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Application News

No. G306A

Gas Chromatography

Analysis of Sulfur Compounds in Natural Gas by Nexis™ SCD-2030 According to ASTM D5504

Varying types and amounts of sulfur-containing compounds are present in gaseous hydrocarbon streams. They contribute to the corrosion of facilities and the inhibition of catalytic reactions, leading to the deterioration of product quality.

For these reasons, identifying and quantifying various sulfur compounds then becomes a fundamental requirement in the petrochemical industry from the viewpoints of quality control, safety, and manufacturing process evaluation of products.

In this document, we analyzed sulfur-containing compounds contained in natural gas samples in accordance with ASTM D5504 using gas chromatography with a sulfur chemiluminescence detector (SCD).

The Nexis SCD-2030 provides high selectivity and linearity for sulfur-containing compounds and minimizes the quenching effects of hydrocarbons.

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Reagent Information

Three kinds of gaseous samples were prepared in different cylinders as follows:

- Gas ① 14 discrete sulfur compounds diluted in helium at 1ppm(V/V)
- Gas ② Nitrogen
- Gas ③ Natural Gas Standard

A 200 mL gas syringe purchased from GL Science was used for diluting and introducing gases.

Table 1 illustrates the detailed composition of these cylinders.

Table 1 Composition of Various Gases Used in Analysis

Gas ① 14 Sulfur Compounds Gas Mixture		
Index	Components	Concentration
Balance	Nitrogen	99.999 %
1	Hydrogen sulfide	0.93 ppm
2	Carbonyl sulfide	0.96 ppm
3	Methyl mercaptan	0.99 ppm
4	Ethyl mercaptan	0.98 ppm
5	Dimethyl sulfide	1.00 ppm
6	Carbon disulfide	1.02 ppm
7	2-Propanethiol	0.95 ppm
8	t-Butanethiol	1.09 ppm
9	1-Propanethiol	1.00 ppm
10	Methyl ethyl sulfide	0.98 ppm
11	Thiophene	1.02 ppm
12	Diethyl sulfide	0.99 ppm
13	n-Butanethiol	0.95 ppm
14	Dimethyl disulfide	0.97 ppm

Gas ② Nitrogen		
Index	Components	Concentration
Balance	Nitrogen	99.9995 %

Gas ③ Natural Gas Standard		
Index	Components	Concentration
Balance	Methane	86.595 %
1	Nitrogen	0.10 %
2	Carbon dioxide	0.30 %
3	Ethane	8.50 %
4	Propane	3.50 %
5	n-Hexane	0.05 %
6	Isopentane	0.05 %
7	n-Pentane	0.05 %
8	Isobutane	0.40 %
9	n-Butane	0.40 %
10	Oxygen	0.06 %

The following document approximately states that the concentration of sulfur compounds in ① is 1 ppm.

Analysis Method

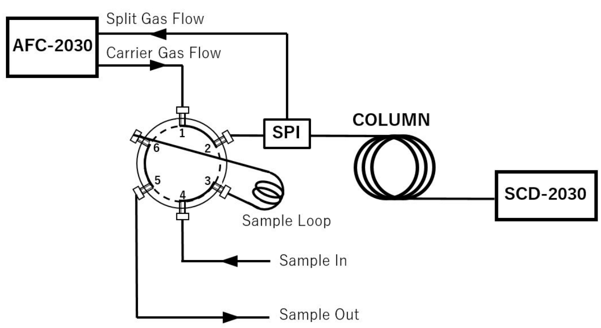

Fig. 1 Schematic of Instrument Configuration

In all evaluations, we used a system configured with a splitter injector (SPI) as a split/splitless vaporization unit. The temperature of the SPI can be controlled independently. Sample introduction was performed via a 6-port gas sample valve interfaced to the SPI.

All sample-paths in the system, such as valves, gas-tubing, SPI, were Sulfinert® treated because volatile sulfur compounds can be highly reactive, absorptive, and adsorptive.

Fig. 1 illustrates a schematic of the instrument configuration.

Table 2 illustrates the details of the analysis method.

Table 2 Instrument Configuration and Analytical Conditions

Instrument Configuration:	
Main Unit	: Nexis GC-2030
Valve	: 6-port Valve (Restek)
Sample Loop Volume	: 1 mL
Injector	: SPI
Column	: SH-1 (60 m × 0.53 mm I.D. df=7 µm) *1
Post Column	: Deactivated Fused Silica Tubing (0.3 m × 0.32 mm)
Detector	: SCD-2030
Analytical Conditions:	
Injector Temp.	: 150 °C
Split Ratio	: 1:9 (10 % to column)
Carrier Gas	: He
Carrier Gas Control	: Constant Column Flow mode (6.0 ml/min)
Column Temp.	: 30 °C (1.5 min) - 10 °C /min - 200 °C (3 min)
SCD	
Interface Temp	: 200 °C
Furnace Temp	: 850 °C
H_2 flow rate	: 100 ml/min
N_2 flow rate	: 10 ml/min
O_2 flow rate	: 12 ml/min
O_3 flow rate	: 25 ml/min

*1 P/N: 227-36108-02

Linearity and Repeatability Evaluation

ASTM D5504 quantifies the amount of each individual sulfur compound using the external standard method so that the linear response for the sulfur compounds is a primary measurement in the SCD.

