APPLICATION NOTE

TN

NEXIS Aqua

ACCURATE, RELIABLE AND ULTRA-FAST TOTAL NITROGEN ANALYSIS IN WATER SAMPLES

INTRODUCTION

This note describes the backgrounds, principle of operation and performance data of the Total Nitrogen analysis in water samples carried out by the NEXIS Aqua model Total Nitrogen Analyzer.

BACKGROUNDS

For many years the standard method for the determination of organic nitrogen in water samples has been based on the Kjeldahl digestion technique that converts organic nitrogen into ammonia, which can then be determined along with any ammonia originally present. However, this method has been experienced by users as time consuming, extensive use of chemicals and the accuracy is variable because the effect of interferences causes unreliable results, especially in complex matrices. An alternative method for the determination of organic nitrogen is the so-called catalytic oxidative combustion method, which is based on an instrumental technique, which will benefit customers in terms of costs of operation.

Total Nitrogen (TN) is the sum of nitrate-nitrogen (NO_3-N), nitrite-nitrogen (NO_2-N), ammonia-nitrogen (NH_3-N) and organically bonded nitrogen. Total Nitrogen (TN) should not be confused with TKN (Total Kjeldahl Nitrogen), which is the sum of ammonia-nitrogen plus organically bound nitrogen but does not include nitrate-nitrogen or nitrite-nitrogen.

TN is sometimes regulated as an effluent parameter for municipal and industrial wastewater treatment plants, but it is more common for limits to be placed on an individual nitrogen form, such as ammonia. Treatment plants that have a TN limit will usually need to nitrify and denitrify in order to achieve the TN limit.
Because nitrogen in wastewater can be found in four major forms (excluding trace amounts of nitrogen gas), each major form is generally analyzed as a separate component, with Total Nitrogen calculated from the sum of the four forms.

Figure 1:
NEXIS Aqua with AS liquid sampler

EST analytical & tHR

Nitrogen in freshly polluted water is originally present in the form of organic nitrogen and ammonia. Natural biochemical processes slowly convert the organic nitrogen into ammonia, which is the form of nitrogen best able to be utilized as a nutrient by microorganisms in the treatment process. Some waste waters may be nitrogen deficient and require supplemental ammonia for adequate reproduction. Under aerobic conditions the conversion of organic nitrogen into ammonia reaches a peak and, under the appropriate biological conditions, is biochemically oxidized first into nitrite, then into nitrate. When nitrite and ammonia nitrogen are at minimum concentration (at or near zero) and nitrate is at a maximum value, the wastewater has been fully nitrified. A fully nitrified wastewater will have little or no organic nitrogen.

EST-TSHR has introduced a new Total Nitrogen water analyzer based upon the combustion nitrogen technique, and in compliance with ASTM D8083 and NEN-EN 12260 methods, which is also known as oxidative combustion method, and detects the Total Nitrogen content, not only that which is contained within proteins.

The combustion method for nitrogen determination is more convenient in many aspects such as speed, safety, cleanliness, productivity and cost per analysis.
The problem in the past was that it was not easy to reproduce the conditions required by the combustion method and for this reason the Kjeldahl technique took the lead, and became considered as the classical method for nitrogen/protein determination. Nowadays, thanks to steps forward in technology, the combustion nitrogen determination is becoming more widespread and accepted in the market.

Results obtained with the combustion nitrogen determination are usually a little bit higher than with Kjeldahl, since even the heterocyclic compounds and nitrogen compounds (e.g. nitrites and nitrates) are detected. In the Kjeldahl method, such compounds are converted into the ammonium ion incompletely or not at all.
The opposite could also happen (rarely), because in this kind of analysis there are lots of variables that could influence the final result. Indeed, there are many minor variants of the Kjeldahl method, involving the use of different catalysts, heating times, volumes and distribution of sulfuric acid and masses of test portion: this shows that the Kjeldahl procedure may be influenced by experimental errors. Recovery is the same for both the methods (≥ 99.5%), whilst the detection limit is lower for Combustion than for Kjeldahl (0.003 mg N absolute vs. ≥ 0.1 mg N absolute).

