

Analysis of Sulfur Compounds in High-Purity Hydrogen

Using an Agilent 8890 gas chromatograph and an Agilent 8355 sulfur chemiluminescence detector

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Abstract

Sulfur compounds in high-purity hydrogen were analyzed on an Agilent 8890 gas chromatography (GC) system equipped with an Agilent 8355 sulfur chemiluminescence detector (SCD). A six-port gas-sampling valve was used to introduce samples into the whole system. Excellent peak shape and resolution were obtained by using an Agilent J&W DB-Sulfur SCD column. Linearity, repeatability, and limit of detection (LOD) were excellent, with correlation coefficients (R^2) ≥ 0.9983 and LOD approximately 10 ppb for all analytes. The typical percent relative standard deviation (RSD) of the peak area ranged from 0.87 to 12.54%.

Introduction

Hydrogen has become one of the preferred sources for green energy because of its high calorific value and clean product. Hydrogen can be produced from many sources, such as natural gas, coal, biomass, or electrolysis of water. However, based on its relatively low cost and more mature technology, hydrogen production from fossil fuels is still the most common method.

The raw materials or reaction processes can introduce impurities into the hydrogen product. Common impurities are CO, CO₂, NH₃, sulfur, formaldehyde, etc.¹ Quality control of hydrogen, especially impurity analysis of different grades, has become an urgent need for both hydrogen manufacturers and users.

Analysis of permanent gas impurities in hydrogen is well reported:

- An Agilent 990 Micro GC system configured with a micro thermal conductivity detector and two analytical channels can provide fast (within 150 seconds) and sensitive analysis of some permanent gases (He, Ne, N₂, Ar, O₂, CO, CO₂) from 2 to 10,000 ppm.²
- The Agilent 8890 GC equipped with pulsed discharge helium ionization detector (PDHID) allows qualitative and quantitative detection of permanent gas impurities and carbon dioxide in the low parts per billion (ppb) range with a single injection.³

In addition, monitoring sulfur compounds in hydrogen is also very important to protect expensive catalysts and ensure product quality. However, the determination of sulfur compounds in hydrogen is a challenge because of their highly reactive, adsorptive, and metal catalytic properties. Obtaining reliable and accurate results requires both high inertness throughout the system and high sensitivity. This application note demonstrates the use of 8890 GC and 8355 SCD systems for analyzing sulfur compounds in hydrogen.

Experimental

Analyses were performed on an 8890 GC configured with an 8355 SCD. Samples were introduced through a six-port gas sampling valve connected directly to an inert volatiles interface (VI). To achieve higher sensitivity, a 2 mL loop was used to introduce more sample into the system. The split-injection approach is recommended to improve the peak shape of hydrogen sulfide, which eluted as the first peak. In another modification to achieve high sensitivity, a small split ratio is preferred. Here, a split ratio of 10:1 is used to balance the peak shape and sensitivity. The instrument conditions are listed in Table 1.

Table 1. Instrument conditions.

Parameter	Value
Agilent 8890 GC	
Sample Introduction	Six-port gas-sampling valve; valve box temperature: 150 °C
Sample Loop	2 mL
Inlet	Volatiles interface; split mode, split ratio 10:1; temperature: 150 °C
Column	Agilent J&W DB-Sulfur SCD, 60 m × 0.32 mm, 4.2 μm (p/n G3903-63001)
Carrier Gas	Helium, 3 mL/min, constant flow
Oven Program	40 °C (1 min), 15 °C/min to 230 °C
Agilent 8355 SCD	
Burner Temperature	800 °C
Base Temperature	280 °C
Upper H ₂ Flow	38 mL/min
Lower H ₂ Flow	8 mL/min
Oxidizer Flow (Air)	50 mL/min
O ₃ Generator Flow	44.15 mL/min
Burner Pressure	383 Torr
Reaction Cell Pressure	4.9 Torr
Data Rate	5 Hz

