

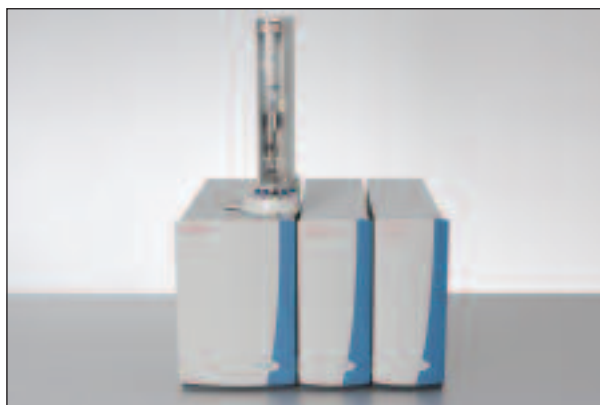
Total Nitrogen analysis in Aromatic Hydrocarbons according ASTM D4629

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Key Words

- TITAN 4000
- ASTM D4629
- Hydrocarbons
- Liquid Petroleum
- Nitrogen

Introduction



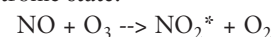
Nitrogen plays an important part in the manufacturing of chemicals and petrochemicals, and knowledge of nitrogen content in petrochemical processes is essential for adherence to stringent pollution laws. Nitrogen content has also been found to be detrimental to the effectiveness of catalysts and shortens their lifespan (adding cost to plan operations). This causes problems for many petrochemical plants which have moved into the production of light products whereby catalysts play an important role in those processes. Aromatics and olefins are particularly susceptible to nitrogen effects when they are saturated by a hydro-treating process.

This application note describes the principle of operation and performance of the Thermo Scientific TITAN 4000 Total Nitrogen configuration for the determination of Total Nitrogen in liquid petroleum hydrocarbons according to ASTM D4629 methodology.

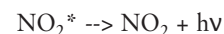
Principle of operation

The TITAN 4000™ Total Nitrogen Analyzer incorporates a Thermo Scientific AI3000 auto sampler for direct liquid injection. An automatic syringe pump is used for precise sample withdrawal and introduction into the injection port. The regulated injection speed ensures complete combustion and superb reproducibility of results. The TITAN 4000 is also fitted with a vertical, patent-pending, folded turbo combustion tube which provides excellent mixing of the sample with oxygen whilst making the TITAN 4000 the smallest bench-top element analyzer in the market place. The combustion process only requires oxygen, making an additional inert gas flow like Argon redundant. Minimum dead volumes and the unique plug-flow principle ensure very short sample resident times resulting in an analysis time of less than two minutes.

To eliminate water effects on the operation of the detectors, a two staged Perma Pure™ dryer is placed between the outlet of the furnace and the remainder of the flow path to the Nitrogen detector. After the combustion stage, the formed NO_x compounds are swept to the detector where it meets a stream of ozone to form NO₂ in an excited electronic state:



Which rapidly returns to ground state, emitting a photon through chemiluminescence:



A PMT detector measures the light intensity and converts it electronically (with reference to stored calibration information) to display the analytical result as a mass of nitrogen or as nitrogen concentration in the sample.

Analysis

The TITAN 4000 was calibrated using a set of pyridine standards solved in xylene. The following standards were prepared: blank, 0.5, 1, 2.5, 5, 10, 25 and 50 mg N/L.

The system settings selected to run this application are shown in table 1.

Parameter	Setting
Injection temperature	70 °C
Furnace 1 temperature	1000 °C
Furnace 2 temperature	1000 °C
Injection speed	1 uL/sec
Injection volume	25 uL
Gasflow oxygen	900 mL/min

Table 1: System settings



Figure 1 shows the calibration line of pyridine standards with concentrations of 0.5 up to 50 ppm. The calibration line shows a good regression.

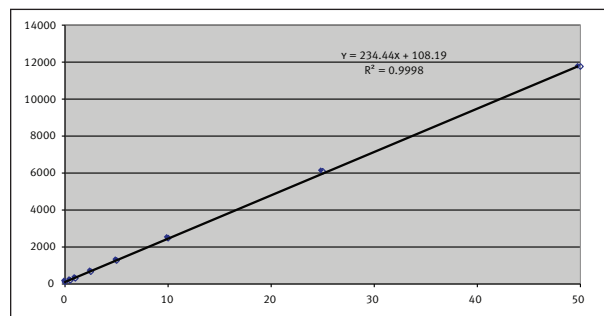


Figure 1: Calibration line 0 – 50 ppm TN

Results

Sample	TN (mg/L)	RSD (%)
Gasoline	2.8	2.4
Gasoil	4.6	0.9
Mineral Oil 1	28.1	0.9
Mineral Oil 2*	540	0.6
Ethanol	1.89	4.2
Cyclo-hexane	1.17	1.5

N = 3

Table 2: Total Nitrogen test results for TITAN 4000

Wherein:

TN = Total Nitrogen concentration determined by TITAN 4000 in mg/L

RSD = relative standard deviation in %

* = 15 times diluted

The example of measurement peaks are displayed in figure 2, which shows for the four analysis repeats of the calibration standards with analytical times of less than two minutes.

Conclusion

The test results obtained with the analysis of a set of practical samples shows a good repeatability and in compliance with ASTM D4629 methodology.

Additionally, the new injection and combustion techniques on the TITAN 4000, combined with chemiluminescence detection, results in analysis times of less than two minutes.

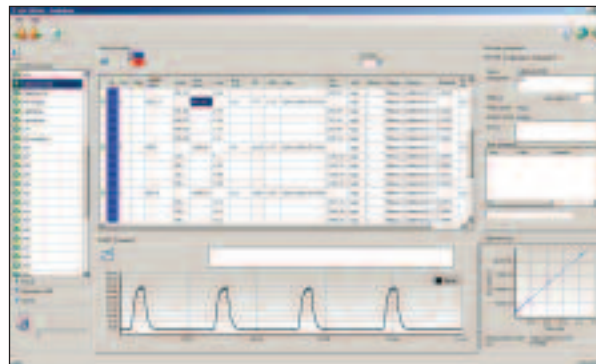


Figure 2: Example of NSX VISUAL software with TN calibration plot. Shows analysis times of less than two minutes.

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