



Automated Simplified Total Kjeldahl Nitrogen (s-TKN™) by Flow Injection Analysis



Abstract:

TKN is the total concentration of organic nitrogen-N + ammonia-N. TKN methodology requires a time consuming, off-line digestion. Automated s-TKN™ is a variation, whereby nitrate/nitrite-N is subtracted from total nitrogen, to give a final value equivalent to TKN.

On the initial channel nitrogen compounds are oxidized in-line to nitrate using alkaline persulfate/UV digestion. Oxidation of nitrogen-containing compounds to nitrate is achieved at 105°C with additional energy supplied by exposure to UV light. The digestion occurs in-line, prior to the injection valve.

After digestion, the nitrate produced in the digestion, plus the nitrate in the original sample, are quantitatively reduced to nitrite by passage of the sample through a copperized cadmium column. The nitrite thus produced (reduced nitrate plus original nitrite) is then determined by diazotization with sulfanilamide under acidic conditions to form a diazonium ion. The diazonium ion is coupled with N-(1-naphthyl) ethylenediamine dihydrochloride. The resulting pink dye absorbs at 520 nm and is proportional to total nitrogen.

On the second channel nitrate-nitrite-N is directly measured by quantitatively reducing the nitrate to nitrite (by passage of the sample through a copperized cadmium column). The nitrite (reduced nitrate plus original nitrite) is then determined by diazotization with sulfanilamide under acidic conditions to form a diazonium ion. The diazonium ion is coupled with N-(1-naphthyl) ethylenediamine dihydrochloride. The resulting pink dye absorbs at 520 nm and is proportional to nitrate-nitrite nitrogen.

By subtracting the nitrate-nitrite value from the determined total nitrogen value, the s-TKN™ value is determined (organic nitrogen and ammonia components of the sample). (i.e. s-TKN™ is defined as the difference between the concentrations of total nitrogen and oxidized nitrogen: $s\text{-TKN}^{\text{TM}} = \text{Total N} - (\text{NO}_3^- \text{-N} + \text{NO}_2^- \text{-N})$).

Scope and Application:

This is a two channel method. Total Nitrogen is measured on Channel 1; Nitrate-nitrite on Channel 2. Automated s-TKN™ is then determined by subtraction. ($\text{TN} - \text{NO}_2 + \text{NO}_3\text{-N} = \text{sTKN}^{\text{TM}}$)

The applicable range is 0.2 to 20.0 mg N/L for both TN and nitrate. The method detection limit is 0.01 mg N/L for the TN application and 0.002 mg N/L for the nitrate/nitrite application. The method throughput is 50 injections per hour.



Laboratory Relevance:

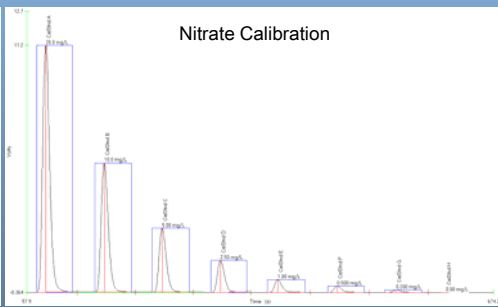
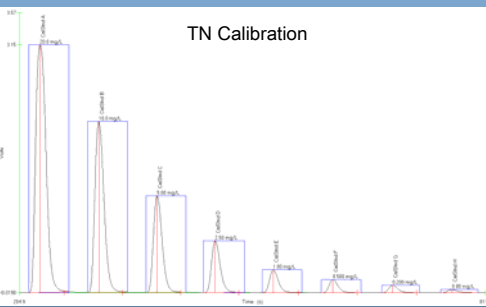
In contrast to the traditional Kjeldahl digestion, the automated s-TKN™ is just that - COMPLETELY AUTOMATED! Just load your samples.

Automated s-TKN™ does not require a digestion block, a fume hood, or expensive glassware. Total cost for the analysis is less than \$1 per sample (TN and $\text{NO}_2 + \text{NO}_3$), including the cadmium columns, with the reagent costs less than 10 cents per sample total for both channels.

