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Analytical and Measuring Instruments

Overcoming Challenges of Sulfur Analysis in Natural Gas and Gaseous Fuels

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Introduction

Identification and quantification of sulfur in natural gas is a critical factor in assessing its quality, ensuring safety, determining the concentration of various additives, and ensuring process control during refining. Sulfur occurs naturally in natural gas and originates from the breakdown of organic material upon its burial and heating and is released along with hydrocarbons as a source rock matures. Sulfur compounds in raw gas typically need to be removed during processing, which is an energy intensive process. Thus, natural gas with high sulfur content, termed "sour gas", commands a lower market price than gas with low sulfur content, or "sweet gas".

The primary reason to determine the sulfur content and speciation within a natural gas sample is to assess its value and determine the best workflow for processing. Many sulfur compounds are corrosive to metals in pipelines and processing plants, causing excess wear and necessitating replacement of pipes, valves, and fittings. Furthermore, sulfur compounds readily poison costly precious-metal catalysts that are used in the refining process, rendering them inefficient or useless.

From a safety and environmental standpoint, understanding sulfur concentrations within a gaseous sample is essential. Certain compounds, such as H_2S, are toxic to humans; at concentrations in the range of ~100 ppm or more, H_2S can be fatal in a short amount of time. Another major goal of sulfur removal is to meet increasingly stringent environmental regulations. When natural gas is burned as a fuel, sulfur compounds are oxidized and expelled into the atmosphere, where they combine with water to form dilute sulfuric acid, or acid rain.

Whether analyzing sulfur for unwanted compounds or for additives such as odorants, understanding its speciation and concentration is important for ensuring efficient processing, providing for the safety of refiners and users, and complying with environmental regulations

Despite the efforts to remove sulfur from natural gas, various sulfur compounds are often added into the product before delivery. As these compounds have a distinct odor at low concentrations, they serve to alert consumers to the presence of a gas leak. Whether analyzing sulfur for unwanted compounds or for additives such as odorants, understanding its speciation and concentration is important for ensuring efficient processing, providing for the safety of refiners and users, and complying with environmental regulations.

GC-SCD for Analysis

There are a variety of methods for analysis of sulfur in natural gas and petrochemicals, but perhaps none more powerful than gas chromatography with sulfur chemiluminescence detection, or GC-SCD. This technology couples the power of a GC to separate sulfur compounds from the matrix of a sample and an SCD for highly selective and sensitive detection of sulfur. A variety of approved test methods exist that specify the use of GC-SCD, including ASTM D5504, D5623, and D7011.

A sulfur chemiluminescence detector operates by detecting photons emitted by excited forms of SO_2 as the molecules relax and electrons fall into a ground state. However, the process to get from sample to detection is complex (Fig. 1). After the sample is injected into the GC, its constituents are separated on the GC column as they would be for any routine analysis. As the sulfur compounds elute off the column, they enter the SCD where they are first oxidized at high temperatures in the presence of oxygen to form SO_2, then reduced in the presence of hydrogen to SO. These processes of oxidation and reduction are commonly termed "redox" processes or reactions. Following that, the reduced species travels to a reaction cell, where they are reacted with ozone (O_3) to form an excited state of SO_2, dubbed SO_2*.

As this excited SO_2* compound loses energy and electrons relax into their stable configuration, a photon of characteristic wavelength is emitted. These photons pass through a wavelength filter and are detected by a photomultiplier tube (PMT), in which they are converted into an electrical signal and fed into a data system to form the peaks that chromatographers are accustomed to.

The selectivity for sulfur in an SCD relies on the fact that non-sulfur compounds either "burn off", pass through the SCD without reacting, or generate a photon that cannot pass through the wavelength filter on the PMT. Regardless of the reason, these compounds remain undetected and do not generate a signal.

