

GC-SCD Analysis of Fuels and Petrochemicals

Application Notebook



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There is perhaps no technique more specific, selective, and sensitive for analysis of sulfur compounds than gas chromatography with sulfur chemiluminescence detection (GC-SCD). As an analytical technique, GC-SCD couples the separations capability of conventional GC with a highly specific detector for sulfur and sulfur species, enabling ppb-level detection of sulfur in a variety of sample matrices.

Many of the common applications of GC-SCD are directed towards the energy, fuels, and petrochemicals industries. Sulfur and sulfur compounds are naturally occurring components in crude oil and natural gas that make their way into processing and refining streams. Accurate and reliable analysis of these compounds is necessary to ensure process efficiency, minimize catalyst poisoning, and to comply with environmental regulations and product specifications.

This application notebook provides an overview of the energy, fuels, and petrochemical applications for which Shimadzu has tested its Nexis™ GC-2030 coupled with its innovative SCD-2030.

Application Notebook

- Determination of Sulfur Compounds in Light Hydrocarbon Liquids (ASTM D5623)
- Reliable Analysis of Sulfur Compounds in Diesel Fuel
- Analysis of Sulfur Compounds in Natural Gas (ASTM D5504)
- Analysis of Trace Thiophene in Benzene using Helium Carrier Gas (ASTM D7011)
- Analysis of Trace Thiophene in Benzene using Nitrogen Carrier Gas (ASTM D7011)
- Analysis of Dibenzyl Disulfide and Total Sulfur in Transformer Insulating Oil
- Comparison of Sensitivity for Sulfur Species: Demonstrating Equimolarity on the SCD-2030



Application News

No. G305

Gas Chromatography

Performance Assessment of Nexis™ SCD-2030 Using Sulfur Compounds Recommended by ASTM D5623

ASTM D5623 provides guidelines for the analysis of sulfur-containing compounds in light petroleum liquids by gas chromatography with a sulfur chemiluminescence detector (SCD). ASTM D5623 applies to petroleum products with a final boiling point of less than 230 °C at standard atmospheric pressure, such as gasoline.

The SCD provides high selectivity and linearity for sulfur-containing compounds and minimizes the quenching effects of hydrocarbons during sample analysis of complex hydrocarbon matrices.

This document introduces the results of using Nexis SCD-2030 to analyze sulfur compounds standards recommended by ASTM D5623.

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Fig. 1 Nexis™ SCD-2030

Analytical Conditions

Table 1 shows instrument configuration details and analytical conditions used for all evaluations.

In order to prevent adsorption of sulfur compounds at low concentrations, a sample vaporization injector SPL-2030 (P/N: S221-77100-61/-64) was subjected to a deactivation treatment and installed on the system.

LabSolutions GC was used for instrument control and data collection.

Table 1 Instrument Configuration and Analytical Conditions

Main Unit	: Nexis GC-2030 /AOC-20i plus
Column	: SH-Rxi™-1MS (30 m × 0.32 mm I.D. df= 4 μm)
Detector	: SCD-2030
Injection Volume	: 1 μL
Injection Mode	: Split
Split Ratio	: 1:9
Injection Unit Temp	: 275 °C
Carrier Gas	: He
Carrier Gas Control	: Constant Column Flow Mode (2.8 mL/min)
Column Temp.	: 40 °C (3 min) - 10 °C/min - 250 °C (16 min)
Interface Temp.	: 200 °C
Furnace Temp.	: 850 °C
Detector Gas	: H ₂ 100 mL/min, N ₂ 10 mL/min, O ₂ 25 mL/min

Analysis of Sulfur Calibration Standard

Nineteen discrete sulfur compounds recommended by ASTM D5623 were separated into two groups for optimal chromatogram separation. Ten out of the nineteen compounds were diluted in n-hexane to yield standard 1 (STD1) and the remaining nine sulfur compounds were diluted in toluene to yield standard 2 (STD2). Diphenyl sulfide was added to each STD at a concentration of 1 ppm(w/w) as an internal standard. Chromatograms of the STD1 and STD2 are shown in Fig. 2.

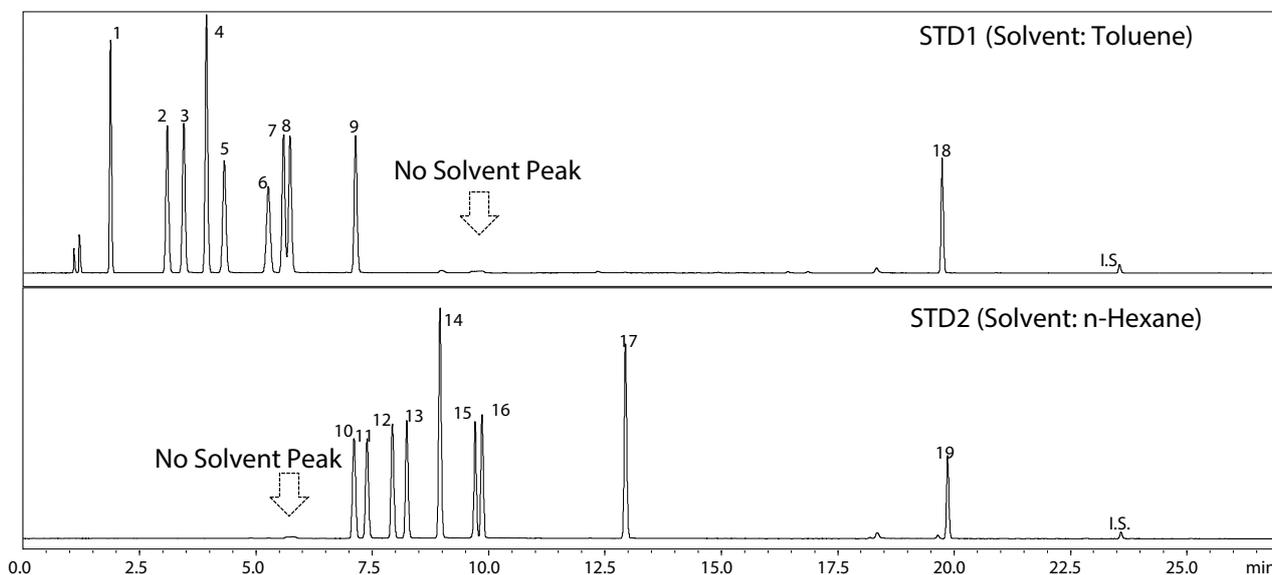


Fig. 2 Chromatograms of 19 Sulfur Compounds (10 ppm)

■ Repeatability and Linearity Evaluation

Nineteen discrete sulfur compounds were diluted to the following concentrations 0.1 ppm, 1 ppm, 10 ppm, and 100 ppm (w/w) according to ASTM D5623. Table 2 illustrates repeatability (%RSD, n=5) and coefficient of determination (R²) for the Nexis SCD-2030 analysis of the sulfur compound standards. The area ratio value of the target compound to the internal standard was used in this evaluation. The results were highly reproducible with excellent linear response for all compounds. Fig. 3 illustrates the calibration curves for 2-propanethiol and methyl disulfide which are representative of the analytes.

