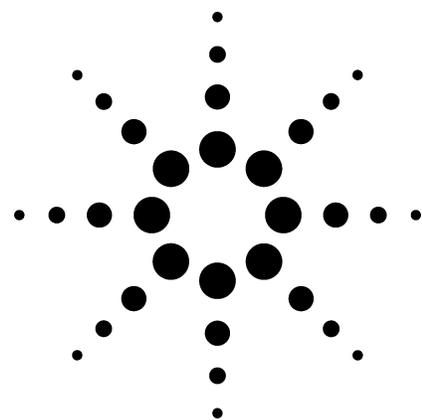


Use of the New 5973 inert for Determination of Low-Level Volatile Sulfur in Gaseous Streams

Application

Gas Chromatography



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Abstract

The enhanced inertness of the new 5973 inert MSD improves analysis of trace level volatile sulfur compounds. When operated in scan or selected ion monitoring mode, excellent sensitivity, selectivity, and peak symmetry are obtained for active compounds. Eight volatile sulfur species are used to demonstrate these attributes in a variety of hydrocarbon matrices. The system is well suited for the characterization of fuel feedstocks and basic petrochemicals, where impurities can poison critical catalytic processes or affect product quality.

Introduction

Sulfur detectors find widespread use in a broad range of applications that span 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 are detailed in previous Agilent application literature [1, 2, 3, 4].

The mass selective detector (MSD) is usually not considered first when the need for low-level volatile sulfur quantitation and speciation arises in the analytical laboratory. Selective detectors such as the flame photometric detector (FPD), pulsed flame photometric detector (PFPD), and sulfur chemiluminescence detector (SCD) have traditionally dominated these applications [1]. The 6890N/5973 inert GC/MSD system is a very capable alternative to these detectors, providing optimized inertness and the benefit of positive compound identification. This application note details how to set up the system for optimum sensitivity and selectivity. The specific hardware configuration is applicable to a wide range of applications where ppb detection of gaseous analytes is required.

A common problem with many sulfur selective detectors is hydrocarbon interference, especially from co-elution [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 5973 inert in selected ion monitoring (SIM) mode can largely overcome quenching caused by co-elution for many applications.



Experimental

The 5973 inert equipped with a new deactivated source was used for all experiments. The 3-mm drawout lens was used to achieve low ppb sensitivity while maintaining linearity over the ppb to low ppm concentration range needed for most sulfur measurements.

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 Siltek™ 1/16-inch tubing. See the sample introduction diagram in Figure 1. The sample loop, tubing, and inlet are Siltek treated for inertness.

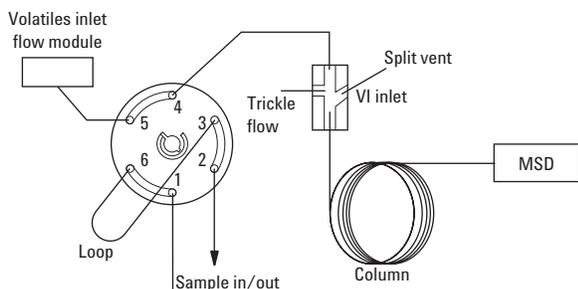


Figure 1. Sample introduction scheme.

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 have been described in detail [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 mm to 3 mm of the column should be visible at the MSD end of the transfer line. See Reference 5 for installation details. See Table 1 for instrument conditions.

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 was used.