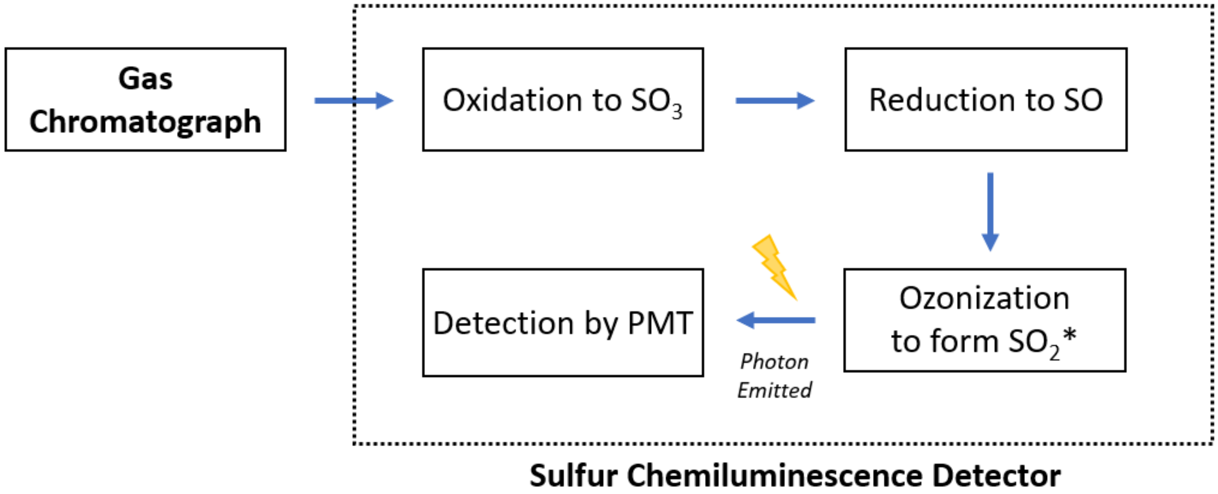

Figure 1: A simplified schematic of the operation of a sulfur chemiluminescence detector.

Challenges with GC-SCD

Historically, there have been challenges associated with GC-SCD analyses. Though easy on paper, the number and complexity of components and processes can lead to erroneous analyses or difficulty in operation and maintenance. Operators of these instruments commonly report poor selectivity for sulfur, with high baseline levels or errant peaks generated as a result of high carrier gas flow and/or the sample matrix itself. Furthermore, incomplete or inefficient redox processes, particularly on high boiling point sulfur compounds, yield differing responses between compounds, despite their sulfur equimolarity. Worse yet, some users have simply found little or no sensitivity to sulfur compounds at all. Additionally, there are well-known difficulties associated with operation and maintenance from ideally conditioning the detector and the pump to cleaning or replacing fragile tubes within the redox cell. For these reasons and others, GC analysts have either avoided harnessing the capabilities of SCDs or merely tolerated their traditional inconveniences.

Though easy on paper, the number and complexity of components and processes can lead to erroneous analyses or difficulty in operation and maintenance of GC-SCDs

Reimagining the SCD

To combat many of the pitfalls and challenges associated with conventional GC-SCD analysis, Shimadzu has reimagined the traditional design of the SCD, creating the Nexis SCD-2030. From the bench-top up, it has been reconfigured compared to traditional designs, including features that make the instrument more sensitive, more selective, more robust, and easier to use.

The Nexis SCD-2030 features the industry's largest redox cell, ensuring complete oxidation and reduction reactions, yielding excellent sensitivity in the low ppb range, even for difficult to oxidize, high boiling-point compounds. Ensuring complete oxidation and reduction not only enhances sensitivity, it also ensures that the responses are equivalent for equimolar compounds, regardless of the boiling point or reactivity of the sulfur-bearing compounds. It also guarantees that there are not incomplete reactions or radicals formed that can generate false or interfering peaks, even when operating at carrier flows as high as 20 mL/minute. Lastly, orienting the redox cell horizontally ensured the shortest possible transfer line between it and the ozone reaction cell, reducing dispersion and minimizing additional reactions before the reaction cell, increasing sensitivity. With its new design and features, the SCD-2030 enables quick, easy, and reliable sulfur-specific detection for gas chromatographs.

