



Designation: D 5762 – 04~~2~~

An American National Standard

Standard Test Method for Nitrogen in Petroleum and Petroleum Products by Boat-Inlet Chemiluminescence¹

This standard is issued under the fixed designation D 5762; 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 nitrogen in liquid hydrocarbons, including petroleum process streams and lubricating oils in the concentration range from 40 to 10 000 $\mu\text{g/g}$ nitrogen. For light hydrocarbons containing less than 100 $\mu\text{g/g}$ nitrogen, Test Method D 4629 can be more appropriate.

1.2 The values stated in SI units are to be regarded as the standard. The values given in parentheses are for information only.

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.* Specific hazard statements are given in Section 6, 7.1, 8.2, and 8.2.2.

2. Referenced Documents

2.1 *ASTM Standards:*

¹ This test method is under the jurisdiction of ASTM Committee D02 on Petroleum Products and Lubricants and is the direct responsibility of Subcommittee D02.03 on Elemental Analysis.

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

- D 4052 Test Method for Density and Relative Density of Liquids by Digital Density Meter²
- D 4057 Practice for Manual Sampling of Petroleum and Petroleum Products²
- D 4177 Practice for Automatic Sampling of Petroleum and Petroleum Products²
- D 4629 Test Method for Trace Nitrogen in Liquid Petroleum Hydrocarbons by Syringe/Inlet Oxidative Combustion and Chemiluminescence Detection²

3. Summary of Test Method

3.1 A hydrocarbon sample is placed on a sample boat at room temperature. The sample and boat are advanced into a high-temperature combustion tube where the nitrogen is oxidized to nitric oxide (NO) in an oxygen atmosphere. The NO contacts ozone and is converted to excited nitrogen dioxide (NO₂). The light emitted as the excited NO₂ 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 Many nitrogen compounds can contaminate refinery catalysts. They tend to be the most difficult class of compounds to hydrogenate, so the nitrogen content remaining in the product of a hydrotreater is a measure of the effectiveness of the hydrotreating process. In lubricating oils the concentration of nitrogen is a measure of the presence of nitrogen containing additives. This test method is intended for use in plant control and in research.

5. Apparatus

5.1 *Boat Inlet System*, capable of being sealed to the inlet of the combustion tube and swept with inert gas. The boats are fabricated from platinum or quartz. To aid quantitative liquid injection, add a small piece of quartz wool to the boat. The boat drive mechanism should be able to fully insert the boat into the furnace tube inlet section. A drive mechanism that advances and withdraws the sample boat into and out of the furnace at a controlled and repeatable rate is required.

5.2 *Chemiluminescence Detector*, capable of measuring light emitted from the reaction between nitric oxide and ozone, and containing a variable attenuation amplifier, integrator, and readout.

NOTE 1—Detectors designed to maintain the chemiluminescence reaction cell at reduced pressure are acceptable for use and were included in the instruments used to determine the precision of this test method.

5.3 *Combustion Tube*, fabricated from quartz. The inlet end of the tube shall be large enough to accept the sample boat and to have side arms for introduction of oxygen and inert gas. The construction is such that the carrier gases sweep the inlet zone transporting all of the volatilized sample into a high-temperature oxidation zone. The oxidation section should be large enough to ensure complete oxidation of the sample. Combustion tubes recommended for the two furnaces in 5.5.1 and 5.5.2 are described in 5.3.1 and 5.3.2. Other configurations are acceptable if precision and bias are not degraded.

5.3.1 Quartz combustion tube for use with the single-zone furnace is illustrated in Fig. 1. A water-jacket around the inlet section can be used to cool the boat prior to sample injection.

5.3.2 Quartz combustion tube for use with the two-zone furnace is illustrated in Fig. 2. Fig. 3 illustrates a combustion tube for a two-zone furnace that is equipped with the ability to switch to a pure oxygen carrier gas flow after the boat has been fully extended into the furnace (consult the instrument manual to determine if the instrument changes to a pure oxygen carrier gas flow after the boat is inserted). The outlet end of the pyrolysis tube is constructed to hold a removable quartz insert tube. The removable quartz insert tube is packed with an oxidation catalyst as recommended by the instrument manufacturer.

