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Application News

No. G330A

Gas Chromatography

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)).

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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 (Sulfinert® 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-1 (30 m × 0.25 mm I.D., 0.25 µm) *1
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

*1 P/N: 221-75719-30

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.

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

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

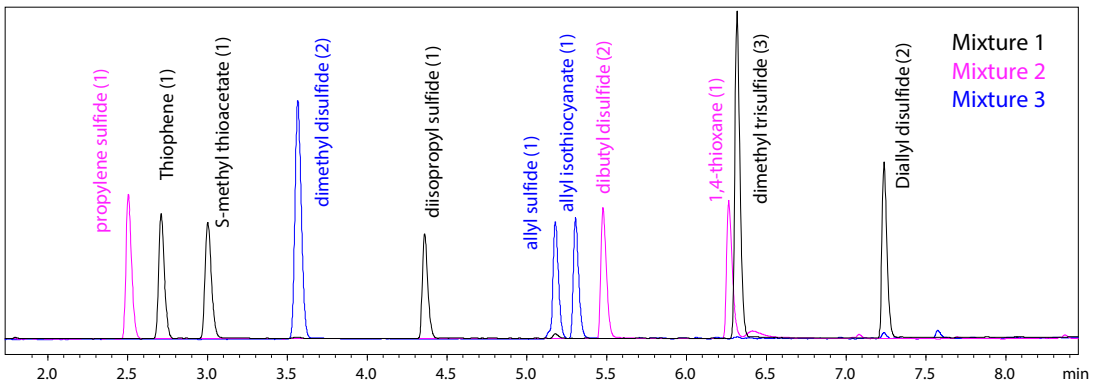

Fig. 1 Chromatograms of Mixed Standard (10 µg/mL in MeOH)
Numbers in parentheses indicate the number of S atoms in molecules.

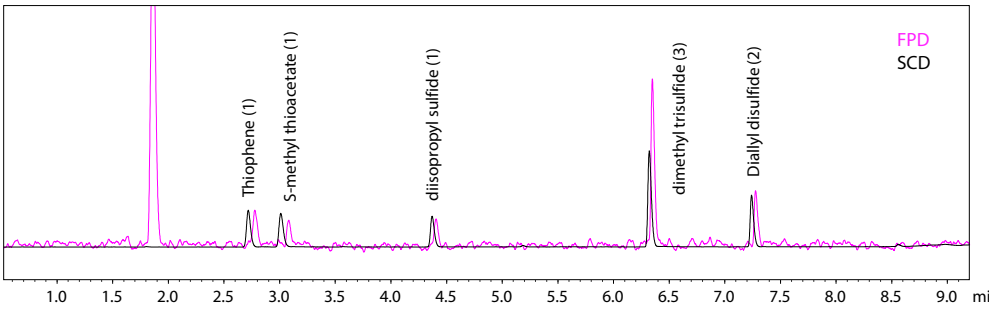

Fig. 2 Comparison of Chromatograms of Mixture 1 by FPD(S) and SCD Numbers in parentheses indicate the number of S atoms in molecules. For comparison, the peak heights by the two methods were adjusted to be approximately the same.

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 S_2 molecule.

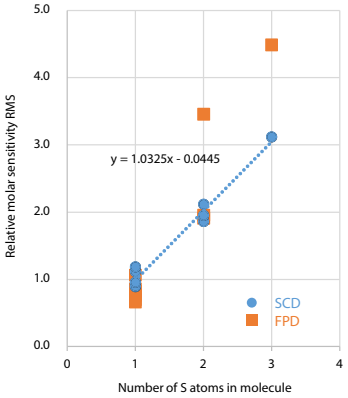

Fig. 3 Comparison of Linearity of Sensitivity for Number of S Atoms in Molecules by SCD and FPD

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.

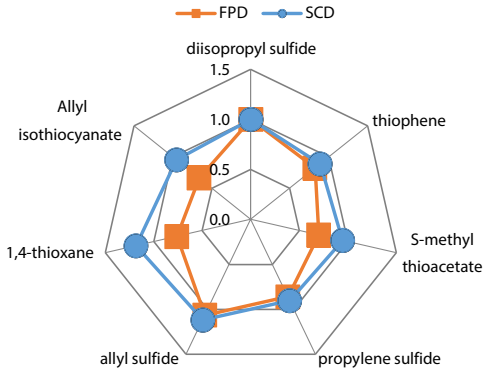

Fig. 4 Radar Chart of RMS for Compounds with 1 S Atom in Molecule

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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