Simultaneous Determination of Total Bound Nitrogen (TN_b) and Total Organic Carbon (TOC) in Aqueous Samples

Introduction

Total bound nitrogen (TN_b) consists of dissolved ammonia, nitrates, nitrites, amines, and other organic nitrogen-containing compounds. TN_b measurements represent an alternative to Total Kjeldahl Nitrogen (TKN) analysis for rapid screening of industrial wastewater, drinking water, agricultural run-off, and surface waters.

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 oxidizes compounds containing carbon into CO_2 and nitrogen compounds into nitric oxide (NO). Oxygen carrier gas transports to CO_2 and NO reaction gases first into a solid-state non-dispersive infrared (SS-NDIR) detector to measure TOC and then into an electrochemical detector to measure TN_b.

This application note describes the use of tandem detectors for simultaneous TN_b and TOC measurements, and oxidation efficiency and conversion of nitrogen compounds into NO using standards and industrial water samples. Instrument operating conditions, calibration data, analytical results, and repeatability are reported.

Keywords

TN_b - Total bound nitrogen
Model 1080 TOC Analyzer
Total Kjeldahl Nitrogen (TKN)

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Principle of Operation

Total Kjeldahl Nitrogen (TKN) is the USEPA-approved parameter for total organic nitrogen. The TKN method measures organic nitrogen and ammonia nitrogen. Total nitrogen is defined by the EPA 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 on a continuous flow analyzer. The TKN method has limited efficiency, requires hazardous reagents, and suffers significant negative bias in the presence of nitrate nitrogen.[1]

An OI Analytical 1080 TOC Analyzer equipped with a TN_b module and 1088 Rotary Autosampler enables rapid (within five minutes) screening of samples for total nitrogen without interference from nitrate nitrogen.

The TN_b module measures nitrogen compounds by electrochemically detecting nitric oxide (see Figure 1). This gas dissolves in water within the electrochemical cell in the following reaction:

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

This reaction occurs at the sensing electrode. Nitric acid then exhibits the following equilibrium reaction.

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

At the counter electrode, the oxygen reacts as follows:

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

The presence of NO in the sample stream is measured as a potential difference between the sensing electrode and counter electrode for calculation of mass and concentration of nitrogen from the sample.

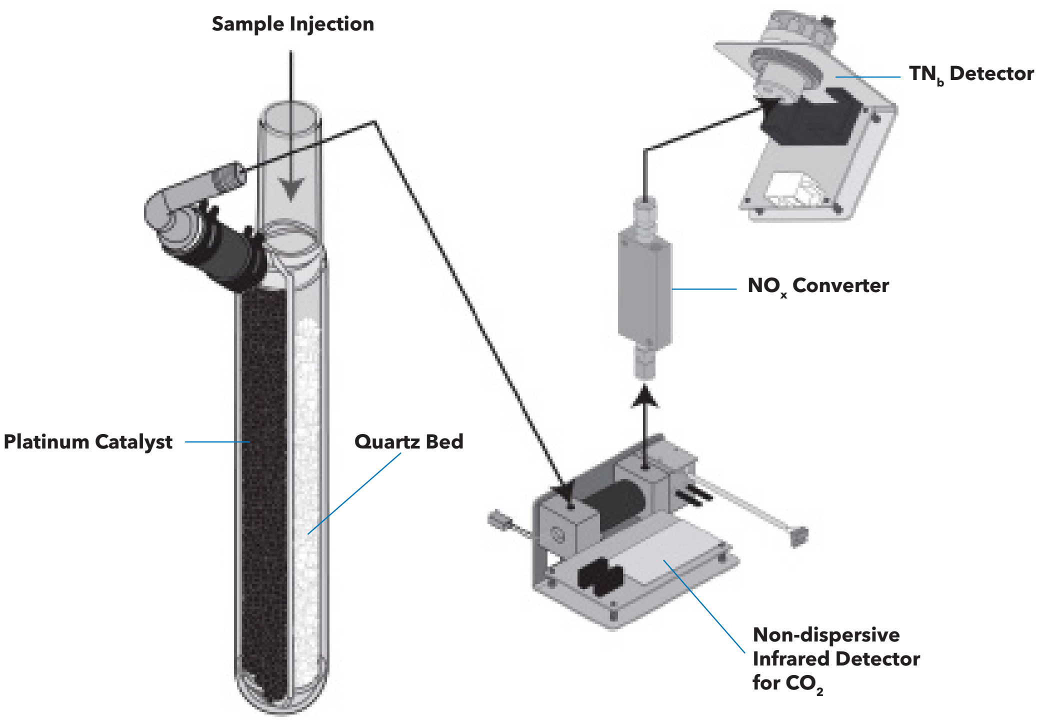

Figure 1. **Schematic of TN_b Analysis Performed with the 1080 TOC Analyzer**

Experimental

Two experiments were performed to demonstrate the reliability and accuracy of the TN_b method. In the first experiment TN_b was analyzed alone, ignoring the instrument's capability to analyze TOC and TN_b simultaneously. 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 settings and calibration data.

