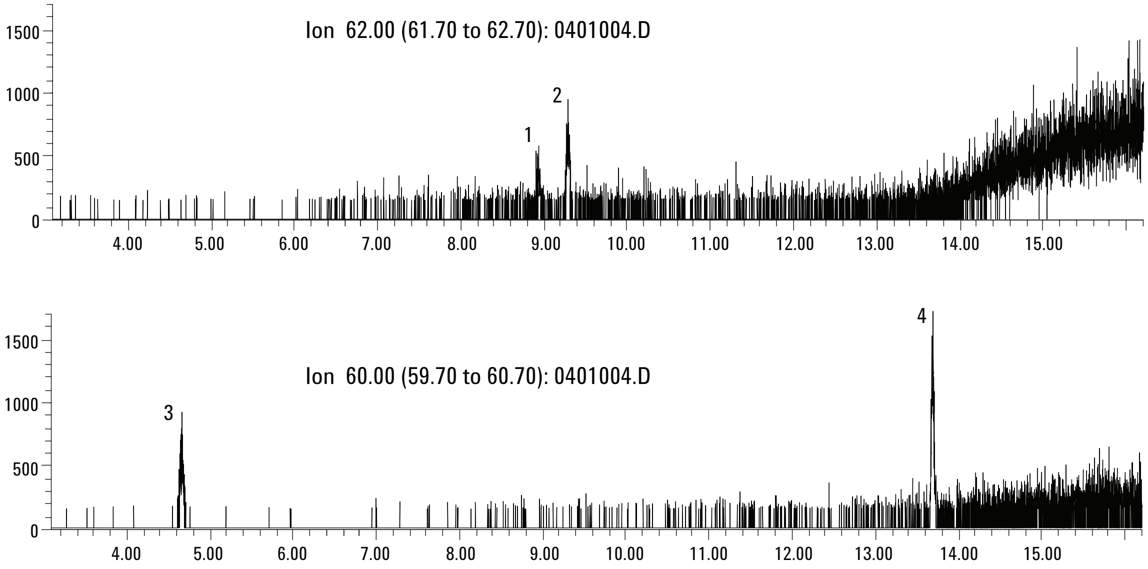


Figure 4. **Extracted ion chromatograms for ions 60 and 62. Concentration is 86 ppb per component. Split ratio 1:1. Peak labels: 1. EtSH, 2. DMS, 3. COS, 4. THT.**

Application of SIM

SIM provides superior sensitivity and selectivity. Since sulfur determinations will normally be done in hydrocarbon matrices, care must be taken to select ions that ideally have no hydrocarbon contribution. If this can be done, excellent selectivity can be achieved even in cases where coelution of sulfur species and hydrocarbon occur. This is an important distinction and advantage of the MSD compared to some of the common gas chromatographic sulfur-selective detectors. Both the FPD and PFPD will suffer from quenching if coelution occurs making accurate quantitation of low-level sulfur impossible [2]. Even the SCD will have problems measuring low ppm sulfur in the presence of a dominant coeluting hydrocarbon. In situations where a unique sulfur ion cannot be found, refinement of the method and chromatographic column/conditions to achieve separation from the interfering hydrocarbon should be tried [2]. Also, when operating the MSD in SIM mode, it is usually best to select low resolution for maximum sensitivity at the expense of some mass selectivity loss.

The SIM ions used for each sulfur compound are listed in Table 4. These ions were chosen to minimize interference from hydrocarbons. To arrive at the ions shown in the table, a scan of the sulfur mix in helium is acquired to identify target ions. Library spectra can also be consulted. Hydrocarbon mixes such as natural gas and refinery gas are then run separately using the SIM table to look for ions that may match those selected for the sulfur. The table may be further refined if hydrocarbon interferences appear. Retention times of the sulfur compounds are also needed to set up the time-programmed groups. These are not the only possible ions that can be used. For some of the compounds other choices or additional ions could be included in the SIM table. While not necessary for this relatively simple sulfur example, the use of second and third qualifier ions may give the analyst a higher level of confidence of a compound's identity by comparing ion ratios to library spectra for a particular compound.

Table 4. Optimized SIM table for selective sulfur detection in hydrocarbon streams. Dwell time for each ion is 100 ms.

