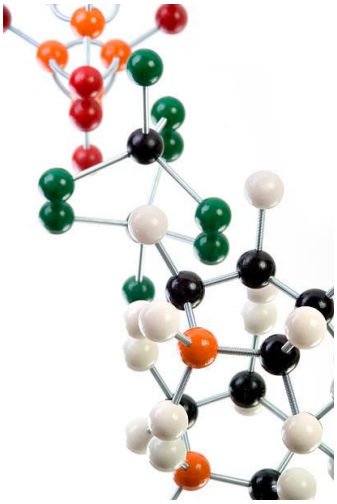
Determination of Nitrogen in Polymers by Boat-inlet Combustion and Chemiluminescence



- Horizontal ElemeNtS allows highly accurate analysis
- Repeatable introduction with the boat-inlet drive (BID)
- Protection of the optics against accidental sooting with the particle filter
- Fast analysis times: Around 5 minutes for both liquids and solids
- Safety as a priority with automatic gas shutoff and furnace cooldown

Keywords: Nitrogen, polymers, chemiluminescence, boat-inlet, ElemeNtS

Introduction:

Polymers are substances consisting of very large molecules, composed of many repeating subunits. In the petrochemical industry, polymers most often are synthetic plastics. Some common examples of these plastics include polyethylene (PE), polypropylene (PP) and polystyrene (PS). They have a wide array of applications such as packaging, tires, insulation and many more.

Plastics very often contain nitrogen compounds as many monomers have a nitrogen atom in their structure, such as acrylonitrile or hexamethylene diamine. Additives can contain nitrogen as well, such as plasticizers, stabilizers and pigments. By determining the nitrogen content, the concentration of monomer or additive can be determined.

Combustion chemiluminescence is an established technique to determine the nitrogen concentration in a wide array of matrices. There are established standard test methods, such as ASTM D4629 and ASTM D5762 for the determination of nitrogen in liquids. These methods are used to conform with both environmental regulations and product specifications. There is no established standard test method for the determination of nitrogen in polymers. But the combustion chemiluminescence technique can still be used for it.

Horizontal ElemeNts

In 2018 PAC successfully introduced the Antek ElemeNtS for total sulfur and nitrogen analyses in liquids and gases. The standard method requirement of a boat-inlet introduction, as well as the ability to analyze viscous liquids and solid samples, have led to the development of the horizontal configuration of the ElemeNtS platform.

The horizontal ElemeNtS offers the same benefits as the vertical configuration. The ability to use the 749 ALS for high liquid sample throughput and the use of the PAC Accura for accurate gas and LPG injection. The 10" touchscreen on the front offers full control 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. In addition, the vertical and horizontal configurations share about 90% of their parts, eliminating the need for different stocks of spare parts and consumables.

Analytically the horizontal ElemeNtS is very similar to its vertical counterpart. It has a wide linear dynamic range of up to 10^3 for nitrogen, allowing for a single calibration curve of 0.1-100 ppm. The working range is up to 1% mass. Its superb repeatability and excellent precision ensure it meets the requirements. Each instrument is factory tested with round-robin samples, covering the range of products as defined in the method scope, and compared to the accepted reference value (ARV). The limit of detection is calculated according to ISO11843 and is <100 ppb for the horizontal ElemeNtS.

Measuring principle

Around 20 mg of polymer is weighed into the sample boat. This sample boat is then inserted into the combustion tube at a controlled rate. The combustion tube is heated to a temperature of 1050°C by a furnace. The nitrogen bound components are vaporized and combusted, the released nitrogen is oxidized to nitrogen oxide (NO) in an oxygen rich atmosphere.

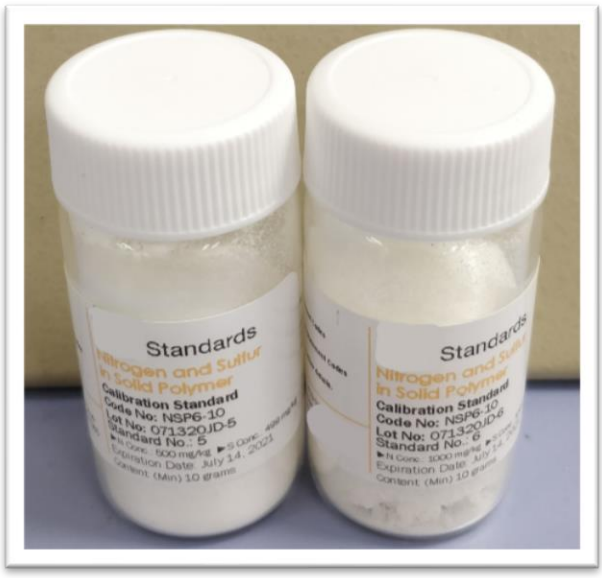
$$R - N + O_2 \xrightarrow{1050°C} CO_2 + NO + H_2O \qquad NO + O_3 \rightarrow NO_2^* + O_2 \qquad NO_2^* \rightarrow NO_2 + hv$$

A stream of inert gas (argon or helium) transfers the reaction products, after removal of the water vapor produced, to a reaction chamber. Here, under reduced pressure (using a build 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 and converts it into 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.

