Detection of Sulfur Compounds in Natural Gas According to ASTM D5504 with Agilent's Dual Plasma Sulfur Chemiluminescence Detector (G6603A) on the 7890A Gas Chromatograph

Application

Hydrocarbon Processing

Authors

Wenmin Liu
Agilent Technologies Co. Ltd.
412 Ying Lun Road
Waigaoqiao Free Trade Zone
Shanghai, 200131
China

Mario Morales
Agilent Technologies, Inc.
2850 Centerville Road
Wilmington, DE 19808
USA

Abstract

An Agilent dual plasma sulfur chemiluminescence detector (DP SCD) combined with an online dilutor was used for the analysis of sulfur compounds. By using this method, the detection limits of the sulfur compounds achieved the ppb level. The stability of the DP SCD was also investigated. The long-term and short-term stability show that the performance of DP SCD is stable, and no hydrocarbon interference was found during the analysis of natural gas samples.

Introduction

Many sources of natural gas and petroleum gases contain varying amounts and types of sulfur compounds. The analysis of gaseous sulfur compounds is difficult because they are polar, reactive, and present at trace levels. Sulfur compounds pose problems both in sampling and analysis. Analysis of sulfur compounds many times requires special treatment to sample pathways to ensure inertness to the reactive sulfur species. Sampling must be done using containers proven to be nonreactive. Laboratory equipment must also be inert and well conditioned to ensure reliable results. Frequent calibration using stable standards is required in sulfur analysis [1].

GC SCD configuration with inert plumbing is one of the best methods to detect sulfur compounds in different hydrocarbon matrices. Sulfur compounds elute from the gas chromatographic column and are combusted within the SCD burner. These combustion products are transferred to the SCD detector box via vacuum to a reaction cell for ozone mixing. This detection technique provides a highly sensitive, selective, and linear response to volatile sulfur compounds.

Agilent Technologies DP technology is the detector of choice for sulfur analysis when dealing with a hydrocarbon matrix. The burner easily mounts on the 6890 and 7890A GCs and incorporates features for easier and less frequent maintenance. In this application, the Agilent 355 DP SCD was used to analyze the gaseous sulfur compounds in natural gas. Detection limits, stability and linearity were investigated.

Experimental

An Agilent 7890A GC configured with a split/splitless inlet (Sulfinert-treated), and an Agilent 355 DP SCD were used. Sample introduction was through a six-port Hastelloy C gas sample valve (GSV) interfaced directly to the sulfur-treated inlet with Sulfinert tubing. An online dilutor was used for preparation of ppb-level sulfur compounds in different matrices. Two four-port valves were used — one for sample introduction and one for static sample injection. The valves were installed sequentially prior to the GSV. Figure 1 illustrates the configuration of the gas blending system and GC SCD.

The sulfur standards were blended in helium at 1 ppm (V/V) and were purchased from Praxair, Inc. (Geismar, LA). See Table 1 for component details.

Table 1. Sulfur Standards in Helium

1.	Hydrogen sulfide	H_2S
2.	Carbonyl sulfide	COS
3.	Methyl mercaptan	CH_3SH
4.	Ethyl mercaptan	CH_4CH_3SH
5.	Dimethyl sulfide	CH_3SCH_3
6.	Carbon disulfide	CS_2
7.	2-propanethiol	$CH_3SHC_2H_5$
8.	Tert-butyl mercaptan	$(CH_3)_3CSH$
9.	1-propanethiol	$CH_3(CH_2)_2SH$
10.	Thiophene	C_4H_4S
11.	n-butanethiol	$CH_3(CH_2)_3SH$
12.	Diethyl sulfide	$CH_3CH_2SCH_2CH_3$
13.	Methyl ethyl sulfide	$CH_3SCH_2CH_3$
14.	2-methyl-1-propanethiol	$(CH_3)_2CHCH_2SH$
15.	1-methyl-1-propanethiol	$CH_3CH_2CHSHCH_3$

Experimental Conditions

GC Conditions

Front Inlet	Split/splitless (Sulfinert-treated capillary inlet system)
Heater	150 °C
Pressure	14.5 psi
Septum purge flow	3 mL/min
Mode	Splitless
Gas saver	20 mL/min after 2 min
Sample loop	1 mL
Oven	30 °C (1.5 min), 15 °C/min 200 °C (3 min)
Column	HP-1 60 m × 0.53 mm × 5 µm
Injection mode	Static flow and dynamic flow modes

SCD Conditions

Burner temperature	800 °C
Vacuum of burner	372 torr
Vacuum of reaction cell	5 torr
H_2	40 mL/min
Air	53 mL/min

Results and Discussion

From the comparative results of the sulfur detectors' sensitivity, it could be seen that SCD is the best detector for sulfur components, especially at low levels [3]. The Agilent DP technology is the most sensitive and selective detector for sulfur-containing gaseous hydrocarbon samples.

