

# Evaluation of the need for preliminary distillation prior to analysis of ammonia using Hach method 10205 (TNTplus™ 830, 831, 832)

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## Hach Applications Laboratory Report

### Background:

Hach's TNTplus™ ammonia reagents can be used for NPDES reporting under USEPA method 350.1. Some Wisconsin laboratories would like to use the TNTplus ammonia reagents for wastewater discharge reporting. However, section NR219.04 Wis. Admin. Code requires that a manual distillation be performed unless comparability data on representative effluent samples show that preliminary distillation is not necessary.

### Project Overview:

A number of Wisconsin laboratories have expressed interest in using Hach method 10205 due to the ease of use and the potential cost advantages the method offers. These laboratories must have data on file to show that preliminary distillation step is not necessary. Most of the registered and smaller certified labs wish to use Hach method 10205, but do not have access to the equipment needed to generate the data to show that distillation is not required.

### Experimental Design:

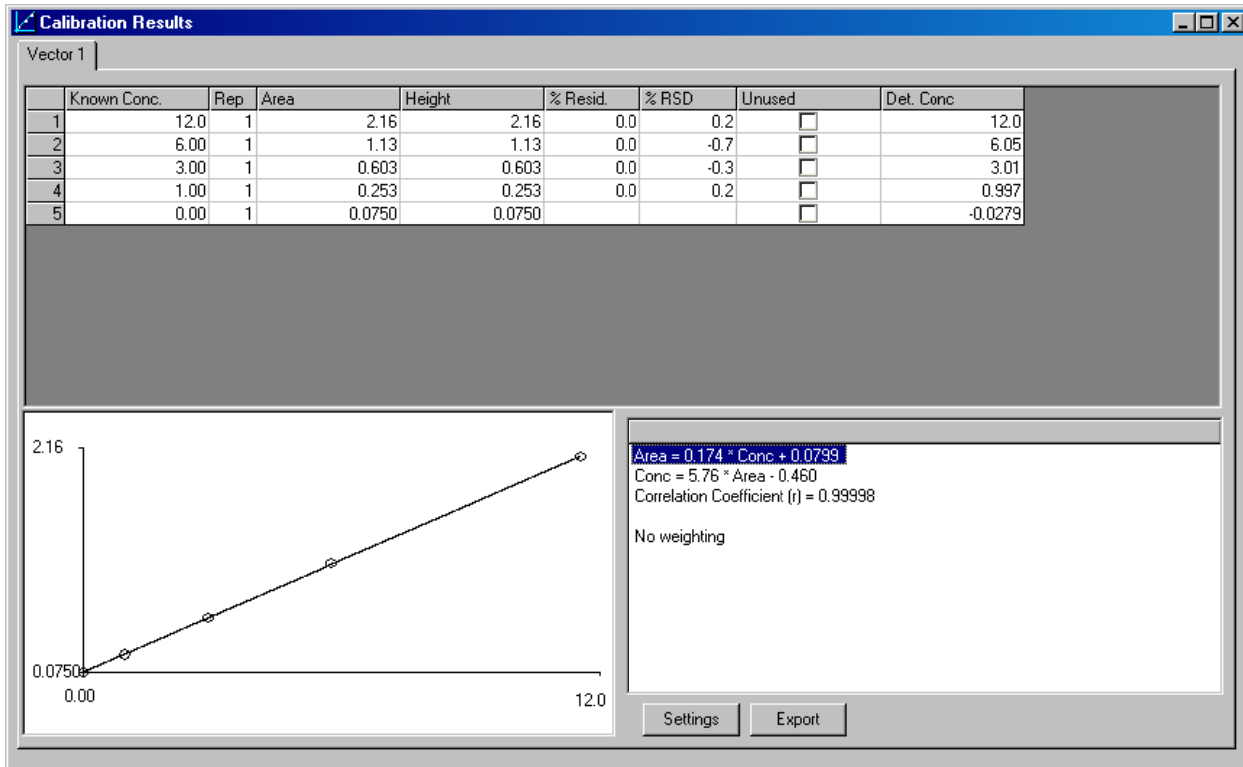
The Wisconsin Department of Natural Resources (DNR) proposed that Hach conduct a study to determine whether the preliminary distillation step is required prior to the analysis of ammonia using Hach method 10205. They proposed Hach analyze 5 different effluent samples that are representative of the treatment process used in Wisconsin. They also proposed Hach analyze a laboratory control (LSC) and reagent blank along with the 5 effluents. Samples selected and their treatment process are as follows:

