



# Standard Test Method for Trace Nitrogen in Aromatic Hydrocarbons by Oxidative Combustion and Reduced Pressure Chemiluminescence Detection<sup>1</sup>

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

D 3437 Practice for Sampling and Handling Liquid Cyclic Products<sup>2</sup>

D 4629 Test Method for Organically Bound 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>

E 691 Practice for Conducting an Interlaboratory Study to Determine the Precision of a Test Method<sup>4</sup>

<sup>1</sup> This test method is under the jurisdiction of ASTM Committee D-16 on Aromatic Hydrocarbons and Related Chemicals and is the direct responsibility of Subcommittee D16.0E on Instrumental Analysis.

Current edition approved Dec. 10, 1996. Published February 1997.

<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.

### 2.2 Other Documents:

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

## 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 it under goes chemiluminescence. Thus, reduced pressure provides improved sensitivity and lower noise.

## 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

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

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 (N<sub>2</sub>) 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.

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,<sup>6</sup> 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:

14.0 = the atomic weight of nitrogen, and

99.1 = the molecular weight of NMP.

8.6 *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 pipetting 10 mL of 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 pipetting 1 mL of the 100 µg-N/mL standard into a

<sup>6</sup> *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 Pharmacopoeia and National Formulary*, U.S. Pharmacopoeial Convention, Inc. (USPC), Rockville, MD.

clean 100-mL volumetric flask and pipetting 2 mL of the 100- $\mu\text{g}$  N/mL standard into a different clean 100-mL volumetric flask and diluting each to volume with solvent.

NOTE 3—Working standards should be prepared on a regular basis depending upon the frequency of use and age. Typically, standards have a useful life of about 3 months.

8.7 *Cupric Oxide (CuO) or Platinum (Pt)*—May be used as an oxidation catalyst, as recommended by the instrument manufacturer.

8.8 *Quartz Wool*—May be needed if recommended by the instrument manufacturer.

## 9. Hazards

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

9.2 High temperature is employed in this test method. **Warning**—Extreme care should be exercised when using flammable materials near the pyrolysis furnace.

## 10. Sample Handling

10.1 Collect the samples in accordance with Practice D 3437.

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 specimen as soon as possible after transferring from the sample container 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 results.

## 11. Instrument Assembly and Preparation

11.1 Install the instrument in accordance with manufacturer's instructions. See Appendix X1 for typical set-up parameters.

11.2 Adjust gas flows and pyrolysis temperature(s) to the operating conditions as recommended by the manufacturer.

11.3 The actual operation of injecting a sample will vary depending upon the instrument manufacturer and the type of inlet system used (see 7.5-7.8).

## 12. Calibration and Standardization

12.1 Prepare the working calibration standards using the stock solution as described in 8.5 and 8.6.

12.1.1 Before injecting a standard or blank, refer to procedures (see Section 13, Procedure), to ensure proper technique for either the direct injection system or the boat inlet system.

12.2 A calibration based on the difference between two gravimetrically prepared standards works well within the limited scope of this procedure. This type of calibration can be used to quantitate nitrogen at the 1.0 ppm (wt/wt) concentration or to determine pass/fail compliance. Two standards are prepared with concentrations that differ by the target specification. Thus, for a 1.0 ppm nitrogen (wt/wt) maximum specification, prepare two standards that differ in concentration by 1.0 ppm (that is, 2.0  $\mu\text{g}$ -N/mL and a 1.0  $\mu\text{g}$ -N/mL standard).

12.2.1 Each standard should be injected in triplicate and the integrator counts averaged and recorded.

## 13. Procedure

13.1 Sample sizes from 5 to 50  $\mu\text{L}$  are acceptable. Although, at the concentration range from 0.2 to 2  $\mu\text{g}$  N/mL, it is recommended that the same size sample be used for all standards and samples analyses.

NOTE 4—When an organic sample is injected into the pyrolysis furnace a pressure wave is formed. The initial flash vaporization forms a positive pressure pulse, thus decreasing detector sensitivity. After pyrolysis of the organic material in the high-temperature furnace a reduced pressure pulse is formed, resulting in increased detector sensitivity. Thus, maintaining the same sample size for all injections (that is, samples and standards) will improve repeatability and reproducibility. As mentioned in 8.4, Solvent, using a solvent with a boiling point similar to that of the sample being analyzed is generally recommended.

