Detection of Sulfur Compounds in Light Petroleum Liquids According to ASTM D5623 with the Agilent Dual Plasma Sulfur Chemiluminescence Detector and the Agilent Intuvo 9000 GC

Application Note

Author

Rebecca Veeneman, PhD
Agilent Technologies, Inc.

Abstract

Sulfur compounds in gasoline samples are detected using an Agilent Intuvo 9000 gas chromatograph configured with an Agilent 8355 dual plasma sulfur chemiluminescence detector (SCD). The 8355 SCD provides linear responses from 0.01 to 1 ppm. Detection of sulfur compounds was achieved down to 2 ppb.

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.

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 examines 23 discrete sulfur compounds with a boiling point ranging from 57–230 °C, as recommended by ASTM D5623.

The Agilent 8355 SCD provides linear 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. The Agilent Intuvo 9000 GC provides a gas chromatograph with a 27 cm footprint, inert flow path, direct heating technology, and ferrule-less connections. This enables a more stable system with an easier and less frequent maintenance model. This Application Note demonstrates the same performance parameters as a previously published Application Note[2] on the Intuvo 9000 GC. Linearity, stability, and practical detection limits of the system with a Intuvo DB-1 column of 1 µm film thickness are shown.

Experimental

An Agilent Intuvo 9000 GC was configured with a deactivated split/splitless inlet, an Agilent 7693A Automatic Liquid Sampler, and a standalone 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. Table 1 shows the compound information. 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 resolution and practical limits of detection.

NIST standard reference material (SRM) 2299: Sulfur in Gasoline, and NIST SRM 2298: Sulfur in Gasoline, High Octane were used as another means of system analysis. The expected total sulfur in NIST 2299 is 13.6 ± 1.5 µg/g. The expected total sulfur in NIST 2298 is 4.7 ± 1.3 µg/g. Diphenyl sulfide (compound 23) was added to each solution as an internal standard at 10 ppm.

Table 1. Sulfur standard components.

	Compound	Formula	Calibration group
1	Ethanethiol	CH_3CH_2SH	1
2	Dimethyl sulfide	$(CH_3)_2S$	2
3	Carbon disulfide	CS_2	3
4	2-Propanethiol	$(CH_3)_2CHSH$	4
5	2-Methyl-2-propanethiol	$(CH_3)_3CSH$	5
6	1-Propanethiol	$CH_3(CH_2)_2SH$	1
7	Ethylmethyl sulfide	$CH_3CH_2SCH_3$	2
8	2-Butanethiol	$CH_3CH_2CH(SH)CH_3$	3
9	Thiophene	C_4H_4S	4
10	2-Methyl-1-propanethiol	$(CH_3)_2CHCH_2SH$	5
11	Diethyl sulfide	$CH_3CH_2SCH_2CH_3$	1
12	*n*-Butanethiol	$CH_3(CH_2)_3SH$	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	$(C_2H_5)_2S_2$	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

Table 2 shows the instrument conditions.

Table 2. Instrument conditions.

Parameter	Value
Agilent Intuvo 9000 GC	
Syringe	10 µL
Solvent washes	pre-injection 3× solvent A, isooctane (2 µL) 2× solvent B, acetone (2 µL) post-injection 2× solvent A, acetone (2 µL) 2× solvent B, acetone (2 µL)
Sample wash	2 × 1 µL
Sample pumps	6
Carrier gas	Helium
Inlet	Split/Splitless inlet in split mode
	300 °C
Split ratio	10:1
Split flow	20 mL/min
Septum purge flow	3 mL/min
Gas saver	20 mL/min after 5 minutes
Intuvo Guard Chip	300 °C
Column	Agilent Intuvo DB1 30 m × 320 µm, 1 µm
Column flow	2 mL/min
Column temperature program	40 °C (0.71 minutes) 14.1 °C to 250 °C (1 minute)
Agilent 8355 SCD	
Base temperature	280 °C
Burner temperature	800 °C
Upper H_2 flow	38 mL/min
Lower H_2 flow	8 mL/min
Oxidizer flow	50 mL/min
Ozonizer (O_2)	36 mL/min
Nominal burner pressure	5 torr
Range	6
Data rate	5 Hz