Case study using ASTM D5504 – Analysis of Sulfur in Natural Gas and Gaseous Fuels by GC-SCD

One of the most common methods for assessing sulfur concentration and speciation within a gaseous sample is ASTM D5504, entitled *Standard Test Method for Sulfur Compounds in Natural Gas and Gaseous Fuels by Gas Chromatography and Chemiluminescence*. This test method addresses the determination of sulfur compounds in high-methane gases and fuels and has also been applied to refinery, landfill, cogeneration, and sewage digester gas. Here, we will outline the results of our assessment of this method with Shimadzu's Nexis GC-2030 gas chromatograph with the SCD-2030 detector.

Reagents

We prepared three gases in sampling cylinders:

1. Nitrogen containing a mixture of 14 sulfur compounds at 1 ppm (v/v)
2. Nitrogen (99.9995%) – diluent gas
3. Sulfur-free natural gas standard

A 200 mL gas syringe from GL Sciences was used for dilution and injection of these gases. Their composition is outlined in Table 1.

Table 1: Composition of Gases Used in Analysis

1) Nitrogen w/ 14 sulfur compounds		
	Component	***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

2) Nitrogen		
	Component	***Concentration***
Balance	Nitrogen	99.9995%

3) Natural Gas Standard		
	Component	***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%

Analytical Conditions

In all evaluations, we used a Shimadzu Nexis GC-2030 configured with a splitter injector (SPI) as a split/splitless vaporization. The temperature of the SPI can be controlled independently, and samples were introduced through a 6-port gas sampling valve on the SPI.

All of the sample-wetted portions of the flowpath, including valves, the gas tubing, and the SPI, were treated with Sulfinert® to minimize their reactivity with volatile sulfur compounds. Figure 2 illustrates the schematic of the instrument used. Table 2 outlines the details of the analytical method.

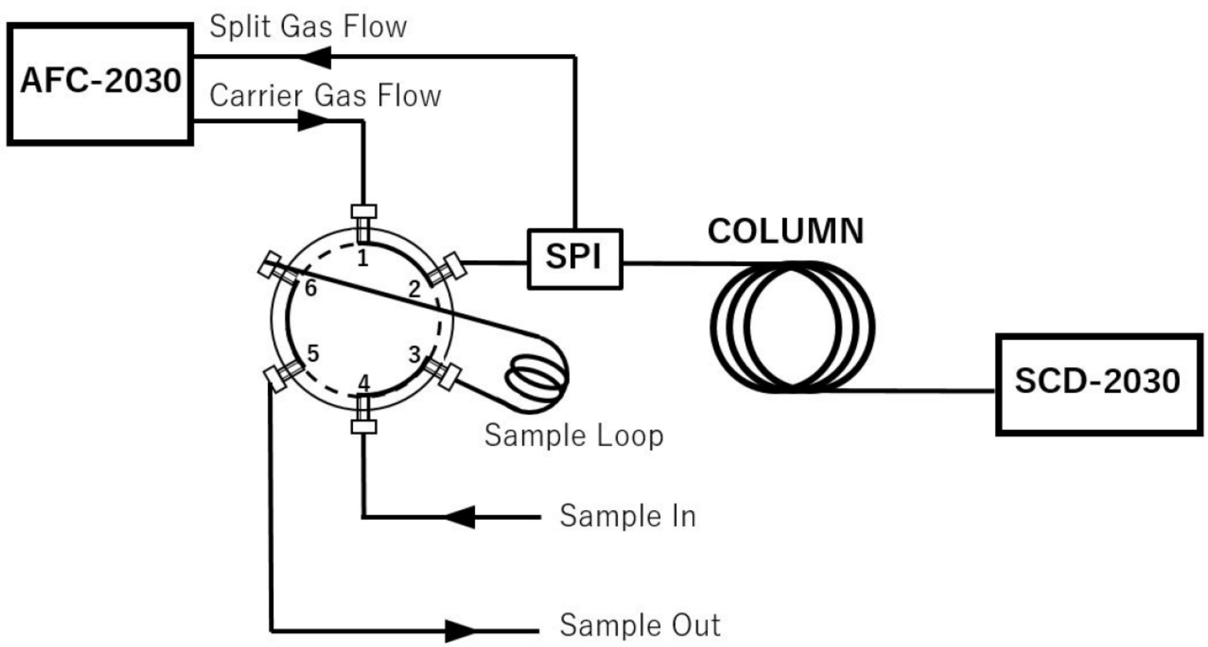

Figure 2: Schematic of instrument configuration.

