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Application Note

Simultaneous detection of Total Bound Nitrogen (TN_b) and Total Organic Carbon (TOC) in aqueous samples

Introduction

Total bound nitrogen (TN_b) is the nitrogen present in dissolved ammonia, nitrates, nitrites, amines, and organic nitrogen-containing compounds.(1) TN_b measurements represent an alternative to both Total Kjeldahl (TKN) and Dumas method nitrogen determination for rapid screening of industrial wastewater, drinking water, agricultural runoff, and surface waters.

TN_b offers a faster, cleaner alternative to the Kjeldahl method—no boiling acid or distillation required. TOC and TN_b together provide a rapid assessment of organic carbon and nitrogen pollution in water.

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TN_b analysis can be performed simultaneously with Total Organic Carbon (TOC) analysis by using detectors selective for nitrogen and carbon in tandem. High-temperature (720 °C) catalytic combustion in an air or oxygen stream oxidizes carbon-containing species into CO_2 and nitrogen-containing compounds into nitric oxide, NO, and carries the reaction products sequentially through:

1. a solid-state non-dispersive infrared (SSNDIR) detector where the CO_2 is measured
2. a polishing afterburner to convert nitrogen species to NO and
3. an electrochemical cell where NO is measured. These are the species measured for TOC and TN_b determinations.(2)

Here we describe the use of tandem detectors for simultaneous TN_b and TOC determinations and the oxidation and conversion efficiency of nitrogen compounds into NO using standards and industrial water samples. Instrument operating conditions, calibration data, analytical results, and repeatability are reported.

Principle of Operation–TOC

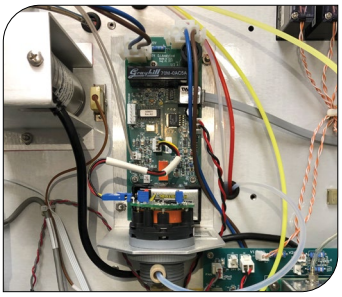
Samples are injected into a catalyst-filled reactor held at 680 °C where they are combusted in an oxygen atmosphere. The combustion effluent is swept through a solid-state non-dispersive infrared detector (SS-NDIR) where the detector response is converted to area counts proportional to the amount of carbon in the sample. To analyze for TOC, rather than total carbon (TC), the inorganic carbon is removed first by acidification to a pH value of less than 2 and sparging to waste.

Principle of Operation–TN_b

Total Kjeldahl Nitrogen (TKN) is the USEPA-approved parameter for total organic nitrogen. The Dumas Method is also used for nitrogen determinations primarily in food and protein or sludge samples and is recognized by AOAC and many other bodies, but not USEPA. USEPA defines total nitrogen as TKN plus nitrate/nitrite nitrogen.

The TKN method requires a preliminary digestion in concentrated sulfuric acid with a metal catalyst followed by distillation and analysis or automated analysis using a continuous flow analyzer. The TKN method has limited efficiency, requires hazardous reagents, and suffers significant negative bias in the presence of nitrate nitrogen. The Dumas method eliminates the use of sulfuric acid,(3) but nitrogen oxides must be reduced to nitrogen gas which is determined by thermal conductivity, whereas the TN_b method eliminates the final reduction step and detection by thermal conductivity.

An OI Analytical 1080 TOC Analyzer equipped with a TN_b module and 1088 Rotary Autosampler enables rapid (within five minutes) screening of a sample for total nitrogen without interference from nitrate nitrogen. Combustion of nitrogen-containing samples is carried out at 720 ˚C to ensure complete oxidation of organic nitrogen.



TN_b Module

The following oxidation reaction occurs at the sensing (working) electrode:

$$NO + 2H_2O \longrightarrow HNO_3 + 3H^+ + 3e^-$$

Nitric acid exhibits the following equilibrium reaction in solution.

$$4HNO_3 \longleftrightarrow 4NO_2 + O_2 + 2H_2O$$

At the counter electrode, the following reduction occurs

$$O_2 + 4H^+ + 4e^- \longrightarrow 2H_2O$$

The presence of NO in the sample stream creates a potential difference between the sensing (working) electrode and the counter electrode for the calculation of the mass and concentration of nitrogen in the sample.

