Total Nitrogen Analysis: A New Perspective on TOC

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Introduction

Monitoring the nitrogen content is of great importance in many industries for many reasons. In waters and wastewaters the most interesting forms of nitrogen, in order of decreasing oxidation state, are nitrate, nitrite, ammonia, and organic nitrogen[1]. Organic nitrogen includes such natural materials as proteins, peptides, nucleic acids, urea, and numerous synthetic organic materials. In excessive amounts, nitrate contributes to the illness known as methemoglobinemia in infants. As a preventative measure, the current EPA-imposed maximum contaminant level (MCL) for nitrate in drinking water is 10 mg/L. Nitrite is an intermediate oxidation state of nitrogen both in the oxidation of ammonia to nitrate and the reduction of nitrate to nitrite. It can enter a water supply system through its use as a corrosion inhibitor in industrial process water. It is also a precursor in the formation of nitrosamines, which are known to be carcinogens. Ammonia is present naturally in surface and wastewaters. At some wastewater treatment plants, it is used as an additive to control residual chlorine. Analytically, ammonia and organic nitrogen can be determined together using a technique called Total Kjedahl Nitrogen (TKN).

In the past, to arrive at an accurate assessment of total nitrogen, the analyst had to separately measure for all of the various nitrogen forms and then combine the results. Consequently, analyzing for total nitrogen proved to be a long and difficult process. What's more, all of the EPA-approved methods for nitrogen analysis were extremely time-consuming. These methods were primarily wet chemical methods requiring extensive sample preparation in the form of digestions and/or titrations. Also, UV/VIS spectroscopy was typically used to measure for the various nitrogen forms (i.e. nitrate plus nitrite) in the wet chemical product. Thus, more time was consumed in waiting for color to fully develop in the absorbing species. As a result, the analysis time for separate nitrogen forms ranged from one to six hours depending upon the nitrogen form being determined and the number of samples being analyzed.

Shimadzu understands the need for quick and accurate analysis of total nitrogen. Combined with our state-of-the-art TOC-V Visionary series Total Organic Carbon analyzer (TOC-V_{CSH}), Shimadzu's Total Nitrogen Module, TNM-1, uses chemiluminescence to measure total nitrogen in less than four minutes! Similar to the TOC analyzer, the TNM-1 is a non-specific measurement of total nitrogen. A nitrogen-based sample is combusted to nitrogen monoxide and nitrogen dioxide. The nitrogen species are then reacted with ozone to form an excited state of nitrogen dioxide. Upon returning to ground state, light energy is emitted. Then, total nitrogen (TN) is measured using a chemiluminescence detector. To add, the combination of the TOC-V_{CSH} and the TNM-1 can simultaneously measure for TOC and TN.

Method and Results

In section 1, the Shimadzu TNM-1 coupled with the TOC-V_{CSH} was used to demonstrate the ability to effectively measure nitrogen at low levels by performing a method detection limit study. In section 2, various forms of nitrogen compounds of known concentrations, including nitrates, nitrites, ammonium, and organic nitrogen, were analyzed at higher ppm ranges for accuracy. Finally, in section 3, mixture compounds of known nitrogen and carbon content were analyzed at higher ppm ranges to demonstrate the ability to simultaneously measure for total nitrogen and total carbon.

Section 1: Total Nitrogen Detection Limit Study

Shimadzu's TNM-1, Total Nitrogen Module, can accurately and precisely analyze a wide range of Total Nitrogen (TN) from 100ppb to 4000ppm. A laboratory blank with deionized water and a 100ppb KNO_3 standard were prepared for determining the Method Detection Limit (MDL).

Method Detection Limit (MDL) Study on Total Nitrogen using the TNM-1

Estimated MDL is 100ppb

Rep #	Area(mV)		Concentration(ppb)
Blank	0.0409		N/A
1	4.279		94.29
2	4.438		97.83
3	4.324		95.29
4	4.548		100.3
5	4.121		90.77
6	4.262		93.91
7	4.558		100.5
Mean Area	4.361	Mean Conc.	96.12

Standard Deviation of Conc. (SD) is 3.578ppb
T-value (t) based on 6 degrees of freedom is 3.14
MDL = t x SD = 11.23ppb

The estimated MDL is based upon the listed specification limits for the TNM-1. This value is somewhat empirical in the sense that an MDL is dependent upon achieving optimal instrument, laboratory and sample matrix conditions. The true calculated MDL of 11.23 ppb was achieved based upon the optimal conditions at Shimadzu's Application Laboratory. It is recommended that a Practical Quantitation Limit (PQL), which is typically five times higher than the MDL, be used as the lowest concentration level that is attainable when generating reproducible and accurate data. Based on the results of this study, a PQL of approximately 56ppb was achieved. Shimadzu is currently in the process of researching lower method detection limits by increasing the maximum injection volume to 2000uL. The current maximum injection volume is 150uL.

Section 2: Nitrate, Nitrite, Ammonium, and Organic Nitrogen Analysis

Nitrate generally occurs in trace quantities in surface water and domestic wastewater, but achieves levels as high as 30 mg/L in the effluent of nitrifying biological treatment plants[1]. Nitrite, due to its propensity to form ammonia or nitrate, does not have any specific expectant concentration ranges in various water sources. Ammonia concentrations may exist in trace amounts in some natural surface and groundwaters and spiral up to more than 30 mg/L in some wastewaters. Typical organic nitrogen concentrations vary from 0.2 mg/L to more than 20mg/L in raw sewage. The goal here is not to show nitrogen sensitivity but rather accuracy at measuring for different nitrogen forms. The TNM-1 is used in series with the TOC-V to accurately measure for Total Nitrogen compounds in the 100ppm range.

