PAC | Application Note

Ultra low Nitrogen in Aromatic Hydrocarbons by Oxidative Combustion and Reduced Pressure Chemiluminescence detection according to ASTM D7184.

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

Keywords: ASTM D7184, ElemeNtS, Aromatic hydrocarbons, Nitrogen, Chemiluminescence, reduced pressure

INTRODUCTION

ASTM D7184 covers the determination of ultra low level total nitrogen in aromatic hydrocarbons, such as benzene, toluene and xylene. This test method is applicable for samples containing nitrogen from 0.1 to 1.2 mg/kg.

ASTM D7184 is the preferred method to detect and quantify nitrogen-containing compounds in light aromatic hydrocarbons used or produced in manufacturing process. These nitrogen-containing compounds are undesirable in finished aromatic products.

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 an aromatic hydrocarbon 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.

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

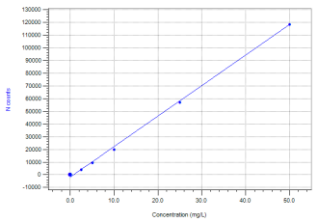
A stream of inert gas (helium or argon) is taking the reaction products, after removal of the produced water vapor, into a reaction chamber. Here, under reduced pressure (using a build-in vacuum pump) the NO molecules are converted to excited NO_2^* by adding ozone and emitting light (chemiluminescence) 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 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, sample scope, level of detection (LOD), recovery and repeatability, to validate its performance according to ASTM D7184.

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. A calibration curve is constructed by the ElemeNtS software based on the four gravimetrically prepared standards (0,05, 0,10, 0,5 and 1,0 mg/L) and blank. The response curve meets the requirement of a minimum R2 of 0,99. The calibration curve is displayed in Figure 1.

Table 1: Response values

Concentration mg/L	Avg Area counts
0.00	136.0
0.05	219.9
0.10	299.8
0.50	1008.5
1.00	1928.3

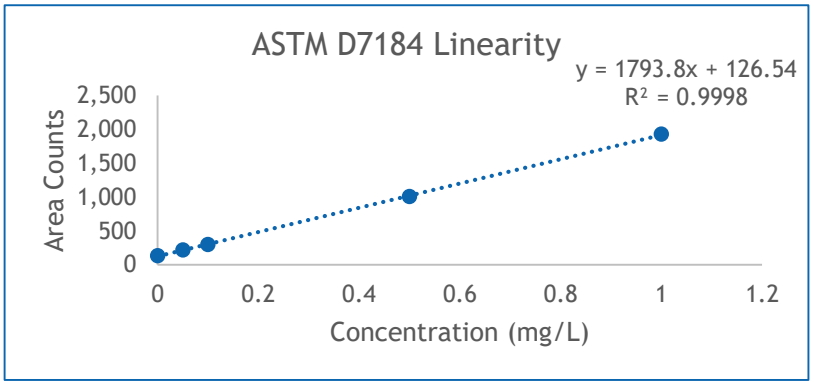


Figure 1: Full range Calibration curve covering total range of ASTM D7184

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.

In case a linear model is selected, we can conclude that for the selected range the response of the ElemeNtS instrument is linear when residuals are evenly distributed over the complete range. In accordance to ISO-11843 a good fit of the model and low RSD's will result in a low calculated limit of detection.

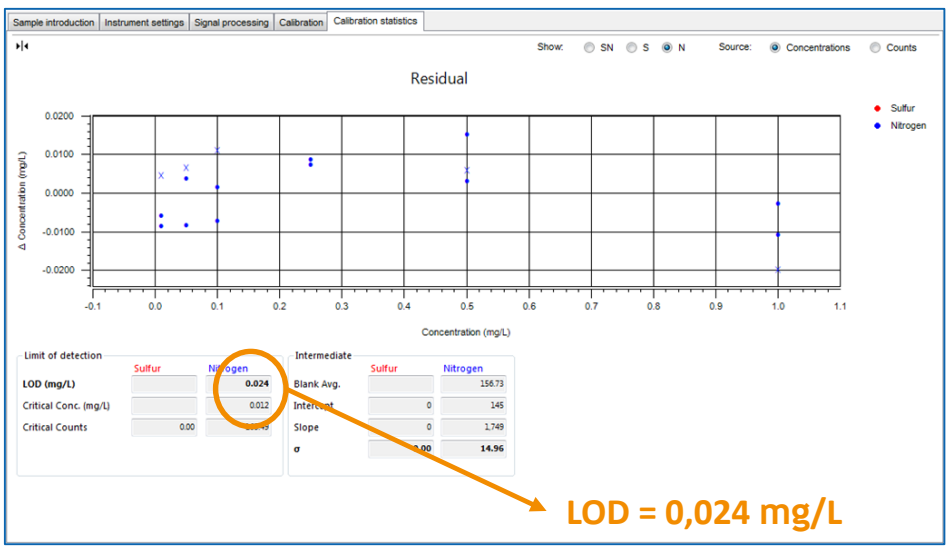


Figure 2: Calculation of LOD according to ISO-11843

SAMPLE SCOPE

Different types of samples were selected to cover the scope of the method (benzene, toluene, xylene's). The blank solvents were spiked with nitrogen containing components to the desired concentration. To obtain one result, each sample is measured three times, and the average detector response is calculated. The results are compared with the gravimetric data of the preparation of the samples. All sample results are within the ASTM D7184 specification limits for the corresponding gravimetric prepared values (table 2). Note: The available benzene standard already contains ~0,5 mg/L total nitrogen.

Table 2: Overview of sample results, compared with gravimetric prepared values and ASTM D7184 precision data.

