Detection of Sulfur Compounds in Light Petroleum Liquids According to ASTM D5623 with an Agilent Dual Plasma Sulfur Chemiluminescence Detector

Application Note

Authors

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Abstract

Sulfur compounds in gasoline samples are detected using an Agilent 7890B gas chromatograph configured with an Agilent 8355 Dual Plasma Sulfur Chemiluminescence Detector (SCD). The 8355 SCD provides linear, equimolar responses from 0.01 to 10 ppm. Detection of sulfur compounds down to 2 ppb is easily obtainable.

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Introduction

The petrochemical industry relies heavily on measuring sulfur throughout various processes. Sulfur-containing compounds present in petroleum feed stocks and products are monitored closely during the entire refinement process. Often sulfur compounds are odorous, disruptive to equipment, and detrimental to downstream processing due to their corrosive nature. Being able to identify and detect discrete sulfur-containing compounds is invaluable for process control. A gas chromatograph (GC) equipped with a sulfur chemiluminescence detector (SCD) provides a rapid and efficient means of identifying and quantifying sulfur compounds present at the various refinement stages. Various detectors exist for the detection of sulfur compounds, but the SCD provides the most specific and sensitive method for analysis.

ASTM D5623 [1] provides guidelines for the determination of volatile sulfur-containing compounds in light petroleum liquids. It applies to petroleum products with a boiling point of 230 °C or lower. While total sulfur is often reported and estimated from the total area sum, this application note examined 23 discrete sulfur compounds with boiling points ranging from 57–230 °C, as recommended by ASTM D5623.

The Agilent 8355 Sulfur Chemiluminescence Detector (SCD) provides linear, equimolar responses to sulfur-containing compounds with minimal hydrocarbon interference. This improves ease-of-use for data collection and analysis since it eliminates the need to linearize the data and determine separate response factors for each compound of interest. The 8355 SCD also provides a stable response that is not quenched by hydrocarbons. This application note demonstrates expected performance of the SCD. Linearity, stability, and practical detection limits of the 8355 SCD installed on an Agilent 7890B GC equipped with a DB-1 column of 1 µm film thickness is shown.

Experimental

An Agilent 7890B GC was configured with a deactivated split/splitless inlet, an Agilent 7650A Automatic Liquid Sampler, and an Agilent 8355 SCD. Stock solutions were made in isooctane with neat compounds obtained from Sigma-Aldrich Corporation at approximately 10,000 ppm. Stock solutions were diluted in isooctane to concentrations ranging from 0.1 to 100 ppm using the Agilent 7696A Sample Prep WorkBench. Compound information can be found in Table 1. For linearity analysis, 22 analytes were separated among five groups, each with a 0.1 ppm, 1 ppm, 10 ppm, and 100 ppm level, for optimal resolution and peak identification. The mixes were then combined and diluted to achieve concentrations of 20 ppb and 10 ppm, which were used to demonstrate chromatographic attributes (resolution), and to demonstrate practical limits of detection. An internal standard was added to each mix to ensure run to run repeatable performance.

Table 1. Sulfur Standards Components

No.	Compound	Formula	Linearity group
1	Ethanethiol	CH_3CH_3SH	1
2	Dimethyl sulfide	$(CH_3)_3S$	2
3	Carbon disulfide	CS_3	3
4	2-Propanethiol	$(CH_3)_3CHSH$	4
5	2-Methyl-2-propanethiol	$(CH_3)_3CSH$	5
6	1-Propanethiol	$CH_3(CH_3)_3SH$	1
7	Ethylmethyl sulfide	$CH_3CH_3SCH_3$	2
8	2-Butanethiol	$CH_3CH_3CH(SH)CH_3$	3
9	Thiophene	C_4H_4S	4
10	2-Methyl-1-propanethiol	$(CH_3)_3CHCH_3SH$	5
11	Diethyl sulfide	$CH_3CH_3SCH_3CH_3$	1
12	*n*-Butanethiol	$CH_3(CH_3)_3SH$	2
13	Dimethyl disulfide	CH_3SSCH_3	3
14	2-Methylthiophene	C_5H_6S	4
15	3-Methylthiophene	C_5H_6S	5
16	3-Chlorothiophene	C_4H_3ClS	5
17	2-Bromothiophene	C_4H_3BrS	2
18	Diethyl disulfide	$(C_3H_5)_2S_3$	1
19	Di-*tert*-butyl disulfide	$(CH_3)_3CSSC(CH_3)_3$	4
20	Thianaphthene	C_8H_6S	1
21	2-Methylbenzothiophene	C_9H_8S	3
22	3-Methylbenzothiophene	C_9H_8S	2
23	Diphenyl sulfide	$(C_6H_5)2S$	ISTD

NIST standard reference material (SRM) 2299, sulfur in gasoline and NIST SRM 2298, sulfur in gasoline (high octane) was used as another means of analysis. The total sulfur in NIST 2299 is 13.6 ± 1.5 µg/g. The total sulfur in NIST 2298 is 4.7 ± 1.3 µg/g. Diphenyl sulfide (compound number 23) was added to each solution as an internal standard at 10 ppm.

