Analysis of Sulfur Compounds in a Petroleum Fraction using Agilent J&W DB-Sulfur SCD GC Column and Inert Flow Path

Application Note

Energy & Chemicals

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Abstract

Sulfur-containing components in gasoline samples were analyzed using an Agilent Inert Flow Path GC/SCD with an Agilent J&W DB-Sulfur SCD column according to ASTM D5623. The 60 m × 0.32 mm id, 4.2-µm film DB-Sulfur SCD column, with low bleed and exceptional inertness, provides good resolution and peak shape to these reactive sulfur compounds. Hydrogen sulfide and carbonyl sulfide can be separated very well at ambient temperature, which avoids cryogenic cooling. Good results confirm that the Inert Flow Path GC/SCD configured with the DB-Sulfur SCD column is a useful tool for analysis of sulfur compounds.

Introduction

Monitoring sulfur compounds in petroleum related products is very important to protect expensive catalysts and ensure product quality. The analysis of sulfur compounds in gasoline can be challenging because they can occur in very complex matrixes and often in widely varying concentrations. Although several methods can be used to simply indicate total sulfur levels in various petroleum liquids, the increasing tendency is to carry out selective detailed analysis of sulfur compounds in these samples.

It is generally accepted that gas chromatography/mass spectrometry (GC/MS) is a useful tool when identifying peaks but, in the case of petroleum matrixes, such attempts are usually frustrated by the disturbing effect of co-eluting hydrocarbons. Gas chromatography with a sulfur specific detector is commonly used to quantify sulfur compounds. Sulfur chemiluminescence detection (SCD) is known as an excellent device for sulfur compound analysis because its response is inherently linear, equimolar, and far less susceptible to hydrocarbon interference. For example, ASTM Method D5623-94 uses SCD for the detection of sulfur compounds in gasoline.

Thick film, 100% dimethylpolysiloxane type columns have been widely adopted for volatile sulfur analyses to achieve good resolution. However, these thick film columns generally exhibit higher bleed levels. 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.

The Agilent DB-Sulfur SCD GC column is specifically developed for sulfur compound analyses and optimized for GC/SCD. This novel wall coated, open tubular column with low bleed and exceptional inertness to sulfur compounds enables separation of a broad range of the active solutes at low concentrations. This application note demonstrates how sulfur compounds in a petroleum fraction are analyzed using gas chromatography with inert flow path components, SCD, and a DB-Sulfur SCD GC column.

Experimental

The experiments were performed on an Agilent 7890 Gas Chromatograph equipped with Agilent 355 DP SCD, and Agilent 7683 Automatic Liquid Sampler (ALS). An Agilent Inert Flow Path split/splitless inlet and Ultra Inert liner and Ultra Inert gold seal were used.

The sulfur standards in toluene were purchased from J&K Chemical (Shanghai, China). The component information is listed in Table 1.

Stock solutions of sulfur standards, including 20 sulfur compounds, were prepared by dissolving them in toluene at concentrations of 100 mg/kg. Diphenyl sulfide was used as the internal standard.

Calibration solutions were prepared in six different concentrations by dilution of sulfur stock solutions in toluene. Each standard solution contained 5 mg/kg of internal standard. A cracked gasoline sample was provided by a local petrochemical company. Internal standard was added to each sample at a concentration of 5 mg/kg before injection.

Conditions, GC

Column:	Agilent J&W DB-Sulfur SCD, 60 m x 0.32 mm, 4.2 µm (p/n G3903-63001)
Inlet:	275 °C, Split ratio 10:1 (Inert Flow Path split/splitless inlet)
Carrier:	Helium, constant flow mode, 2.8 mL/min
Oven:	35 °C for 3 min, 35 °C to 250 °C at 10 °C/min, 250 °C for 10 min
Injection volume:	1 µL

Conditions, SCD

Burner temperature:	800 °C
Vacuum of burner:	364 torr
Vacuum of reaction cell:	5 Torr
Hydrogen:	40 mL/min
Air:	60 mL/min

