Measuring Ammonia in Kjeldahl Digestates from Municipal Wastewater Influent and Effluent Samples Using the Timberline TL 2800 Ammonia Analyzer

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INTRODUCTION

Kjeldahl Digestion, also called Total Kjeldahl Nitrogen or TKN, is considered by many to be the one of the oldest analytical procedures still in use. The basic principle of the digestion has remained essentially the same since its introduction. The purpose of the digestion procedure is for determining the organic nitrogen (N) content by oxidation to ammonium ion (NH_4^{+1}). Kjeldahl digestion, named for its inventor, Johan Kjeldahl, was first described in 1883 at a meeting of the Danish Chemical Society and subsequently published in *Zeitschrifte fur Analytische Chemie* the same year.

Johan Kjeldahl's original technique was to heat the sample in a solution of concentrated fuming sulfuric acid and potassium permanganate ($KMnO_4$) to near its boiling point of 330 ^{0}C (1). He also added phosphoric anhydride to speed up the digestion, probably because the phosphoric anhydride allowed a higher boiling point. Since then a variety of metal catalysts, including mercury, copper, iron and titanium dioxide, have been employed to reduce the digestion time and improve the degree of digestion. In the current Standard Methods procedure, method 4500-Norg B, the digest solution uses concentrated sulfuric acid, copper sulfate as a catalyst, and potassium sulfate to provide a higher boiling point. Typical digestion times are 30 minutes to 120 minutes depending on the sample being digested. It is important to note that nitrate and nitrite are not converted to ammonia in a TKN digest; in fact higher concentrations of nitrate and nitrite can interfere with complete digestion of organic nitrogen.

Since the result of digestion is ammonium ion and many samples contain ammonium ion prior to digestion, it is often necessary to measure ammonium before and after digestion. A number of different analytical methods have been used to quantitate ammonia before and after digestion. One of the first required neutralizing the digestion solution with base, converting ammonium to ammonia, followed by distillation of the ammonia into a weakly acidic solution and acid/base titration to determine the ammonia concentration present. Other methods include KI/KIO_3 reaction and titration of the liberated iodine, colorimetric methods (for example phenol-hypochlorite, sodium salicylate-chlorine with nitroprusside or Nessler's reagent), and membrane diffusion/conductivity. Some methods require ammonium distillation after digestion; some only require dilution of the digestate.

ANALYTICAL METHOD

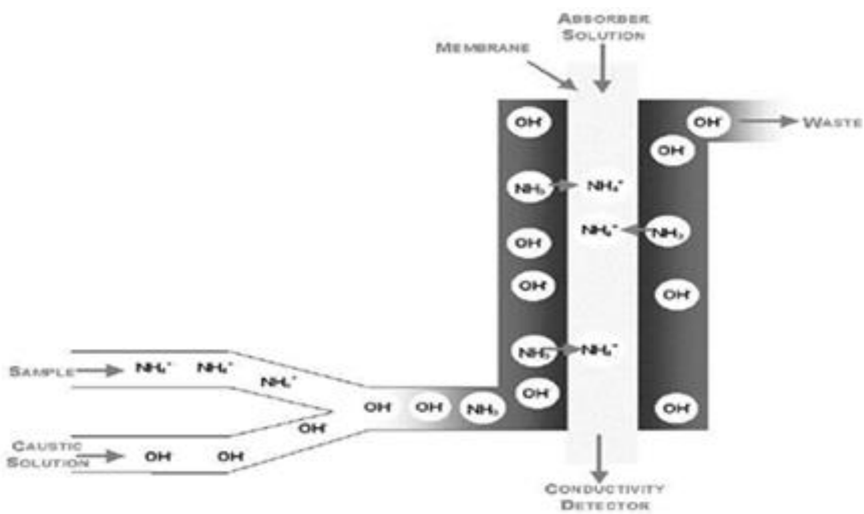
In this paper we will present the analysis for ammonia in a Kjeldahl digestate of influent and effluent samples from the local municipal water treatment plant in Boulder, CO. All samples were digested at the Boulder Water Quality and Environmental Services Lab. Samples are analyzed for ammonia at the Boulder Water Quality and Environmental Services Lab as well as at the Timberline Lab, each using a Timberline TL-2800 Ammonia/Nitrate Analyzer, . Both labs followed the EPA Method "Timberline-001" which covers the analysis of ammonia in Kjeldahl digestates. The method is also cited in Standard Methods in method 4500-N D. The Timberline method for ammonia uses flow injection with membrane diffusion and conductivity detection. This method does not require distillation after digestion and requires only a simple 1:1 dilution with DI water of the digestate sample. The analysis time is approximately 2 minutes. Samples are measured for residual ammonia prior to digestion, then digested following Standard Methods method 4500-Norg B. Post digestion samples are analyzed using the Timberline Ammonia/Nitrate Analyzer which uses membrane diffusion of dissolved ammonia gas from a basic sample stream into a slightly acidified buffer stream, where the dissolved ammonia gas is converted to aqueous ammonium ion, followed by conductivity detection. Specifically, the on-board peristaltic pump directs sample and caustic streams together to mix. The resulting solution has a pH sufficiently high (pH 11-13) to convert all the ammonium ions present in the sample to dissolved ammonia gas. Referring to Figure 1, this basic solution containing the dissolved ammonia gas then flows to the outside of the diffusion membrane tube. The peristaltic pump separately directs a dilute boric acid solution, pH 6.5, to the inside of the diffusion membrane tube. The sample/caustic solution flows past the outside of the membrane that is permeable to gases but not to liquids or dissolved ionic species. The dissolved ammonia gas in the sample/caustic mixture diffuses across the membrane from the high pH caustic solution to the acidic boric acid solution on the inside of the membrane where ammonia gas is re-dissolved in the acidic buffer and converted back to ammonium ions according to Equation 1 .

