

Analysis of Sulfur Compounds in Petroleum Gases and Natural Gas

Application Note

Energy & Chemicals

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Abstract

Agilent J&W DB-Sulfur SCD columns were evaluated by analyzing different sulfur gaseous standards. Sulfur compounds in petroleum gases and natural gas samples were also analyzed using an Agilent Inert Flow Path GC/SCD with the DB-Sulfur SCD column according to ASTM D5504. The column, with low bleed and exceptional inertness, provided good resolution and peak shape to these reactive sulfur compounds. Good results confirmed that the Inert Flow Path GC/SCD configured with the DB-Sulfur SCD column was a useful tool for analysis of sulfur compounds.

Introduction

Petroleum gases and natural gas are well-established contributors to the world's energy needs. Monitoring sulfur compounds in these products is very important, not only to protect expensive catalysts and ensure product quality, but also to protect the environment and human health. The analysis of gaseous sulfur compounds is challenging because they are polar, reactive, and present in widely varying concentrations. The sulfur chemiluminescence detector (SCD) is known as an excellent device for sulfur compound analysis because its response is inherently linear, equimolar, and far less susceptible to hydrocarbon interferences. For example, ASTM Method D5504 [1] uses SCD for the detection of sulfur compounds in gaseous fuels and natural gas, but the SCD requires low-bleed GC columns to be used to avoid fouling of the SCD ceramics, and decreasing sensitivity. In addition, volatile sulfur compounds are highly reactive and have absorptive, adsorptive, and metal-catalytic properties. Therefore, analysis of sulfur compounds requires that sample pathways, especially the GC column, be inert to ensure reliable results.



Agilent Technologies

The Agilent J&W DB-Sulfur SCD GC column with low bleed and exceptional inertness is specifically developed for sulfur compound analyses and optimized for GC/SCD. This application note demonstrates the performance of the DB-Sulfur SCD column in analyzing sulfur compounds in petroleum gases and natural gas using an Agilent Inert Flow Path GC/SCD.

Materials and Methods

The experiments were performed on two sets of Agilent 7890A GC configured with an Agilent 355 SCD with dual plasma burner. Split/splitless inlet and volatiles interface (VI) were equipped with GC/SCD. Sample introduction consisted of a six-port gas sample valve connected directly to the split/splitless inlet or VI with inert Agilent UltiMetal tubing. A point-of-use gas blending system controlled by auxiliary EPC was used for preparation of low level samples.

Table 1 lists the sulfur compounds included in the study. All sulfur standards were purchased from Beijing AP BAIF Gases Industry Company. All sulfur standards were blended in nitrogen and the concentrations were modified by the point-of-use gas blending system.

GC conditions 1

Columns:	Agilent J&W DB-Sulfur SCD, 70 m × 0.53 mm, 4.3 μm (p/n G3903-63003)
Tubing:	Deactivated fused silica, 1 m × 0.18 mm (p/n 160-2615-1)
Union:	Deactivated Ultimate union (p/n G3182-60580)
Carrier:	Helium, constant pressure mode, 8.6 psi
Inlet:	Inert flow path split/splitless inlet, 240 °C, split ratio 10 :1
Liner:	Ultra Inert liner (p/n 5190-2295)
Oven:	35 °C for 2 min, 35 °C to 80 °C at 10 °C/min, 80 °C for 6 min, 80 °C to 220 °C at 15 °C /min, 220 °C for 10 min
Sample loop:	1 mL
Detector:	Agilent 355 SCD
SCD conditions	
Burner temperature:	800 °C
Vacuum of burner:	350 Torr
Vacuum of reaction cell:	5 Torr
H ₂ :	40 mL/min
Air:	60 mL/min

GC conditions 2

Columns:	Agilent J&W DB-Sulfur SCD, 70 m × 0.53 mm, 4.3 μm (p/n G3903-63003)
Carrier:	Helium, constant pressure mode, 8.6 psi
Inlet:	Volatiles interface inlet, 200 °C , split ratio 4:1
Oven, sample loop, and SCD conditions as for Conditions 1	

Table 1. Sulfur standards.

