



Designation: D 6366 – 99

# Standard Test Method for Total Trace Nitrogen and Its Derivatives in Liquid Aromatic Hydrocarbons by Oxidative Combustion and Electrochemical Detection<sup>1</sup>

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 ( $\epsilon$ ) 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<sup>2</sup>

D 3852 Practice for Sampling and Handling Phenol and Cresylic Acid<sup>2</sup>

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

E 29 Practice for Using Significant Digits in Test Data to

Determine Conformance with Specifications<sup>4</sup>

### 2.2 Other Document:

OSHA Regulations, 29 CFR, paragraphs 1910.1000 and 1910.1200<sup>5</sup>

## 3. Terminology

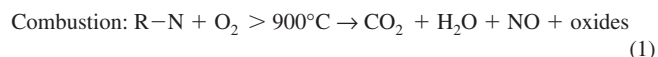
### 3.1 Definitions:

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:



## 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

<sup>1</sup> 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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<sup>2</sup> Annual Book of ASTM Standards, Vol 06.04.

<sup>3</sup> Annual Book of ASTM Standards, Vol 05.02.

<sup>4</sup> Annual Book of ASTM Standards, Vol 14.02.

<sup>5</sup> Available from Superintendent of Documents, U.S. Government Printing Office, Washington, DC 20402.

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 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 *Pyrolysis 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 alkali-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- $\mu$ L 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  $\mu$ g N/mL*—Prepare a stock solution by accurately weighing to the nearest 0.1 mg, 1.195 g of carbazole or 0.565 g of pyridine into a tared 100 mL volumetric flask. A small amount of acetone may be used to dissolve the carbazole. Dilute to volume with selected solvent. This stock may be further diluted to desired sulfur concentrations, using the following equation:

$$1000 \mu\text{g N/mL} = W \times 14.0 \times 1000 \mu\text{g/mg} / 100 \text{ mL} \times MW \quad (2)$$

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  $\mu$ g N/mL*—The working standards are prepared by dilution of the stock solution with the solvent. Prepare a 100- $\mu$ g N/mL standard by accurately pipetting 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- $\mu$ g N/mL by accurately pipetting 1, and 2 mL of the 100- $\mu$ g N/mL standard into separate clean 100-mL volumetric flasks and diluting each to volume with solvent.