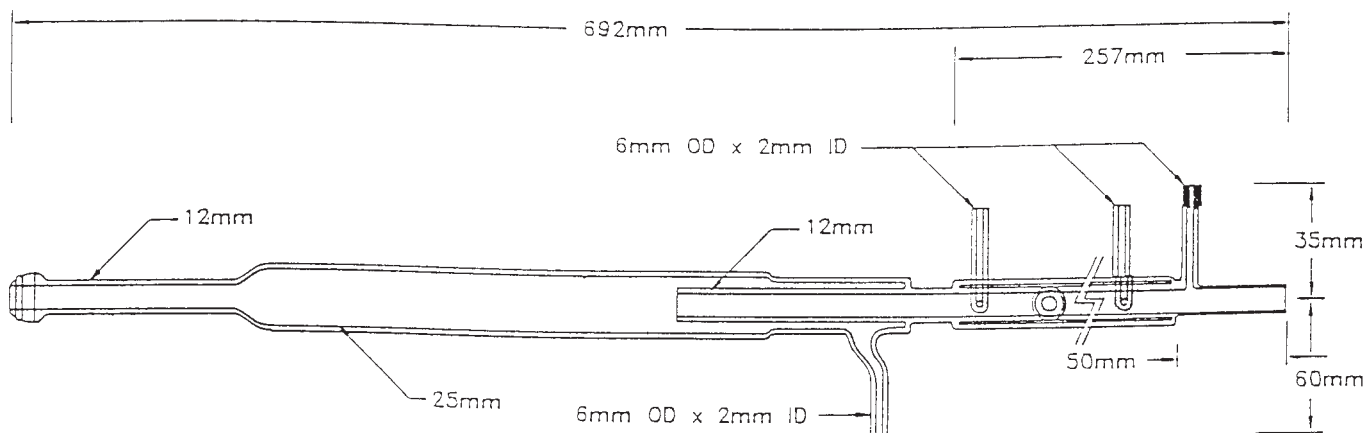


FIG. 1 Quartz Combustion Tube (Single-Zone Furnace)

² Annual Book of ASTM Standards, Vol 05.02.

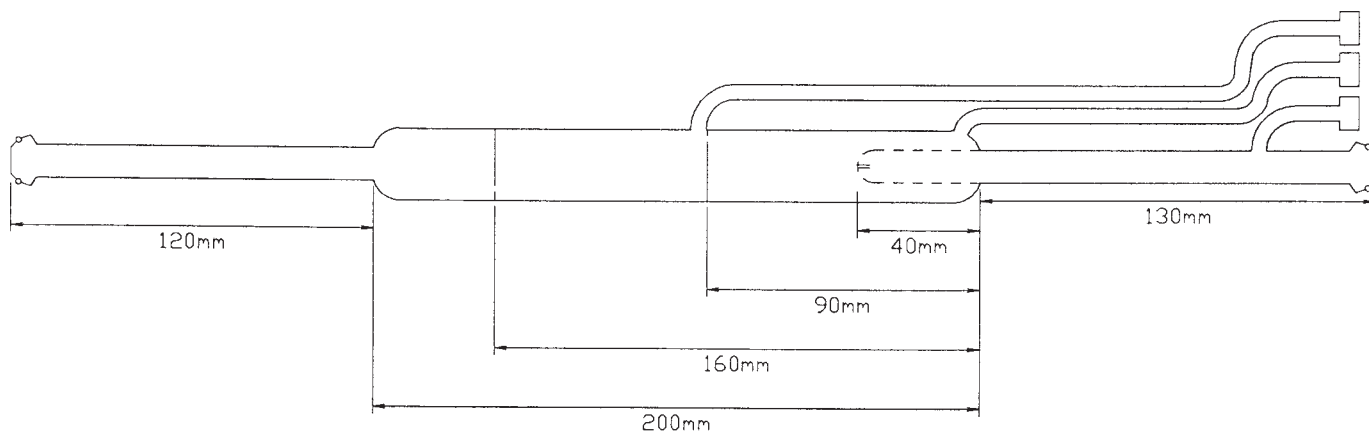


FIG. 2 Quartz Combustion Tube (Two-Zone Furnace)