Table 2 Repeatability and Linearity of Sulfur Compounds

No.	Analytes	Concentration (ppm)				STD No	R ² (0.1-100 ppm)
		0.1	1	10	100		
1	Methyl mercaptan	7.1 %	1.8 %	5.1 %	3.0 %	1	0.9999
2	Ethyl mercaptan	6.5 %	1.5 %	3.7 %	2.3 %	1	0.9999
3	Dimethyl sulfide	6.8 %	1.3 %	3.7 %	2.4 %	1	0.9999
4	Carbon disulfide	7.3 %	1.9 %	4.4 %	2.7 %	1	0.9999
5	2-Propanethiol	6.7 %	1.4 %	2.9 %	2.0 %	1	0.9999
6	2-Methyl-2-propanethiol	9.7 %	2.8 %	2.5 %	1.9 %	1	0.9999
7	1-Propanethiol	6.3 %	1.4 %	2.9 %	1.9 %	1	0.9999
8	Ethyl methyl sulfide	7.7 %	1.8 %	2.8 %	2.2 %	1	0.9999
9	Thiophene	6.7 %	1.7 %	2.8 %	2.0 %	1	0.9999
10	2-Butanethiol	8.5 %	3.4 %	1.7 %	2.4 %	2	0.9999
11	2-Methyl-1-propanethiol	8.5 %	3.1 %	1.7 %	2.3 %	2	0.9999
12	Diethyl sulfide	4.8 %	2.9 %	1.9 %	2.3 %	2	0.9999
13	1-Butanethiol	9.1 %	3.8 %	1.8 %	2.4 %	2	0.9999
14	Methyl disulfide	1.9 %	2.6 %	2.1 %	2.3 %	2	1.0000
15	2-Methylthiophene	9.7 %	3.2 %	1.8 %	2.3 %	2	0.9999
16	3-Methylthiophene	6.0 %	2.8 %	1.5 %	2.4 %	2	0.9999
17	Diethyl disulfide	3.7 %	2.8 %	1.8 %	2.4 %	2	0.9999
18	5-Methylbenzothiophene	9.4 %	1.5 %	1.9 %	1.8 %	1	0.9999
19	3-Methylbenzothiophene	9.6 %	4.1 %	1.7 %	2.5 %	2	0.9999

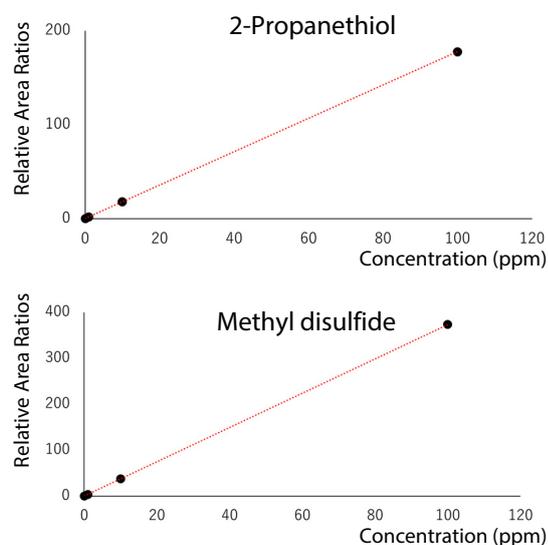


Fig. 3 Calibration Curve for 2-Propanethiol and Methyl Disulfide

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■ Long-Term Stability Evaluation

Long-term stability of a detector is one key measure of performance that directly impacts data reliability. 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.

In Table 2, a 10 ppm (w/w sulfur) standard 3 (STD3), containing all nineteen sulfur compounds, was analyzed for sixteen days continuously. Diphenyl sulfide was added to the sample at a concentration of 1 ppm as an internal standard.

Fig. 4 illustrates the results of relative response factor stability and absolute area stability for the four components (1-butanethiol, methyl disulfide, diethyl disulfide, 3-methylbenzothiophene) in STD3 with boiling points ranging from 98 °C to 273 °C. Each plot represents the daily mean value of the analysis result, and the error bar represents the value of three standard deviations (3σ).

The relative standard deviations of the relative response factors and absolute area for 1-butanethiol, methyl disulfide, diethyl disulfide and 3-methylbenzothiophene are shown in Table 3.

The results of this evaluation showed excellent long-term stability and diurnal variation. The Nexis SCD-2030 not only provides a stable relative response but also a stable absolute response over time.

Table 3 Long-Term Stability for Representative Analytes

Analytes	1-Butanethiol	Methyl disulfide	Diethyl disulfide	3-Methylbenzothiophene
Response Factor RSD(%)	1.4	1.2	1.9	1.6
Absolute Area RSD(%)	3.5	3.6	3.8	3.4

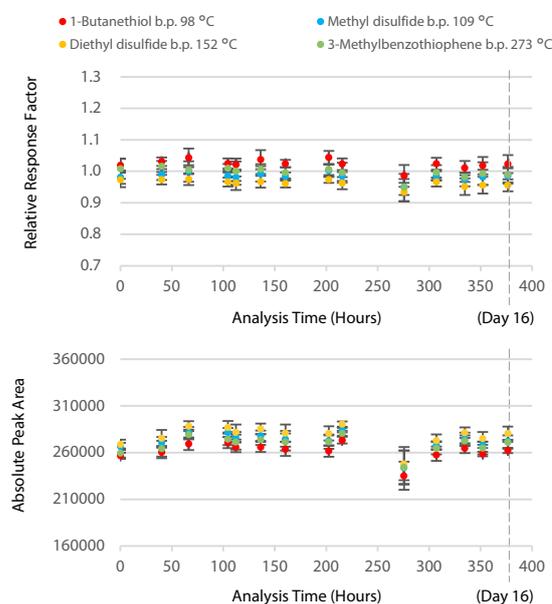


Fig. 4 Relative Response Factors and Absolute Peak Area Over 16 Days



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GC Nexis™ GC-2030

Reliable Sulfur Compounds Analysis in Diesel using Sulfur Chemiluminescence Detector Nexis SCD-2030

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User Benefits

- ◆ Sulfur Chemiluminescence Detector (SCD) Nexis SCD-2030 enables the sensitive and selective analysis of sulfur compounds in high matrix petrochemical samples without adverse matrix effects
- ◆ Its high reproducibility and excellent recovery ensure reliable detection and quantitation of the sulfur components
- ◆ The equimolarity of Nexis SCD-2030 eliminates the need for an individual calibration of target compounds, facilitating the quantitation process for complex mixtures and minimizing calibration standard costs

Introduction

Sulfur compounds are of high importance in petrochemical products. Besides the health risk H₂S poses by itself, they are responsible of atmospheric pollutions (SO₂ and SO₃)⁽¹⁾ and are proven to be poison for catalysts used in refining⁽²⁾. The sulfur amount in the fuels is steadily decreasing to the higher level of 10 ppm for diesel and gasoline. Since even low sulfur concentrations are harmful, already trace-level identification of potential poisons is essential. This creates the demand for a highly sensitive detector, which can also cope with the high matrix interference seen as the goal is to analyse the undiluted petrochemical sample wherever possible. The detection method of choice is sulfur chemiluminescence detection (SCD): Not only is this technique sensitive and selective to sulfur, but it additionally shows the benefit of equimolar response, which facilitates quantitation of especially complex mixtures as it erases the need for an individual calibration of each target compound⁽²⁾.

Using the example of diesel matrix, an investigation of petrochemical samples via gas chromatography (GC) combined with sulfur chemiluminescence detector (SCD) is presented. Selectivity, reproducibility, equimolarity and recovery of the setup are examined to judge reliability of the sulfur content determination.



Fig. 1 Nexis™ SCD-2030

Sample Preparation and Calibration

To investigate the selectivity, reproducibility and equimolarity, a matrix of desulfurized diesel (remaining sulfur content below 10 mg/L) was spiked with a mix of seven different sulfur compounds belonging to different sulfur substance groups relevant for diesel samples: sulfides, mercaptans and thiophenes. To investigate potential matrix effects and the recovery of the system, the spiked diesel matrix sample was compared to a pure solvent sample, in which the same compounds were spiked into hexane matrix. The investigation range was chosen as 10, 100 and 500 mg/L per target substance since higher levels of a single compound are highly unlikely to occur in diesel samples. This resulted in concentrations sulfur

of 1 to 4 mg/L S for the lowest level (level 1), 16 to 40 mg/L S for the medium level (level 2) and 82 to 200 mg/L S for the highest level (level 3) investigated, respectively (Table 1).

