Total Nitrogen Methods Fact Sheet

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Total Nitrogen Methods Fact Sheet
July 21, 2014

Summary:

The SFWMD Laboratory is changing the way it determines total nitrogen (TN) in water samples. The approach for many years has been to determine two forms of nitrogen in the sample, Total Khejdahl Nitrogen (TKN) and NOX (nitrite + nitrate as N) and add them together to calculate the total (TN = TKN + NOX). While this approach has provided acceptable results, the TKN procedure is labor intensive (the sample must be evaporated at high temperature and ambient pressure and brought back to volume after digestion) and requires specialized equipment to perform the necessary digestion (including costly digestion tubes and a dedicated fume hood with specialized ventilation to remove acid fumes generated during digestion). In the new procedure TN is determined directly by digesting a portion of the water sample in a closed vessel at elevated temperature and pressure. This procedure does not require bringing the sample back to original volume and acid fumes are not released during digestion. In addition, this new procedure provides the added benefit of lower detection limits with lower levels of associated uncertainty than the traditional method of calculating TN from TKN and NOX.

There is also a new counterpart, TDN (Total Dissolved Nitrogen), to the new TN parameter for the determination of total nitrogen in a filtered sample. This parameter will replace TDKN, the similar counterpart to TKN.

Method Development and Certification:

The Laboratory conducted extensive development and optimization for this procedure to assure minimal impacts on sample collection and laboratory workflows. The method was validated with multiple proficiency testing studies and by conducting comparative analysis with 773 typical SFWMD surface water samples. In 2013, the Laboratory submitted an application for certification to the Florida Department of Health, Bureau of Laboratories. In April 2014, the DOH conducted an on-site inspection and approved certification of the method.

Implications of the Method Change:

The use of the new method will require some changes to existing monitoring permits and parameter lists to fully implement. In cases where only the measurement of TN is needed for permit compliance, the requested parameter list can be reduced from TKN and NOX to TN only. For permits that require that both TN and NOX be measured for compliance, the requested parameter list will need to be changed to include TN instead of TKN. If there are permits that specifically require a determination of TKN for compliance, the permit conditions will need to be revised with TKN being replaced by TN. The reference method for the new TN parameter is Standard Methods SM4500NC (Standard Methods for the Examination of Water and Wastewater, 21st Edition). The SFWMD SOP for this parameter is SFWMD-SOP-3090-003. The new TN method has a detection limit of 0.02 mg/L while the effective detection limit for calculated TN is the detection limit of TKN (0.05 mg/L) plus the detection limit of NOX (0.005) or 0.055 mg/L. Samples for TN and TDN will be collected and preserved in the same bottles and with the same filters and preservatives used for TKN and TDKN; and there is no change in the sample volume required for analysis.

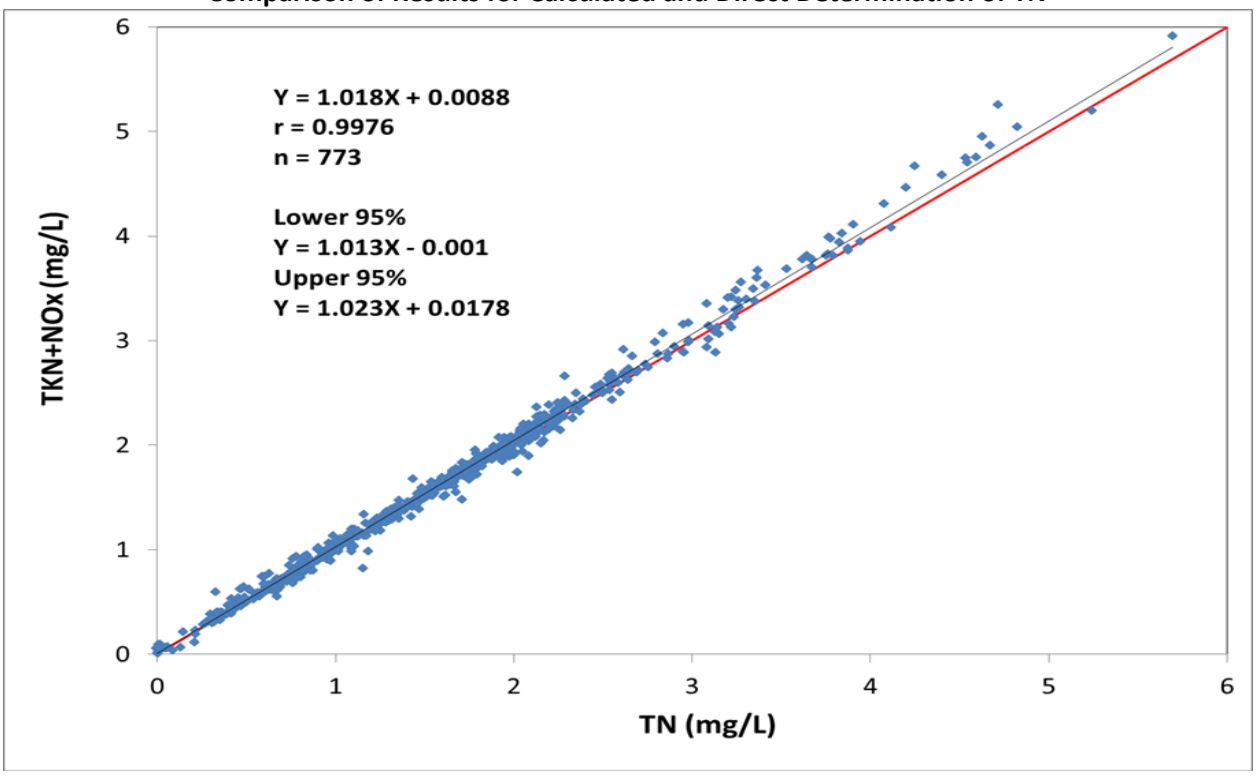
With the new direct TN method, it will now be possible to run TN analysis from the same auto sampler collected bottle used for TP. This was not possible with calculated TN because the NOX sample required filtration prior to preservation.

