



A Honeywell Company

Trace Nitrogen in Liquid Hydrocarbons by Oxidative Combustion with Chemiluminescence Detection

UOP Method 981-14

Scope

This method is for determining nitrogen in liquid hydrocarbons at concentrations ranging from 30 to 600 ng/g (mass-ppb). It is applicable to highly volatile samples, such as pentane, through the use of a cooled sampling system. Higher concentrations can be determined by ASTM Methods D4629, "Trace Nitrogen in Liquid Petroleum Hydrocarbons by Syringe/Inlet Oxidative Combustion and Chemiluminescence Detection," D6069, "Trace Nitrogen in Aromatic Hydrocarbons by Oxidative Combustion and Reduced Pressure Chemiluminescence Detection," and D7184, "Ultra Low Nitrogen in Aromatic Hydrocarbons by Oxidative Combustion and Reduced Pressure Chemiluminescence Detection," using the cooled sampling system described herein for highly volatile matrices. Halogens and sulfur interfere at concentrations greater than approximately 1%.

References

ASTM Method D4052, "Density and Relative Density of Liquids by Digital Density Meter," www.astm.org

ASTM Method D4629, "Trace Nitrogen in Liquid Petroleum Hydrocarbons by Syringe/Inlet Oxidative Combustion and Chemiluminescence Detection," www.astm.org

ASTM Method D6069, "Trace Nitrogen in Aromatic Hydrocarbons by Oxidative Combustion and Reduced Pressure Chemiluminescence Detection," www.astm.org

ASTM Method D7184, "Ultra Low Nitrogen in Aromatic Hydrocarbons by Oxidative Combustion and Reduced Pressure Chemiluminescence Detection," www.astm.org

Jones, B.M. and Daughton, C.G., *Anal. Chem.*, **57**, 2320-2325 (1985)

UOP Method 999, "Precision Statements in UOP Methods," www.astm.org

Outline of Method

A commercial instrument is set up and calibrated with liquid standards. For samples containing volatile components such as pentane, a temperature control system must be used to stabilize the temperature of the sample tray and the syringe at 15 °C. Using an autosampler, the sample is directly injected into the combustion tube where it vaporizes into an argon carrier and is mixed with oxygen at high temperature. The organic material is converted to carbon dioxide and water. The nitrogen in the sample is converted to nitric oxide. This is further reacted in the detector with ozone to produce

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nitrogen dioxide in an excited state. The excited state nitrogen dioxide molecules relax to the ground state, producing light (chemiluminescence), which is detected by a photomultiplier tube. The signal is proportional to the total nitrogen in the sample. The detector is operated at reduced pressure to decrease the probability of excited state nitrogen dioxide molecules colliding with other molecules before emitting light, thus increasing sensitivity and signal-to-noise ratio.

This procedure has a low sensitivity to diatomic nitrogen (N_2), but only during the combustion of the hydrocarbon and has reduced sensitivity to compounds with nitrogen-nitrogen bonds that decompose to produce nitrogen gas. The relative responses of some nitrogen compounds have been determined and tabulated by Jones and Daughton.

Apparatus

References to catalog numbers and suppliers are included as a convenience to the method user. Other suppliers may be used.

Balance, analytical, readable to 0.0001 g

Flasks, volumetric, Class A, borosilicate glass, 100- and 250-mL, Fisher Scientific, Cat. Nos. 10-210-8C and -8E, respectively

Nitrogen Chemiluminescence Analyzer, with attached furnace, autosampler, vacuum pump, controls and computer. This method was developed and validated using the Mitsubishi analyzer, Model TS-100V, with ND-100 Nitrogen Detector and STC-210 Sample Temperature Controller, Mitsubishi Chemical Analytech, available from COSA Instrument. It has also been validated on the Mitsubishi NSX-2100V, with ND-210 Nitrogen Detector and STC-210 Sample Temperature Controller. The procedure for analysis may be different for other instruments and all other instruments need to be validated before using for this method.

The Mitsubishi analyzer must be equipped with the following accessories:

Autosampler, Mitsubishi Model ASC-150L or ASC-250L, COSA Instrument

Autosampler syringes, gas tight, 100- μ L, Mitsubishi, Cat. No. MSSG10, COSA Instrument

Autosampler vials, rinse, Mitsubishi Cat. No. TX3LSW, COSA Instrument. These are also used as pre-fill vials and wash bottles, see *Preparation of Apparatus*.