Supplies

Septum:	Non-stick bleed and temperature optimized (BTO) septum (p/n 5183-4757)
Liner:	Ultra Inert liner (p/n 5190-2295)
Seal:	Ultra Inert gold seal and washer (p/n 5190-6144)
Syringe:	5 µL tapered, fixed needle 23-26s/42/HP (p/n 5181-1273)

Table 1. Sulfur standards

No.	Compound	CAS No.	Formula	Concentration (mg/kg)
1	Hydrogen sulfide	7783-06-4	H_2S	2000
2	Carbonyl sulfide	463-58-1	COS	2000
3	Methanethiol	74-93-1	CH_3SH	2000
4	Ethanethiol	75-08-1	C_2H_5SH	2000
5	Dimethyl sulfide	75-18-3	$(CH_3)_2S$	2000
6	Carbon disulfide	75-15-0	CS_2	2000
7	2-Propanethiol	75-33-2	C_3H_8S	2000
8	2-methyl-2-Propanethiol	75-66-1	$C_4H_{10}S$	2000
9	1-Propanethiol	107-03-9	C_3H_8S	2000
10	Ethyl methyl sulfide	624-89-5	$C_2H_5SCH_3$	2000
11	Thiophene	110-02-1	C_4H_4S	2000
12	2-methyl-1-Propanethiol	513-44-0	$C_4H_{10}S$	2000
13	Diethyl sulfide	352-93-2	$(C_2H_5)_2S$	2000
14	1-Butanethiol	109-79-5	$C_4H_{10}S$	2000
15	Dimethyl Disulfide	624-92-0	$(CH_3S)_2$	2000
16	2-Methylthiophene	554-14-3	C_5H_6S	2000
17	3-Methylthiophene	616-44-4	C_5H_6S	2000
18	Diethyl disulfide	110-81-6	$(C_2H_5S)_2$	2000
19	5-Methylbenzo[b]thiophene	14315-14-1	C_9H_8S	2000
20	3-Methylbenzothiophene	1455-18-1	C_9H_8S	2000
21	**Diphenyl sulfide	139-66-2	$C_{12}H_{10}S$	2000

** Internal standard

Results and Discussion

Resolution

The volatility, polarity, and reactivity of the sulfur compounds normally lead to the choice of a nonpolar thick film column for their separation. Typically, a 30 m, 0.32 mm id fused silica column coated with a 4.0 µm thick film of bonded, nonpolar (dimethylpolysiloxane) stationary phase is used to obtain sufficient retention of the volatile sulfur compounds. In addition, the initial oven starting temperature is below ambient temperature to separate sulfur compounds, which means cryogenic cooling should be installed.

In this work, a 60 m × 0.32 mm id, 4.2 µm film DB-Sulfur SCD GC column was used and the analysis was initiated at 35 °C. As shown in Figure 1, the column provided satisfactory separation of sulfur standards in toluene. In particular, good resolution and retention of hydrogen sulfide and carbonyl sulfide can be achieved at ambient temperature, which avoids the need for cryogenic cooling. Thiophene and 2-methyl-1-propanethiol normally co-elute on a 30 m × 0.32 mm, 4 µm nonpolar column, but they can be baseline separated on the DB-Sulfur SCD.

Better resolution can be obtained with a lower oven temperature rate of 5 °C/min, and better sensitivity can be achieved if the flow rate is reduced by half. However, run time will be increased.

