ANALYSIS OF SULPHUR IN LIGHT HYDROCARBONS ACCORDING TO ASTM D5623 USING SHIMADZU'S SCD-2030

Sulphur in fossil fuels generates environmentally-harmful sulphur oxides within exhaust gases as a byproduct of combustion. As a result, the concentration of sulphur in common fuels is regulated to 10 ppm or less in many major countries. Regulations on the concentration of sulphur in fuel are becoming increasingly strict in developing countries, and stricter quality control of sulphur concentration in fuel is required worldwide.

Analysis of the sulphur content of fuels is critical to ensuring quality and meeting environmental regulations. Sulphur oxides produced during combustion of fossil fuels reacts with atmospheric water to generate acid rain and can also cause respiratory problems in the humans.

The EDXRF method specified in ASTM D4294 is useful for the screening analysis of sulphur compounds at relatively high concentrations, such as marine fuel, but gas chromatography (GC) methods are preferred for the detailed, trace analysis of sulphur compounds. Two common detection methods include Flame Photometric Detector (FPD) and Sulphur Chemiluminescence Detector (SCD). Although both are widely used in the petrochemical industry, SCD demonstrates increased selectivity sensitivity for sulphur, provides a linear and equimolar response, and does not suffer from matrix quenching when compared to FPD.

Method

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

Table 1 shows the details of the instrument configuration and analytical conditions used for all analyses.

To prevent adsorption of sulphur compounds on the injector at low concentrations, a sample vaporisation injector SPL-2030 was subject to deactivation treatment and installed on the system.

LabSolutions GC was used for instrument control, as well as data collection and processing. Automation functions within the software ensure ease of start-up and shut-down of the GC-2030 and SCD-2030.

Repeatability and Linearity Evaluation

19 discrete sulphur compounds were diluted to 0.1 ppm, 1 ppm, 10 ppm, and 100 ppm (w/w), according to ASTM D5623.

The 19 compounds were separated into two groups for optimal chromatographic separation. Ten compounds were diluted in toluene to yield STD 1 and the remaining 9 compounds were diluted in n-hexane to yield STD 2. Diphenyl sulphide was added to each standard at a concentration of 1 ppm as an internal standard. Chromatograms of the STD 1 and STD2 are shown in Figure 1.

Note *– STD 1 and STD 2 concentrations are concentration of the sulphur-containing compound, and the concentrations of STD 3 shown below are concentrations of sulphur itself to assess long-term stability and equimolar response.*

Table 1: Instrument configuration and analytical conditions

Main Unit	Nexis GC-2030 /AOC-20i plus
Column	SH-Rxi-1MS (30 m x 0.32 mm I.D. df= 4 µm)
Detector	Nexis 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 12 mL/min, O_3 25 mL/min

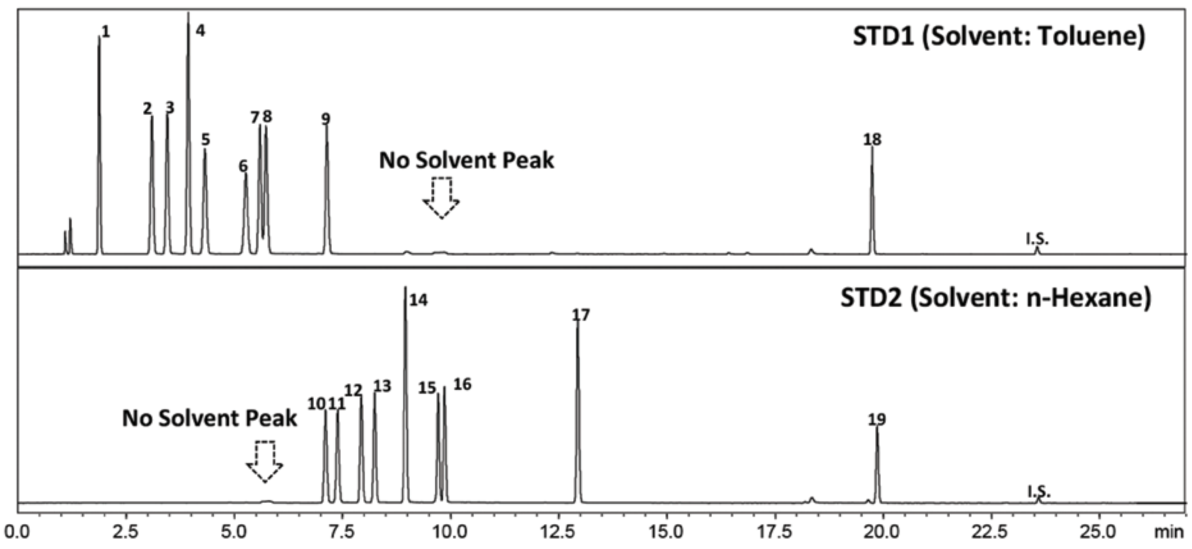

Figure 1: Chromatograms of 19 sulphur compounds (10 ppm)

Table 2: Repeatability and Linearity of sulphur compounds

No.	Analytes	0.1 ppm	1 ppm	10 ppm	100 ppm	STD No.	R^2 (0.1-100ppm)
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 sulphide	6.8%	1.3%	3.7	2.4	1	0.9999
4	Carbon disulphide	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 sulphide	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 sulphide	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 disulphide	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 disulphide	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

Table 2 contains the repeatability (% RSD, n=5) and coefficient of determination (R^2) for the sulphur compounds analysed using the Nexis SCD-2030. The area ratio value of the target compound relative to the internal standard was used in this evaluation to normalise for instrumental drift. The low RSD values and R^2 values at or near 1.0 demonstrate the high repeatability and linearity of the Nexis SCD-2030.