Table 1. Instrument Conditions

6890N GC		5973 inert MSD	
Injection port	Volatiles interface	Mass range	33–100 and 12–100 amu
Temperature	150 °C	Scans	13.1/s and 15.9/s
Split ratios	1:1 up to 50:1	Samples	2
Carrier gas	Helium	Threshold	150
Constant Flow Mode	1.9 mL/min	EM Voltage	BFB.U tune voltage
Injection source	6-port gas sampling valve	Solvent delay	3.00 min
Material	Hastelloy C	Source	Surface deactivated
Temperature	150 °C	Drawout lens	3 mm
Loop	Siltek, 0.5 cc	Source temperature	230 °C
Column	60 m × 0.320 mm × 5.0 μm DB-1	Quad temperature	150 °C
Initial temperature	40 °C	Transfer line	280 °C
Initial time	5 min		
Temperature ramp	25 °C/min		
Final temperature	270 °C		
Final time	2 min		

Calibrations are linear in both matrices for all eight sulfur compounds. Refer to Table 3 where the regression coefficient r^2 values are shown. This is an indication that not only is the system response linear, but also that adsorption is not occurring in the GC or MSD from active sites. If adsorption were present, then one would expect a drop off at the lower end of the calibration curve. This is a direct benefit of the new inert MSD source.

Two calibration plots, as produced by the MSD ChemStation, are shown in Figures 2 and 3 for the calibration of H₂S and COS in natural gas, respectively. These are two challenging compounds with respect to activity, and they help illustrate the effectiveness of the inert system.

The 3-mm Drawout Lens

The 3-mm lens offers excellent sensitivity-optimized performance for this application. The 3-mm drawout was chosen for this work to meet the objective of reliable low ppb sulfur analysis. In addition, linearity over only a part of the MSD's dynamic range was required. Calibrations from 20 ppb to 5 ppm cover expected impurity ranges in real world samples and show excellent linearity with the 3-mm lens including samples run in a natural gas matrix where significant hydrocarbon fragmentation occurs.

Table 2. Calibration Levels for Checking System Linearity. Sulfur Concentrations in ppb.

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	--	--

Table 3. Calibration Regression Coefficient r^2 Values

Compound	Helium	Natural gas
H ₂ S	0.998	0.998
COS	0.998	0.999
CH ₃ SH	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

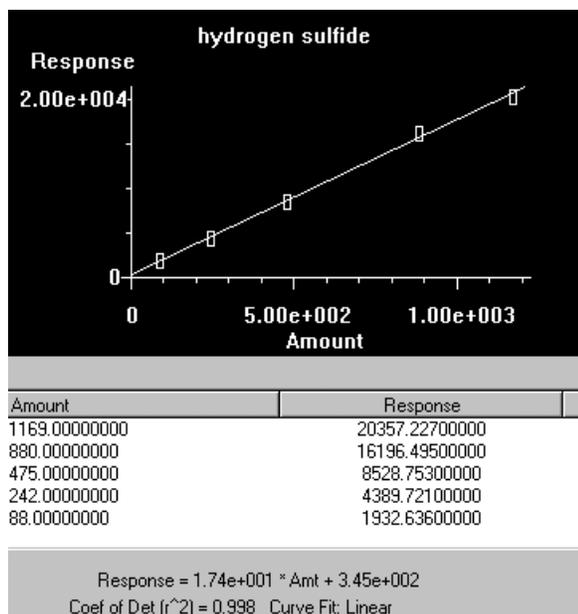


Figure 2. Five level calibration plot of H₂S in natural gas diluent. Calibration range is from 88 ppb to 1170 ppb.

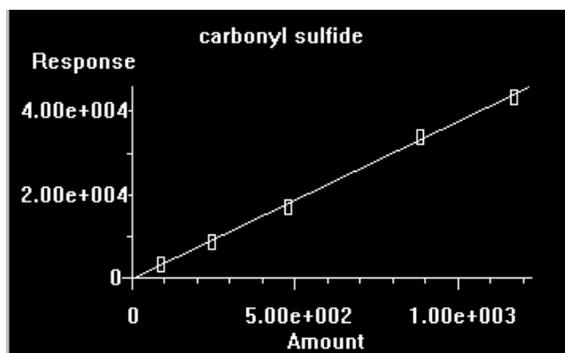


Figure 3. Five level calibration plot of COS in natural gas diluent. Calibration range is from 88 ppb to 1170 ppb.

