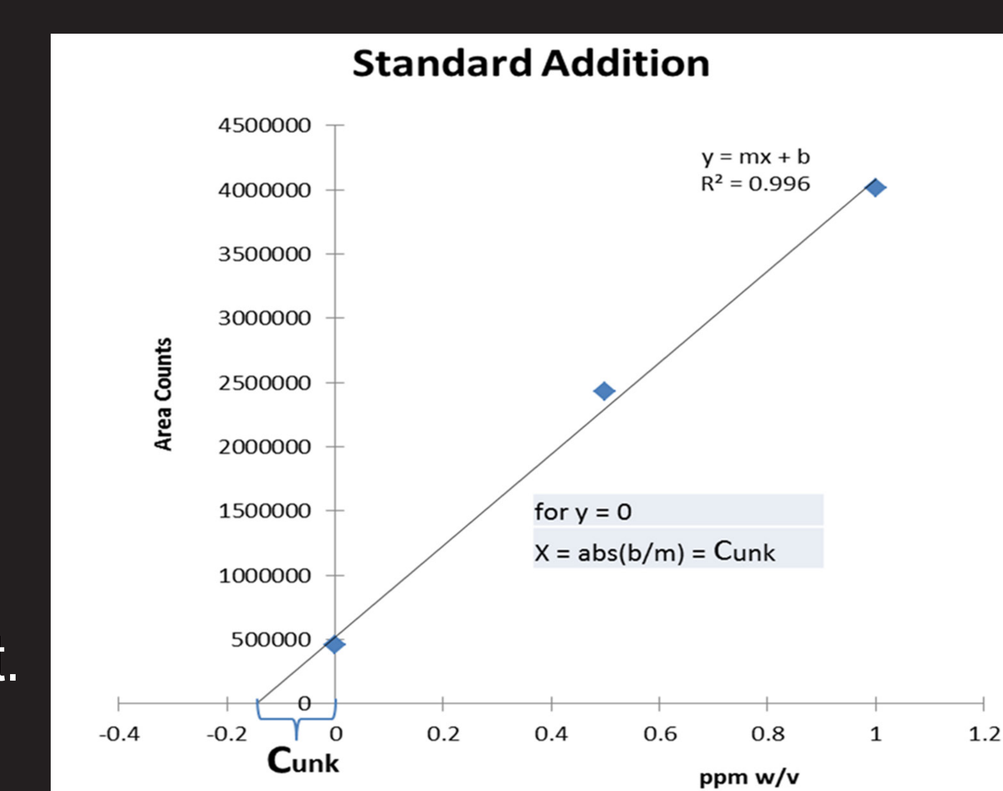
Trace Nitrogen Applications in Catalytic Naphtha and Feed Stocks by Combustion and Chemiluminescence Analysis

By Aaron Mendez Ph.D. and Lisa Houston - PAC L.P.

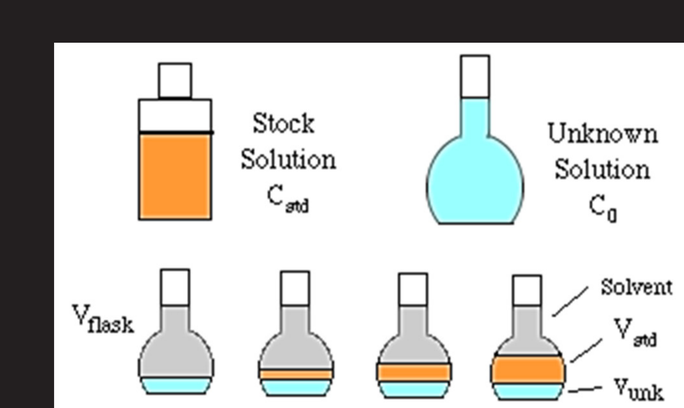
Introduction

The total nitrogen in naphtha range samples and other trace nitrogen containing liquid hydrocarbons can be determined by four different ASTM standard methods: ASTM D4629, D5762, D6069 and D7184.

D4629 and D5762 are performed at atmospheric pressure. ASTM D6069 and D7184 are performed under reduced pressure and, as such, require a trace nitrogen kit comprised of a vacuum pump, a needle valve for pressure control and a restrictor to regulate the ozone concentration in the reaction chamber that would affect the sensitivity of the measurement. This application utilizes the Standard Addition Method, which has following characteristics:



- Need to eliminate matrices effects
- No need for calibration
- No need for real blanks
- Needs linearity response of detector
- Can reach very low LOD's



Experimental

Standard addition method ,also known as spiking, is used in very complex mixtures. It is an attempt to make corrections for uncontrollable random errors caused by other components in the analytical system. Changes in instrument response are only due to changes in the analyte concentration.

