GC Nexis™ GC-2030

Total Sulfur Content in Diesel – Reliable Analysis using Sulfur Chemiluminescence Detector Nexis SCD-2030

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User Benefits

- Sulfur Chemiluminescence Detection (SCD) with Nexis SCD-2030 enables the reliable analysis of total sulfur content in petrochemical samples
- Additionally, and in contrast to classical total sulfur approaches, it offers the possibility to detect and quantify individual sulfur compounds, revealing the sulfur pattern of a certain sample

■ Introduction

Sulfur compound content is critical for petrochemical products, as sulfur species not only are responsible for atmospheric pollutions (SO_2 and SO_3)[1)], but also are poisonous for catalysts used in refining[2)]. Since this is true for any sulfur containing molecule down to trace-level amounts, the biggest demand for an analytical system is to detect the total sulfur content, meaning the sum of all sulfur species, down to low absolute values – despite the high matrix load of an undiluted petrochemical sample. Classical total sulfur analysis methods involve e. g. oxidative microcoulometry, UV fluorescence, titration or gravimetric methods[3)]. However, these techniques only determine the total sulfur content and cannot give information on the sulfur component pattern of a certain sample. To do so, the instrument of choice is sulfur chemiluminescence detection (SCD): It combines not only the selectivity and sensitivity necessary for the analysis of the total sulfur content but also offers the advantage to additionally determine individual sulfur species in a certain sample and quantitate single compound amounts via its equimolar response[2)].

Using the example of a diesel sample, an investigation of the total sulfur content in petrochemical samples via gas chromatography (GC) combined with sulfur chemiluminescence detection (SCD) is presented. Two approaches are compared: A high-throughput setup using a short tubing without stationary phase, that gives the total sulfur content as one peak without chromatographic separation, against a more flexible setup with a regular analytical column, additionally allowing for the investigation of single peaks due to the chromatographic separation of the sulfur compounds.

■ Sample Preparation and Calibration

The diesel sample is injected undiluted into the gas chromatograph. For the short tubing approach, quantitation of the total sulfur content is realized using a 3-level standard addition. Due to the equimolarity of SCD-2030 a single sulfur compound standard is sufficient. In case an analytical column with chromatographic separation is used, as alternative to the standard addition method the addition of an internal standard (ISTD) to quantify the sulfur compounds based on area ratios is possible, given sufficient separation between the ISTD peak and the sulfur target signals. The standard of choice in this study is 2-bromothiophene. For the ISTD method the standard was added at 20 ppm S, whereas in the standard addition setup, the 2-bromothiophene concentrations were in the range from 2 to 6 ppm, knowing that the sulfur sample investigated had a low ppm sulfur content.

■ Results

Using an analytical column, its compound separation enables the observation of individual sulfur species in a certain sample. Fig 1 shows the chromatograms of three diesel samples with low, medium, and high sulfur contents, predetermined by a total sulfur analyzer. The total sulfur content is determined as sum of the individual compound groups being integrated. The longer analysis time of this setup limits the sample throughput but allows for a thorough investigation of the sulfur pattern. Care should be taken about the column performance to ensure reliable quantitation of low ppm sulfur samples.

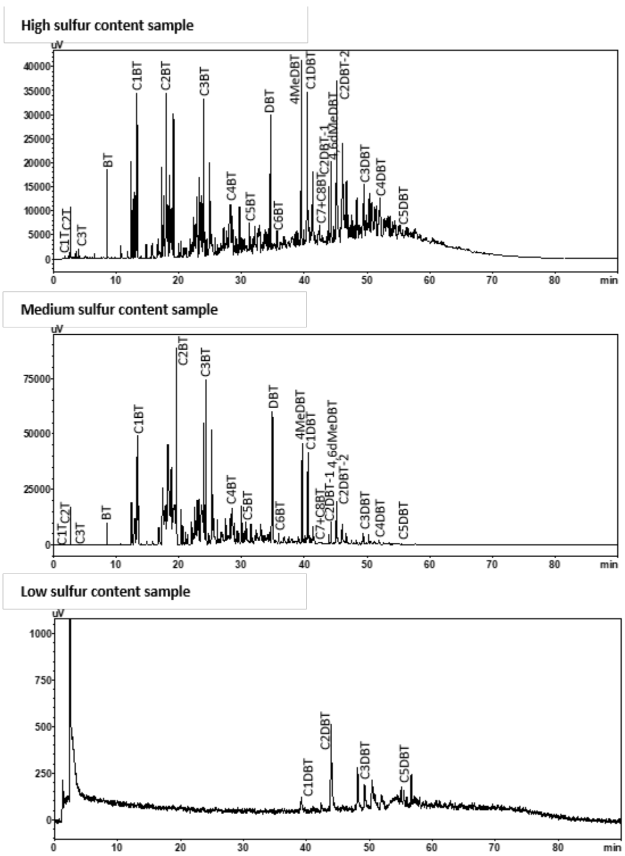

Fig. 1 Chromatograms of high, medium, and low sulfur content samples analyzed with the analytical column setup

Using a short tubing without stationary phase, all sulfur compounds elute as one peak (Fig. 2). This drastically shortens the chromatographic runtime increasing sample throughput. It facilitates the quantitation of very low sulfur content samples, making it beneficial especially for low ppm S samples, but compromises the sulfur pattern information.

