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Chemiluminescence Detection for Nitrogen Containing Compounds Compared to Other Approved Techniques

Application Note

Abstract

Nitrogen monitoring is important for process control, regulations, and economic reasons. There are several techniques that can be used to monitor nitrogen, some of which can be time consuming, labor intensive, and may have waste disposal concerns. This study examines using a high temperature combustion (HTC) Total Organic Carbon (TOC)/Total Nitrogen (TN) Analyzer with chemiliumunescence detection (CLD) to monitor nitrogen in samples. By using HTC TN, both TOC and TN can be determined simultaneously, analysis is completed faster, real time analysis can be done, and many matrices can be used. This study will also compare nitrogen analysis with HTC TN to other known nitrogen testing methods.

Torch TOC Combustion Analyzer with TN Module

Introduction

The United States Environmental Protection Agency (USEPA) limits the amount of nitrates (measured as nitrogen) to a maximum contaminant level (MCL) of 10ppmN. Long-term exposure to nitrates greater than the MCL can lead to methemoglobinemia, a blood disorder.[1] .Because of the possible health effects on the population, it is necessary to have accurate means for nitrogen analysis. The current standard method for wastewater nitrogen analysis is the Total Kjeldahl Nitrogen (TKN) wet chemistry method, a labor-intensive analysis.

The TKN method is a wet chemistry analysis which converts nitrogen to ammonia. For analysis using the

TKN, samples are digested in sulfuric acid for one to three hours in the presence of a mercuric oxide catalyst. Not only does the use of sulfuric acid have environmental concerns, problems with digestion can occur if the proper amount of acid is not used. If the amount of acid is too high, nitrogen will be lost and if the amount of acid is too low, digestion of the nitrogen will not go to completion.[2] Another health and safety concern with TKN analysis is with the use of mercuric oxide, which is toxic.

TKN is then determined either by titration of the ammonia formed in the digestion, or through the use of a

spectrophotometer. Using this method to determine nitrogen content in a sample is time consuming and disposal is an environmental and health issues due to the sulfuric acid and mercuric oxide used during analysis.

The use of a high temperature combustion (HTC) Total Organic Carbon (TOC)/Total Nitrogen (TN)

Analyzer offers a safe and effective alternative to the TKN method of nitrogen analysis. Nitrogen analysis by HTC TN allows a 15-20 minute analysis and offers simultaneous TOC analysis. This requires little sample preparation and handling, and because sample volumes are small, less reagents are used for analysis.

For nitrogen analysis using HTC TOC/TN, the sample is injected into the combustion furnace and the nitrogen in the sample is converted to nitric oxide (NO). At the same time, the carbon present in the sample is converted to CO_2. The carrier gas sweeps the sample into the nondispersive infrared detector (NDIR) where the CO_2 concentration is measured. From the NDIR, the sample gas is swept to the nitrogen module where NO is mixed with ozone (O3). Excited state nitrogen dioxide (NO2*) is formed and when NO2* relaxes to its ground state (NO2), the extra energy is given of as light (hv). This reaction is illustrated in Figure 1. A chemiliuminescence detector with a photomultiplier tube is used to convert the light signal to an electronic signal for quantitation.

$$NO + O_3 \longrightarrow NO_2^*$$
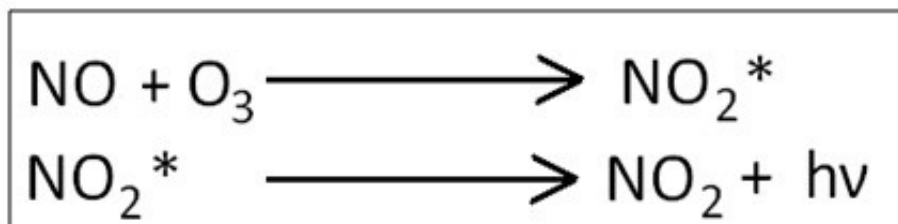$$NO_2^* \longrightarrow NO_2 + hv$$

Figure 1: Analysis of Nitrogen using HTC TOC/TN

This study will employ a Teledyne Tekmar Torch Combustion TOC Analyzer with TN Module to demonstrate the suitability of HTC TOC/TN analysis for nitrogen analysis.

Experimental-Instrument Conditions

For this study the default TN Wastewater Method was used for analysis and has an optimal range of 1-20ppmN. Table 1 outlines the method parameters.