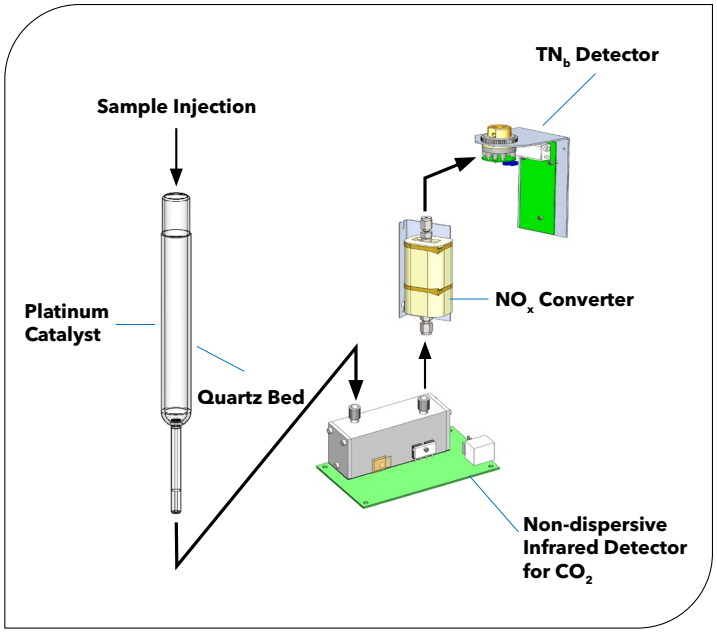


Figure 1. Schematic of TOC/TN$_b$ analysis performed with the 1080 TOC analyzer

Experimental

Two experiments were conducted to demonstrate the accuracy and reliability of the TN$_b$ method and TOC measurements were used as a reference. In the first experiment, TN$_b$ was analyzed alone, ignoring the instrument's capability to simultaneously analyze TOC and TN$_b$. The analyzer is calibrated with nitrogen standards prepared from potassium nitrate, taking advantage of the Model 1080 autocalibration feature to prepare the calibration curve. See Table 1 for instrument parameters and calibration data.

Table 1. Instrument operating parameters for TN$_b$ calibration and calibration results.

TN$_b$-Only calibration	
System parameter	**Setting or value**
Sample volume	80 µL
System pressure	20 psi
Detect time	5 minutes
Detect temperature	720 °C
Calibration type	Autogenerated
Number of standards	3
Dilution factor	2:1
Dilution volume	20 mL
Correction method	Subtract offset

Calibration results		
R^2	0.9958	
Offset	3677	
Calibration point	**Detector area counts**	**%RSD**
RW	349	3.63
12.5 mg N/L	27816	1.82
25 mg N/L	54072	1.77
50 mg N/L	104843	3.95
100 mg N/L	195325	4.37

A second experiment demonstrates the capability of simultaneous determination of organic carbon and total nitrogen. In this experiment, the calibration was made using organic carbon standards prepared from primary standards potassium hydrogen phthalate (KHP) and potassium nitrate. Again, the autocalibration feature of the 1080 was used to prepare the standard curve.

Results

TN_b-only analysis

The calibration data showed acceptable linearity over the calibration range and a coefficient of determination (R^2) of 0.9958. Checks performed by reanalysis of calibration standards were within 90-110% recovery. Certified simple and complex nutrient wastewater samples from two suppliers from two suppliers (Agilent catalog numbers QCI-745A and QCI-745B; and Waters ERA catalog numbers 739 and 741) were obtained for this study. (4,5) The simple nutrient check standards contain nitrogen as ammonia and nitrate; the complex nutrient check standards certify the nitrogen content as TKN. Values for the total nitrogen in the simple nutrient standards were calculated by adding the theoretical concentrations of nitrate and ammonia nitrogen.

Samples were analyzed in duplicate and on two separate Model 1080 instruments. The second instrument provides an indication of multiple laboratory/multiple user precision and bias. The same calibration standards and check standards were used in all analyses.

Table 2. Quality control recoveries for nutrient samples

Sample		Expected value mg/L	Instrument 1 mg/L	Instrument 2 mg/L
Agilent	Simple	19.7	19.6	20.6
	Simple		19.9	20.5
Agilent	Complex	16.4	17.3	19.8
	Complex		17.4	17.8
Waters ERA	Simple	26.6	27.2	27.2
	Simple		27.1	27.0
Waters ERA	Complex	19.2	20.6	20.8
	Complex		20.9	20.8

Calibration

Simultaneous TOC and TN_b analysis Calibration of TOC and TN_b combined resulted in coefficients of determination of 0.9998 and 1.000, respectively. The R^2 of the TN_b calibration likely improved because, in this test, the calibration was over a narrower concentration range. Calibration standards were reanalyzed as unknowns with recoveries well within the range of 90-110%.