- The sample is splt in several aliquots of the same volume stock standard solution of known concentration is added in increasing volumes to the subsequent flasks or aliquots. The instrument response is measured for all the solutions and the data is plotted with volume standard added vs. Instrument response.
- Linear regression will produce the slope and offset of the calibration curve.
- Conceptually for y=0 which is for zero amount of standard added the amount of the sample would be the ratio of b/m

$$R\text{-}N + O_2 \longrightarrow CO_2 + H_2O + NO + MOx \quad (1)$$

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

$$NO_2^* \longrightarrow NO_2 + h\upsilon \quad (3)$$

Instrumentation

Antek MultiTek® Vertical configuration with nitrogen detection and liquid autosampler.

Instrument Parameters:

Sample Volume (µL)	20
GFC 1- Ar carrier (ml/min)	130
GFC 2- Pyro O2 (ml/min)	450
GFC 3- Ozone O2 (ml/min)	35
GFC 4- Carrier O2 (ml/min)	25
GFC 5- Auxiliary O2 (ml/min)	25
Furnace (°C)	1050
Nitrogen PMT voltage (V)	700

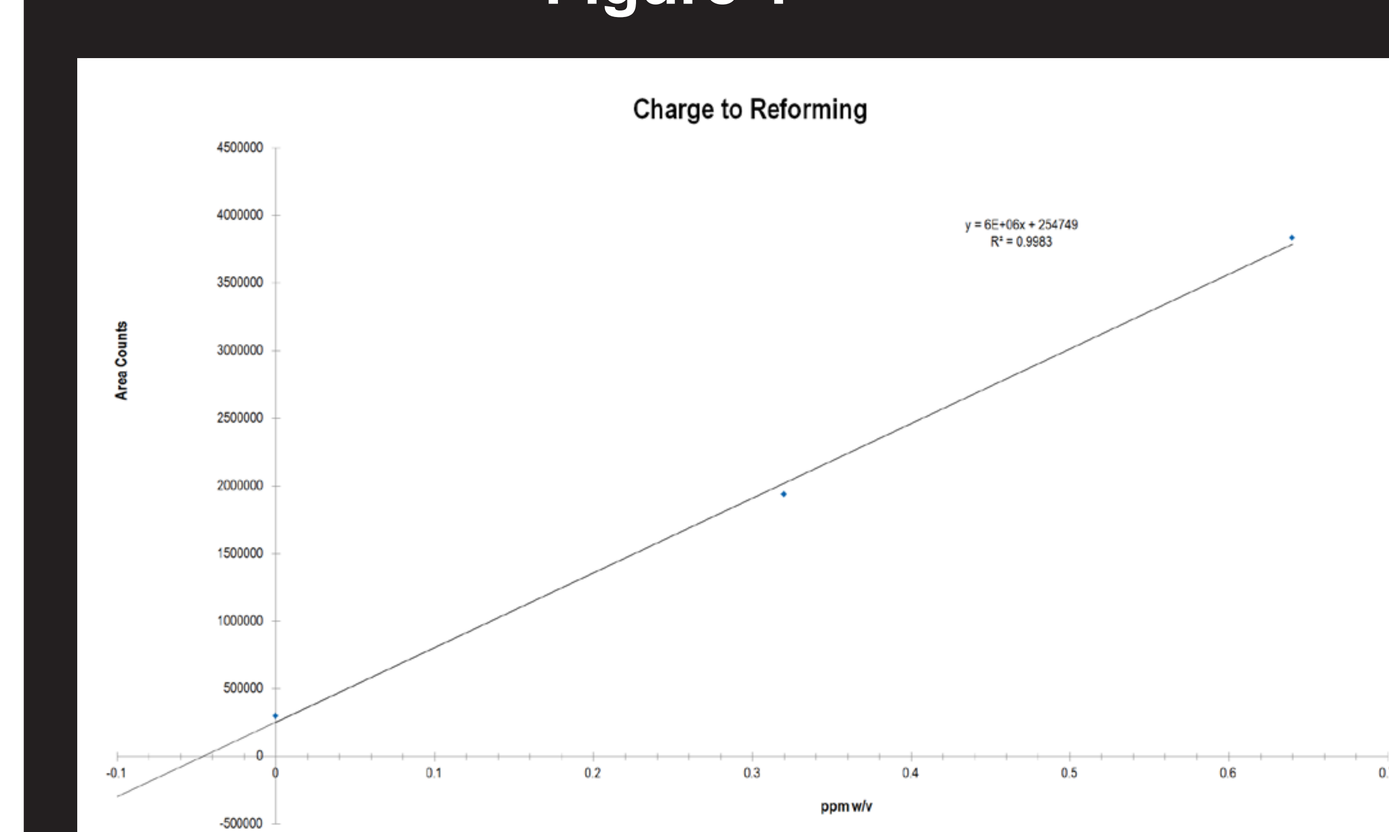
Discussion

Figures 1 and 2 show the trace N results for charge and product of naphtha reforming by standard addition. In order to validate the method, a reformate feed and a sweet naphtha, shown in Figures 3 and 4, were analyzed by the conventional method utilizing the calibration represented in Figure 5. As it can be seen the values obtained correspond exactly to those from the standard addition method. The table shown in Figure 5 displays an excellent agreement between the two methods.

Figure 6 shows the simultaneous analysis for S and N in one ASTM D7184 ILS sample.