GROUP	START TIME (min)	TARGET and QUALIFIER IONS	COMPOUND
1	3.00	33,34	H_2S
2	4.20	60	COS
3	6.00	45,47	MeSH
4	8.00	47	EtSH
5	9.10	45,47,62	DMS
6	9.70	44,76	CS_2
7	10.20	57,90	t-ButylSH
8	11.80	45,60,88	THT

Fuel Cell Natural Gas Feedstocks: Composition and Impurities

The TIC of a natural gas scan and sulfur mix SIM runs are overlaid for illustration purposes in Figure 5. Note that with the 60 m × 0.32 mm × 5.0 µm DB-1 column, all hydrocarbons and CO_2 are separated. Natural gas compounds in order of elution are: O_2/N_2, CH_4, CO_2, ethane, propane, i-butane, n-butane, i-pentane, and n-pentane. From the overlay, it can be seen that seven of the eight sulfurs do not coelute with natural gas components; only COS and propane show potential overlap. This also demonstrates the utility of the system for fuel cell feed streams, providing both hydrocarbon composition and gas impurity analysis.

The chromatogram shown in Figure 6 of the sulfur mix in helium was produced using the SIM parameters in Table 3. The offsets seen in the baseline are a result of the MSD switching from group to group and should not be interpreted as a chromatographic problem. Excellent signal to noise is seen for all components at the 46 ppb level. The sulfur mix was then further diluted to 16 ppb per component. The resulting chromatograms for H_2S and COS, the most challenging analytes, and tetrahydrothiophene are shown in Figure 7.

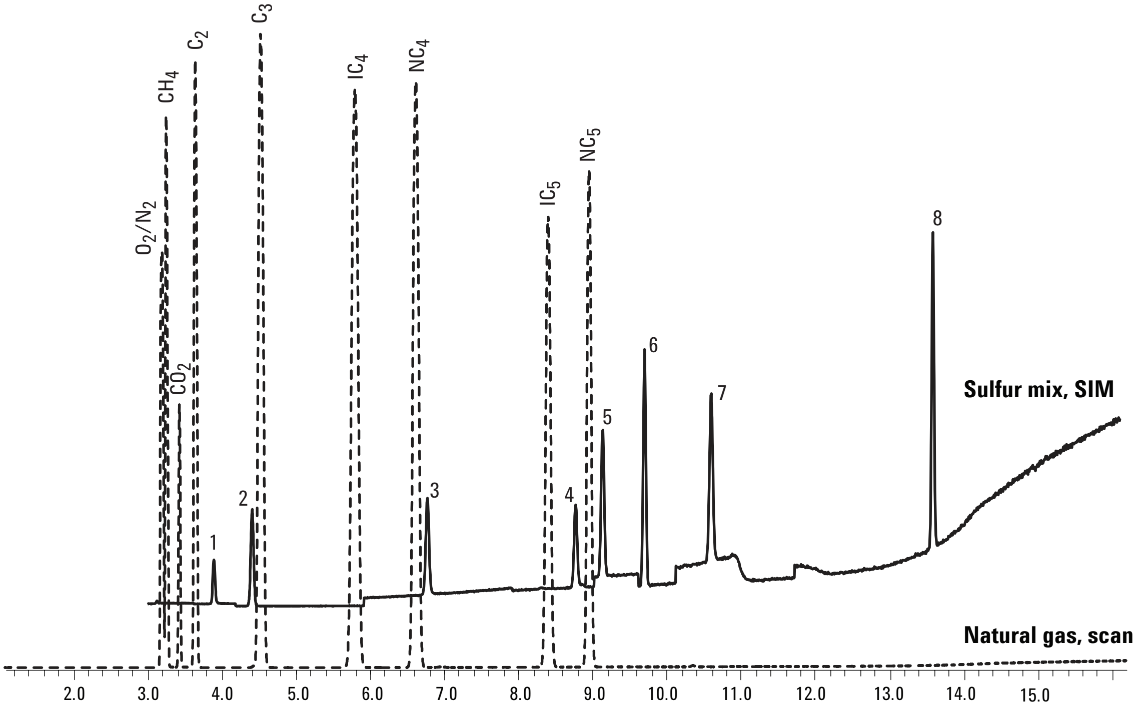


Figure 5. Overlay of two runs: natural gas scan (12 to 100 amu) and sulfur mix at 4.5 ppm in SIM mode. Split ratio 20:1. Sulfur peak labels same as in Figure 3.