Table 1 Concentrations of the target substances

No.	Compound	Level 1 (mg/L S)	Level 2 (mg/L S)	Level 3 (mg/L S)
1	Thiophene	4.02	40.18	200.89
2	Butyl mercaptan	3.62	36.25	181.23
3	2-Methylthiophene	3.39	33.87	169.34
4	tert-Butyl disulfide	3.97	39.72	198.61
5	Benzothiophene	2.56	25.59	127.97
6	Ethyl phenyl sulfide	2.29	22.95	114.74
7	Dibenzothiophene	1.65	16.54	82.69

Results

Comparison of Chromatograms

Comparing the desulfurized diesel matrix sample with the hexane solvent matrix sample, no negative matrix effects were observed (Fig. 2). The signals in the diesel sample are not shifted significantly compared to the hexane sample and show similar base widths proving that no severe peak broadening occurs due to the diesel matrix. This not only allows for convenient comparison of diesel and hexane samples with just one processing method, but also ensures detection limits to be as good in the diesel as in pure solvent, enabling sensitive, yet selective detection of the target compounds down to trace levels despite the high matrix load in the diesel sample.

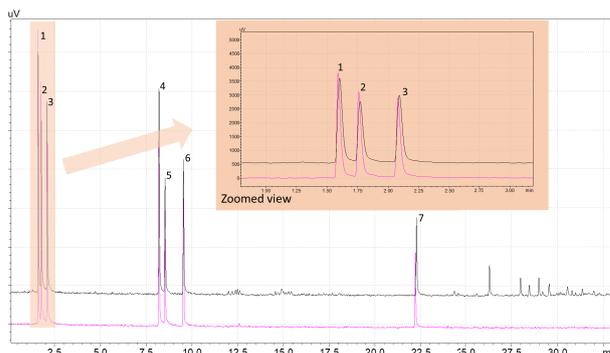


Fig. 2 Comparison view of the chromatograms for level 1 sulfur standard in desulfurized diesel matrix (black) and hexane solvent matrix (pink), chromatograms are base shifted for better visibility

• Reproducibility

Calculation of the relative standard deviation (%RSD) for retention times and peak areas at level 1 revealed the reliability of the setup (Table 2). Retention times were found to be highly stable with a reproducibility below 0.05 % for all target compounds. Area reproducibility was below 4 % for all spiked components, ensuring reliable detection and quantitation of the sulfur targets even at low concentrations.

Table 2 Relative standard deviations at level 1 of the diesel matrix sample for n = 6 consecutive measurements

No.	Compound	Ret. Time (min)	%RSD Ret. Time	%RSD Area
1	Thiophene	1.61	0.02	1.33
2	Butyl mercaptan	1.78	0.03	1.90
3	2-Methylthiophene	2.10	0.04	2.99
4	tert-Butyl disulfide	8.21	0.04	2.75
5	Benzothiophene	8.54	0.04	2.78
6	Ethyl phenyl sulfide	9.55	0.03	1.17
7	Dibenzothiophene	22.28	0.01	3.93

• Equimolarity

Equimolarity of sulfur compound detection facilitates target substance calibration by providing a response for different compounds solely dependent on the amount of sulfur (in moles) being present. To provide a measure for this, relative response factors (RRF) can be used. The response factors (RF) calculated from area and concentration S for each compound are averaged over all compounds to determine values for the single response factors relative to the average value (RRF). In a perfectly equimolar detection, the response factors for all components are the same, resulting in an RRF value of 100 for

Table 3 Relative response factors (RRF) determined for the hexane solvent samples at level 1, 2 and 3

No.	Compound	Level 1	Level 2	Level 3
1	Thiophene	103.5	98.4	106.3
2	Butyl mercaptan	104.5	93.5	100.2
3	2-Methylthiophene	105.5	95.1	103.0
4	tert-Butyl disulfide	94.3	97.8	94.7
5	Benzothiophene	89.7	99.2	90.8
6	Ethyl phenyl sulfide	109.1	114.7	106.7
7	Dibenzothiophene	93.3	101.3	98.3

Table 4 Relative response factors (RRF) determined for the desulfurized diesel matrix samples at level 1, 2 and 3

No.	Compound	Level 1	Level 2	Level 3
1	Thiophene	103.7	98.3	104.8
2	Butyl mercaptan	93.7	74.8	81.4
3	2-Methylthiophene	107.9	99.5	104.5
4	tert-Butyl disulfide	100.6	100.9	98.1
5	Benzothiophene	90.5	98.5	92.9
6	Ethyl phenyl sulfide	107.4	120.2	113.1
7	Dibenzothiophene	96.2	108.0	105.1

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every compound. For the samples diluted in hexane, RRF values were between 90 and 115 for all compounds at all concentration levels (Table 3); in the diesel matrix samples, RRF values were between 75 and 120 (Table 4). This demonstrates good equimolarity for not only the monosulfur compounds belonging to different substance groups, but also for the disulfide, independent of the chosen concentration level.

• Recovery

The recovery of the sulfur compounds in diesel matrix was investigated by comparing the response in the desulfurized diesel matrix with the response in the hexane solvent matrix for all three concentration levels. The resulting recovery values were in the range 0.8 to 1.1 for all compounds at all levels (Table 5), ensuring reliable recovery regardless the target component concentration.

Table 5 Recovery determined at level 1, 2 and 3

No.	Compound	Level 1	Level 2	Level 3
1	Thiophene	1.03	1.01	1.01
2	Butyl mercaptan	0.92	0.81	0.83
3	2-Methylthiophene	1.05	1.06	1.04
4	tert-Butyl disulfide	1.09	1.04	1.06
5	Benzothiophene	1.03	1.00	1.05
6	Ethyl phenyl sulfide	1.01	1.06	1.08
7	Dibenzothiophene	1.06	1.08	1.09

■ Conclusion

Sulfur chemiluminescence detection using SCD-2030 enables selective detection of sulfur compounds in high matrix load petrochemical samples down to low concentration levels. Its excellent selectivity and reproducibility ensure reliable results, while equimolarity for different sulfur target species facilitates the analysis of unknown sulfur compounds. Additionally, providing good recovery independent of the sulfur component concentration, SCD-2030 allows to accurately determine sulfur target substances both in lower and higher concentrations relevant for petrochemical samples.

The methodology reported in this application was developed in partnership with Total Refining and Chemicals, Total Research & Technology Gonfreville, Harfleur, France.



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- (1) R. L. Tanner, J. Forrest, L. Newman, "Determination of atmospheric gaseous and particulate sulfur compounds. [Atmospheric SO₂ sampling, calibration, and data processing]," Brookhaven National Laboratory, Upton, NY, USA, Tech. Rep. BNL-23103. Jan. 1977.
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Application News

No. G306

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			Gas ② Nitrogen		
Index	Components	Concentration	Index	Components	Concentration
Balance	Nitrogen	99.999 %	Balance	Nitrogen	99.9995 %
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 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

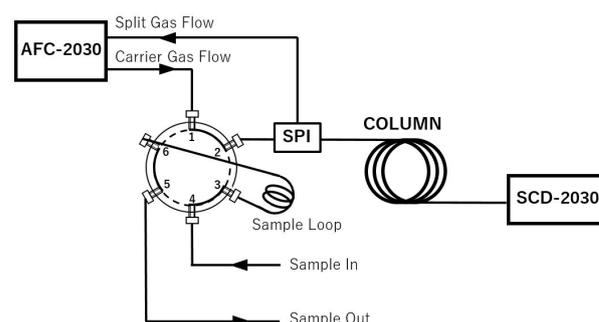


Fig. 1 Schematic of Instrument Configuration

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-Rtx™-1 (60 m × 0.53 mm I.D. df=7 μm)
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

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.