Parts-per-billion (ppb) calibration standards were prepared using a pneumatic control module (PCM) and a newly designed gas blending module. This module, known as a mini gas blender, is an integrated, single-stage dynamic flow dilutor designed to be installed at any available electronic pneumatic control (EPC) slot of the 8890 GC. Compared to the previous version, it is much more compact and easier to install. A constant stream of a calibration gas mixture blends with a stream of matrix gas inside the blender to produce the desired concentration. Figure 1 shows the sample dilution, introduction, and analysis setup. In this study, high-purity hydrogen is used as the diluent gas. The dilution ratio is determined by the calibration mix flow (F_1) and matrix flow (F_2). The dilution formula is:

$$C_2 = C_1 \times \left(\frac{F_1}{F_1 + F_2} \right)$$

Equation 1.

where C_2 is diluted concentration, C_1 is original calibration concentration, F_1 is calibration mixture flow rate, and F_2 is diluent matrix gas flow rate.

The sulfur gas standard was purchased from Air Liquide. To minimize adsorption of active sulfur components, the standard gas cylinder was connected to the system using an inert regulator and inert tubing. Table 2 lists the composition and concentration of the sulfur gas

standard. Table 3 shows the volume concentrations (v/v) of each component at different calibration levels for eight mix/diluent combinations (starting from a sulfur calibration mix of approximately 1 ppm).

The Agilent OpenLab chromatography data system (CDS) was used to control the GC system and to provide data acquisition and quantitative analysis. A data acquisition rate of 5 Hz/0.04 minutes yielded an acceptable baseline.

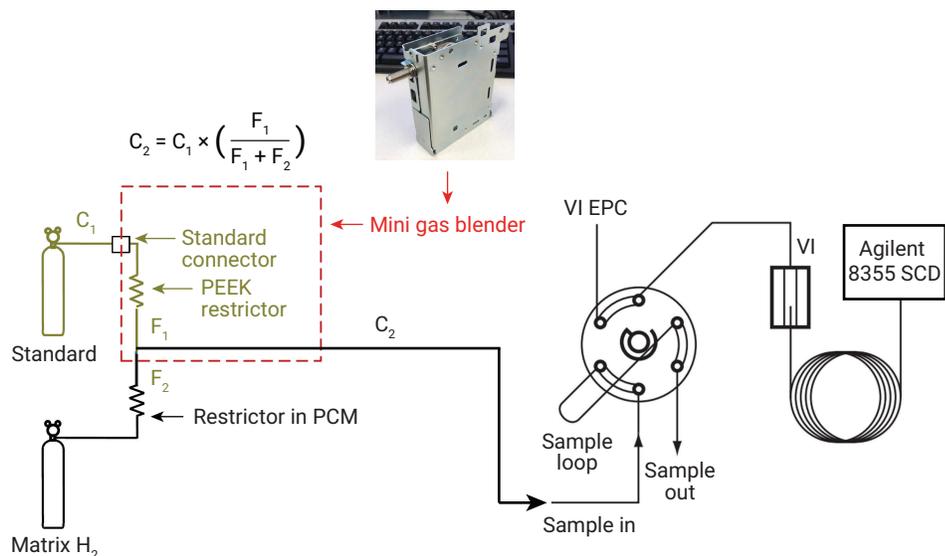


Figure 1. Layout of the dynamic blending system and configuration of the Agilent 8890 GC for sulfur compounds analysis. The dilution formula is defined in Equation 1.

Table 2. Standard mix gas (balance gas: H_2).

No.	Compound Name	Formula	Concentration ($\mu\text{mol/mol}$, ppm)
1	Hydrogen sulfide	H_2S	0.992
2	Carbonyl sulfide	COS	1.01
3	Methyl mercaptan	CH_3SH	0.999
4	Ethyl mercaptan	C_2H_5SH	0.990
5	Dimethyl sulfide	CH_3SCH_3	1.01
6	Carbon disulfide	CS_2	1.01
7	Thiophene	C_4H_4S	1.01

Table 3. Dilution table (starting calibration mix at about 1 ppm per component).

