⊕PAC

Determination of Nitrogen in liquid hydrocarbons, petroleum and petroleum products by boat-inlet chemiluminescence according to ASTM D5762

- Horizontal ElemeNtS allows highly accurate analysis according to ASTM D5762

- Fast analysis times: 5 minutes for both liquids and solids, shorter for gases

- High level of automation with the 749 ALS, resulting in lower cost per analysis

- Safety as a priority with automatic gas shutoff and furnace cooldown

- Optionally cooled boat-inlet drive allows wide scope of samples

**Keywords**: Nitrogen, ASTM D5762, Chemiluminescence, boat-inlet, ElemeNtS

Introduction:

While the nitrogen content of fuels and refined products is often not directly regulated, it can have an impact on specifications such as gum content, storage stability and thermal stability. The presence of nitrogen containing compounds can also have an impact on process operation as well as catalyst selection, degradation and lifetime. Therefore, the concentration of nitrogen in intermediate streams and end-products needs to be accurately monitored to ensure optimum process control and conformance to product specifications.

ASTM D5762 is the preferred method for the quantification of nitrogen in liquid hydrocarbons, petroleum and petroleum products with concentrations ranging from 40 mg/kg up to 10000 mg/kg. For lighter products with concentrations below 40 mg/kg, ASTM D4629 is more appropriate. The difference between these two methods is D5762's requirement to use a boat-inlet drive to introduce the sample, while this is optional with D4629. ASTM D5762 additionally requires a dilution of at least 5 times.
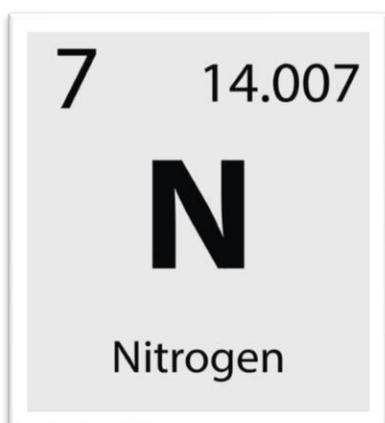
Either manually or automatically, 5 µL of sample is introduced into a sample boat. This sample boat is then inserted into the combustion tube at a controlled speed. The combustion tube is heated by a furnace to a temperature of 1100°C. The nitrogen bound components are vaporized and combusted, the released nitrogen is oxidized to nitrogen oxide (NO) in an oxygen rich atmosphere.

$$R - N + O_2 \xrightarrow{1100°C} CO_2 + NO + H_2O \qquad NO + O_3 \rightarrow NO_2^* + O_2 \qquad NO_2^* \rightarrow NO_2 + h\nu$$
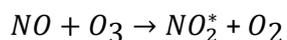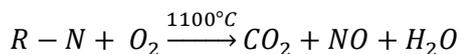
A stream of inert gas (argon or helium) transfers the reaction products, after removal of the water vapor produced, to a reaction chamber. Here, under reduced pressure (using a build in vacuum pump) the NO molecules are converted to excited NO_2^* by the addition of ozone. It emits light (chemiluminescence) 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.

