



Designation: D8083 – 16

Standard Test Method for Total Nitrogen, and Total Kjeldahl Nitrogen (TKN) by Calculation, in Water by High Temperature Catalytic Combustion and Chemiluminescence Detection¹

This standard is issued under the fixed designation D8083; 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 total nitrogen (TN) and total dissolved nitrogen (TDN) in surface water, seawater, groundwater, wastewater, and wastewater effluents in the range from 0.2–10 mg/L N. Concentrations from 10–500 mg/L are possible when used in conjunction with manual or automatic dilution, or automatic injection of less sample volume. The EPA 40 CFR Part 136 Appendix B Method Detection Limit (MDL) is 0.05 mg/L N. Higher concentrations may be determined by sample dilution. Lower concentrations may be possible by injecting larger sample volumes. Follow the manufacturer's instructions.

1.2 The sample is injected onto a platinum catalyst heated at $\geq 720^\circ\text{C}$. The sample converts into a gaseous phase and is forced through a layer of catalyst ensuring conversion of all nitrogen containing compounds to nitrogen oxide (NO). Reaction with ozone converts the NO to an excited NO_2 . As the excited NO_2 returns to the ground state, it emits radiation that is measured photo-electrically.

1.3 Total and dissolved organic carbon analysis by Test Method [D7573](#) can be analyzed at the same time on the same sample simultaneously using a properly equipped analyzer. (See [Appendix X1](#) for an example of simultaneous TOC data.)

1.4 This test method quantitatively recovers nitrogen from a large range of organic and inorganic nitrogen compounds (see [Table 1](#) and [Table 2](#)). The test method does not measure nitrogen gas (N_2). It is the user's responsibility to ensure the validity of this test method for waters of untested matrices.

1.5 This test method is applicable only to nitrogenous matter in the sample that can be introduced into the reaction zone. The syringe needle or injector opening size generally limits the maximum size of particles that can be so introduced. Optional automatic sample homogenization may be used.

1.6 This test method is performance based. You may make modifications that improve the test method's performance but do not change the oxidation or detection technique.

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

1.8 *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.*

2. Referenced Documents

2.1 ASTM Standards:²

- [D1129 Terminology Relating to Water](#)
- [D1193 Specification for Reagent Water](#)
- [D1426 Test Methods for Ammonia Nitrogen In Water](#)
- [D2777 Practice for Determination of Precision and Bias of Applicable Test Methods of Committee D19 on Water](#)
- [D3370 Practices for Sampling Water from Closed Conduits](#)
- [D3590 Test Methods for Total Kjeldahl Nitrogen in Water](#)
- [D3867 Test Methods for Nitrite-Nitrate in Water](#)
- [D4327 Test Method for Anions in Water by Suppressed Ion Chromatography](#)
- [D4448 Guide for Sampling Ground-Water Monitoring Wells](#)
- [D5847 Practice for Writing Quality Control Specifications for Standard Test Methods for Water Analysis](#)
- [D6089 Guide for Documenting a Groundwater Sampling Event](#)
- [D6538 Guide for Sampling Wastewater With Automatic Samplers](#)
- [D6759 Practice for Sampling Liquids Using Grab and Discrete Depth Samplers](#)
- [D6919 Test Method for Determination of Dissolved Alkali and Alkaline Earth Cations and Ammonium in Water and Wastewater by Ion Chromatography](#)

¹ This test method is under the jurisdiction of ASTM Committee [D19](#) on Water and is the direct responsibility of Subcommittee [D19.06](#) on Methods for Analysis for Organic Substances in Water.

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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.

TABLE 1 Nitrogen Recoveries from Various Compounds in Presence of Organic Carbon

Compound	Nitrogen	ppm Carbon
Potassium Nitrate (100 ppm N)	100%	0
Potassium Hydrogen Phthalate (0 ppm)	ND	100
Acetonitrile (58.6 ppm N)	104%	100
Caffeine (58.9 ppm N)	90%	100
Nicotinic Acid (20 ppm N)	99%	100
Urea (233 ppm)	91%	100
Nicotinic Acid (100 ppm N)	97%	98%

TABLE 2 Nitrogen Recoveries for a Range of Nitrogen Sources

Compound	TN (mg/L)	Recovery (%)
Ammonium Chloride	0.01	102
Ammonium Sulfate	2	102
Ammonium Sulfate	100	100
Aniline	0.014	101
Arginine	0.007	99
Calcium Nitrate	10	99
Glutamic Acid	0.013	98
Glycine	0.016	103
L-glutamic Acid	2	102
1,6-Hexanediamine	50	101
Imidazole	0.011	100
Nitro aniline	50	100
Nitro phenol	50	102
Potassium Nitrate	10	99
Potassium Nitrate	0.009	99
Potassium Nitrate	50	105
Proline	0.01	99
RNA	0.018	103
Sodium Nitrite	0.009	101
Tri-peptide (Glu-Cys-Gly)	0.014	99
Tryptophan	0.009	103
Urea	0.013	99