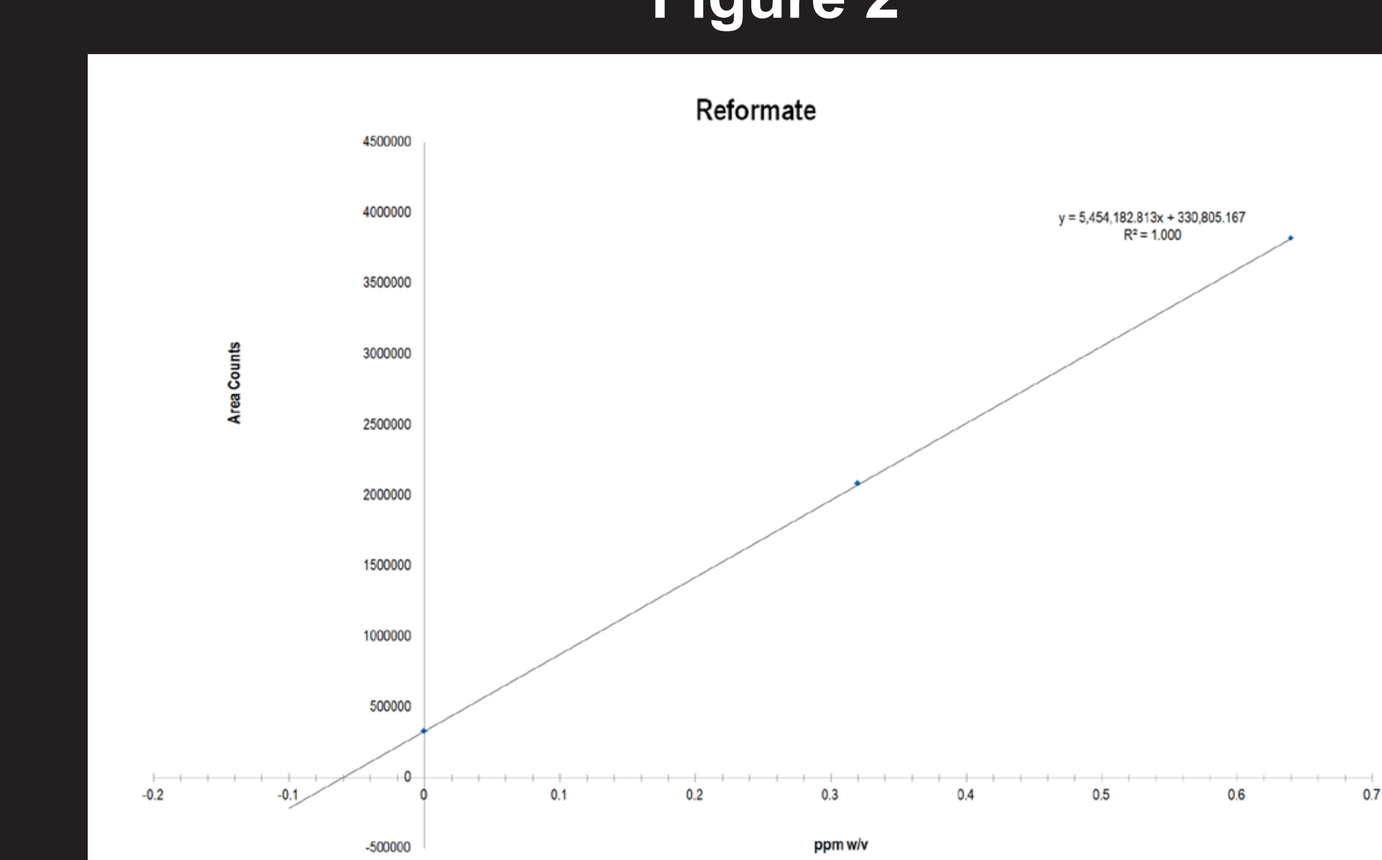
Experimental Results

Figure 1