Membrane drier, Perma Pure, Model MD-110-24F-4 or Mitsubishi Tube Dryer, Cat. No. TN6RPC, COSA Instrument (see *Note 1*)

Sample temperature controller, Mitsubishi Model STC-210, COSA Instrument

Vacuum pump, Vacuubrand, Model MD4CNT and Ulvac GLS-050 vacuum pumps meet this requirement; other vacuum pumps must be evaluated before use, COSA Instrument (see *Note 2*)

Pipet, volumetric, Class A, 0.5-, 1-, 2-, and 5-mL, Fisher Scientific, Cat. No. 13-650-2A, -2B, -2C, and -2F, respectively

Pipet filler, VWR, Cat. No. 53497-055

Refrigerator, laboratory, explosion proof or flammable storage, Fisher Scientific, Cat. No. 97-950

Regulator, argon, single-stage, with stainless steel diaphragm, delivery pressure range 30-700 kPa (4-100 psi), Matheson Tri-Gas, Cat. No. 3231. This regulator is installed downstream of the two-stage regulator to provide better flow control.

Regulator, argon, two-stage, with stainless steel diaphragm, delivery pressure range 30-700 kPa (4-100 psi), Matheson Tri-Gas, Cat. No. 3104-580

Regulator, oxygen, single-stage, with stainless steel diaphragm, delivery pressure range 30-700 kPa (4-100 psi), Matheson Tri-Gas, Cat. No. 3231. This regulator is installed downstream of the two-stage regulator to provide better flow control.

Regulator, oxygen, two-stage, with stainless steel diaphragm, delivery pressure range 30-700 kPa (4-100 psi), Matheson Tri-Gas, Cat. No. 3104-540

Reagents and Materials

References to catalog numbers and suppliers are included as a convenience to the method user. Other suppliers may be used.

The following items are required to perform the analysis. Additional reagents and materials may be required depending on the specific instrument.

Air, compressed, dry, oil-free, for membrane drier (if instrument does not purge the drier with argon)

Alumina balls, Mitsubishi, Cat. No. TS3CAT, COSA Instrument

Argon, compressed gas, 99.99% minimum purity, UHP, local supply

Autosampler vials, 15x45 mm, Grace Davison Discovery Sciences, Cat. No. 98008

Catalyst, Mitsubishi, Cat. No. TN5CAT, COSA Instrument

Isooctane, should be as low in residual nitrogen as possible to minimize the blank value, B&J Brand, Burdick & Jackson, Cat. No. BJ362-1, VWR, or Fisher Pesticide grade, Fisher Scientific, Cat. No. O297-4. Test each new lot of solvent before use.

Oxygen, compressed gas, 99.98% minimum purity, UHP, local supply

Perfluoropolyether vacuum pump oil (PFPE), Krytox 1525, DuPont

Pipet, transfer, disposable plastic, 152-mm length, Fisher Scientific, Cat. No. 13-711-SA

Pyridine, 99+%, Sigma-Aldrich, Cat. No. 36,057-0

Quartz wool, Mitsubishi, Cat. No. TNQWL, COSA Instrument

Toluene, B&J Brand, Burdick & Jackson, Cat. No. BJ347-4, VWR

Procedure

The analyst is expected to be familiar with general laboratory techniques, nitrogen analysis, and the equipment being used. Dispose of used supplies and samples in an environmentally safe manner according to applicable regulations.

Preparation of Standards

Pyridine stock solution, 1000-µg N/mL

1. Tare a clean, dry 250-mL volumetric flask. Dispense 1.41 ± 0.005 g of pyridine and record the mass to the nearest 0.1 mg.
2. Dilute to the mark with toluene. Cap and mix well.
3. Calculate the actual concentration of the stock solution using Equation 1:

$$N, \mu\text{g/mL} = \frac{A(0.1771)10^6}{250} \quad (1)$$

where:

A = mass of pyridine, g
0.1771 = N mass-fraction of pyridine (**14.01/79.10**)
14.01 = molecular mass of nitrogen, g/mol
79.10 = molecular mass of pyridine, g/mol
250 = dilution volume, mL
10⁶ = factor to convert g to μg

Pyridine stock solution, 10- μg N/mL

1. Dispense 1.0 mL of the 1000- μg /mL N stock solution using a volumetric pipet into a clean, dry 100-mL volumetric flask.
2. Dilute to the mark with low N isooctane. Cap and mix well.
 - The actual concentration is 1/100th the concentration of the stock solution above.

