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Application News

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 H_2S poses by itself, they are responsible of atmospheric pollutions (SO_2 and SO_3) [(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.

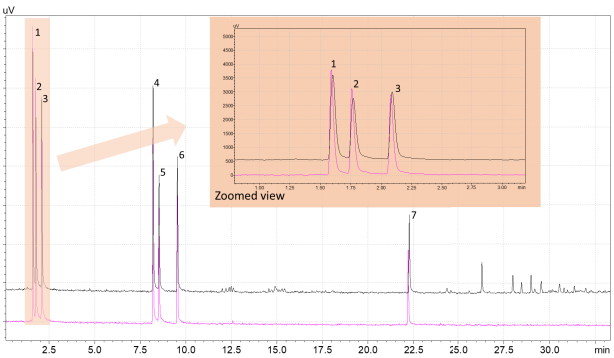

Fig. 2 Comparison view of the chromatograms for level 1 sulfur standard in desulfurized diesel matrix (black) and hexane solvent matrix (pink), chromatograms are base shifted for better visibility

• 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 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.

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

• 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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