Long-term Stability Evaluation

Long-term stability of the detector is a key measure of performance that directly impacts data reliability. The Nexis SCD-2030 is configured with the industry's first horizontal redox cell, which promotes the oxidation-reduction reaction of samples by ensuring sufficient reaction area and reaction time in the cell to achieve stable analysis.

To assess long-term stability of the SCD-2030, a standard (STD 3) containing 10 ppm (w/w) of all 19 sulphur compounds shown in Table 2 was analysed repeatedly over 16 days. As an internal standard, 1 ppm Diphenyl sulphide was added to the sample.

Figure 2 illustrates the results of relative response factor for four components in STD 3 with different boiling points (1-Butanethiol, Methyl disulphide, Diethyl disulphide, 3- Methylbenzothiophene with boiling points ranging from 98°C to 273°C). Each plot represents the mean value of the analysis result for each day, and the error bar represents the value of three standard deviations (3σ).

The relative standard deviations of the relative response factors for 1-Butanethiol, Methyl disulphide, Diethyl disulphide and 3-Methylbenzothiophene were 1.4%, 1.2%, 1.9%, and 1.6% respectively. The relative response factor for each day did not deviate more than three standard deviations.

The results of this evaluation demonstrate excellent long-term stability with minimal variation day-over-day. The Nexis SCD-2030 not only provides a stable relative response but also a stable absolute response over an extended time.

Equimolar Response Evaluation

The relative area ratio of sulphur compounds was evaluated via ASTM D5623 and calculated based on equation 1. Using the analytical conditions outlined in ASTM D5623, various sulphur compounds at a sulphur concentration of 10 ppm (w/w) were measured, and the relative area ratio for each component was calculated with respect to the area value for diphenyl sulphide.

Equation 1: Relative response factor (R_{rn}) for given compound calculated where C_n = concentration of sulphur in compound, A_r = peak area of reference standard, C_r = concentration of sulphur in reference standard, and A_n = peak area of compound.

$$R_{rn} = \frac{C_n \times A_r}{C_r \times A_n}$$

Table 3 illustrates the relative area ratio of sulphur compounds. The results of this evaluation show that regardless of the compound, the Nexis SCD-2030 gave a similar response. This demonstrates that oxidation and detection of sulphur in the SCD-2030 is not preferential to any compound and the detector yields an equimolar response. This is critical to ensuring accurate quantitation across a variety of compounds and their boiling points.

Conclusion

The Nexis SCD-2030 shows excellent linearity and repeatability for all sulphur compounds tested. Additionally, the Nexis SCD-2030 demonstrates excellent long-term stability, ensuring quality analyses day-over-day.

The Nexis SCD-2030 is compliant with ASTM D5623 and other trace sulphur analysis standards for petroleum products, such as ASTM D5504. The dramatically enhanced sensitivity and reliability, the ease of maintenance, and the industry-first automation functions will improve laboratory productivity.

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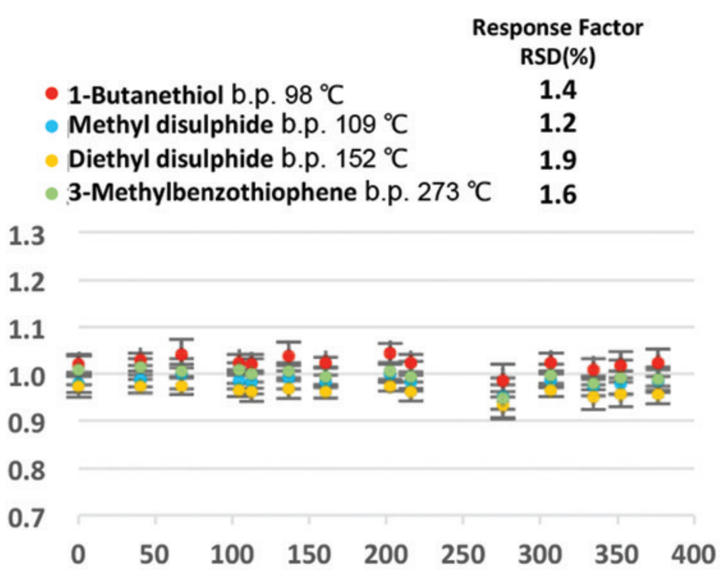

Figure 2: Relative Response Factors over 16 days

Table 3: Relative area ratio of sulphur compounds

sulphur Compounds	Relative Area Ratio
Thiophene	1.07
2-Methyl-1-propanethiol	1.07
Diethyl sulphide	1.03
1-Butanethiol	1.01
Methyl disulphide	0.97
2-Methylthiophene	1.08
3-Methylthiophen	0.96
Diethyl disulphide	0.97
5-Methylbenzothiophene	0.94
3-Methylbenzothiophene	1.01
Diphenyl sulphide (Internal Standard)	1.00

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