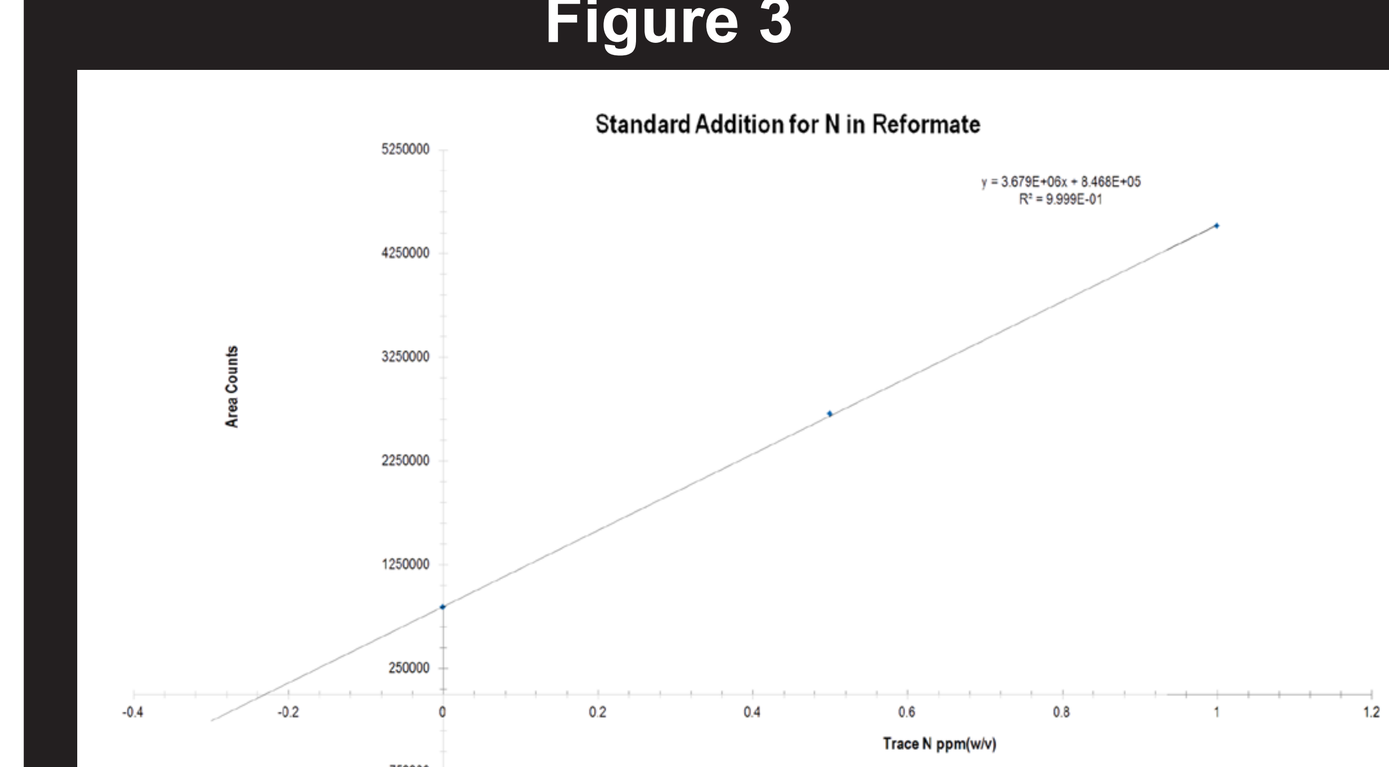
SLOPE =	5521053.1
INTERCEPT =	254748.7
Cunk(ppm) =	0.046

