

Application Note

NSX-5000V/SD

Jun. 2022 v.1



- **Total sulfur in liquid petroleum products by UVFL according to ASTM D5453**
 - **Easy automatic measurement**
 - **Employed using different standard test methods**

Keyword:

ASTM D5453/D7183

DIN EN ISO 20846, JIS K2541-6

UVFL, Sulfur, Biofuels, Diesel, Gasoline, Jet fuel

Sulfur oxides contained in automobile exhaust gases cause acid rain and lead directly to environmental load. It is necessary to reduce and manage sulfur compounds in petroleum products. NSX-5000V/SD allows rapid and fully automated determination of total sulfur in these materials.

- **Scope**

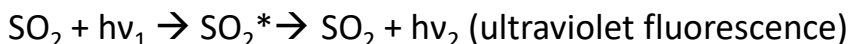
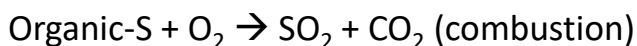
ASTM D5453 is an established test method for the determination of total sulfur in liquid hydrocarbons containing 1.0 to 8000 mg/kg-S, boiling in the range from approximately 25 to 400 degC and with viscosities between approximately 0.2 and 20 cSt (mm²/s) at room temperature. This test method is applicable to the liquid hydrocarbons containing less than 0.35 wt% of halogen(s).

- **Relevant standard**

ASTM D5453/D7183
UOP 987 Part-A
DIN EN ISO 20846/EN 15486
JIS K2541-6

- **Outline of method**

The sample is injected into a high temperature combustion tube where the sulfur is oxidized to sulfur dioxide (SO₂) in an oxygen rich atmosphere. The sample combustion gases are next exposed to ultraviolet (UV) light. The SO₂ absorbs the energy from the UV light and is converted to excited sulfur dioxide (SO₂*). The fluorescence emitted from SO₂* as it returns to a stable state, SO₂, is detected by a photomultiplier tube and the resulting signal is a measure of the sulfur contained in the sample.



- **Preparation**

System: NSX-5000V/SD with ASC-550L

Reagents and samples:

Dibutyl sulfide, >98.0%(CAS 544-40-1) Tokyo Chemical Industry

Dibutyl disulfide, 99.5+%(CAS 629-45-8) FUJIFILM Wako Pure Chemical

Isooctane, GR (CAS 540-84-1) FUJIFILM Wako Pure Chemical

Toluene, GR (CAS 108-88-3) FUJIFILM Wako Pure Chemical

Commercially available Solvents, Kerosene, Gasoline, Diesel oil, Biodiesel, Jet aviation fuel, Engine oil and others

Method Description



Method Parameters

Table 1: Parameters

Furnace temperature	Inlet 900 degC
	Outlet 1000 degC
Gas flow	Ar 100 mL/min
	O ₂ 500 mL/min
ASC-550L	Injection rate 1.2 μL/sec
Integration time	300 sec max.
Calibration standard	Dibutyl sulfide in isooctane or toluene
Sample volume	2 - 90 μL

Calibration

The calibration of the NSX-5000V/SD was carried out by different concentrated liquid standards (0 to 1000 mg/L), based on dibutyl sulfide in isooctane standards. Each calibration solution and blank is measured three times. Although the NSX-5000V/SD system is linear in response in the range from 0 to 1000 mg/L, typical calibration curves have been created according to the suggested ranges in ASTM D5453 (Fig.1).