Table 2 gives the instrument conditions.

Table 2. Instrument Conditions

Agilent 7890B GC conditions	
Front inlet	Split/Splitless inlet
Temperature	275 °C
Septum purge flow	3 mL/min
Mode	Split
Split ratio	10:1
Split flow	20 mL/min
Gas saver	20 mL/min after 5 minutes
Oven	40 °C (0.71 minutes) 14.1 °C to 250 °C
Column	DB1 30 m × 320 µm, 1 µm (p/n 123-1033)
Constant flow	2 mL/min
Agilent 8355 SCD conditions	
Base temperature	250 °C
Burner temperature	800 °C
Upper H_2 flow	38 mL/min
Lower H_2 flow	8 mL/min
Oxidizer flow	60 mL/min
Ozonizer (O_2)	40 mL/min
Nominal burner pressure	366 torr
Nominal reaction cell vacuum	3–5 torr

Results and Discussion

Repeatability and linearity

Linearity was evaluated for 22 analytes ranging from 0.1 to 100 ppm injected. The equivalent on-column concentration was 0.01 to 10 ppm given the 10:1 split ratio. Repeatability was calculated by determining the RSD from five replicate injections, and repeated for each analyte at each concentration. Table 3 gives repeatability along with R^2 values. Diphenyl sulfide was used as an internal standard, and was included in each dilution at approximately 30 ppm (~5 ng S). The average area RSD for the 0.1 ppm standard was 5.9%. The average area RSD improved for higher concentrations to be 2.6%, 2.8%, and 2.7% for 1 ppm, 10 ppm, and 100 ppm, respectively. The linearity was found to be 0.999 or better for all but 2-methylbenzothiophene, which had a slightly lower R^2 value of 0.996.

Table 3. Repeatability and Linearity for the 22 Sulfur Compounds Analyzed

No.	Analyte	0.1 ppm	1 ppm	10 ppm	100 ppm	R^2
1.	Ethanethiol	6.7%	3.1%	6.1%	4.7%	0.9992
2.	Dimethyl sulfide	8.4%	5.1%	4.6%	4.5%	0.9995
3.	Carbon disulfide	9.5%	3.8%	4.3%	6.4%	0.9992
4.	2-Propanethiol	6.1%	4.2%	3.3%	3.7%	0.9996
5.	2-Methyl-2-propanethiol	8.0%	1.8%	3.3%	2.5%	0.9997
6.	1-Propanethiol	7.6%	2.4%	4.6%	3.2%	0.9999
7.	Ethylmethyl sulfide	8.1%	3.9%	3.5%	3.8%	0.9996
8.	2-Butanethiol	4.9%	1.3%	3.4%	3.6%	0.9997
9.	Thiophene	2.6%	3.2%	3.5%	3.7%	0.9997
10.	2-Methyl-1-propanethiol	5.8%	2.4%	2.6%	2.3%	0.9998
11.	Diethyl sulfide	7.1%	1.8%	3.0%	2.1%	0.9997
12.	*n*-Butanethiol	6.4%	2.9%	1.6%	2.1%	0.9994
13.	Dimethyl disulfide	5.6%	2.6%	3.0%	4.0%	0.9997
14.	2-Methylthiophene	3.6%	2.4%	2.1%	2.1%	0.9998
15.	3-Methylthiophene	6.1%	1.4%	2.8%	2.1%	0.9997
16.	3-Chlorothiophene	5.6%	1.7%	2.7%	1.9%	0.9997
17.	2-Bromothiophene	4.3%	2.2%	0.88%	1.5%	0.9998
18.	Diethyl disulfide	4.2%	0.94%	0.84%	0.97%	0.9999
19.	Di-*tert*-butyl disulfide	2.3%	1.9%	0.80%	0.62%	0.9999
20.	Thianaphthene	6.1%	2.5%	1.3%	0.78%	0.9994
21.	2-Methylbenzothiophene	8.1%	3.5%	0.92%	1.7%	0.9955
22.	3-methylbenzothiophene	3.4%	2.0%	1.9%	1.8%	0.9999

Linearity was very good for all of the compounds evaluated. Figure 1 shows a log-log calibration plot for four analytes of interest. The log-log plot is shown to better demonstrate the linearity across a wide concentration range. Although it is not easily seen, there are five data points plotted for each of the four concentrations. This demonstrates superior confidence of repeatability. The four analytes chosen are representative of the 22 compounds evaluated.