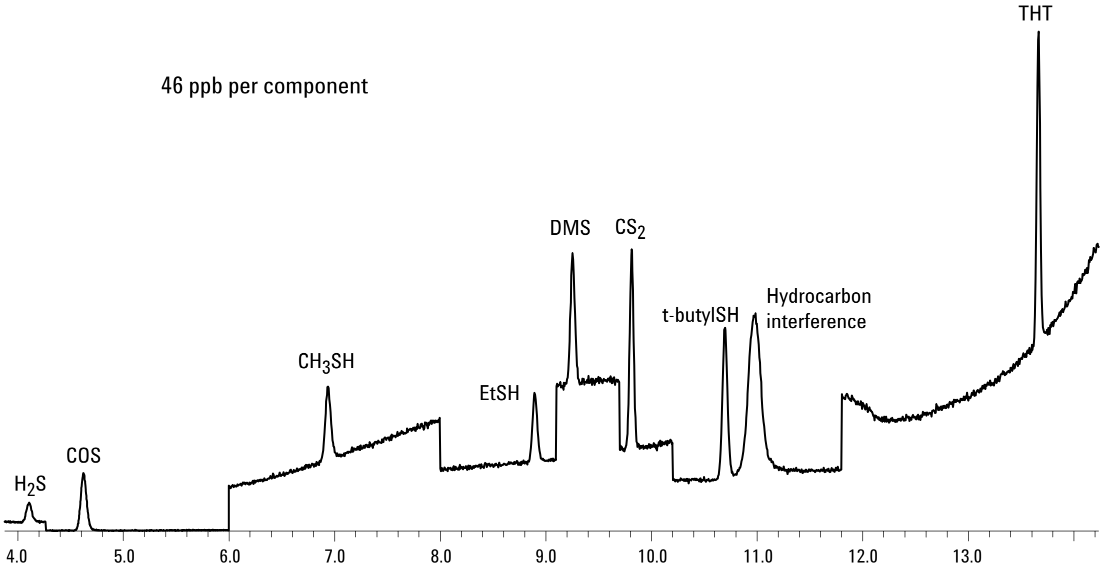


Figure 6. Eight-component sulfur mix in helium at 46 ppb per component in SIM mode. Split ratio 0.5:1.

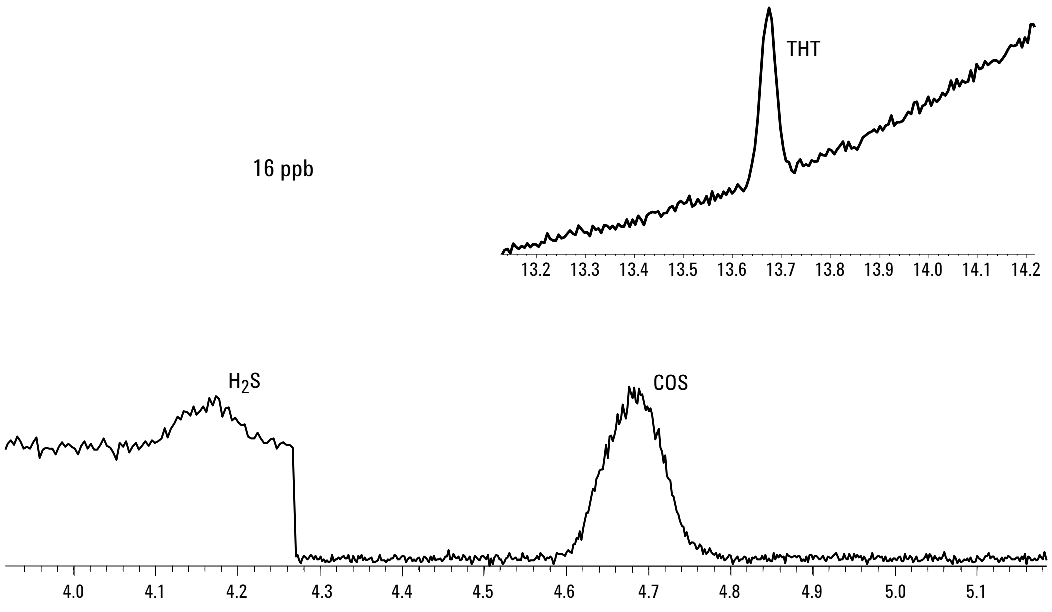


Figure 7. H_2S, COS and tetrahydrothiophene (insert) at 16 ppb each. SIM was used.

For ppb sulfur analysis, it is recommended that the pure matrix be run separately using the sulfur SIM acquisition parameters. Ideally, no response would be seen. If ions of the hydrocarbon matrix are seen, they can be noted and not mistaken for sulfur compounds. This is illustrated in Figure 8 for natural gas streams. Chromatograms of the sulfur mix in scan mode and pure natural gas in SIM mode are overlaid for illustrative purposes. Both are drawn to the same scale. This is a good practice to follow not only for sulfur but also for any impurity analysis using SIM.