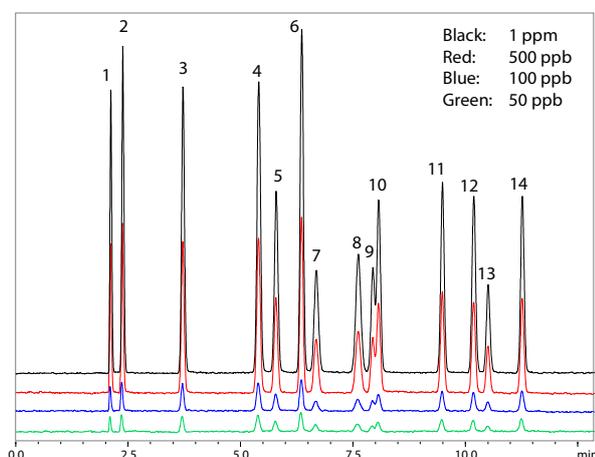


Fig. 2 Chromatogram of 14 Sulfur Compounds Mixture at 50 ppb, 100 ppb, 500 ppb, 1 ppm

Table 3 Linearity and Repeatability Results

Index	Components	Linearity (50 ppb, 100 ppb, 500 ppb, 1 ppm)	Repeatability n=5 (1 ppm)
		R ²	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.

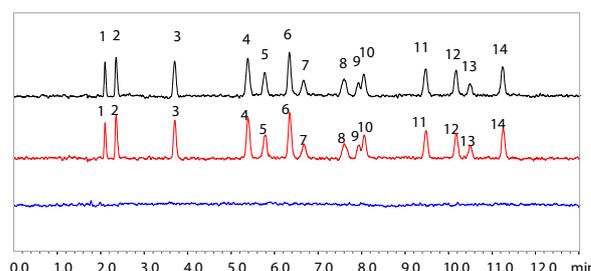


Fig. 3 Chromatogram Comparison of Standard Sulfur Mixture, Natural Gas Sulfur Mixture, and Gas ③

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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Application News

No. G307

Gas Chromatography

Analysis of Trace Thiophene in Benzene According to ASTM D7011 Using Nexis™ SCD-2030

Thiophene and other sulfur compounds are known for generating sulfur oxide upon combustion and also known as poisons in catalyst. For this reason, the quality control of petroleum products requires high-sensitivity analysis of sulfur compounds. In Application News No. G291, we introduced an analysis that employs gas chromatography using a Flame Photometric Detector (FPD).

ASTM D7011 introduces a method for analyzing trace thiophene in benzene by Sulfur Chemiluminescence Detector (SCD) at a level of approximately 0.03 mg/kg which is lower than what is conventionally analyzed with FPD.

The Nexis SCD-2030 next-generation sulfur chemiluminescence detection system (Fig. 1) with its best-in-class sensitivity and stability is capable of selectively detecting sulfur compound types with high sensitivity. This article shows an example of the analysis of thiophene in benzene at high sensitivity in conformance with ASTM D7011 and using the Nexis SCD-2030.

Y. Nagao



Fig. 1 Nexis™ SCD-2030

Instrument Configuration and Analysis Conditions

Table 1 lists the instrument configuration and analysis conditions. The GC analytical conditions according to ASTM D7011.

Table 1 Instrument Configuration and Analysis Conditions

Main Unit	: Nexis GC-2030/AOC-20i plus
Column	: SH-Rtx™-WAX (30 m × 0.32 mm I.D., df = 1 μm)
Detector	: SCD-2030
Injection Volume	: 1 μL
Injection Mode	: Split
Split Ratio	: 1 : 5
Injection Unit Temp.	: 125 °C
Carrier Gas	: He
Carrier Gas Control	: Constant Column Flow Mode (2.00 mL/min)
Column Temp.	: 40 °C (2 min) – 10 °C/min – 100 °C (1 min)
Interface Temp.	: 200 °C
Furnace Temp.	: 850 °C
Detector Gas	: H ₂ 100 mL/min, N ₂ 10 mL/min, O ₂ 12 mL/min, O ₃ 25 mL/min

Analysis of Trace Thiophene

Standard solutions were prepared by diluting thiophene in thiophene-free benzene to concentrations between 10 and 1000 ppb (v/v) *1.

Fig. 2 shows four chromatograms comparing the thiophene elution positions of 10 ppb and 50 ppb thiophene, thiophene-free benzene and high purity benzene. As shown in Fig. 2, high purity benzene may contain several ppb of thiophene; consequently, and thiophene-free benzene is required in order to analyze thiophene in low ppb level.

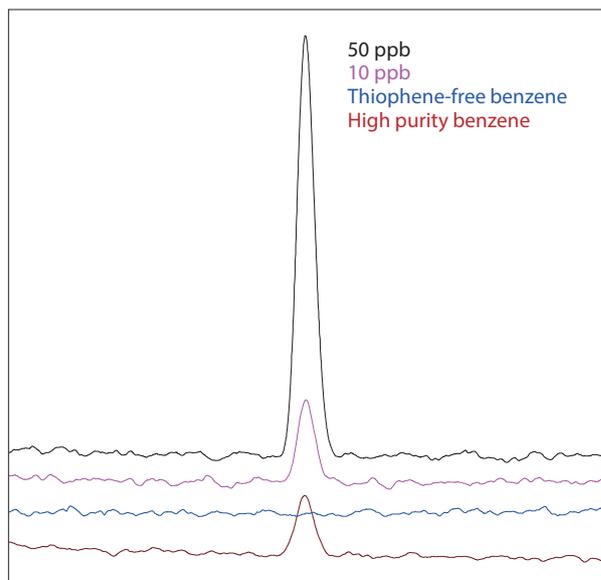


Fig. 2 Comparison of Thiophene Elution Positions of Trace Thiophene and Two Types of Benzenes (Only high purity benzene was measured on a different day. The retention time was adjusted for comparison.)

*1 1000 ppb (v/v) ≈ 1.2 mg/kg

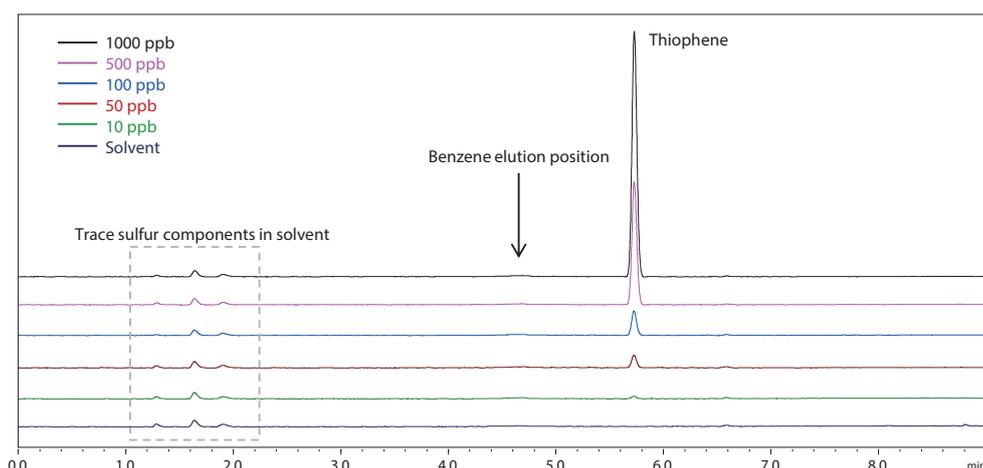


Fig. 3 Comparison of Chromatograms of Thiophene Standard Solutions (10 to 1000 ppb) and Solvent (Thiophene-Free Benzene)

■ Analysis of Standard Samples

Fig. 3 shows the results of analyzing the standard solutions. The baseline has been shifted in these results for comparing chromatograms. Note that the thiophene-free benzene used in this analysis contained trace sulfur components that were eluted one to two minutes into the retention time.

Table 2 lists the retention time and area repeatability (RSD%) and S/N average values obtained in analysis with $n = 6$. A sensitivity of $S/N = 5.37$ was observed for the 10 ppb thiophene. If we take the quantitative lower limit to be $S/N = 10$, the quantitative lower limit of this analysis can be calculated to be approximately 18 ppb. This demonstrates that this analysis system has a level of sensitivity capable of quantifying concentrations of thiophene lower than the 0.03 mg/kg (≈ 25 ppb (v/v)) specified in ASTM D7011.