- 1) Ladysmith, WI (Aerated Lagoon (AL), 0.8 MGD)
- 2) Cambridge-Oakland (Suspended Media-SBR, 0.6 MGD)
- 3) Beaver Dam (Suspended Media-Activated Sludge, 3.5 MGD)
- 4) Broadhead (Suspended Media-Oxidation Ditch, 0.29 MGD)
- 5) Whitewater (Fixed Media-RBC, 1.6 MGD)
- 6) 5 mg/L NH<sub>3</sub>-N Laboratory Standard

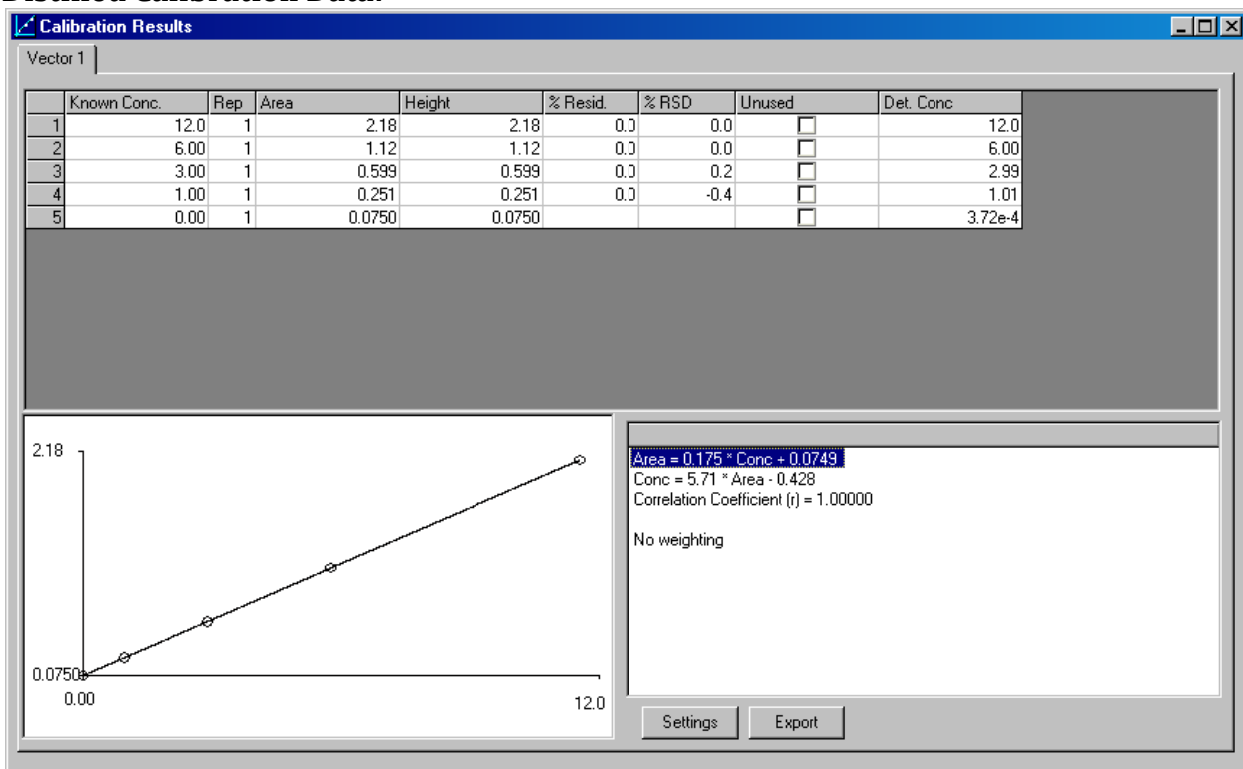
The samples were analyzed following Hach method 10205, with reagent kit TNT831 that has a concentration range of 1-14 mg N/L. The samples, QC and calibration standards were distilled following Lachat Instruments MicroDist™ procedure for Ammonia-1: Phenate and ISE method, the MicroDist™ distillation procedure is equivalent to Standard Methods method 4500-NH<sub>3</sub>-B, 20<sup>th</sup> edition.

# Results:

## Non-Distilled Calibration Data:



## Distilled Calibration Data:



The calibration series was 1, 3, 6, and 12 mg/L NH<sub>3</sub>-N, including a reagent blank. The standards for the distilled calibration were carried through the same distillation as the samples, LCS and reagent blanks.

The samples from Broadhead, Whitewater, and Cambridge had NH<sub>3</sub> concentrations that were below the optimal lower level of 1 mg N/L for TNT831 method (0.276, 0.141, 0.211 mg NH<sub>3</sub>-N/L, respectively). These three samples were spiked at a concentration of 5 mg/L NH<sub>3</sub>-N.

