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Standard Test Method for Trace Nitrogen in Liquid Petroleum Hydrocarbons by Syringe/Inlet Oxidative Combustion and Chemiluminescence Detection¹

This standard is issued under the fixed designation D4629; the number immediately following the designation indicates the year of original adoption or, in the case of revision, the year of last revision. A number in parentheses indicates the year of last reapproval. A superscript epsilon (ϵ) indicates an editorial change since the last revision or reapproval.

This standard has been approved for use by agencies of the U.S. Department of Defense.

1. Scope

1.1 This test method covers the determination of the trace total nitrogen naturally found in liquid hydrocarbons boiling in the range from approximately 50 °C to 400 °C, with viscosities between approximately 0.2 cSt and 10 cSt (mm²/s) at room temperature. This test method is applicable to naphthas, distillates, and oils containing 0.3 mg/kg to 100 mg/kg total nitrogen. For liquid hydrocarbons containing more than 100 mg/kg total nitrogen, Test Method D5762 can be more appropriate. This test method has been successfully applied, during interlaboratory studies, to sample types outside the range of the scope by dilution of the sample in an appropriate solvent to bring the total nitrogen concentration and viscosity to within the range covered by the test method. However, it is the responsibility of the analyst to verify the solubility of the sample in the solvent and that direct introduction of the diluted sample by syringe into the furnace does not cause low results due to pyrolysis of the sample or solvent in the syringe needle.

1.2 The values stated in SI units are to be regarded as standard. No other units of measurement are included in this standard.

1.3 *This standard does not purport to address all of the safety concerns, if any, associated with its use. It is the responsibility of the user of this standard to establish appropriate safety and health practices and determine the applicability of regulatory limitations prior to use. See 6.2, 6.4, 6.5, 6.9, and Section 7.*

1.4 *This international standard was developed in accordance with internationally recognized principles on standardization established in the Decision on Principles for the Development of International Standards, Guides and Recom-*

mendations issued by the World Trade Organization Technical Barriers to Trade (TBT) Committee.

2. Referenced Documents

2.1 ASTM Standards:²

D1298 Test Method for Density, Relative Density, or API Gravity of Crude Petroleum and Liquid Petroleum Products by Hydrometer Method

D4052 Test Method for Density, Relative Density, and API Gravity of Liquids by Digital Density Meter

D5762 Test Method for Nitrogen in Petroleum and Petroleum Products by Boat-Inlet Chemiluminescence

D6299 Practice for Applying Statistical Quality Assurance and Control Charting Techniques to Evaluate Analytical Measurement System Performance

3. Summary of Test Method

3.1 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 the excited NO₂ decays is detected by a photomultiplier tube and the resulting signal is a measure of the nitrogen contained in the sample.

4. Significance and Use

4.1 Some process catalysts used in petroleum and chemical refining may be poisoned when even trace amounts of nitrogenous materials are contained in the feedstocks. This test method can be used to determine bound nitrogen in process feeds and may also be used to control nitrogen compounds in finished products.

¹ This test method is under the jurisdiction of ASTM Committee D02 on Petroleum Products, Liquid Fuels, and Lubricants and is the direct responsibility of Subcommittee D02.03 on Elemental Analysis.

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² For referenced ASTM standards, visit the ASTM website, www.astm.org, or contact ASTM Customer Service at service@astm.org. For *Annual Book of ASTM Standards* volume information, refer to the standard's Document Summary page on the ASTM website.

5. Apparatus

5.1 *Furnace*, electric, held at a temperature sufficient to volatilize and pyrolyze all of the sample and oxidize the organically bound nitrogen to NO. Furnace temperature(s) shall be as recommended by the manufacturer (typically around 1000 °C).

5.2 *Combustion Tube*, fabricated to meet the instrument manufacturer's specifications.