Fig. 4 shows the calibration curve obtained from these standard samples. The R^2 value is higher than 0.9999, indicating good linearity. As with the GC-FPD method, introduced in Application News No. G291, due to its detection principle, a linear calibration curve must be created using the double logarithms of concentration and area for sulfur compounds. On the other hand, SCD allows the creation of a linear calibration curve based on the actual values of concentration and area of sulfur compounds.

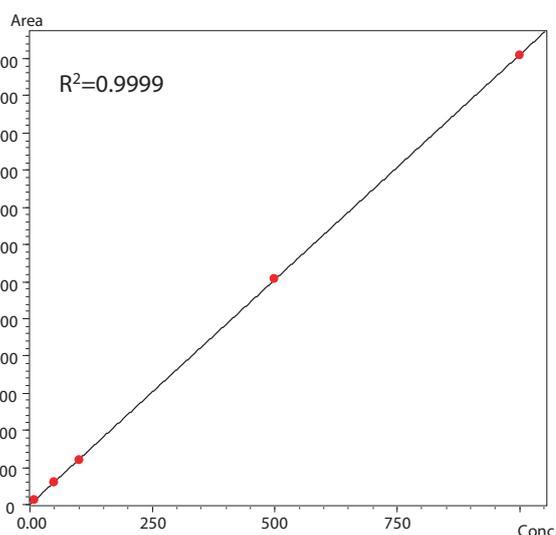


Fig. 4 Calibration Curve for Thiophene (10 to 1000 ppb)

Table 2 Retention Time and Area Repeatability and S/N Average with $n=6$

Concentration (ppb)	Retention time RSD (%)	Area RSD (%)	S/N Average
10	0.027	9.47	5.37
50	0.006	0.58	30.0
100	0.015	0.39	57.9
500	0.011	0.57	280
1000	0.013	0.51	544

■ Conclusion

We performed analysis of trace thiophene in benzene in conformance with ASTM D7011 using the Nexis SCD-2030 next-generation sulfur chemiluminescence detection system.

The Nexis SCD-2030 has best-in-class sensitivity and stability and demonstrated favorable sensitivity, repeatability, and linearity in this analysis. We determined that analyses according to ASTM D7011 are achievable by using this system.

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Trace Thiophene in Refined Benzene by GC with Nexis™ SCD-2030 Using Nitrogen Carrier Gas

■ Introduction

Determination of trace amounts of thiophene in refined benzene can be challenging due to the sensitivity required and potential detection of interference from the benzene matrix. Because of its sensitivity as well as selectivity, a gas chromatograph (GC) with sulfur chemiluminescence detector (SCD) allows trace amounts of thiophene to be accurately determined in a benzene matrix. Traditionally SCD requires using helium (He) carrier gas, which can be very costly due to a global supply shortage. In this application, we demonstrate that trace concentrations of thiophene can be successfully quantified in a benzene matrix using a Shimadzu Nexis™ SCD-2030 with nitrogen carrier gas.

■ Samples and Analytical Conditions/Experimental

An ASTM D7011 standard set was purchased from a chemical company, which contains the following standards: 0.02 mg/kg, 0.2 mg/kg, 0.5 mg/kg, 1.0 mg/kg and 2.0 mg/kg thiophene in benzene, as well as an unspiked benzene (blank). A Shimadzu GC-2030 equipped with a split/splitless injector and an SCD detector (Nexis™ SCD-2030) was used for this assay. The instrument settings are shown in Table 1.

Table 1: Instrument Configuration and Analysis Conditions

GC System	Shimadzu GC-2030 with SCD-2030 and AOC-20i Plus autosampler
Column	SH-Stabilwax, 30m x 0.32mm x 1.00µm
Injector Mode	Split at 1:5 ratio
Injection Volume	1µL
Carrier Gas	Nitrogen
Flow mode	Constant column flow at 2mL/min
Column Temp	40°C, 2 min – 10°C/min – 100°C, 1 min (total GC program 9min)
Interface Temp	150°C
SCD Furnace Temp	850°C
Detector Gases	H ₂ 100 mL/min, N ₂ 10 mL/min, O ₂ 12 mL/min, O ₃ 25 mL/min

■ Results and Discussion

The thiophene standards were assayed using nitrogen carrier gas per conditions described in ASTM D7011 method. Minimal interference was seen from benzene. However, a thiophene peak was observed in the purportedly thiophene-free, unspiked benzene blank. As shown in Figure 1, a significant thiophene peak is seen in the benzene blank (black trace). In contrast, no peak was seen in a hexane blank assayed after the highest calibration standard (pink trace).



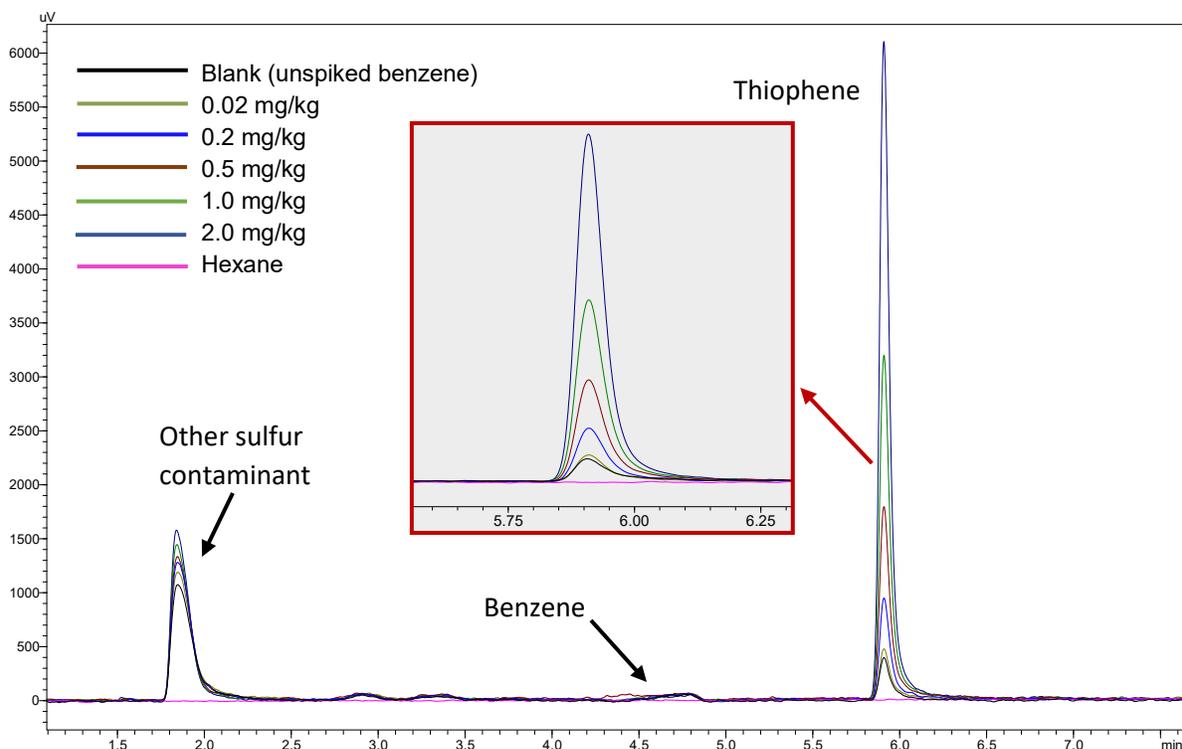


Figure 1: Example chromatograms of thiophene in benzene standards.

To investigate whether this was either an artifact of the system or the result of carryover, a sample of hexane was assayed before and after the benzene/thiophene samples. No thiophene peak was detected in the hexane injections before or after sample injections, indicating that the unspiked benzene blank contained a quantifiable amount of thiophene. This is not surprising, as it is very common for benzene to be contaminated with small amount of thiophene.

