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Trace N Determination in Catalytic Naphtha by Standard Addition and Combustion Chemiluminescence Analysis

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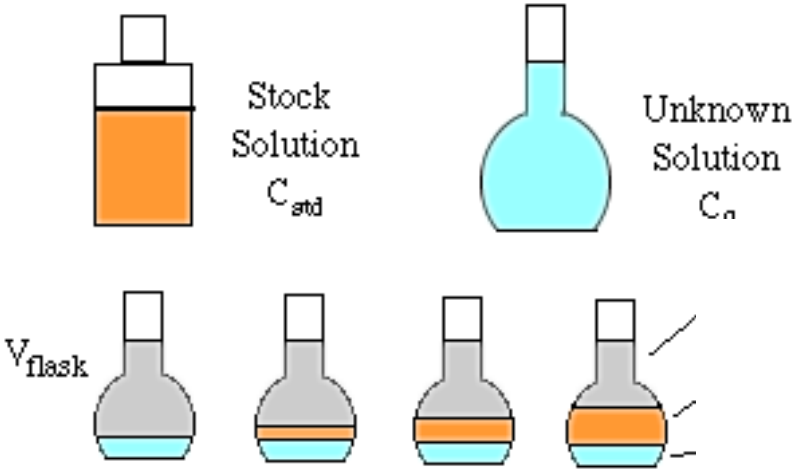
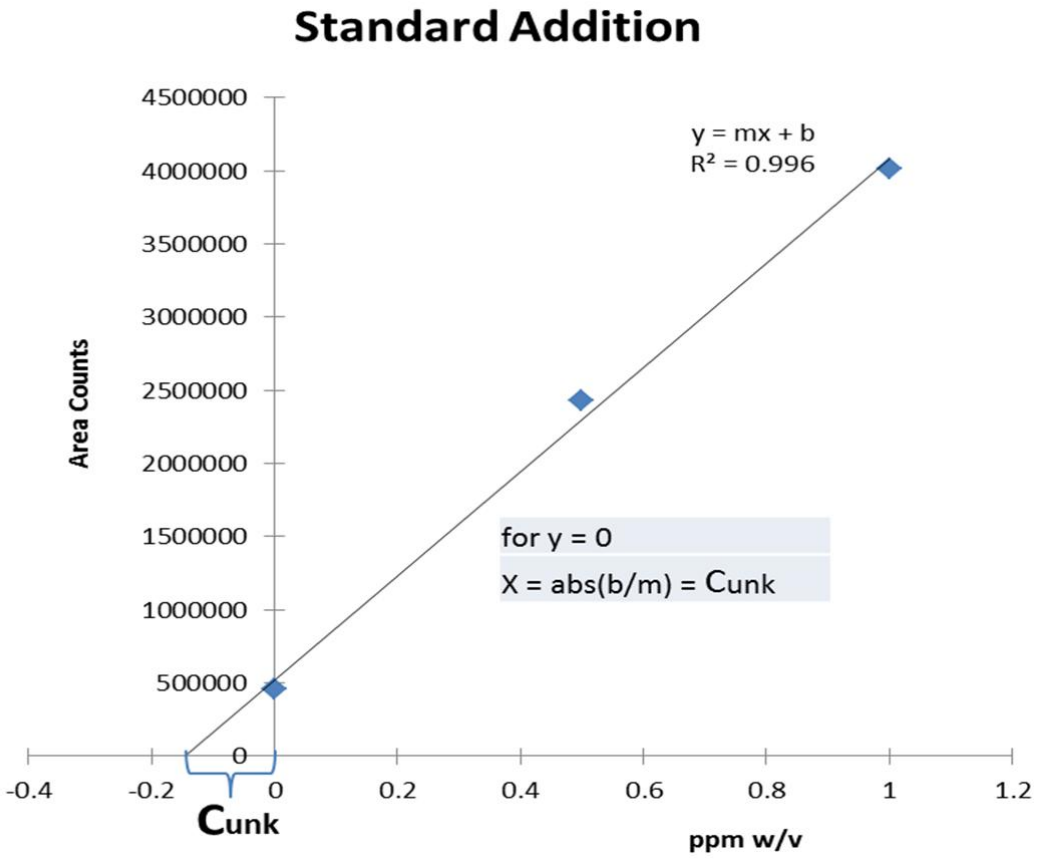
Introduction