No.	Compound	CAS No.	Formula
1	Hydrogen sulfide (H ₂ S)	7783-06-4	H ₂ S
2	Sulfur dioxide (SO ₂)	7446-9-5	SO ₂
3	Carbonyl sulfide (COS)	463-58-1	COS
4	Methanethiol (MeSH)	74-93-1	CH ₃ SH
5	Ethanethiol (EtSH)	75-08-1	C ₂ H ₅ SH
6	Dimethyl sulfide (DMS)	75-18-3	(CH ₃) ₂ S
7	Carbon disulfide (CS ₂)	75-15-0	CS ₂
8	2-Propanethiol (i-PrSH)	75-33-2	C ₃ H ₈ S
9	2-methyl-2-Propanethiol (t-BSH)	75-66-1	C ₄ H ₁₀ S
10	1-Propanethiol (n-PrSH)	107-03-9	C ₃ H ₈ S
11	Ethyl methyl sulfide (MES)	624-89-5	C ₂ H ₅ SCH ₃
12	1-methyl-1-Propanethiol (s-BuSH)	513-53-1	C ₄ H ₁₀ S
13	Thiophene (TP)	110-02-1	C ₄ H ₄ S
14	2-methyl-1-Propanethiol (i-BuSH)	513-44-0	C ₄ H ₁₀ S
15	Diethyl sulfide (DES)	352-93-2	(C ₂ H ₅) ₂ S
16	1-Butanethiol (n-BuSH)	109-79-5	C ₄ H ₁₀ S
17	Dimethyl disulfide (DMDS)	624-92-0	(CH ₃ S) ₂
18	Tetrahydrothiophene (THT)	110-01-0	C ₄ H ₈ S
19	Ethyl methyl disulfide (MEDS)	20333-39-5	C ₃ H ₈ S ₂
20	Dipropyl sulfide (DPS)	111-47-7	C ₆ H ₁₄ S
21	Diethyl disulfide (DEDS)	110-81-6	(C ₂ H ₅ S) ₂
22	Dimethyl trisulfide (DMTS)	3658-80-8	C ₂ H ₆ S ₃

Results and Discussion

GC conditions 1

To achieve better resolution of COS and SO₂, 1-m deactivated fused silica tubing was used as a restrictor, connected to a 70 m × 0.53 mm, 4.3 μm DB-Sulfur SCD GC column. Different sulfur gaseous standards applicable to different applications were tested and the analysis initiated at 35 °C. Compared to a typical initial temperature at 30 °C or below ambient temperature, the GC system was more stable, no cryogenic cooling was required, and the system was suitable for different laboratory conditions.

As shown in Figure 1, the column provided satisfactory separation for most of 1# and 2# sulfur standards. In particular, good resolution and retention of carbonyl sulfide and hydrogen sulfide were achieved at ambient temperature. According to chromatogram overlays of 1# and 2# standards, carbonyl sulfide and sulfur dioxide normally coelute on a regular 60 m × 0.53 mm, 4 μm nonpolar column, but they can be partially separated on the 70-m DB-Sulfur SCD column with 1-m deactivated fused silica tubing. This is confirmed by analysis of a sulfur gaseous mix that was made by mixing 1# and 2# sulfur standards, and adding some common sulfur compounds.

