APPLICATION NOTE

MultiTek® Trace Nitrogen in Liquid Aromatic Samples by Chemiluminescence - ASTM D6069 & D7184

- **Automatic and Accurate Determination of Trace levels of Nitrogen**
- **Excellent Linearity, Sensitivity and Repeatability**
- **Comparative Study of Reduced Pressure and Atmospheric Pressure Conditions**

Keywords:
MultiTek®, Trace Nitrogen, Combustion Analysis, Chemiluminescence, Ozone

INTRODUCTION

The analysis of total trace nitrogen in organic solvents can be utilized in the refining industry for product quality control and to prevent corrosion and deactivation of catalysts of processes like reforming, isomerization and hydrogenation. The amount of nitrogen has been determined according to the ASTM standards D6069 and D7184.

The principle of operation for nitrogen analysis begins with the complete, oxidative combustion of the entire sample matrix. The sample is combusted with excess oxygen at a temperature of 1050°C.

$$R\text{-}N + O_2 \xrightarrow{1050^\circ C} CO_2 + H_2O + NO + MO_x \quad (1)$$

The combustion gases are routed through a membrane drying system to remove the water and then to the nitrogen detector module for quantitation.

Nitric oxide is reacted with ozone, produced by an onboard ozone generator, to form NO_2^* excited according to the first reaction (2). As the excited species relaxes to its ground state, light is emitted at a broad band of wavelengths in the red and NIR as per second reaction (2). Emitted energy is proportional to the amount of nitrogen in the sample and is detected by a photomultiplier tube (PMT). This ozone induced chemiluminescence is an equimolar process, characterized by a linear response and a large dynamic range higher than 10^3.

$$NO + O_3 \longrightarrow NO_2^* + O_2 \longrightarrow NO_2 + h\nu + O_2 \quad (2)$$

EXPERIMENTAL CONDITIONS

▪ **Instrumentation**

Antek MultiTek® Vertical Nitrogen analyzer, liquid autosampler and trace nitrogen kit.

▪ **Instrument Parameters**

Sample Volume (µL)	20
GFC 1- Ar carrier (ml/min)	130
GFC 2- Pyro O_2 (ml/min)	450
GFC 3- Ozone O_2 (ml/min)	35
GFC 4- Carrier O_2 (ml/min)	25
N detector Temperature (°C)	5
Furnace (ºC)	1050
Nitrogen PMT voltage (V)	700

Two calibrations were performed from 0 - 1 and 0 - 2 mg/Kg at reduced pressure. For comparative purposes, the same analysis was performed only with the difference that the vacuum pump, restrictor and needle valve were removed maintaining the same instrumental parameters listed above.

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- ■ **Sample Results**

Table 1 below compares the results of aromatic samples at normal and reduced pressures. Two QC samples were included as a mean to establish the validity of the results.

Aromatic Hydrocarbons	D7184	Ambient
Sample ID	N mg/Kg	N mg/Kg
A	0.291	0.289
B	1.094	1.178
C	0.9	0.865
D	0.467	0.494
QC(0.6ppm)	0.547	0.597
QC(0.060 mg/Kg)	0.054	

Table 1. Samples results (n=5)

- ■ **Calibration Curve**

Calibration was performed with toluene standards with acridine as per ASTM D7184 as shown below.
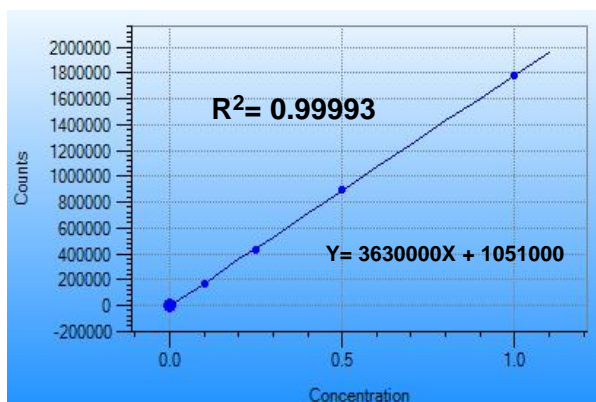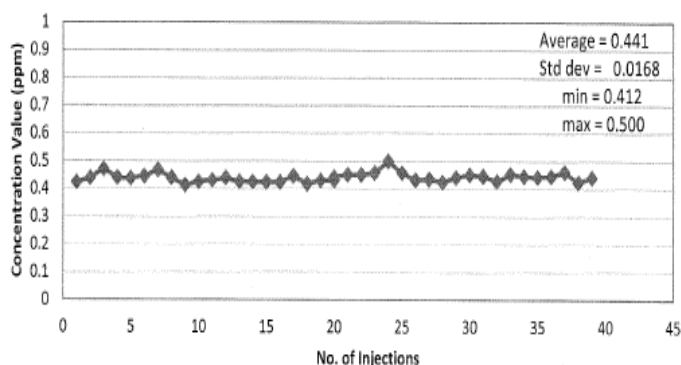

R^2= 0.99993

Y= 3630000X + 1051000

Figure 1. Calibration Results for Nitrogen

- ■ **Stability Test**

The N detector stability was determined over 40 consecutive injections of a ASTM ILS sample. Figure 2 below shows the stability results as well as the statistic for the experiment.
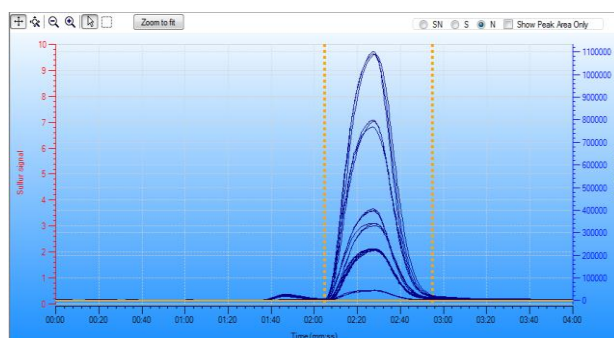

Average = 0.441
Std dev = 0.0168
min = 0.412
max = 0.500

- ■ **LOD Results**

$Y= \mu_D + K_D\sigma_b$		
Y=	1128202	
Y = mx + b =	1128202	
m=	3630000	
b =	1051000	
X =	0.02127	ppm
	21.27	ppb

- ■ **Experimental samples**

The results in figure 2 show complete stability by overlaying the five consecutive injections of each of the aromatic streams analyzed.

Figure 2. Nitrogen distribution of 8 samples of Benzene, Toluene and Xylenes analyzed by ASTM D7184

CONCLUSION

The MultiTek® Analyzer demonstrates the ability to accurately determine the total trace nitrogen content in organic solvents and organic compounds in general. The analysis allows the user to monitor the feeds and products of catalytic refining processes to assist the engineers in preserving installations and catalysts as well as to determine the quality of final products. LOD values were determined at 21.3 ppb at 3σ signal to noise ratio. Results show excellent stability and no major differences in the experimental reaction chamber total pressure.

The Antek MultiTek® is the only instrument on the market that combines sulfur, nitrogen, and halides analysis all in one. Compact, powerful, automated, and able to analyze gas, liquid, or solid samples, it's the perfect solution to today's increasing demand worldwide for fast, accurate detection and analysis of contaminants, and corrosive elements. Because MultiTek® delivers precise results with high sensitivity and unmatched versatility, it's a valuable process optimization tool that will deliver faster ROI and a better bottom line.

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