5.3 *Drier Tube*—The reaction products include water vapor that must be eliminated prior to measurement by the detector. This can be accomplished with a magnesium perchlorate $Mg(ClO_4)_2$ scrubber or a membrane drying tube (permeation drier), or by whatever other means the instrument manufacturer specifies as appropriate for the instrument being used.

5.4 *Chemiluminescent Detector*, capable of measuring light emitted from the reaction between NO and ozone.

5.5 *Totalizer*, having variable attenuation, and capable of measuring, amplifying, and integrating the current from the chemiluminescent detector. A built in microprocessor or attached computer system may perform these functions.

5.6 *Micro-litre Syringe*, of 5 μ L, 10 μ L, 25 μ L, 50 μ L, or 250 μ L capacity capable of accurately delivering micro-litre quantities is required. The needle should be long enough to reach the hottest portion of the inlet section of the furnace when injecting the sample. The syringe may be part of an automatic sampling and injection device used with the instrument.

5.7 *Strip Chart Recorder* (Optional).

5.8 *Sample Inlet System*—One of the following must be used:

5.8.1 *Manually Operated Syringe*.

5.8.2 *Syringe*, with a constant rate injector system, capable of delivering a sample at a precisely controlled rate.

5.8.3 *Boat Inlet System*, to facilitate analysis of samples that would react with the syringe or syringe needle. The pyrolysis tube for boat inlet use may require specific construction to permit insertion of a boat fully into the inlet section of the furnace. The boat inlet system external to the furnace may be cooled to a temperature below room temperature to aid in dissipating the heat from the boat when it is removed from the furnace. Cooling the boat inlet system may also reduce the chances of the sample combusting in the boat before introduction into the furnace and may be necessary when running volatile samples such as naphtha using a boat inlet system.

5.9 *Quartz Insert Tube* (Optional), may be packed with cupric oxide (CuO) or other oxidation catalyst as recommended by the instrument manufacturer, to aid in completing oxidation. This is inserted into the exit end of the pyrolysis tube.

5.10 *Vacuum System* (Optional), The chemiluminescence detector may be equipped with a vacuum system to maintain the reaction cell at reduced pressure (typically 20 mm to 25 mm Hg). This can improve the signal to noise ratio of the detector.

5.11 *Analytical Balance* (Optional), with a precision of ± 0.01 mg.

6. Reagents

6.1 *Purity of Reagents*—Reagent grade chemicals shall be used in all tests. Unless otherwise indicated, it is intended that all reagents shall conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society,³ where such specifications are available. Other grades may be used, provided it is first ascertained that the reagent is of sufficiently high purity to permit its use without lessening the accuracy of the determination.

6.2 *Magnesium Perchlorate* $Mg(ClO_4)_2$, for drying products of combustion (if permeation drier is not used.) (**Warning**—Strong oxidizer, irritant.)

6.3 *Inert Gas*, argon or helium, ultra-high purity grade (UHP).

6.4 *Oxygen*, (99.8 % or better, 99.996 % is recommended.) (**Warning**—Vigorously accelerates combustion.)

6.5 *Solvents*, for diluting and matrix matching such as, toluene, isooctane, xylene, acetone, cetane. (Other solvents similar to those occurring in samples to be analyzed are also acceptable). Solvents should contain less than 0.1 μ g N/mL. (**Warning**—Flammable solvents.)

6.6 *Nitrogen Stock Solution*, 1000 μ g N/mL, Prepare a stock solution by accurately weighing approximately 1.195 g of carbazole or 0.565 g of pyridine to the nearest milligram, into a tared 100 mL volumetric flask (see 6.6.1). Fifteen millilitres of acetone may then be added when using carbazole to help dissolve it. Dilute to volume with the selected solvent. Calculate the exact concentration of the stock solution based on the actual mass of pyridine or carbazole used and corrected for any known purity factors for the specific lot of pyridine or carbazole. This stock may be further diluted to desired nitrogen concentrations.

6.6.1 Calibration standards from commercial sources may be used if they conform to the requirements of the test method.

NOTE 1—Pyridine should be used with low boiling solvents (<220 °C).