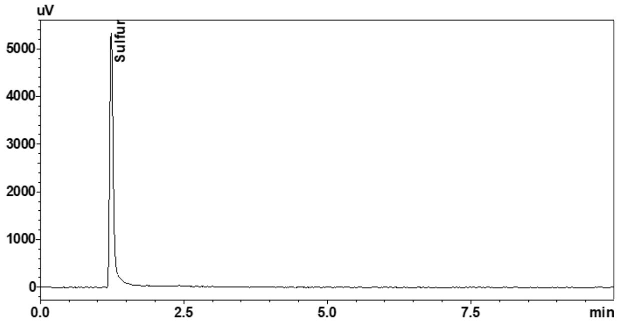

Fig. 2 Low sulfur content sample analyzed with the short tubing setup

Table 1 summarizes the sulfur contents found for the diesel samples, additionally stating the values measured for the samples via Total Sulfur Analyzer (TSA). The SCD approaches give the same result for the low sulfur content sample and show a deviation of 5.1 % from the TSA result. Independent of the sulfur content value the SCD analysis gives values within 10% deviation of the TSA result, proving the reliability of the total sulfur determination via sulfur chemiluminescence detection.

Table 1 Total sulfur content results in the diesel samples

	TSA	SCD w column	SCD w tubing
Total sulfur low content sample	7.9 mg/kg	8.3 mg/kg	8.3 mg/kg
Total sulfur medium content sample	5040 mg/kg	5298 mg/kg	-
Total sulfur high content sample	11100 mg/kg	12128 mg/kg	-

The analytical column approach additionally reveals the sulfur content per compound group (table 2).

Table 2 Sulfur content values per compound group determined with the analytical column setup

Compound groups	High S content sample	Medium S content sample	Low S content sample
Thiophene, sulfurs, mercaptans	1	n.d.	0.3
C1 thiophenes	2	1	n.d.
C2 thiophenes	10	n.d.	n.d.
C3+ thiophenes	58	3	n.d.
Benzothiophene	59	21	n.d.
C1 benzothiophenes	507	544	n.d.
C2 benzothiophenes	767	1327	n.d.
C3 benzothiophenes	967	1173	n.d.
C4 benzothiophenes	646	533	n.d.
C5 benzothiophenes	689	411	n.d.
Dibenzothiophene	n.d.	195	n.d.
C6 benzothiophenes	693	198	n.d.
4M dibenzothiophene	234	148	n.d.
C1 dibenzothiophenes (w/o 4M)	623	250	0.1
C7+C8 benzothiophenes	425	38	n.d.
4,6DM dibenzothiophene	141	32	n.d.
C2 dibenzothiophenes (w/o 4,6DM)	1518	248	0.8
C3 dibenzothiophenes	1237	94	1.1
C4 dibenzothiophenes	980	46	n.d.
C5+ dibenzothiophenes	2410	34	5.9

Fig. 3 Nexis™ GC-2030 equipped with Nexis SCD-2030 detector

■ The Package

The recommended analytical hardware and software configuration is listed below.

❑ *Main Unit*

Nexis GC-2030 plus Nexis SCD-2030: Gas chromatograph plus sulfur chemiluminescence detector

❑ *Accessory*

AOC™-30i autosampler: Liquid autosampler with 30 vials capacity

❑ *Main Consumables*

SH-1 column (30 m x 0.32 mm x 1 µm; P/N 227-36099-01)

Non-polar Fused Silica tubing (15 m x 0.2 mm; Merck, P/N 25755)

❑ *Software*

LabSolutions™ LC/GC

■ Conclusion

Sulfur chemiluminescence detection using Nexis SCD-2030 enables the reliable determination of the total sulfur content in petrochemical samples. A retention gap approach offers fast investigation of the total sulfur amount, whereas a separation column approach allows for the additional detection and quantitation of individual sulfur compounds revealing the sample's sulfur pattern.

■ Acknowledgements

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TotalEnergies

■ References

1) R. L. Tanner, J. Forrest, L. Newman, "Determination of atmospheric gaseous and particulate sulfur compounds. [Atmospheric SO_2 sampling, calibration, and data processing]," Brookhaven National Laboratory, Upton, NY, USA, Tech. Rep. BNL-23103. Jan. 1977.
2) X. Yan, "Unique selective detectors for gas chromatography: Nitrogen and sulfur chemiluminescence detectors," J. Sep. Sci., vol. 29, pp. 1931-1945, Jun. 2006.
3) S. C. Bajia, R. J. Singh, B. Bajia, S. Kumar, "Determination of sulfur content in petroleum products – an overview," J. Sulfur Chem, vol. 38, pp. 450–464, Feb. 2017.

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