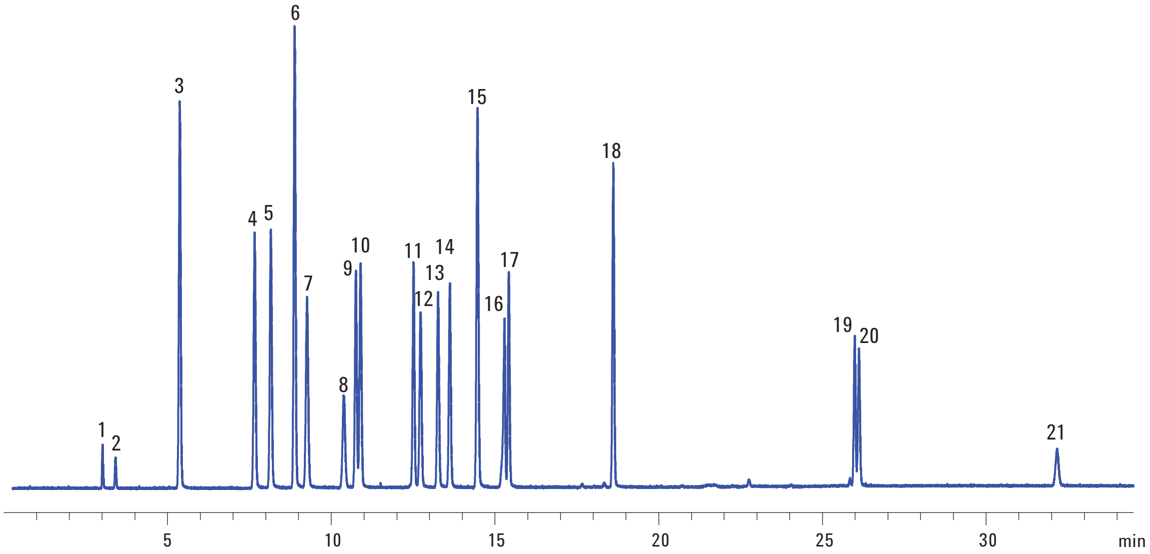

Figure 1. Chromatogram of sulfur standards in toluene using an Agilent GC/SCD system and Agilent J&W DB-Sulfur SCD column Refer to Table 1 for peak identification.

Figure 2 shows the chromatogram and signal-to-noise of each sulfur standard at 0.1 mg/kg (about 0.01 ng on column). With the low bleed of the DB-Sulfur SCD the detector remains stable throughout the evaluation and shows no sign of instability.

The DB-Sulfur SCD column can provide excellent resolution, peak shape, and response for these polar and reactive sulfur compounds due to its low bleed and improved inert performance.

Linearity

Calibration curves were constructed from data obtained from six concentration levels of standards. The test method is applicable to the determination of most target sulfur standards at levels of 0.1 to 10 ppm. Due to volatility and polarity, the concentration range for hydrogen sulfide and carbonyl sulfide is from 2 to 25 ppm, and thiophene from 0.1 to 50 ppm because its concentration is relatively high in the sample. The SCD response to sulfur is linear and essentially equimolar for all sulfur compounds within the scope of this method. Correlation coefficients of the tested sulfurs were better than 0.997 (R^2). Table 2 shows the linearity of each sulfur compound.

Table 2. Linear range of target sulfur compounds

Compound	**Concentration range (ppm)**	**Linearity (R^2)**
Hydrogen sulfide	2 – 25	0.9976
Carbonyl sulfide	2 – 25	0.9990
Methanethiol	0.1 – 10	0.9987
Ethanethiol	0.1 – 10	0.9995
Dimethyl sulfide	0.1 – 10	0.9991
Carbon disulfide	0.1 – 10	0.9990
2-Propanethiol	0.1 – 10	0.9998
2-methyl-2-Propanethiol	0.1 – 10	0.9989
1-Propanethiol	0.1 – 10	0.9990
Ethyl methyl sulfide	0.1 – 10	0.9998
Thiophene	0.1 – 50	0.9997
2-methyl-1-Propanethiol	0.1 – 10	0.9991
Diethyl sulfide	0.1 – 10	0.9992
1-Butanethiol	0.1 – 10	0.9990
Dimethyl disulfide	0.1 – 10	0.9987
2-Methylthiophene	0.1 – 10	0.9985
3-Methylthiophene	0.1 – 10	0.9994
Diethyl disulfide	0.1 – 10	0.9990
5-Methylbenzo[b]thiophene	0.1 – 10	0.9984
3-Methylbenzothiophene	0.1 – 10	0.9978