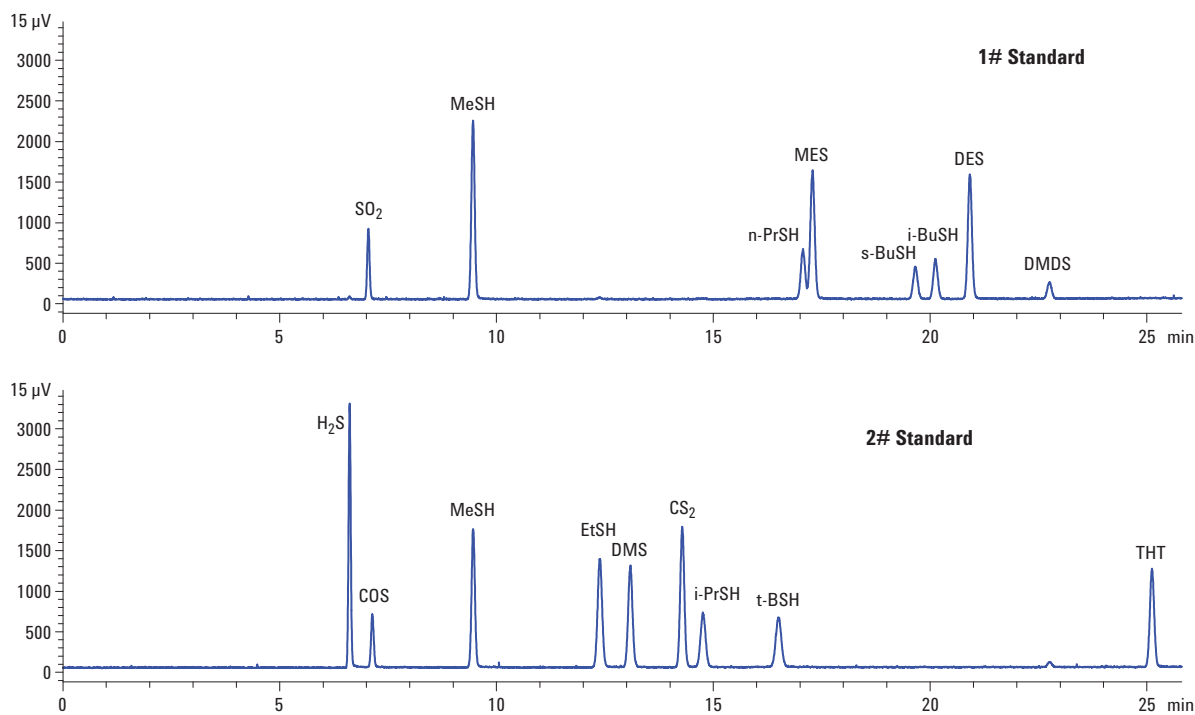


Figure 1. Chromatogram overlays of sulfur standards using an Agilent GC/SCD system and Agilent J&W DB-Sulfur SCD column.

Figure 2 shows the chromatogram of the 22 sulfur compounds. Most of the peaks were well resolved on the DB-Sulfur SCD column with excellent peak shapes. Resolution of carbonyl sulfide and sulfur dioxide was about 0.8. 1-methyl-1-propanethiol, thiophene, and 2-methyl-1-propanethiol are normally difficult to separate because they often show coelution on commonly used nonpolar (dimethylpolysiloxane) stationary phase GC columns. Figure 2 exhibits improved separation of these three compounds using the DB-Sulfur SCD column.

Better resolution can be obtained with a lower initial oven temperature and longer GC columns with deactivated fused silica tubing. Due to complete sulfur compounds combustion, better sensitivity can be achieved if a relatively lower flow rate is selected. However, run time will be increased.