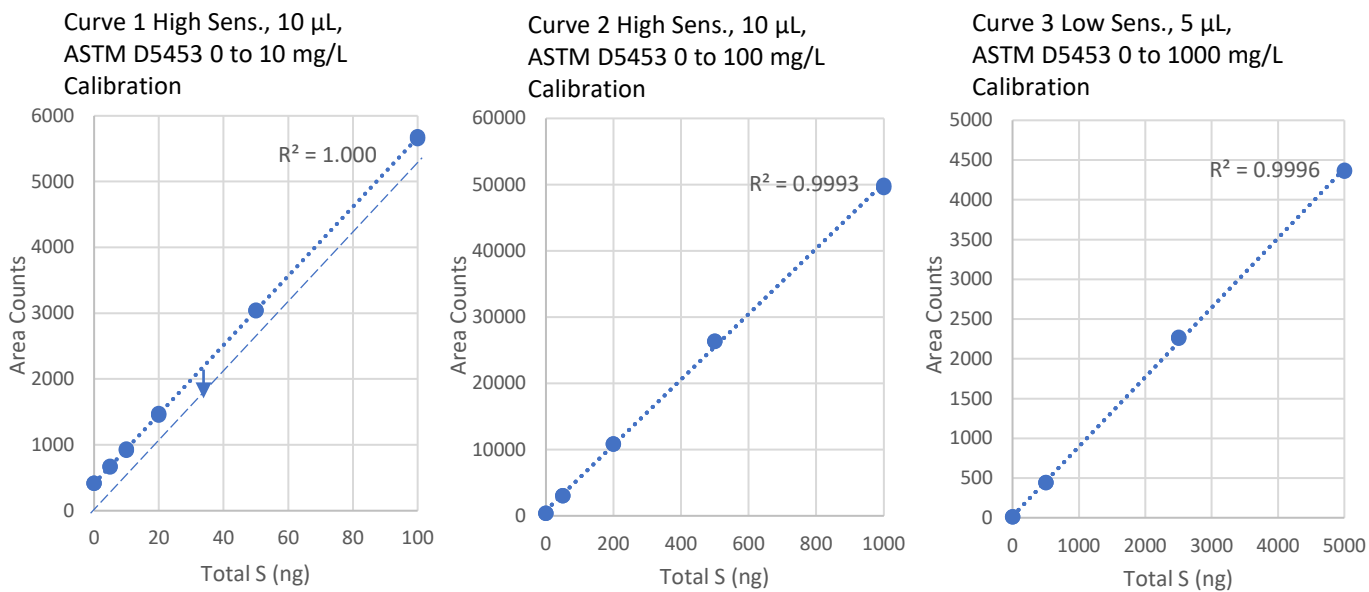


Fig.1: Calibration curve and its linearity

All above use standard of dibutyl sulfide in isooctane. In case high blank value due to the solvent specimen, NSX-5000 enables to set shifted regression line as a calibration curve which is set intercept at 0 to avoid negative leverage as in Curve 1.



• LOQ and quantification range

To calculate LOQ (limit of quantification), one needs to calibrate it at 0 to 1 mg/L of calibration curve with 90 μ L injection. Each level shall be conducted in 5 times of repeated analysis and 10 times of blank analysis. From 10 times of standard deviation value of blank and gradient of the curve, LOQ is calculated at 0.02 mg/L-Sulfur (2 ng-S).

Upper limit of quantification is confirmed and calculated by the calibration curve at 2000, 5000 and 10000 mg/L-Sulfur with 2 μ L injection. From the data of 3 times analysis for each level, NSX-5000V/SD performs good coefficient of determination and repeatability with this range. It shows availability of quantification range as 2 to 20000 ng of Sulfur.

• Repeatability

Two samples were analyzed 10 times with 10 μ L of injection in a row to determine standard deviation (SD). As shown in Table 2, repeatability (r) is well within the repeatability limit stated in ASTM D5453.

Table 2: Overview of repeatability, High Sens.

Measurement	1	2	...	9	10	Average \pm SD	r (SD x 2.77)	r _{D5453}	Within limit
Biodiesel 1	9.49	9.40	9.44	9.42	9.44 \pm 0.08 mg/kg	0.22 mg/kg	0.96 mg/kg	Yes
Gasoline 1	36.9	36.8	38.0	37.9	37.5 \pm 0.6 mg/L	1.7 mg/L	2.7 mg/L	Yes

• Sample scope and reproducibility

Different types of samples were selected to cover the scope of the method. To obtain one result, each sample is measured 3 times, and the average detector response is calculated. The results are compared with reference values provided by the authority. All sample results which have target values are within the reproducibility limit stated in ASTM D5453 as shown in Table 3. ASTM D7183, UOP 987 Part-A, DIN EN ISO 20846/EN 15486 and JIS K2541-6 will be able to perform on NSX-5000V/SD also as in table 4 with an appropriate calibration curve.