Equation 1

$$NH_4^{+1}\,(aq) + OH^{-1}\,(aq) \rightarrow NH_3(g) + H_2O\,(liq) \xrightarrow{\text{Membrane}} NH_3(g) + H_3BO_3 \rightarrow NH_4^{+1}(aq) + H_2BO_3^{-1}(aq)$$

Finally, the boric acid solution, containing ammonium ions from the sample, flows through the conductivity cell. The ammonium ions are detected in the cell as an increase in conductivity as compared to the lower conductivity of the boric acid solution background.

Figure 1



SAMPLE ANALYSIS PROCEDURE

Municipal Plant Influent and Effluent samples were collected and digested using the Standard Methods method 4500-N_{org} B. Four sets of samples, Influent pre and post TKN digest, and Effluent pre and post TKN digest were analyzed at Boulder Water Quality and Environmental Services Lab and at Timberline Lab. Pre-digestion samples were analyzed with the typical 5%w/w NaOH (1.9N) as the caustic concentration. Post digestion samples were analyzed with 15% w/w NaOH (5.67N) concentration as the caustic stream. The higher NaOH concentration combined with a 1:1 dilution with DI water is required to completely neutralize the high concentration of sulfuric acid (approximately 2.5N) in the post digestate sample solution and allow for excess NaOH to convert all the ammonium to ammonia in the sample stream. See Equation 2. (Note: Standard Methods Method 4500-N_{org} B specifies 268 mLs concentrated H_2SO_4 diluted to 2L in the TKN digestate)

Equation 2

a.) (268 mLs conc H_2SO_4(1L/1000mL)(36.8 moles H_30^{+1}/L))/(2L) = 4.93N H_30^{+1} (1:1 dilution) = 2.47N H_30^{+1}

b.) 5.67N NaOH - 2.47N H_30^+ = **3.2N NaOH excess caustic**

Samples were analyzed after instrument calibration. At the Timberline Lab, the instrument was calibrated from 2.5 ppm to 50.0 ppm N as ammonia plus a DI water blank and for Influent samples, and from 0.05 ppm to 2.5 ppm N as ammonia plus a DI water blank for Effluent samples. The calibration R^2 was 0.9999 for both calibrations using second order fit. A similar set of calibrations was used at the Boulder Water Quality and Environmental Services Lab. Regular check samples and spike samples were run at both labs to ensure consistent instrument performance.

DATA AND ANALYSIS

Effluent samples were digested by Boulder Water Quality and Environmental Services Lab and analyzed for ammonia by both labs on 11/14/18. Influent samples were similarly digested by Boulder Water Quality and Environmental Services Lab and analyzed for ammonia by both labs on 11/16/18. Effluent pre-digest sample ammonia concentrations ranged from less than the limit of detection (LOD) to 0.1 ppm-N as ammonia. The Effluent post-digest sample ammonia concentrations range from approximately 0.5 ppm-N as ammonia to approximately 2.0 ppm-N as ammonia.