Validation

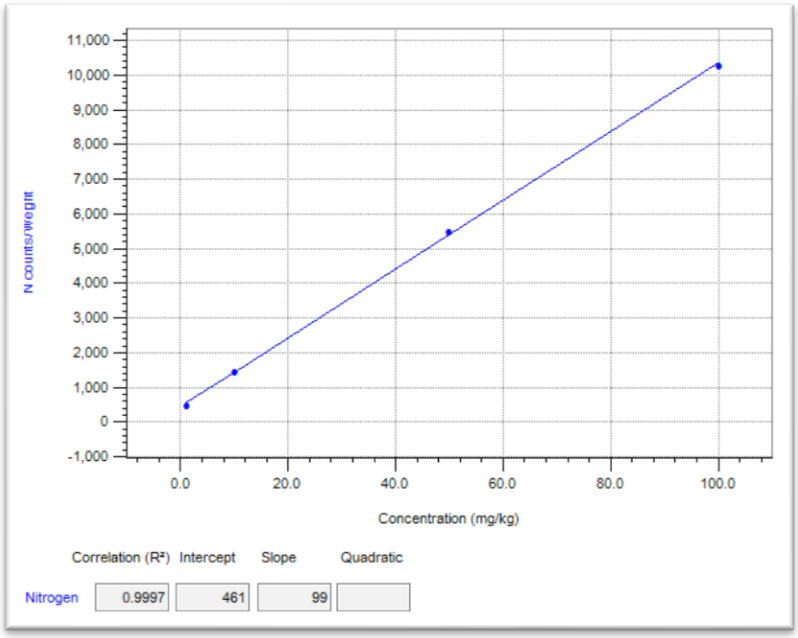
The horizontal ElemeNtS total nitrogen analyzer system and methodology is rigorously tested for linear response, recovery, precision and repeatability, to validate its performance.

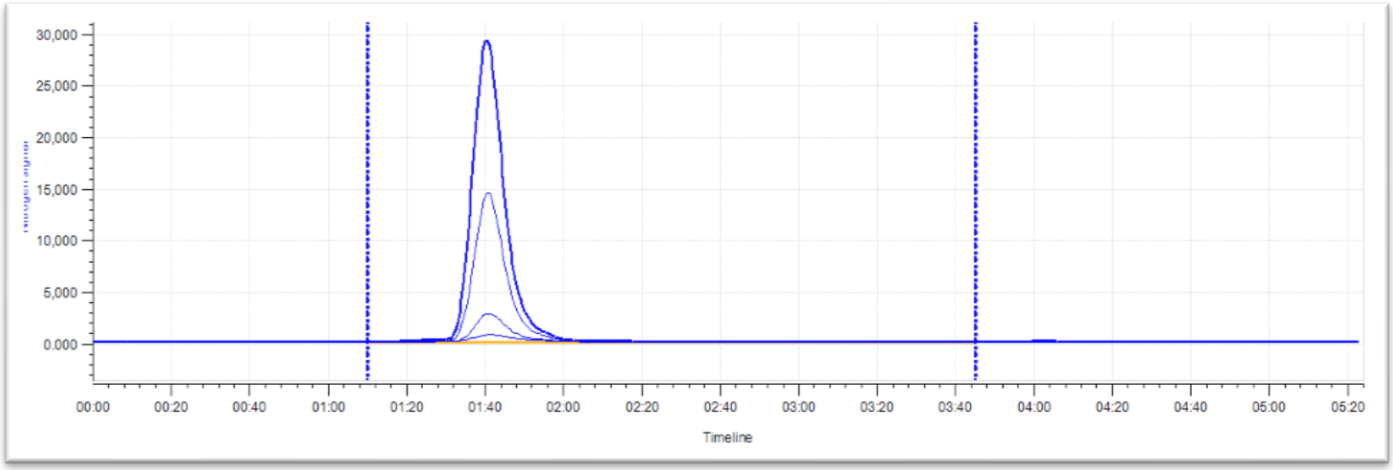


Calibration

The ElemeNtS is calibrated using nitrogen in polymer standards. A single calibration of 1-100 mg/kg is performed with 3 analyses per standard. The obtained correlation of 0.9997 is excellent, showcasing the superb linearity of the instrument.

