

Application Note

NSX-5000V/ND

Jun. 2022 v.1



- **Total nitrogen in liquid petroleum products by CLD according to ASTM D4629**
 - Easy automatic measurement
 - Employed using different standard test methods

Keyword:

ASTM D4629/D6069/D7184

DIN 51444, JIS K2609

**Chemiluminescence, CLD, Nitrogen,
Petroleum hydrocarbons, Biofuels, Gasoline, Heavy oil**



Introduction

In order to realize a sustainable environment, it is necessary to grasp and reduce the amount of nitrogen compounds emitted into the atmosphere and water.

NSX-5000V/ND helps reduce the environmental burden by measuring and managing the nitrogen content in raw materials or emissions.

- **Scope**

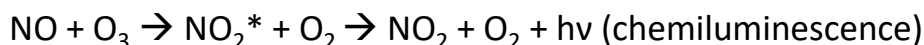
ASTM D4629 covers the determination of the trace total nitrogen found in liquid hydrocarbons containing 0.3 to 100 mg/kg-N, boiling in the range from approximately 50 to 400 degC and with viscosities between approximately 0.2 and 10 cSt (mm²/s) at room temperature. This test method is applicable to naphtha, distillates, and oils.

- **Relevant Standard**

ASTM D4629/D6069/D7184
UOP 971/981
DIN 51444, JIS K2609

- **Outline of Method**

The sample of liquid petroleum hydrocarbon is introduced either by syringe or boat inlet system, into a stream of inert gas (helium or argon). The sample is vaporized and carried to a high temperature zone where oxygen is introduced and organically bound nitrogen is converted to nitric oxide (NO). The NO contacts ozone and is converted to excited nitrogen dioxide (NO₂*). The light emitted as NO₂* decays is detected by a photomultiplier tube and the resulting signal is a measure of the nitrogen contained in the sample.



- **Preparation**

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

Reagents and samples:

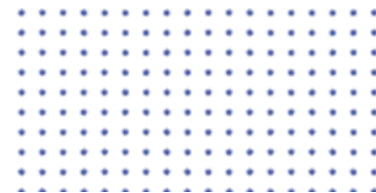
Pyridine, 99.5+%, Infinity Pure(CAS 110-86-1) FUJIFILM Wako Pure Chemical

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

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

Commercially available Solvents, Gasoline, Biodiesel, Jet aviation fuel, Engine oil and Heavy oil

Method Description



Method Parameters

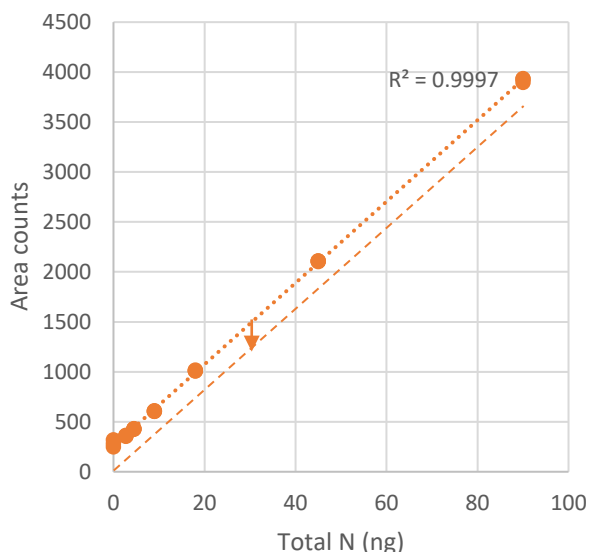
Table 1: Parameters

| | |
|-----------------------------|----------------------------------|
| Furnace temperature | Inlet 800 degC |
| | Outlet 900 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 | Pyridine in isooctane or toluene |
| Sample volume | 2 - 90 μL |

Calibration

The calibration of the NSX-5000V/ND was carried out by different concentrated liquid standards (0 to 100 mg/L), based on pyridine in isooctane standards. Each calibration solution and blank is measured three times. Typical calibration curves have been created according to the range of sample concentration as shown in Fig.1.