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-Rtx®-1 (60 m × 0.53 I.D. df = 7 µm)
Post-column	Deactivated fused silica tubing (0.3 m × 0.32 mm)
Detector	SCD-2030
GC Conditions	
Injector Temp.	150° C
Split Ratio	1:9 (10% to column)
Carrier Gas	He
Carrier Gas Control	Constant Column Flow (6.0 mL/min)
Column Temp.	30° C (1.5 min hold) ramped at 10 C/min to 200 C (3 min hold)
SCD Conditions	
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

Linearity and Repeatability

A key metric of compliance with ASTM D5504 is ensuring appropriate linearity of signal response on the detector and repeatability of results of multiple analyses. To assess both linearity and repeatability, we blended the nitrogen with 14 sulfur compounds (gas 1) with the blank nitrogen (gas 2) to generate gas standards at the following concentrations: 50 ppb, 100 ppb, 500 ppb, and 1000 ppb (v/v).

Figure 3 is a series of stacked chromatograms of the standards and Table 3 outlines the results of the assessment. For all compounds, the r^2 value of the calibration curves is ≥0.9994 and the peak area %RSD is ≤2.31 (n = 5), with most ≤1.09 %RSD.

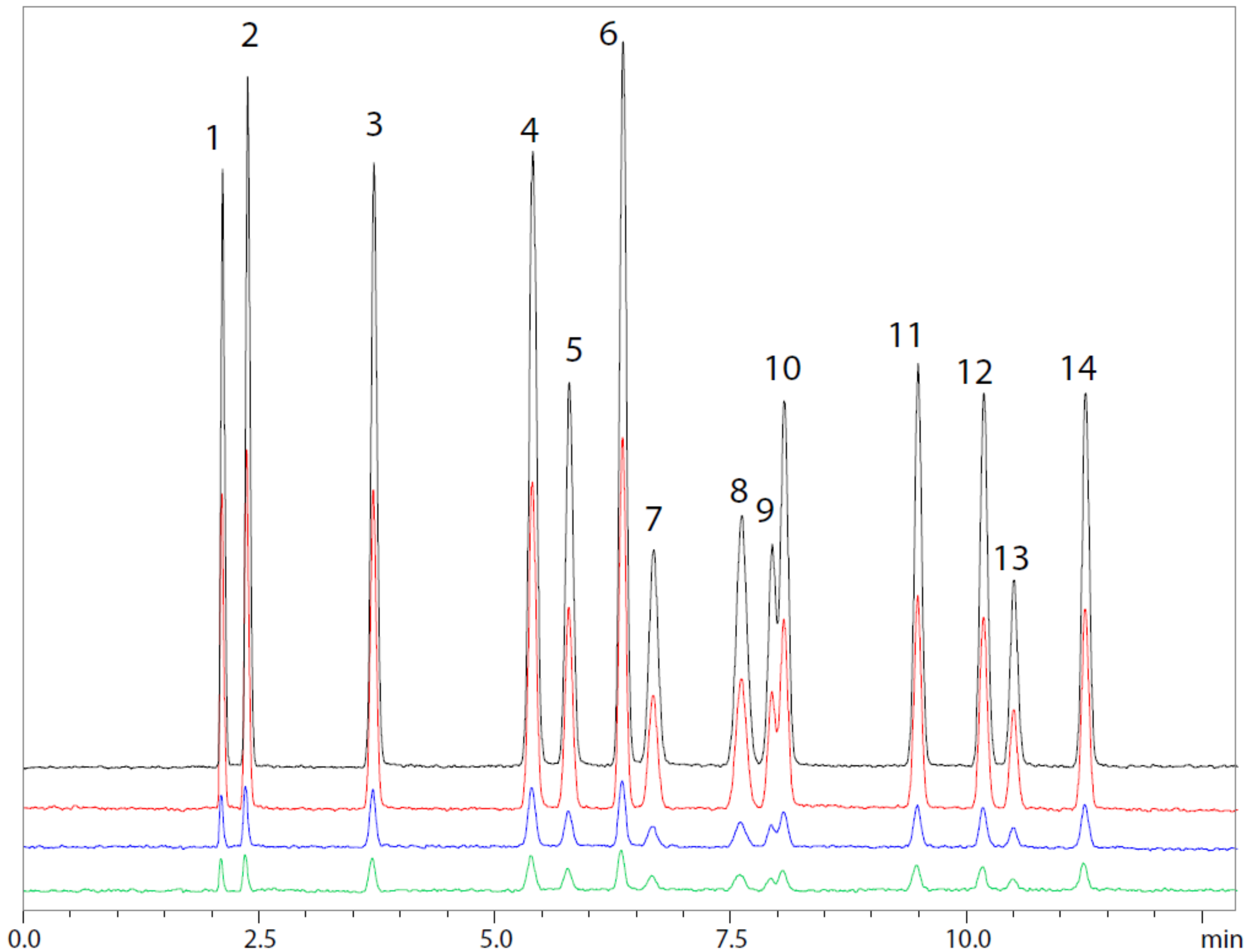

Figure 3: Stacked chromatograms of the calibration curve standards. Green = 50 ppb sulfur (v/v), Blue = 100 ppb, Red = 500 ppb, and Black = 1000 ppb. Note that the baselines have been shifted for comparative purposes.

Table 3: Linearity and Repeatability Results

	Component	**Linearity (r^2)***	**Repeatability (%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	Dimethyl disulfide	0.9997	0.87