TN Analysis

Solutions of each compound were made so that the nitrogen concentration was fixed at 100ppm. A calibration curve was created using a 100ppm potassium nitrate solution. All compounds were then analyzed as samples against this curve. The 100ppm potassium nitrate solution was used as a control.

Injection Volume: 80㎖L

Calibration Curve

Standard	Formula	Area	Conc. (ppm)
Potassium Nitrate	KNO_3	1771	100

Results

Compound Name	Formula	Theoretical Conc. (ppm)	Actual Conc. (ppm)	% Recovery
Potassium Nitrate	KNO_3	100	97.62	98
Sodium Nitrite	$NaNO_2$	100	96.17	96
Ammonium Nitrate	NH_4NO_3	100	98.20	98
Nicotinic Acid	$C_6H_5NO_2$	100	100.6	101
Urea	CH_4N_2O	100	97.60	98

The recoveries of the various nitrogen compounds were in the range of 96-101%.

Section 3: Simultaneous Carbon and Nitrogen Analysis

In fresh and salt waters, nitrogen is well known as an eutrophying agent. Eutrophication is the process in which nitrogen unintentionally enriches or "fertilizes" carbon-containing compounds found in various types of industrial wastes[2]. Nitrogenous compounds supply nutrients to algae which proliferate so abundantly that a large proportion die for lack of light; their decomposition products deplete the water of its dissolved oxygen causing the death of fish and other marine life. Thus, the ability to accurately monitor both carbon and nitrogen is of great importance. It has been shown that substances containing high ppm (~100ppm) concentrations of total carbon present a negative interference when determining total nitrogen. Thus, the TNM-1 is used in series with the TOC-V_{CSH} analyzer to simultaneously determine total nitrogen and 100 ppm range total organic carbon in less than four minutes.

TC/TN Analysis

Solutions of each compound were made so that the carbon concentration was fixed at 100ppm. Two calibration curves were created, one for carbon and one for nitrogen. The carbon calibration curve was created using a 100ppm potassium hydrogen phthalate (KHP) solution. The nitrogen calibration curve was created using a 100ppm potassium nitrate solution. All compounds were then analyzed as samples against these two curves. The 100ppm KHP and potassium nitrate solutions were used as controls.

Injection volume: 80㎖L

Calibration Curves

Standard	Formula	Area	Conc. (ppm)
Potassium Hydrogen Phthalate (KHP)	$KC_8H_5O_4$	753.7	100
Potassium Nitrate	KNO_3	1874	100

Results

Compound Name	Formula	Theoretical Conc. (ppm)		Actual Conc. (ppm)		% Recovery	
		TC	TN	TC	TN	TC	TN
Potassium Hydrogen Phthalate (KHP)	$KC_8H_5O_4$	100	-	100.2	-	100.2	-
Potassium Nitrate	KNO_3	-	100	-	100.2	-	100
Acetonitrile	C_2H_3N	100	58.6	93.93	61.00	94	104
Caffeine	$C_8H_{10}N_4O_2$	100	58.9	93.64	53.22	94	90
Nicotinic Acid	$C_6H_5NO_2$	100	20	104.20	19.65	104	99
Urea	CH_4N_2O	100	233	97.58	212.4	98	91

The recoveries for the various TC compounds analyzed were in the range of 94-104%. The recoveries for the TN compounds analyzed were in the range of 91-104%.

Conclusion

In Section 1 of this discussion, the TNM-1 achieved a calculated MDL of 11.23 ppb. Meaning that the practical quantitation limit (PQL), which is a factor of approximately 5 times higher than the MDL, was approximately 56ppb. The results of the detection limit study demonstrated that the TNM-1 could accurately and precisely determine nitrogen levels at 56ppb.

In Section 2, various forms of nitrogen were analyzed strictly for accuracy at the 100 ppm range. A 100 ppm Potassium Nitrate solution represented the nitrate form and gave a recovery of 98%. The nitrite form of nitrogen was analyzed and gave a recovery of 96%. A 100 ppm Ammonium Nitrate solution was selected to represent the ammonia form of nitrogen, and the recovery was 98%. Finally, two compounds of 100 ppm nicotinic acid and 100 ppm urea represented the organic nitrogen form of nitrogen. The recoveries were 101% and 98%, respectively.

In Section 3, known mixture compounds of nitrogen and carbon content were analyzed for accuracy. Acetonitrile, caffeine, nicotinic acid, and urea gave excellent total nitrogen and total carbon recoveries. For acetonitrile, the total nitrogen recovery was 104% and the total carbon recovery was 94%. Caffeine gave total nitrogen and total carbon recoveries of 90% and 94%, respectively. Nicotinic Acid gave total nitrogen and total carbon recoveries of 99% and 104%, respectively. Urea gave recoveries of 91% and 98% for total nitrogen and total carbon, respectively. Regardless of the high TC concentrations, the TN concentrations were accurately determined.

In addition to being capable of effectively measuring total nitrogen at trace ppb levels, the Shimadzu TNM-1 coupled with the TOC-V_{CSH} demonstrated the ability to accurately measure all forms of nitrogen compounds. Moreover, the TNM-1/TOC-V_{CSH} combination simultaneously determined total nitrogen and total carbon concentrations with a high degree of accuracy.

References

1. Standard Methods for the Examination of Water and Wastewater, 20th Edition, 4500-N Nitrogen, pages 4-99 and 4-100.

2. Hawley's Condensed Chemical Dictionary, 11th Edition, "Eutrophication", page 502.