PRINCIPLE OF OPERATION

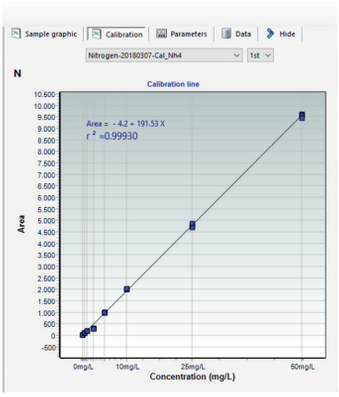
Combustion nitrogen determination requires well homogenized samples, heated in a high-temperature furnace where the combustion takes place rapidly through a catalyst-based furnace tube at minimum 650°C in the presence of pure oxygen. This produces mostly water, carbon dioxide and nitrogen as several oxides (NyOx). This gas mixture is passed through a permapure dryer tube in order to remove the water and directly transfer to a chemiluminescence detector where the Total Nitrogen content is measured.

INSTRUMENT SETTINGS

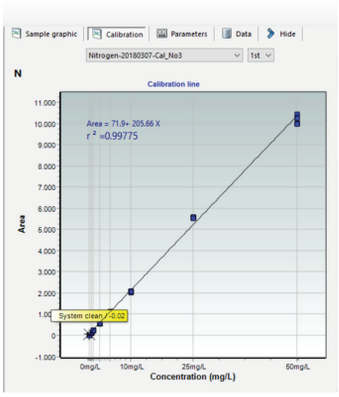
Parameter	System Value
Oxygen gas	320 mL/min
Furnace temperature	680 °C
Injection volume	20 µL

Table 1:
Typical NEXIS Aqua model instrument settings

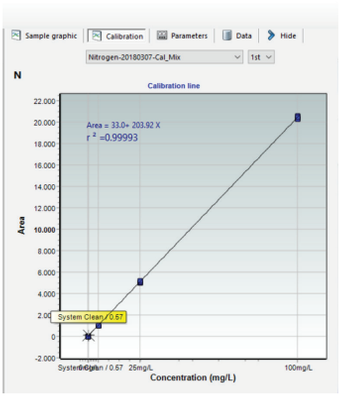
PERFORMANCE DATA



Calibration NH_4 0 – 50 ppm



Calibration NO_3 0 – 50 ppm



Calibration mix 0 – 100 ppm

Figure 2:
Calibration performance data

EST analytical & tsHR

RESULTS CUSTOMER SAMPLES

Based on above mix calibration line (0 – 100 ppm) customer QC samples with concentrations of 5, 25 and 100 ppm were analyzed as four replicates and calculated the total nitrogen content as given in below table 2.

nr	pos	sig	name	type	area	conc	c. unit	mean	sd	rsd
65	40		QC Mix c5ppm	calibration	1082.26	5.15	mg/L			
66	40		QC Mix c5ppm	calibration	1033.80	4.91	mg/L			
67	40		QC Mix c5ppm	calibration	1035.64	4.92	mg/L			
68	40		QC Mix c5ppm	calibration	1051.35	4.99	mg/L	4.99	0.11	2.20
69	41		QC Mix 25ppm	calibration	5040.68	24.56	mg/L			
70	41		QC Mix 25ppm	calibration	5072.97	24.72	mg/L			
71	41		QC Mix 25ppm	calibration	5115.69	24.92	mg/L			
72	41		QC Mix 25ppm	calibration	5235.92	25.51	mg/L	24.93	0.42	1.68
73	42		QC Mix 100ppm	calibration	20589.58	100.81	mg/L			
74	42		QC Mix 100ppm	calibration	20357.63	99.67	mg/L			
75	42		QC Mix 100ppm	calibration	20307.52	99.42	mg/L			
76	42		QC Mix 100ppm	calibration	20460.24	100.17	mg/L	100.02	0.61	0.61