NOTE 2—Carbazole should be used with high boiling solvents (>220 °C).

NOTE 3—Working standards should be remixed on a regular basis depending upon frequency of use and age. Typically, standards have a useful life of about 3 months, and should be refrigerated when not being used.

6.7 *Cupric Oxide Wire*, as recommended by instrument manufacturer.

6.8 *Quartz Wool* (optional), or other suitable absorbent material that is stable and capable of withstanding temperatures inside the furnace (**Note 4**).

NOTE 4—Materials meeting the requirements in 6.8 are recommended to be used in sample boats to provide a more uniform injection of the

³ *Reagent Chemicals, American Chemical Society Specifications*, American Chemical Society, Washington, DC. For suggestions on the testing of reagents not listed by the American Chemical Society, see *Analar Standards for Laboratory Chemicals*, BDH Ltd., Poole, Dorset, U.K., and the *United States Pharmacopeia and National Formulary*, U.S. Pharmacopeial Convention, Inc. (USPC), Rockville, MD.

sample into the boat by wicking any remaining drops of the sample from the tip of the syringe needle prior to introduction of the sample into the furnace. Consult instrument manufacturer recommendations for further guidance.

6.9 *Pyridine*. (**Warning**—Flammable, irritant.)

6.10 *Carbazole*.

7. Hazards

7.1 High temperature is employed in this test method. Exercise care when using flammable materials near the pyrolysis furnace.

8. Sampling

8.1 To preserve volatile components, which may be in some samples, do not uncover samples any longer than necessary. Analyze samples as soon as possible after taking from the bulk supplies to prevent loss of nitrogen or contamination due to exposure or contact with sample container.

9. Assembly Apparatus

9.1 Assemble apparatus in accordance with manufacturer's instructions.

9.2 Adjust the gas flows and the pyrolysis temperature as recommended by the instrument manufacturer.

10. Calibration and Standardization

10.1 Prepare a series of calibration standards from the stock solution (see 6.6) covering the range of operation and consisting of nitrogen type and matrix similar to samples to be analyzed. There shall be a minimum of two calibration standards in addition to the solvent blank, used to generate the calibration curve.

10.2 Determine the volume or mass of the material to be analyzed by using one of the volumetric or gravimetric methods described below.

10.2.1 Volumetric measurement of the injected material is obtained by filling the syringe to the 80 % level, retracting the plunger so that the lower liquid meniscus falls on the 10 % scale mark, and recording the volume of liquid in the syringe. After the material has been injected, again retract the plunger so that the lower liquid meniscus falls on the 10 % scale mark and record the volume of liquid in the syringe. The difference between the two volume readings is the volume of material injected.

10.2.2 Alternatively, an automatic sampling and injection device may be used to volumetrically inject a reproducible volume of the material into the furnace.

10.2.3 Gravimetric measurement of the injected material is obtained by weighing the syringe before and after injection to determine the amount of material injected. This procedure provides greater precision than the volumetric procedure, provided a balance with a precision of at least ± 0.01 mg is used.

10.3 To introduce the sample into the furnace, insert the syringe needle through the inlet septum up to the syringe barrel and inject the sample or standard at a uniform rate as specified by the instrument manufacturer (typically 0.2 $\mu\text{L/s}$ to

1.0 $\mu\text{L/s}$). Rate of injection is dependent on such factors as viscosity, hydrocarbon type, and nitrogen concentration. Each user must adopt a method whereby a consistent and uniform injection rate is ensured. An automatic sampling and injection device may be used to introduce the material at a reproducible rate. If an automatic sampling and injection device is not being used, determine the quantity of material injected using either 10.2.1 (volumetric injection procedure) or 10.2.3 (gravimetric injection procedure).

NOTE 5—For the most consistent injection rate and best analytical results, a constant rate injection unit or automatic sampling and injection device may be helpful. Coke formation at the outlet of the combustion tube may indicate too rapid of an injection rate. Consult manufacturer for recommendations.