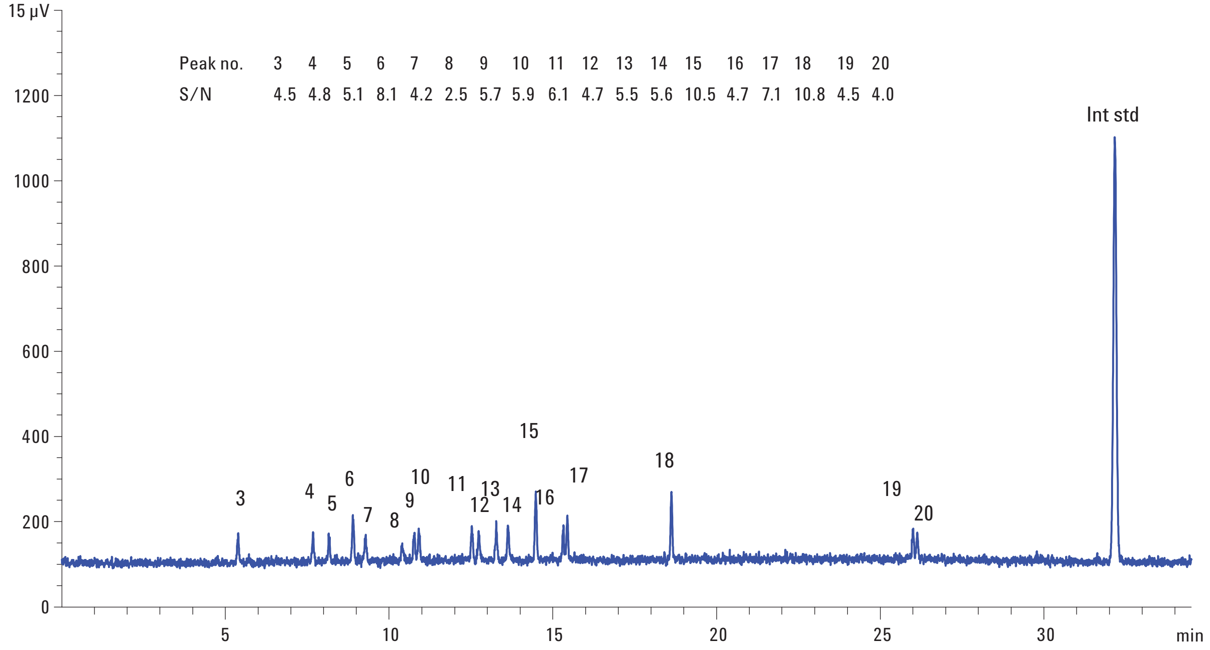

Figure 2. Chromatogram and signal-to-noise of sulfur standards at 0.1 mg/kg (approximately 0.01 ng on column). Refer to Table 1 for peak identification.

Repeatability

The repeatability was tested and the results are shown in Table 3. All data were based on six replicates of target sulfur compounds at different concentrations. Figure 3 shows good repeatability for hydrogen sulfide and carbonyl sulfide at 2 ppm with relative standard deviation (RSD) less than 3.5%.

Table 3. Repeatability of sulfur compounds at different concentrations

		10 ppm	1 ppm	0.1 ppm
No	**Compound**	**RSD%**	**RSD%**	**RSD%**
1	Methanethiol	2.94	4.46	5.12
2	Ethanethiol	2.53	3.00	4.38
3	Dimethyl sulfide	2.53	2.79	4.79
4	Carbon disulfide	2.13	3.29	5.43
5	2-Propanethiol	2.49	3.98	4.85
6	2-Methyl-2-propanethiol	2.89	4.47	4.41
7	1-Propanethiol	2.81	3.88	4.91
8	Ethyl methyl sulfide	2.34	4.17	5.24
9	Thiophene	2.24	3.06	3.49
10	2-Methyl-1-propanethiol	1.87	2.31	5.86
11	Diethyl sulfide	2.00	2.97	4.80
12	1-Butanethiol	2.46	3.36	6.47
13	Dimethyl disulfide	3.62	4.15	4.23
14	2-Methylthiophene	3.59	4.62	5.95
15	3-Methylthiophene	2.85	3.90	4.90
16	Diethyl disulfide	2.74	3.16	6.34
17	3-Methylbenzothiophene	2.48	4.87	5.29
18	5-Methylbenzo(b)thiophene	2.42	4.25	7.37

Petroleum fraction analysis

Equimolar response of a detector refers to the property of the detector that yields equal responses to equal amounts of analytes on a molar basis. Relying on the equimolarity of the Agilent SCD, petroleum fraction samples were detected and the mass concentrations of total sulfur in samples were calculated by summing the sulfur content of all sulfur components (known and unknown) in the sample, to arrive at its total sulfur value as recommended by ASTM D5623.