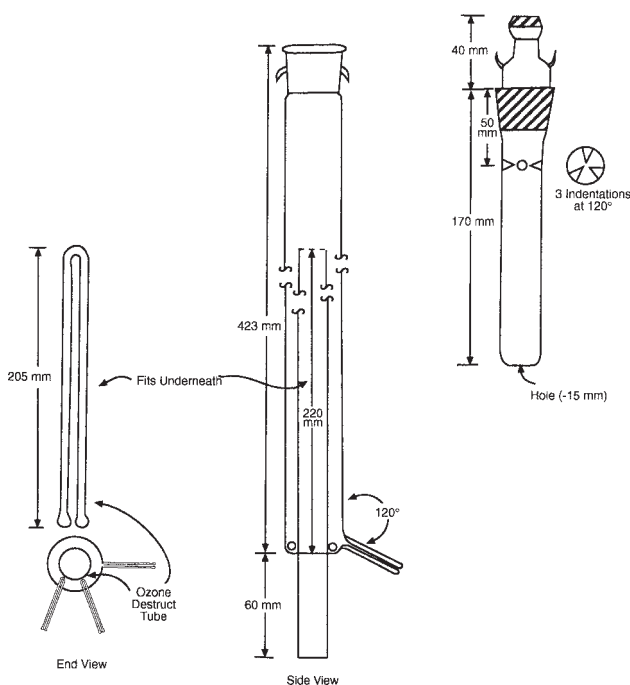


FIG. 3 Quartz Combustion Tube (for two zone furnace equipped with the ability to switch to pure oxygen carrier gas flow)

5.4 *Drier Tube*, for the removal of water vapor. The reaction products include water vapor that shall be eliminated prior to measurement by the detector. This can be accomplished with a magnesium perchlorate, $Mg(ClO_4)_2$, scrubber, a membrane drying tube permeation drier, or a chilled dehumidifier assembly.

5.5 *Furnace, Electric*, held at a temperature sufficient to pyrolyze all of the sample and oxidize the nitrogen to NO. The following furnace designs may be used. All furnace assemblies include a method for gas flow control, such as needle valves, flow restrictors or mass flow controllers. Furnaces that are operated at temperatures below 1050°C shall be capable of switching to 100% oxygen carrier gas flow after the boat has been fully extended into the furnace.

5.5.1 Single-zone tube furnace with temperature controller capable of maintaining a stable furnace temperature of 1100 (\pm 25°C).

5.5.2 Two-zone tube furnace with temperature controllers capable of maintaining the temperature of each furnace zone independently from 950 to 1050°C (see 5.5). Or two-zone tube furnace equipped with the ability to change to a pure oxygen carrier gas flow after the boat is fully extended in to the furnace and temperature controllers capable of maintaining the temperature of each furnace zone independently to 950°C.

5.6 *Microlitre Syringe*, of 5 or 10- μ L capacity, capable of accurately delivering microlitre quantities.

5.7 *Ozone Generator*, to supply ozone to the detector reaction cell.

5.8 *Recorder (Optional)*, for display of chemiluminescence detector signal.

6. Reagents and Materials

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 where such specifications are available.³ 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 *Acridine*, C₁₃H₉N, molecular weight 179.21, 7.82 mass % nitrogen. (**Warning**—Irritant.)

6.3 *Oxidation Catalyst: Cupric Oxide Wire, CuO, or Platinum Catalyst, PtAl₂O₃*, as recommended by the instrument manufacturer.

6.4 *Inert Gas*—Argon or Helium only, high-purity grade (that is, chromatographic or zero grade), 99.998 % minimum purity, 5 ppm maximum moisture.

6.5 *Anhydrous Magnesium Perchlorate*, Mg(ClO₄)₂, for drying products of combustion (if permeation drier or chilled drier is not used). (**Warning**—Strong oxidizer, irritant.)

6.6 *Nitrogen Stock Solution*, 500 ng nitrogen/μL—Accurately weigh (to the nearest 0.1 mg) approximately 0.64 g of acridine into a tared 100-mL volumetric flask. Add xylene to dissolve, then dilute to volume with xylene. Calculate the nitrogen content of the stock solution to the nearest milligram of nitrogen per litre. This stock can be further diluted to desired nitrogen concentrations. (**Warning**—Remake standard solutions on a regular basis depending upon frequency of use and age. Typically, standards have a useful life of approximately three months.)