Table 3: Overview of reproducibility, High Sens., 10 μ L

Measurement	Target	Result	Delta	R _{D5453} /√2	Within limit
Kerosene by NIST	8.41 mg/kg	8.30 mg/kg	0.11 mg/kg	2.0 mg/kg	Yes
Diesel oil by JPI	49.8 mg/kg	50.4 mg/kg	0.6 mg/kg	7.7 mg/kg	Yes
Gasoline 2 by NIST	40 mg/kg	42.9 mg/kg	2.9 mg/kg	6.7 mg/kg	Yes

Table 4: Overview of sample results

Measurement	Sens.	Volume	Average \pm SD
Dibutyl disulfide in Toluene	High	10 μ L	4.91 \pm 0.10 mg/L
Biodiesel 2 (Palm)	High	10 μ L	6.79 \pm 0.05 mg/kg
Jet aviation fuel	Low	5 μ L	474 \pm 5 mg/kg
Engine oil, diluted by isooctane	Low	5 μ L	2013 \pm 11 mg/kg
Heavy oil, diluted by isooctane	Low	5 μ L	0.232 \pm 0.000 wt%



• Analytical chart

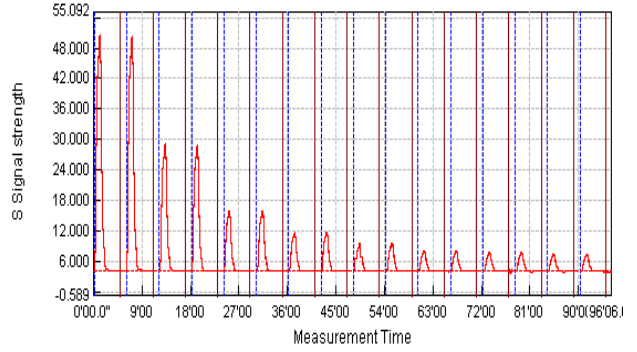
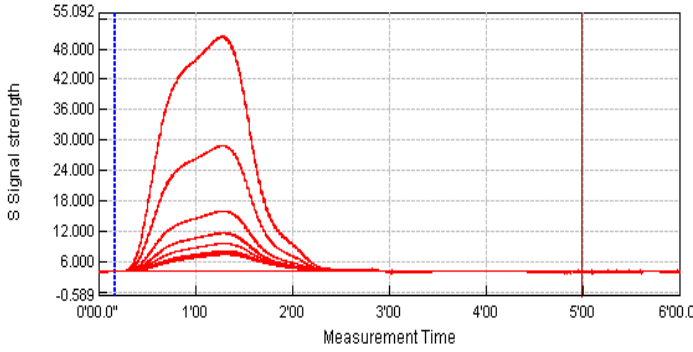