*Linearity of 4-point calibration curve (50 ppb, 100 ppb, 500 ppb, 1000 ppb)
**%RSD of 1 ppm standard (n = 5)

Selectivity
The other crucial aspect of sulfur chemiluminescence detection is selectivity, that is that the detector does not exhibit response for non-sulfur compounds and that the detector does not lose sensitivity due to matrix effects, such as quenching often seen in hydrocarbon matrices on flame photometric detectors (FPD).

To assess the selectivity of the SCD-2030 for sulfur and only sulfur, we prepared two gases at 50 ppb (v/v) of the 14 sulfur compounds by mixing the standard gas (Table 1, gas 1) with high purity nitrogen (gas 2) to produce a sample of 50 ppb of the sulfur compounds in nitrogen and the standard gas with the blank natural gas (gas 3) to produce 50 ppb of the sulfur compounds in natural gas.

The results of this selectivity evaluation are shown in Figure 4. The black chromatogram of sulfur compounds in nitrogen demonstrate the separations and detection ability of the GC-2030 with the SCD-2030 and the blue line shows that no sulfur compounds are detected within the blank natural gas matrix. The analysis of the natural gas sample spiked with sulfur compounds, shown in red, demonstrates the same separation, resolution, and response as those in the nitrogen matrix. This shows that the SCD is not generating any errant peaks unrelated to sulfur compounds and that the detector does not suffer from matrix quenching when analyzing hydrocarbon-based samples.