6.7 *Oxygen*, high-purity grade (that is, chromatographic or zero grade), 99.75 % minimum purity, 5 ppm maximum moisture, dried over molecular sieves. (**Warning**—Vigorously accelerates combustion.)

6.8 *Quartz Wool*.

6.9 *Silver Wool*, as recommended by the instrument manufacturer.

6.10 *Xylene*. (**Warning**—Flammable, health hazard.)

7. Sampling

7.1 Obtain a test sample in accordance with Practice D 4057 or D 4177. (**Warning**—Samples that are collected at temperatures below room temperature can undergo expansion at laboratory temperatures and rupture the container. For such samples, do not fill the container to the top. Leave sufficient air space above the sample to allow room for expansion.) (**Warning**—To minimize loss of volatile components, which can be present in some test samples, do not uncover any longer than necessary. Test samples should be analyzed as soon as possible after taking from bulk supplies to prevent loss of nitrogen or contamination due to exposure or contact with sample container.)

7.2 If the test sample is not used immediately, then thoroughly mix it in its container prior to taking a test specimen. Some test samples require heating in order to thoroughly homogenize.

8. Preparation of Apparatus

8.1 Assemble apparatus in accordance with the manufacturer's instructions.

8.2 Adjust the oxygen flow for the ozone generator in accordance with the manufacturer's instructions. Adjust the combustion tube gas flows and the pyrolysis temperature to the desired operating conditions using the following guidelines for each furnace type. (**Warning**—Ozone is extremely toxic. Make sure that appropriate steps are taken to prevent discharge of ozone within the laboratory work area.)

8.2.1 For the single-zone furnace without the ability to change to a pure oxygen carrier gas flow after the boat has been fully extended into the furnace, adjust the combustion tube gas flows to the following values: pyrolysis oxygen, 360 mL/min; inlet oxygen, 60 mL/min; and inert carrier inlet, 155 mL/min. Set the furnace temperature to 1100 ± 25°C. Adjust the boat drive mechanism to obtain a drive rate of 150 ± 10 mm/min. Refer to the manufacturer's instructions for descriptions of these settings.

8.2.2 For the two-zone furnace without the ability to change to a pure oxygen carrier gas flow after the boat has been fully extended into the furnace, adjust the combustion tube gas flows to the following values: combustion oxygen, 165 mL/min; inlet inert carrier, 85 mL/min; and boat inert carrier, 50 mL/min. Set the inlet furnace temperature to 1050 ± 25°C, and the outlet furnace temperature to 925 ± 25°C. Adjust the boat drive mechanism to obtain a drive rate of 150 ± 10 mm/min (boat speed number 4). Refer to the manufacturer's instructions for the description of these settings. (**Warning**—High temperature is employed in this test method. Use flammable materials with care near the pyrolysis furnace.)

8.2.3 For the two-zone furnace with the ability to change to a pure oxygen carrier gas flow after the boat has been fully extended in to the furnace, adjust the combustion tube gas flows to the following values: main oxygen, 400 mL/min; inlet argon carrier, 0.4 L/min, and inlet oxygen carrier, 0.4 L/min. Set the inlet furnace temperature to 600 ± 25°C, and the outlet (catalyst) temperature to 950 ± 25°C. Set the automatic boat control as follows: 1 Fuc FWD 125 speed 10 time 30, 2 Fuc 285 speed 05 time 30, 5 Fuc time 30, 6 Fuc time 90, A Fuc time 60. Refer to manufacturer's instructions for a description of these settings.

8.3 Insert boat into furnace for a minimum of 2 min to remove any residual nitrogen species.

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.

9. Calibration and Standardization

9.1 Prepare calibration standards containing 1, 5, 10, 50, and 100 ng nitrogen/ μL in xylene by volumetric dilution of the 500-ng nitrogen/ μL nitrogen stock solution.

9.2 Five microlitres of the material to be analyzed (see Note 1) shall be quantitatively placed in the sample boat for measurement of chemiluminescence response. There are two alternative injection procedures available, the volumetric and the gravimetric procedures.

NOTE 1—The formation of NO and NO₂ from oxidative combustion of nitrogen containing hydrocarbons is dependent on combustion conditions such as temperature and oxygen concentration. Injection of a constant solution volume, and dilution of all test specimens and standards with a common solvent, maintain consistent combustion conditions for test specimens and standards.