Influent pre-digest sample ammonia concentrations ranged from LOD to 31 ppm-N as ammonia. Influent post-digest sample ammonia concentrations range from less than LOD to 50 ppm-N as ammonia.. Overall the accuracy of spiked samples and check standards recovery ranged from 93.9% to 107% and averaged 101% with a standard deviation of 5.2 and an RSD of 5.1%.

The data generated by each lab correlated well, as shown by the Graph below. The slope of the trendline is 0.961, indicating the Boulder Water Quality and Environmental Services Lab data is generally slightly lower than the Timberline Lab data but only by 4% on average. A slope of nearly 1.00 combined with a correlation coefficient of 0.998, demonstrates the correlation between labs using the Timberline method for ammonia in TKN samples is excellent.

CONCLUSION

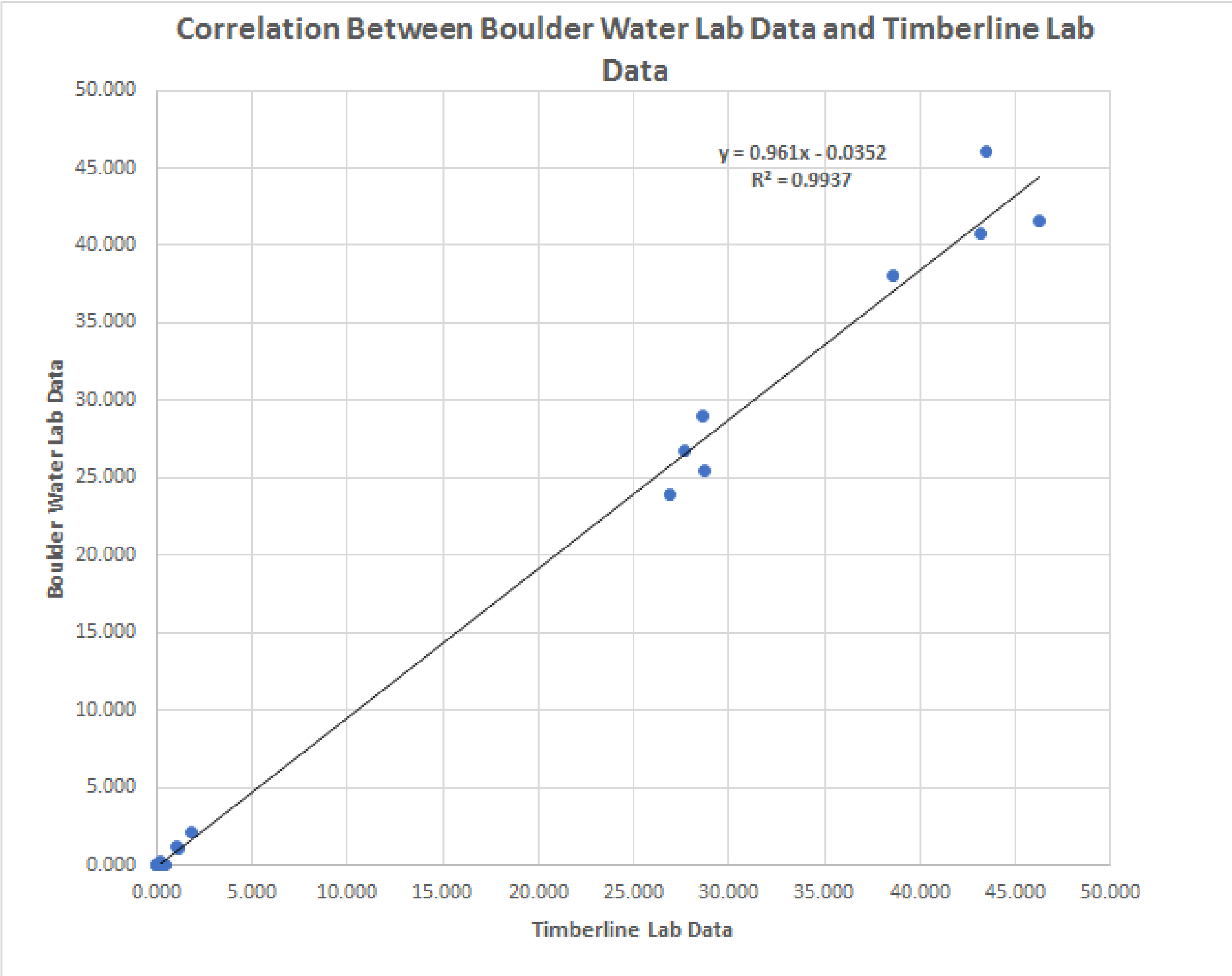
As expected, the Influent samples showed much higher ammonia concentrations than the Effluent samples, indicating the water treatment process is reducing the ammonia concentration in the effluent by as much as two orders of magnitude and is doing its job. Timberline Lab data displayed excellent recovery for check standards and spiked samples. Both labs reported less than LOD for four samples. The fact that the recovery of check standards and spiked samples, as well as the correlation between the two data sets, were very good for both the Influent and Effluent post-digest samples demonstrates that the Timberline Membrane/Conductivity method for measuring ammonia in post TKN digest samples with a simple 1:1 DI water dilution is a fast, easy, and reliable way to measure ammonia in TKN digest samples, eliminating the need for digest sample distillation prior to analysis.

