

TRACE NITROGEN IN LIGHT AROMATIC HYDROCARBONS BY CHEMILUMINESCENCE

UOP Method 971-00

SCOPE

This method is for determining total nitrogen in light aromatic hydrocarbons, such as benzene. It is applicable to quantitative determination of nitrogen at a level of 30 to 400 ng/g. Samples containing more than 400 ng/g nitrogen can be analyzed according to ASTM D 4629 or D 6069. Halogen and sulfur-containing compounds can interfere if any one or all of these elements are present in a sample in concentration greater than 10%.

OUTLINE OF METHOD

The sample is injected by an autosampler into a quartz-wool filled sample boat. The volatile components are allowed to evaporate into an argon stream that carries them into the combustion furnace. The boat is then moved into the furnace and the residual material is combusted in oxygen. The organic material is converted to carbon dioxide and water. The nitrogen in the sample is converted to nitric oxide that is further reacted in the detector with ozone to produce nitrogen dioxide that is generated in an excited state. The excited state nitrogen dioxide molecules relax to the ground state, producing light (chemiluminescence), that 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 is not sensitive to diatomic nitrogen (N_2) 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.

IT IS THE USER'S RESPONSIBILITY TO ESTABLISH APPROPRIATE PRECAUTIONARY PRACTICES AND TO DETERMINE THE APPLICABILITY OF REGULATORY LIMITATIONS PRIOR TO USE. EFFECTIVE HEALTH AND SAFETY PRACTICES ARE TO BE FOLLOWED WHEN UTILIZING THIS PROCEDURE. FAILURE TO UTILIZE THIS PROCEDURE IN THE MANNER PRESCRIBED HEREIN CAN BE HAZARDOUS. MATERIAL SAFETY DATA SHEETS (MSDS) OR EXPERIMENTAL MATERIAL SAFETY DATA SHEETS (EMSDS) FOR ALL OF THE MATERIALS USED IN THIS PROCEDURE SHOULD BE REVIEWED FOR SELECTION OF THE APPROPRIATE PERSONAL PROTECTION EQUIPMENT (PPE).

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UOP Methods are available through ASTM International, 100 Barr Harbor Drive, PO Box C700, West Conshohocken PA 19428-2959, United States. The Methods may be obtained through the ASTM website, www.astm.org, or by contacting Customer Service at service@astm.org, 610.832.9555 FAX, or 610.832.9585 PHONE

Chemiluminescence analyzer, Mitsubishi TN-110 analyzer with an automatic boat controller module, Cosa Instruments. This method was developed using the Mitsubishi analyzer. The procedure for analysis may be different for other instruments. The Mitsubishi analyzer must be equipped with the following accessories:

Autosampler, Mitsubishi Cat. No. ASC-150L, Cosa Instruments

Autosampler syringes, gas tight, 100- μ L, Mitsubishi Cat. No. MSSG10, Cosa Instruments

Autosampler vials, rinse, Mitsubishi Cat. No. TX3LSW, Cosa Instruments

Autosampler vials, sample, Mitsubishi Cat. No. TX3LSV, Cosa Instruments

Vacuum pump, 50 L/min minimum flow capacity, Sinku Kiko GLS-050 (Mitsubishi), Cosa Instruments. See *NOTE 1*.

Filter capsule, particulate, HEPA-Cap 36, glass fiber, Fisher Scientific, Cat. No. 09-744-12. Connect this filter before the membrane drier.

Flasks, volumetric, glass, Class A, 25-, 50 (two required), and 100-mL, Fisher Scientific, Cat. Nos. 10-210A, B and C, respectively

Membrane drier, Perma Pure, MD-110-12F. See *NOTE 2*.

Regulator, air, stainless steel, two-stage, high purity, Matheson Gas Products, Model 3810-590

Regulator, argon, stainless steel, two-stage, high purity, Matheson Gas Products, Model 3810-580

Regulator, oxygen, stainless steel, two-stage, high purity, Matheson Gas Products, Model 3810-540

Syringes, gas tight, 50 and 100 μ L, Fisher Scientific, Cat. Nos. 14-824-30 and 13-684-100. The syringe used for pure pyridine should not be used for low nitrogen samples without first being thoroughly cleaned.

REAGENTS AND MATERIALS

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

Air, compressed, dry, oil-free air for Perma Pure membrane drier

Aluminum foil, optional, see *NOTE 3*, local supply

Argon, high purity, 99.98+%, Matheson Gas Products

Benzene, low nitrogen, as an alternative to isooctane, local supply

Catalyst, Mitsubishi Cat. No. TN5CAT, Cosa Instruments

Isooctane, should be as low in residual nitrogen as possible to minimize the blank value, Pesticide grade, Fisher Scientific, O297-4. If available, benzene containing very low concentrations of nitrogen compounds could be substituted. The blank value must be determined for each new bottle of solvent used for making standards.