### Non-distilled Samples

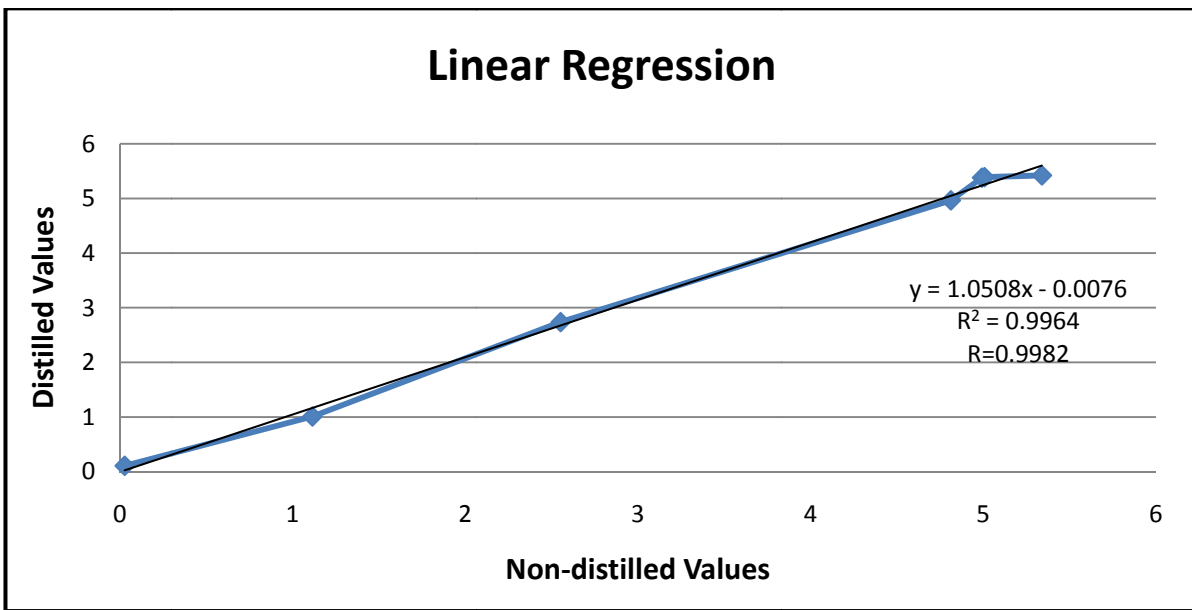
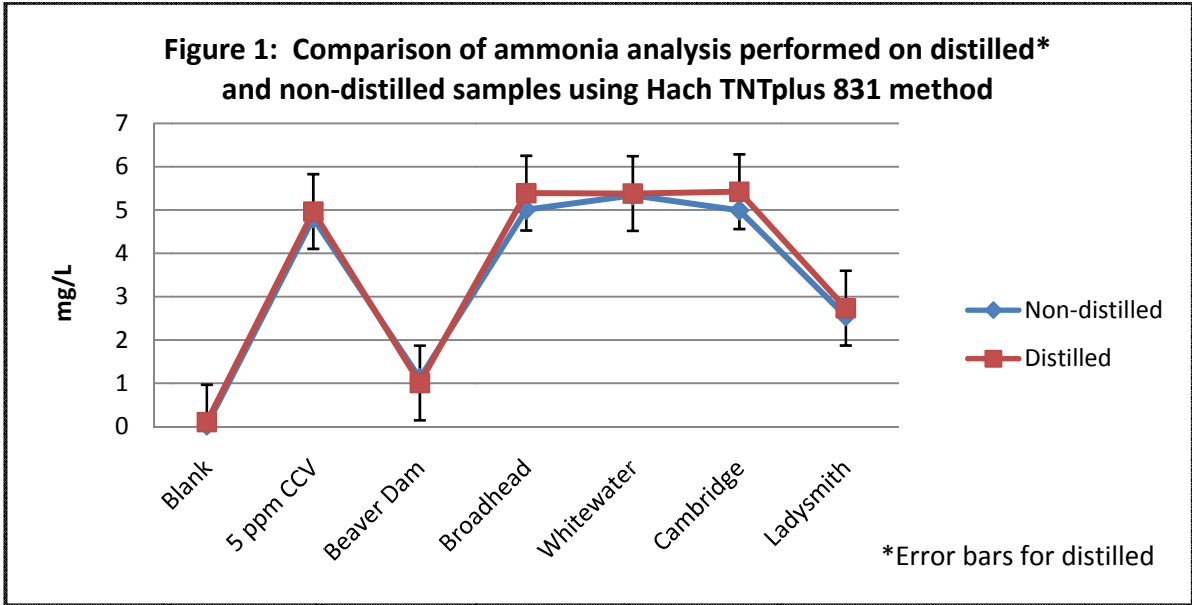
Sample	Blank	5 mg/L LCS	Beaver Dam	Broadhead	Whitewater	Cambridge	Ladysmith
Rep 1	0.03	4.86	1.10	4.97	5.39	5.05	2.56
Rep 2	0.019	4.80	1.11	5.02	5.36	4.89	2.52
Rep 3	0.035	4.78	1.12	5.06	5.26	4.97	2.54
Rep 4	0.027	4.81	1.13	4.98	5.35	5.06	2.59
AVG	0.028	4.81	1.12	5.01	5.34	4.99	2.55
STDEV	0.007	0.034	0.013	0.041	0.056	0.079	0.030
% RSD	24.15	0.71	1.16	0.82	1.05	1.59	1.17
95% confidence	0.007	0.033	0.013	0.040	0.055	0.078	0.029
% REC	-	96.25	-	-	-	-	-

