Designation: D 6366 – 99

Standard Test Method for Total Trace Nitrogen and Its Derivatives in Liquid Aromatic Hydrocarbons by Oxidative Combustion and Electrochemical Detection[1]

This standard is issued under the fixed designation D 6366; 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.

1. Scope

1.1 This test method covers the determination of the total trace nitrogen (organic and inorganic) naturally found in liquid aromatic hydrocarbons, its derivatives and related chemicals.

1.2 This test method is applicable for samples containing nitrogen from 0.05 to 100 mgN/kg. For higher concentrations refer to Test Method D 4629.

1.3 The detector response for the technique within the scope of this test method is linear with nitrogen concentration.

1.4 The following applies to all specified limits in this test method: for purposes of determining conformance with this test method, an observed value or a calculated value shall be rounded off “to the nearest unit” in the last right-hand digit used in expressing the specification limit, in accordance with the rounding-off method of Practice E 29.

1.5 *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.* For specific hazard statements, see Section 9 and Note 2, Note 3, Note 4, and Note 8.

2. Referenced Documents

2.1 *ASTM Standards:*

D 3437 Practice for Sampling and Handling Liquid Cyclic Products[2]

D 3852 Practice for Sampling and Handling Phenol and Cresylic Acid[2]

D 4629 Test Method for Trace Nitrogen in Liquid Petroleum Hydrocarbons by Syringe/Inlet Oxidative Combustion and Chemiluminescence Detection[3]

E 29 Practice for Using Significant Digits in Test Data to Determine Conformance with Specifications[4]

2.2 *Other Document:*

OSHA Regulations, 29 CFR, paragraphs 1910.1000 and 1910.1200[5]

3. Terminology

3.1 *Definitions:*

3.1.1 *oxidative combustion*, *n*—a process in which a sample undergoes combustion in an oxygen-rich environment at temperatures greater than 650°C and compounds decompose to form carbon dioxide, water and elemental oxides.

4. Summary of Test Method

4.1 A sample of liquid aromatic hydrocarbon is injected, at a controlled rate, into a stream of inert gas (helium or argon) or inert gas mixed with oxygen. The sample is vaporized and carried to a high temperature zone (> 900°C), where oxygen is introduced. Organic and inorganic nitrogen compounds, present in the specimen, are converted to nitric oxide (NO). Nitric oxide is reacted with the sensing electrode in a 3-electrode electrochemical cell. This reaction produces a measurable current that is directly proportional to the amount of nitrogen in the original sample material.

4.1.1 The reaction that occurs is as follows:

$$\text{Combustion: } R{-}N + O_2 > 900°C \rightarrow CO_2 + H_2O + NO + \text{oxides} \quad (1)$$

$$\text{Detection: } NO + 2\,H_2O \text{ electrolyte } HNO_3 + (3H^+) + (3e^-)$$

5. Significance and Use

5.1 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 total nitrogen in process feeds and may also be used to control nitrogen compounds in finished products that fall within the scope of this test method.

NOTE 1—Virtually all organic and inorganic nitrogen compounds will detected by this technique.

5.2 This technique will not detect diatomic nitrogen and it will produce an attenuated response when analyzing compounds (that is, 5-triazine and azo compounds, etc.) that form

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[1] This test method is under the jurisdiction of ASTM Committee D16 on Aromatic Hydrocarbons and Related Materials, and is the direct responsibility of Subcommittee D16.04 on Instrumental Analysis.

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[2] *Annual Book of ASTM Standards*, Vol 06.04.

[3] *Annual Book of ASTM Standards*, Vol 05.02.

[4] *Annual Book of ASTM Standards*, Vol 14.02.

[5] Available from Superintendent of Documents, U.S. Government Printing Office, Washington, DC 20402.

nitrogen gas (N_2) when decomposed.

6. Interferences

6.1 Moisture produced during the combustion step can interfere if not removed prior to the detector.

7. Apparatus

7.1 *Pyrolsis Furnace*, capable of maintaining a temperature sufficient to volatilize and combust all of the sample and oxidize the organically bound nitrogen to NO. The furnace temperatures for petroleum substances shall be as recommended by the manufacturer.

7.2 *Quartz Combustion Tube*, capable of withstanding 900 to 1200°C. The inlet end of the tube holds a septum for syringe entry of the sample and has inlet fittings or side arms for the introduction of oxygen (O_2) and inert gas. The construction is such that the inert gas (or inert gas and oxygen mixture) sweeps the inlet zone, transporting all of the volatilized sample into a high-temperature oxidation zone. The oxidation section shall be large enough to ensure complete oxidation of the sample.