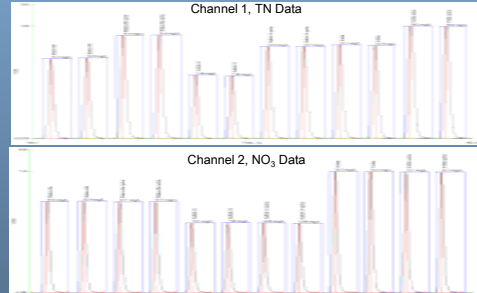
Automated s-TKN™ is a low-cost, safer TKN method. The method gives operators an improved tool for process control. Real-time results also eliminate the delays caused by having samples analyzed at an outside lab, providing an effective tool for making necessary process adjustments.

Nitrate Interference:

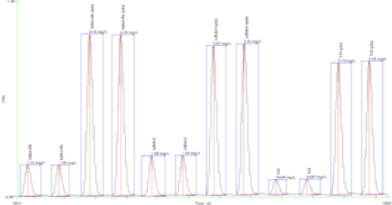
Samples that have a high nitrate to ammonia/TKN ratio can be problematic analytically for the traditional TKN digestion. When nitrate is at a concentration level that is ten times or greater than the TKN level, the ammonia generated during the TKN digestion is oxidized by the elevated nitrate concentrations to nitrous oxide, producing a negative interference. The negative nitrate interference has no effect on the s-TKN™ persulfate digestion, making the s-TKN™ application superior to the traditional TKN analysis when measuring samples with nitrate concentrations that are ten times greater than the original TKN sample concentration.



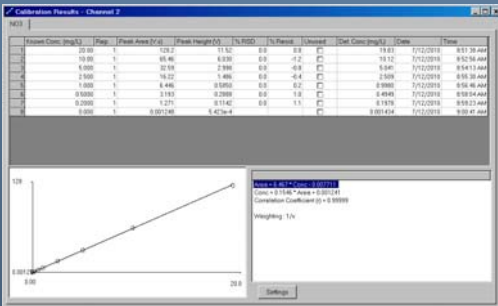
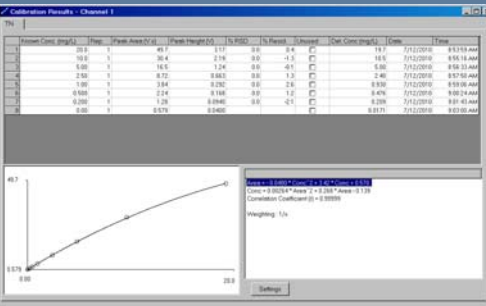
TN recoveries on Channel 1 and NO_3 recoveries on Channel 2, subtraction of the NO_3 results from the TN results produce the Automated s-TKN™ values:



TKN digestion recoveries for the same wastewater spikes:



Conclusion: For 5 out of 6 samples and spikes the % difference was below 15%. The only sample (Suffolk Ct) that was outside this percent range was with a concentration below 0.5 mg N/L, which will produce higher percentages of error. The % difference when the Suffolk Ct sample was spiked was less than 4%. 5-Mile sample and spike TKN values were lower than the S-TKN values, this is most likely due to the high nitrate concentration of the sample (12 mg N/L). Nitrate values >10 mg N/L will produce a negative interference for traditional TKN digestions because the elevated levels of nitrate will oxidize ammonia to nitrous oxide. This problem of >10 mg N/L nitrate concentrations are not an issue for the Automated s-TKN™ application.



Comparisons between traditional TKN and s-TKN™

Sample	TKN (mg N/L)	Automated s-TKN™ (mg N/L)	% Difference
Batesville	1.30	1.22	6.15%
Batesville Spike	6.30	6.29	0.16%
Suffolk Ct	1.66	0.42	74.7%
Suffolk Ct Spike	5.90	5.68	3.73%
5-Mile	0.67	0.8	16.3%
5-Mile Spike	5.22	6.0	13%

Sample	TN (mg N/L)	NO_3 (mg N/L)	Spike (mg N/L)	%Recovery	Automated s-TKN™ (mg N/L)
Batesville	10.35	9.14	---	---	1.22
Batesville Spike	15.4	9.11	5.0	101%	6.29
Suffolk Ct	7.43	7.01	---	---	0.42
Suffolk Ct Spike	12.65	6.98	5.0	104.5%	5.68
5-Mile	13.0	12.2	---	---	0.8
5-Mile Spike	18.1	12.1	5.0	102%	6.0