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 of ASTM D5762. 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. The vertical configuration is preferred when analyzing ultra-trace samples of <100 ppb.
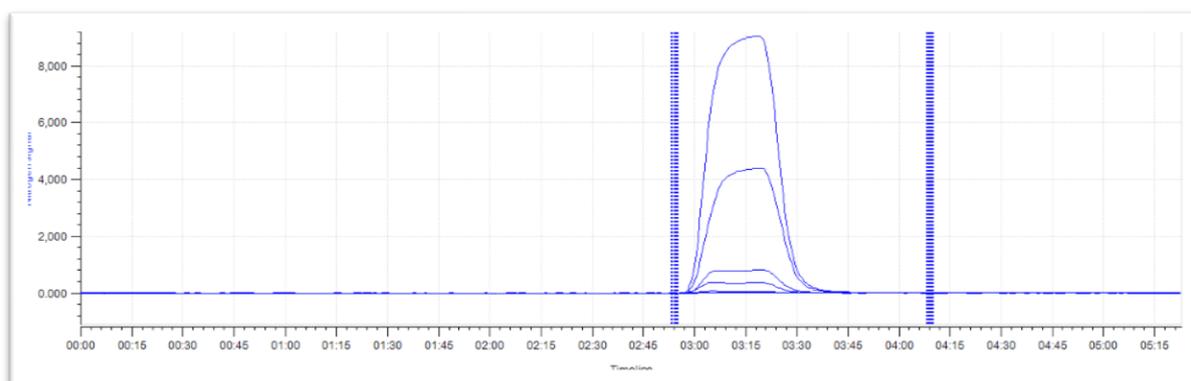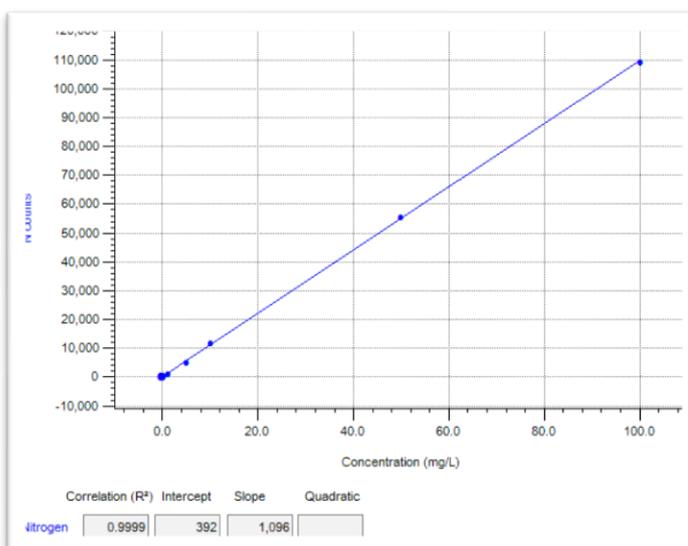
Validation

The horizontal ElemeNtS total nitrogen analyzer system and methodology is rigorously tested for linear response, recovery, precision and repeatability, to validate its performance according to ASTM D5762.

Calibration

ASTM D5762 describes a calibration curve of 0-100 mg/L of nitrogen, using acridine in xylene as standards. The blank and each standard is injected 3 times and the average signal used to calculate the calibration curve.

ASTM D5762 nitrogen 0-100 mg/L	
Conc. mg/kg	Area
0	103
1	1303
5	5464
10	11920
50	55916
100	109633
Slope	1096
Intercept	392
Correlation	0.9999

Recovery and precision

To validate recovery and precision, a number of check standards covering the scope of the method were analyzed. These standards are certified reference materials of ASI standards, with the exception of the heating oil which is derived from a round robin study. Concentrations ranged from 55 mg/kg up to 1% and the samples were thus diluted to fall within the calibration range. The obtained results were compared to the reference value, using the reproducibility of the D5762 method.