We evaluated the linearity of the Nexis SCD-2030 using samples prepared by mixing Gas ① with Gas ② to the following concentrations: 50 ppb, 100 ppb, 500 ppb, and 1 ppm(v/v). Fig. 2 illustrates chromatograms of 14 discrete sulfur compound samples. Table 3 illustrates the results of the coefficient of determination (R2) ranging from 50 ppb to 1 ppm and peak area repeatability at 1 ppm (%RSD, n = 5) of each of the sulfur compounds.

The Nexis SCD-2030 is configured with an industry-first horizontal redox cell, which promotes the complete oxidation-reduction reaction of samples by ensuring sufficient reaction area and reaction time in the cell to achieve stable analysis. Use of this configuration lead to excellent linear and stable response for sulfur compounds.

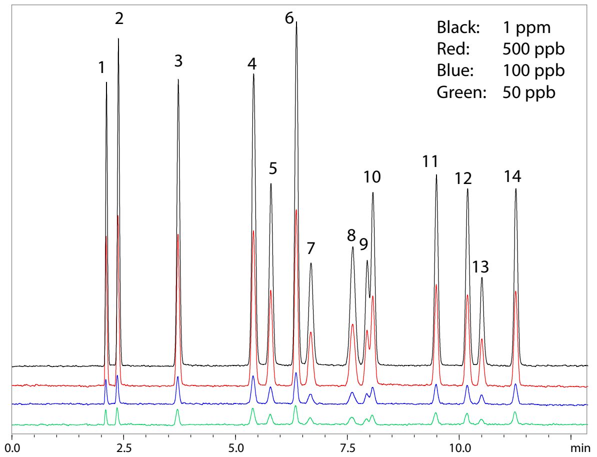

Fig. 2 Chromatograph of 14 Sulfur Compounds Mixture at 50 ppb, 100 ppb, 500 ppb, 1 ppm

Table 3 Linearity and Repeatability Results

Index	Components	Linearity (50 ppb, 100 ppb, 500 ppb, 1 ppm) R^2	Repeatability n=5 (1 ppm) Peak Area RSD%
1	Hydrogen sulfide	0.9999	1.09
2	Carbonyl sulfide	0.9999	0.35
3	Methyl mercaptan	0.9998	0.91
4	Ethyl mercaptan	1.0000	0.90
5	Dimethyl sulfide	0.9998	0.68
6	Carbon disulfide	1.0000	0.29
7	2-Propanethiol	0.9998	1.39
8	t-Butanethiol	0.9999	0.51
9	1-Propanethiol	0.9994	2.15
10	Methyl ethyl sulfide	0.9995	0.68
11	Thiophene	0.9998	1.06
12	Diethyl sulfide	0.9996	0.85
13	n-Butanethiol	0.9997	2.31
14	Dimethyldisulfide	0.9997	0.87

Selectivity Evaluation

A sulfur chemiluminescence detector can selectively detect sulfur compounds even during analysis of samples with high concentrations of hydrocarbons. Therefore, the ASTM D5504 specifies SCD users to evaluate selectivity and quenching effect of the SCD as a part of the system suitability test.

We used two mixtures of fourteen discrete sulfur compounds at 50 ppb in this evaluation — the Standard Sulfur Mixture and the Natural Gas Sulfur Mixture. The Standard Sulfur Mixture was prepared by diluting Gas ① with Gas ② to 50 ppb. The Natural Gas Sulfur Mixture was prepared by diluting Gas ① with Gas ③ to 50 ppb. Fig. 3 shows the chromatogram of Standard Sulfur Mixture, Natural Gas Sulfur Mixture, and Gas ③.

The black line is the chromatogram of the Standard Sulfur Mixture, which illustrates that all fourteen sulfur compounds can be detected in trace-level concentrations. The blue line is the chromatogram for Gas ③ and illustrates no response for all compounds contained in the sulfur-free natural gas. The chromatogram of the Natural Gas Sulfur Mixture, shown by the red line, revealed that all fourteen sulfur compounds were detected in the same manner as the Standard Sulfur Mixture. Therefore, the Nexis SCD-2030 can selectively detect sulfur compounds without being affected by the quenching of hydrocarbons.

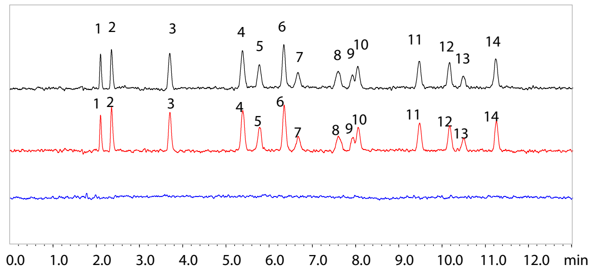

Fig. 3 Chromatogram Comparison of Standard Sulfur Mixture, Natural Gas Sulfur Mixture, and Gas ③

Black: 14 Discrete Sulfur Compounds In Nitrogen (50 ppb each)

Red: 14 Discrete Sulfur Compounds In Natural Gas (50 ppb each)

Blue: Sulfur-free Natural Gas Standard (Chromatogram baseline-shifted for comparison)

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First Edition: Mar. 2019
Revision A: Mar. 2023