STANDARD ADDITION METHOD

- 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

Standard Addition Method





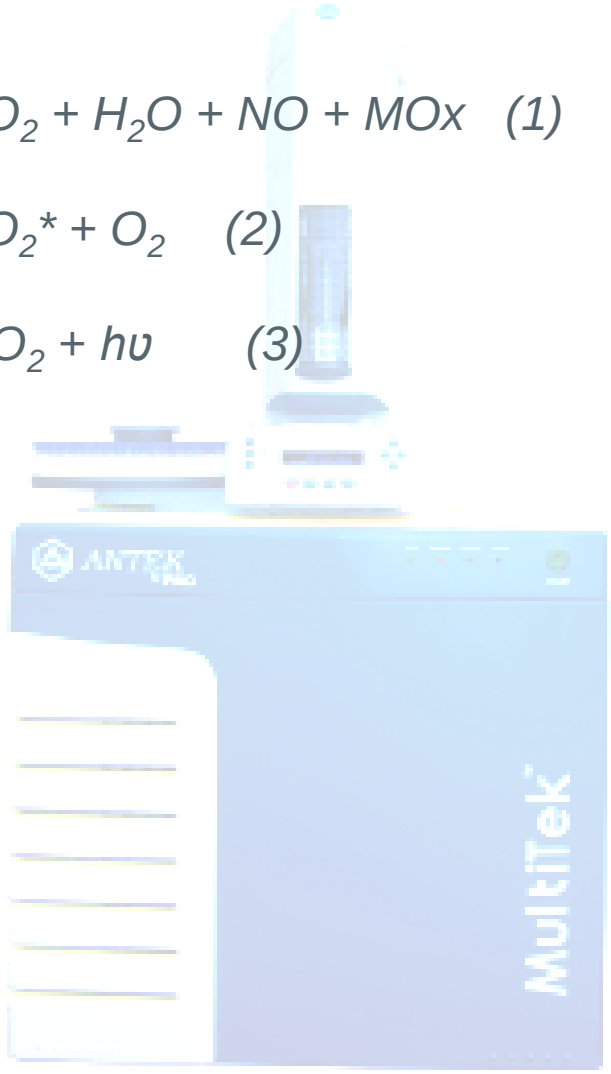
Experimental

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

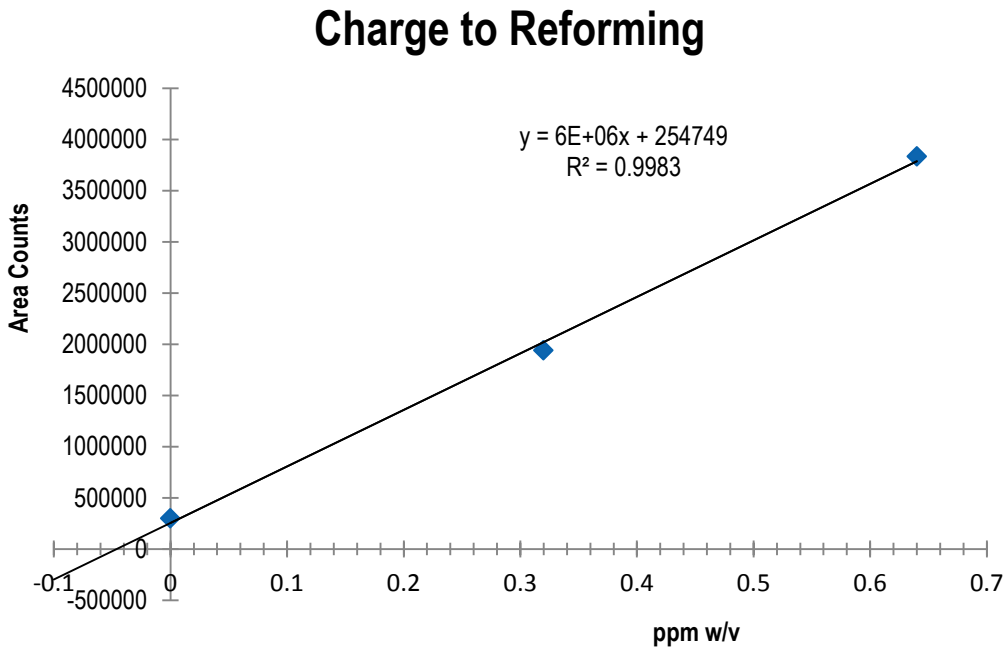
$$NO + O_3 \longrightarrow NO_2^* + O_2 \quad (2)$$

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

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
GFC 5- Auxiliary O_2 (ml/min)	25
Furnace (ºC)	1050
Nitrogen PMT voltage (V)	700