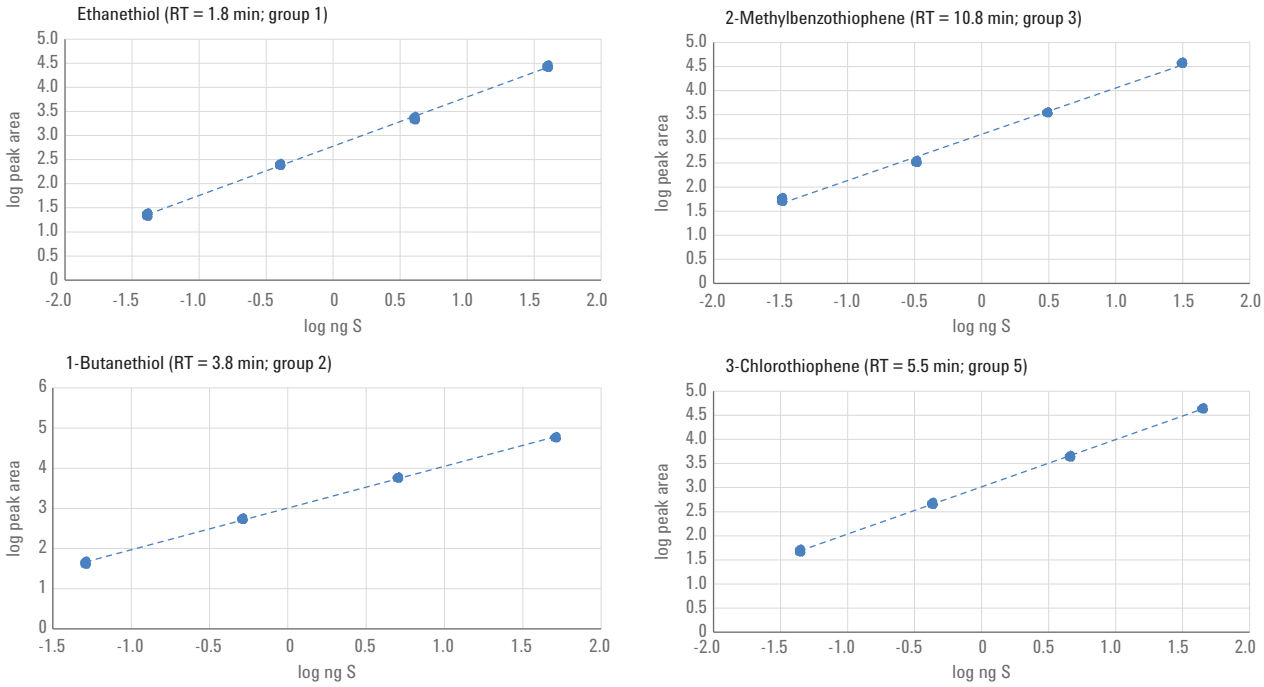

Figure 1. Calibration plots are show for four sulfur compounds of interest. These plots are representative of the 22 analytes examined.

Limit of detection (LOD) evaluation

To determine a practical LOD for the SCD, the 22 analytes were combined into one mix, along with diphenyl sulfide as the internal standard. The chromatograms in Figure 2 show the SCD response to the combined mix at both 10 ppm (Figure 2A) and 20 ppb (Figure 2B). Peak identification can be found in Table 1. At 10 ppm, most of the analytes show excellent peak shape and resolution, although diethyl sulfide (peak 11) and 1-butanethiol (peak 12) show some broadening. All 23 peaks were eluted in less than 14 minutes. At 20 ppb (Figure 2B), a large majority of the analytes can be resolved from the baseline noise. This indicates a practical LOD of 2 ppb since the 20 ppb standard was split 10:1.