Fig.2: Curve 1 High Sens., 10 µL, ASTM D5453 0 to 10 mg/L Calibration

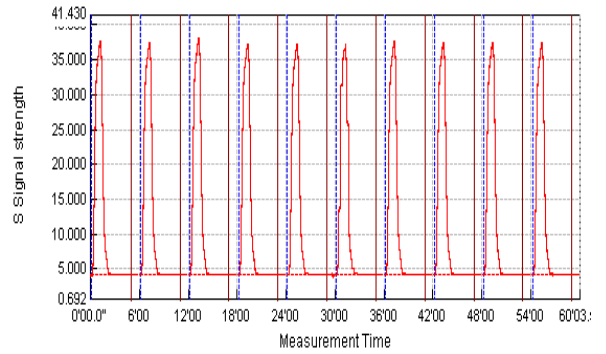
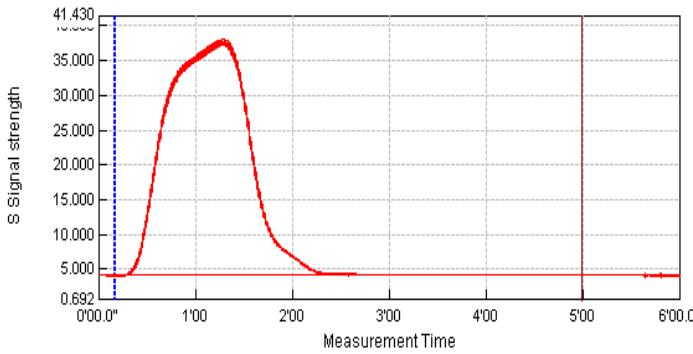


Fig.3: Repeatable Biodiesel 1 Analysis (n=10), High Sens., 10 µL

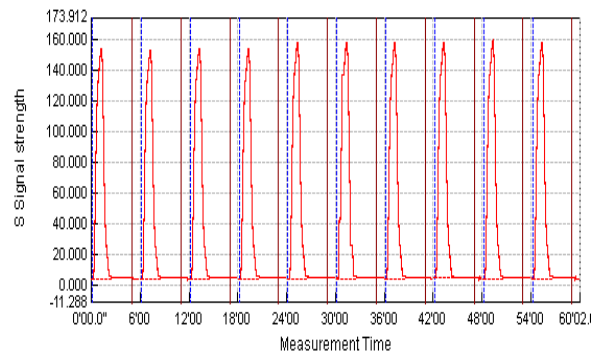
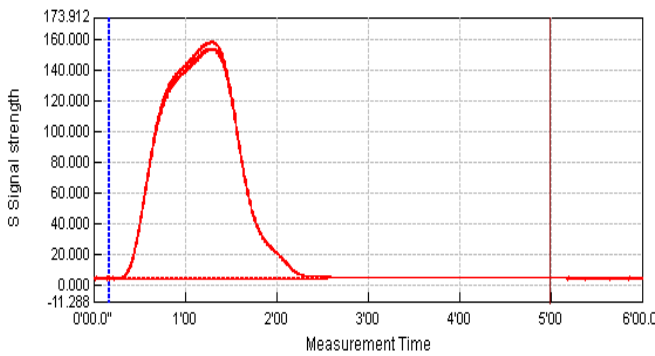


Fig.4: Repeatable Gasoline 1 Analysis (n=10), High Sens., 10 µL

Summary



- **Conclusions about NSX-5000V/SD**
- A wide range of quantification up to 10^4 ng of Sulfur
Measuring range: 2 to 20,000 ng-S
- Able to perform for linearity, precision and accuracy conforming to ASTM D5453 and other related methods as ASTM D7183, UOP 987 Part-A, DIN EN ISO 20846 and JIS K2541-6.
Tested with samples, covering the range of products as defined in the scope, show good agreement with the reference values.

- **Specification**

Samples	Liquid
Analytical method	Oxidative combustion and UV fluorescence detection
Furnace	Max.1,100°C, Openable electric furnace, 2-section type
Measuring range	2 to 20,000 ng of Sulfur LOQ: 0.02 mg/L
Sample size	Liquid : max. 200 μ L
Measuring time	Less than 3 min
Gas	Argon: Purity 99.98 % or more, 0.3 ± 0.1 MPa Oxygen: Purity 99.7 % or more, 0.3 ± 0.1 Mpa
Dimensions	VF-500: 500(W) x 430(D) x 500(H)mm, approx. 35 kg SD-500: 220(W) x 375(D) x 500(H), approx. 21 kg ASC-550L: 460(W) x 320(D) x 470(H), approx. 16 kg

Note: *This sheet is provided as a reference and does not guarantee analytical values. Optimal conditions may vary depending on external factors such as the environment of analysis or the nature of the sample. Follow instructions in manuals to install, connect and operate the instruments correctly.
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