Calibration Mix Flow (mL/min)	PCM (H_2) Flow (mL/min)	Concentration (ppbv)
1	99	10
1	65.67	15
1	49	20
1	39	25
1	19	50
1	9	100
1	5.67	150
1	4	200

Results and discussion

Achieving system equilibrium with sulfur compounds

The biggest challenge for analyzing sulfur at low concentrations (ppb) is minimizing the adsorption of active sulfur compounds and quickly establishing sulfur "saturation" on the sample flow path. Passivation of the complete sample flow path is recommended, including the gas cylinder regulator, connection tubing, mini gas blender, valve sample loop, VI inlet, analytical column, and detector, to minimize the active sites. It was found that, in addition to passivation, a priming process was required to presaturate sulfur analytes on the passivated flow path. The priming time mainly depended on the sample concentration used for priming the flow path.

During the priming process, an increase in peak area was observed for some compounds when the system was initially exposed to sulfur compounds (Figure 2). This incremental response phenomenon is most pronounced for highly reactive compounds, such as hydrogen sulfide, methyl mercaptan, and ethyl mercaptan. In this study, hydrogen sulfide did not appear at all in the first run, while methyl mercaptan and ethyl mercaptan showed very low

initial responses. For these compounds, a long sequence was set up to prime the system. When the priming was done, stable response could be obtained when repeatedly injecting the ppb calibration samples (Figure 3). In addition, after the priming procedure, the relative responses of H₂S and COS at the lowest and highest calibration level were similar. This similarity showed that priming the system was effective. In this study, the

concentration of priming substance used was less than 1 ppm. It was assumed that the higher the priming sample concentration, the faster the sample flow path was saturated by sulfur compounds.

If the primed system is idle for several days, usually the first two to three injections after the standby should be discarded. The subsequent injections can be used for quantitative analysis.

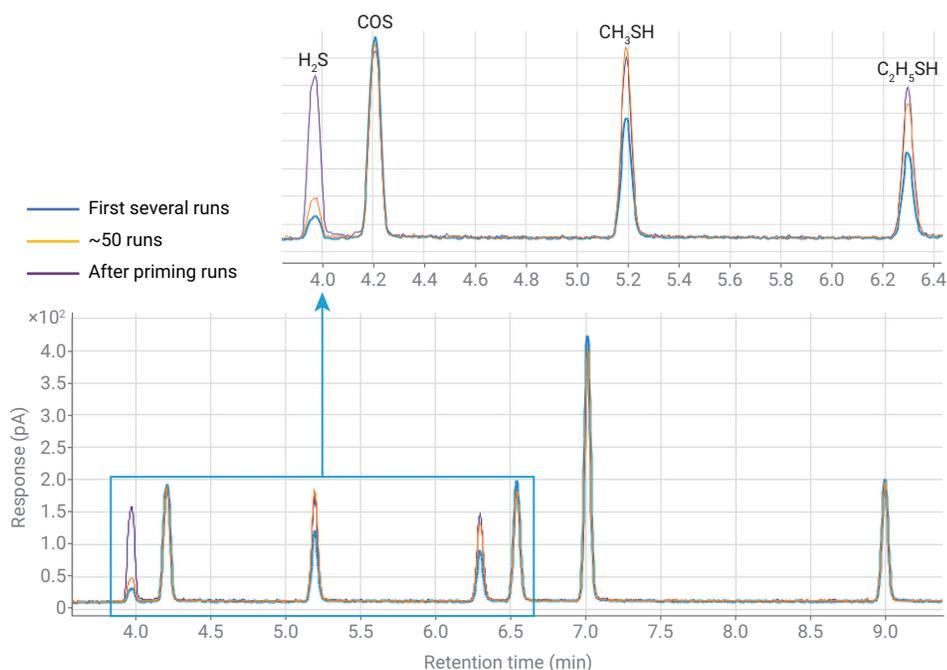


Figure 2. System behavior when the system is initially exposed to sulfur compounds. The concentration of each compound is 200 ppb.