Calibration standard solution, 50-ng N/mL

1. Dispense 0.5 mL of the 10- μg /mL N stock solution using a volumetric pipet into a clean, dry 100-mL volumetric flask.
2. Dilute to the mark with low N isooctane. Cap and mix well.
 - The actual concentration is 1/200th the concentration of the nominal 10- μg N/mL stock solution above.

Calibration standard solution, 25-ng N/mL

1. Dispense 2 mL of the 50-ng/mL N standard solution using a volumetric pipet into a clean, dry vial, such as an autosampler vial.
2. Dispense 2 mL of the low N isooctane into the vial using a volumetric pipet. Cap and mix well.
 - The actual concentration is 1/2 the concentration of the 50-ng N/mL standard solution above.
 - Other volumes can be used with a larger vial, as long as the standard:isooctane ratio remains 1:1.

Calibration standard solution, 100-ng N/mL

1. Dispense 1.0 mL of the 10- μg /mL N stock solution using a volumetric pipet into a clean, dry 100-mL volumetric flask.
2. Dilute to the mark with low N isooctane. Cap and mix well.
 - The actual concentration is 1/100th the concentration of the nominal 10- μg N/mL stock solution above.

Calibration standard solution, 200-ng N/mL

1. Dispense 2.0 mL of the 10- μg /mL N stock solution using a volumetric pipet into a clean, dry 100-mL volumetric flask.
2. Dilute to the mark with low N isooctane. Cap and mix well.
 - The actual concentration is 1/50th the concentration of the nominal 10- μg N/mL stock solution above.

Calibration standard solution, 500-ng N/mL

1. Dispense 5.0 mL of the 10- μg /mL N stock solution using a volumetric pipet into a clean, dry 100-mL volumetric flask.
2. Dilute to the mark with low N isooctane. Cap and mix well.

- The actual concentration is 1/20th the concentration of the nominal 10- μ g N/mL stock solution above.

The stock solutions can be retained, if refrigerated, for up to six months. The 100-, 200-, and 500-ng N/mL standard solutions can be retained, if refrigerated, for up to four weeks. The 50-ng N/mL standard solution should be made fresh weekly. The 25-ng N/mL standard solution should be made fresh daily.

Preparation of Apparatus

1. Set up the instrument according to the manufacturer's instructions. New combustion tubes need to be conditioned with catalyst before use, following the manufacturer's procedure. For Mitsubishi instruments, procedure ZINF026 must be followed. Connect the membrane drier in series between the combustion tube and the detector. For the NSX-2100V, the mixing chamber is not used between the membrane drier and the detector. Allow the instrument to warm up and the baseline to stabilize before injecting samples. Suggested Operating Conditions for the Mitsubishi TS-100V analyzer are listed in Table 1 and for the NSX-2100V in Table 2.

Table 1
Suggested Operating Conditions for Mitsubishi TS-100V/ND-100

Upper temperature	800 °C
Lower temperature	900 °C
Argon main	100 mL/min
Oxygen main	400 mL/min
Argon auxiliary	50 mL/min
Oxygen auxiliary	50 mL/min
Ozone	150 mL/min
Gain	ultra
Normal end	off
Timer start	3 sec
Timer end	240 sec
Minimum area	5000
Base line	25%
Syringe pre-fill	10 μ L
Injection rate	1.2 μ L/sec

Table 2
Suggested Operating Conditions for Mitsubishi NSX-2100V/ND-210

Inlet heater temperature	800 °C
Outlet heater temperature	900 °C
Argon	100 mL/min
Oxygen	500 mL/min
Argon time	30 sec
Oxygen time	120 sec
Ozone	200 mL/min
PMT sensitivity	high (for low concentration)
Type	timer
Waiting time	5 sec
Measurement time	250 sec
Syringe pre-fill	10 μ L
Injection rate	1.2 μ L/sec
Precedent rinse	enable

2. Set the STC-210 temperature set points to 15 °C for both the sample tray and the syringe. Allow at least 30 minutes for the temperature to stabilize before injecting samples.

3. Fill the rinse and pre-fill vials with low nitrogen isooctane. Empty the waste bottle.
 - Dispose of all materials in an environmentally safe manner according to local regulations.
4. Before starting to measure either calibration standards or samples, run an instrument program with 3 (or more) injections of isooctane to condition the instrument. The response should be stable before proceeding.

