Designation: D7184 – 15

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

1. 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 0.1 to 1.2 mg N/kg. For higher nitrogen concentrations refer to Test Method D4629. With careful analytical technique, this method can be used to successfully analyze concentrations below the current scope (see Appendix X1).

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

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 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.

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

---

[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.

Current edition approved June 1, 2015. Published June 2015. Originally approved in 2007. Last previous edition approved in 2013 as D7184 – 13. DOI: 10.1520/D7184-15.

[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**

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 0.1 to 1.2 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 %.

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.

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

where:

% nitrogen in pyridine = 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:

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

or

---

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

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

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

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' 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 8.5 and 8.6.

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

12.3 A calibration based on the four gravimetrically prepared standards works well within the limited scope of this procedure. This type of calibration can be used to quantitate nitrogen at the 0.1 to 1.2 mg N/kg concentration range.

12.4 Run a calibration program for linear regression in accordance with the instrument manufacturer's recommendations. The correlation coefficient should be a minimum of 0.99.

12.5 Inject each standard and blank at least 3 times.

NOTE 3—The calibration corrects for residual nitrogen content of the solvent used to make the standards (often greater than 0.05 mg N/L) by generating the regression line as a standard addition to the solvent blank. The slope generated is used to create a calibration line starting at the origin, that is, zero signal for nitrogen.

13. Procedure

13.1 Sample size from 5 to 250 µL is acceptable.

13.2 When using a constant rate injector always flush the syringe several times with the material to be injected to prevent contamination. Do not return the first few flushes back into the specimen bottle.

13.3 If using an auto-sampler set the program to the instrument manufacturer's recommendations.

NOTE 4—Follow instrument manufacturer's recommendations for sample size.

13.4 Set the automatic boat control to the instrument manufacturer's recommendations. Cycle the empty boat in and out of the combustion furnace to remove any residual contamination until you see a minimum peak on your baseline as a result of the cycling of the empty boat.

13.5 Fill the auto-sampler vials with the samples and place the vials into the rack.

13.6 Using a constant rate injector fill the syringe past the desired volume to be injected, (that is, if you are going to inject 50 µL fill the syringe to 60 µL and then back to 50 µL), taking care not to pull air bubbles into the syringe with the sample. With the syringe needle pointed up, push the plunger 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 volumes and can not be tolerated.

NOTE 6—If the detector response continuously increases or decreases, this is an indication of contamination. Check with the instrument manufacturer's recommendations for decontamination of the instrument.

13.7 Insert the syringe needle through the inlet septum as far as it will go (the syringe barrel should be touching the septum). Inject the sample in accordance with the instrument manufacturer's recommendations.

13.8 Repeat 13.7 and 13.8 analyzing each sample or standard 3 times. Average the 3 results for each sample and record the results.

14. Calculation

14.1 All calculations are performed automatically by the manufacturer's software, and results are displayed and printed out in µg N/kg (ng/g) or mg N/kg (µg/g) as appropriate, see manufacturer's software manual. The density is filled in during sample data entry and is used by the instrument to convert results from mg N/L to mg N/kg.

14.2 Calculate the concentration of nitrogen by using the instrument software.

$$mg\ N/kg = \frac{W}{V \times D} \qquad (4)$$

where:

W = µg of the nitrogen in sample
V = volume of sample injected, mL
*Density** = density of sample, g/ml

*Density can be used from the supplier, measured directly or taken out of the SDS sheet of the used sample.

15. Report

15.1 Report the nitrogen results as mg N/kg of the sample. Report to the nearest 0.01 mg N/kg.

16. Precision and Bias(see Practice E691)[5]

16.1 An ILS was conducted with eight laboratories participating, testing nitrogen in aromatic hydrocarbons. Three laboratories ran samples twice using either different instruments or different calibration standards resulting in eleven sets of results. Every analyst reported duplicate test results for each unknown in this study. Practice E691 was followed for the study design. The details are given in ASTM Research Report No. RR:D16-1044.

16.2 *Repeatability Limit(r)*—Two test results obtained within one laboratory shall be judged not equivalent if they differ by more than the "*r*" value for that material; "*r*" is the interval representing the critical difference between two test results for the same material, obtained by the same operator using the same equipment on the same day in the same laboratory.

TABLE 1 Nitrogen in Aromatics (mg N/kg)

Material	Average[A]	Repeatability Limit r	Reproducibility Limit R
p-Xylene Level 5	0.06	0.04	0.09
p-Xylene Level 3	0.11	0.03	0.20
p-Xylene Level 4	0.13	0.03	0.22
Toulene Level 3	0.14	0.04	0.24
p-Xylene Level 1	0.38	0.15	0.23
p-Xylene Level 2	0.57	0.08	0.25
Benzene Level 1	0.88	0.16	0.34
Benzene Level 2	1.19	0.13	0.28

[A] The average of the laboratories' calculated averages.