D7573 Test Method for Total Carbon and Organic Carbon in Water by High Temperature Catalytic Combustion and Infrared Detection

D7781 Test Method for Nitrite-Nitrate in Water by Nitrate Reductase

3. Terminology

3.1 Definitions:

3.1.1 For definitions of terms used in this standard, refer to Terminology **D1129**.

3.2 Definitions of Terms Specific to This Standard:

3.2.1 *dissolved inorganic nitrogen (DIN)*, *n*—nitrogen in the form of ammonium, nitrate ion, or nitrite ion determined in a filtered sample.

3.2.2 *dissolved nitrogen (DN)*, *n*—nitrogen determined in a filtered sample.

3.2.3 *dissolved organic nitrogen (DON)*, *n*—organic nitrogen determined in a filtered sample.

3.2.4 *particulate nitrogen (PN)*, *n*—nitrogen bound to particulate materials that do not pass through a filter.

3.2.5 *refractory material*, *n*—that which cannot be completely oxidized under the test method conditions.

3.2.6 *total inorganic nitrogen (TIN)*, *n*—nitrogen in the form of ammonium ion, nitrite ion, or nitrate ion.

3.2.7 *total Kjeldahl nitrogen (TKN)*, *n*—the sum of nitrogen contained in free ammonia and other nitrogen compounds which are converted to ammonium sulfate [(NH₄)₂SO₄] under the conditions of Test Method **D3590**.

3.2.8 *total nitrogen (TN)*, *n*—the sum of TIN and TON.

3.2.9 *total organic nitrogen (TON)*, *n*—nitrogen in the form of organic compounds.

4. Summary of Test Method

4.1 *Fundamentals*—Nitrogen can occur in water as inorganic or organic compounds, or both. This test method can be used to measure TN, and can also determine TON by the difference of TN and TIN measured by other methods, such as Test Method **D4327** plus Test Method **D6919**, Test Method **D1426** plus Test Method **D7781**, or Test Methods **D1426** plus Test Method **D3867**. DON is determined on samples that have been filtered through a quartz fiber filter.

4.2 TON and DON procedures require that samples have been preserved with acid before it is analyzed for organic nitrogen content.

4.3 TN minus nitrate nitrite nitrogen is equivalent to TKN in most samples.

5. Significance and Use

5.1 This test method is used for determination of the total or dissolved nitrogen content of water from a variety of natural, domestic, and industrial sources. In its most common form, this test method is used to measure nitrogen as a means of monitoring nutrient pollutant in industrial wastewater, domestic wastewater, and ambient water. These measurements may also be used in monitoring waste treatment processes.

5.2 This test method measures oxidized ammonia and organic nitrogen (as nitrate) and soluble nitrate simultaneously, subtracting the nitrate + nitrite value from a non-digested sample gives total Kjeldahl nitrogen (TKN).

$$\begin{aligned} \text{TN} &= \text{TKN} + (\text{NO}_3^- - \text{N}) + (\text{NO}_2^- - \text{N}) \\ \text{TKN} &= \text{NH}_3 - \text{N} + \text{Organic N} \end{aligned}$$

When using this test method:

$$\begin{aligned} \text{TN} &= \text{Digested Sample} - \text{Non-Digested Sample} \\ \text{TKN} &= \text{TN} - [\text{NO}_3^- - \text{N} + \text{NO}_2^- - \text{N}] \end{aligned}$$

where:

TN = total nitrogen, and
TKN = total Kjeldahl nitrogen.

6. Interferences

6.1 The conversion of dissolved inorganic and organic nitrogen to NO is brought about at high temperatures (≥720°C) in the presence of oxygen. A catalyst promotes the process and the resulting nitrogen oxide is converted by ozone to nitrogen dioxide (NO₂). The NO₂ is measured by a chemiluminescence detector. Suspended and refractory materials are completely oxidized under these conditions.

6.2 Acid preservation minimizes interference that can cause results to be low.

6.3 Total organic carbon (TOC) up to 300 mg/L does not interfere. Dissolved salts up to 31 000 mg/L do not interfere.

6.4 Homogenizing may be necessary for samples with a high particulate loading.

6.5 Inorganics dissolved in the sample are not volatilized into gas and remain on the catalyst or quartz surface of the combustion tube. High amounts of solids eventually react with the quartz causing devitrification, or solidify in the catalyst bed decreasing flow rates. Limit sample volume injected to reduce the amount of soluble salts and to reduce cooling of the reaction chamber. Buildup of salts; reduction of flow rate, or large injection volumes could result in peak splitting.