Scan Results

The total ion chromatogram (TIC) of the eight-component sulfur mix at 1.3 ppm in helium using a split ratio of 0.5 to 1 is shown in Figure 4. As is evident in the figure, H₂S is close to the minimum detection level (MDL) for this particular set of operating conditions. Symmetric peak shapes are seen for all components including adsorptive H₂S and COS.

Application of SIM

SIM provides the best sensitivity and selectivity for target analytes. 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 co-elution 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 co-elution occurs, making accurate quantitation of low-level sulfur problematic [2]. Even the SCD will have problems measuring low ppm sulfur in the presence of a dominant co-eluting 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 attempted [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 resolution loss.

Refer to Reference 6 for guidelines for setting SIM parameters and instructions on using the AutoSIM feature available in the MSD ChemStation, G1701DA.

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 sulfur. The table may be further refined if hydrocarbon interferences appear. 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.

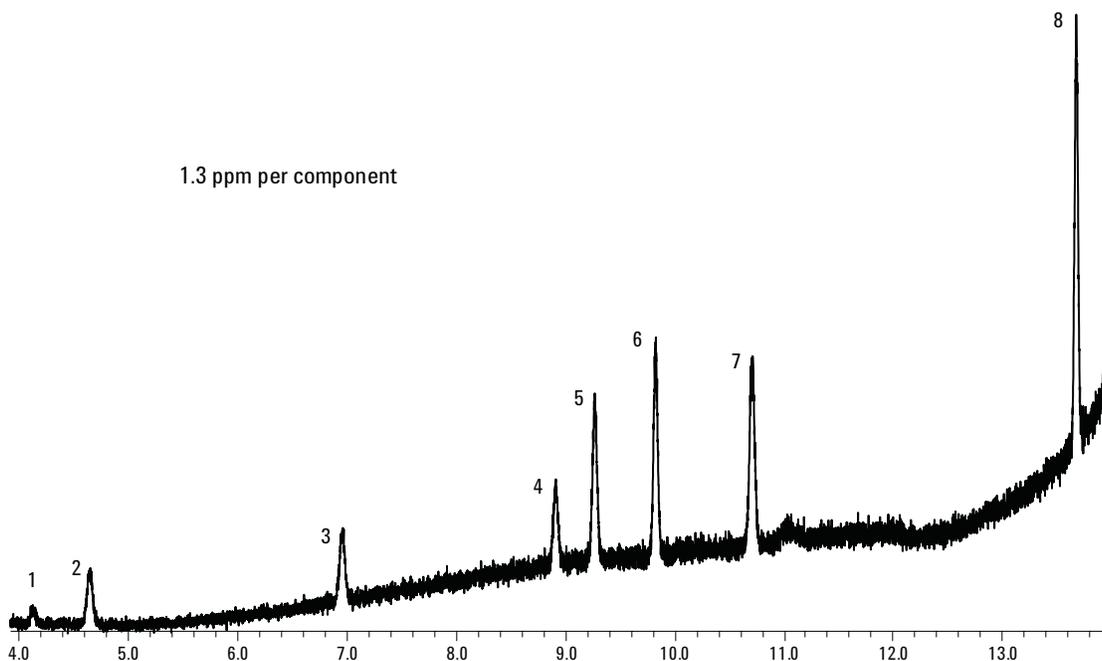


Figure 4. TIC of the eight-component sulfur mix at 1.3 ppm per component. Scan 33–100 amu. Peak labels: 1. hydrogen sulfide, 2. carbonyl sulfide, 3. methyl mercaptan, 4. ethyl mercaptan, 5. dimethyl sulfide, 6. carbon disulfide, 7. t-butyl sulfide, 8. tetrahydrothiophene.

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 ₂ S
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

The sulfur mix chromatogram shown in Figure 5 was produced using the SIM parameters shown in Table 4. The offsets seen in the baseline are a result of the MSD switching from group to group and are not chromatographic. Excellent signal-to-noise and peak shape are 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 H₂S, COS, and THT, the most challenging analytes, appear in Figure 6. At these levels, any problems with system or source activity would be evident. Sensitivity and peak shape are maintained, indicating excellent source inertness.