Parameters		Advanced Parameters	
Variable	Value	Variable	Value
Sample Volume	0.10mL	Needle Rinse Volume	2.5mL
Water Chase Volume	1.50mL	Vial Prime Volume	2.0mL
Dilution	1:1	Baseline Stabilize Time	0.25min
Number of Injection Line Rinses	1	Detector Pressure Flow (mL/min)	175
Injection Line Rinse volume	0.5mL	Syringe Speed Waste	10
Carrier Gas Delay Time	0.40min	Syringe Speed DI Water	7
Detector Sweep Flow (mL/min)	500	NDIR Pressurization	50psig
Furnace Sweep Time	1.00min	Syringe Speed Sample Dispense	7
System Flow (mL/min)	200	Syringe Speed Sample Aspirate	7
		Syringe Speed IC Dispense	7
		Syringe Speed IC Aspirate	5
		NDIR Pressure Stabilize	0.60min
		Syringe Speed Furnace Dispense	3
		Syringe Speed Furnace Aspirate	5
		Furnace Temperature	750 °C
		TN Expansion Stabilize Time	0.25min
		TN Detector Sweep Time	1.25min

Table 1: Torch TN Wastewater Method Parameters

Sample Preparation

For analysis using a high temperature combustion (HTC) Total Organic Carbon (TOC)/Total Nitrogen (TN) Analyzer, a five-point curve was made from a 20ppmN nitrogen solution from 1.00ppmN - 20.0ppmN using the autocalibration feature as seen in Figure 2. After analyzing the nitrogen containing samples, check standards, standards at known concentrations, were ran to validate the curve.

Stock solutions of several nitrogen containing compounds were prepared at 1000ppm Nitrogen (ppmN) in a 1L volumetric flask as shown in Table 2. From the stock solutions, 5ppmN solutions were made to verify that the analyzer was able to process the compounds and also to calculate percent yield and percent relative standard deviation (%RSD). Blanks followed each standard to asses cross contamination.

Compound	Molecular Weight	Percent Nitrogen (%)	g material for 1000ppmN
Dicyanodiamide	84.08	66.65	1.50
Glutamic Acid	147.13	9.52	10.50
Glycine	75.07	18.66	5.36
Isonicotinic Acid	123.11	11.38	8.79
Nicotinic Acid	123.11	11.38	8.79
p-Nitrophenol	139.11	10.07	9.93
Thiourea	76.12	36.81	2.72

Table 2: % Nitrogen Values and Sample Dilutions of the Nitrogen-Containing Compounds

Results

Using the autodilution feature on the Torch with TN module, a curve was prepared using a 20ppm nitrates as nitrogen (N) standard. Figure 2 illustrates the result of the curve from 1.0 – 20ppmN with the default TN Wastewater Method. Tables 3-4, shows the calibration and check standard data.
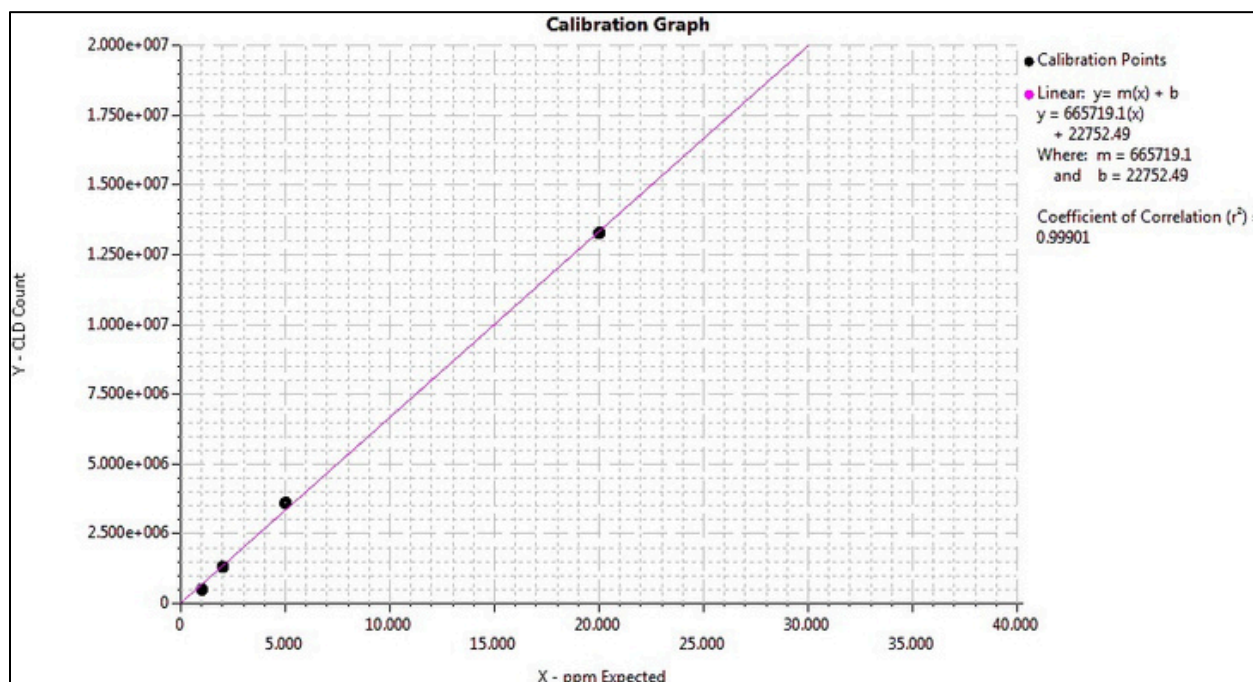