9.2.1 For volumetric measurement of the material by microlitre syringe, flush the microlitre syringe several times with the material, discarding the flushed liquid each time. Fill the 10- μL syringe to the 5- μL level. Retract the plunger so that the lower liquid meniscus falls on the 10 % scale mark. When bubbles are present within the liquid column, flush the syringe and withdraw a new aliquot of the liquid. Record the volume of liquid in the syringe. Immediately inject the liquid into the boat, being careful to displace the last drop by touching the edge of the boat, or the quartz wool if present, with the syringe needle. After the injection, again retract the plunger so that the lower liquid meniscus falls on the 10 % scale mark and record the volume of liquid in the syringe. The difference between the two volume readings is the volume of liquid injected.

NOTE 2—An automatic sampling and injection device can be used in place of the described manual injection procedure.

9.2.2 For gravimetric measurement of the solution, fill the syringe as indicated in 9.2.1. Weigh the microlitre syringe and its contents, and record the mass to the nearest 0.01 mg. Immediately inject the liquid into the boat, being careful to displace the last drop by touching the edge of the boat, or quartz wool if present, with the syringe needle. After the injection, remove the syringe and again weigh the syringe and its contents. Record the mass to the nearest 0.01 mg. The difference between the two weighings is the mass of liquid injected. The gravimetric procedure is more precise than the volumetric procedure, provided a balance with a precision of ± 0.01 mg is used.

9.3 Activate the boat drive mechanism to insert the boat into the furnace. The instrument baseline should remain stable until the boat approaches the furnace and volatilization of injected material begins. After the measurement is complete, retract the boat. The instrument baseline should reestablish before the boat has completely emerged from the furnace. Record the integrated chemiluminescence response. Allow the boat to cool for at least 1 min before the next injection.

9.4 Calibrate the instrument using one of the following two techniques.

9.4.1 Perform measurements for the calibration standards and blank using the procedure described in 9.2 and 9.3. Measure the calibration standards and blank three times each, and determine the average integrated chemiluminescence response for each. Construct a curve plotting average integrated detector response (*y*-axis) versus nanograms of nitrogen injected (*x*-axis).

9.4.2 If the system features an internal calibration routine, measure the calibration standards and blank three times each using the procedure described in 9.2 and 9.3. Calibrate the analyzer in accordance with the manufacturer's instructions using the average of the three measurements for each standard and blank.

9.5 If analyzer calibration is performed using only a subset of the calibration standards listed in 9.1, the calibration standards closest in concentration to the measured solution(s) must be included in the subset (that is, if the concentration of the test specimen solution is 20 ng nitrogen/ μL , include the 10 and 50-ng nitrogen/ μL standards in the calibration). System performance must be checked with the calibration standards at least once per day.

10. Quality Assurance

10.1 A sample of known nitrogen content will be run after each calibration. The sample can also be analyzed periodically throughout a series of analyses to check the functioning of the instrument and the validity of the calibration curve. This sample can be a National Institute for Standards and Technology Standard Reference Material (SRM) material, an acridine in xylene standard prepared to have a nitrogen value not used to calibrate the instrument, or any other material that has been analyzed repeatedly such that sufficient data are available to determine a statistical mean. The results of the analysis of the known sample will be within 10 % of the certified or accepted value for the operation and calibration of the instrument to be considered acceptable. If the results are not within 10 % of the accepted value, perform appropriate corrective maintenance on the instrument and repeat the calibration procedure described in 9.4.

11. Procedure

11.1 Obtain a test specimen using the procedure described in Section 7. Prepare a test specimen solution by dilution of the test specimen in xylene. Use a dilution factor of at least 1:5 (see Note 1). The nitrogen concentration in the test specimen solution shall be less than the concentration of the highest standard used in calibration and greater than 3 ng nitrogen/ μL . The dilution can be performed either on a weight or volume basis.

11.1.1 For gravimetric dilution, record the mass of the test specimen and the total mass of the test specimen and solvent.

11.1.2 For volumetric dilution, record the mass of the test specimen and the total volume of the test specimen and solvent.

11.2 Measure the chemiluminescence response for the test specimen solution using the procedure described in 9.2 and 9.3.

11.3 If the chemiluminescence response from the test specimen solution is greater than the response from the highest calibration standard used, repeat the test specimen dilution described in 11.1 using a higher dilution factor. Repeat the analysis procedure described in 9.2 through 9.3 on this new test specimen solution.

