SULFUR IN GASOLINE:
LIGHT PETROLEUM LIQUIDS ACCORDING TO ATSM D5623

Technology Advantage: Agilent Intuvo 9000 GC with SCD

Introduction

Reliable sulfur measurements are a requirement in many areas of the petrochemical industry. Sulfur-containing compounds are present in petroleum feed stocks and products. This class of compounds is odorous, often disruptive to equipment, and detrimental to downstream processing. Therefore, sulfur-containing compounds are monitored through the entire refinement process.

While the analysis of sulfur-containing compounds is easily achieved with conventional gas chromatography systems, the Agilent Intuvo 9000 GC equipped with an Agilent 8355 Sulfur Chemiluminescence Detector (SCD) provides a unique solution with additional advantages:

- Smaller footprint
- Increased stability
- Easier maintenance

At only 27 cm, the Intuvo 9000 GC is approximately half the size of a conventional GC. A proprietary flow path and connection paradigm yields a more robust analysis, while enabling faster column changes for method development.

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Experimental

To demonstrate equivalent chromatographic performance to conventional gas chromatographs, standards were used as in a previously published Application Note[1] demonstrating the capabilities of the 8355 SCD. Standards containing 22 sulfur-containing compounds were made in isooctane with concentrations ranging from 0.1 to 100 ppm, and were used to demonstrate linearity and repeatability. Standards diluted to 20 ppb and 10 ppm were used to demonstrate resolution, and determine practical limits of detection (LODs).

Split injections (10:1) were performed, and the analysis was achieved with a 30 m Agilent Intuvo DB1 column following a standard oven program. The SCD was maintained with recommended temperatures and flow rates. The full method details are available in a separate Application Note[2].

Results and Discussion

Four standards ranging from 0.1 to 100 ppm were evaluated with the Agilent Intuvo 9000 and a stand-alone SCD. Across 22 compounds, the average peak area RSD for five consecutive injections was 4.1 %, 3.2 %, 2.9 %, and 2.2 % for 0.1 ppm, 1 ppm, 10 ppm, and 100 ppm, respectively. The average R^2 value was 0.999.

Figures 1A and 1B show the 22 analytes at 10 ppm and 20 ppb. Diphenyl disulfide was included as an internal standard. At 10 ppm, all analytes show excellent peak shape. At 20 ppb, a majority of the analytes can be differentiated from the baseline, with over 50 % giving a signal-to-noise ratio (S/N) greater than 3 (Table 1).

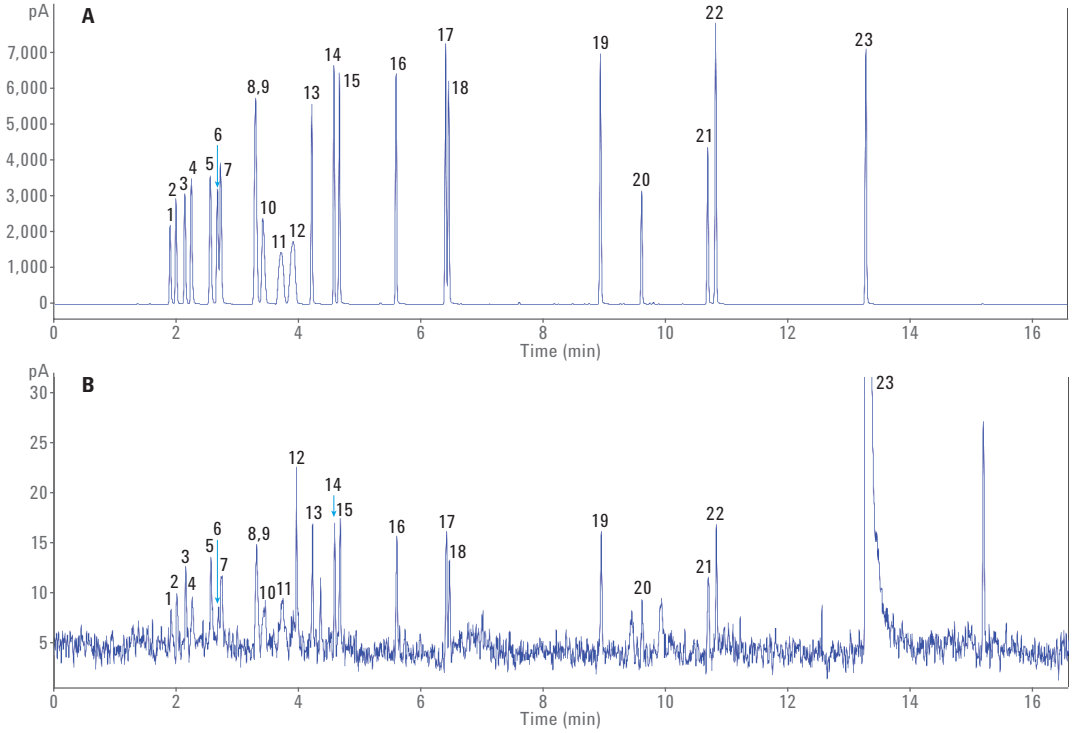

Figure 1. Chromatograms at 10 ppm (A) and 20 ppb (B) for the 22 sulfur compounds analyzed. Peak shape is well maintained for both concentrations.

Table 1. Peak identification for the sulfur compounds shown in Figure 1, listed with the S/N determined from the 20 ppb standard.

Peak	Analyte	S/N (20 ppb)
1	Ethanethiol	1.76
2	Dimethyl sulfide	2.43
3	Carbon disulfide	3.34
4	2-Propanethiol	2.04
5	2-Methyl-2-propanethiol	3.34
6	1-Propanethiol	1.48
7	Ethylmethyl sulfide	2.46
8	2-Butanethiol	4.01
9	Thiophene	ND
10	2-Methyl-1-propanethiol	2.00
11	Diethyl sulfide	1.34
12	1-Butanethiol	6.45
13	Dimethyl disulfide	4.79
14	2-Methylthiophene	4.83
15	3-Methylthiophene	5.04
16	3-Chlorothiophene	4.44
17	2-Bromothiophene	4.83
18	Diethyl disulfide	3.81
19	Di-*tert*-butyl disulfide	4.44
20	Thianaphthene	2.40
21	2-Methylbenzothiophene	3.31
22	3-Methylbenzothiophene	4.79
23	Diphenyl sulfide	ISTD

Conclusion

The Agilent Intuvo 9000 GC, equipped with an Agilent 8355 SCD and an Intuvo column, yields equivalent performance to that of a conventional GC equipped with the same detector and an Agilent J&W DB1 column. Area repeatability and linearity is excellent across a wide range of concentrations. The ability to differentiate the analytes of interest from the baseline gives a practical LOD of 2 ppb given the 10:1 split ratio. However, the innovative flow path affords a smaller footprint, more robust connections, and simplified maintenance, thus providing another method to

make reliable sulfur measurements.

References

1. Veeneman, R.; Smith, A. Detection of Sulfur Compounds in Gasoline According to ASTM D5623 with Agilent's Dual Plasma Sulfur Chemiluminescence Detector (8355), *Agilent Technologies Application Note*, publication number 5991-6577EN, **2016**.

2. Veeneman, R. Detection of Sulfur Compounds in Gasoline According to ASTM D5623 with Agilent's Intuvo GC and Dual Plasma Sulfur Chemiluminescence Detector, *Agilent Technologies Application Note*, publication number 5991-7215EN, **2016**.

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