A five-point calibration curve was generated using the standards described above. The benzene blank still contains trace amount of thiophene. As a result, the calibration curve does not go through zero. Despite that, excellent linearity with $R^2 > 0.9999$ is obtained as can be seen in Figure 2.

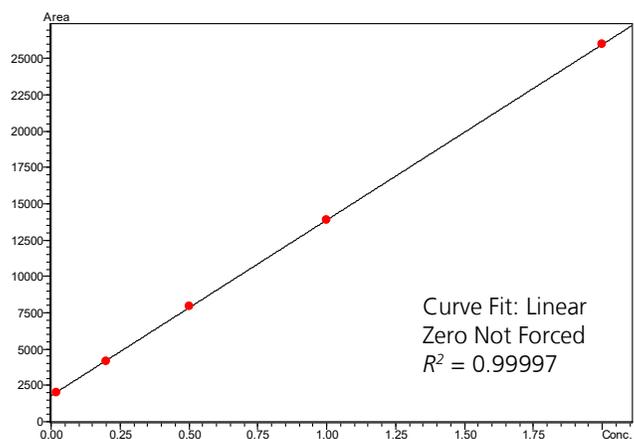


Figure 2: Five-point calibration curve of thiophene.

When using the standard addition calibration method, the concentration of thiophene in the benzene blank was determined to be 0.148 mg/kg. Unfortunately, this is above the amount allowed by the ASTM method (<0.02 mg/kg) to be considered thiophene-free benzene. Therefore, a future study using benzene of a higher purity grade will be needed.

Each standard and blank were analyzed four times and the results are shown in Table 2.

Table 2: Retention time and Area Repeatability and S/N for multiple injections (n=4).

Standard Sample	Retention Time % RSD	Area % RSD	Average S/N
0.02 mg/kg	0.0288	2.335	14.19
0.2 mg/kg	0.0123	2.732	33.85
0.5 mg/kg	0.0043	1.358	60.95
1.0 mg/kg	0.0138	0.665	107.89
2.0 mg/kg	0.0146	1.003	216.46
Blank (unspiked)	0.0302	1.982	13.07

The relative standard deviation (RSD) for multiple injections (n=4) are all under 3%, showing excellent repeatability. The % RSD for overall retention time for all 24 analyses in the table is 0.0207. Average signal to noise (S/N) for each sample is also shown.

■ Conclusion

Trace amounts of thiophene can easily be measured using Shimadzu GC with SCD-2030, due to the excellent sensitivity and selectivity. Furthermore, the Shimadzu SCD-2030 can work with nitrogen carrier gas in addition to traditional helium carrier gas, greatly reducing the cost of analysis. The SCD-2030 offers seamless integration with the GC system and software control, automatic start up, shutdown and conditioning, making operation of this detector streamlined and hassle-free.

■ References

- ASTM D7011-15, Standard Test Method for Determination of Trace Thiophene in Refined Benzene by Gas Chromatography and Sulfur Selective Detection, ASTM International, West Conshohocken, PA, 2015, www.astm.org
- Shimadzu application news No. G307, Analysis of Trace Thiophene in Benzene According to ASTM D7011 Using Nexis™ SCD-2030

■ Consumables

- 227-36252-01: SH-Stabilwax, 0.32mm x 1µm x 30m
- 227-35007-01: Deactivated split liners
- 036-11203-84: O-ring for liners
- 221-76650-01: Inlet septa
- 221-84141-41: SCD-2030 consumable kit

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Analysis of Dibenzyl Disulfide and Total Sulfur in Insulating Oil Using SCD

In an oil-filled transformer, sulfur-containing compounds in insulating oil are known to cause sulfide corrosion of the transformer. Specifically, dibenzyl disulfide (DBDS), an additive of insulating oil as a metal deactivator, has been reported as a cause of sulfide corrosion. The International Electrotechnical Commission (IEC) has issued the analytical standard for DBDS in insulating oil as IEC62697-1. A sulfur chemiluminescence detector (SCD) that can be used as one of gas chromatographs can selectively analyze sulfur-containing compounds with a high sensitivity. This detector has a high selectivity and avoids the effects of contaminants and enables accurate quantification of sulfur-containing compounds. This article introduces an analysis of DBDS in insulating oil using an SCD in accordance with IEC 62697-1, and it also reports on analysis of the quantity of total sulfur in insulating oil using the equimolar response of SCD.

Y. Takemori

Sample Preparation

[Standard samples]

- [1] Dibenzyl disulfide (DBDS) was dissolved in toluene to make a concentration of 100 mg/kg.
- [2] Diphenyl disulfide (DPDS) was dissolved in toluene to make a concentration of 500 mg/kg.
- [3] [1] was added to mineral oil to make concentrations of 0.1 - 100 mg/kg.
- [4] 0.25 g of each of the DBDS samples prepared in [3] was weighed and dissolved in 5 ml of isoctane.
- [5] 0.1 ml of [2] was added as an internal standard to each of the DBDS samples prepared in [4], and analyzed as standard samples.

[Insulating oil samples]

- [6] 0.25 g of each of 5 types of insulating oil was weighed and dissolved in 5 ml of isoctane.
- [7] 0.1 ml of [2] was added as an internal standard to each of solutions prepared in [6] and analyzed as insulating oil samples.

Analytical Method/Conditions

The conditions for quantitative analysis of DBDS and conditions for separation analysis of other sulfur-containing compounds are shown in Table 1. The conditions for analysis of total sulfur in insulating oil which is not separated by a column are shown in Table 2.

Table 1 Conditions for Quantitative Analysis of DBDS and Separation Analysis of Other Sulfur-Containing Compounds

Model	: Nexis™ GC-2030 / SCD-2030	
Injection Volume	: 1 μL	
Injection	: SPL	
Injection Temp.	: 275 °C	
Injection Mode	: Split	
Split Ratio	: 1:5	
Carrier Gas	: He	
Carrier Gas Control	: Linear velocity (45.0 cm/s)	
Column	: SH-Rtx™-5 (30 m × 0.32 mm I.D., 0.25 μm)	
Column Temp.	: 90 °C-10 °C/min-275 °C (20 min)	
Interface Temp.	: 250 °C	
Electric Furnace Temp.	: 850 °C	
Detector Gas	: H ₂ 100.0 mL/min	: N ₂ 10.0 mL/min
	: O ₂ 12.0 mL/min	: O ₃ 25.0 mL/min

Table 2 Conditions for Analysis of Total Sulfur in Insulating Oil Not Separated by Column

Model	: Nexis GC-2030 / SCD-2030	
Injection Volume	: 0.5 μL	
Injection	: SPL	
Injection Temp.	: 280 °C	
Injection Mode	: Split	
Split Ratio	: 1:50	
Carrier Gas	: He	
Carrier Gas Control	: Pressure (10 kPa)	
Column	: Deactivated fused silica tube (15 m × 0.2 mm I.D.)	
Column Temp.	: 280 °C (hold time: 10 minutes)	
Interface Temp.	: 250 °C	
Electric Furnace Temp.	: 850 °C	
Detector Gas	: H ₂ 100.0 mL/min	: N ₂ 10.0 mL/min
	: O ₂ 12.0 mL/min	: O ₃ 25.0 mL/min

Chromatogram and Calibration Curve of Standard Samples

The chromatogram and calibration curve of standard samples are shown in Fig. 1 and Fig. 2, respectively. Concentrations as low as 0.1 mg/kg could be detected.