Figure 2



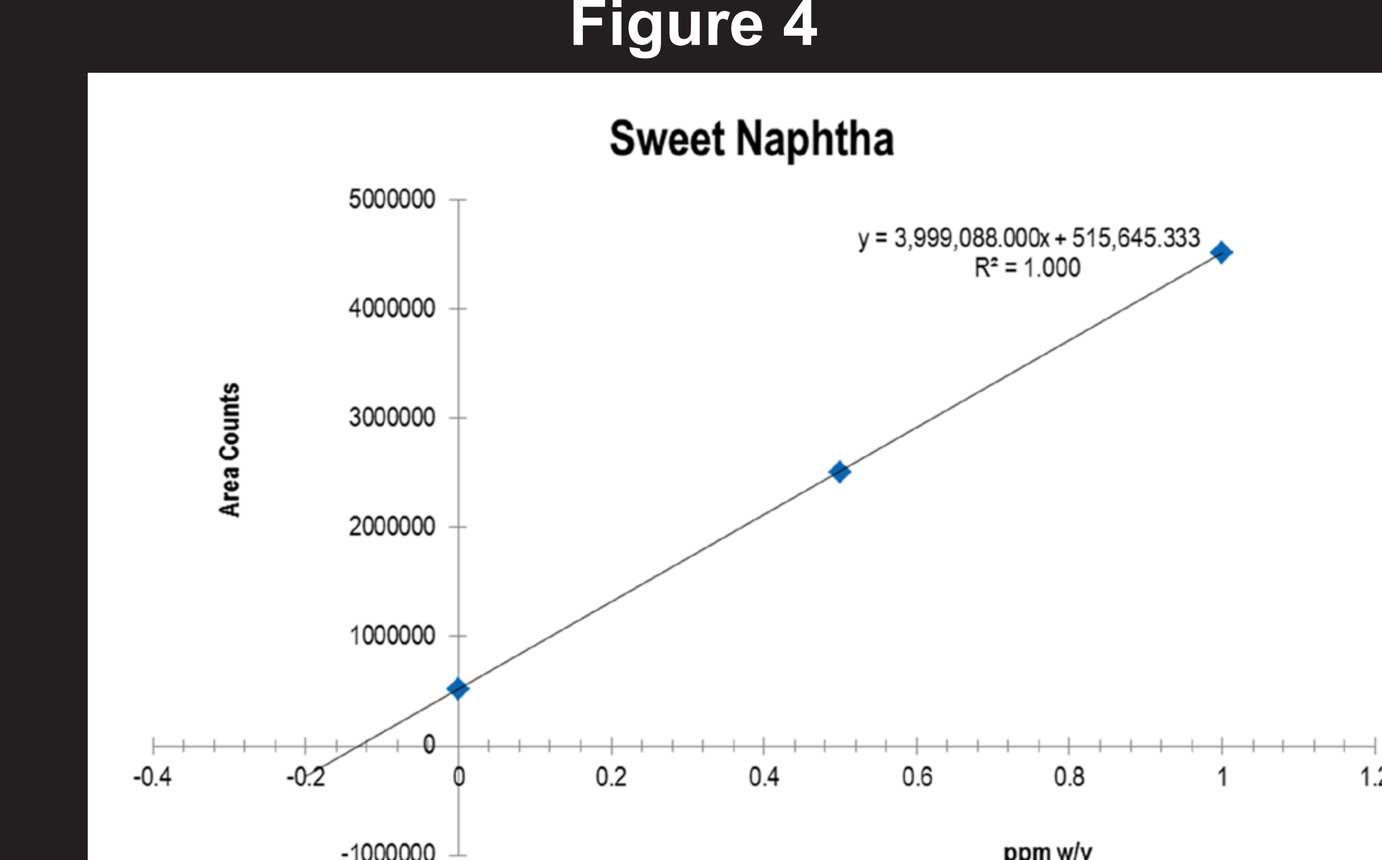
SLOPE =	5454182.8
INTERCEPT =	330805.1667
Cunk(ppm) =	0.061