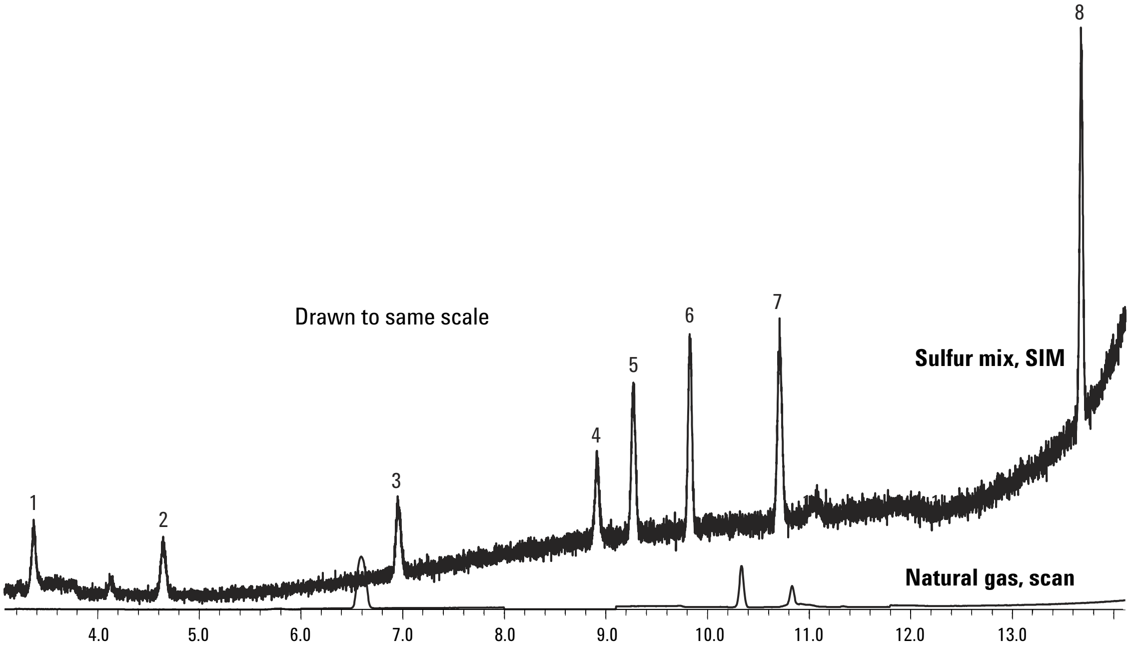


Figure 8. Overlay of sulfur mix in scan (33-100 amu) and natural gas (using sulfur SIM table). Ideally the natural gas chromatogram would be blank. Same scale used for both.

Analysis of COS in Propylene and Propane

Measurement of ppb COS in propylene and propane can be a challenging analytical problem due to coelution of COS/propylene on the preferred methyl silicone columns. This coelution is illustrated in Figure 9 where two independent (separate runs) are overlaid. Both the FPD and PFPD will be unsuccessful with this analysis due to quenching. The SCD's selectivity can also be exceeded for low ppb COS analysis

SIM (ion 60) was employed for the analysis of COS. To avoid overloading the source, the split ratio was increased to 50:1. To determine the effect of coeluting propylene on COS response, two runs were performed at identical concentrations of 105 ppb COS. The diluents for the first and second runs were helium and propylene, respectively. Chromatograms for both runs are shown in Figure 10. The helium chromatogram shows the true COS area unaffected by any other coeluting compound. This area is then compared to that of COS in propylene diluent using the area ratio (COS propylene/COS helium) to indicate how coelution has affected the MSD response. This ratio of 0.77 indicates that COS in propylene response is suppressed by only 23%, probably due to a reduction in ionization efficiency. Moreover, a subsequent experiment that constructed a five level calibration of COS in propylene showed linear behavior over the range of 20 to 1200 ppb. Therefore, using a carefully constructed SIM method, the MSD has the capability of quantifying ppb level COS in coeluting 99+% propylene. It follows, in the general case, that coeluting analytes do not preclude quantification even when concentration differences exceed 10^5 provided unique ions can be identified for the component of interest.

These results and conclusions are relevant to fuel cell developers who are using high propane (for example 50 to 99%) as a feedstock. The performance, chromatographic behavior, and minimal detectable impurity levels will be very similar. Under the conditions used the retention time of propane will differ by less than 0.1 minute from propylene (see propane retention time in Figure 5). Sulfur impurities other than COS can be easily measured.