Solids 1-100 mg/kg	
Conc. mg/kg	**Counts/mg**
1	494
10	1472
50	5497
100	10305
Slope	99
Intercept	461
Correlation	0.9997

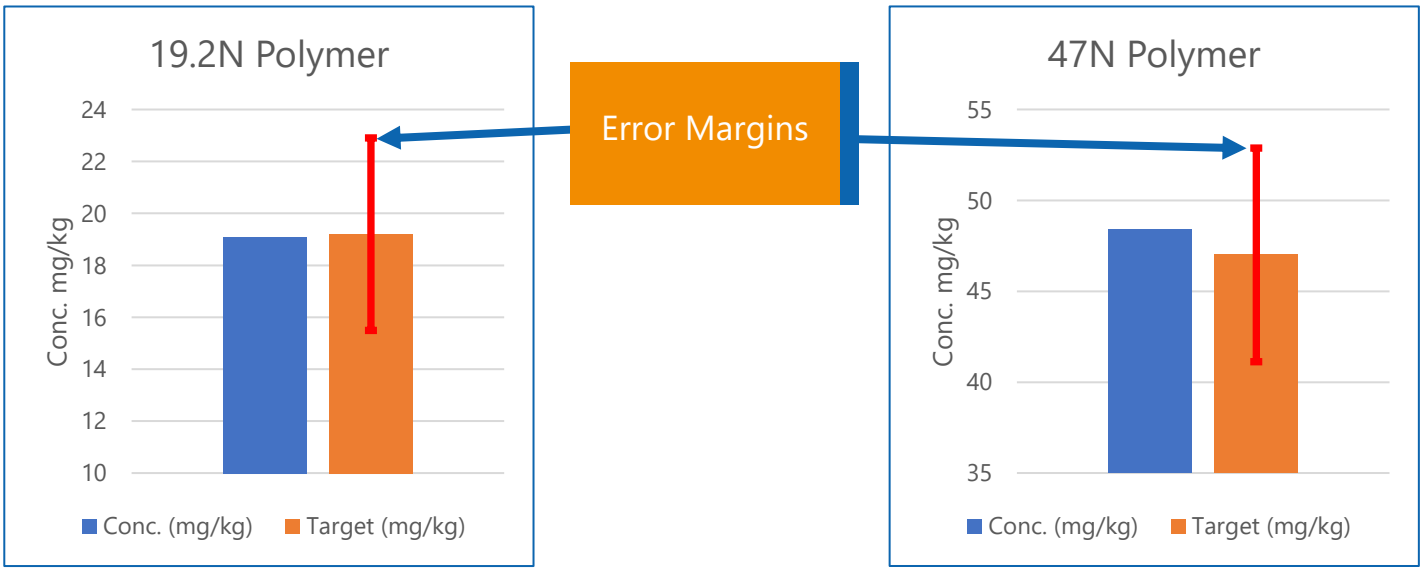




Recovery and precision

To validate recovery and precision, two polymer samples with known nitrogen concentrations are analyzed. The quantification of both samples is done using the calibration curve. Deviation from the known value is compared to the maximum allowed deviation from ASTM D4629, although polymers are not included in its scope, as an indicator of the system performance.

Recovery and precision					
Sample name	**Counts/mg**	**Conc. (mg/kg)**	**Target (mg/kg)**	**Δ Analysis (mg/kg)**	**D4629 R/√2 (mg/kg)**
19.2N Polymer	2250	19.1	19.2	-0.1	2.6
47N Polymer	5030	48.4	47.0	1.4	4.2

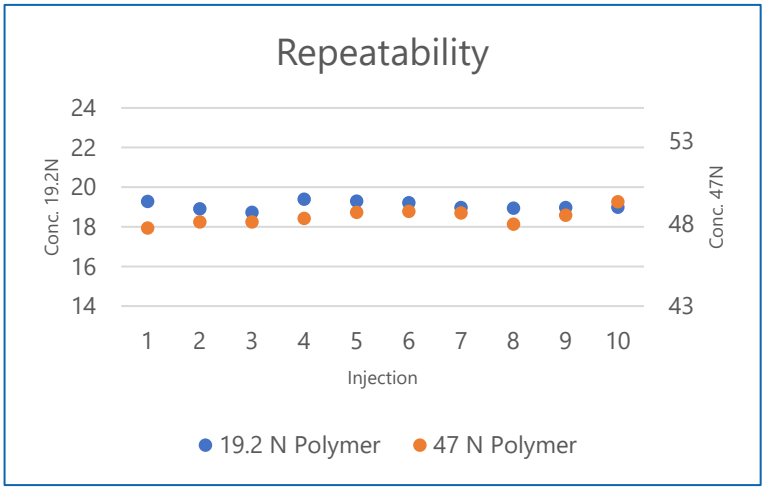


The quantified concentrations are within the reproducibility limits of D4629, it can be concluded that the obtained results are significantly identical to the reference values.