Calibration

Calibrate weekly when in use.

1. Rinse each autosampler vial with approximately 1 mL of the fill material, dump and then fill the autosampler vial with the sample.
2. Fill several autosampler vials, one each with the solvent used to make the standard solutions (solvent blank) and the 25-, 50-, 100-, 200-, and 500-ng N/mL calibration standards.
 - Rinse each autosampler vial with approximately 1 mL of the fill material, dump and then fill the autosampler vial with the sample.
3. Cycle the instrument (Step 4 in the *Preparation of Apparatus* section) while the temperature of the standard solutions equilibrates to 15 °C.
4. Run a calibration program with multiple 80-μL injections of the solvent blank and each standard. It is recommended to inject each standard or blank at least 4 times. The injections contain approximately 0, 2, 4, 8, 16, and 40 ng of added nitrogen.
 - Relative standard deviation (RSD), as calculated by the instrument software for the blank, should be within 25%. The RSD for the standards should be within 10%.
 - If an outlier occurs in one of the four replicates, it may be excluded if it is statistically valid to do so.
5. Create a regression line using the instrument software using the blank and the three standards. Set the regression line to “ $y=bx+c$ ”.
 - The calibration corrects for the residual diatomic nitrogen content of the solvent used to make the standards. Nitrogen solubility in hydrocarbons will result in a non-zero intercept.

Sample Analysis

1. Fill the autosampler vials with sample and place in the cooled sample tray.
2. Enter the sample parameters into the instrument software to create a sample method. Set injection volume to 80 μL. Each sample should be injected at least four times.
 - More than four injections are recommended for samples expected to be below 100 ng N/g.
 - The 80-μL injection volume is necessary for the required sensitivity. Do not inject less than 80 μL for samples containing less than 200 ng N/g.
3. Combust and analyze at least 3 injections of isooctane to condition the instrument before starting the samples.
4. Rinse the autosampler vial with approximately 1 mL of the sample, dump and then fill the autosampler vial with the sample. Place the vial onto the autosampler rack and repeat for all remaining samples.
5. Inject and analyze the samples using 80-μL injections.
 - Each sample should be injected and analyzed at least 4 times.
 - If the detector becomes contaminated (trace off scale), continue to inject blanks until the response stabilizes. Then verify that the instrument sensitivity is unchanged by analyzing a calibration standard or QC sample before analyzing unknown samples.

Calculations

All calculations are performed by the instrument software, and results are displayed and printed in mass-ppm (mg/kg) or mass-ppb (ng/g). The density of the sample is input during sample data entry and is used by the instrument to convert results from mass/volume to mass/mass. If the density is unknown, it can be determined by ASTM D4052, "Density and Relative Density of Liquids by Digital Density Meter," or other technique.

- Multiple injections of the same sample are averaged by the instrument software. The values from each of the replicate runs should not deviate from the average by more than 0.01 mg/kg (< 0.3 mg/kg) or 0.02 mg/kg (> 0.3 mg/kg). If greater deviations occur, make certain that there are no problems with the equipment or the procedure, and then make additional runs until the expected repeatability is obtained.

Report

Report mg/kg (mass-ppm) results to two decimal places.

Notes and Precautions

1. The membrane drier is used to remove the water produced during combustion. If not removed, the water vapor would enter the detector and result in a reduction of the chemiluminescence intensity. The membrane drier consists of a thin walled Nafion™ tube within a larger plastic tube. The combustion product gas flows through the Nafion™ tube. Dry air or other dry gas flows counter-current through the outer plastic tube. The Nafion™ membrane allows water to pass through and be carried away by the air stream on the other side. The membrane drier was determined to be superior to a phosphoric acid scrubber to remove water without reducing sensitivity.
2. The vacuum pump is required to reduce the pressure in the detector to improve sensitivity, and also to draw the combustion product gas into the detector. This requires a pump capable of handling high flow rates. The Ulvac rotary pump listed provides for a minimum capacity of 50 L/min capacity. Pump stability is very important as pressure fluctuations will strongly affect sensitivity. Other types of vacuum pumps (diaphragm, scroll, etc.) may be suitable depending on pump capabilities and need to be validated for this method. Rotary pumps need to be operated with PFPE pump oil (e.g. Krytox, Fomblin).
3. Since this method is for use with very low levels of nitrogen, care must be taken to prevent contamination of the sample. The containers used for the samples and standards must not contaminate the solutions. The autosampler vial septum could also be a source of nitrogen contamination. Fill an autosampler vial with isooctane and cap. Analyze immediately from this container, and again, several hours later. Any increase in nitrogen level is an indication of contamination from the container. Autosampler bottles, such as the recommended part from Grace, do not contribute nitrogen to the samples. The samples should not be left uncovered any longer than necessary. This prevents loss of volatile components and/or entry of contaminants.
4. The sample must not burn too quickly. Incomplete combustion will result in carbon monoxide, and even particulate carbon, entering the detector and causing a positive interference.
5. With direct injection instruments, it is recommended that the same injection volume be used for both the standards and the samples.
6. Samples containing long chain n-paraffins, such as n-C₁₆ or longer, should be heated to 25-30 °C to prevent solidification. Pentane and hexane samples should be cooled to 15 °C. Most liquid hydrocarbons should be analyzed at 15 or 20 °C for improved precision.