Natural Gas and Refinery Gas: Composition and Impurities

The TIC of a natural gas scan and sulfur mix SIM runs are overlaid for illustration purposes in Figure 7. Note that with the 60 m × 0.32 mm × 5.0 μm DB-1 all hydrocarbons and CO₂ are separated. Natural gas compounds in order of elution are: O₂/N₂, CH₄, CO₂, 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 co-elute with natural gas components; only COS and propane have nearly identical retention times. Even with co-elution, SIM makes it possible to quantify the COS; this will be addressed in the following section on propylene impurities.

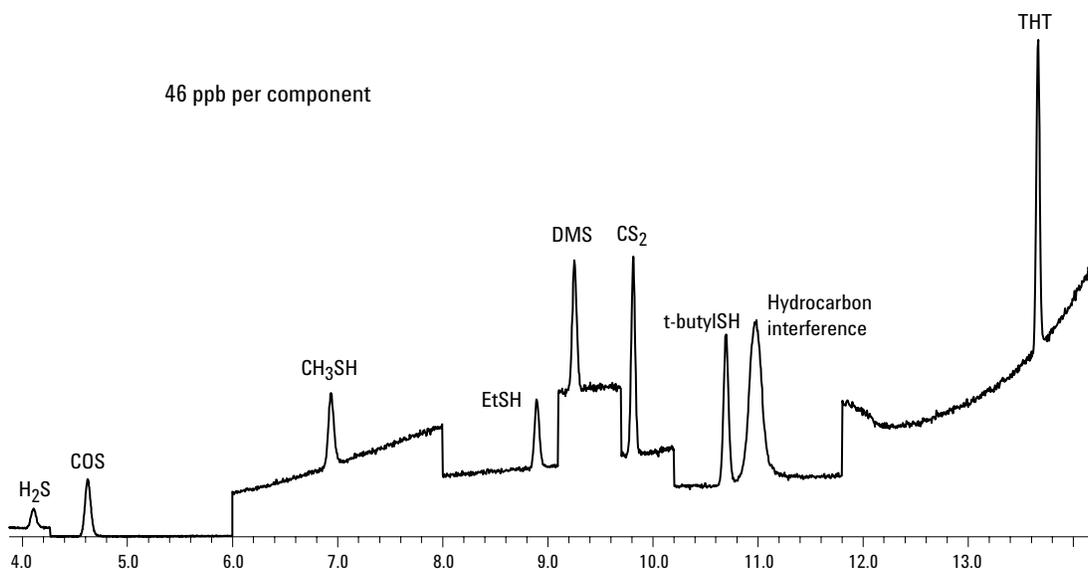


Figure 5. Eight-component sulfur mix in helium at 46 ppb per component in SIM mode. Split ratio 0.5:1. Refer to Figure 4 for peak identification.