Figure 2 is the chromatogram of low-level sulfur compounds at 1.35 ppb (H_2S), which is prepared by the point-of-use gas blending system. Table 2 is the calculated signal to noise (S/N) of each compound, from the achieved data. It can be seen that DP SCD can detect low-level sulfur compounds.

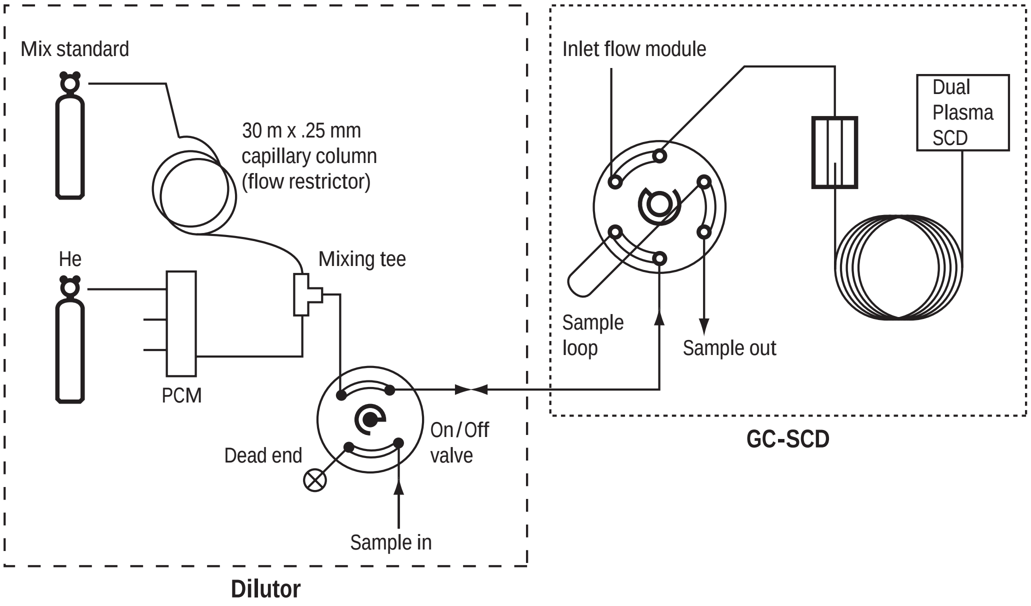

Figure 1. Diagram of online dilutor GC-DP SCD.

Table 2. S/N of Each Sulfur Component at 1.35 ppb (Refer to Table 1 for peak identification.)

Peak No.	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15
S/N	12.0	5.0	2.1	2.6	4.9	11.5	4.0	2.7	3.7	9.1	7.6	2.3	5.7	1.0	1.1

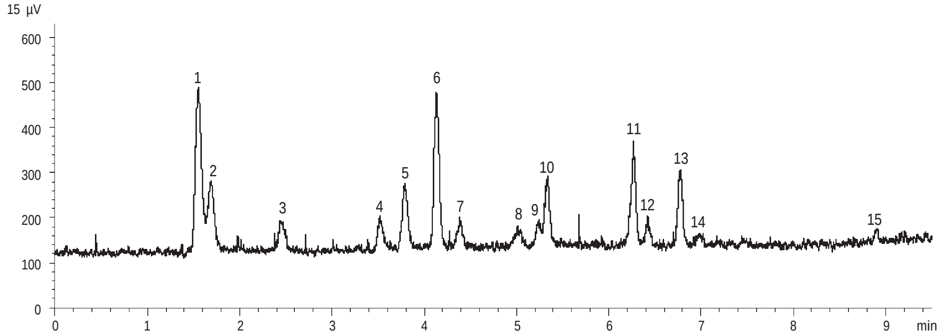

Figure 2. Chromatogram of sulfur compounds in helium at 1.35 ppb. (Refer to Table 1 for peak identification.)

Because the low-level sulfur components were prepared by the online dilutor system, which was prepared by adjusting the aux EPC to get appropriate diluent flow, high diluent flow could have the potential to cause high pressure in the sample loop, which results in the amount of the sample in the loop being different when the diluent flow changes from low to high. In this application, two sample injection modes, static and dynamic, were investigated. The mode is actuated by the on/off valve installed prior to GSV. When using static injection mode, the valve is switched to the off position, the pressure in the sample loop balances to ambient pressure, and then the sample is injected into the GC.

