

Total Chemically Bound Nitrogen in Water by Pyrolysis and Chemiluminescence Detection according to ASTM D5176

- Highly accurate analysis according to ASTM D5176
- Boat-inlet drive allows wide sample scope
- Total nitrogen content within 5 minutes
- High level of automation with the 749 ALS
- Automatic safety features



Keywords: Nitrogen, Water, ASTM D5176, Chemiluminescence, boat-inlet, ElemeNtS

Introduction:

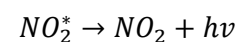
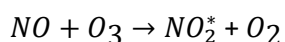
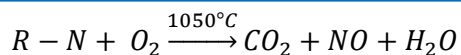
Total nitrogen content is an important quality criterium for many types of water, but especially for wastewater, such as process effluents. High nitrogen concentrations in rivers and lakes can cause explosive bacterial and algae growth, depleting dissolved oxygen, which in turn leads to mass starvation of fish. Therefore, lowering the nitrogen concentration of the effluent is one of the main reasons for treating wastewater. Nitrogen removal is done by means of bacteria that convert organic and inorganic nitrogen through several steps into nitrogen gas, which leaves the effluent into the air.

The total nitrogen concentration can be obtained by summing the concentrations of the different kinds of nitrogenous components, as they may be present in wastewater. The traditional methods only determine one or more types of nitrogen like total Kjeldahl nitrogen (TKN), which determines ammonia and organic nitrogen, and total inorganic nitrogen (TIN), which determines all inorganic nitrogen. They usually involve digestion and can take hours to complete. In addition to that, they require hazardous chemicals and take up valuable operator time.



Combustion chemiluminescence is a well-established test method for the determination of total nitrogen i.e., all possible types of nitrogen as they may be present in the water. It typically takes about 5 minutes for an analysis and doesn't require hazardous chemicals or a high amount of operator time.

The combustion chemiluminescence analysis technique is based on the combustion of the sample followed by a chemical reaction of the combustion products with ozone, and finally measuring the light emitted from the reaction. Either manually or automatically, 5 μL of sample is introduced into a sample boat. This sample boat is then inserted into the combustion tube, which is heated by a furnace to 1050°C, at a controlled rate. The nitrogen bound components are vaporized and combusted, the released nitrogen is oxidized to nitrogen oxide (NO) in an oxygen rich atmosphere. Both organic and inorganic nitrogen is converted to NO.



A stream of inert gas (argon or helium) takes the reaction products, after removal of the produced water vapor, into a reaction chamber. Here, under reduced pressure (using a built in vacuum pump) the NO molecules are converted to excited NO_2^* by the addition of ozone. It emits light (chemiluminescence) upon falling back to the ground state.

A photomultiplier tube measures the emitted light, converting it to an electronic signal. This response signal is integrated to calculate the area. The nitrogen concentration of an unknown sample is calculated using the linear regression function of the concentration standard mixtures versus integrated area.

Horizontal ElemeNtS

The vertical configuration of the ElemeNtS total sulfur and nitrogen analyzer was introduced in 2018 and a great number of them have been sold. The standard method requirement of a boat-inlet introduction, as well as the better performance with heavy and solid samples, led to the development of the horizontal configuration of the ElemeNtS platform.



The horizontal ElemeNtS offers the same benefits as the vertical configuration. The possibility to use the 749 ALS for high sample throughput and the use of the Accura for accurate gas and LPG injection. It has the 10" touchscreen on the front, allowing full operation of the instrument in addition to the automated vacuum and pressure tests for easy leak detection. The front maintenance door allows easy access to the consumables, eliminating the need to access the back of the instrument. Furthermore, the vertical and horizontal configurations share about 90% of their parts, allowing fast shipment of spare parts and consumables.

Analytically the horizontal ElemeNtS is very comparable to its vertical counterpart. It has a large linear dynamic range of up to 10^3 for nitrogen, allowing a single calibration curve of 0.5-500 ppm. The working range is even up to 1% mass. The repeatability can be called very good and complies with the requirements set out by ASTM D5176. The precision is excellent with each instrument tested with round-robin samples, covering the range of expected samples, and compared to the accepted reference value (ARV).