11.4 Inspect the boat and combustion tube to verify complete combustion of the test specimen solution. Increase the residence time for the boat in the furnace if coke or soot is observed on the boat. Decrease the boat drive introduction rate if coke or soot is observed on the exit end of the combustion tube. Clean any coked or sooted parts. After any cleaning or adjustment, repeat instrument calibration prior to reanalysis of the test specimen.

11.5 Measure each test specimen solution three times and calculate the average chemiluminescence response.

12. Calculation

12.1 For analyzers calibrated using a standard curve, calculate the nitrogen content of the test specimen in micrograms per gram ($\mu\text{g/g}$) as follows:

$$\text{Nitrogen, } (\mu\text{g/g}) = \frac{(I - Y)}{S \times M \times K_g} \quad (1)$$

or,

$$\text{Nitrogen, } (\mu\text{g/g}) = \frac{(I - Y)}{S \times V \times K_v} \quad (2)$$

where:

D = density of test specimen solution, g/mL,

I = average of integrated detector response for test specimen solution, counts (or found ng nitrogen),

K_g = gravimetric dilution factor, mass of test specimen/mass of test specimen and solvent, g/g,

K_v = volumetric dilution factor, mass of test specimen/volume of test specimen and solvent, g/mL,

M = mass of test specimen solution injected, either measured directly or calculated from measured volume injected and density, $V \times D$, mg,

S = slope of standard curve, counts/ng nitrogen (or found ng nitrogen/ng nitrogen),

V = volume of test specimen solution injected, either measured directly or calculated from measured mass injected and density, M/D , μL , and

Y = y-intercept of standard curve, counts (or found ng nitrogen).

12.2 For analyzers calibrated using an internal calibration routine, calculate the nitrogen content of the test specimen in micrograms/gram ($\mu\text{g/g}$) as follows:

$$\text{Nitrogen, } (\mu\text{g/g}) = \frac{I}{M \times K_g} \quad (3)$$

or,

$$\text{Nitrogen, } (\mu\text{g/g}) = \frac{I}{V \times K_v} \quad (4)$$

where:

D = density of test specimen solution, g/mL,

I = average of visual display readings of test specimen solution, ng nitrogen,

K_g = gravimetric dilution factor, mass of test specimen/mass of test specimen and solvent, g/g,

K_v = volumetric dilution factor, mass of test specimen/volume of test specimen and solvent, g/mL,

M = mass of test specimen solution injected, either measured directly or calculated from measured volume injected and density, $V \times D$, mg, and

V = volume of test specimen solution injected, either measured directly or calculated from measured mass injected and density, M/D , μL .

13. Precision and Bias ⁴

13.1 *Repeatability*—The difference between two test results obtained by the same operator with the same apparatus under constant operating conditions on identical test material would, in the long run, in the normal and correct operation of the test method, exceed the following values in only one case in twenty, where X = the average of the two test results.

$$r = 0.087 \times X \mu\text{g/g} \quad (5)$$

13.2 *Reproducibility*—The difference between two single and independent results obtained by different operators working in different laboratories on identical test material would, in the long run, in the normal and correct operation of the test method, exceed the following values in only one case in twenty, where X = the average of the two test results.

⁴ Supporting cooperative data are available from ASTM International Headquarters. Request RR:D02-1370 or RR:D02-1507.

$$R = 0.266 \times X \mu\text{g/g} \quad (6)$$

13.3 *Bias*—An NIST SRM was analyzed by the cooperators participating in the repeatability and reproducibility determination. This test method showed no significant bias for this sample within the repeatability of this test method.

14. Keywords

14.1 chemiluminescence; nitrogen

SUMMARY OF CHANGES

Subcommittee D02.03 has identified the location of selected changes to this standard since the last issue (D 5762–9801) that may impact the use of this standard.

~~(1) Updated furnace descriptions, Section 5.~~

~~(2) Added additional oxidation catalyst, Section 6.~~

~~(3) Update~~ Inserted a new Note 1 to reflect that the use of detectors operated under vacuum is acceptable since they were included in the instruments used to determine the precision statement and research report availability, Section 13, of this test method.

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