	D7184			Prepared value	Determined value	Blank corrected value	RSD
	R	LSL	USL	mg/L	mg/L	mg/L	N=3
Blank p-Xylene				0.00	0.00	n.a.	
p-Xylene + 0.25 mg/L	0.23	0.13	0.45	0.29	0.30	0.30	5.5%
p-Xylene + 0.75 mg/L	0.25	0.64	0.99	0.81	0.89	0.89	0.4%
Toluene blank				0.00	0.01	n.a.	
Toluene + 0.10 mg/L	0.24	0.00	0.27	0.10	0.11	0.10	3.9%
Toluene + 0.25 mg/L	0.24	0.10	0.44	0,27	0.25	0.24	1.5%
Toluene + 0.75 mg/L	0.24	0.62	0.98	0.79	0.74	0.73	2.9%
Blank benzene				0.00	0.54	n.a.	
Benzene + 1.0 mg/L	0.28	0.81	1.21	1.01	1.65	1.11	1.0%

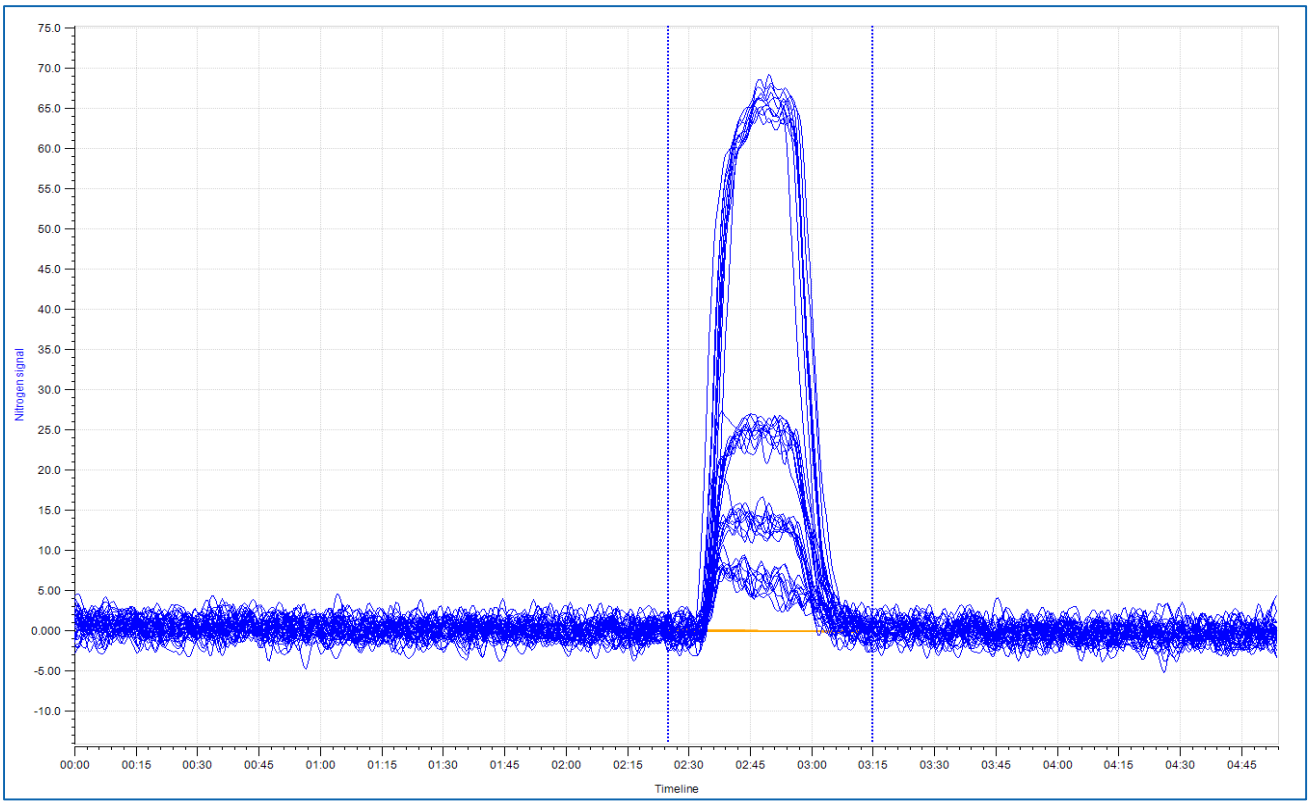


Figure 3: Overlay Blank Toluene spiked with ~0.10; ~0.25 and 0.75 mg/L (n=10)

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 ASTM D7184.

Table 3: Repeatability values of three different gravimetric reference samples compared with precision statement of ASTM D7184.

Run	Toluene (mg/L)	p-Xylene (mg/L)	p-Xylene (mg/L)
1	0.11	0.31	0.93
2	0,11	0.34	0.92
3	0.10	0.32	0.93
4	0.11	0.32	0.91
5	0.13	0.32	0.92
6	0.13	0.29	0.91
7	0.11	0.32	0.92
8	0.11	0.31	0.90
9	0.11	0.30	0.90
10	0.11	0.32	0.89
Average	0.11	0.32	0.91
Standard deviation (SD)			
Measurement	0.0065	0.0125	0.0139
Method SD ($r_{D7184}/2.77$)	0.0397	0.0542	0.0578
Relative standard deviation (RSD %)			
Measurement	5.9	3.9	1.5
Method RSD ($r_{D7184}/2.77$)/mean	36.1	16.9	6.4

CONCLUSION

These results demonstrate that the ElemeNtS analyzer is a powerful tool for the determination of ultra low nitrogen in aromatic hydrocarbons, like benzene, toluene and xylene, based on the exceptional calibration linearity, low limit of detection, excellent repeatability and recovery.
The **Antek ElemeNtS** total nitrogen analyzer is meeting the ASTM D7184 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.