TNb Only Calibration		
System	**Model 1080 with TN_b**	
Sample Volume	80 µL	
System Pressure	20 psi	
Detect Time	5 min	
Detect Temperature	720 °C	
Calibration		
Type	Autogenerated	
Standards	3	
Dil. Factor	2:1	
Dil. Volume	20 mL	
Sampling	Subtract Offset	
Results		
R2	0.9958	
offset	3677	
	Area Counts	**% RSD**
RW	349	3.63
12.5	27816	1.82
25	54072	1.77
50	104843	3.95
100	195325	4.37

Table 1. Instrument Operating Parameters for TN_b Calibration

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 standard potassium hydrogen phthalate (KHP) and from potassium nitrate. Again, the autocalibration feature of the 1080 was used to prepare the standard curve.

Results and Discussion

TN_b-only analysis

The calibration data showed acceptable linearity throughout 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 separate suppliers (Ultra Scientific[(2)] (Catalog numbers QCI-745A and QCI-745B respectively) and Environmental Resource Associates[(3)] (Catalog numbers 739 and 741 respectively)) were obtained for this study. 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/user precision and bias. The same calibration standards and check standards were used in all analyses.

The results are shown in Table 2. With the exception of one result on the Ultra Scientific simple nutrient sample with instrument 2, all values obtained were within the stated quality control limits.

Sample		Expected Value	Expected Range	Instrument 1	Instrument 2
Ultra Scientific	Simple	19.67± 0.15	16.38 - 22.7	19.698	20.622
	Simple			19.941	20.570
Ultra Scientific	Complex	16.4±0.2	12.6 - 19.5	17.368	19.869
	Complex			17.423	17.871
ERA QC	Complex	19.2	16.2 - 21.6 $_{QC}$	20.698	20.835
	Complex		12.7 - 24.7 $_{PT}$	20.998	20.864
ERA QC	Simple	26.6	23.8 - 29.3 $_{QC}$	27.200	27.276
	Simple		20.7 - 32.0 $_{PT}$	27.157	27.087

Table 2. Quality Control Recovery Test

TOC and TN_b-Simultaneous 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 improved because, in this test, the calibration was made over a narrower concentration range. Calibration standards were reanalyzed as unknowns with recoveries well within 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 DIN: ISO 19905-2[(4)] and EN 12260.[(5)] These standards were prepared at 1 ppm C/1 ppm N and 10 ppm C/10 ppm N.