Oxygen, high purity, 99.7+%, Matheson Gas Products

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

Quartz Wool, Mitsubishi Cat. No. TNQWL, Cosa Instruments

Toluene, Fisher Scientific, Cat. No. T324-4

PROCEDURE

Preparation Of Standard Solutions

Pyridine stock solution, 100 µg N/mL

1. Dispense 58 µL of pyridine using a microliter syringe into a clean, dry 100 mL volumetric flask.
2. Dilute to the mark with toluene. Cap and mix well.

The identity below shows the calculation of the concentration of nitrogen in the stock solution:

$$100\mu\text{g N/mL} = \frac{(58)(0.978)(14.01)(1000)}{(79.10)(100)}$$

where:

0.978 = density of pyridine at 20°C, mg/µL

14.01 = molecular mass of nitrogen, g/mol

58 = volume of pyridine, µL

100 = dilution volume, mL

79.10 = molecular mass of pyridine, g/mol

1000 = factor to convert mg to µg

Calibration standard solution, 50 ng N/mL

1. Dispense 25 µL of the pyridine stock solution with a microliter syringe into a clean, dry 50-mL volumetric flask.
2. Dilute to the mark with a low nitrogen solvent, either isooctane or benzene. Cap the flask and mix well.
 - The actual concentration of this standard will be 1/2000th of the pyridine stock solution.

Calibration standard solution, 100 ng N/mL

1. Dispense 50 µL of the pyridine stock solution with a microliter syringe into a clean, dry 50-mL volumetric flask.
2. Dilute to the mark with the low nitrogen solvent used above. Cap the flask and mix well.
 - The actual concentration of this standard will be 1/1000th of the pyridine stock solution.

Calibration standard solution, 200 ng N/mL

1. Dispense 50 μ L of the pyridine stock solution with a microliter syringe into a clean, dry 25-mL volumetric flask.
2. Dilute to the mark with a low nitrogen solvent used above. Cap the flask and mix well.
 - The actual concentration of this standard will be 1/500th of the pyridine stock solution.

The stock solution can be retained, if refrigerated, for up to three months. The standard solutions can be retained, if refrigerated, for one week. Do not refrigerate stock and standard solutions if prepared in benzene as the benzene will freeze, causing erratic results.

Sampling

Some organic nitrogen compounds will adsorb on the walls of metal sample containers. It is, therefore, recommended that analysis by this procedure be available in the refinery where sampling takes place. If samples must be shipped to another site for analysis, use pressure-tight glass containers and the fastest form of transport available. Analyze samples as soon as possible after sampling.

Instrument Set Up

1. Set up the instrument according to the manufacturer's instructions. Connect the filter capsule and membrane drier in series in the line from the combustion tube to the detector. Allow the instrument to warm-up and the baseline to stabilize before injecting samples. Suggested Operating Conditions for the Mitsubishi TN-110 analyzer are listed in Table 1.

Table 1
Suggested Operating Conditions for Mitsubishi TN-110:

Furnace inlet temperature	600°C
Catalyst bed temperature	900°C
Argon carrier	170 mL/min
Oxygen	110 mL/min
Ozone	190 mL/min
Integrate delay	0 sec
Slope start	200
Slope end	20
End thrsh	10 %
Normal end	Off
Timer end	325 sec
Base correct	Off
Minimum area	5000
Base line	25 %
Interval end	350 sec

2. Disconnect the tubing from the combustion tube to the detector to prevent carbon build-up in membrane drier, tubing, and detector during the burn profiling steps.

3. Determine proper settings for automatic boat controller programs for 40 μL injection of calibration standard solvent and for 80 μL injections of each type of hydrocarbon sample (benzene, toluene, ethylbenzene, etc.). See *NOTES 4 and 5*.
 - Different hydrocarbons require different temperatures in order to vaporize at a controlled rate and burn completely.
 - The programs need to be set the first time the instrument is run. Future runs can use the same settings as long as the instrument parameters (flow rates, temperatures, etc.) are not changed.
4. Reconnect the tubing from combustion tube to the detector.

Calibration

Calibrate daily when in use.

1. Fill autosampler vials, one each, with the solvent used to make the standard solutions (solvent blank) and the 50, 100, and 200 ng/mL nitrogen calibration standards.
2. Cycle the empty boat in and out of the combustion furnace to remove any residual contamination.
3. Run a calibration program with multiple 40 μL injections of the solvent blank and each standard. It is recommended to inject each standard or blank at least 5 times. The injections contain 0, 2, 4 and 8 ng of added nitrogen.
 - Relative standard deviation (RSD), as calculated by the instrument for the blank, should be within 25%. The RSD for the standards should be within 15%.
 - Smaller, 40 μL injections are used for standards to minimize residual nitrogen from the solvent during calibration.
4. Create a regression line using the instrument software using the blank and the three standards. Set the regression line to “ $y=bx$ ” instead of “ $y=bx+c$ ”.
 - The calibration corrects for the residual nitrogen content of the solvent used to make the standards (solvent blank, often greater than 50 ng/g) by generating the regression line as a standard addition to the solvent blank to calibrate the sensitivity to added nitrogen. The slope generated is used to create a calibration line starting at the origin, i.e., zero signal for zero nitrogen.