16.3 *Reproducibility Limit (R)*—Two test results shall be judged not equivalent if they differ by more than the "*R*" value for that material; "*R*" is the interval representing the critical difference between two test results for the same material, obtained by different operators using different equipment in different laboratories.

16.3.1 Results should not be suspect unless they differ by more than shown in Table 1. Results differing by less than "*r*" and "*R*" have a 95 % probability of being correct.

16.4 *Bias*—At the time of the study, no accepted reference material suitable for determining the bias for this test method was available, therefore no statement on bias is being made.

17. Quality Guidelines

17.1 It is recommended that the operator of this test method select and perform relevant QA/QC activities like the ones in Guide D6809 to help ensure the quality of data generated by this test method.

18. Keywords

18.1 chemiluminescence; nitrogen; reduced pressure

APPENDIX

(Nonmandatory Information)

X1. OPERATIONAL CONDITIONS FOR SUCCESSFUL TRACE NITROGEN ANALYSIS

X1.1 This method can be used to successfully analyze concentrations below the current scope. Careful analytical technique and adherence to the instrument manufacturer's instructions and recommendations will yield analysis to trace levels down to ≤30 ppb nitrogen. The following is provided as information on the factors required.

X1.2 Prepare the instrument in accordance with manufacturer's instructions. The sample flow path must be leak free when pressure tested in accordance with the manufacturer's recommended procedure.

X1.3 Trace analysis cannot be achieved if contamination is present in the supply gas, flow path, standards and/or samples. Contamination in supply gas(es) and/or flow path can be identified by performing an analysis in which no sample is injected while allowing the analyzer to go through its analytical program. If found, identify the cause and eliminate.

X1.4 Calibration standards must be prepared with solvent materials that have minimal or no contamination. Contribution from solvent materials and impurity of source material must be corrected for by either using a blank correction procedure or by

---

[5] Supporting data have been filed at ASTM International Headquarters and may be obtained by requesting Research Report RR:D16-1044. Contact ASTM Customer Service at service@astm.org.

entering the corrected concentrations based on standard addition during the calibration.

X1.5 Trace amounts of nitrogen may be changed by the slightest mistakes in sample handling. Extreme care must be taken not to contaminate the standards or samples. The sample may need to be refrigerated. Ensure that sample vial caps are properly seated. This will prevent evaporation and provide for accurate sampling.

X1.6 All glassware, syringes and any other apparatus used should be clean and free of nitrogen compounds to avoid possible contamination. Do not touch any sample introduction device (that is, syringe needle, quartz sample boat, etc.). This may contaminate the device with nitrogen.

X1.7 Prior to analysis, be certain that the detector baselines are stable and noise free. For a given gain factor, photomultiplier tube voltage may be adjusted to insure maximum sensitivity while maintaining a stable, noise-free baseline.

X1.8 Flow path back pressure during normal reduced pressure operation must be stable to achieve repeatable results.

X1.9 Gas supplies to various points in the sample path must be consistently controlled to allow for smooth, complete combustion of the sample.

X1.10 Always ensure that the gas flows and temperatures are correct and stable before introducing sample materials into the system.

X1.11 Use of an autosampler is strongly recommended to achieve maximum repeatability and reproducibility for trace level analysis.

X1.12 Avoid removing the sample introduction device (that is, syringe, quartz sample boat, etc.) before the sample material is completely combusted.

X1.13 Residence time of the needle in the inlet area must be consistent following the injection of the sample.

X1.14 A wait of at least two to three minutes between sample introductions is strongly recommended. This will allow the membrane dryer to regenerate and the baseline to fully stabilize. For an apparatus that utilizes a desiccant as an indicator of dryness, replace the drying agent when a color change (blue to pink) indicates the need to do so.

X1.15 Ensure that at least two rinses are purged through the syringe assembly between analyses.

X1.16 Always operate within the calibrated range, extrapolation is not recommended.

X1.17 Confirm the validity of the calibration curve on a daily basis by analyzing at least one material of known concentration. The result should be within normal analytical error.

X1.18 When constructing a calibration curve, select instrument settings that will yield at least three times baseline noise for the lowest point on the calibration curve.

X1.19 Frequently inspect the inlet and exit portions of the pyrotube for any carbon residue. If residue is found, immediately clean the residue from the system and check for gas leaks, proper gas flows, correct sample introduction technique, and suitable sample size.

SUMMARY OF CHANGES

Committee D16 has identified the location of selected changes to this standard since the last issue (D7184-13) that may impact the use of this standard. (Approved June 1, 2015.)

(1) Updated Scope Section 1.2.
(2) Updated Section 5.1.
(3) Updated Section 12.3.
(4) Updated Section 16.1.
(5) Updated Table 1.