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 from five replicate injections, and repeated for each analyte at each concentration. Table 3 gives the repeatability and R^2 values. Diphenyl sulfide was used as an internal standard, and was included in each standard for each level at approximately 30 ppm (~5 ng S). The average area RSD for the 0.1 ppm standard was 4.1 %. The average area RSD improved for higher concentrations to 3.2 %, 2.9 %, and 2.2 % for 1 ppm, 10 ppm, and 100 ppm, respectively. The correlation coefficients were found to be 0.999 or better for a majority of the analytes. Figure 1 shows the log-log calibration plot for four analytes of interest, including two analytes that had slightly lower R^2 values. A log-log plot is shown to better demonstrate the linearity across the wide concentration range. In addition, there are five data points plotted for each of the four concentrations. This demonstrates high confidence in repeatability. The four analytes chosen are representative of the 22 compounds evaluated.

Table 3. Repeatability and linearity for the 22 sulfur compounds analyzed.

Analyte	0.1 ppm (%)	1 ppm (%)	10 ppm (%)	100 ppm (%)	R^2
Ethanethiol	8.5	4.6	5.4	3.9	0.998
Dimethyl sulfide	5.5	5.9	6.9	4.1	0.997
Carbon disulfide	3.9	6.8	4.0	7.3	0.997
2-Propanethiol	3.1	3.6	3.9	3.7	0.999
2-Methyl-2-propanethiol	4.3	2.6	1.6	1.0	0.999
1-Propanethiol	6.7	2.2	5.3	2.9	0.999
Ethylmethyl sulfide	3.8	5.3	5.1	3.0	0.999
2-Butanethiol	3.1	4.2	2.4	3.8	0.999
Thiophene	3.9	3.6	4.5	4.0	0.999
2-Methyl-1-propanethiol	3.0	3.2	1.4	1.1	0.999
Diethyl sulfide	6.9	2.6	3.7	1.9	0.999
n-Butanethiol	4.0	3.7	3.7	1.9	0.994
Dimethyl disulfide	3.3	3.5	2.2	4.0	0.999
2-Methylthiophene	2.8	3.5	2.7	1.7	0.999
3-Methylthiophene	4.4	3.3	1.5	0.9	0.999
3-Chlorothiophene	4.7	3.2	1.2	0.8	0.999
2-Bromothiophene	2.8	0.9	2.30	0.5	0.999
Diethyl disulfide	3.1	1.20	1.60	0.56	0.999
Di-*tert*-butyl disulfide	2.5	1.9	0.66	0.74	0.999
Thianaphthene	4.7	0.7	1.2	0.54	0.999
2-Methylbenzothiophene	2.7	1.4	1.20	0.6	0.998
3-methylbenzothiophene	1.5	2.4	0.6	0.2	0.999

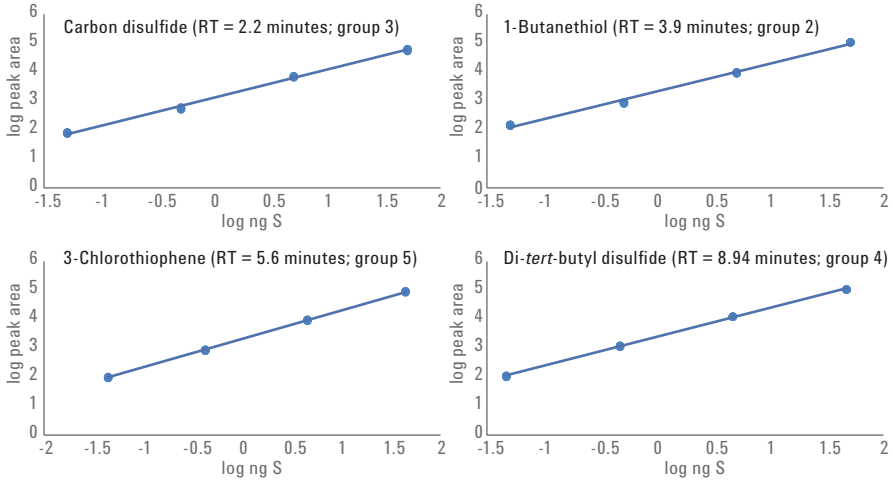

Figure 1. Calibration plots for four sulfur compounds of interest highlighting the repeatability of the system. Five data points are plotted at each concentration. These plots are representative of the 22 analytes examined.

