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Standard Test Method for Trace Nitrogen in Liquid Petroleum Hydrocarbons by Syringe/Inlet Oxidative Combustion and Chemiluminescence Detection[1]

This standard is issued under the fixed designation D4629; 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.

This standard has been approved for use by agencies of the U.S. Department of Defense.

1. Scope

1.1 This test method covers the determination of the trace total nitrogen naturally found in liquid hydrocarbons boiling in the range from approximately 50 °C to 400 °C, with viscosities between approximately 0.2 cSt and 10 cSt (mm^2/s) at room temperature. This test method is applicable to naphthas, distillates, and oils containing 0.3 mg/kg to 100 mg/kg total nitrogen. For liquid hydrocarbons containing more than 100 mg/kg total nitrogen, Test Method D5762 can be more appropriate. This test method has been successfully applied, during interlaboratory studies, to sample types outside the range of the scope by dilution of the sample in an appropriate solvent to bring the total nitrogen concentration and viscosity to within the range covered by the test method. However, it is the responsibility of the analyst to verify the solubility of the sample in the solvent and that direct introduction of the diluted sample by syringe into the furnace does not cause low results due to pyrolysis of the sample or solvent in the syringe needle.

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

1.3 *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.* See 6.2, 6.4, 6.5, 6.9, and Section 7.

1.4 *This international standard was developed in accordance with internationally recognized principles on standardization established in the Decision on Principles for the Development of International Standards, Guides and Recommendations issued by the World Trade Organization Technical Barriers to Trade (TBT) Committee.*

2. Referenced Documents

2.1 *ASTM Standards:*[2]

D1298 Test Method for Density, Relative Density, or API Gravity of Crude Petroleum and Liquid Petroleum Products by Hydrometer Method

D4052 Test Method for Density, Relative Density, and API Gravity of Liquids by Digital Density Meter

D5762 Test Method for Nitrogen in Petroleum and Petroleum Products by Boat-Inlet Chemiluminescence

D6299 Practice for Applying Statistical Quality Assurance and Control Charting Techniques to Evaluate Analytical Measurement System Performance

3. Summary of Test Method

3.1 The sample of liquid petroleum hydrocarbon is introduced either by syringe or boat inlet system, into a stream of inert gas (helium or argon). The sample is vaporized and carried to a high temperature zone where oxygen is introduced and organically bound nitrogen is converted to nitric oxide (NO). The NO contacts ozone, and is converted to excited nitrogen dioxide (NO_2). The light emitted as the excited NO_2 decays is detected by a photomultiplier tube and the resulting signal is a measure of the nitrogen contained in the sample.

4. Significance and Use

4.1 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 bound nitrogen in process feeds and may also be used to control nitrogen compounds in finished products.

[1] This test method is under the jurisdiction of ASTM Committee D02 on Petroleum Products, Liquid Fuels, and Lubricants and is the direct responsibility of Subcommittee D02.03 on Elemental 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.

5. Apparatus

5.1 *Furnace,* electric, held at a temperature sufficient to volatilize and pyrolyze all of the sample and oxidize the organically bound nitrogen to NO. Furnace temperature(s) shall be as recommended by the manufacturer (typically around 1000 °C).

5.2 *Combustion Tube,* fabricated to meet the instrument manufacturer's specifications.

5.3 *Drier Tube*—The reaction products include water vapor that must be eliminated prior to measurement by the detector. This can be accomplished with a magnesium perchlorate $Mg(ClO_4)_2$ scrubber or a membrane drying tube (permeation drier), or by whatever other means the instrument manufacturer specifies as appropriate for the instrument being used.

5.4 *Chemiluminescent Detector,* capable of measuring light emitted from the reaction between NO and ozone.

5.5 *Totalizer,* having variable attenuation, and capable of measuring, amplifying, and integrating the current from the chemiluminescent detector. A built in microprocessor or attached computer system may perform these functions.

5.6 *Micro-litre Syringe,* of 5 µL, 10 µL, 25 µL, 50 µL, or 250 µL capacity capable of accurately delivering micro-litre quantities is required. The needle should be long enough to reach the hottest portion of the inlet section of the furnace when injecting the sample. The syringe may be part of an automatic sampling and injection device used with the instrument.

5.7 *Strip Chart Recorder* (Optional).

5.8 *Sample Inlet System*—One of the following must be used:

5.8.1 *Manually Operated Syringe.*

5.8.2 *Syringe*, with a constant rate injector system, capable of delivering a sample at a precisely controlled rate.

5.8.3 *Boat Inlet System,* to facilitate analysis of samples that would react with the syringe or syringe needle. The pyrolysis tube for boat inlet use may require specific construction to permit insertion of a boat fully into the inlet section of the furnace. The boat inlet system external to the furnace may be cooled to a temperature below room temperature to aid in dissipating the heat from the boat when it is removed from the furnace. Cooling the boat inlet system may also reduce the chances of the sample combusting in the boat before introduction into the furnace and may be necessary when running volatile samples such as naphtha using a boat inlet system.

5.9 *Quartz Insert Tube* (Optional), may be packed with cupric oxide (CuO) or other oxidation catalyst as recommended by the instrument manufacturer, to aid in completing oxidation. This is inserted into the exit end of the pyrolysis tube.

5.10 *Vacuum System* (Optional), The chemiluminescence detector may be equipped with a vacuum system to maintain the reaction cell at reduced pressure (typically 20 mm to 25 mm Hg). This can improve the signal to noise ratio of the detector.

5.11 *Analytical Balance* (Optional), with a precision of ±0.01 mg.

6. Reagents

6.1 *Purity of Reagents*—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,[3] 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.

6.2 *Magnesium Perchlorate $Mg(ClO_4)_2$,* for drying products of combustion (if permeation drier is not used.) (**Warning—** Strong oxidizer, irritant.)

6.3 *Inert Gas,* argon or helium, ultra-high purity grade (UHP).

6.4 *Oxygen,* (99.8 % or better, 99.996 % is recommended). (**Warning—**Vigorously accelerates combustion.)

6.5 *Solvents,* for diluting and matrix matching such as, toluene, isooctane, xylene, acetone, cetane. (Other solvents similar to those occurring in samples to be analyzed are also acceptable). Solvents should contain less than 0.1 µg N/mL. (**Warning—**Flammable solvents.)

6.6 *Nitrogen Stock Solution,* 1000 µg N/mL, Prepare a stock solution by accurately weighing approximately 1.195 g of carbazole or 0.565 g of pyridine to the nearest milligram, into a tared 100 mL volumetric flask (see 6.6.1). Fifteen millilitres of acetone may then be added when using carbazole to help dissolve it. Dilute to volume with the selected solvent. Calculate the exact concentration of the stock solution based on the actual mass of pyridine or carbazole used and corrected for any known purity factors for the specific lot of pyridine or carbazole. This stock may be further diluted to desired nitrogen concentrations.

6.6.1 Calibration standards from commercial sources may be used if they conform to the requirements of the test method.

NOTE 1—Pyridine should be used with low boiling solvents (<220 °C).

NOTE 2—Carbazole should be used with high boiling solvents (>220 °C).

NOTE 3—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, and should be refrigerated when not being used.

6.7 *Cupric Oxide Wire,* as recommended by instrument manufacturer.

6.8 *Quartz Wool (optional),* or other suitable absorbent material that is stable and capable of withstanding temperatures inside the furnace (Note 4).

NOTE 4—Materials meeting the requirements in 6.8 are recommended to be used in sample boats to provide a more uniform injection of the

[3] *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.