Determination of Nitrogen in Lubrication Oils using Boat-Inlet Combustion and Chemiluminescence

- Accurate analysis according to standard test methods
- Boat-inlet drive suitable for lubrication oil
- Analysis time of 5 minutes
- Fully automated analysis
- Repeatability and precision exceeding method requirements

Keywords: Nitrogen, Lubrication oil, Chemiluminescence, boat-inlet, ElemeNtS

Introduction:

Lubrication oils find their usage in a wide variety of applications. The largest usage, and probably best known, is in the automotive industry. Here lubrication oils are used to lubricate the moving parts of the engine. Modern lubrication oils often contain a wide variety of additives to improve certain characteristics. Examples of additives are detergents, oxidation inhibitors and viscosity improvers. Some of these additives contain nitrogen and thus by determining the nitrogen concentration, the concentration of these additives can be determined.

A commonly used technique to determine the nitrogen concentration in lubricants is combustion chemiluminescence. This is a technique standardized in several standard test methods, such as ASTM D5762, which describes the introduction of samples through a boat inlet device.

Either manually or automatically, 10 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.

$$R - N + O_2 \xrightarrow{1100°C} CO_2 + NO + H_2O \qquad NO + O_3 \rightarrow NO_2^* + O_2 \qquad NO_2^* \rightarrow NO_2 + hv$$

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.

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 standard test methods like 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 ISO 11843 and is <100 ppb for the horizontal ElemeNtS. The vertical configuration is preferred when analyzing ultra-trace samples of <100 ppb.

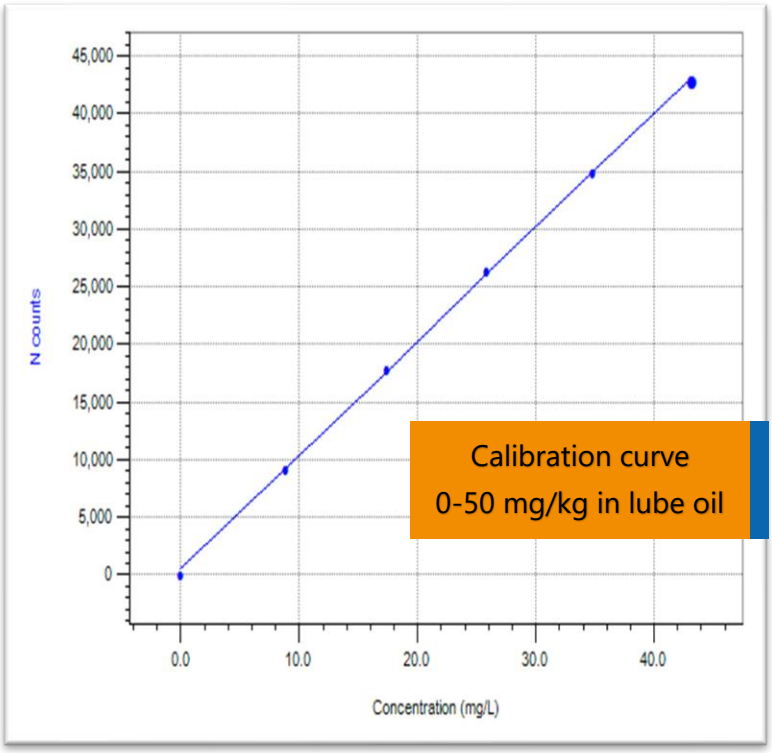
Validation

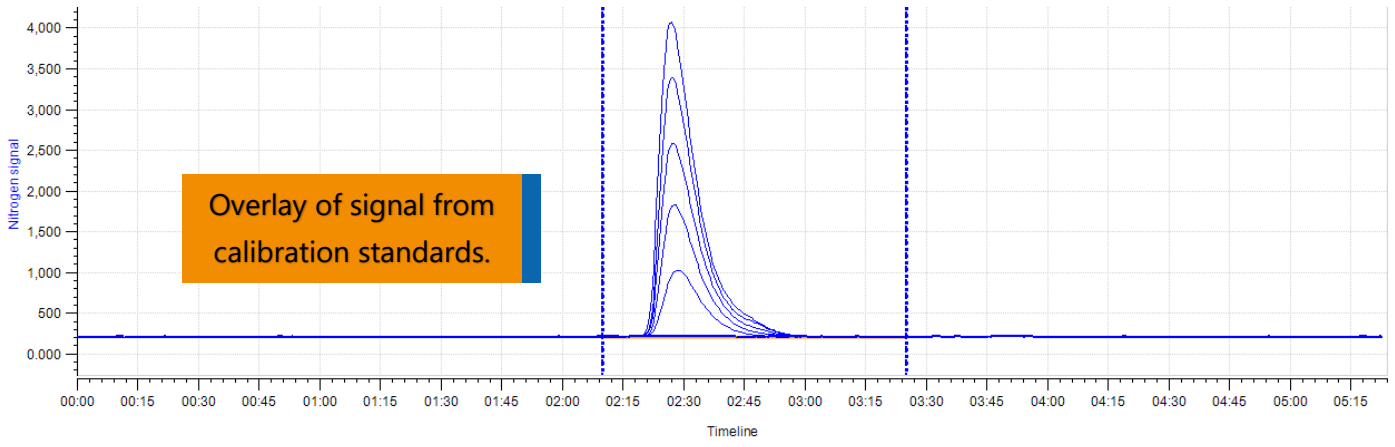
The horizontal ElemeNtS total nitrogen analyzer system and methodology is rigorously tested for linear response, recovery, precision, and repeatability, to validate its performance.