Sample Analysis

1. Enter the sample parameters into the software to create a sample method. Set injection volume to 80 μL . Each sample should be injected at least four times.
 - More than five injections are recommended for samples expected to be below 100 ng/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/g.
2. Cycle the empty boat in and out of the combustion furnace to remove any residual contamination.
3. Fill the autosampler vials with the samples and place the vials onto the autosampler rack.
4. Inject and analyze the samples using the automatic boat controller parameters optimized for 80 μL injections.
 - If the detector becomes contaminated (trace off scale), continue to inject blanks until the response stabilizes.

CALCULATIONS

All calculations are performed by the software, and results are displayed and printed in ppb (ng/g) or ppm ($\mu\text{g/g}$) as appropriate. The density is input during sample data entry and is used by the instrument to convert results from wt/vol to wt/wt.

REPORT

Report mass-ppb (ng/g) results to the nearest unit.

NOTES AND PRECAUTIONS

1. 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 pump specified provides for a minimum of 50 L/min capacity (60 L/min for operation with 60 Hz power). Pump stability is very important as pressure fluctuations will strongly affect sensitivity.
2. The Perma Pure 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 NafionTM tube within a larger plastic tube. The combustion product gas flows through the Nafion tube. Dry air or nitrogen is flowed 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 the phosphoric acid scrubber to remove water without reducing sensitivity.
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 thereafter. Any increase in nitrogen level is an indication of contamination from the container. If all available septa cause a high level of nitrogen contamination, use aluminum foil in place of the septum. 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. The sample should evaporate and burn completely at least 10 seconds before the boat is inserted into the furnace.
5. This method can be extended to non-aromatic hydrocarbons by creating an appropriate automatic boat controller program for the hydrocarbon matrix. The program should be checked to confirm proper evaporation and combustion before it is used for analysis.
6. An instrument using a constant rate injector can be substituted for the autosampler and boat drive system. Follow the manufacturers directions for recommended conditions. With direct injection instruments, it is recommended that the same injection volume be used for both the standards and the samples.

PRECISION

The precision statements were determined using UOP Method 999.

ASTM Repeatability

A nested design was carried out for determining nitrogen in benzene with two analysts in one laboratory. Each analyst carried out tests at two concentrations on two separate days, performing four tests each day. The total number of tests at each concentration was 16. Using a stepwise analysis of variance procedure, the within-day estimated standard deviation (esd) was calculated for each concentration and is listed in Table 2. Two tests performed by the same analyst on the same day should not differ by more than the ASTM allowable difference shown in Table 2 with 95% confidence.

UOP Repeatability

A nested design was carried out for determining nitrogen in benzene with two analysts in one laboratory. Each analyst carried out tests at two concentrations on two separate days, performing four tests each day. The total number of tests at each concentration was 16. Using a stepwise analysis of variance procedure, the within-lab estimated standard deviation (esd) was calculated for each concentration and is listed in Table 2. Two tests performed in one laboratory by different analysts on different days should not differ by more than the UOP allowable difference shown in Table 2 with 95% confidence.

The data in the Table is a short-term estimate of repeatability. When the test is run routinely, a control standard and chart should be used to develop a better estimate of the long-term repeatability.

Reproducibility

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

Table 2
ASTM and UOP Repeatability, ng/g

<u>Mean Concentration</u>	<u>ASTM Repeatability</u>		<u>UOP Repeatability</u>	
	<u>Within-Day esd</u>	<u>Allowable Difference</u>	<u>Within-Lab esd</u>	<u>Allowable Difference</u>
27	6	19	11	30
77	8	26	14	40

TIME FOR ANALYSIS

The elapsed time for one analysis including calibration is 3 hours. The labor requirement is 1 hour. Each additional sample analysis adds 0.5 hour elapsed time and 0.1 hour labor time.

REFERENCES

ASTM Methods D 4629 and D 6069, www.astm.org
Jones, B.M. and Daughton, C.G., *Anal. Chem.*, **57**, 2320-2325 (1985)
UOP Method 999, "Precision Statements in UOP Methods"

SUGGESTED SUPPLIERS

Aldrich Chemical Co., Inc., 1001 West Saint Paul Avenue, Milwaukee, WI 53201 (414-273-3850)
www.sigma-aldrich.com
Cosa Instruments Co., 55 Oak Street, Norwood, NJ 07648 (201-767-6600) www.cosainstrument.com
Fisher Scientific, 711 Forbes Ave., Pittsburgh, PA 15219 (412-562-8300) www.fishersci.com
Matheson Gas Products, P.O. Box 85, East Rutherford, NJ 07073 (201-933-2400)
www.mathesontrigas.com
Perma Pure Inc., 8 Executive Dr., Toms River, NJ 08754 (732-244-0010) www.permapure.com