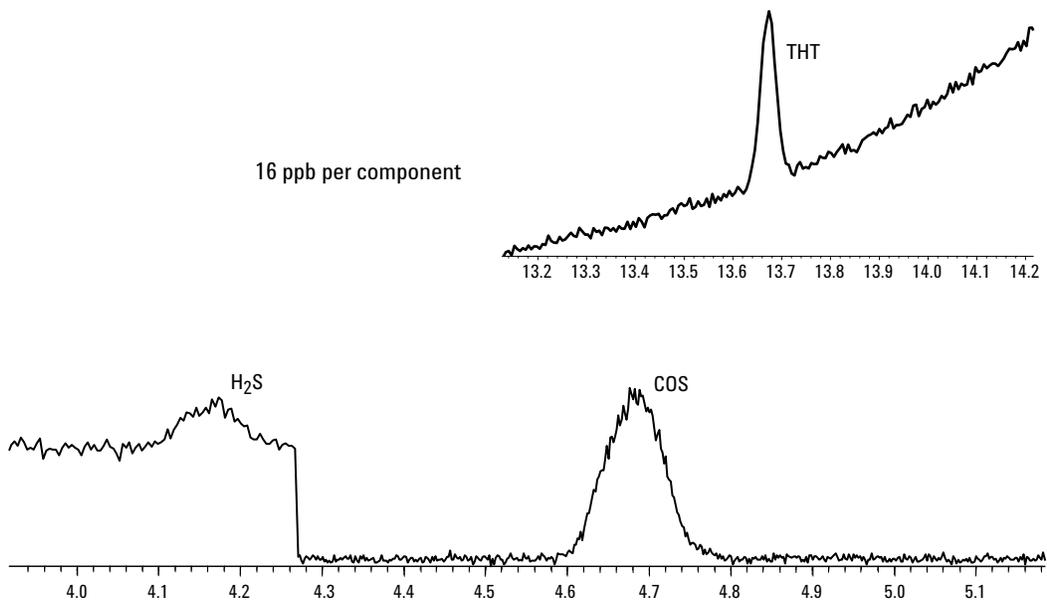


Figure 6. H₂S, COS and tetrahydrothiophene (insert) at 16 ppb each.

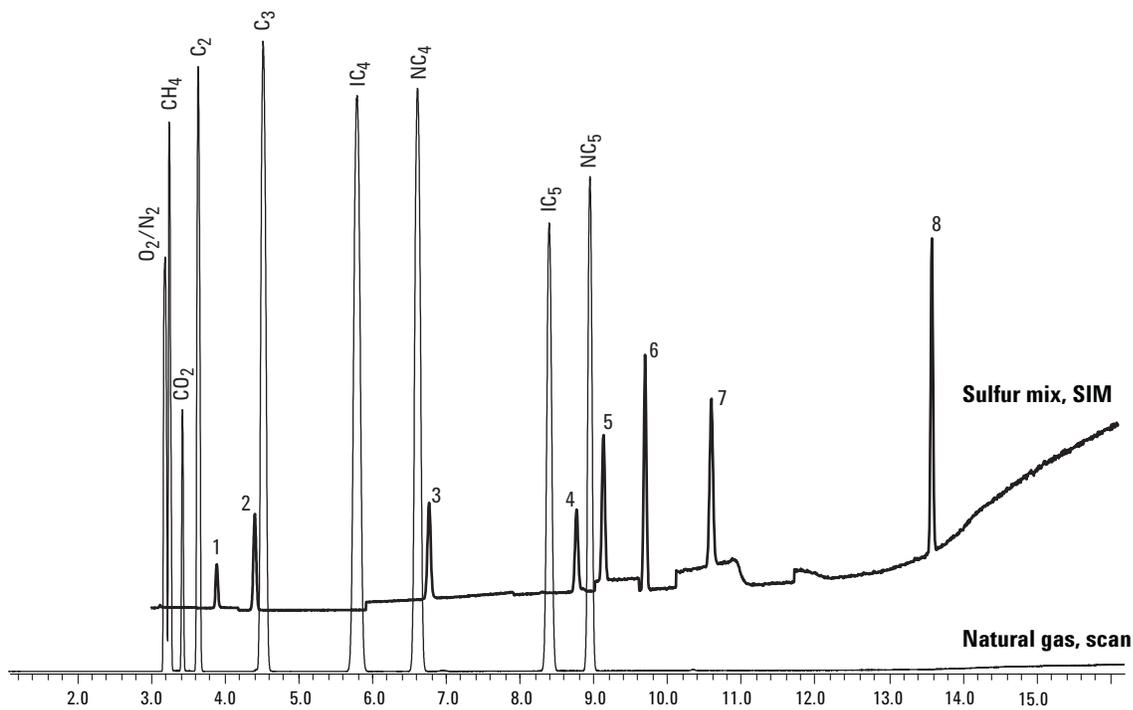


Figure 7. Overlay of two runs: natural gas scan (12–100 amu), and sulfur mix at 4.5 ppm in SIM mode. Split ratio 20:1. Peak numbering same as Figure 4.