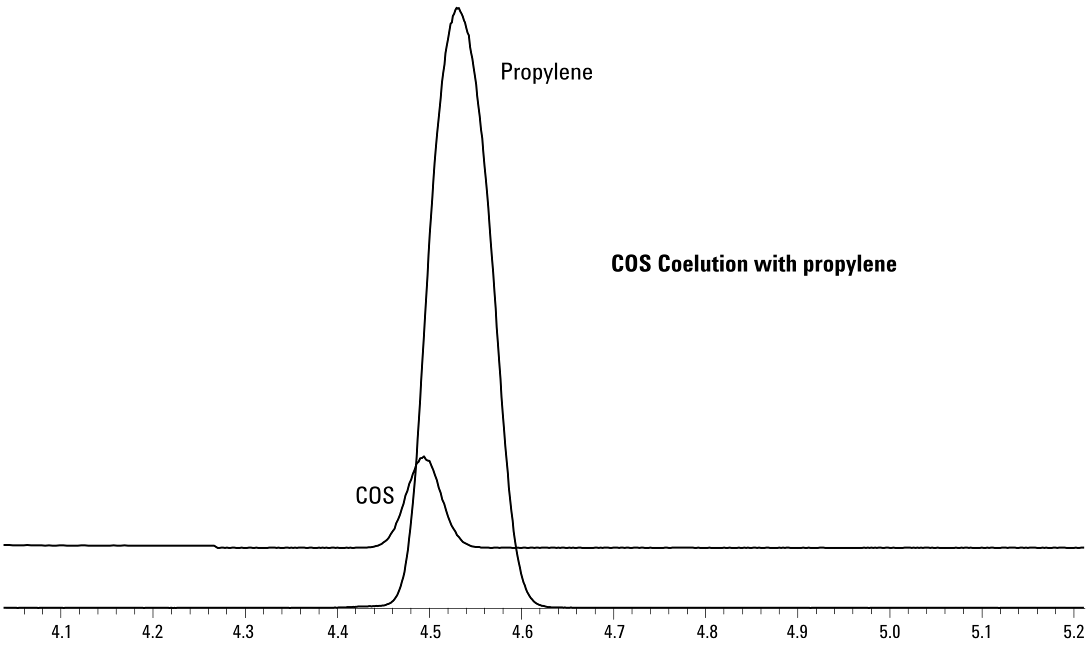
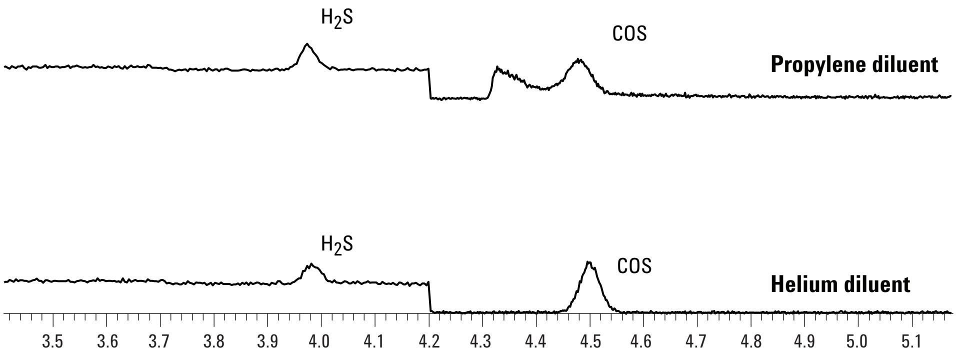


Figure 9. **Two separate chromatograms (from separate runs) superimposed showing the coelution of COS with propylene. Split ratio 50:1.**



105 ppb each H_2S and COS
Area ratio: COS in Propylene/COS in Helium = 0.77

Figure 10. Comparison of COS response (SIM mode) in helium and propylene. Split ratio 50 to 1.

Conclusions

The hardware and associated methods outlined in this paper demonstrate the MSD's capabilities as a sensitive and selective detector for gaseous analytes. It has the added advantage of providing structural information. Sulfur detection at low ppb levels is easily achieved through use of a time programmed SIM table consisting of unique ions for the compounds of interest. This minimizes hydrocarbon interference making it possible to quantitate low-level analytes such as COS with coeluting propylene.

The 6890N/5973N system is also a powerful tool for fuel cell developers, providing detailed composition and impurity analyses of common fuels. The examples shown here demonstrate how natural gas feed could be characterized providing complete speciation of sulfur compounds including odorants or naturally occurring impurities such as H_2S. The system can also be used to monitor the performance of desulfurization beds and reformer output.

References

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