Determination of TKN by Subtraction using ASTM D8083-16 and ASTM D7781-14

William Lipps, Shimadzu Scientific Instruments, Inc.

Introduction

The USEPA Clean Water Act (CWA) requires national approval for all methods used for CWA compliance(1). There are approved methods for the determination of inorganic nitrogen (NO_3-N, NO_2-N, and NH_3-N), and for organic nitrogen (TKN – NH_3-N). There are no EPA approved methods for the determination of total nitrogen although it is a required parameter in many USEPA permits, including monitoring of nutrient pollution for ambient water criteria. Because Part 136.3 Table 1b methods are required, laboratories have no recourse but to measure total nitrogen as the sum of TKN, NO_3-N , and NO_2-N (2).

ASTM D8083-16, a new method for Total Nitrogen and TKN by Calculation

This new method (3) couples the Shimadzu TOC-L (Figure 1) High Temperature Catalytic Oxidation (or Combustion) Total Organic Carbon (TOC) analyzer with the Shimadzu TNM chemiluminescent nitrogen detector. The combustion temperature is 720 ºC.

Nitrogen containing compounds in the sample introduced into the combustion tube convert to nitrogen monoxide (reactions 1 and 2). Nitrogen gas in the carrier gas (air) does not interfere. The carrier gas containing the nitrogen monoxide (NO) passes through a thermoelectric cooler. The cooled and dehumidified gas then enters the chemiluminescence analyzer where the NO reacts with ozone (O3) and converts to a combination of nitrous oxide (NO2) and excited nitrous oxide (NO2*) (reactions 3 and 4). As the NO2* returns to the ground state, it emits radiation that is measured photo-electrically (reaction 5). The detector signal generates a peak that is proportional to the nitrogen concentration in the sample.

(1) $4NH_3 + 5O_2 \rightarrow 4NO + 6H_2O$
(2) $2(NH_2)_2CO + 5O_2 \rightarrow 4NO + 4H_2O + CO_2$
(3) $NO + O_3 \rightarrow NO_2 + O_2$
(4) $NO + O_3 \rightarrow NO_2^* + O_2$
(5) $NO_2^* \rightarrow NO_2 + hv$

Description of ASTM D8083-16

The Shimadzu TOC-L with TN module converts all nitrogen compounds to NO at 720 ºC. The instrument uses an auto-sampler to automatically inject sample onto a platinum catalyst inside the heated combustion chamber. The instrument automatically calibrates from a single 10 mg/L N solution to establish a multiple point calibration curve from 0.2 – 10 mg/L N. The instrument automatically dilutes (or injects less sample aliquot) off-scale peaks, enabling quantitation up to 500 mg/L. Concentrations higher than 500 mg/L N are diluted manually. Total analysis time, per injection, is 2-5 minutes. The Method Detection Limit (MDL) is 0.05 mg/L N.

Figure 1: Shimadzu TOC-L with TN Module

Measure Nitrate/Nitrite Nitrogen with ASTM D7781-14

This ASTM method (4) determines nitrate using discrete analyzers capable of very fast determinations equaling or exceeding 60 determinations per hour. Other method for nitrate plus nitrite, such as EPA 353.2 and EPA 353.1 determine nitrite after a reduction of nitrate to nitrite using cadmium metal or hydrazine respectively. ASTM D7781-14 reduces nitrate to nitrite using an environmentally benign enzyme (Figure 2) making it a “green” chemistry.

Comparison of ASTM D8083-16 TN with EPA TN methods

Fifty-two samples were analyzed by the EPA calculation for TN and compared to TN determined by the new ASTM method. These results are statistically the same (Figure 2)

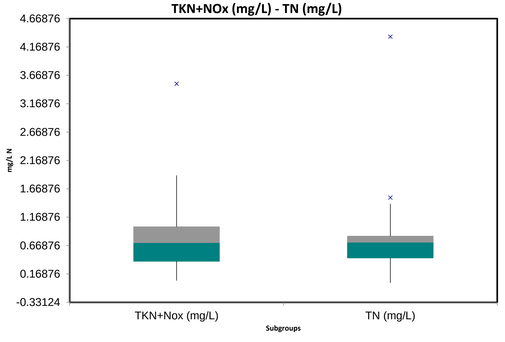

Figure 2: Comparison of EPA TN and ASTM D8083

Inter-laboratory Study data

The ASTM D19.06 task group validating ASTM D7781-14 conducted an inter-lab study in accordance with the USEAP ATP protocol and ASTM D8083-16 accordance with ASTM Practice D2777 –13, Complex matrices including POTW matrices, and pulp and paper effluent were used. Laboratories received each matrix, with the exception of a Laboratory Control Sample (LCS), as blind samples. Table 1 and Table 2 list the statistical summary for all the inter-laboratory study results.

Matrix	Average Spike Recovery (%)	Average RPD (%)
WW treatment plant influent	94.1	3.7
wastewater treatment plant effluent #1	99.7	8.1
wastewater treatment plant effluent #2	97.9	2.7
Paper Mill waste stream effluent	102	1.9
metal finisher wastewater effluent	98.0	15.3
commercial laundry wastewater effluent	101	3.2
ERA #507 Hardness	95.2	5.9
Confined Animal Feeding Operation (CAFO) effluent	91.5	16.6
Low Nutrient Seawater	93.5	1.6

Table 2: Summary of ILS results for ASTM D7781-14

Matrix	Source of N	Known N (mg/L)	Found N (mg/L)	% Recovery	% RSD (multiple operator)	% RSD (single operator)
1	Glycine	5.00	5.15	103	3.56	1.49
		4.00	4.04	101	4.89	0.93
2	Nicotinic Acid	2.00	1.93	97	4.71	1.20
		1.61	1.54	96	4.75	1.06
3	Glycine	0.514	0.496	97	6.03	2.81
		0.313	0.303	97	12.2	4.56
4	Mix of NH_3-N and NO_3-N	10.0	9.70	97	7.94	1.99
5	NH_3-N	30.0	28.5	95	9.50	2.98
6	unknown		29.6		7.74	2.71
7	unknown		4.41		11.5	6.80
8	unknown		9.30		31.0	3.42
9	unknown		339		37.9	6.76

Table 1: Summary of ILS results

Conclusion

ASTM D8086-16 is a new method for the determination of total nitrogen, and TKN by calculation, in water samples. Used with ASTM D7781-14 for nitrate / nitrite determination, TKN is now greener, faster, and much less dangerous. Results compare favorably with the current EPA approved calculated total nitrogen in samples without interferences..

(1) https://www.epw.senate.gov/water.pdf, Secs 301(a), 304 (h), and 501(a), accessed February 10, 2017
(2) Code of Federal Regulations, Protection of the Environment, Title 40, Chapter 1, Subchapter D, Part 136.3
(3) ASTM D8083-16, Standard Test Method for Total Nitrogen, and Total Kjeldahl Nitrogen (TKN) by Calculation, in Water by High Temperature Catalytic Combustion and Chemiluminescence Detection, ASTM International, West Conshohocken, PA, 2016, www.astm.org
(4) ASTM D7781-14, Standard Test Method for Nitrate-Nitrite in Water by Nitrate Reductase, ASTM International, West Conshohocken PA, 2014, www.astm.org