Excellence in Science

Application News

No. G334

Gas Chromatography

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 g/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 isooctane.

[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 isooctane.

[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 O_2 12.0 mL/min	N_2 10.0 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 O_2 12.0 mL/min	N_2 10.0 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.

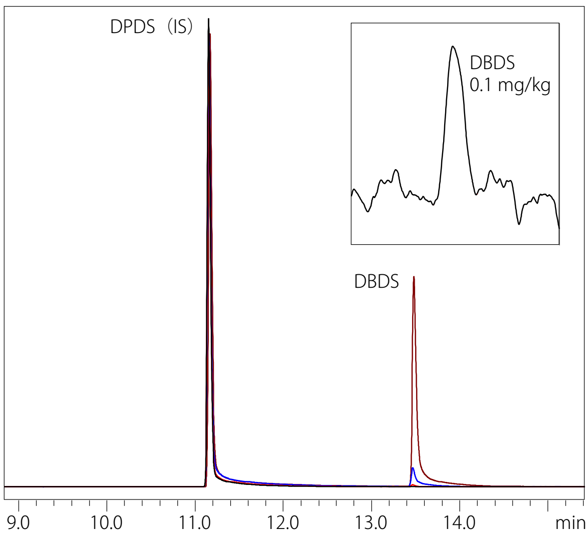

Fig. 1 Chromatogram of Standard Samples (0.1 - 100 mg/kg)

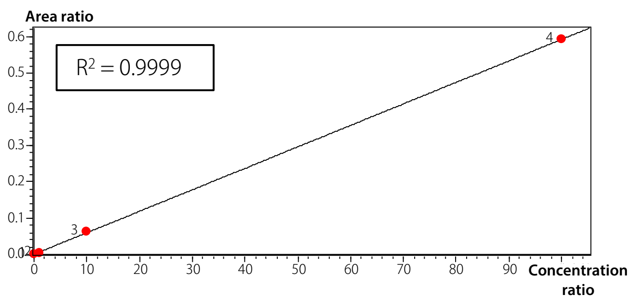

Fig. 2 Calibration Curve

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.

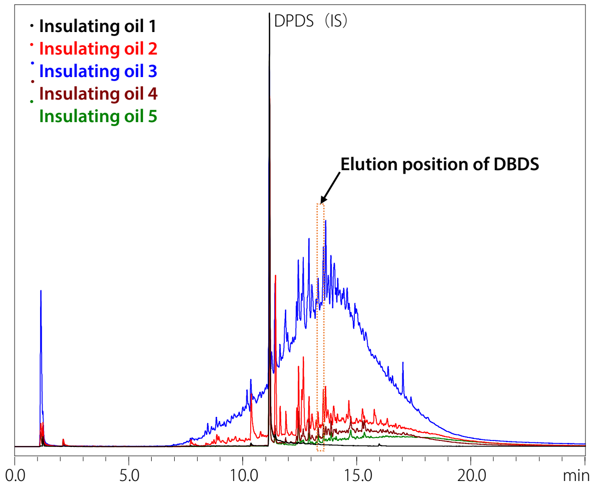

Fig. 3 Chromatograms of Insulating Oil Samples

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.

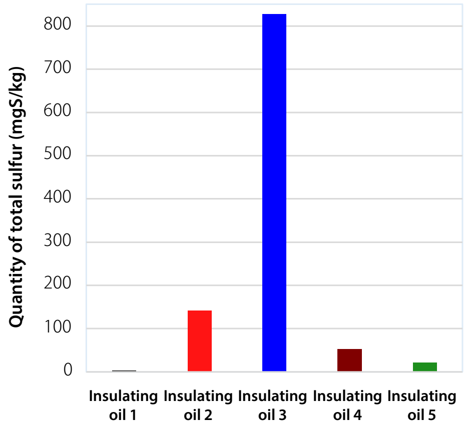

Fig. 4 Comparison of Quantity of Total Sulfur in Separated Samples Calculated Using Calibration Curve of DBDS

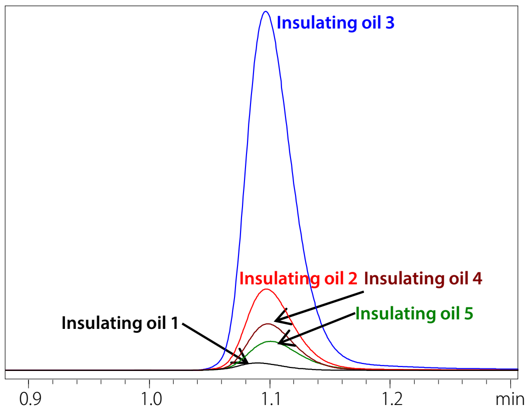

Fig. 5 Comparison of Unseparated Insulating Oil Samples

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.

First Edition: Aug. 2020

SHIMADZU

Shimadzu Corporation

www.shimadzu.com/an/