A mixed TOC and TN_b standard prepared from KHP and KNO_3 was analyzed with recovery of 98.8% TOC and 103% TN_b. Standards prepared from ammonium sulfate and nitric acid were also analyzed. Ammonium sulfate is specified in EN ISO 20236:2024.(6) These standards were prepared at concentrations of 1 mg C/L, 1 mg N/L and 10 mg C/L, 10 mg N/L.

Recovery of these check standards were well within 90-110% for both concentrations (Figures 2 and 3). This data show that the determination of TOC and TN_b in the same solution can be achieved with acceptable accuracy. A second test was made using urea. Although urea may be considered a “simple” molecule, it is a very common constituent in industrial and municipal wastewater. Urea is 46.65% nitrogen by mass and 20.00% carbon by mass, with a ratio of 2.33:1 nitrogen to carbon ratio. Standards were prepared from urea with a concentration of 1 mg C/L and 5 mg C/L and analyzed for TOC and TN_b. The nitrogen to carbon ratio was calculated and data are presented in Table 3.

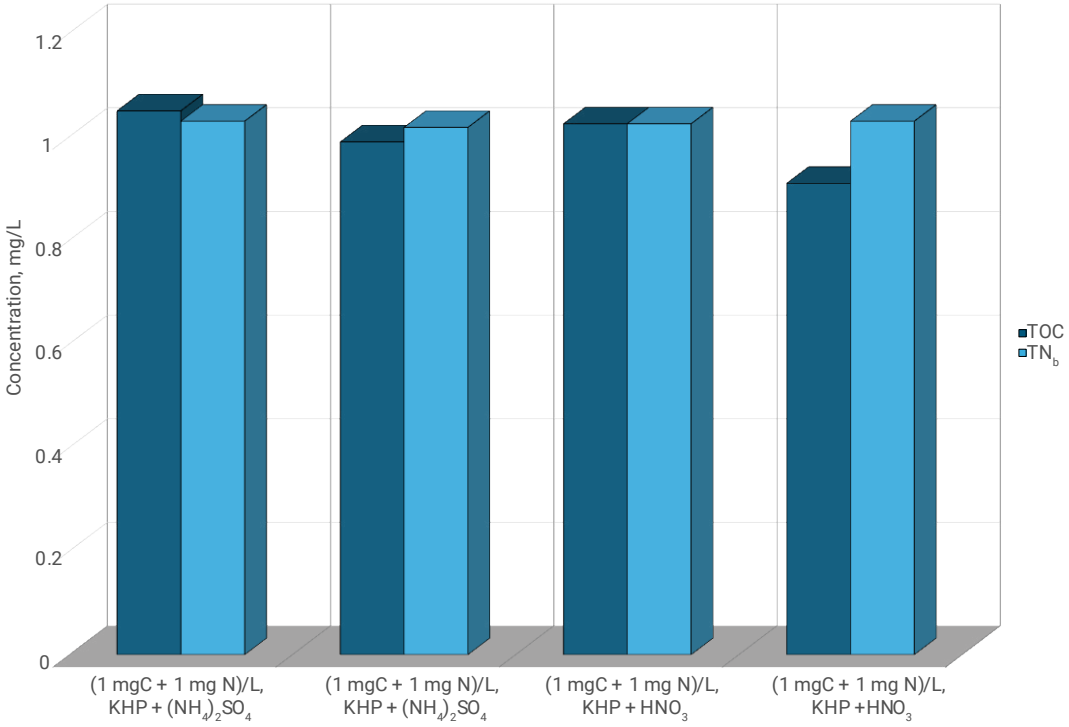


Figure 2. Mixed standard recoveries at 1 mg/L

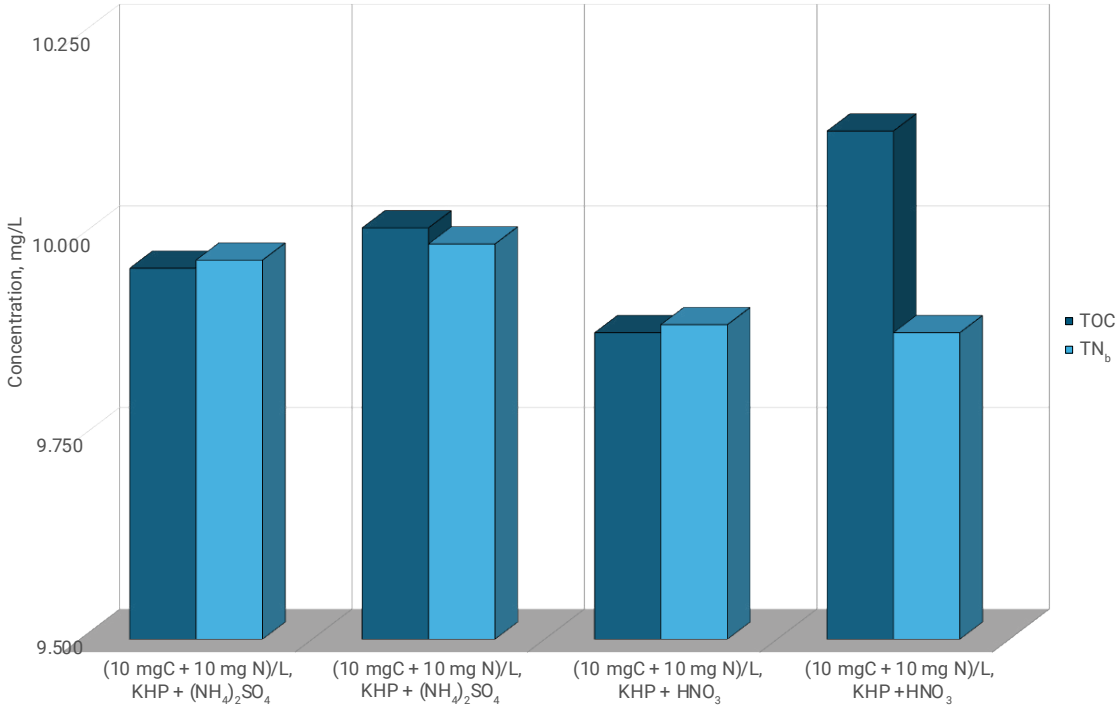


Figure 3. Mixed standard recoveries at 10 mg/L

Table 3. Nitrogen and carbon ratio from urea standards

Urea	TOC, mg/L	TN_b, mg/L	N:C ratio
Sample 1a	0.92	2.43	2.64
Sample 1b	0.99	2.43	2.45
Sample 2a	5.03	11.4	2.27
Sample 2b	5.19	11.5	2.22

Conclusion