Calibration

Good calibration is important to obtain correct results. In this case the ElemeNtS was calibrated using a lubrication oil with a known nitrogen concentration. By diluting with toluene, a calibration curve of 0-50 mg/kg was obtained. Similar results will be obtained when the instrument is calibrated using Xylene samples as prescribed by ASTM D5762.

Lube oil nitrogen 0-50 mg/kg	
Conc. mg/kg	**Area**
0	94
10.1	9141
20.0	17951
29.8	26490
40.1	34974
49.8	42759
Slope	**990**
Intercept	**461**
Correlation	**0.9995**

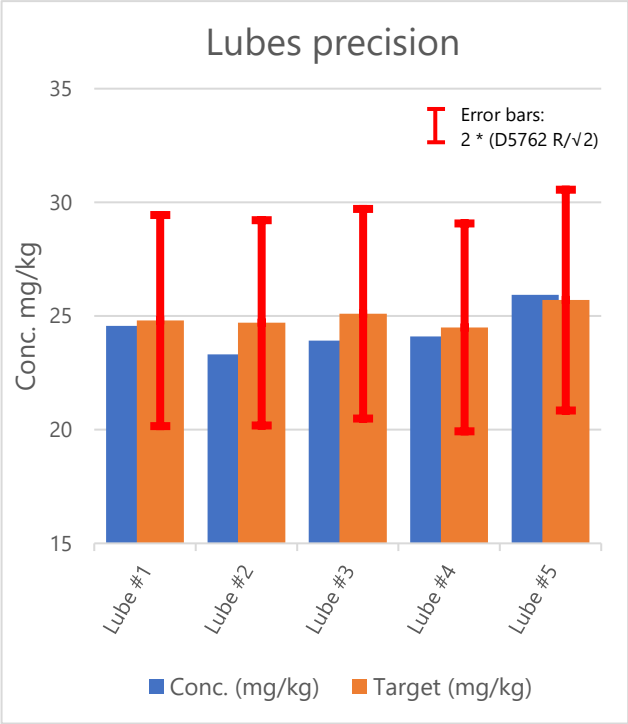




Recovery and precision

To validate recovery and precision, a total of five samples were analyzed. These samples have known concentrations of nitrogen and are diluted to a concentration of 25 mg/kg to fall within the calibration curve. Then the obtained concentration is compared to the theoretical concentration using the ASTM D5762 reproducibility as a guideline.

The obtained concentrations are very close to the target concentrations and well within the limits set by ASTM D5762. This means that the actual found concentration is significantly equal to the target concentration.

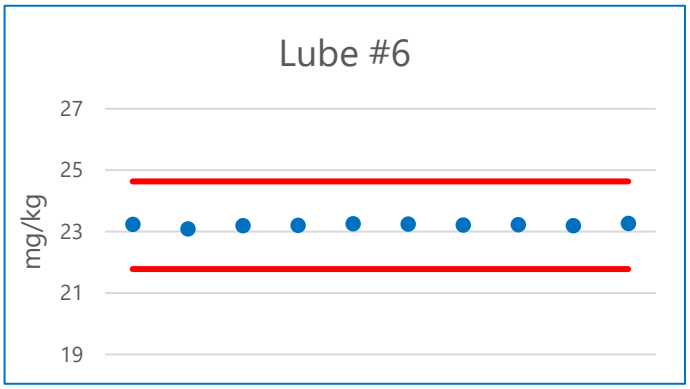


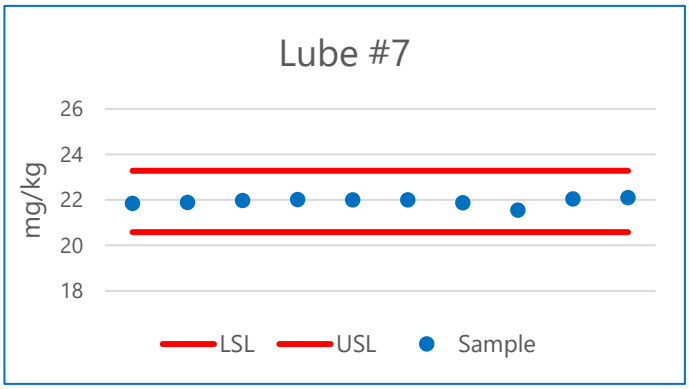
Lubricant oil precision				
Sample name	**Target (mg/kg)**	**Conc. (mg/kg)**	**Δ (mg/kg)**	**D5762 R/√2**
Lube #1	24.8	24.6	-0.2	4.6
Lube #2	24.7	23.3	-1.4	4.5
Lube #3	25.1	23.9	-1.2	4.6
Lube #4	24.5	24.1	-0.4	4.6
Lube #5	25.7	25.9	0.2	4.9

Repeatability

To validate the repeatability of the ElemeNtS analyzer, two samples were injected 10 times each. The repeatability standard deviation is then calculated and multiplied by 2.77 to obtain the repeatability r. This repeatability is then compared to the repeatability of ASTM D5762.

Repeatability obtained is well within the specified limits. This demonstrates that the ElemeNtS is very repeatable.





Lubricant repeatability		
Injection	**Lube #6 (mg/kg)**	**Lube #7 (mg/kg)**
1	23.23	21.85
2	23.08	21.89
3	23.19	21.97
4	23.20	22.01
5	23.26	22.00
6	23.24	22.01
7	23.21	21.88
8	23.22	21.55
9	23.19	22.05
10	23.26	22.10
Average	23.2	21.9
Standard deviation	0.050	0.155
r (Analysis)	0.14	0.43
r (D5762)	2.02	1.91

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 more than 0.999 over the concentration range used. Precision is very good, with all samples analyzed within the reproducibility of D5762. The ElemeNtS has unrivalled repeatability, with the obtained results much better than typical method repeatability.

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.

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