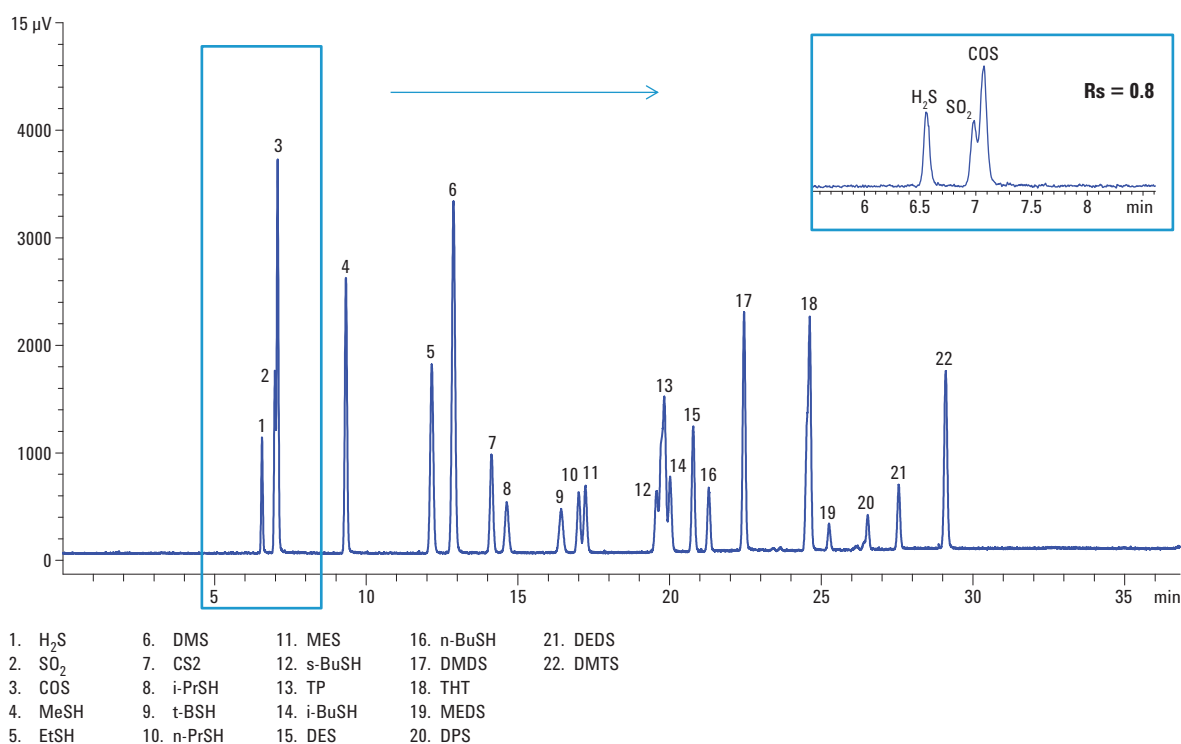


Figure 2. Chromatogram of sulfur gaseous mix using an Agilent GC/SCD system and Agilent J&W DB-Sulfur SCD column.

Figure 3 shows the chromatogram of the 2# sulfur standard and 1# sample (LPG sample after desulfurization) that included a large amount of light hydrocarbons. Good resolution and repeatability also indicated no hydrocarbon interferences in the analysis.

Equimolar response of a detector refers its ability to yield equal responses to equal amounts of analytes on a molar basis. Relying on the equimolarity of the Agilent 355 SCD, the 1# sample (LPG sample after desulfurization) was detected,

and the mass concentrations of total sulfur in the sample were calculated by summing the sulfur content of all sulfur components (known and unknown) in the sample. The total amount of sulfur for the 1# sample was 62 ppm. Individual sulfur compounds in the 1# sample could be identified by retention time. Each major individual sulfur compound was calculated by external standardization. Thus, hydrogen sulfide was 20.46 ppm, COS was 17.22 ppm, and MeSH and CS₂ were 0.75 ppm and 10.41 ppm, respectively.