Table 3 shows the linear ranges of the two injection modes. The two injection modes have no difference from a linearity perspective, which means that the two injection modes are both suitable when using the 1-mL sample loop. The 1-mL sample loop's resistance is not high enough to cause variation in the sample injection amount.

Table 3 Linear Ranges of Two Injection Modes (Refer to Table 1 for peak identification.)

	1	2	3	4	5	6	7	8
Linear range (ppb)				**6.24-544.5**				
Static mode	1	0.99996	0.99995	0.99999	0.99996	0.99999	0.99996	0.99999
Dynamic mode	1	0.99996	0.99997	0.99997	0.99996	0.99999	0.99998	0.99998
	9	**10**	**11**	**12**	**13**	**14**	**15**	
Linear range (ppb)				**6.24-544.5**				
Static mode	0.99995	0.99994	0.99996	0.99996	0.99996	0.99998	0.99998	
Dynamic mode	0.99998	0.99997	0.99998	0.99998	0.99998	1	0.99998	

Table 4 shows the long-term (72 hours) and short-term (8 hours) stability of the SCD at different concentration levels.

In an effort to investigate the coelution of hydrocarbon and sulfur, the same sulfur standards in natural gas were analyzed on the SCD. Figure 3 shows the chromatogram; no quenching was found.

Table 4 The Long-Term and Short-Term Stability of SCD (Refer to Table 1 for peak identification.)

	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15
20.79 ppb S.T. RSD (%)	2.7	2.6	2.9	3.0	0.9	1.4	2.8	4.0	2.6	1.7	1.7	3.3	3.2	8.6	7.9
L.T. RSD (%)	3.0	2.7	2.4	2.5	1.4	1.5	2.6	4.3	3.8	2.7	2.0	4.9	3.2	7.9	6.9
1.38 ppb S.T. RSD (%)	6.6	10.1	11.7	22.8	30.4	4.1	6.9	18.7	10.7	25.1	5.1	11.1	5.8	29.6	24.1
L.T. RSD (%)	14.4	7.5	16.3	20.8	21.7	4.6	6.1	27.7	23.7	25.3	12.2	24.6	6.1	35.7	38.4

ST: Short term (8 hours); LT: Long term (72 hours)

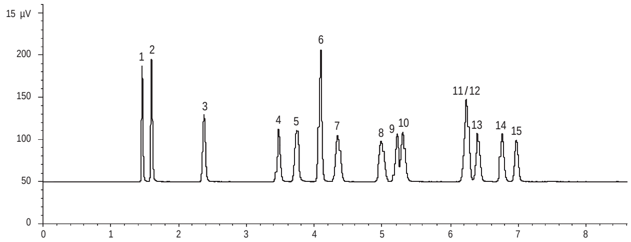

Figure 3. **Chromatogram of sulfurs in natural gas. (Refer to Table 1 for peak identification.)**

Natural Gas Sample Analysis

Three natural gas samples were analyzed by using the GC DP SCD system. Because the concentration of the target compounds is at ppm level, split mode was used and the method was recalibrated at ppm level. Table 5 shows the result of the three gas samples.

Table 5. **Result of the Three Real Samples**

Samples		H_2S	COS	Methyl Mercaptan
BLEND AL	Conc. (ppm, v/v)	2.3	2.0	2.0
	RSD (%, n = 5)	2.3	0.3	1.4
BLEND 6	Conc. (ppm, v/v)	27.1	21.9	17.3
	RSD (%, n = 5)	1.2	0.4	2.3
BLEND 12	Conc. (ppm, v/v)	15.0	9.2	10.1
	RSD (%, n = 5)	0.7	0.6	0.6
Standard	Conc. (ppm, v/v)	2.0	0.8	0.9
natural gas	RSD (%, n = 5)	1.7	2.5	1.7

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Conclusions

An online dilutor combined with a GC DP SCD is suitable for gaseous sulfur components analysis, especially for the low-level components. The online dilutor offers an automatable means of system calibration and the detection limits for the trace sulfur detection are down to ppb level. By using an on/off valve prior to the GSV, both the static and dynamic injection modes of the sample gas blending system can be used. The static injection mode is important when a small sample loop with a large resistance is used. The diluter system with GC/SCD is available as an Agilent SP1, please refer to SP1 7890-0375 for order information.

References

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