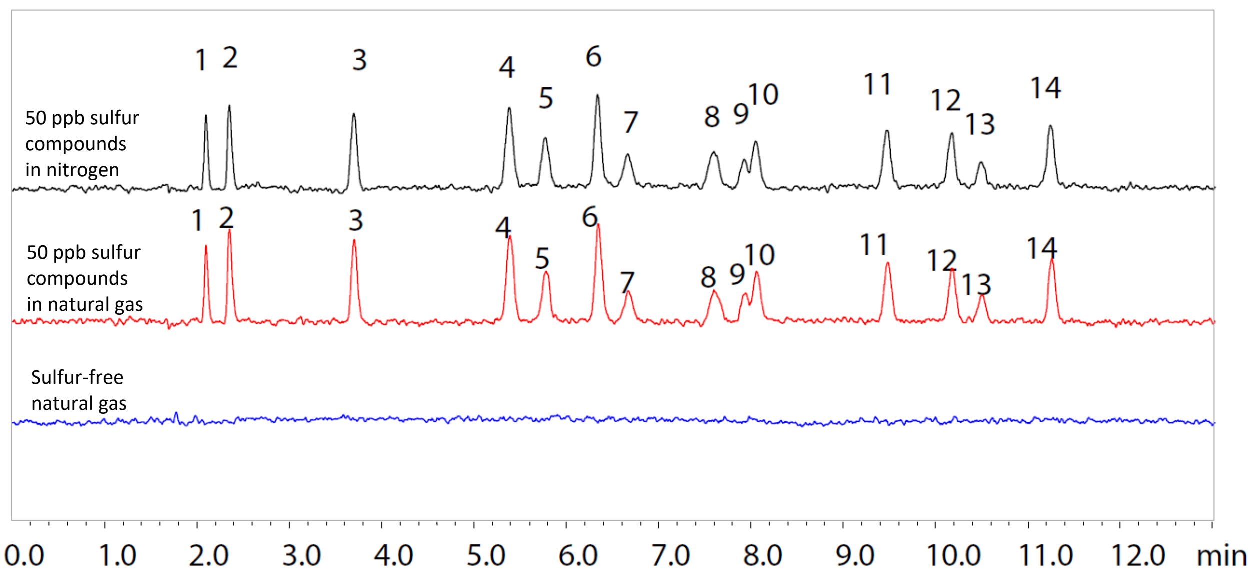

Figure 4: Stacked chromatograms showing the SCD-2030 response for a 50 ppb mix of sulfur compounds in nitrogen (black), in natural gas (red), and a blank, sulfur-free natural gas standard (blue). Note that the baselines have been shifted for comparative purposes.

Conclusions

Sulfur compounds are a natural component of natural gas, crude oil, and associated hydrocarbons. Understanding the speciation and concentration of sulfur within natural gas and gaseous samples is a critical aspect of quality and process control as well as for conforming with safety and environmental regulations.

Sulfur chemiluminescence detection coupled with gas chromatography is one of the most powerful techniques available for these sorts of analyses. However, SCDs have historically been known for their temperamental nature and difficulty of operation.

With the advent of a new design and modernized software functionality that enhances automation, Shimadzu's Nexis SCD-2030 overcomes many of the traditional difficulties with GC-SCD analysis

With the advent of a new design and modernized software functionality that enhances automation, Shimadzu's Nexis SCD-2030 overcomes many of the traditional difficulties with GC-SCD analysis, such as poor sensitivity and selectivity for sulfur, unequal responses between equimolar compounds, and difficulty in operation and maintenance. The SCD-2030 is the next industry standard for sulfur-specific detection for gas chromatography.

The data outlined here demonstrate the compliance of the Nexis GC-2030 with the SCD-2030 with ASTM D5504, a commonly-used method for sulfur analysis within the energy, petrochemical, and gas processing industries. With its compliance to D5504 and other ASTM methods, such as ASTM D5623 and D7011, the GC-2030 with SCD-2030 can meet a variety of petrochemical laboratory demands.

We invite you to learn more about Shimadzu's entire range of energy and petrochemical solutions at www.RefineYourLab.com.

■ References and Comments

- ASTM D5504-12, Standard Test Method for Determination of Sulfur Compounds in Natural Gas and Gaseous Fuels by Gas Chromatography and Chemiluminescence, ASTM International, West Conshohocken, PA, 2012, www.astm.org
- ASTM D5623-19, Standard Test Method for Sulfur Compounds in Light Petroleum Liquids by Gas Chromatography and Sulfur Selective Detection, ASTM International, West Conshohocken, PA, 2019, www.astm.org
- ASTM D7011-15(2019), Standard Test Method for Determination of Trace Thiophene in Refined Benzene by Gas Chromatography and Sulfur Selective Detection, ASTM International, West Conshohocken, PA, 2019, www.astm.org

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