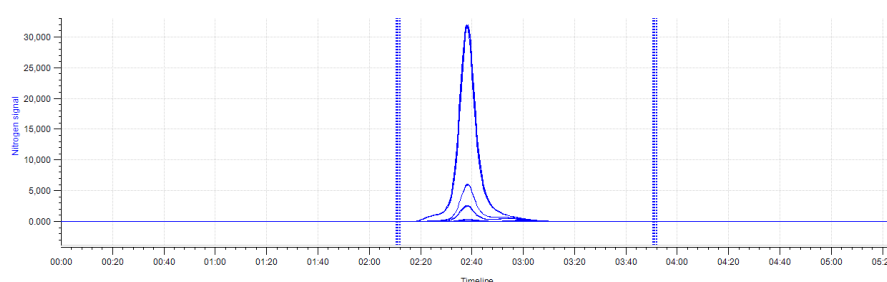
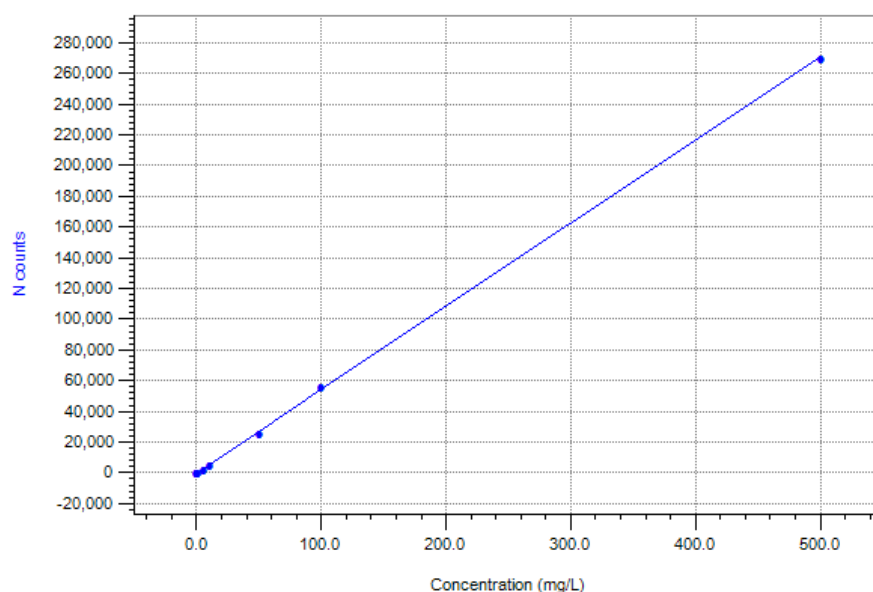
Validation

The system and methodology of the horizontal ElemeNtS total nitrogen analyzer is thoroughly tested for response linearity, recovery, precision, and repeatability, to validate its performance according to ASTM D5176.

Calibration

ASTM D5176 describes a calibration curve of 0-1000 mg/L of nitrogen, using pyridine in water as standards. In this case the ElemeNtS is calibrated up to 500 mg/L, closer to expected wastewater concentrations. The blank and each standard is injected 3 times and the average signal used to calculate the calibration curve.

ASTM D5176 nitrogen 0-500 mg/L	
Conc. mg/L	Area
0	-4
0.5	162
1.0	289
5.0	2215
10	5011
50	26196
100	55919
500	270505
Slope	
	542
Intercept	
	-99
Correlation	
	0.9999



Recovery and bias

To validate the recovery and bias, two samples containing 10 and 100 mg/L of total nitrogen were prepared. Approximately 1/3 each of ammonium sulfate, potassium nitrate, and pyridine contributed to the total nitrogen concentration, representing the typical types of nitrogenous components that may be present in wastewater. The samples were each injected 5 times with the concentration obtained, and the deviation from the reference value, compared to the precision stated in ASTM D5176.

