Validation of a Green Chemistry Method for the Determination of Total Nitrogen and Total Phosphorus Levels in Pulp and Paper Mill Wastewaters: NCASI Method TNTP W10900

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Abstract

Many states already have or are developing nutrient criteria based on total nitrogen (TN) and total phosphorus (TP) measurements. The current approach for determining TN is to measure total Kjeldahl nitrogen (TKN) and nitrate/nitrite and add them to obtain TN. To provide a "green chemistry" approach that will improve accuracy, precision, and sensitivity when assessing TN and TP in pulp and paper mill wastewaters, concentrations and QA/QC results obtained using NCASI TNTP-W10900 (an alkaline to acidic persulfate digestion) were compared to EPA monitoring methods (EPA 365.1 and 365.4 for TP; EPA 351.2 for TKN). In contrast to TKN methods, this digestion is conducted in sealed vials, no fumes are released, lower method detection limits are obtained, waste is non-hazardous, simultaneous digestion for TP and TN occurs, and costs are reduced.

TP and TN concentrations obtained using NCASI TNTP-W10900 are comparable to EPA's monitoring methods. Reproducibility for the TP methods yielded relative percent differences (RPDs) for replicate samples ranging from <0.01 to 14.3% except for EPA 365.4 using copper sulfate ($CuSO_4$) (44 and 50% RPDs). Precision for matrix spikes and matrix spike duplicates ranged from <0.1 to 18.6% RPD for all TP methods with the exception of two samples analyzed using EPA 365.4 ($CuSO_4$) that yielded 47.1 and 96.1% RPDs. TN assessments of precision yielded RPDs ranging from 0.20 to 15.3% except for one sample in which EPA 351.2 ($CuSO_4$) yielded 32.4% RPD. NCASI TNTP-W10900 matrix spike recoveries for TP and TN were within EPA standardized acceptance criteria. Similar results were observed for continuing and independent calibration verifications and independent recovery (digestion) spikes in the TP and TN methods.

NCASI Method TNTP-W10900 provided results comparable to EPA methods for TP and TN in 16 matrices and QA/QC results indicated better accuracy and precision than the reference methods, thus providing a method for simultaneous digestion of TN and TP in pulp and paper mill wastewaters that reduces costs, eliminates hazardous waste, provides greater sensitivity for TN measurements, and exhibits excellent precision and accuracy.

Study Design

A single laboratory method comparison study was conducted at the NCASI West Coast Regional Center (WCRC) laboratory by analyzing samples for TN and TP using the methods specified in Table 1. The sampling and analysis scheme encompassed the requirements of EPA's ATP process (USEPA 1999), along with additional samples to address the use of independent reference standards (IRS) as presented in Table 2 (NCASI 2010; USEPA 1974, 1978, 1993a,b).

Table 1. TKN, TN, TP, and Nitrate Methods Investigated

Method	Analytes	Digestion	Species Detected
NCASI TNTP-W10900	TN and TP	Alkaline to acidic persulfate	Orthophosphate and nitrate
EPA 365.4	TP	Kjeldahl	Orthophosphate
EPA 365.1	TP	Acidic persulfate	Orthophosphate
EPA 351.2	TKN	Kjeldahl	Ammonia
NCASI LTRWS TNTP	TN and TP	Alkaline to acidic persulfate	Orthophosphate and nitrate
EPA 353.2	Nitrate/nitrite	None	Nitrate/nitrite

Table 2. Overview of Study Plan and Analysis Scheme

Analyses	Sample Count	Frequency
Calibration blank	1	daily with each sample set
Calibration curve	5	daily with each sample set
Method blank (MB)	2	twice daily with each sample set
Continuing calibration verification (CCV)	2 to 5	one every ten samples
Independent calibration verification (ICV)	3	one every ten samples
Sample sets (duplicate or triplicate)	16	divided into three sample sets
MS/MSD pairs	>5	minimum of five pairs per study
Independent reference spiked sample	>2	minimum of two per study
Independent reference standard (IRS)	2	one every ten samples

NCASI TNTP-W10900 utilizes a modified digestion based on an oxidizing reagent composed of 2% potassium persulfate ($K_2S_2O_8$) in 0.12 M sodium hydroxide (NaOH) at a pressure of 15 psi for 30 minutes to convert nitrogen forms to nitrate-nitrogen and phosphorus forms to orthophosphate. This mix of reagents results in a gradual decrease in pH from ~12 to 2 during digestion (Ebina, Tsutsui, and Shirai 1983; Hosomi and Sudo

Study Design (continued)

1986). Under the initially alkaline conditions, dissolved and suspended nitrogen are oxidized to nitrate. As the digestion proceeds, bisulfate ions resulting from thermal decomposition of persulfate neutralize and acidify the reaction mixture until the solution approaches pH 2. Under the acidic digestion conditions, dissolved and organic phosphorus are hydrolyzed to orthophosphate. Following digestion the orthophosphate is measured using a modification of EPA 365.1 via semi-automated colorimetry in which ammonium molybdate and antimony potassium tartrate react in an acid medium to form an intensely blue complex that is measured colorimetrically using an autoanalyzer. TN as nitrate is measured using EPA 353.2.