Figure 2: TN Calibration curve on Torch used to analyze check standards and samples.
TN Calibration curve data: y = 665719.1(x) +22752.49, R2=0.99901

Pos	Analysis Type	Concentration (ppmN)	Stock Conc. (ppmN)	Dil.	Sample ID	Results (Cld)	Std. Dev. (Cld)	RSD
A	TN	1.000	20.0	1:20	[TN] TN [1.000]	726020	4795	0.66%
A	TN	2.000	20.0	1:10	[TN] TN [2.000]	1323510	36801	2.78%
A	TN	5.000	20.0	1:4	[TN] TN [5.000]	3611869	106805	2.96%
A	TN	10.000	20.0	1:2	[TN] TN [10.000]	7614377	71927	0.94%
A	TN	20.000	20.0	1:1	[TN] TN [20.000]	14202898	947241	6.67%

Table 3: Torch TN Calibration Data using Default TN Wastewater Method

Pos	BAT	Concentration (ppmN)	Dil.	Sample ID	Min / Max (% dev)	Result	Std. Dev.	RSD
A	TN	1.000	1:20	[TN] TN [1.000ppm]	0.9000 / 1.1000 (90% / 110%)	1.0519 ppmN (PASS)	0.0613 ppmN	5.83%
A	TN	4.000	1:5	[TN] TN [4.000ppm]	3.6000 / 4.4000 (90% / 110%)	4.0119 ppmN (PASS)	0.2191 ppmN	5.46%
A	TN	6.667	1:3	[TN] TN [6.667ppm]	6.0000 / 7.333 (90% / 110%)	7.0230 ppmN (PASS)	0.2100 ppmN	2.99%

Table 4: TN Check Standards Data using Default TN Wastewater Method

Results

Solutions of the nitrogen-containing compounds were prepared at known concentrations and were analyzed using the HTC TOC/TN Analyzer. The data from the HTC TOC/TN was then compared to the theoretical concentrations to determine the percent yield and percent relative standard deviation (%RSD). Table 5 illustrates the results. Each analysis was done in triplicate.

Compound	Theoretical Concentration	Actual Concentration	%Recovery	%RSD
Dicyanodiamide	5.00	4.7290	94.50	4.04
Glutamic Acid	10.00	9.3160	93.16	3.81
Glycine	5.00	4.6703	93.41	3.19
Isonicotinic Acid	5.00	5.0028	100.06	2.07
Nicotinic Acid p-	2.50	2.3114	92.46	3.07
Nitrophenol	5.00	4.6810	93.62	4.07
Thiourea	5.00	4.4498	89.00	2.57

Table 5: Summary of Results for Nitrogen-Containing Compounds

Conclusions

The Teledyne Tekmar Torch TOC Combustion /TN Analyzer used in this study proves to be a fast and efficient alternative to the wet chemistry TKN method for monitoring nitrogen. As seen in Table 3, all nitrogen compounds used in this study were able to be recovered with excellent precision illustrated by low %RSDs. Analysis time for each compound, run in triplicate, was approximately 20 minutes, a fraction of the time required by Total Kjeldahl Nitrogen (TKN) testing. Using HTC TOC/TN also eliminates the environmental concerns that accompany the use of sulfuric acid and mercuric oxide in TKN analysis. Complete automation requires less sample handling and ease of use, while small sample volumes reduce the amount of reagent used. The Torch TOC/TN Analyzer is an alternative to the TKN method that is fast and reliable.

References

1. US EPA Drinking Water Contaminants: http://water.epa.gov/drink/contaminants/index.cfm
2. Standard Methods for the Examination of Water and Wastewaster, 20th Edition, A.D.Eaton, L.S.Clesceri and A.E. Greenberg., APHA/AWWA/WEF, Washingoton, DC, 2002.