ASTM D5176 Recovery and bias					
Sample name	Area counts	Conc. (mg/L)	Target (mg/L)	Δ mg/L	Max Δ D5762
10 ppm	5012	9.433	10	0.6	1.5
100 ppm	55490	102.6	100	2.6	10

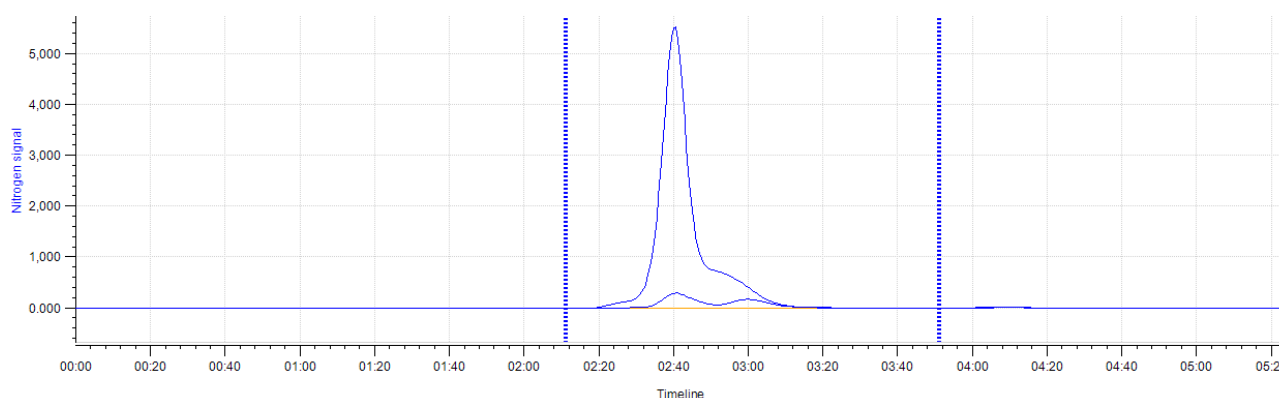
The results for both samples displayed a better precision than specified in the "Precision and bias" statement of ASTM D5176. The ElemeNtS can therefore be regarded as being very precise.

Repeatability

Because the before mentioned samples were injected 5 times, the repeatability can also be determined. The standard deviations obtained were compared to the standard deviation as specified in the "Precision and bias" statement of the method.

The repeatability standard deviations as obtained are all well within the maximum deviation as allowed by the method. This demonstrates the excellent repeatability of the analyzer.

ASTM D5176 repeatability		
Injection	10 ppm	100 ppm
1	9.313	102.5
2	9.449	102.7
3	9.596	102.6
4	9.354	105.5
5	9.453	102.7
Average	9.443	102.6
Standard deviation	0.109	0.102
Std dev (D5176)	0.4	1.0



Sample scope and configurations

Focus of this application highlight has been on the analysis of wastewater, but the method may of course also be used for other aqueous samples. Process water, surface water, and even seawater may be analyzed using the ElemeNtS. Samples with high concentrations of salt are also recommended to be analyzed using boat-introduction, as these salts otherwise deposit into the pyrotube.

The experiments shown here were also performed on a vertical configuration of the ElemeNtS, to satisfactory results. Since wastewater can contain high concentrations of suspended matter, it is advised to use a horizontal boat introduction. The suspended matter may clog the needle of the autosampler syringe in a vertical direct injection configuration. In the vertical configuration the needle is exposed to the high temperature of the furnace, while in the horizontal configuration the needle stays cool

Conclusion

The results demonstrate that the ElemeNtS analyzer is a powerful tool, that meets and exceeds the requirements of ASTM D5176. It has an excellent linearity, with a correlation coefficient of 0.9999 over the concentration range used. The recovery and bias are very good, with the concentration obtained for both samples analyzed well within the allowed deviation. The ElemeNtS has unrivalled repeatability, with the results far exceeding the precision statement of the method.

In addition to the analytical performance, the ElemeNtS has several other distinct advantages. Each analyzer is tested in the factory and is delivered with a start-up kit, making fast commissioning possible. High level of automation with the 749 ALS and short analysis times of 5 minutes, allows for large sample throughput. Automated leak tests and the front maintenance door allows for easy upkeep, making sure the analyzer keeps its superior performance. The safety features build into the ElemeNtS will prevent hazardous situations from happening, which will protect employees and assets from injuries and damage.

Contact your local PAC representative for more information or a quote. We can arrange (online) demonstrations as well as the analysis of your samples, so you can observe the performance of the best sulfur and nitrogen analyzer on the market yourself.