7.2.1 *Quartz Combustion Tube Devitrification*—the suggested maximum temperature for a quartz combustion tube is 1200°C. Samples containing alkai-metals (elements from the Periodic Group IA (that is, Na, K, etc.)) or alkaline earth (elements from the Periodic Group IIA (that is, Ca, Mg, etc.)) will cause quartz to devitrify (that is, become milky white and brittle).

7.3 *Drying Tube*, a magnesium perchlorate $Mg(ClO_4)_2$ scrubber or a membrane drying tube (permeation drier), or both, for removing water vapor produced during the reaction. Such water vapor must be removed prior to measurement by the electrochemical detector.

7.4 *Electrochemical Detector*, capable of measuring NO in the combustion gas stream.

7.5 *Data Reduction System*, having the capability of measuring, amplifying, and integrating the current from the electrochemical detector. The amplified or integrated output signal shall be applied to a digital display or some other data reporting device.

7.6 *Microliter Syringe*, of 5, 10, 25, 50, or 100-µL capacity capable of accurately delivering microliter quantities. The needle should be long enough to reach the hottest portion of inlet section of the furnace when injecting the sample.

7.7 *Recorder*, optional.

7.8 *Constant Rate Injector or Automatic Sampler System(s)*, optional, capable of delivering a sample at a precisely controlled rate.

8. Reagents

8.1 *Purity of Chemicals*—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, 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.

8.2 *Magnesium Perchlorate $Mg(ClO_4)_2$*—for drying products of the combustion (if a permeation drier is not used).

NOTE 2—**Warning:** Strong oxidizer, irritant.

8.3 *Inert Gas*—Either argon (Ar) or helium (He) may be used; the purity should be no less than 99.99 mol %.

8.4 *Oxygen*—The purity should be no less than 99.99 mol %.

NOTE 3—**Warning:** Vigorously accelerates combustion.

8.5 *Solvent*—The solvent of choice should be capable of dissolving the nitrogen-containing compound used to prepare the standard and, if necessary, the samples. The solvent of choice should have a boiling point similar to the samples being analyzed, and it should contain less nitrogen than the lowest sample to be analyzed. Suggested possibilities include, but are not limited to: toluene, *iso*-octane, methanol, cetane, or other solvent similar to compound present in the sample to be analyzed.

NOTE 4—**Warning:** Flammable solvents.

NOTE 5—A quick screening can be conducted by injecting the solvent and sample once or twice and comparing relative integral response.

8.6 *Nitrogen Stock Sample, 1000 µg N/mL*—Prepare a stock solution by accurately weighing to the nearest 0.1 mg, 1.195 g of carbozole or 0.565 g of pyridine into a tared 100 mL volumetric flask. A small amount of acetone may be used to dissolve the carbozole. Dilute to volume with selected solvent. This stock may be further diluted to desired sulfur concentrations, using the following equation:

$$\mu g\ N/mL = W \times 14.0 \times 1000\ \mu g/mg\ /100\ mL \times MW \qquad (2)$$

where:

W = exact weight of pyridine or carbazole, mg, and

MW = the mass weight of the reference material weighed.

NOTE 6—Carbazole may be used for calibration throughout the boiling range of this test method.

NOTE 7—Pyridine should be used with low boiling solvents (< 230°C).

8.7 *Acetone (C_3H_6O)*—mw 58.08.

NOTE 8—**Warning:** Flammable.

8.8 *Carbazole ($C_{12}H_9N$)*—mw 167.20.

NOTE 9—**Warning:** Irritant.

8.9 *Pyridine (C_5H_5N)*—mw 79.10.

NOTE 10—**Warning:** Flammable, irritant.

8.10 *Nitrogen Working Standard Solutions, 1.0 and 2.0 µg N/mL*—The working standards are prepared by dilution of the stock solution with the solvent. Prepare a 100-µg N/mL standard by accurately pippetting 10 mL of the stock solution into a 100-mL volumetric flask and diluting to volume with solvent. This standard is further diluted to 1.0- and 2.0-µg N/mL by accurately pippetting 1, and 2 mL of the 100-µg N/mL standard into separate clean 100-mL volumetric flasks and diluting each to volume with solvent.

NOTE 11—**Caution:** 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.

9. Hazards

9.1 Consult current OSHA regulations,[5] suppliers' Materials Safety Data Sheets, and local regulations for all materials used in this test method.

9.2 High temperature is employed in this test method. Extra care must be exercised when using flammable materials near the high temperature furnace.