Curve 1 High Sens., 90 μL,
0 to 1 mg/L Calibration



Curve 2 High Sens., 20 μL,
0 to 100 mg/L Calibration

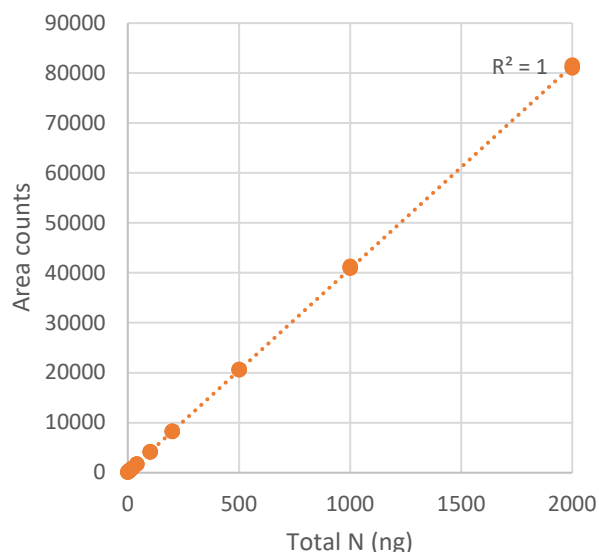


Fig.1: Calibration curve and its linearity

All above use standard of pyridine 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 0.03 mg/L-Nitrogen (3 ng-N).

Upper limit of quantification is confirmed and calculated by the calibration curve at 2000, 5000 and 10000 mg/L-Nitrogen with 2 μ L injection. From the data of 5 times analysis for each level, NSX-5000V/ND performs good coefficient of determination and repeatability with this range. It shows availability of quantification range as 3 to 20000 ng of Nitrogen.

• Repeatability

Two samples were analyzed 10 times with 20 μ L of injection in a row to determine standard deviation (SD). As shown in Table 2, repeatability (r) is well within the limit stated in the ASTM D4629.

Table 2: Overview of repeatability, High Sens.

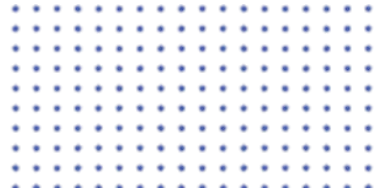
| Measurement | 1 | 2 | ... | 9 | 10 | Average \pm SD | r (SD \times 2.77) | r_{D4629} | Within limit |
|-------------|------|------|------|------|------|----------------------|---------------------------|-------------|--------------|
| Biodiesel 1 | 28.6 | 28.9 | | 28.1 | 28.0 | 28.4 \pm 0.3 mg/kg | 0.8 | 1.0 | Yes |
| Gasoline 1 | 15.5 | 15.4 | | 15.4 | 15.3 | 15.4 \pm 0.1 mg/L | 0.3 | 0.7 | Yes |

• Sample scope

Different types of samples were selected to cover the scope or other methods. To obtain one result, each sample is measured 3 times, and the average detector response is calculated. ASTM D6069/D7184, UOP 971/981, DIN 51444 and JIS K2609 will be able to perform on NSX-5000V/ND also as in Table 3 with an appropriate calibration curve.

Table 3: Overview of sample results

| Measurement | Sens. | Volume | Average \pm SD |
|--------------------------------|-------|------------|-----------------------|
| Heavy oil, diluted by toluene | High | 20 μ L | 0.060 \pm 0.001 wt% |
| Engine oil, diluted by toluene | High | 20 μ L | 595 \pm 5 mg/kg |
| Pyridine in toluene | High | 20 μ L | 0.60 \pm 0.01 mg/L |
| Gasoline 2 | High | 20 μ L | 0.15 \pm 0.02 mg/kg |
| Biodiesel 2 (Palm) | High | 20 μ L | 2.64 \pm 0.03 mg/kg |
| Jet aviation fuel | High | 20 μ L | 3.51 \pm 0.02 mg/kg |



• Analytical chart

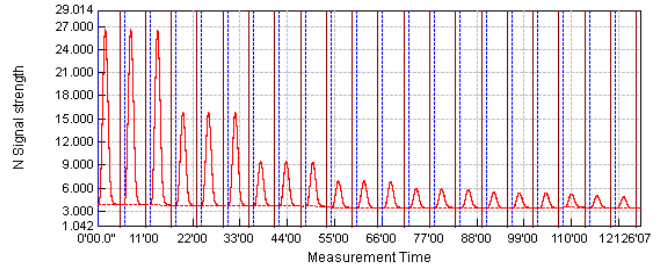
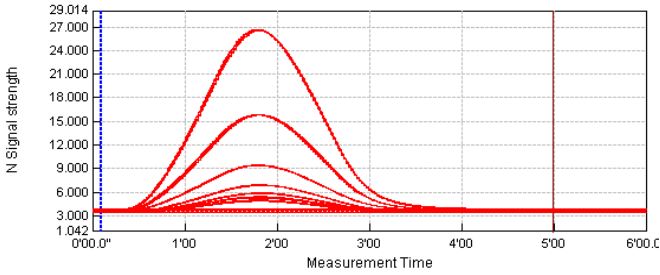