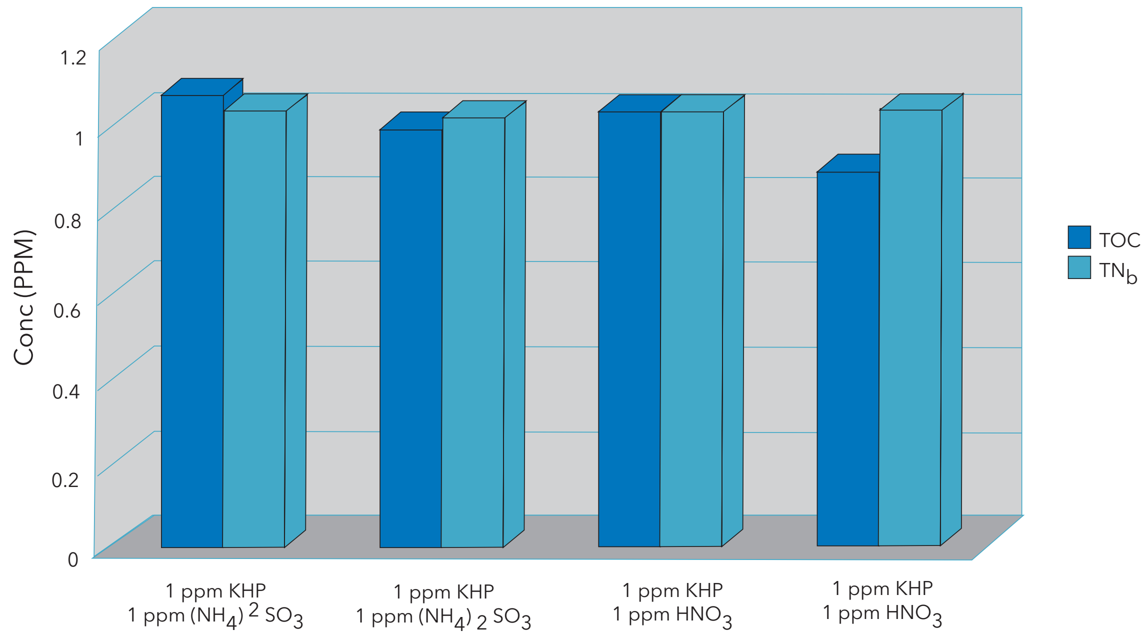

Figure 2. Mixed Standard Recoveries at 1 ppm

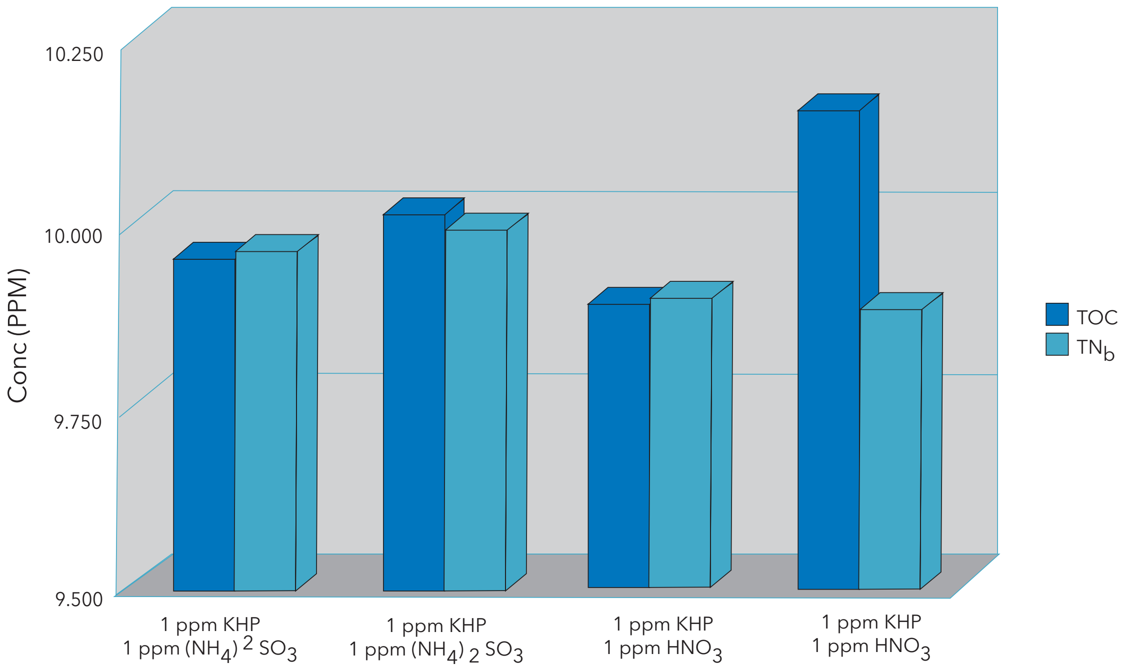

Figure 3. Mized Standard Recoveries at 10 ppm

Recovery of these check standards were well within 90–110% for both concentrations (Figures 2 and 3). These data show that the determination of TOC and TN in the same sample solution can be achieved with acceptable accuracy and precision.

A second test was made using urea, which contains one carbon and one nitrogen. Although urea may be considered a "simple" molecule, it is a very common constituent in industrial and municipal wastewater. The urea molecule is theoretically 46.46% nitrogen and 20% carbon with a 2.3:1 nitrogen to carbon ratio. Standards were prepared from urea with a normal 1 ppm and 5 ppm carbon concentration and analyzed for TOC and TNb. The nitrogen to carbon ratio was calculated and data are presented in Table 3.

Urea	TOC ppm	TN_b ppm	N/C
Sample 1	0.92	2.43	2.6
Sample 1	0.99	2.43	2.4
Sample 2	5.03	11.4	2.3
Sample 2	5.19	11.5	2.2

Table 3. Nitrogen and Carbon Ratio from Urea Standards

Summary and Conclusions

Total bound nitrogen analysis provides a cost effective, safe, and accurate alternative to traditional methods for determination of TN in water samples. Current methods for TN, including TKN, require preliminary manual digestion steps and are subject to interferences. The TNb method has a further advantage of simultaneous determination of TOC. The rapid screening of samples for TOC and TN can provide commercial and process control laboratories valuable data within minutes allowing near real-time decisions to be made.

References

1. U.S. EPA Method 351.3, Total Kjeldahl Nitrogen by Potentiometry.

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4. DIN: ISO 11905-2: 1997. Water Quality - Determination of Nitrogen - Part 2: Determination of Bound Nitrogen, After Combustion and Oxidation to Nitrogen Dioxide, Chemiluminescence Detection.

5. EN 12260: 2003. Water Quality - Determination of Nitrogen - Determination of Bound Nitrogen (TN_b), Following Oxidation to Nitrogen Oxides.

O·I·Analytical
a xylem brand

151 Graham Road
PO Box 9010
College Station, Texas
77842-9010

(979) 690-1711
(800) 653-1711 USA/Canada
FAX (979) 690-0440

www.oico.com
E-mail: oi-info@xyleminc.com

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