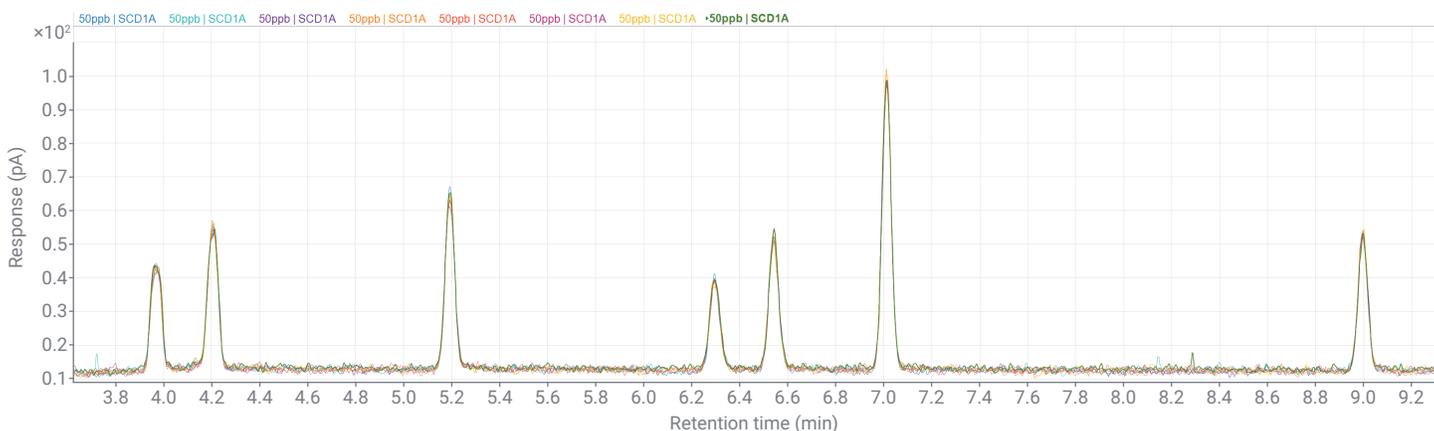


Figure 3. Overlaid chromatograms of eight repeat injections of 50 ppb after priming.

Chromatogram

The 8355 SCD is a highly selective detector for the analysis of trace sulfur-containing compounds without interference from hydrocarbons. It can provide linear and essentially equimolar response for all sulfur within the scope of this method. A J&W DB-Sulfur SCD column coated with 4.2 μm nonpolar stationary phase was connected to the 8355 SCD for the analysis of the volatile, polar, and reactive sulfur compounds. As shown in Figure 4, the whole system can provide good resolution, excellent peak shape, and sensitive response for the target sulfur compounds. This performance is due to the inert flow path, low bleeding, and improved inertness of the analytical column. The percent relative standard deviation (% RSD) of molar response factor for sulfur in each analyte at 100 ppb was 12.1%, which demonstrated the equimolar response of the 8355 SCD for sulfur.

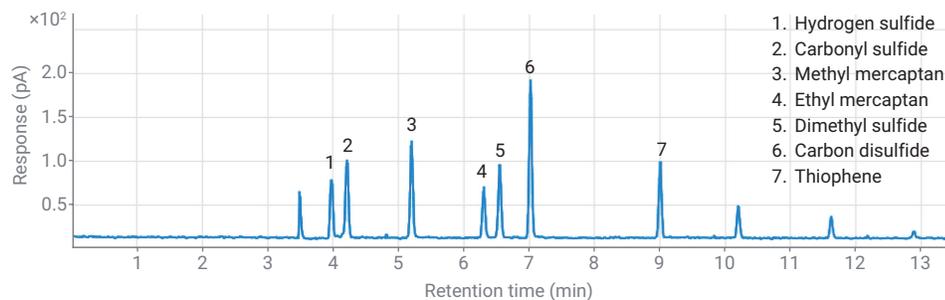


Figure 4. Chromatogram of sulfur standards at a concentration of 100 ppb.