10. Sample Handling

10.1 Collect the samples in accordance with Practice D 3437 or D 3852 as appropriate.

10.2 To preserve sample integrity (consistency) and prevent the loss of 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.

10.3 Since this procedure is intended for trace level contamination, care must be taken to ensure the containers used for the sample, the specimen, and the working standard do not alter the sample result.

11. Preparation of Apparatus

11.1 Assemble the apparatus in accordance with manufacturer's instructions.

11.2 Adjust the gas flows and the combustion temperature to the desired operating conditions.

12. Calibration and Standardization

12.1 Prepare a series of calibration standards using a stock solution covering the range of operation as described in 8.6-8.10 and consisting of nitrogen type and matrix similar to samples to be analyzed.

12.2 Volumetric measurement of the injected sample can be 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 volume of liquid in the syringe. After the sample 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 sample injected.

12.3 Alternatively, the sample injection device may be weighed before and after injection to determine the amount of sample injected. This test method provides greater precision than the volume delivery method, provided a balance with a precision of ± 0.01 mg is used.

12.4 Insert the syringe needle through the inlet septum up to the syringe barrel and inject the sample or standard at a uniform rate of 0.2 to 1.0 µL/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.

NOTE 12—For the most consistent injection rate and best analytical results, a constant rate injection system or automatic sampling system may be helpful. Consult manufacturer for recommendations.

NOTE 13—With direct injection below 2 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.

12.5 For the method blank, rinse the syringe thoroughly with the solvent blank. Then inject the same amount of solvent blank as utilized with standards and obtain the reading. Measure the blank a second time and average the results. The solvent blank should contain less than 0.1 mg/kg of nitrogen.

12.6 If the system features an automatic calibration procedure, repeat the measurement of each calibration standard three times. All calibration points shall be used to construct a calibration curve. System performance shall be checked with suitable a calibration standard each day, and when changing concentration ranges.

12.7 For those analyzers not equipped with an automatic calibration procedure, construct a standard curve by first repeating the determination of each calibration standard and the blank three times to determine the average net response for each standard. Then construct a curve plotting milligrams of nitrogen injected versus detector response (integration count). The response curve should be linear and shall be checked at least once per week.

13. Procedure

13.1 Use sample sizes ranging from 3 to 40 µL. Use sizes of injected sample that are similar to the size of injected standard.

13.2 Use experience to dictate the best sample size. A typical sample size for the scope of this test method is 5 to 20 µL.

13.3 Flush the microliter syringe several times with the unknown sample. Determine the sample size as described in 13.2 and inject it at an even rate as described in 12.4.

14. Calculation

14.1 For analyzers equipped with an automatic calibration, calculate the nitrogen content (N) of the sample in parts per million by weight (mg/kg) as follows:

$$N = (I - B) \times K/V \times D \tag{3}$$

or,

$$N = (I - B) \times K/M \tag{4}$$

where:
D = density of sample, g/mL,
K = dilution factor,
V = volume of sample, µL,
M = mass of sample, mg,
I = visual display reading of sample, and
B = average of visual display readings of blank.

14.2 For analyzers not equipped with automatic calibration, calculate the nitrogen content of the sample (N) in parts per million by weight (mg/kg) as follows:

$$N = I \times S \times K/V \times D \tag{5}$$

where:
S = slope of standard curve, mg N/count,
I = detector response, integration counts, and
K = dilution factor (when applicable).

15. Precision and Bias

15.1 *Precision*—Based on limited information (10 analyses by one operator) from one laboratory, the absolute standard deviation of 0.02 mg/kg at the 1.00 mg/kg level of nitrogen was obtained. See Table 1.

15.1.1 *Intermediate Precision*—The 95 % repeatability limits at the 1.00 mg/kg level are approximately ± 0.06.

15.1.2 The reproducibility of this test method is being determined and will be available by December 2003.

TABLE 1 Precision Data

Analysis Number	Integral Response	Concentration, ppm
1	34 657	1.00
2	34 231	0.99
3	34 485	0.99
4	34 739	1.00
5	33 515	0.97
6	33 821	0.98
7	35 399	1.02
8	36 022	1.04
9	34 729	1.00
10	34 998	1.01
Average	34 660	1.00
Standard Deviation	727	0.02

15.2 *Bias*—Since there is no accepted reference material suitable for determining the bias in this test method for measuring total nitrogen in aromatic hydrocarbons, bias has not been determined.

16. Keywords

16.1 aromatic hydrocarbons; catalyst; electrochemical; nitrogen content; oxidative combustion; oxygenated aromatics; petroleum hydrocarbons; poison

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