No.	Analyte	No.	Analyte
1.	Ethanethiol	13.	Dimethyl disulfide
2.	Dimethyl sulfide	14.	2-Methylthiophene
3.	Carbon disulfide	15.	3-Methylthiophene
4.	2-Propanethiol	16.	3-Chlorothiophene
5.	2-Methyl-2-propanethiol	17.	2-Bromothiophene
6.	1-Propanethiol	18.	Diethyl disulfide
7.	Ethylmethyl sulfide	19.	Di-*tert*-butyl disulfide
8.	2-Butanethiol	20.	Thianaphthene
9.	Thiophene	21.	2-Methylbenzothiophene
10.	2-Methyl-1-propanethiol	22.	3-methylbenzothiophene
11.	Diethyl sulfide	23.	Diphenyl sulfide (IS)
12.	*n*-Butanethiol		

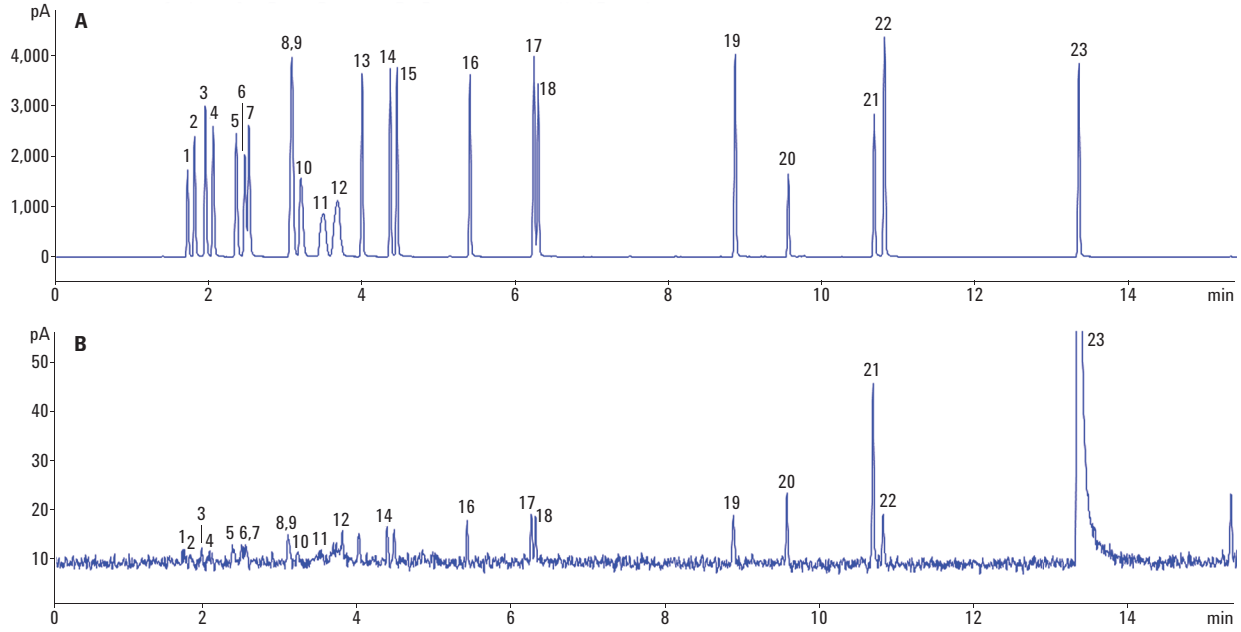

Figure 2. A) Chromatogram for the 10 ppm standard containing all 22 sulfur compounds, with diphenyl sulfide as the internal standard. B) Chromatogram for the 20 ppb standard containing all 22 sulfur compounds with diphenyl sulfide as the internal standard.

NIST Standard reference material evaluation

As a practical demonstration of the SCD's capabilities, NIST SRMs were evaluated. Figure 3 shows chromatograms from NIST SRM 2299 (Figure 3A) and NIST SRM 2298 (Figure 3B). Diphenyl sulfide (added as the ISTD at 10 ppm) is the large peak at approximately 13.5 minutes, and is not included in the total sulfur determination. Total sulfur for NIST 2299 was determined to be 12.5 µg/g. Total sulfur for NIST 2298 was determined to be 3.5 µg/g. Both were found to be within the expected tolerances. Peak shape and resolution appear to be very good for these reference samples as well.