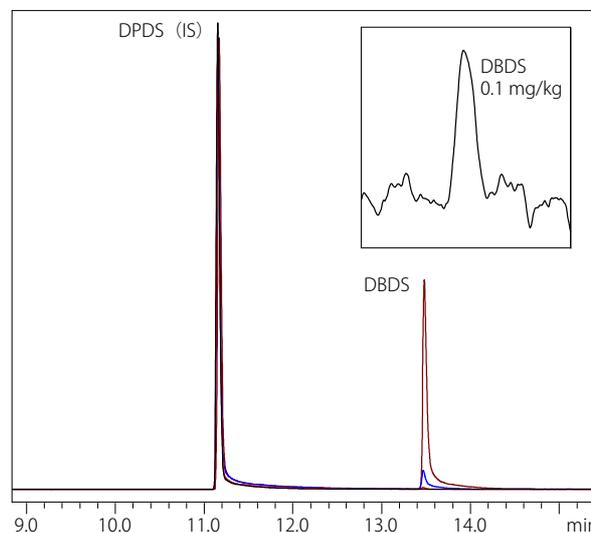


Fig. 1 Chromatogram of Standard Samples (0.1 - 100 mg/kg)

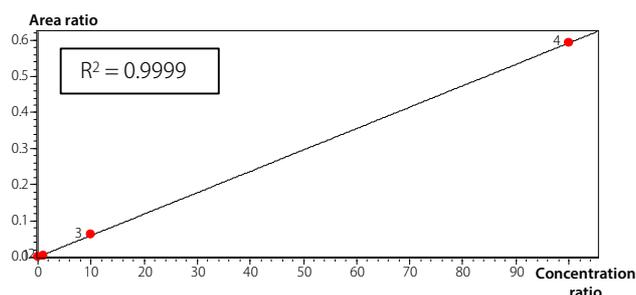


Fig. 2 Calibration Curve

Quantitative Results of DBDS

Fig. 3 shows the chromatogram of 5 types of insulating oil samples. Table 3 shows the results of DBDS quantification based on the calibration curve using the internal standard method.

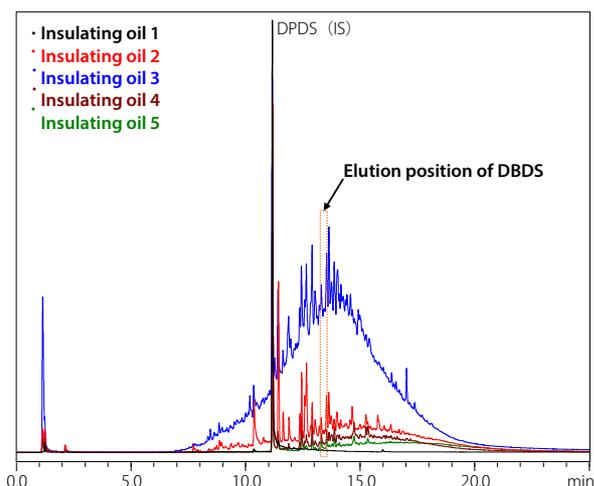


Fig. 3 Chromatograms of Insulating Oil Samples

Table 3 Quantitative Results of DBDS

Insulating oil sample	DBDS concentration (mg/kg)
Insulating oil 1	0.1
Insulating oil 2	2.6
Insulating oil 3	92.2
Insulating oil 4	0.8
Insulating oil 5	0.5

Analysis of Quantity of Total Sulfur Using the Characteristics of SCD

As shown in Fig. 3, many sulfur-containing compounds were detected from the insulating oil samples. In this analysis, the quantities of total sulfur in insulating oil samples were determined by and compared between the following two methods. Similar quantities of total sulfur in the samples separated or unseparated were obtained.

[1] Analysis of the quantity of total sulfur in the normally separated samples (analytical conditions: Table 1)

SCD exhibits the same sensitivity (equimolar sensitivity*), regardless of sulfur-containing compound structure, when the same number of sulfur atoms is introduced into the SCD. This characteristic of SCD allows the use of a calibration curve as shown in Fig. 2 to quantify and aggregate all detected peaks of sulfur-containing compounds and determine the quantity of total sulfur in each sample, as shown in Fig. 4 (*For the details of equimolar sensitivity, refer to G330).

[2] Analysis of the quantity of total sulfur in the unseparated samples (analytical conditions: Table 2)

SCD, in principle, has no sensitivity to compounds other than those containing sulfur. Using this characteristic, the sample injection was connected to SCD with a deactivated fused silica tube, and the unseparated insulating oil samples were introduced into the SCD. Fig. 5 compares the peaks of each of the samples as the quantity of total sulfur.

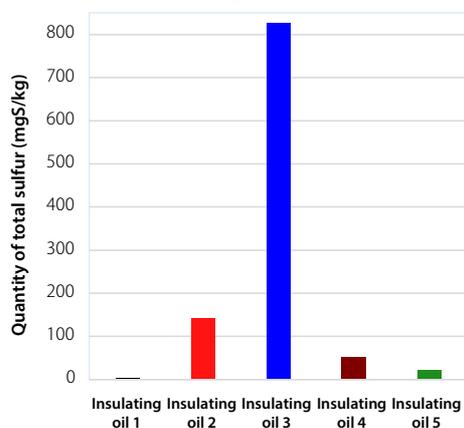


Fig. 4 Comparison of Quantity of Total Sulfur in Separated Samples Calculated Using Calibration Curve of DBDS

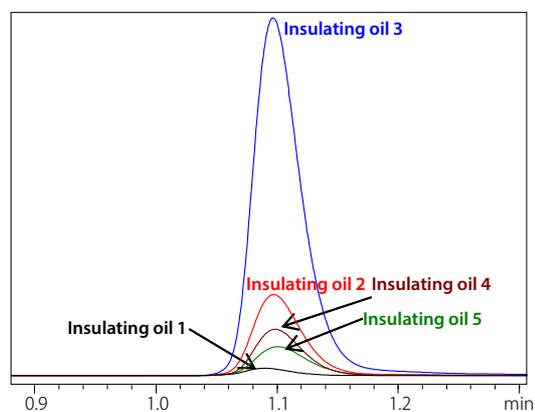


Fig. 5 Comparison of Unseparated Insulating Oil Samples

Conclusion

SCD could determine the quantity of DBDS in insulating oil with a high sensitivity. The use of the characteristics of SCD also enables the quantity of total sulfur to be determined.

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Comparison of Sensitivity for Sulfur Compound Species by Nexis™ SCD-2030: Equimolar Sensitivity Measurement

The Sulfur Chemiluminescence Detector (SCD) has the characteristic of linear response in proportion to the number of sulfur atoms (S atoms) introduced into the detector. Accordingly, the SCD is known to display the same sensitivity (i.e. equimolar sensitivity) regardless of compound species as long as the same number of S atoms (i.e. S mol number) is introduced. Furthermore, if 2 or 3 S atoms exist in a compound, the sensitivity of the SCD increases linearly by 2 or 3 times corresponding to the total number of S atoms introduced into the detector.

This equimolar sensitivity characteristic becomes particularly useful when sulfur compounds to be quantitated have unknown structures. For example, the SCD can be applied to quantitative analysis where the total number of S atoms in a sample is measured.

This article examined the equimolar sensitivity characteristic for multiple sulfur compounds, using a Shimadzu Nexis™ SCD-2030. In addition, a comparison experiment was conducted with another selective and highly sensitive detector for sulfur the Flame Photometric Detector (FPD(S)).

Y. Nagao

Analysis Conditions

Table 1 shows the instrument composition and analysis conditions of this experiment.

Table 1 Instrument Composition and Analysis Conditions

Model	: Nexis GC-2030/AOC-20i Plus
Injection volume	: 0.5 µL
Injection temp.	: 220 °C
Injection unit	: SPL (Sulfiner® treatment completed)
Injection mode	: Split
Split ratio	: 1:50
Carrier gas	: He
Carrier gas control	: Linear velocity (30 cm/s)
Purge gas	: 3.0 mL/min
Column	: SH-Rtx™-1 (30 m × 0.25 mm I.D., 0.25 µm)
Column temp.	: 50 °C (3.5 min) - 30 °C /min - 200 °C - 25 °C /min - 250 °C (2 min)
Detector	: Sulfur chemiluminescence detector (SCD-2030)
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

Sulfur Compounds: Mixed Standards

Three types of mixed standards were prepared as shown in Table 2 with each compound diluted to 10 µg/mL. Table 2 also lists the number of S atoms in each compound. Fig. 1 shows the chromatogram obtained with the standard mixtures.