Table 4. Repeatability results for sulfur compounds.

No.	Compound	Area RSD % (n = 8)		
		Low (15 ppb)	Mid (50 ppb)	High (200 ppb)
1	Hydrogen sulfide	7.3	2.13	1.69
2	Carbonyl sulfide	4.54	3.16	2.21
3	Methyl mercaptan	5.72	3.85	1.67
4	Ethyl mercaptan	7.56	2.67	1.5
5	Dimethyl sulfide	12.54	3.37	1.36
6	Carbon disulfide	4.76	1.77	0.87
7	Thiophene	8.78	3.03	1.08

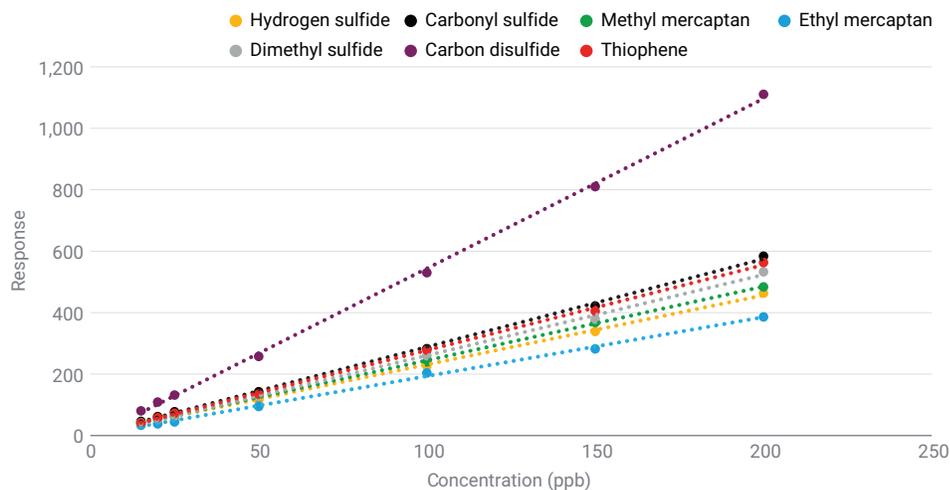


Figure 5. Calibration plots of sulfur compounds analyzed.

Table 5. Linearity results for sulfur compounds.

No.	Compound	Retention Time (min)	CF Formula	R ²
1	Hydrogen sulfide	3.976	$y = 2.2524x + 6.0381$	0.9987
2	Carbonyl sulfide	4.206	$y = 2.8622x + 2.0716$	0.9991
3	Methyl mercaptan	5.193	$y = 2.4045x + 3.9397$	0.9998
4	Ethyl mercaptan	6.295	$y = 1.9226x + 1.0020$	0.9983
5	Dimethyl sulfide	6.543	$y = 2.6252x - 2.1923$	0.9986
6	Carbon disulfide	7.013	$y = 5.5277x - 9.1795$	0.9993
7	Thiophene	8.997	$y = 2.7757x - 0.2334$	0.9991

Repeatability and linearity

The repeatability was tested, and the results are shown in Table 4. All data were collected for three calibration levels (low, middle, and high), with eight replicates at each level. As shown in Table 4, the average area RSD for 15 ppb calibrants was 7.4%, with a maximum of 12.54%. The concentration of 15 ppb is very close to method quantitation limits, so an average area RSD of 7.4% at this level is a very good performance. The area precision improved significantly as the concentration increased. The area RSDs were 1.77 to 3.85% for 50 ppb and 0.87 to 2.21% for 200 ppb.

Linearity was evaluated for the seven compounds at seven concentration levels ranging from 15 to 200 ppb. Correlation coefficients (R^2) of those sulfur components were better than 0.998. Figure 5 shows calibration plots of the target compounds, and Table 5 shows the detailed results for each compound.

