Designation: ~~D7184 – 07~~ D7184 – 12

Standard Test Method for
Ultra Low Nitrogen in Aromatic Hydrocarbons by Oxidative Combustion and Reduced Pressure Chemiluminescence Detection[1]

This standard is issued under the fixed designation D7184; 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~~ Scope*

1.1 This test method covers the determination of total nitrogen in aromatic hydrocarbons, such as benzene, toluene, and xylene.

1.2 This test method is applicable for samples containing nitrogen from ~~0.03~~0.38 to ~~1~~1.2 mg N/kg. For higher nitrogen concentrations refer to Test Method D6069 or D4629.

1.3 In determining the conformance of the test results using this method to applicable specifications; results shall be rounded off in accordance with the rounding-off method of Practice E29.

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

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.

2. Referenced Documents

2.1 *ASTM Standards:*[2]

D3437 Practice for Sampling and Handling Liquid Cyclic Products

D4629 Test Method for Trace Nitrogen in Liquid Petroleum Hydrocarbons by Syringe/Inlet Oxidative Combustion and Chemiluminescence Detection

D6069 Test Method for Trace Nitrogen in Aromatic Hydrocarbons by Oxidative Combustion and Reduced Pressure Chemiluminescence Detection

D6809 Guide for Quality Control and Quality Assurance Procedures for Aromatic Hydrocarbons and Related Materials

E29 Practice for Using Significant Digits in Test Data to Determine Conformance with Specifications

E691 Practice for Conducting an Interlaboratory Study to Determine the Precision of a Test Method

2.2 *Other Documents:*

OSHA Regulations, 29 ~~CFR,~~CFR paragraphs 1910. 1000 and 1910.1200 [3]

3. Terminology

3.1 *Definitions:*

3.1.1 *oxidative pyrolysis, n*—a process in which a sample undergoes combustion in an oxygen rich environment at temperatures greater than 900°C.

3.1.2 *pyrolytic decomposition, n*—combusting a compound to decompose it to carbon dioxide, water and elemental oxides.

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

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[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] 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.

[3] Available from U.S. Government Printing Office Superintendent of Documents, 732 N. Capitol St., NW, Mail Stop: SDE, Washington, DC 20401, http://www.access.gpo.gov.

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

4. Summary of Test Method

4.1 A specimen is introduced into a carrier gas stream, at a controlled rate, and incorporated into a high temperature furnace (900 to 1150°C) where an excess of oxygen is added. Pyrolysis converts hydrocarbons 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 or by a photodiode 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 molecule colliding with other molecules before it undergoes chemiluminescence. Thus, reduced pressure provides improved sensitivity and lower noise.

5. Significance and Use

5.1 This test method is useful to detect and quantify nitrogen-containing compounds at a concentration of 0.03 to 1 mg N/kg in light aromatic hydrocarbons used or produced in manufacturing process. These nitrogen-containing compounds are undesirable in finished aromatic products and may be used in setting specification for determining the total nitrogen content in aromatic hydrocarbons.

5.2 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 N/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 in the sample produced during the combustion step can interfere if not removed prior to the gas entering the detector cell.

7. Apparatus

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

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

7.3 *Chemiluminescence Detector*—Capable of operation at reduced pressure (less than 760 mm mercury) and able to measure light emitted from the reaction between NO and ozone.

7.4 *Microliter Syringe*—5 to 250 µL or as recommended by instrument manufacturer.

7.5 *Constant Rate Injector System*—If the sample is to be introduced into the pyrolysis furnace via syringe, use a constant rate injector or a liquid introduction module or as recommended by instrument manufacturer.

7.6 *Liquid Auto-Sampler*—Capable of injecting 5 to 250 µL of sample or as recommended by instrument manufacturer.

7.7 *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.

7.8 *Automatic Boat Drive System*—If the instrument is equipped with a boat inlet system the boat should be introduced into the furnace at a controlled rate.

7.9 *Membrane Dryer*—Removes moisture of combustion before the detector.

8. Reagents[4]

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, 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 shall be no less than 99.99 mol %.

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

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[4] *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 Pharmacopeial and National Formulary*, U.S. Pharamacopeial Convention, Inc. (USPC) Rockville, MD.

8.4 *Solvent*—The solvent of choice should be capable of dissolving the nitrogen sample. The solvent of choice should have a boiling point similar to the sample being analyzed. The solvent should contain less than 0.05 mg N/L. The blank value must be determined for each new bottle of solvent. Suggested possibilities include, but not limited to methanol, iso-octane and p-xylene.

NOTE 1—A quick screening can be conducted by injecting the solvent and sample once or twice and comparing relative area counts.

8.5 *Nitrogen Stock Solution, approximately 1000 mg N/L*—Prepare a stock solution by weighing, to the nearest 0.1 mg approximately 0.57 g of pyridine into a 100 ml volumetric flask. Dilute to the mark with solvent. Calculate the actual concentration of nitrogen using Eq 1. This standard may also be purchased.

$$\text{mg N/L} = \frac{(\text{Wt. of pyridine in grams}) \times (.1771) \times (10^6)}{100 \text{ ml of solvent}} \tag{1}$$

~~*where:*~~

where:

% nitrogen in pryridine = 17.71

8.6 *Nitrogen Working Standard Solution*—Calculate the correct concentration obtained from the nitrogen stock solution prepared in 8.5 and prepare the working standards by diluting the stock solution with the solvent. Prepare approximately 10.0 mg N/L standard by accurately pipeting 1.0 mL of the stock solution into a 100 ml volumetric flask and dilute to mark with solvent. This Standard is further diluted to 0.05, 0.10, 0.5 and 1.0 mg N/L by accurately pipeting 0.5, 1.0, 5 and 10.0 mL of standard into four separate 100 mL volumetric flasks and dilute to the mark with solvent. The working standards will be approximately blank, 0.05, 0.1, 0.5, and 1.0 mg N/L. Calculate the correct concentrations using the calculation:

$$mg\ N/L = (mg\ N/L\ in\ working\ standard) \times (ml\ pipeted)/(100\ ml) \tag{2}$$

or

$$mg\ N/Kg = (mg\ N/L\ in\ working\ standard) \times (ml\ pipeted)/(100\ ml) * (Density\ of\ solution\ g/ml) \tag{3}$$

~~Alternate volumes of solutions may be prepared so long as the preparation meets the concentration specified.~~

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NOTE 2—Working standards should be prepared on a regular basis depending upon the frequency of use and age. The stock solution can be retained, if refrigerated, for up to three months. Do not refrigerate stock solution if prepared in benzene as the benzene will freeze and cause erratic results.

8.7 *Cupric Oxide (CuO or Platinum (Pt)*—May be used as an oxidation catalyst in the combustion tube, 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, chemical suppliers' Material Safety Data Sheets, and local regulations for all material used in this test method.

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

9.3 Ozone can be hazardous so use of good vented room is necessary.

10. Sample Handling

10.1 Collect the sample in accordance with Practice D3437.

10.2 To preserve sample integrity and prevent the loss of volatile components, which may be in some samples, do not expose samples to the atmosphere 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 analysis, care must be taken to ensure that the sample container, and working standards containers are clean and do not contaminate the sample.

11. Instrument Assembly and Preparation

11.1 Setup the instrument in accordance with the instrument manufacturer's instructions.

11.2 Set instrument parameters in accordance with instrument manufacturer's recommendations.

11.3 Adjust gas flows and pyrolysis temperatures to the operating conditions as recommended by the instrument manufacturer.

11.4 The actual operation of injecting a sample will vary depending upon the instrument manufacturer and 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 and 8.5 and 8.6.