The SFWMD laboratory will continue to conduct TKN analyses as needed until all permit modifications are accomplished.

Method Comparison:

The two methods for determination of TN, calculation as NOX + TKN, and direct determination of TN using SM4500NC produce comparable results as shown in the graph below that charts the results of 773 determinations of TN using both methods in the SFWMD laboratory for a variety of routine water samples. Performance testing on blind samples from the Environment Canada and Quality Assurance of Information for Marine Environmental Monitoring in Europe (QUASIMEME) programs using the new TN method also show good agreement with consensus means and do not indicate any significant bias in freshwaters, low salinity estuarine waters, or seawater. Details of recent results from both Performance Testing (PT) programs are included at the end of this document. The SFWMD laboratory will utilize the new TN method for all performance evaluation studies conducted in the future.

Comparison of Results for Calculated and Direct Determination of TN



Environment Canada Proficiency Testing (PT) Program

This PT Study provides results and evaluations for inorganic parameters in nutrients in natural waters – below are the results for TN determinations conducted on the 10 blind samples that were submitted for

the round ending March 19, 2014. The samples are prepared in natural background waters from lakes, rivers or rainwater, and are fortified. The PT study reports feature tabulation of all results and provide extensive evaluations. Proficiency is ranked in terms of the number of biased parameters (systemic bias) and flagged results (precision measurement). Each laboratory receives a formal appraisal and z-score summary indicating the proficiency for each parameter submitted.

LAB RESULTS

Sample#	1	2	3	4	5	6	7	8	9	10
SFWMD [TN] (mg/L)	0.577	3.12	2.21	0.498	0.481	0.542	0.602	1.14	0.164	0.28
ASSIGNED VALUE *	0.570	3.20	2.24	0.505	0.497	0.545	0.593	1.164	0.168	0.283
R-STD DEV *	0.0273	0.113	0.057	0.0267	0.0253	0.0207	0.0364	0.0457	0.0106	0.0188
Z-Score Summary	0.25	-0.70	-0.52	-0.26	-0.63	-0.14	0.24	-0.52	-0.37	-0.15

Laboratory appraisal – Ideal, no biases

QUASIMEME Laboratory Performance Studies

The test materials (Exercise 1023) were prepared using seawater collected from the Atlantic Ocean. The three test materials differed from each other in respect of their nutrient concentrations (salinity >30 psu).

Following usual practices e.g. ISO 43, the z-scores can be interpreted as follows for laboratories which take part in QUASIMEME to assure the quality of their data for use in international marine monitoring programs.

$\|Z\| < 2$	Satisfactory performance
$2 < \|Z\| < 3$	Questionable performance
$\|Z\| > 3$	Unsatisfactory performance

Exercise 1023 – R73 Nutrients in Seawater & Concentrates: Oct 2013 – Feb 2014

Matrix	***Determinand***	***SFWMD [TN]***	***Units***	***Assigned Value***	***Total Error***	***Z Score***	***z***	***Total Dupl.***
QNU256SW	TOTAL-N	7.920	µmol/l	8.315	1.289	-0.3	S	1
QNU257SW	TOTAL-N	19.00	µmol/l	19.17	1.400	-0.1	S	1
QNU258SW	TOTAL-N	12.90	µmol/l	14.12	1.097	-1.1	S	1

The letters in the *z* column indicate: S – Satisfactory, Q – Questionable, U – Unsatisfactory

The test materials (Exercise 1024) were prepared using seawater collected from the Atlantic Ocean (estuarine water), and from the Baltic Sea (low salinity open seawater). The four test materials differed from each other in respect of their nutrient concentrations and the salinity of the water. The salinity of the water was approximately 7-15 psu.

Exercise 1024 – R73 Nutrients in Estuarine and low salinity seawater: Oct 2013 – Feb 2014

Matrix	*Determinand*	*SFWMD [TN]*	*Units*	*Assigned Value*	*Total Error*	*Z Score*	*z*	*Total Dupl.*
QNU259EW	TOTAL-N	33.30	µmol/l	32.99	2.230	0.1	S	1
QNU260EW	TOTAL-N	79.20	µmol/l	80.85	5.101	-0.3	S	1
QNU261EW	TOTAL-N	23.30	µmol/l	23.65	1.669	-0.2	S	1
QNU262EW	TOTAL-N	17.60	µmol/l	18.54	2.568	-0.4	S	1

The letters in the *z* column indicate: S – Satisfactory, Q – Questionable, U – Unsatisfactory