| ASTM D5762 Recovery and precision							
Sample name	Area counts	Conc. Diluted (mg/L)	Dilution factor	Conc. (mg/kg)	Target (mg/kg)	Δ mg/kg	D5762 R/√2
Heating oil	10508	9.23	6.80	62.8	55.6	7.2	10
Kerosene	48684	44.06	6.11	269	250	19	47
Heavy mineral oil	52419	47.47	22.3	1059	1001	58	188
Residual oil	71476	64.86	77.2	5007	5000	7	940
Crude oil	75516	68.54	144	9870	10000	-130	1881
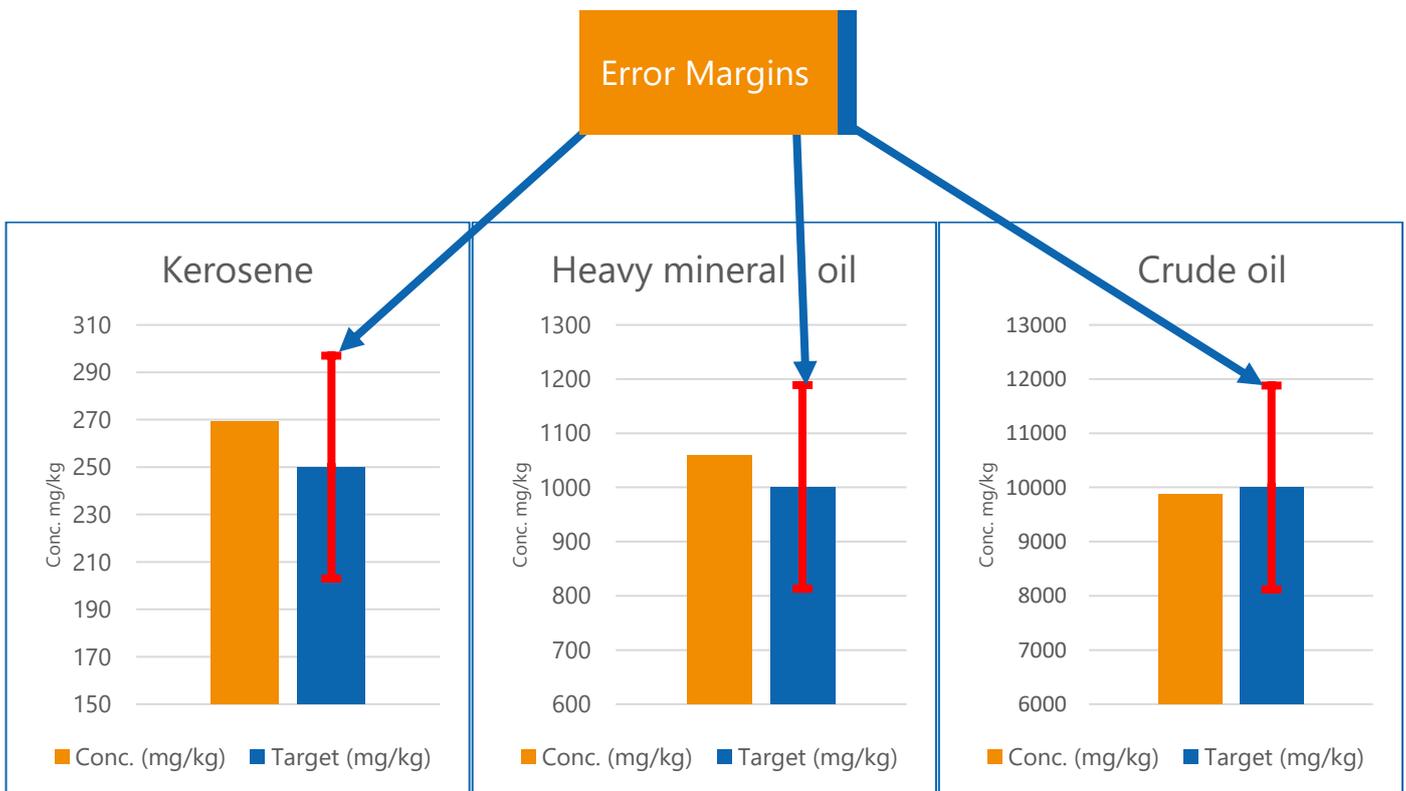
All samples are within the reproducibility limits of ASTM D5762, it can be concluded that the obtained results are significantly identical to the reference values.

Repeatability

To validate the repeatability of the ElemeNtS analyzer, 3 of the check standards were injected 10 times. The repeatability standard deviation is calculated and compared to the repeatability as stated in D5762.

The repeatability obtained is well within the specified limits. This demonstrates the analyzer's excellent repeatability.