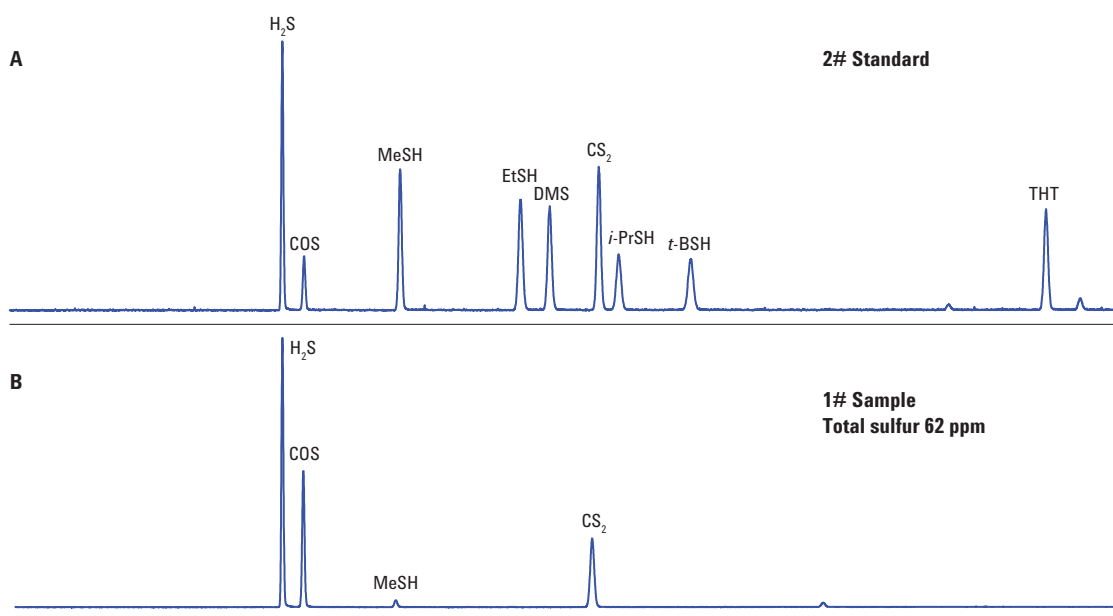


Figure 3. Chromatograms of sulfur standard (A) and 1# sample (LPG sample after desulfurization) (B).

GC Conditions 2

Some previous publications have discussed how SCD offers equimolar/sulfur-specific detection to ppb level [2,3,4]. The DB-Sulfur SCD column is specifically developed for sulfur compound analyses and optimized for SCD. The column was configured with a volatiles interface inlet and SCD detector to measure the total sulfur amount of natural gas before and after desulfurization.

As shown in Figure 4, the concentration of some major sulfur compounds varied greatly before and after desulfurization, especially H_2S . A wide linear range (that is, from 10 ppb to 10 ppm) for major sulfur compounds was required. R^2 correlation coefficients of the tested sulfurs in this study were better than 0.997. Figure 5 shows the chromatogram of the 3# standard and Figure 6 demonstrates the chromatogram of each major sulfur compound at 15 ppb. Signal-to-noise ratios of H_2S , COS, and DMS were 4.8, 11.2, and 9.3, respectively.