Relative Molar Sensitivity

The mol number of each compound in the standards was calculated to determine the molar sensitivity (i.e. peak area/mol number). The relative molar sensitivity (RMS) with respect to the molar sensitivity of diisopropyl sulfide (DIPS) containing 1 S atom was calculated by Eq. (1). Table 2 lists the average values (n = 6) of the RMS of each compound.

The equimolar sensitivity characteristic was satisfactory for all the compounds as the RMS values are close to the number of S atoms in the molecules.

$$\text{Relative molar sensitivity (RMS)} = \frac{\text{Peak area} / \text{Mol number}}{\text{Peak area of DIPS} / \text{Mol number of DIPS}} \quad (1)$$

Table 2 Standard Mixtures of Sulfur Compounds (10 µg/mL each in MeOH)

Mix	Compounds	b.p. (deg.)	Number of S atoms	Average value of RMS (n = 6)
1	thiophene	84	1	0.89
	S-methyl thioacetate	98	1	0.95
	diisopropyl sulfide	121	1	1.00
	dimethyl trisulfide	170	3	3.12
	diallyl disulfide	185	2	1.86
2	propylene sulfide	73	1	0.90
	dibutyl disulfide	117	2	1.95
	1,4-thioxane	147	1	1.18
3	dimethyl disulfide	110	2	2.12
	allyl sulfide	139	1	1.12
	allyl isothiocyanate	148	1	0.96

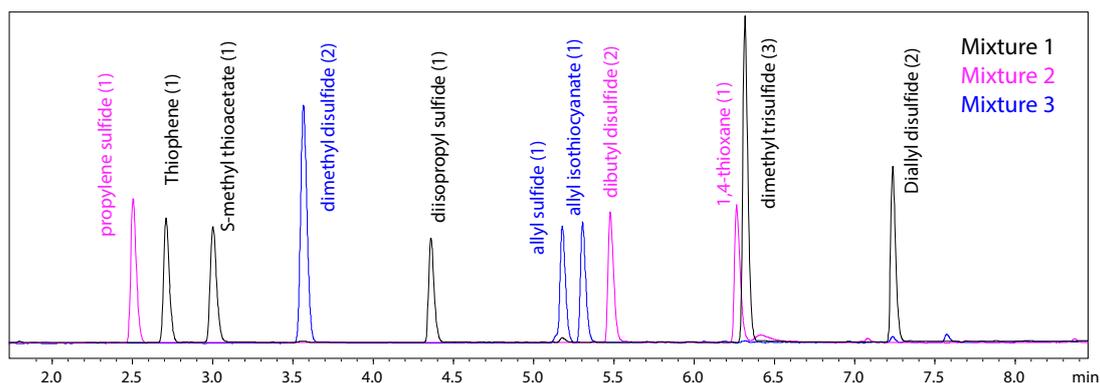


Fig. 1 Chromatograms of Mixed Standard (10 µg/mL in MeOH)
Numbers in parentheses indicate the number of S atoms in molecules.

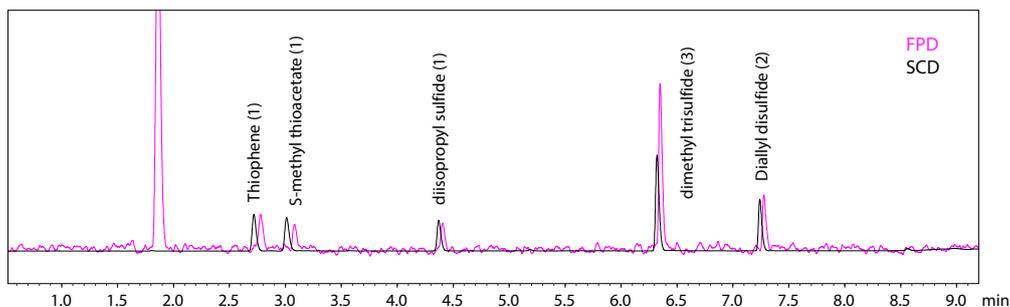


Fig. 2 Comparison of Chromatograms of Mixture 1 by FPD(S) and SCD Numbers in parentheses indicate the number of S atoms in molecules. For comparison, the peak heights by the two methods were adjusted to be approximately the same.

■ Comparison with FPD(S)

The same standards were also analyzed under the same injection conditions using the FPD(S) another selective and highly sensitive detector. Fig. 2 shows a comparison of the chromatograms for Mixture 1. The peak heights by the FPD and the SCD were adjusted to be approximately the same.

Although both devices are selective and highly sensitive detectors for sulfur compounds, the RMSs of the two detectors for the measured compounds were different.

■ Linearity of Sensitivity for Number of S Atoms

Using the results shown in Table 2, Fig. 3 shows the relationship between RMS and the number of S atoms in the molecules. When a regression line is drawn as in Fig. 3, its slope is an indicator of the equimolar sensitivity characteristic. With the SCD, the coefficient of the line was approximately 1.03, confirming the equimolar sensitivity characteristic among the compounds with molecules containing multiple S atoms.

When the correlation of the FPD was examined in the same manner, a linear relationship was not obtained. With the FPD, RMS varied widely for compounds such as dimethyl disulfide (the number of S atoms in molecule: 2) and dimethyl trisulfide (the number of S atoms: 3) likely because the FPD is based on the detection of light emission from the S₂ molecule.

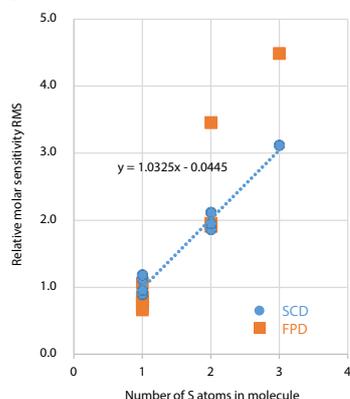


Fig. 3 Comparison of Linearity of Sensitivity for Number of S Atoms in Molecules by SCD and FPD

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■ Radar Chart of RMS

In order to visualize the RMS of the two detection methods for compounds with one S atom in the molecule, a radar chart (Fig. 4) was drawn to illustrate the molar sensitivity of each compound when the molar sensitivity of diisopropyl sulfide (DIPS) is defined as 1. From this chart, it can be observed visually that the SCD has a better RMS in comparison with the FPD.

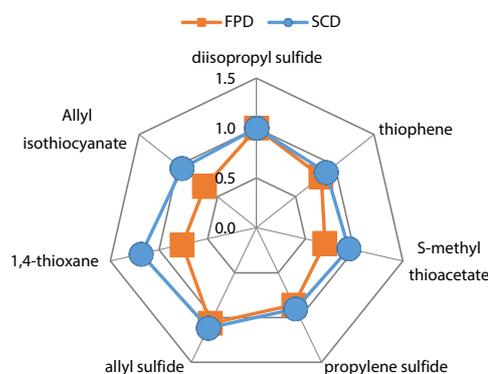


Fig. 4 Radar Chart of RMS for Compounds with 1 S Atom in Molecule

■ Discussion and Conclusion

The equimolar sensitivity characteristic of the SCD for multiple sulfur compounds was investigated using a Nexis SCD-2030. The equimolar sensitivity was confirmed by first calculating the molar sensitivity for each compound tested (i.e. peak area/ mol number) and subsequently examining the relative molar sensitivity (RMS) with respect to diisopropyl sulfide.

A good equimolar sensitivity characteristic was confirmed for the tested compounds having molecules containing 1, 2 and 3 S atoms. Based on this result, approximate quantitation of unknown sulfur compounds as well as the total sulfur content in a sample is feasible with the Nexis SCD-2030.



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