7. Apparatus

7.1 *Sampling Devices*, manually operated or automatically operated sampling valves, or syringes are typically used with this test method.

7.2 *Apparatus for Nitrogen Determination*—This instrument consists of reagent and sample introduction mechanism, the high temperature combustion chamber with catalyst, an ozone generator, a NO₂-specific chemiluminescence detector, a control system, and a display. Fig. 1 shows a diagram of such an arrangement.

7.2.1 *Combustion Chamber*—A heated catalyst contained in a quartz tube, may contain quartz wool, quartz shards, or other items to protect the catalyst from dissolved salts to extend its life.

7.2.2 *Ozone Generator*, converts NO gas emerging from the combustion chamber to NO₂.

7.2.3 *Detector*—The excited NO₂ in the gas stream relaxing to ground state NO₂ is detected by a NO₂-specific chemiluminescence detector.

7.2.4 *Detector Response*—Area integration accurately quantifies nitrogen content in the event of split or overlapping peaks that result from furnace cooling or variable combustion rates of different organic molecules contained in a sample.

7.2.5 *Presentation of Results*—The detector output is related to stored calibration data and then displayed as milligrams of nitrogen per litre.

8. Reagents and Materials

8.1 *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 pure enough to be used without lessening the accuracy of the determination.

8.2 *Purity of Water*—Unless otherwise indicated, references to water shall be understood to mean reagent water conforming to Specification D1193, Type I or Type II.

8.3 *Acid*—Acid is used for sample preservation and interference removal. Follow the manufacturer's suggestions for acid and acid concentration. Do not use nitric acid.

8.4 *Total Nitrogen Stock Calibration Standard Solution (1000 mg/L)*—Weigh 3.609 g of potassium nitrate (KNO₃) and 2.360 g of ammonium sulfate ((NH₄)₂SO₄) previously dried for two hours at 120°C and quantitatively transfer to a 1000-mL volumetric flask containing about 500 mL of reagent water. Stir to dissolve and add 1 mL of concentrated hydrochloric acid (HCl), dilute to the mark with reagent water and mix. Transfer to an amber glass reagent bottle and cap for storage. This stock solution, or dilutions of it, is used to calibrate and test performance of the nitrogen analyzer.

NOTE 1—Alternative nitrogen compounds, such as glycine, may be used as the stock calibrant providing all QC acceptance criteria is met.

8.5 *Total Nitrogen, Stock Laboratory Control Sample (LCS) Solution (1000 mg/L)*—Weigh 7.218 g of potassium nitrate (KNO₃) previously dried at 120°C for two hours and quantitatively transfer to a 1000-mL volumetric flask containing about 500 mL of reagent water. Stir to dissolve and add 1 mL of concentrated hydrochloric acid (HCl), dilute to the mark

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.

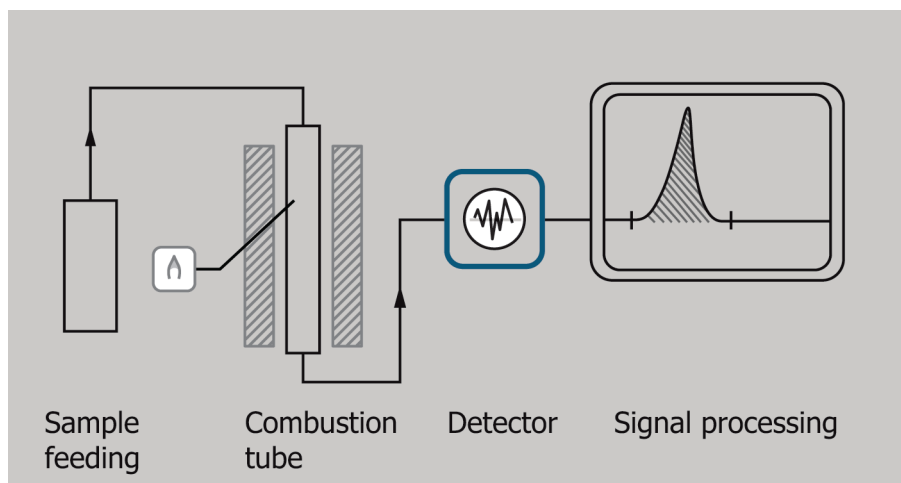


FIG. 1 Diagram of Apparatus

with reagent water and mix. Transfer to an amber glass reagent bottle and cap for storage. This solution, or dilutions of it, is used to verify calibration accuracy and test performance of the nitrogen analyzer.