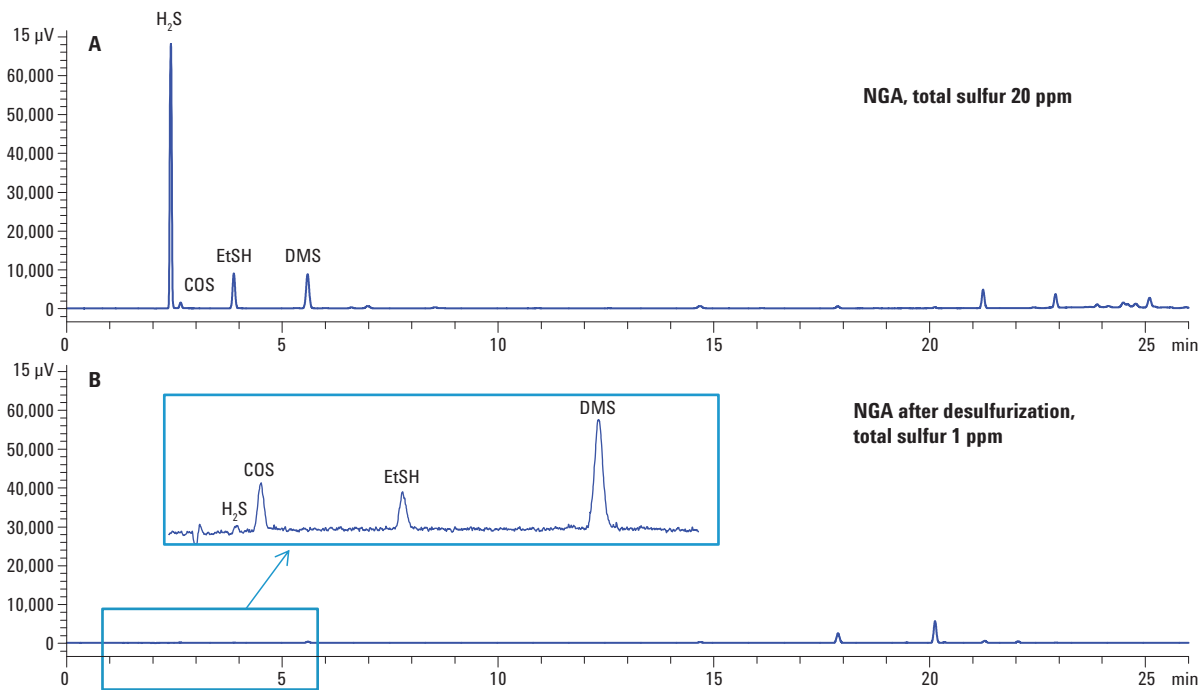


Figure 4. Chromatograms of real samples; natural gas (A) and natural gas after desulfurization (B).

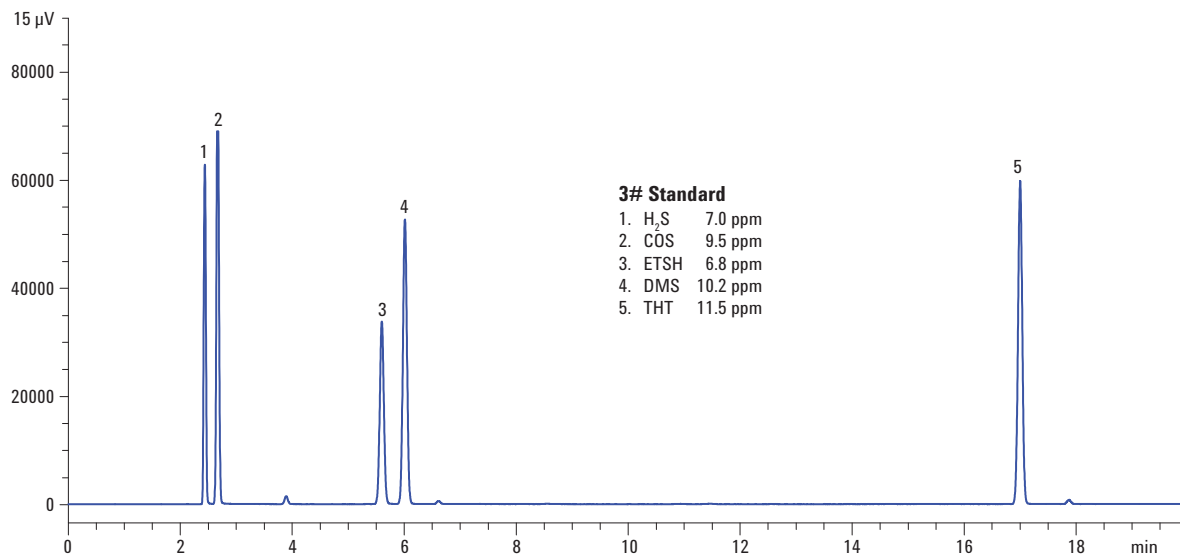


Figure 5. Chromatogram of the 3# standard.