Total bound nitrogen analysis provides a safe, accurate and precise alternative to traditional methods for determination of TN in water samples. TOC and TN data from the same sample can be collected contemporaneously and quickly relative to other current methods for TN, including TKN and Dumas methods. The speed, convenience, and analytical utility of the TOC/TN_b measurement makes it a good method for screening at least in commercial and process control laboratories. Allowing for near real-time decision making can potentially eliminate the need for organic nitrogen analyses that require preliminary manual digestion or complete conversion to nitrogen gas.

References

1. Nitrogen, Kjeldahl, Total (Colorimetric; Titrimetric; Potentiometric). Methods for the Chemical Analysis of Water and Wastes; EPA/600/4-79/020; U.S. Environmental Protection Agency, Office of Research and Development, Environmental Monitoring Systems Laboratory: Cincinnati, OH 1974; Method 351.3

2. Model 1080 Operator's Manual, OI Analytical, 777 Graham Rd, Suite 101, College Station, TX 77845

3. Soil Quality – Determination of total nitrogen content by dry combustion ("elemental analysis") ISO 138768:1998.

4. Agilent Technologies/Ultra Scientific, 250 Smith Street, North Kingstown, RI 02852, USA, www.agilent.com

5. Waters ERA. 6000 West 54th Ave, Arvada, CO 80002, USA, www. eraqc.com

6. Water Quality – Determination of Total Organic Carbon (TOC), Dissolved Organic Carbon (DOC), Total Bound Nitrogen (TN_b) And Dissolved Bound Nitrogen (DNb) After High Temperature Catalytic Oxidative Combustion. DIN EN ISO 20236:2024

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