### Distilled Samples

Sample	Blank	5 mg/L LCS	Beaver Dam	Broadhead	Whitewater	Cambridge	Ladysmith
Rep 1	0.11	5.03	1.01	5.20	5.31	5.44	2.69
Rep 2	0.11	4.97	1.02	5.37	5.33	5.48	2.74
Rep 3	0.10	4.94	1.01	5.49	5.55	5.35	2.75
Rep 4	0.10	4.92	0.99	5.50	5.33	5.42	2.76
AVG	0.105	4.96	1.01	5.39	5.38	5.42	2.74
STDEV	0.006	0.048	0.013	0.140	0.114	0.054	0.031
% RSD	5.50	0.97	1.25	2.59	2.11	1.00	1.14
95% confidence	0.006	0.047	0.012	0.137	0.111	0.053	0.030
% REC	-	99.3	-	-	-	-	-

**Percent difference between non-distilled and distilled samples**

Sample	Blank	5 mg/L LCS	Beaver Dam	Broadhead	Whitewater	Cambridge	Ladysmith
% Diff	26.43	3.07	9.64	7.10	0.74	7.93	6.67



**Discussion:**

The results from this study displayed that these samples didn't show an appreciable difference between the non-distilled and distilled samples. The highest percent difference between the non-distilled and distilled sample was 9.64% for Beaver Dam (excluding the reagent blank). The % difference slightly was higher than the other samples tested due to the low sample concentration; the distilled value was 1.01 and the non-distilled was 1.12 mg/L. However, there was little actual difference between these two values.

A paired Student's t-test was performed on the differences between the two methods. The null hypothesis for this test is that the difference is equal to zero (i.e., results are comparable). The mean difference for the 7 pairs was -0.165 (Non-distilled – Distilled) with a 95% confidence interval for the mean difference of -0.341 to 0.010. The probability value was 0.06, indicating that the mean difference was not significantly different from zero.

All of the data quality objectives for the study plan were met.

- 1) Verify the calibration curve has a correlation coefficient is  $\geq 0.995$ : Non-distilled curve = 0.99998, distilled curve = 1.0000
- 2) Verify the method blanks are similar or better for the direct analysis as compared to those analyzed with preliminary distillation: Non-distilled blank = 0.028 mg/L and distilled blank = 0.11 mg/L.
- 3) Assess precision expressed as percent standard deviation (%RSD) and verify that it is similar or better for the direct analysis compared to those analyzed with preliminary distillation: The %RSDs for both sets of data are low, the highest is 2.59%, excluding the blanks.
- 4) Confirm the mean of the LCS results are within  $\pm 10\%$  (90 – 110% recovery) of the true value for both the direct and preliminary distillation: Non-distilled = 96.25% recovery, distilled = 99.30%.
- 5) Compare the means of the direct and preliminary distillation samples using a scatter plot. The correlation coefficient should be  $\geq 0.995$ : the  $R = 0.998$  ( $R^2 = 0.996$ ).
- 6) Perform a test of significance to determine whether the means of the replicates are significantly different at the 5% probability level using a paired Student t-test of some other test of significance: The probability value was 0.06, indicating that the mean difference was not significantly different from zero.

## Conclusion:

The data from this study show that the preliminary distillation of domestic wastewater effluent samples from Wisconsin is not required prior to the analysis of ammonia using Hach method 10205.

## Acknowledgements:

Samples provided by the following individuals: Rod Minnema, Beaver Dam, WI; Rich Vogel, Broadhead, WI; Steve Sainsbury and Kevin Taylor, Cambridge, WI; Matt Boehmer, Ladysmith, WI; and Melody Wunderlin, Whitewater, WI. All analyses were performed by Scott Tucker, Hach Company, 5600 Lindbergh Drive, Loveland, CO 80539. Report was prepared by Scott Tucker, with the assistance of Jim Burke, Hach Company.