Fig.2: Curve 1 High Sens., 90 μ L, 0 to 1 mg/L Calibration

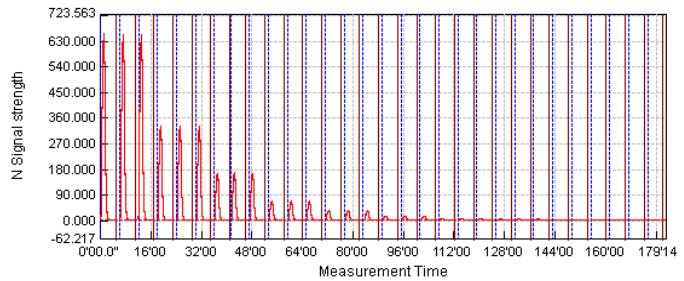
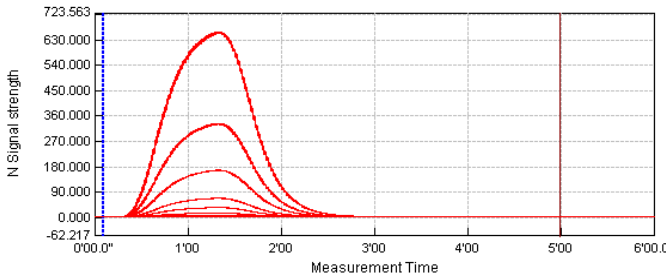


Fig.3: Curve 2 High Sens., 20 μ L, 0 to 100 mg/L Calibration

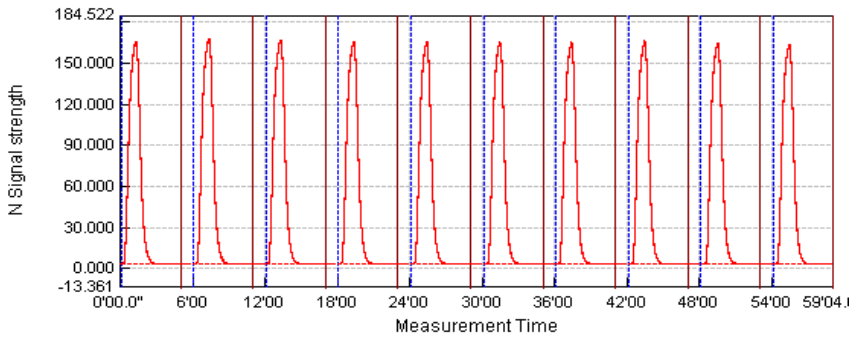


Fig.4: Repeatable Biodiesel 1 Analysis (n=10), High Sens., 20 μ L

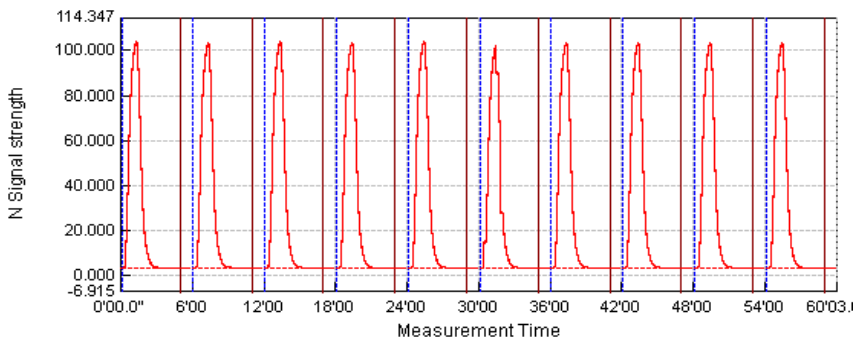


Fig.5: Repeatable Gasoline 1 Analysis (n=10), High Sens., 20 μ L

Summary



- **Conclusions about NSX-5000V/ND**
- A wide range of quantification up to 10^4 ng of Nitrogen
Measuring range: 3 to 20,000 ng-N
- Able to perform for linearity, precision and accuracy conforming to ASTM D4629 and other related methods as ASTM D6069/D7184, UOP 971/981, DIN 51444 and JIS K2609.
Tested with samples, covering the range of products as defined in the scope, show good agreement with the reference value.
- **Specification**

| | |
|--------------------|---|
| Samples | Liquid |
| Analytical method | Oxidative combustion and chemiluminescence detection |
| Furnace | Max. 1,100 °C, Openable electric furnace, 2-section type |
| Detector and range | 3 to 20,000 ng of Nitrogen LOQ: 0.03 mg/L |
| Sample size | Liquid : max. 200 μ L |
| Measuring time | Less than 3 min |
| Gas | Argon: Purity 99.98% or higher, 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), approx. 35 kg ND-500: 220(W) x 375(D) x 500(H), approx. 22 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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