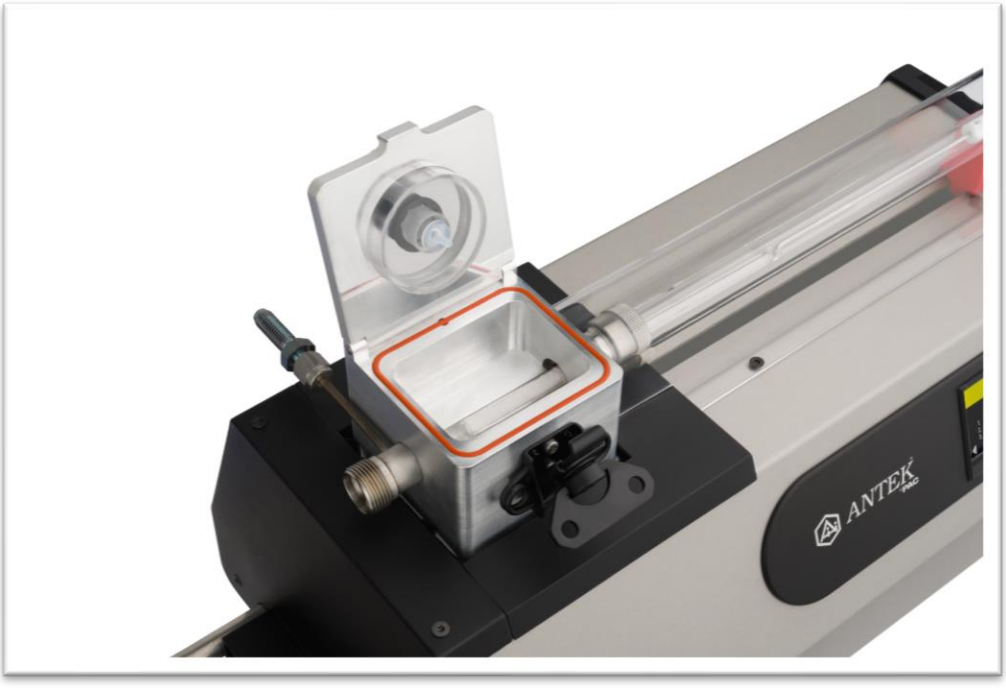
Repeatability

To validate the repeatability of the ElemeNtS analyzer, the reference materials were analyzed 10 consecutive times. The repeatability (r) was then calculated using the obtained standard deviation and compared to the method repeatability of ASTM D4629. Although this method, again, does not include polymers in its scope, it's a good indication of the system performance.

The repeatability obtained is smaller than specified by ASTM D4629. This demonstrates the analyzer's excellent repeatability.



Repeatability		
Injection	**19.2 N Polymer**	**47 N Polymer**
1	19.3	47.7
2	18.9	48.1
3	18.7	48.1
4	19.4	48.3
5	19.3	48.7
6	19.2	48.7
7	19.0	48.6
8	18.9	48.0
9	19.0	48.5
10	19.0	49.3
Average	19.1	48.4
Std. Dev.	0.215	0.462
Repeatability (r)	0.59	1.28
Method Repeatability (r_{D4629})	0.83	1.35



Conclusion

The results demonstrate that the Antek ElemeNtS is a powerful tool, that meets and exceeds the requirements. It has an excellent linearity, with a correlation coefficient of higher than 0.999 over the concentration range of the method. Superb recovery, precision and repeatability comply with the demands set by ASTM D4629. Even though this method does not include polymers in its scope, it is a good indication of the performance of the instrument.

In addition to the analytical performance, the ElemeNtS has several other distinct advantages. Each analyzer is factory tested and comes with a start-up kit, allowing for fast commissioning. High degree of automation with the 749 ALS and short analysis times of 5 minutes, enables large sample throughput. The 10" touchscreen can be used to fully control the instrument during daily use. Automated leak testing and the front maintenance door allow easy maintenance, making sure the analyzer maintains its superior performance. The safety features build into the ElemeNtS prevents hazardous situations and protects employees and assets from injuries and damage.

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