Limit of detection (LOD) evaluation

To determine a practical LOD for the system, 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. All 23 peaks were eluted in less than 14 minutes. At 20 ppb (Figure 2B), a large majority of the analytes can be differentiated from the baseline. This indicates a practical LOD of 2 ppb, since the 20 ppb standard was split 10:1.

NIST standard reference material evaluation

As a practical demonstration of the instrument'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 (averaged from five injections) for NIST 2299 was determined to be 14.4 ± 0.6 µg/g. Total sulfur for NIST 2298 was determined to be 4.0 ± 0.1 µg/g (averaged from four injections). Both were found to be within the expected tolerances. Peak shape and resolution appear to be very good for these reference samples as well.

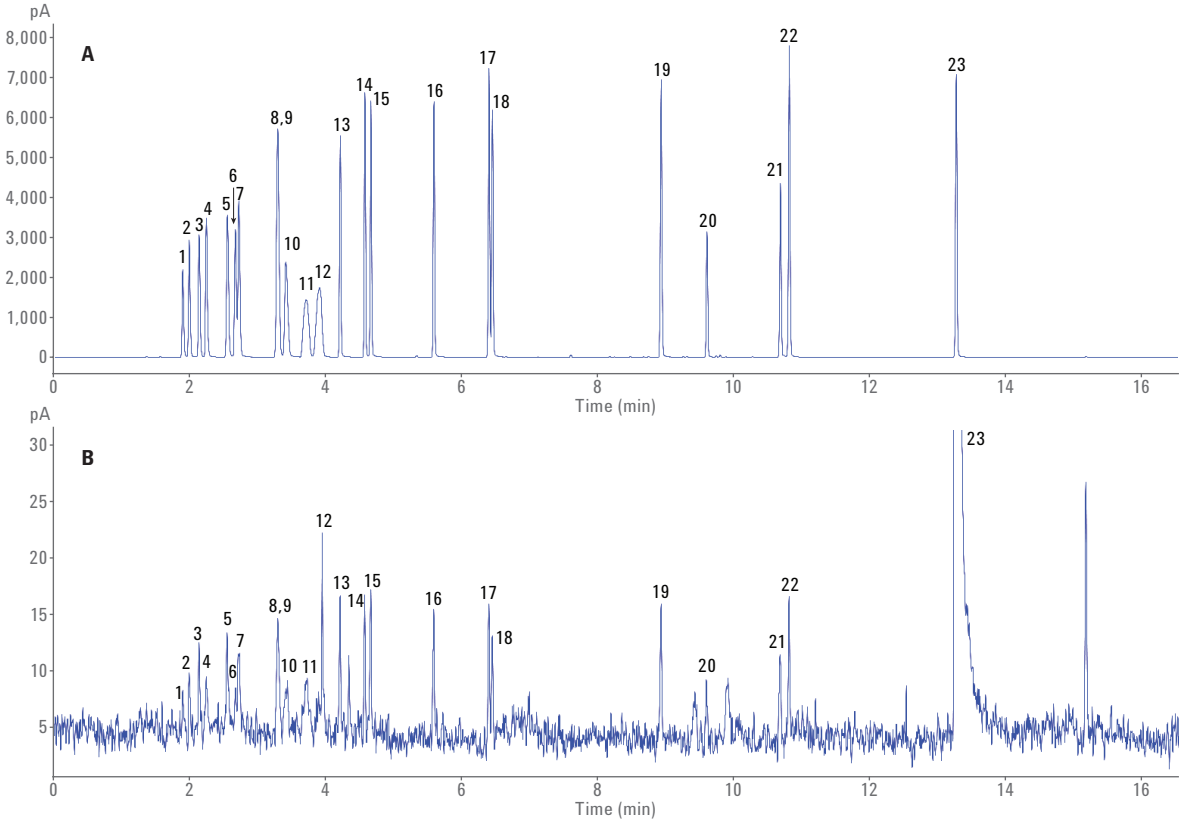

Figure 2. A) Chromatogram of the 10 ppm standard, containing all 22 sulfur compounds, with diphenyl sulfide as the internal standard. B) Chromatogram of the 20 ppb standard, containing all 22 sulfur compounds, with diphenyl sulfide as the internal standard.