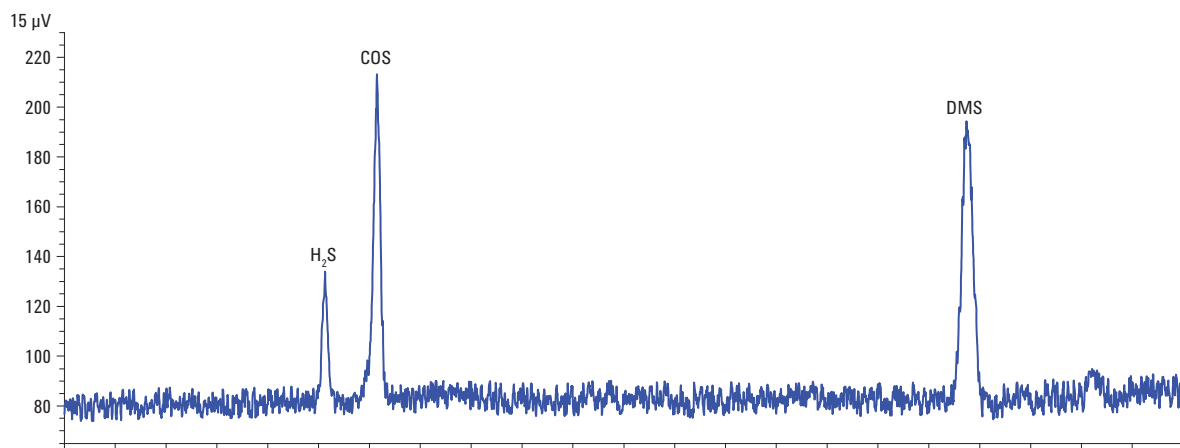


Figure 6. Chromatogram of major sulfur compounds at 15 ppb.

To check suitability, a calibration gas was analyzed several times. Excellent repeatability of major sulfur compounds was obtained, as shown in Table 2, with RSD% below 2.25%.

Table 2. Repeatability of major sulfur compounds.

Run	H ₂ S (ppm)	COS (ppm)	DMS (ppm)
1	8.33	10.15	11.18
2	8.36	10.42	11.27
3	8.62	10.00	10.76
4	8.74	10.18	11.18
5	8.63	10.09	10.94
6	8.30	10.14	10.95
Average	8.50	10.16	10.95
RSD%	2.24	1.38	1.74

The total amount of sulfur was calculated by summing all peak areas in the chromatogram of natural gas and quantitated using the response factor of COS. Table 3 shows the results of the natural gas samples. No hydrocarbon interferences were found in the analysis.

Table 3. Major individual sulfur compounds and total sulfur amount in natural gas.

Sulfur compound	Average content (ppm) before desulfurization	Average content (ppm) after desulfurization
H ₂ S	8.98	0.01
COS	0.21	0.04
EtSH	5.07	0.10
DMS	0.02	0.00
Total sulfur	20.21	1.37

Conclusions

The Agilent J&W DB-Sulfur SCD column was evaluated by analyzing different sulfur gaseous standards and common GC/SCD configurations. The results showed that the column could provide good resolution and symmetrical peak shape for polar and reactive sulfur compounds due to its low bleed and improved inertness performance. In particular, using a 70-m DB-Sulfur SCD column with 1-m deactivated fused silica tubing, resolution of hydrogen sulfide and sulfur dioxide was about 0.8. Hydrogen sulfide and carbonyl sulfide could be baseline separated at ambient temperature without cryogenic cooling. Excellent linearity, repeatability, and response were achieved for major sulfur compounds when the DB-Sulfur SCD column was used with the volatiles interface and SCD. In summary, the combination of an Agilent Inert Flow Path, DB-Sulfur SCD column, and Agilent 355 sulfur chemiluminescence detector can offer excellent performance in the analysis of sulfur components in fuel gases and natural gas.

References

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