13.1.1 Always flush the syringe several times with the material to be injected. To prevent contamination do not return the first couple of flushes back into the specimen bottle.

13.1.2 If the instrument is equipped with a pyrolysis tube for direct syringe injection, see 13.2. If the instrument is equipped with a boat inlet system, see 13.3.

13.2 Fill syringe to approximately 1.5 times the volume to be injected (that is, to inject 10  $\mu\text{L}$ , fill a 25- $\mu\text{L}$  syringe with 15 to 20  $\mu\text{L}$  of sample or standard), taking care not to pull air bubbles into the syringe with the sample. With the syringe needle pointed up, push the plunger in to the desired volume, tap the last drop off the needle point, and pull the plunger back until air can be seen in the syringe barrel.

NOTE 5—The inherent accuracy of this technique is dependent upon the ability of the analyst to repeatedly inject the same volume for each injection. Air bubbles lodged between the syringe plunger and the specimen will result in variable specimen volumes. If bubbles persist, try cleaning the syringe with a different solvent or try inserting the needle into a septum and gently putting pressure on the syringe plunger (this may cause persistent bubbles to break free).

NOTE 6—If the detector response continuously increases or decreases, this is indicative of contamination. If this occurs, continue injecting the specimen until the detector signal shows a typical variance.

13.2.1 Insert the syringe needle through the inlet septum as far as it will go (the syringe barrel should be touching the septum). Allow the residual sample in the needle to burn-off. When the instrument returns to a stable baseline, zero or clear the detector display and inject the specimen or standard at a constant rate of 0.5 to 1.0  $\mu\text{L}/\text{s}$ .

13.2.2 If an autosampler is used the detector will be automatically zeroed prior to injection.

13.2.3 Repeat 13.2 analyzing each standard and sample in triplicate. Average the three results for each standard or sample and record the results.

13.3 With the boat inlet system, a specimen is injected into a cool boat and the boat carried into the pyrolysis furnace. Before analyzing standards or samples introduce the boat into the furnace to burn-off any possible contamination.

13.3.1 Fill the syringe as described in 13.2. Inject the standard or specimen into the cooled boat. Move the boat containing the specimen into the furnace at a controlled and repeatable rate.

NOTE 7—The boat may be stopped at the furnace inlet to permit evaporation, if a controlled combustion is necessary. Although, if the boat is stopped, it must then be stopped at the same place and for the same length of time for all analyses (see Note 4, Note 5, and Note 6).

13.3.2 Repeat 13.3 analyzing each sample, or standard in triplicate. Average the three results for each sample and record the results.

## 14. Calculation

14.1 Calculate the concentration of nitrogen as follows:

$$\text{Nitrogen, mg/kg} = \frac{I_{sx} \times (C_{std2} - C_{std1}) \times V_{std}}{(I_{std2} - I_{std1}) \times V_{sx} \times D_{sx}} \quad (2)$$

where:

- $I_{sx}$  = detector response of sample, integration counts,
- $I_{std2}$  = highest standard's average detector response, integration counts,
- $I_{std1}$  = lowest standard's average detector response, integration counts,
- $C_{std2}$  = concentration of higher standard,  $\mu\text{g N/mL}$ ,
- $C_{std1}$  = concentration of lower standard,  $\mu\text{g N/mL}$ ,
- $D_{sx}$  = density of the sample,  $\text{g/mL}$ ,
- $V_{sx}$  = volume of sample injected,  $\mu\text{L}$ , and
- $V_{std}$  = volume of standard solution injected,  $\mu\text{L}$ .

**TABLE 1 Repeatability and Reproducibility<sup>A</sup>**

Nitrogen Concentration, mg/kg	Repeatability	Reproducibility
0.32	0.09	0.25
0.60	0.15	0.26
0.88	0.19	0.34

<sup>A</sup> Repeatability and Reproducibility determined at the 95 % confidence level.

**TABLE 2 Estimated Bias**

Solvent	Nitrogen Spike, mg N/kg	Average of 10 Laboratories Nitrogen Results Based on the ILS, mg N/kg	Absolute Difference
Xylene	0.32	0.32	0.00
Xylene	0.60	0.60	0.00
Xylene	0.88	0.87	0.01

## 15. Precision and Bias

15.1 *Precision*—The following criteria<sup>7</sup>, conducted under the guidelines of Practice E 691, should be used to judge the acceptability (95 % probability) of the results obtained by this test method. The criteria were derived from a interlaboratory study between ten laboratories. Standards and samples were analyzed in duplicate on the same day by a single operator. Each analysis represented triplicate injections.