Figure 4a shows the chromatogram of a cracked gasoline sample that includes more than about 63.5% aromatic hydrocarbons and 25% nonaromatic hydrocarbons. Figure 4b shows the chromatogram of the sulfur standards at 5 ppm.

Individual sulfur compounds in cracked gasoline samples could be identified by retention time. GC/MS was used for further identification and confirmation. Each major individual sulfur compound was calculated by internal standardization. The RSD for target sulfur compounds ranged from 2.74 to 4.34%.

The total amount of sulfur was calculated by summing all the peak areas in the chromatogram of cracked gasoline, and quantitated using the response factor of thiophene. Table 5 shows the duplicate analysis of cracked gasoline samples with good repeatability, and RSD less than 4.85%, which also indicates no hydrocarbon interferences in the analysis.

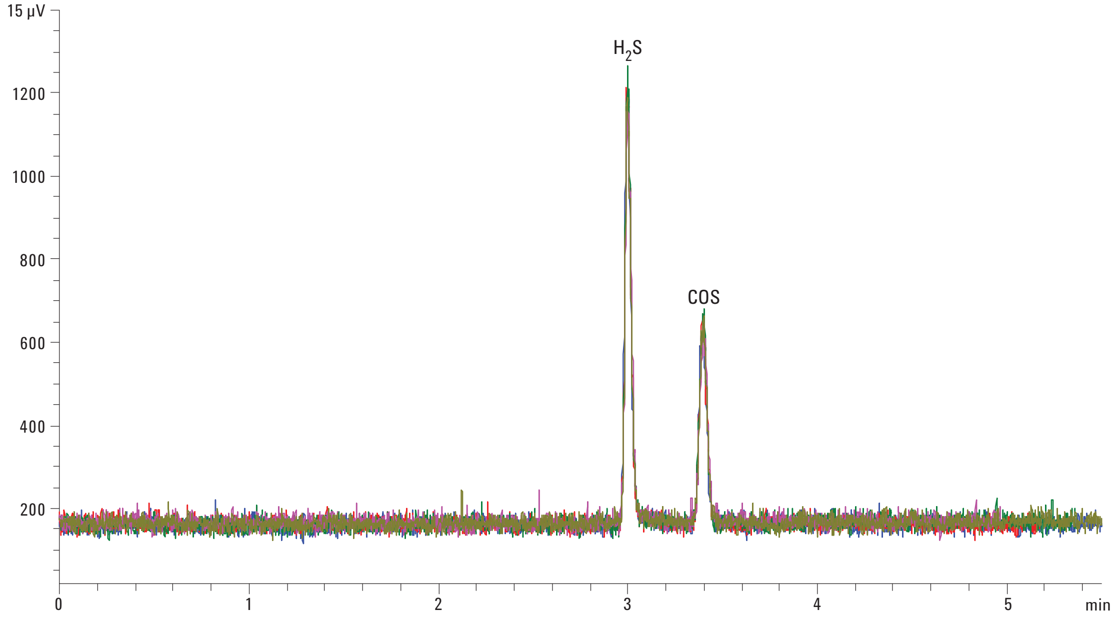

Figure 3. Chromatogram overlay of hydrogen sulfide and carbonyl sulfide at 2 ppm

Table 4. Major individual sulfur compounds in cracked gasoline

Sulfur compounds	Average content (mg/kg)	RSD% (n = 5)
Carbon disulfide	3.58	2.74
Thiophene	30.75	4.08
2-Methylthiophene	8.72	4.34
3-Methylthiophene	6.98	3.75

Table 5. Repeatability data of total sulfur in cracked gasoline

Sample	Total sulfur (mg/kg)					Mean	RSD%
Cracked gasoline	91.46	91.60	100.60	94.89	100.88	95.89	4.84