Figure 3



SLOPE =	3678571
INTERCEPT =	846774.8
Cunk(ppm) =	0.230

Figure 4



SLOPE =	3999088
INTERCEPT =	515645.33
Cunk(ppm) =	0.129

Experimental Results

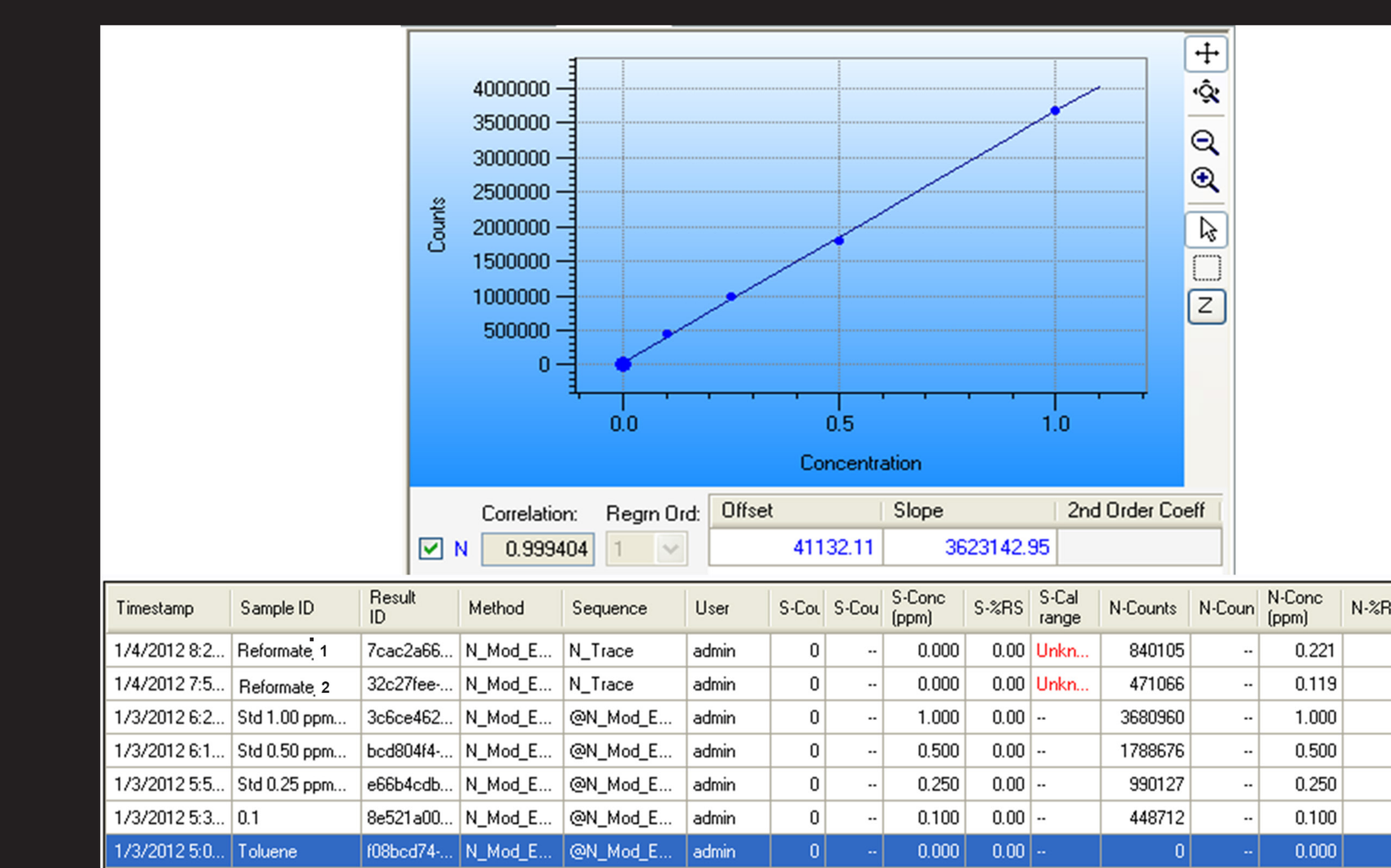


Figure 5: Trace Level Nitrogen by Multipoint Calibration

Experimental Results

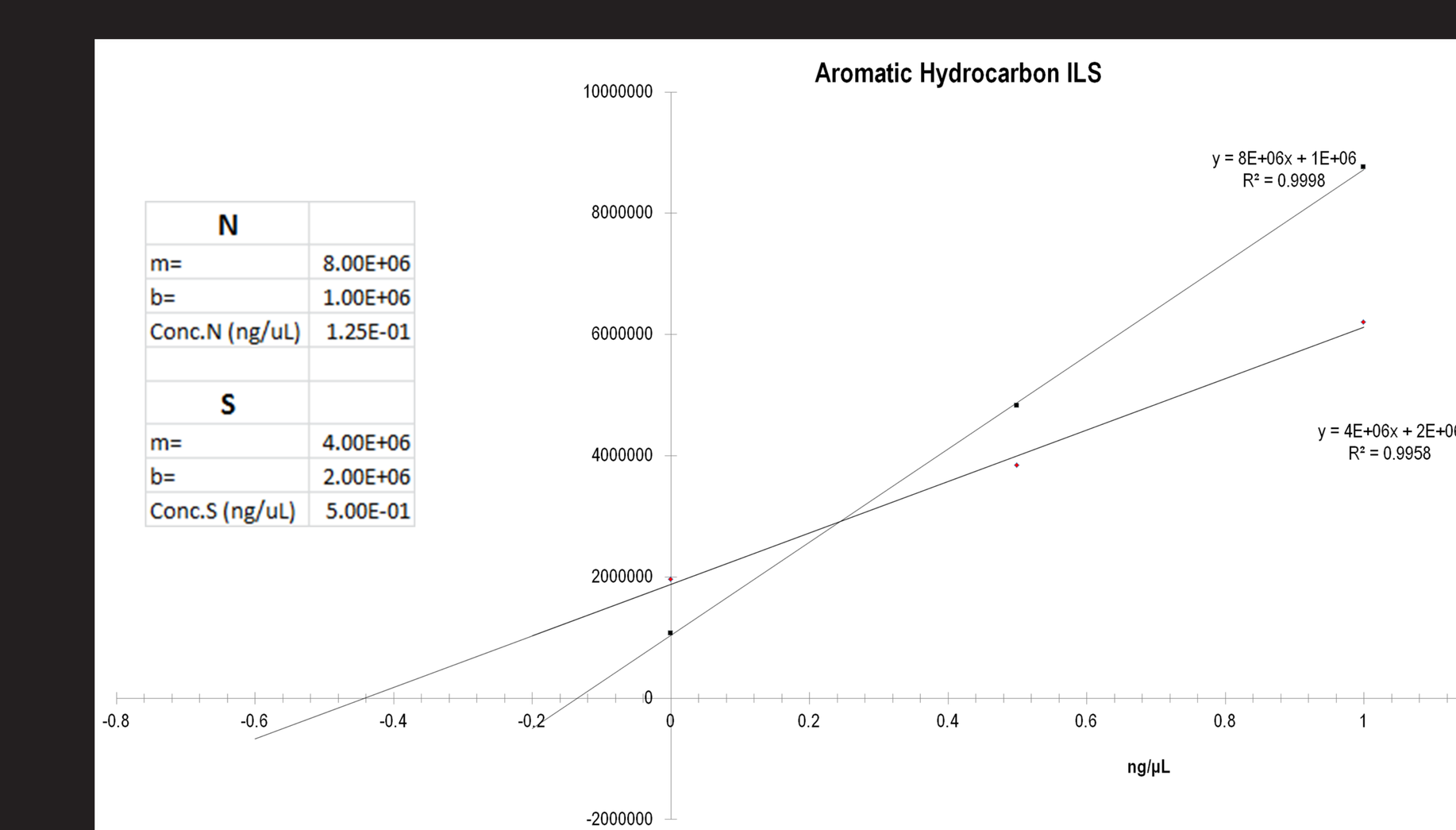


Figure 6: Simultaneous S and N by Standard Addition

Conclusion

- Standard addition methods have proven suitable for analyzing trace level nitrogen and sulfur samples with no matrix effects. The MultiTek provides a good alternative and is easy to set up.
- MultiTek® accurately determines very low levels of nitrogen even when not configured with a vacuum pump as demanded by ASTM standard methods D6069 and D7184.
- Results showed excellent stability, and similarities with or without the vacuum system.
- MultiTek ® can optimize your refining catalytic processes by:
  - Reducing operational costs
  - Controlling the quality of final products

PAC

www.paclp.com

ANTEK by PAC