15.1.1 *Repeatability*—Results within laboratory results by the same operator with the same equipment over the shortest practicable period of time should not be considered suspect unless they differ by more than the amount shown in Table 1.

15.1.2 *Reproducibility*—Results submitted by two laboratories should not be considered suspect unless they differ by more than the amount shown in Table 1.

15.2 *Bias*—Systematic error that contributes to a difference between the mean and an accepted reference value. Since all organic solvents can contain nitrogen, an absolute statement of bias could not be determined from this study. Although, an estimate of bias was determined by spiking a single solvent (xylene) with three different concentrations of nitrogen. These three spiked samples were then analyzed as unknowns in the interlaboratory study (see Table 2).

## 16. Keywords

16.1 chemiluminescence; nitrogen

<sup>7</sup> Supporting data are available from ASTM Headquarters. Request RR:D 16-1024.

**APPENDIX**
**(Nonmandatory Information)**
**X1. TYPICAL SET-UP CONDITIONS**

X1.1 Table X1.1 illustrates two instrument's parameters and settings.

**TABLE X1.1 Typical Set-Up Conditions<sup>A,B</sup>**

<b>Instrument 1 Parameters</b>		<b>Instrument 1 Settings</b>		
Syringe Drive Rate for Direct Injection		(700–750) 1 $\mu$ L/second		
Boat Drive Rate for Boat Inlet		(700–750) 140–160 mm/min		
Furnace Temperature		1050 $\pm$ 25°C		
Furnace Oxygen Flowmeter Setting		(3.8–4.1) 450–500 cc/min		
Inlet Oxygen Flowmeter Setting		(0.4–0.8) 10–30 cc/min		
Inlet Carrier Flowmeter Setting		(3.4–3.6) 130–160 cc/min		
Ozone Oxygen Flowmeter Setting		(1.5–1.7) 35–45 cc/min		
Pyro-tube Back Pressure		1–2.5 psi		
Gain		High		
Attenuation		50		
Sample Size		20 $\mu$ L		
<b>Instrument 2 Parameters</b>		<b>Instrument 2 Settings</b>		
Automatic Boat Control	1 Fuc	FWD 140	Speed 10	Time 30
	2 Fuc	FWD 285	Speed 05	Time 30
	5 Fuc			Time 30
	6 Fuc			Time 90
	AFuc			Time 60
Furnace Temperatures	Inlet	600°C		
	Catalyst	950°C		
Gas Flow Setting	Main Oxygen	400 cc/min		
	Inlet Oxygen	0.4 L/min		
	Inlet Argon	0.4 L/min		
Range		Low		
Attenuation		2		
Sample Size		20 $\mu$ L		

<sup>A</sup>The sole source of supply of the apparatus for Instrument 1, Antek Model 7000 known to the committee at this time is Antek Instruments, Inc., Houston, TX. If you are aware of alternative suppliers, please provide this information to ASTM Headquarters. Your comments will receive careful consideration at a meeting of the responsible technical committee<sup>1</sup>, "which you may attend."

<sup>B</sup>The sole source of supply of the apparatus for Instrument 2, Mitsubishi Model TN-10 known to the committee at this time is COSA Instrument Corp., Norwood, NJ. If you are aware of alternative suppliers, please provide this information to ASTM Headquarters. Your comments will receive careful consideration at a meeting of the responsible technical committee<sup>1</sup>, "which you may attend."

 **D 6069**

*The American Society for Testing and Materials takes no position respecting the validity of any patent rights asserted in connection with any item mentioned in this standard. Users of this standard are expressly advised that determination of the validity of any such patent rights, and the risk of infringement of such rights, are entirely their own responsibility.*

*This standard is subject to revision at any time by the responsible technical committee and must be reviewed every five years and if not revised, either reapproved or withdrawn. Your comments are invited either for revision of this standard or for additional standards and should be addressed to ASTM Headquarters. Your comments will receive careful consideration at a meeting of the responsible technical committee, which you may attend. If you feel that your comments have not received a fair hearing you should make your views known to the ASTM Committee on Standards, 100 Barr Harbor Drive, West Conshohocken, PA 19428.*