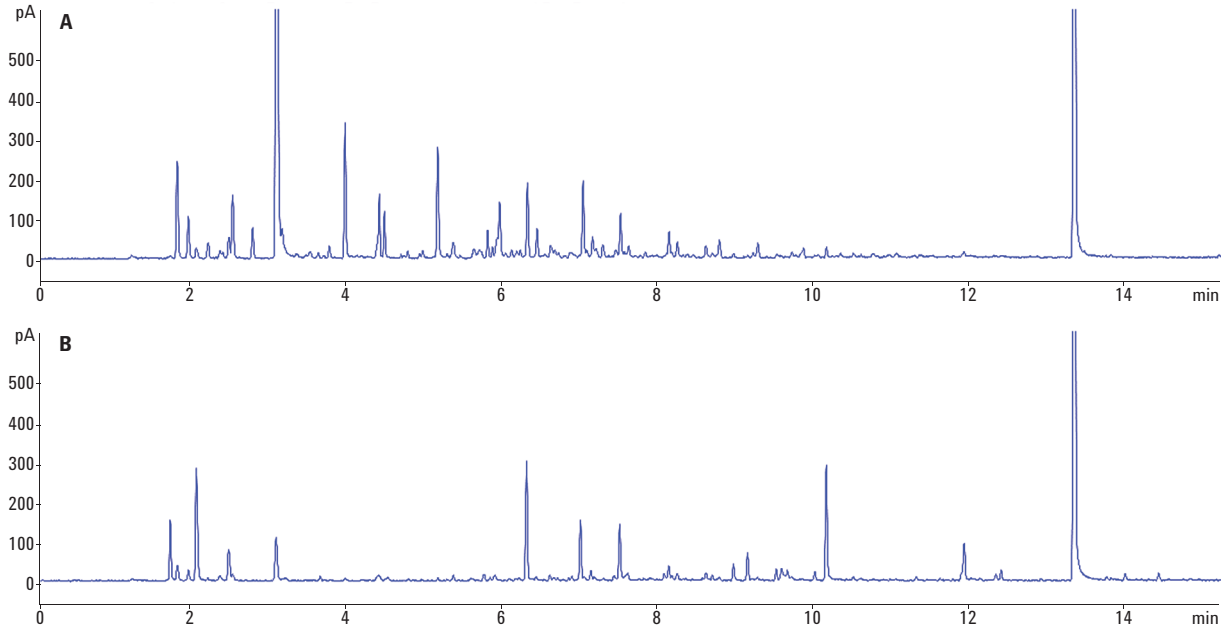

Figure 3. A) Chromatogram for the analysis of NIST SRM 2299 (sulfur in gasoline). B) Chromatogram for the analysis of NIST SRM 2298 (sulfur in gasoline, high octane).

Stability analysis

The SCD provides a relatively stable response over time. The relative response factor of t-butyl disulfide (~3 ng S) was monitored over time, and illustrates the stability of this detector. Nearly 240 runs were completed over the course of two weeks by analyzing the stability mix at the beginning and end of each sequence run (for example, linearity and NIST SRM evaluation). The average relative response factor was found to be 0.96. The standard deviation and RSD were 0.02 and 2.1%, respectively. Over the course of two weeks, the relative response factor was very stable. Figure 4 shows the average relative response factor each day that stability data was collected over the two-week test period. Each data point is bracketed with error bars showing three standard deviations based on the average value for that day. The gaps in data represent when the unit sat in standby mode. This demonstrates that the unit can be put into sleep or standby mode, and brought back into operation quickly and reliably.

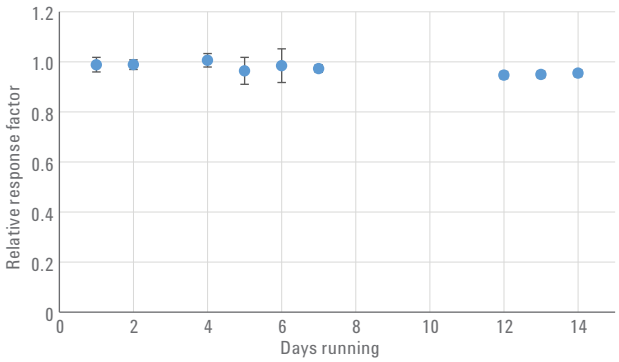

Figure 4. Two-week relative response factor data. For 238 runs collected over a two-week time period, the relative response factor did not deviate more than three standard deviations.

Conclusions

The Agilent 8355 Dual Plasma Sulfur Chemiluminescence Detector provides a linear response for a wide range of sulfur-containing compounds. The 8355 SCD provides an equimolar response that does not require linearization. This provides measureable advantages over other techniques such as the pulsed flame photometric detector, the flame photometric detector, and flame ionization detector when analyzing light petroleum liquids.

Area repeatability is very good across the 10^3 range measured. Linearity was very good, with 95% of the compounds achieving 0.999 or better. Sulfur-containing compounds were easily identified from a 20 ppb standard (corresponding to 2 ppb on-column), which indicates a practical LOD that is more than adequate to address not only the ASTM D5623 method, but other ASTM methods aimed at determining sulfur compounds in various matrices. The 8355 SCD also yielded exceptional results for NIST gasoline standards, and demonstrated stable relative response factors for over two weeks.

Reference

1. ASTM 5623: Standard test method of sulfur compounds in light petroleum liquids by gas chromatography and sulfur selective detection.

For More Information

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