NCASI LTRWS TNTP is based on the same chemistry as NCASI TNTP-W10900, but uses a slightly less basic solution of sodium hydroxide (0.08 M) during initial digestion.

EPA 351.2 renders organic nitrogen forms to ammonia-nitrogen, referred to as TKN. EPA 365.4 converts organic phosphorus and other phosphorus forms to orthophosphate. These semi micro Kjeldahl block digestions decompose samples in sulfuric acid using mercury sulfate or copper sulfate as the catalyst. Digestion proceeds for 2.5 hours in open 100 mL tubes at high temperatures (160 to 380°C). To assess the impact of the catalyst used to conduct Kjeldahl digestions, each sample was digested using both mercury sulfate and copper sulfate. EPA 351.2 does not include nitrogen in the form of nitrate and nitrite and therefore does not represent the TN in a sample. Two analyses are required to obtain a value for TN: one to determine the nitrate concentration and another to determine the TKN concentration (as ammonia). These values are added together to determine TN. In this study, once the digestates were prepared orthophosphate was analyzed using the same modification of EPA 365.1 discussed under NCASI TNTP-W10900. The resulting ammonia was analyzed using EPA 351.2 via a segmented flow automated colorimetric procedure in which an emerald green color is formed by the reaction of ammonia, sodium salicylate, sodium nitroprusside, and hypochlorite in a buffered alkaline medium at pH 12.5 to 13.5.

EPA 365.1 utilizes an acidic persulfate solution to convert all forms of phosphorus to orthophosphate. Orthophosphate is measured colorimetrically as an antimony-phospho-molybdate complex of phosphomolybdic acid that is reduced to an intensely blue-colored complex of molybdenum blue by ascorbic acid.

Samples utilized during this study were collected from 16 pulp and paper mill wastewater treatment plants (WWTP) (Table 3) by mill personnel, preserved at pH 2 with sulfuric acid, and stored at 4°C prior to shipping to the NCASI WCRC via overnight courier. High organic carbon (>150 mg/L) in samples is known to impact the digestion efficiency of the alkaline to acidic persulfate method (Patton and Kryskalla 2003); dilution was employed to eliminate this issue. All preserved samples were digested within seven days of collection. The digestates have a holding time of 28 days and were stored at room temperature prior to analysis.

Samples were analyzed using a segmented flow Autoanalyzer 3 by Bran and Luebbe. Autoanalyzer methods have a narrower calibration range (0.01 to 5.0 mg N/L and 0.01 to 3.0 mg P/L), thus sample dilution was required prior to digestion and analysis.

Table 3. Mill Wastewater Treatment Plants Sampled

Mill Code	Sample Numbers[a]	Sampling Set	Mill Furnish[b]	Process Type[c]	WWTP[d]
A	24413, 24412	1	SW, OCC	kraft, recycle	ASB
B	24415, 24414	1	SW, HW	recycle, kraft	AS
C	24417, 24416	1	SW	dissolving kraft	ASB
D	24419, 24418	1	HW, SW	kraft	ASB
E	24421, 24420	1	SW, HW, deink	kraft, recycle	ASB
F	24478, 24477	2	SW, HW	kraft, NSSC, recycle	AS
G	24479, 24480	2	SW, HW	kraft	AS
H	24481, 24482	2	SW, HW, deink, OCC	NSSC, recycle, kraft	ASB
I	24484, 24483	2	HW, SW	kraft	AS
J	24486, 24485	2	SW, deink	recycle, RMP	AS
K	25001, 25000	3	SW, HW	kraft	ASB
L	25008, 25007	3	SW, HW, recycle	Recycle	AS
M	25009, 25010	3	SW, HW	kraft, NSSC	ASB
N	25012, 25011	3	SW, HW	kraft	ASB
O	25076, 25075	3	SW, HW	kraft	ASB
P	25014, 25013	3	SW	RMP, TMP, recycle	AS

[a] preserved sample listed first, unpreserved sample listed second
[b] HW = hardwood; SW = softwood; OCC = old corrugated containers
[c] RMP = residential mixed paper; TMP = thermo-mechanical pulping; NSSC = neutral sulfite semi-chemical
[d] AS = activated sludge; ASB = aerated stabilization basin

Method Comparison Results

Concentration data obtained for TP in the samples listed in Table 3 for the five methods assessed were compared using a multiple variable analysis in Statgraphics®. The Pearson product moment correlation (PPMC) measures the strength of the linear relationship between each pair of concentrations. The PPMCs ranged from 0.9887 to 0.9900 across all methods. These methods yielded comparable results for TP concentrations. The p-values, which test the statistical significance of the estimated correlations, were all <0.05, indicating statistically significant non-zero correlations at the 95% confidence level. These relationships are illustrated in Figure 1. Graphic data for each method are provided in relationship to every other method by examining the box in which the method titles intersect. For example, the letter A represents the graph of TP concentrations obtained using NCASI TNTP-W10900 (Y-axis) and LTRWS TNTP (X-axis); B represents LTRWS TNTP plotted on the Y-axis and TNTP-W10900 plotted on the X-axis.