ASTM D5762 repeatability			
Injection	Kerosene	H. Min. oil	Crude oil
1	269.0	1058.6	9859.4
2	271.4	1059.7	9898.8
3	269.6	1060.5	9888.7
4	269.1	1060.7	9877.3
5	268.9	1059.4	9880.9
6	268.9	1058.5	9862.0
7	269.0	1057.8	9863.3
8	268.9	1056.7	9867.3
9	268.8	1057.3	9859.8
10	268.3	1056.6	9845.3
Average	269.2	1058.6	9870.3
Standard deviation	0.84	1.5	16.0
r (Analysis)	2.32	4.10	44.2
r (D5762)	23.4	92.1	859
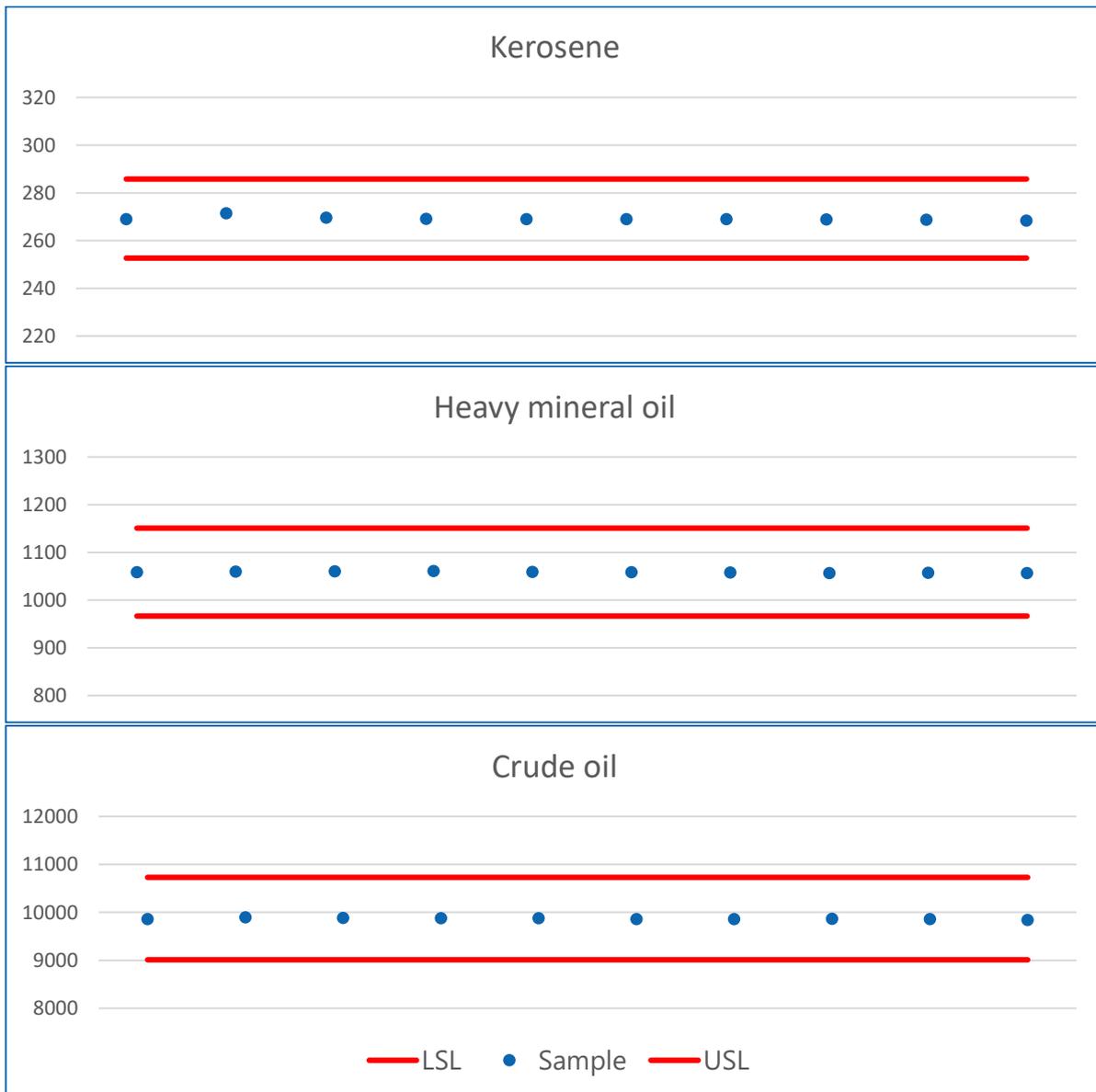
Conclusion

The results demonstrate that the ElemeNtS analyzer is a powerful tool, that meets and exceeds the requirements of ASTM D5762. It has an excellent linearity, with a correlation coefficient of 0.9999 over the concentration range of the method. Recovery and precision are very good, with all samples analyzed within the reproducibility of D5762. The ElemeNtS has unrivalled repeatability, with the results exceeding the requirements of the method.

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.