8.6 *Organic Nitrogen, Stock TON Test Solution (1000 mg/L)*—Weigh 7.964 g of glycine (C₂H₄NO₂-HCL) and transfer to a 1000-mL volumetric flask containing about 500 mL of reagent water. Mix to dissolve, dilute to the mark, and mix.

8.7 *Calibration Solutions*—TN.

8.7.1 *TN Calibration Solutions*—At least four calibration concentrations and a calibration blank (CB) are used to prepare an initial calibration curve. Standards are prepared to cover the concentration of interest from the total nitrogen stock calibration solution. Calibration standards are prepared in reagent water and preserved to pH ≤2 with concentrated H₂SO₄. Filtration of these standards is unnecessary. These standards may be used for TN and DN calibrations. The calibration blank (CB) should be compensated either by running a 0.0 mg N/L standard or by blank subtraction. These standards, if stored in the dark, are stable for about 30 days and may be used to recalibrate the instrument within the 30-day period. See [Table 3](#) for an example of calibration standard preparation. Different calibration standards may be needed depending upon the concentration of nitrogen in the samples analyzed.

8.8 *Gas Supply*—High-purity compressed air or high purity oxygen free of CO₂ and of organic matter is required. Use gas purity as specified by the equipment manufacturer.

9. Sampling and Sample Preservation

9.1 Collect the sample in accordance with Practices [D3370](#), Guide [D4448](#), Guide [D6538](#), or Practice [D6759](#). Document the field activities according to Guide [D6089](#).

9.2 To preserve samples for this analysis, store samples in high density polyethylene or glass at just above freezing to 6°C. Acidify the samples to a pH ≤2 with H₂SO₄. Analyze within 28 days of collection.

9.3 DON or DN must be filtered in the field or in the laboratory within 48 hours of collection and prior to acidification and analysis. After filtration, the sample is acidified to a pH ≤ 2 and stored at above freezing to 6°C. The sample must be analyzed within 28 days of collection.

9.4 For monitoring of waters containing solids or immiscible liquids that are to be injected into the heated reaction zone use a mechanical homogenizer or ultrasonic disintegrator. Filtering or screening may be necessary after homogenization to reject particle sizes that are too large for injection.

NOTE 2—Samples up to 500 mg/L total suspended solids may be analyzed. Constantly stir with a magnetic stirrer during sample introduction.

9.5 For wastewater streams where nitrogen concentrations are greater than the desired range of instrument operation, dilute the samples as necessary.

10. Instrument Operation

10.1 Follow the manufacturer's instructions for instrument warm-up, combustion temperature, gas flows, and liquid flows.

11. Calibration

11.1 Prior to calibration, monitor the background levels for at least 30 minutes or until the background signal reaches the manufacturer's recommended level. Adjust instrument temperatures, flow rates, and reagent settings according to the manufacturer's instructions. Perform multiple injections of reagent water until three consecutive injections fall within 20 % of their mean.

11.2 A new calibration curve is generated when fresh standards are made, or when continuing calibrations verification standards (CCV) fall outside of quality control (QC) Limits. Use a CB and at least four calibration standards to span the expected concentration range of the samples to be analyzed. The lowest calibration standard must be at the minimum reporting level (MRL). Inject standards from low to high (in triplicate for greatest accuracy) to calibrate the instrument. Triplicate measurements, if made, should be within 5 % of their mean. See [Fig. 2](#) for an example of a calibration curve.

11.3 After the instrument has been calibrated, verify the calibration with an initial calibration verification standard (ICV) prepared at the midpoint of the curve. The ICV should be within 10 % of its known value.

11.4 Record the data from the calibration in an instrument log or laboratory notebook. This calibration serves as a historical record of instrument performance. Compare subsequent calibrations, recording the data each time. If the slope of a calibration changes significantly such that QC criteria cannot be met, consult the instrument manual or laboratory SOP for corrective action, which may include replacement of the combustion tube, catalyst, or combinations thereof.

12. Procedure

12.1 Mix or blend each sample thoroughly and carry out any necessary dilution to bring the nitrogen content within range of the instrument. Since some high molecular weight, organic compounds may precipitate upon cooling, warm the sample

TABLE 3 Example Preparation of Calibration Curve Standards for Total and Dissolved Nitrogen Analysis

Cal Level	Concentration of Stock (mg/L)	Volume of Stock (mL)	Final Volume of Calibration Standard (mL)	Final Concentration of Calibrations Standard (mg/L)
Calibration Blank (CB)	—	0.0	1000	0.0
1	1000	0.20	1000	0.20
2	1000	0.50	1000	0.50
3	1000	1.00	1000	1.00
4	1000	5.00	1000	5.00
5	1000	10.0	1000	10.0