Limit of detection evaluation

The standard mix gas was diluted to determine a practical LOD on the 8355 SCD for the seven sulfur compounds. The chromatograms in Figure 6 show the response to the standard mix at 10 ppb (Figure 6A) and 15 ppb (Figure 6B). All analytes can be resolved from the baseline noise with sharp peak shape. The signal-to-noise ratio (S/N) (ASTM) was used for the LOD evaluation, and the S/N values for all analytes at 10 ppb and 15 ppb are shown in Figures 6A and 6B, respectively. The S/N values are much greater than 3, which means that the LODs of those compounds are less than 10 ppb. The S/N values are slightly greater than 10 in Figure 6B, from which it can be concluded that the limit of quantitation of each analyte is approximately 15 ppb.

Conclusion

The Agilent 8890 gas chromatography system coupled with an Agilent 8355 sulfur chemiluminescence detector provides good linearity and repeatability performance for the analysis of sulfur compounds. A practical LOD was also evaluated in this study, which showed excellent sensitivity of the whole system. The features of the total system—inert flow path, sample valve connected via a volatiles interface, mini gas blender, Agilent J&W DB-Sulfur SCD column, and coupled SCD—ensure accurate qualitative and quantitative analysis of trace amounts of sulfur compounds in high-purity hydrogen.

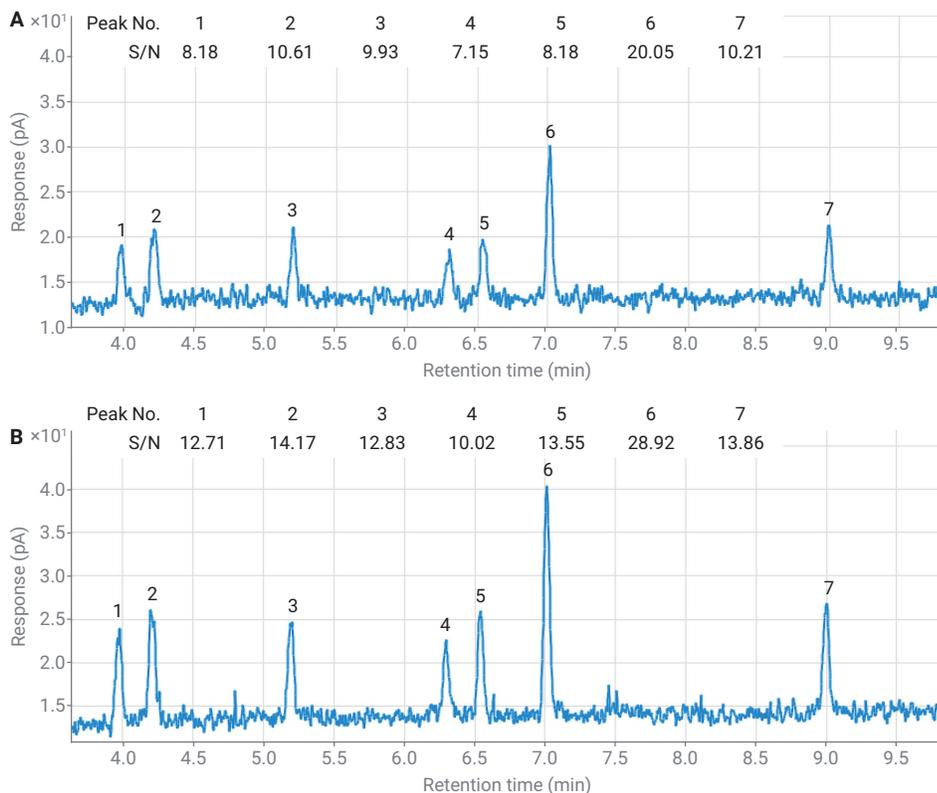


Figure 6. Chromatogram and signal-to-noise of sulfur standards at low concentrations: (A) 10 ppb; (B) 15 ppb. See Figure 4 for peak identification.

References

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