Precision

Precision statements were determined using UOP Method 999, "Precision Statements in UOP Methods," from precision data obtained using an autosampler.

Repeatability and Site Precision

A nested design was carried out for determining nitrogen in five samples by two analysts, with each analyst performing analyses on two separate days, performing five analyses each day for a total of 100 analyses. Using a stepwise analysis of variance procedure, the within-day estimated standard deviations (esd) were calculated at the concentration means listed in Table 3. Two analyses performed in one laboratory by the same analyst on the same day should not differ by more than the repeatability allowable differences shown in Table 3 with 95% confidence. Two analyses performed in one laboratory by different analysts on different days should not differ by more than the site precision allowable differences shown in Table 3 with 95% confidence.

Table 3
Repeatability and Site Precision, Nitrogen, mg/kg (mass-ppm)

<u>Sample</u>	<u>Mean</u>	<u>Repeatability</u>		<u>Site Precision</u>	
		<u>Within-Day esd</u>	<u>Allowable Difference</u>	<u>Within-Lab esd</u>	<u>Allowable Difference</u>
Hexane	0.12	0.012	0.03	0.014	0.04
Naphtha A	0.03	0.005	0.02	0.006	0.02
Naphtha B	0.10	0.005	0.02	0.006	0.02
Naphtha C	0.16	0.009	0.03	0.010	0.03
Isooctane	0.32	0.007	0.02	0.008	0.02

The data in Table 3 represent short-term estimates of the repeatability of the method. When the test is run routinely, use of a control standard and a control chart is recommended to generate an estimate of long-term repeatability.

Reproducibility

There is insufficient data to calculate the reproducibility of the test at this time.

Time for Analysis

The elapsed time for one analysis, including calibration, is 4 hours. The labor requirement is 2 hours. Each succeeding analysis requires 0.5 hour.

Suggested Suppliers

Burdick & Jackson, 1953 S. Harvey St., Muskegon, MI 49442, USA, 1-800-368-0050,
www.burdickandjackson.com

COSA Instrument Corp., 84G Horseblock Rd., Yaphank, NY 11980, USA, 1-631-345-3434,
distributor for Mitsubishi Chemical Analytech, 370 Enzo, Chigasaki, Kanagawa Pref., 253-0084,
Japan, +81-467-86-3864, www.cosa-instrument.com

DuPont, 1007 Market St., Wilmington, DE 19898, USA, 1-800-424-7502, www.krytox.com

Fisher Scientific, 300 Industry Dr., Pittsburgh, PA 15275, USA, 1-412-490-8300,
www.fishersci.com

Grace Davison Discovery Sciences, 2051 Waukegan Rd., Deerfield, IL 60015, USA, 1-847-948-8600, www.discoverysciences.com

Matheson Tri-Gas, 166 Keystone Dr., Montgomeryville, PA 18936, USA, 1-215-641-2700,
www.mathesontrigas.com

Perma Pure Inc., 8 Executive Dr., Toms River, NJ 08754, USA, 1-732-244-0010,
www.permapure.com

Sigma-Aldrich, 3050 Spruce St., St. Louis, MO 63103, USA, 1-314-771-5765,
www.sigma-aldrich.com

VWR International, 1310 Goshen Pkwy., West Chester, PA 19380, USA, 1-610-431-1700,
www.vwr.com