Effluent - Pre-Digest 11/14/18			
Sample Name	**Timberline NH_3 Conc.**	**Boulder Water NH_3 Conc.**	**% Recovery**
1.0 ppm chk std	1.00		100.
BC61	0.102	0.120	
BCADC	0.030	0.040	
CCKEN	<LOD	<LOD	
Effluent 1113	0.050	0.060	
1.0 ppm chk std	0.990		99.0
BCCU	<LOD	<LOD	
BCCU spike 2.0 ppm	2.20		101
BCCU spike 2.0 ppm dup	2.22		102
1.0 ppm drift std	1.02		101

Effluent - Post Digest 11/14/18			
Sample Name	**Timberline NH_3 Conc.**	**Boulder Water NH_3 Conc**	**% Recovery**
2.50 chk std	2.50		100.
DI Blank	0.010		
TKN Blank	0.028	0.060	
1.0 ppm chk std	1.01		101
BC61 digest	0.477	0.510	
BCADC digest	1.14	1.11	
CCKEN digest	1.06	1.19	
Effluent 1113 digest	1.81	2.15	
BCCU digest	0.209	0.220	
BCCU digest spike 2.0 ppm	2.08		95.5
BCCU digest spike 2.0 ppm dup.	2.10		96.2
1.0 ppm drift std	0.972		97.2

Influent - Pre Digest 11/16/18			
Sample Name	**Timberline NH_3 Conc.**	**Boulder Water NH_3 Conc.**	**% Recovery**
10 ppm chk std	9.95		99.5
ABI 1031	28.6	29.0	
Inf 1031	27.7	26.7	
Inf 1113	26.9	23.9	
Inf 1106	28.8	25.4	
LEX 1023	<LOD	<LOD	
10 ppm chk std	10.04		100.
ABI 1031 + 10 ppm	43.8		105
ABI 1031 +10 ppm dup.	44.1		106
25 ppm drift std	25.4		102

Influent - Post Digest 11/16/18			
Sample Name	**Timberline NH_3 Conc.**	**Boulder Water NH_3 Conc.**	**% Recovery**
50 ppm N chk Std	50.8		102
DI Blank	<LOD		
TKN Blank	<LOD	0.060	
10 ppm chk std	10.7		107
ABI 1031 digest	38.6	38.0	
Inf 1031 digest	43.5	46.1	
Inf 1113 digest	43.2	40.8	
Inf 1106 digest	46.2	41.6	
Lex 1023 digest	<LOD	<LOD	
ABI 1031 digest + 5.0 ppm	47.6		94.8
ABI 1031 digest + 5.0 ppm dup.	47.1		93.9
25 ppm drift std	26.4		106


Correlation Between Boulder Water Lab Data and Timberline Lab Data
y = 0.961x - 0.0352
R² = 0.9937
Boulder Water Lab Data
Timberline Lab Data
0.000
5.000
10.000
15.000
20.000
25.000
30.000
35.000
40.000
45.000
50.000