NOTE 6—With direct injection below 5 mg/kg of nitrogen, the needle septum blank may become increasingly important. Error due to this can be avoided by inserting the syringe needle into the hot inlet and allowing the needle-septum blank to dissipate before injecting the sample.

10.4 If a boat inlet system is used, then the material to be analyzed is injected into a quartz boat using one of the procedures described in 10.2.1, 10.2.2, or 10.2.3 and the quartz boat is moved into the hot portion of the combustion tube. Refer to the manufacturer's instructions for selecting the rate of boat movement into the furnace and boat residence time in the hot portion of the combustion tube.

10.5 Calibration curves shall be generated in one of the following manners depending on the capability of the instrumentation used.

10.5.1 For systems that use a microprocessor or computer system for data collection and calibration curve generation, the calibration curve shall be based on the linear regression of a minimum of three repeat measurements of each calibration standard.

10.5.2 For those detectors not equipped with a microprocessor or computer system for generating a calibration curve, construct a standard curve as follows. Repeat the determination of each calibration standard and the blank three times to determine the average net response for each. Construct a curve plot of detector response (integration counts) versus nanograms of nitrogen injected and apply the best straight line fit through the plotted data.

10.6 The response curve should be linear with a minimum R^2 of 0.999. The intercept should not be forced through zero. The calibration curve shall be checked each day that the instrument is used (see Section 14).

11. Procedure

11.1 Obtain a test specimen using the procedure in Section 8. The nitrogen concentration in the test specimen must be less than the concentration of the highest standard used in the calibration. Injection volumes ranging from 3 μL to 100 μL are acceptable depending on the instrument being used. The size of the injected sample shall be similar to the size of the injected standards used for calibration.

11.2 Flush a clean microlitre syringe several times with the sample to be determined, and introduce it into the furnace using the procedure outlines in 10.2 – 10.4 (depending on whether a boat inlet system is being used). For samples with

total nitrogen concentration in the range 1 mg/kg to 100 mg/kg, sample sizes injected are typically up to 10 µL. For samples with total nitrogen concentration less than 1 mg/kg, injected sample size can be up to 100 µL. Follow the instrument manufacturer's recommendation on sample size based on type of sample and level of nitrogen present.

11.3 To obtain one result, measure each test specimen a minimum of three times and calculate the average detector response.

12. Calculation

12.1 For samples introduced volumetrically (10.2.1 or 10.2.2), density values used for calculations are to be measured using Test Method D1298, Test Method D4052 or their equivalent, at ambient temperature.

12.2 Calculate the nitrogen content of the sample in mg/kg for the average of the three determinations that make up a single result as follows:

$$\text{nitrogen, mg/kg} = (I - I_0) \times K / (S \times V \times D) \quad (1)$$

or

$$\text{nitrogen, mg/kg} = (I - I_0) \times K / (S \times M) \quad (2)$$

where:

- D = density of sample, g/mL,
- S = slope of the calibration curve, counts/ng N,
- V = volume of sample, µL,
- K = dilution factor,
- M = mass of sample, mg,
- I = average detector response, integration counts, and
- I_0 = intercept of the calibration curve, integration counts.

12.3 For analyzers equipped with a calibration adjust, calculate the nitrogen content of the sample in mg/kg as follows (the average of three determinations make up a single result):

$$\text{nitrogen, mg/kg} = (I - B) \times K / (V \times D) \quad (3)$$

or

$$\text{nitrogen, mg/kg} = (I - B) \times K / M \quad (4)$$

where:

- D = density of sample, g/mL,
- S = slope of the calibration curve, counts/ng N,
- V = volume of sample, µL,
- K = dilution factor,
- M = mass of sample, mg,
- I = visual display reading of the sample, ng N
- B = average of visual display readings of the blank, ng N.

