

Determination of bound Nitrogen in Petroleum products by Combustion and Chemiluminescence according to DIN 51444

- Rapid and Accurate Determination of Trace levels Nitrogen
- Fully Automated Combustion system
- Excellent Sensitivity, Repeatability & Linearity

Keywords: DIN 51444, ElemeNTS, Petroleum products, Nitrogen, Chemiluminescence



INTRODUCTION

DIN 51444 covers the determination of bound Nitrogen in concentrations ranging from about 0.3 to 300 mg/kg in petroleum products having a boiling point range of 50°C to 400°C and viscosities between 0.2 and 10 mm²/s at ambient temperature.

DIN 51444 is a German standard that is the preferred method in many countries to detect and quantify Nitrogen containing compounds in all kinds of petroleum products. These compounds can have detrimental effects on many processes and are undesirable in finished products. Therefore it is important to monitor the concentration of these compounds.

Operating the detector at a reduced pressure lowers the probability of the excited Nitrogen dioxide molecule colliding with other molecules before it undergoes chemiluminescence. Thus, reduced pressure provides improved sensitivity and lower noise.

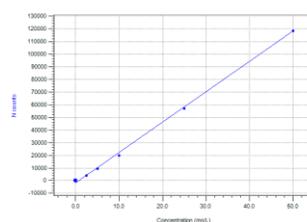
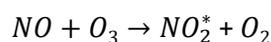
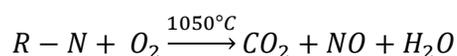
MEASURING PRINCIPLE

A sample of a petroleum product is directly injected, by a fully automated liquid sampler, into a dual zone high temperature combustion tube where the Nitrogen containing components are vaporized and combusted. The released Nitrogen is oxidized to nitric oxide (NO) in an oxygen rich atmosphere.

A stream of inert gas (Helium or Argon) is taking the reaction products, after removal of the produced water vapor, into a reaction chamber. Here, under reduced pressure (using a build-in vacuum pump) the NO molecules are converted to excited NO₂* by adding ozone and emitting light (chemiluminescence) while it relaxes to a stable state.

A photomultiplier tube measures the emitted light signal.

The response signal is integrated to calculate the area. The Nitrogen concentration of an unknown product is calculated using the linear regression function of the of the concentration of standard mixtures versus integrated area.



VALIDATION

The system and methodology of the ElementS total Nitrogen analyzer is thoroughly tested for response linearity, level of detection (LOD), recovery, precision and repeatability, to validate its performance according to DIN 51444.

CALIBRATION

Calibration curves are composed using pyridine in iso-octane standards. Each calibration solution and blank (iso-octane) is measured three times to determine the average net response for each. The ElementS is linear in the complete range of the method, but for improved precision the recommended calibration curves from the method can also be used.

Table 1: Full calibration DIN 51444

DIN 51444 Nitrogen 0-300 mg/kg	
Conc. mg/kg	Area
0	617
1	1680
2	2858
3	3975
4	5225
5	6355
10	13013
20	26119
30	40891
40	55115
50	69720
75	105706
100	142681
125	180003
150	212414
250	349473
300	421485
Slope	1408
Intercept	-175
Correlation	0,9999

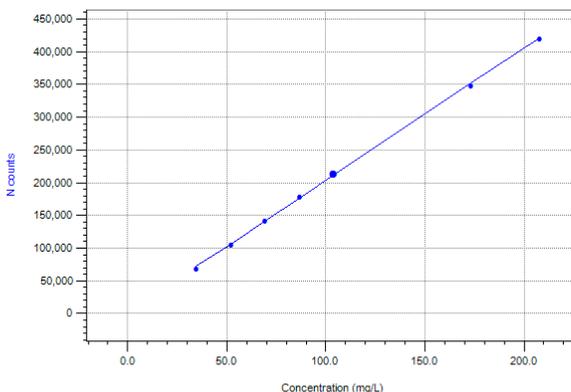
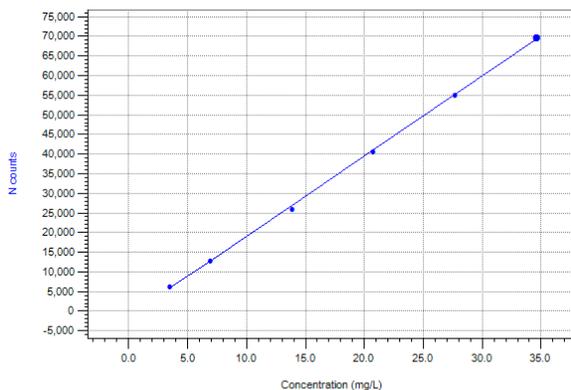
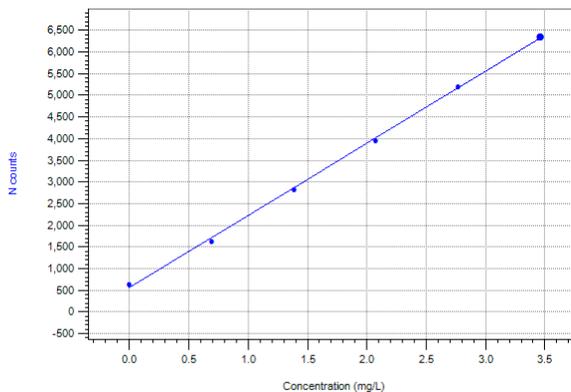


Figure 1: Recommended calibration ranges of DIN 51444

LIMIT OF DETECTION

The new ElemeNtS software has an integrated LOD calculation according to ISO-11843 helping to determine the performance of the ElemeNtS instrument. The statistical tab shows detailed information used to calculate the limit of detection and a graphical overview of the residuals. The residuals are calculated relative to the best fit correlation as displayed in the calibration tab.