Table 2:
Results of TN analysis in customer QC samples

A set of customer urea, ammonia and nitrate standard samples with 20 ppm nitrogen concentration were analyzed as 4 replicates and calculated the Total Nitrogen concentrations of these respective standard samples as per below table 3.

nr	pos	sig	name	type	area	conc	c. unit	mean	sd	rsd
51	36		Customer 20ppm NH4	sample	4084.44	19.87	mg/L			
52	36		Customer 20ppm NH4	sample	4088.74	19.89	mg/L			
53	36		Customer 20ppm NH4	sample	3781.23	18.38	mg/L			
54	36		Customer 20ppm NH4	sample	4185.10	20.36	mg/L	19.62	0.86	4.38
55	37		Customer 20ppm NO3	sample	4226.36	20.56	mg/L			
56	37		Customer 20ppm NO3	sample	4085.58	19.87	mg/L			
57	37		Customer 20ppm NO3	sample	4350.08	21.17	mg/L			
58	37		Customer 20ppm NO3	sample	4039.74	19.65	mg/L	20.31	0.69	3.40
59	38		Customer 20ppm Urea	sample	3598.79	17.49	mg/L			
60	38		Customer 20ppm Urea	sample	3656.43	17.77	mg/L			
61	38		Customer 20ppm Urea	sample	3540.59	17.20	mg/L			
62	38		Customer 20ppm Urea	sample	3546.41	17.23	mg/L	17.42	0.26	1.52

Table 3:
Results of TN analysis in customer standard samples

Figure 3 shows the sample peak of a mixed ammonia/nitrate sample, which distinguishes the presence of both compounds in the sample.

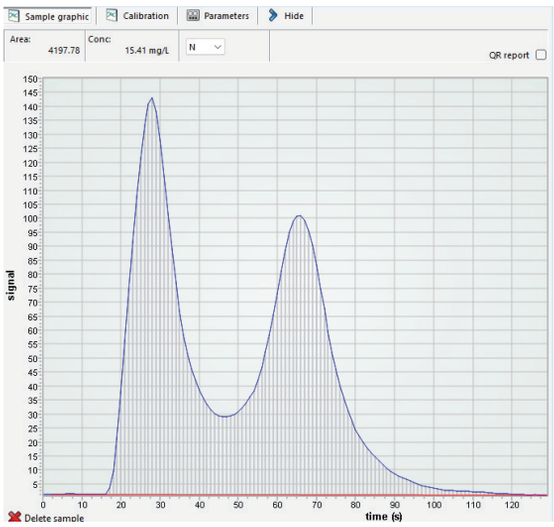


Figure 3:
Sample peak of a TN measurement using NEXIS Aqua generated by NEXIS LINK software

DISCUSSION

The performance data of customer QC samples analyzed on the NEXIS Aqua, shows a very good repeatability (RSD < 3%) and accuracy based on the prepared calibration standards range.

The analysis of a 20 ppm NH_4 and NO_3 gives excellent results and the 20 ppm urea a lower recovery, which is very common in this type of analysis. Also, the NEXIS Aqua is able to distinguish the ammonia and nitrate in the sample, which will support the information of presence of the individual compounds in the sample.

In this way an automated highly sophisticated and most compact instrument has been developed which is capable of measuring the Total Nitrogen content of various type of water samples within 2 minutes.

CONTACT INFO

E-mail: **sales.tshr@estanalytical.com**

E-mail (US only): **sales@estanalytical.com**

Our website: **www.estanalytical.com**

Visit our website to find your local TSHR distributor

EST analytical & tshr

YOUR PARTNER IN COMBUSTION ELEMENTAL ANALYSIS

300.AN.TN013.V1.0