Designation: D 4629 – 96

An American National Standard

Designation: 379/88

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 D 4629; 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 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 and 10 cSt (mm^2/s) at room temperature. This test method is applicable to naphthas, distillates, and oils containing 0.3 to 100 mg/kg total nitrogen.

1.2 *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 Sections 5.2, 5.4, 5.5, 5.10, and 6.0.

1.3 The values stated in acceptable SI units are to be regarded as the standard.

2. Summary of Test Method

2.1 The sample of liquid petroleum hydrocarbon is injected 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 organic and bound nitrogen is converted to nitric oxide (NO). The NO contacts ozone and is converted to excited nitrogen oxide (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.

3. Significance and Use

3.1 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 which fall within the scope of the test method.

4. Apparatus[2] (Figs. 1-3)

4.1 *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) for petroleum substances shall be as recommended by the manufacturer.

4.2 *Combustion Tube*, fabricated from quartz. The inlet end of the tube holds a septum for syringe entry of the sample and has a side arm for introduction of oxygen (O_2) and inert gas. The construction is such that the inert gas sweeps the inlet zone transporting all of the volatilized sample into a high temperature oxidation zone. The oxidation section shall be large enough (see Fig. 1 and Fig. 3) to ensure complete oxidation of the sample. Fig. 1 and Fig. 3 depict conventional pyrolysis tubes. Other configurations are acceptable if precision is not degraded.

4.3 *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 both.

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

4.5 *Totalizer*, having variable attenuation, and capable of measuring, amplifying and integrating the current from the chemiluminescent detector. The amplified or integrated output signal shall be applied to a digital display and to strip chart recorder if desired.

[1] This test method is under the jurisdiction of ASTM Committee D-2 on Petroleum Products and Lubricants and is the direct responsibility of Subcommittee D02.03.0B on Spectrometric Methods.

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[2] The apparatus described in (4.1-4.11) is manufactured in several variations by the Antek Instruments Inc. of Houston, TX and Dohrmann Division, Xertex Corp. of Santa Clara, CA. Both have been found to meet all essential requirements.

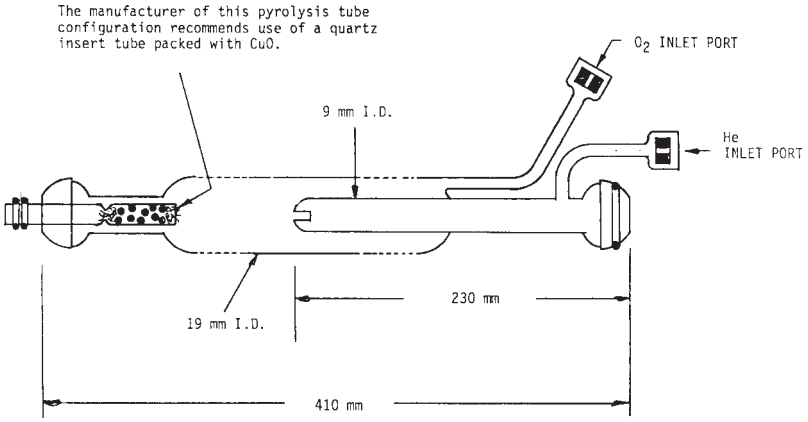

FIG. 1 Quartz Pyrolysis Tube

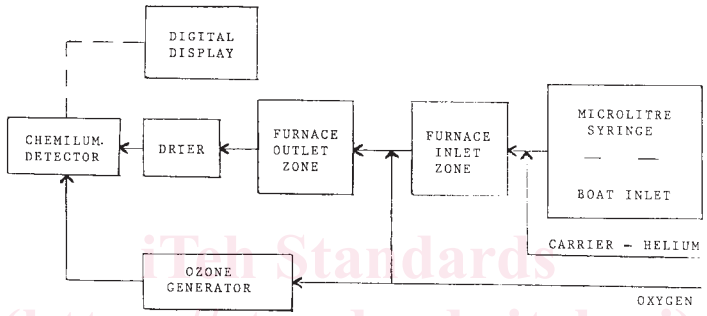

FIG. 2 Typical Instrument Block Diagram

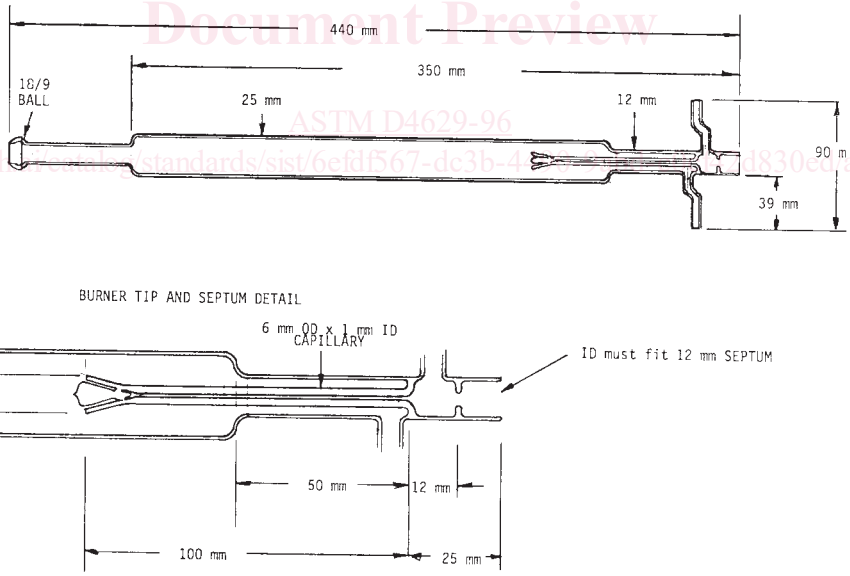

FIG. 3 Quartz Pyrolysis Tube

4.6 *Microlitre Syringe*, of 5, 10, 25, 50, or 250 µL capacity capable of accurately delivering microlitre quantities is required. The needle should be long enough to reach the hottest portion of *inlet* section furnace when injecting the sample.

4.7 *Recorder (Optional)*.

4.8 *Constant Rate Injector System (Optional)*, capable of delivering a sample at a precisely controlled rate may have independent signal processing and data display capabilities (optional).