The LOD calculation of ISO 11843 is always based of a particular calibration. The ElemeNtS can reach a LOD as low as 30 ppb for Nitrogen, based on a 0-1 ppm calibration. The LOD based on this particular 0-5 mg/kg calibration is 133 ppb.

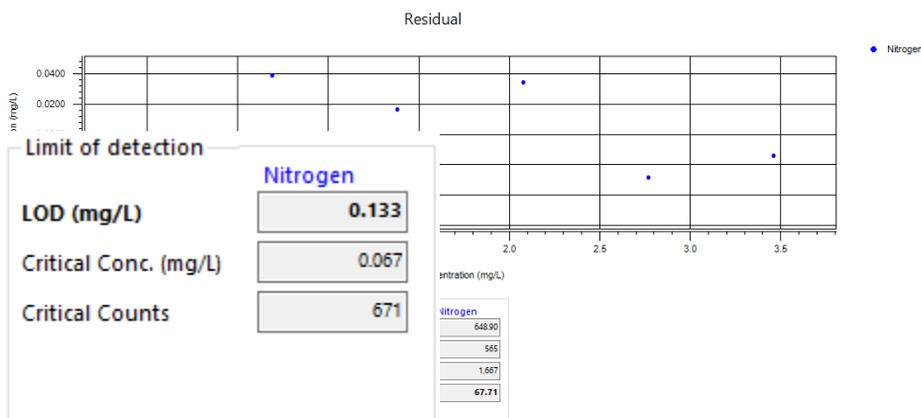


Figure 2: Calculation of LOD according to ISO-11843

PRECISION

Different types of samples were selected to cover the scope of the method. Each sample is measured three times to obtain one result. The resulting area is calculated to a corresponding concentration using the applicable calibration line. The results are compared to the consensus values obtained during a Proficiency Testing Program (PTP), giving an indication of the precision. All the results were within the DIN 51444 reproducibility limits.

Table 2: Overview of sample results, compared with PTP values and DIN 51444 precision data.

Results recovery / bias DIN 51444					
Sample name	Part #	Target concentration (ppm)	Result concentration (ppm)	Difference	DIN 51444 R/√2
Gasoline BOB	00.02.734	1,29	1,39	0,10	0,35
Gasoline Enhanced	00.02.733	1,35	1,10	0,25	0,35
Diesel B7	00.02.735	39,9	40,9	1,0	13,2
Heating Oil	00.02.737	55,6	55,3	0,3	18,2

REPEATABILITY

Area (concentration) is the primary measurement in total Nitrogen analysis. The precision in which it is measured ultimately determines the validity of the generated quantitative data. Area precision requires that all parameters (temperatures, pressure, flow, injection) are controlled to exact tolerances. Furthermore, the inertness of the flow path can considerably affect area precision, especially for active Nitrogen components at low levels.

Concentration repeatability for the ElementS total Nitrogen analyzer is measured for 10 consecutive runs for three gravimetrically prepared samples. Repeatability standard deviation of total Nitrogen is well within the precision statement of DIN 51444.

Table 3: Repeatability values of four samples

Repeatability Nitrogen DIN 51444				
Run	Gasoline BOB	Gasoline Enhanced	Diesel B7	Heating Oil
1	1,44	1,12	40,9	55,1
2	1,53	1,15	40,2	55,3
3	1,39	1,08	40,7	55,5
4	1,39	1,04	41,2	55,5
5	1,40	1,10	41,0	55,4
6	1,34	1,10	40,9	55,5
7	1,39	1,16	40,8	55,3
8	1,34	1,12	40,9	55,2
9	1,37	1,07	40,9	55,4
10	1,35	1,10	41,2	55,3
Average	1,39	1,10	40,9	55,3
Standard deviation (SD)				
Measurement	0,056	0,037	0,273	0,133
Method SD (r DIN/2.77)	0,108	0,108	0,444	0,617
Relative standard deviation (RSD)				
Measurement	4,02%	3,31%	0,67%	0,24%
Method RSD (r DIN/2.77)	7,77%	9,82%	1,09%	1,12%

CONCLUSION

These results demonstrate that the ElementS analyzer is a powerful tool for the determination of bound Nitrogen in petroleum products, like gasoline, diesel and heating oil, based on the exceptional calibration linearity, low limit of detection, excellent repeatability and precision.

The **Antek ElementS** total Nitrogen analyzer is meeting the DIN 51444 requirements.

Antek's lab instruments provide reliable, precise elemental analysis for total Nitrogen and Sulfur, speciated Nitrogen and Sulfur, Fluoride, Chloride, and Bromide. Antek products are recognized by global regulating bodies, leading scientific research institutions, and process laboratories as the instrument of choice for selective multi-element detection.