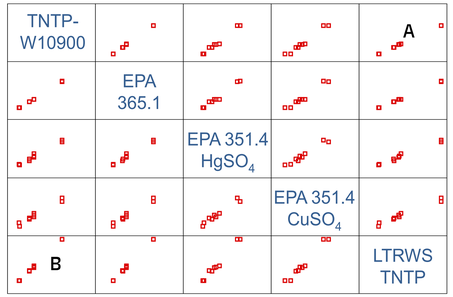

Figure 1. TP Method Comparison: Multiple Variable Analysis (mg P/L)

Data obtained for TN are provided in Figure 2 for the four methods assessed. The PPMC between each pair of concentrations ranged from 0.6968 to 0.9929. Each method yielded comparable results for TN concentrations. The p-values were all <0.05, indicating statistically significant non-zero correlations at the 95% confidence level.

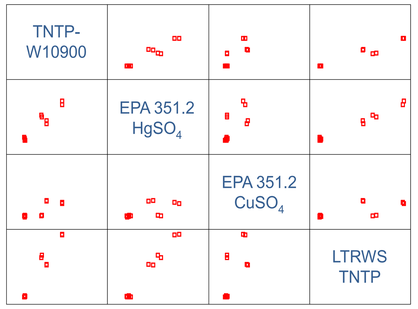

Figure 2. TN Method Comparison: Multiple Variable Analysis (mg P/L)

QC and QA experiments indicated that NCASI TNTP-W10900 provided consistently reproducible and accurate results (summarized in Table 4) for all matrices assessed during this study.

Table 4. QA/QC Summary

Method	RPD Range	MS/MSD RPD Range	MS/MSD Recovery Range	CCV, ICV, IRS Recovery Range
Total Phosphorus				
NCASI TNTP-W10900	<0.01 – 11.8	<0.5 - 8.5	94 - 104	86.0 - 107
EPA 365.1	<0.01 – 4.11	0.8 - 11.6	80.3 - 105	75.0 - 103
EPA 365.4 ($HgSO_4$)	<0.01 – 14.3	<0.5 - 18.6	86.8 - 115	72.0 - 115
EPA 365.4 ($CuSO_4$)	<0.01 – 50	<0.5 - 96.3	67.0 - 103	95.5 - 106
LTRWS TNTP	<0.01 - 2.8	0.5 - 3.6	97.4 - 100	98.7 - 104
Total Nitrogen				
NCASI TNTP-W10900	0.29– 6.42	<0.01 - 6.5	81.3 - 98.9	95.8 - 107
EPA 351.2 ($HgSO_4$)	1.80 – 14.2	0.5 - 6.8	105 - 169	75.3 - 110
EPA 351.2 ($CuSO_4$)	1.30 – 32.4	<0.5 - 27.3	57 - 106	86.0 - 109
LTRWS TNTP	0.2 - 3.40	0.01 - 7.3	90.3 - 134	93.7 - 95.5

Study Findings

NCASI Method TNTP-W10900, based on alkaline to acidic persulfate digestion and automated colorimetric analysis for simultaneous determine of TN and TP in pulp and paper mill biologically treated wastewaters, was compared to EPA Methods 365.1 (TP by acidic persulfate digestion), 365.4 (TP by Kjeldahl digestion), and 351.2 (TKN by Kjeldahl digestion) and to NCASI Method LTRWS TNTP. All samples in this study were analyzed for nitrate and nitrite in order to provide data for calculating TN from TKN results (TN = (NO_3+NO_2) + TKN). Results were evaluated using statistical and graphical techniques.

- Nitrate and nitrite concentrations provided only minor contributions (<0.05 mg N/L) to overall TN concentrations in 15 of the 16 pulp and paper mill biologically treated wastewaters assessed during this study.
- TN and TP results obtained for replicates in 16 matrices showed that a significant relationship existed for concentrations obtained using NCASI TNTP-W10900 and the other methods assessed when a multiple variable analysis was applied (p-values <0.05). TN results for EPA 351.2 using copper sulfate as the catalyst did not have a consistently linear relationship for the concentrations obtained using the other methods evaluated during this comparison study.
- QC and QA experiments indicated that NCASI TNTP-W10900 provided consistently reproducible and accurate results for all matrices assessed during this study.

In conclusion, NCASI Method TNTP-W10900 provided results comparable to the reference methods for TP and TN in the 16 matrices assessed, thus providing a method for simultaneous digestion of TN and TP in pulp and paper mill wastewaters that reduces costs in terms of energy consumption and time required to prepare digestates, eliminates hazardous waste, provides greater sensitivity for TN measurements, and exhibits excellent precision and accuracy.

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