



Designation: D 6069 – 01

Standard Test Method for Trace Nitrogen in Aromatic Hydrocarbons by Oxidative Combustion and Reduced Pressure Chemiluminescence Detection¹

This standard is issued under the fixed designation D 6069; 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 total nitrogen (organic and inorganic) in aromatic hydrocarbons, their derivatives and related chemicals.

1.2 This test method is applicable for samples containing nitrogen from 0.2 to 2 mgN/kg. For higher nitrogen concentrations refer to Test Method D 4629.

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

1.3 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.

1.4 *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.

2. Referenced Documents

2.1 ASTM Standards:

D 1555 Test Method for Calculation of Volume and Weight of Industrial Aromatic Hydrocarbons²

D 3437 Practice for Sampling and Handling Liquid Cyclic Products²

D 4629 Test Method for Organically Bound Trace Nitrogen in Liquid Petroleum Hydrocarbons By Syringe/Inlet Oxidative Combustion and Chemiluminescence Detection³

¹ This test method is under the jurisdiction of ASTM Committee D16 on Aromatic Hydrocarbons and Related Chemicals 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.

E 29 Practice for Using Significant Digits in Test Data to Determine Conformance with Specifications⁴

E 691 Practice for Conducting an Interlaboratory Study to Determine the Precision of a Test Method⁴

2.2 Other Documents:

OSHA Regulations, 29 CFR, paragraphs 1910.1000 and 1910.1200⁵

3. Terminology

3.1 Definitions:

3.1.1 *reduced pressure chemiluminescence*—a chemical reaction at pressure less than 760 mm mercury (Hg) in which light is emitted.

3.1.2 *oxidative pyrolysis*—a process in which a sample under goes combustion in an oxygen rich environment at temperatures greater than of 650°C.

3.1.2.1 *Discussion*—Organic compounds pyrolytically decompose to carbon dioxide, water and elemental oxides.

4. Summary of Test Method

4.1 A specimen is introduced into a gas stream, at a controlled rate, and carried into a high temperature furnace (>900°C) where an excess of oxygen is added. Pyrolysis converts organic material in the specimen to carbon dioxide and water. Organic nitrogen and inorganic nitrogen compounds, present in the specimen, are converted to nitric oxide (NO). Nitric oxide reacts with ozone in the detector producing nitrogen dioxide molecules in an excited state. As the excited nitrogen dioxide molecules relax to ground state, light is emitted. This light is detected by a photomultiplier tube with the resulting signal proportional to the concentration of nitrogen in the sample. Operating the detector at a reduced pressure, lowers the probability of the excited nitrogen dioxide molecules colliding with other molecules before they undergo chemiluminescence. Thus, reduced pressure provides improved sensitivity and lower noise.

⁴ Annual Book of ASTM Standards, Vol 14.02.

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

*A Summary of Changes section appears at the end of this standard.

5. Significance and Use

5.1 This method has been prepared to detect and quantitate nitrogen-containing compounds such as *N*-formylmorpholine (4-formylmorpholine, Chemical Abstract Service numbers (CAS) No. 250-37-6) or 1-methyl-2-pyrrolidinone (NMP) (CAS) No. 872-50-42 at a concentration of 1.0 mgN/kg or less in aromatic hydrocarbons used or produced in manufacturing processes. These nitrogen-containing compounds are undesirable in the finished aromatic products and may be the result of the aromatic extraction process. This test method may be used in setting specifications for determining the total nitrogen content in aromatic hydrocarbons.

NOTE 1—Virtually all organic and inorganic nitrogen compounds will be 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, *s*-triazine and azo compounds, etc.) that form nitrogen gas (N₂) when decomposed.

5.3 This test method requires the use of reduced pressure at the detector. Loss of vacuum or pressure fluctuations impact the sensitivity of the detector and the ability to determine nitrogen concentrations less than 1 mg/kg.

6. Interferences

6.1 Chlorides, bromides, and iodides can interfere if any one or all of these elements are present in a sample in concentrations greater than 10 % by total weight of halogen in the sample.

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

7. Apparatus

7.1 *Pyrolysis Furnace*—A furnace capable of maintaining a temperature sufficient to volatilize and pyrolyze the sample and oxidize organically bound nitrogen to NO. The actual temperature(s) should be recommended by the specific instrument manufacturers.

7.2 *Quartz Pyrolysis Tube*—Capable of withstanding 900 to 1200°C.

7.2.1 *Quartz Pyrolysis Tube*—The suggested maximum temperature for a quartz pyrolysis tube is 1200°C. Samples containing alkali-metals (elements from the Periodic Group IA (that is, Na, K, etc.)) or alkaline earths (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 *Chemiluminescent Detector*—Capable of operation at reduced pressures (less than 760 mm mercury) and able to measure light emitted from the reaction between NO and ozone. Includes ozone generator.

7.4 *Microlitre Syringe*—Capable of delivering from 5 to 50 µL of sample. Check with the instrument manufacturer for recommendations for specific sample needs.

7.5 *Constant Rate Injector System (Optional)*—If the sample is to be introduced into the pyrolysis furnace via syringe, a constant rate injector should be used.

7.6 *Boat Inlet System (Optional)*—If the instrument is equipped with a boat inlet system, care must be taken to ensure the boat is sufficiently cooled between analyses to prevent the

sample from vaporizing as it is injected into the boat. The sample should start vaporizing as it enters the furnace. It is critical that the sample vaporize at a constant and reproducible rate. This type of inlet system offers advantage when the sample is viscous or contains heavy components not volatile at temperatures of approximately 300°C, or for samples that contain polymers or high concentrations of salts that could result in plugging of the syringe needle.

7.7 *Automatic Boat Drive System (Optional)*—If the instrument is equipped with a boat inlet system, a device for driving the boat in to the furnace at a controlled and repeatable rate may improve data repeatability and reproducibility.

7.8 *Oxidation Catalyst (Optional)*—Catalyst (that is, cupric oxide (CuO) or Platinum (Pt)) may be packed into the pyrolysis tube to aid in oxidation efficiencies (see manufacturer's recommendations).

8. Reagents

8.1 *Purity of Reagents*—Reagent grade chemicals shall be used in all tests. It is intended that all reagents shall conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society,⁶ where such specifications are available, unless otherwise indicated. 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 *Inert Gas*—Either argon (Ar) or helium (He) may be used. The purity should be no less than 99.99 mol %.

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

8.4 *Solvent*—The solvent chosen 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, methanol, tetrahydrofuran, *iso*-octane.

NOTE 2—A quick screening can be conducted by injecting the solvent and sample once or twice and comparing relative area counts.

8.4.1 *Solvent*—Toluene, relative density at 60°F/60°F 0.8718 (see Test Method D 1555).

8.5 *Nitrogen Stock Solution, 1000 µg N/mL*—Prepare a stock solution by accurately weighing, to the nearest 0.1 mg, approximately 707.7 mg of 1-methyl-2-pyrrolidinone (NMP) (CAS No. 872-50-4) into a 100-mL volumetric flask. Fill to volume with solvent as follows:

$$\mu\text{g N/mL} = \frac{\text{exact weight of NMP (mg)} \times 14.0 \times 1000 (\mu\text{g/mg})}{100 \text{ mL} \times 99.1} \quad (1)$$

where:

⁶ *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.