13. Report

13.1 For results equal to or greater than 1 mg/kg, report the nitrogen result to two significant figures when two or more significant figures are available. For results less than 1 mg/kg, report the nitrogen result to the nearest tenth of a mg/kg. State that results were obtained according to Test Method D4629.

TABLE 1 Repeatability and Reproducibility

Concentration (mg/kg N)	r	R
100	2.0	8.7
75	1.7	7.5
50	1.4	6.1
25	1.0	4.2
10	0.6	2.6
1	0.18	0.81
0.3	0.10	0.44

14. Quality Assurance/Quality Control (QA/QC)

14.1 Confirm the performance of the instrument and the test procedure by analyzing a quality control (QC) sample.

14.1.1 When QA/QC protocols are already established in the testing facility, these may be used when they confirm the reliability of test results.

14.1.2 When there is no QA/QC protocol established in the testing facility, Appendix X1 may be used as the QA/QC system.

14.2 Users of this test method are advised that in contractual agreements, one or more of the contracting parties can and may make Appendix X1 a mandatory practice.

15. Precision and Bias⁴

15.1 The precision of this test method as determined by statistical examination of interlaboratory results is as follows (see Table 1):

15.1.1 *Repeatability*—The difference between two test results obtained by the same operator with the same apparatus under constant operating conditions on identical test material would, in the long run, in the normal and correct operation of the test method, exceed the following values in only one case in twenty, where X = the average of the two test results.

$$r = 0.1825(X)^{0.5149} \quad (5)$$

15.1.2 *Reproducibility*—The difference between two single and independent test results obtained by different operators working in different laboratories on identical test material would, in the long run, in the normal and correct operation of the test method, exceed the following values in only one case in twenty, where X = the average of the two test results.

$$R = 0.8094(X)^{0.5149} \quad (6)$$

15.2 The bias of this test method cannot be determined since an appropriate standard reference material containing a known trace level of nitrogen in a liquid petroleum hydrocarbon is not available to form the basis of a bias study.

16. Keywords

16.1 liquid hydrocarbons; total nitrogen

⁴ Supporting data have been filed at ASTM International Headquarters and may be obtained by requesting Research Reports RR:D02-1199 and RR:D02-1527. Contact ASTM Customer Service at service@astm.org.

APPENDIX**(Nonmandatory Information)****X1. QUALITY CONTROL (QC) MONITORING**

X1.1 Confirm the performance of the instrument or the test procedure by analyzing QC sample(s).

X1.2 Prior to monitoring the measurement process, determine the average value and control limits of the QC sample. Refer to Practice **D6299** and ASTM MNL 7.⁵

X1.3 Record the QC results and analyze by control charts or other statistically equivalent techniques to ascertain the statistical control status of the total test process.⁶ Refer to Practice **D6299** and ASTM MNL 7.⁵ Investigate any out-of-control data for root cause(s). The results of this investigation may, but not necessarily, result in instrument recalibration.

X1.4 The frequency of QC testing is dependent on the criticality of the quality being measured, the demonstrated

stability of the testing process, and customer requirements. Generally, a QC sample is analyzed each testing day with routine samples. The QC frequency should be increased if a large number of samples are routinely analyzed. However, when it is demonstrated that the testing is under statistical control, the QC testing frequency may be reduced. The QC sample precision should be periodically checked against the ASTM method precision to ensure data quality. Refer to Practice **D6299** and ASTM MNL 7.⁵

X1.5 It is recommended that, if possible, the type of QC sample that is regularly tested be representative of the material routinely analyzed. An ample supply of QC sample material should be available for the intended period of use, and must be homogenous and stable under the anticipated storage conditions.

X1.6 See Practice **D6299** and ASTM MNL 7⁵ for further guidance on QC and control charting techniques.

⁵ MNL 7, *Manual on Presentation of Data and Control Chart Analysis*, ASTM International, West Conshohocken, PA.

⁶ In the absence of explicit requirements given in the test method, this clause provides guidance in QC testing frequency.

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