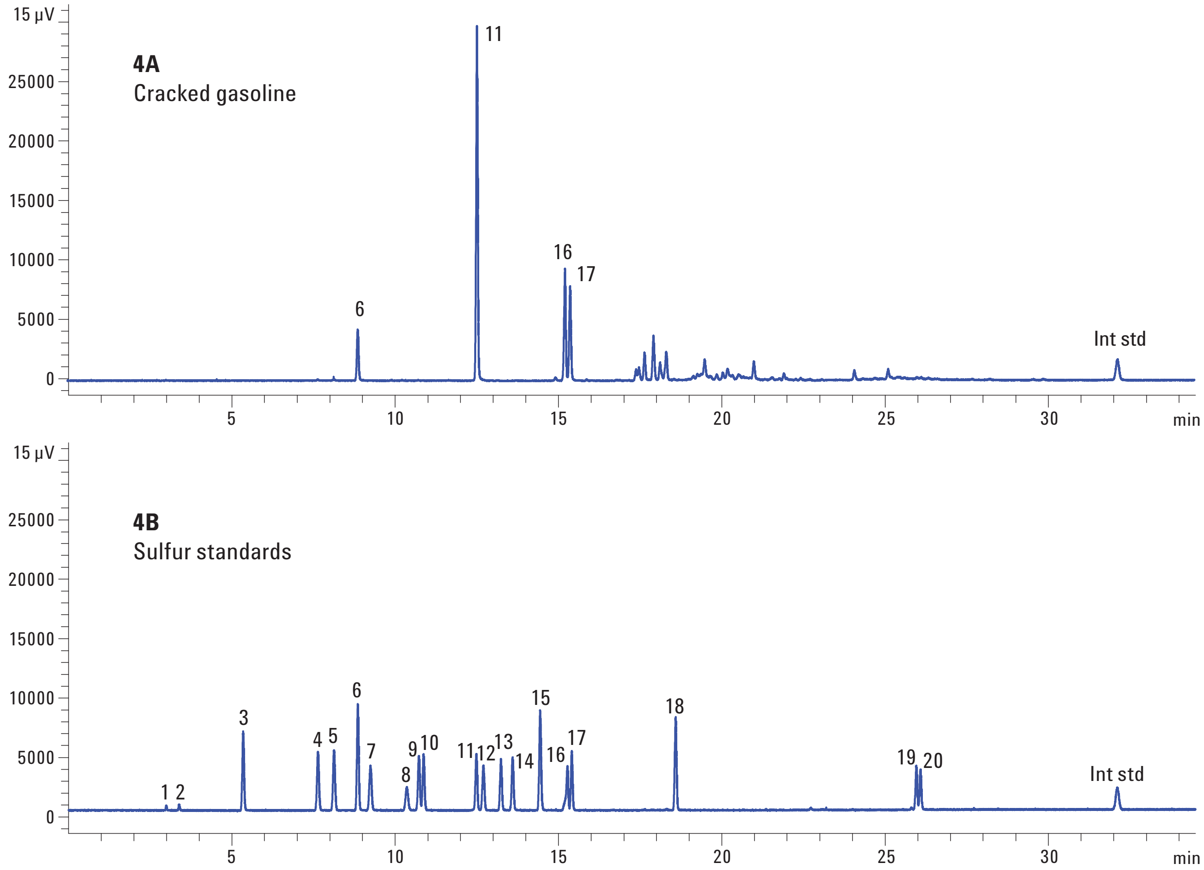

Figure 4. The chromatogram of a cracked gasoline sample that included more than about 63.5% aromatic hydrocarbons and 25% nonaromatic hydrocarbons (above). Chromatogram of sulfur standards at 5 ppm (below).

Conclusions

The Agilent J&W DB-Sulfur SCD column was evaluated for petroleum fraction analysis with GC/SCD detection. The results show that the column provided good resolution and symmetrical peak shape for about 20 sulfur compounds. In particular, hydrogen sulfide and carbonyl sulfide could be separated at ambient temperature without cryogenic cooling. Good linearity and repeatability were achieved for all targeted compounds. The combination of an Inert Flow path, the DB-Sulfur SCD column and a sulfur chemiluminescence detector ensures accurate quantitative and qualitative analysis of volatile sulfur compounds in petroleum samples.

References

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Printed in the USA
September 5, 2013
5991-3108EN

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