PAC | Application Note

Trace Nitrogen in Liquid Petroleum Hydrocarbons by Syringe/Inlet Oxidative Combustion and Chemiluminescence Detection according to ASTM D4629.

- Rapid and Accurate Determination of Chemically bound Nitrogen
- Fully Automated Injection and Combustion system
- Excellent Sensitivity, Repeatability & Linearity

Keywords: ASTM D4629, ElemeNtS, Nitrogen, Chemiluminescence

INTRODUCTION

ASTM D4629 covers the determination of the trace total nitrogen naturally found in liquid hydrocarbons containing 0.3 to 100 mg/kg total nitrogen, boiling in the range from approximately 50 to 400 °C and with viscosities between approximately 0.2 and 10 cSt (mm2/s) at room temperature This test method is applicable to naphtha's, distillates, and oils.

ASTM D4629 is the preferred method for the quantification of trace nitrogen in hydrocarbon samples like feedstock, intermediate streams and finished hydrocarbon products due to its sensitivity, linearity, dynamic range and ruggedness. Since nitrogen is an ubiquitous element in hydrocarbon streams responsible for many undesirable effects like catalyst poisoning, detrimental product quality and ecosystem pollution, there is a need to quantify and monitor its content in every step of the industry´s technical operations.

MEASURING PRINCIPLE

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

$$R - N + O_2 \xrightarrow{1050°C} CO_2 + NO + H_2O$$

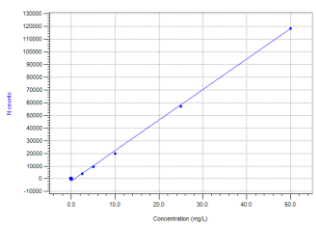
A stream of inert gas (helium or argon) is taking the reaction products, after removal of the produced water vapor, into a reaction chamber. Here, under reduced pressure (using a build-in vacuum pump) the NO molecules are converted to excited NO_2^* by adding Ozone and emitting light (chemiluminescence) while it relaxes to a stable state.

$$NO + O_3 \rightarrow NO_2^* + O_2$$

$$NO_2^* \rightarrow NO_2 + hv$$

A Photomultiplier tube measures the emitted light signal.

The response signal is integrated to calculate the area. The sulfur 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, sample scope, recovery and repeatability.

CALIBRATION

Calibration curves are composed using Pyridine in i-octane standards. Each calibration solution and blank (i-octane) is measured three times to determine the average net response for each. A calibration curve is constructed by the ElemeNtS software. The response curve meets the requirement of a minimum R^2 of 0,999. The intercept should not be forced through zero. The full range (0 – 100 mg/L) calibration curve is displayed in Figure 1.

Concentration mg/L	Avg Area Counts
0	146
0.25	549
0.5	1025
0.75	1402
1	1952
2.5	4700
5	9879
10	20144
25	54831
50	109395
100	214414

Table 1: Response values

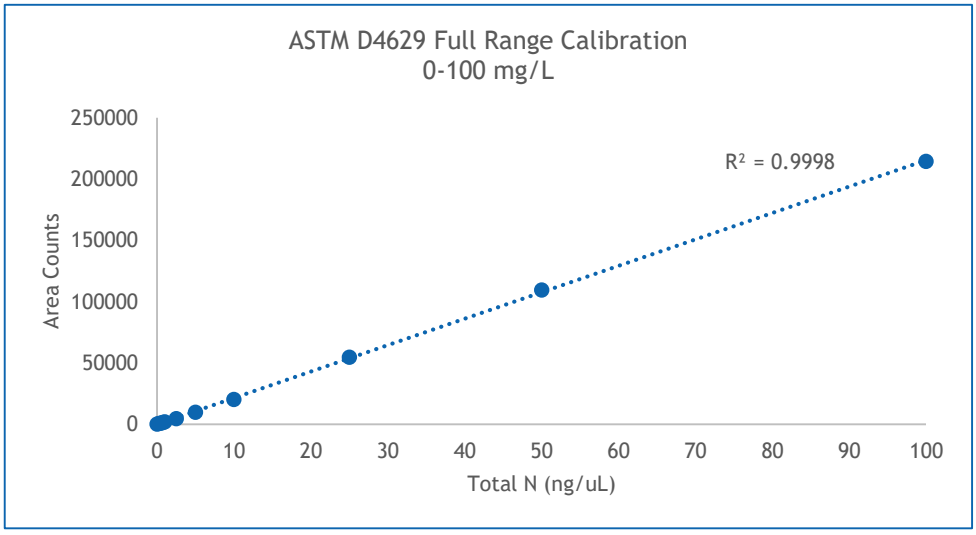


Figure 1: Calibration curve covering full range of ASTM 4629

SAMPLE SCOPE

Different types of samples were selected to cover the whole boiling point range of the scope of the method (Gasoline BOB, Gasoline Enhanced/Premium, Gasoline E85, Diesel B7, Jetfuel, heating oil). To obtain one result, each sample is measured three times, and the average detector response is calculated. The results are compared with the consensus values obtained during a Proficiency Testing Program (PTP). All sample results are within the ASTM D4629 precision limits for the corresponding consensus target values (table 2).

AC part #	Type	PTP mean mg/kg	Result (mg/kg)	Delta	D4629 R/√2
00.02.729	Diesel B7	62	58	4	5
00.02.730	E85	n.a.	2.4		
00.02.732	Jetfuel	n.a.	7.8		
00.02.733	Gasoline enhanced	1.4	1.3	0.1	0.7
00.02.734	Gasoline BOB	1.3	1.8	0.5	0.7
00.02.735	Diesel B7	40	38	2	4
00.02.736	Jetfuel	n.a.	3.0		
00.02.737	Heating oil	56	54	2	5

Table 2: Overview of sample results, compared with consensus values of PTP (if applicable)

REPEATABILITY

Area is the primary measurement in total nitrogen analysis. The precision in which it is measured ultimately determines the precision of the generated quantitative data. Area precision require that all parameters (temperatures, pressure, flow, injection) are controlled to exacting 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 on three QC reference samples. Repeatability standard deviation of Total nitrogen is well within the precision statement of ASTM D4629.

Run	Sample 00.02.733 Gasoline	Sample 00.02.732 Jetfuel	Sample 00.02.737 Heating oil
	mg/kg N	mg/kg N	mg/kg N
1	1.37	7.79	54.3
2	1.33	7.77	54.2
3	1.32	7.76	54.3
4	1.34	7.76	54.3
5	1.30	7.77	54.1
6	1.33	7.77	54.1
7	1.30	7.75	54.1
8	1.32	7.77	54.0
9	1.33	7.69	54.0
10	1.30	7.59	53.9
Average	**1.33**	**7.74**	**54.1**
Standard deviation (SD)			
Measurement	0.021	0.0586	0.1401
Method SD (r_{D4629}/2.77)	0.08	0.19	0.51
Relative standard deviation (RSD)			
Measurement	1.59%	0.76%	0.26%
(r_{D4629}/2.77)	5.75%	2.44%	0.95%

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CONCLUSION

These results demonstrate that the analyzer is a powerful tool for the determination of nitrogen in Liquid Petroleum Hydrocarbons, like Spark Ignition Engine Fuel, Diesel Engine Fuel, and Jetfuel, based on the exceptional calibration linearity, low limit of detection, excellent repeatability and recovery.
The **Antek ElemeNtS** total Nitrogen analyzer is meeting the ASTM D4629 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.