Low level (350 ppb) sulfur gases in a representative refinery gas matrix are shown in Figure 8. Again, good peak shape and signal-to-noise are seen. Only methyl mercaptan is lost to hydrocarbon interference.

Analysis of COS in Propylene

Measurement of ppb COS and H₂S in propylene or propane can be challenging due to the co-elution of COS/propylene and the reactivity of H₂S. The COS co-elution is illustrated in Figure 9, where two independent separate runs are superimposed.

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 co-eluting 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 co-elution. This area is then compared to that of COS in propylene diluent using the area ratio (COS propylene/COS helium) to indicate how co-elution has affected the 5973 inert 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 ppb to 1200 ppb. Therefore, using a carefully constructed SIM method, the 5973 inert equipped with 3-mm drawout has the capability of quantifying ppb level COS in co-eluting propylene. Co-eluting active analytes do not preclude quantification even when concentration differences exceed 105 provided unique ions can be identified for the component of interest.

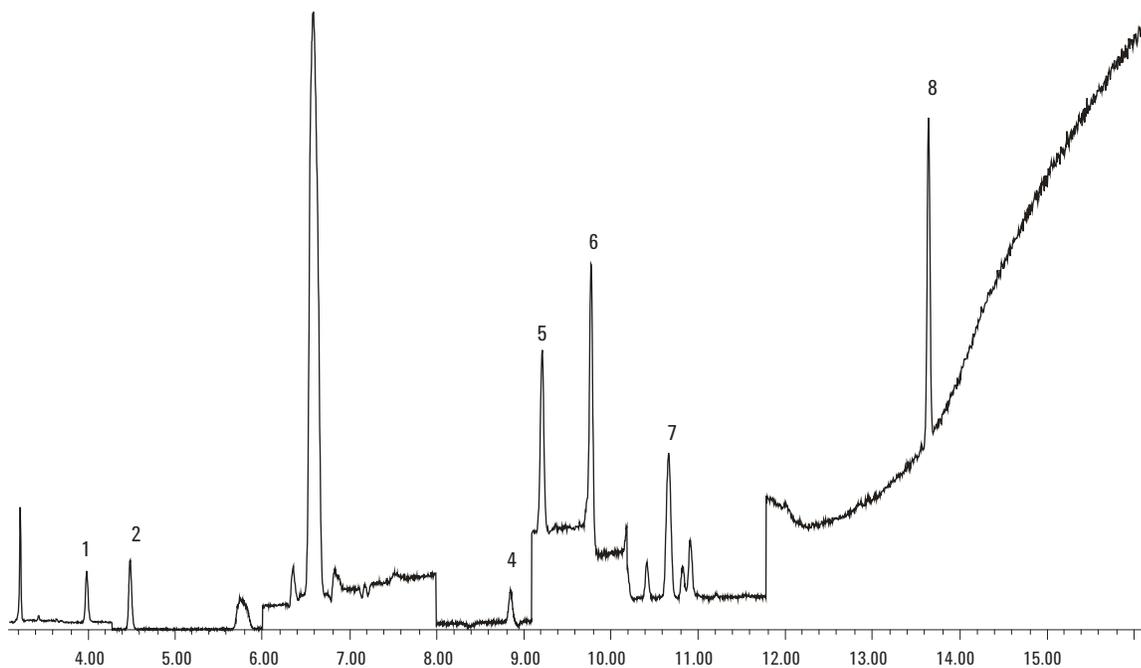


Figure 8. Three hundred fifty ppb sulfur mix in refinery gas. Peak identifications same as Figure 4. Good peak symmetry and sensitivity seen.