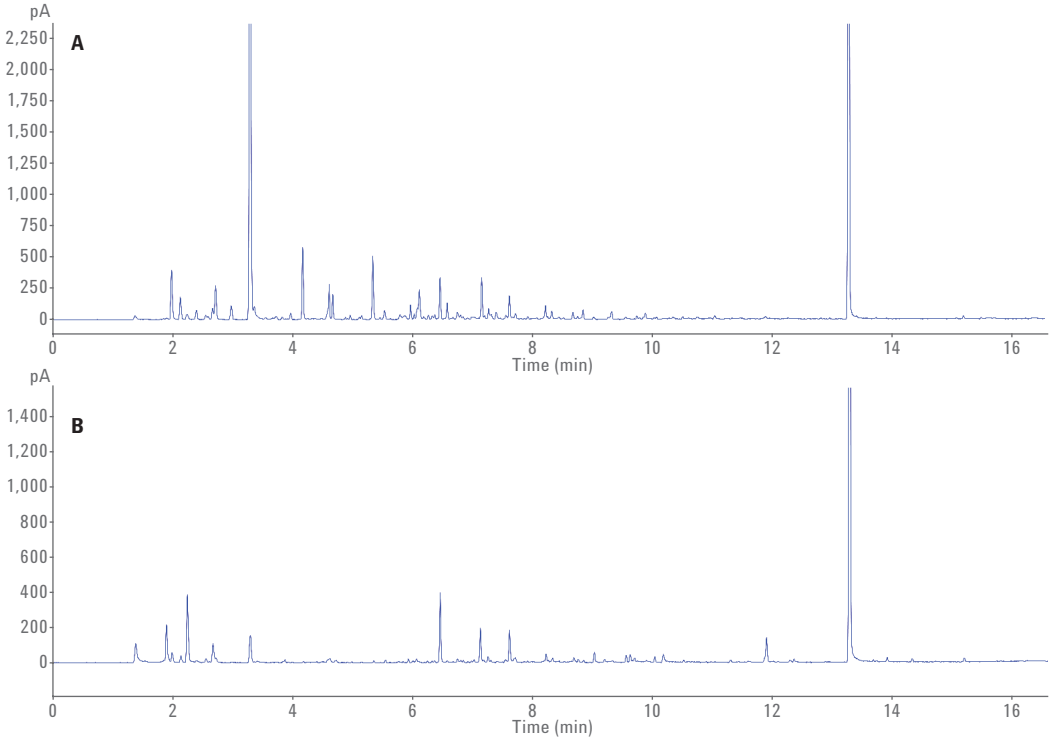

Figure 3. A) Chromatogram for the analysis of NIST SRM 2299 (Sulfur in Gasoline). B) Chromatogram for the analysis of NIST SRM 2298 (Sulfur in Gasoline, High Octane).

Conclusions

The Agilent 8355 dual plasma sulfur chemiluminescence detector combined with the Agilent Intuvo 9000 GC and an Intuvo DB1 column provided a linear response for a wide range of sulfur-containing compounds. Area repeatability was very good across the three orders of magnitude measured. Linearity was very good, with the majority of compounds achieving 0.999 or better. Sulfur-containing compounds were easily identified from a 20 ppb standard (corresponding to 2 ppb on-column). This 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 with the Intuvo 9000 GC also and an Intuvo DB1 column yielded exceptional results for NIST gasoline standards.

The Intuvo 9000 GC, equipped with a standalone 8355 SCD, provides a small, stable platform capable of detecting a wide range of sulfur-containing compounds down to 2 ppb. The Intuvo inert flow path and ferrule-less connections provide a reliable and robust sample path, while the SCD delivers stable species-specific detection.

References

1. ASTM D5623: Standard test method of sulfur compounds in light petroleum liquids by gas chromatography and sulfur selective detection.

2. Veeneman, R.; Smith, A. Detection of Sulfur Compounds in Light Petroleum Liquids According to ASTM D5623 with an Agilent Dual Plasma Sulfur Chemiluminescence Detector, *Agilent Technologies Application Note*, publication number 5991-6577EN.

www.agilent.com/chem

Published in the USA, September 1, 2016
5991-7215EN