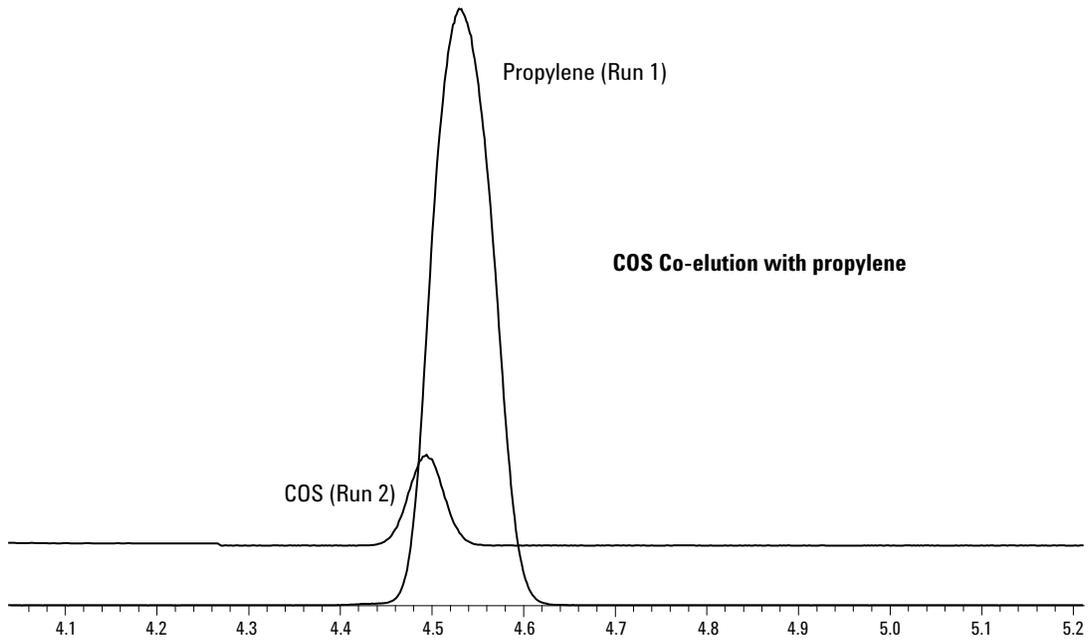


Figure 9. Two separate chromatograms superimposed showing the co-elution of COS with propylene. Split ratio 50:1.

105 ppb each H₂S and COS

Area ratio: COS in Propylene/COS in Helium = 0.77

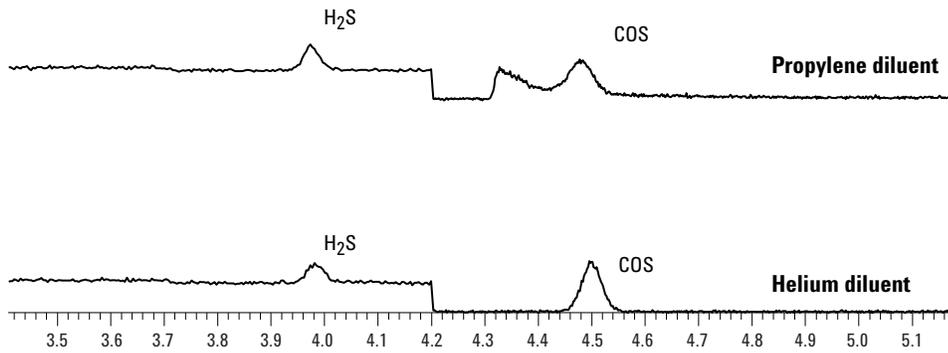


Figure 10. Comparison of COS response (SIM mode) in helium and propylene. Split ratio 50:1.

Conclusions

The importance of inertness cannot be over emphasized when analyzing and quantifying ppb level volatile sulfur compounds. The 5973 inert has excellent capabilities as a sensitive, repeatable, and selective detector for active gaseous analytes at low levels. 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 co-eluting propylene.

Use of the new inert source leads to excellent detection limits of active, adsorptive compounds with minimal peak tailing. Good peak symmetry is maintained at the ppm and ppb level for H₂S, COS, and other light organo-sulfur compounds. Detection of low-level polar analytes in general will improve with the 5973 inert.

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