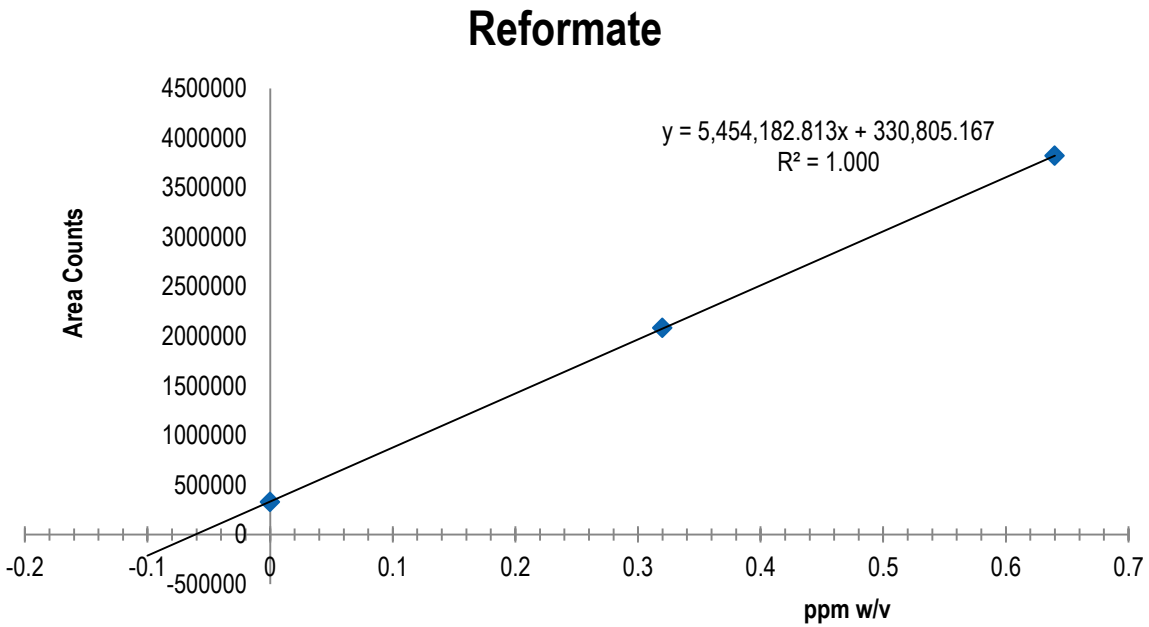


Experimental Results



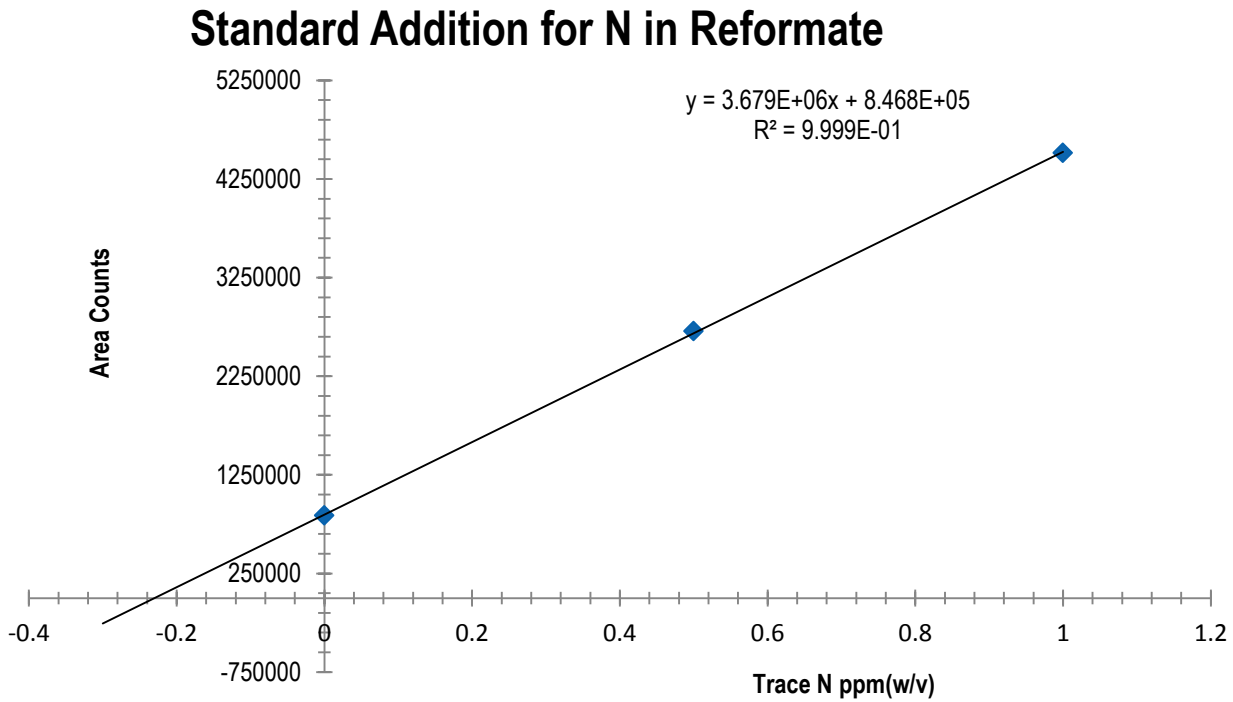
SLOPE =	5521053.1
INTERCEPT =	254748.7
$C_{unk(ppm)}$ =	0.046

Experimental Results



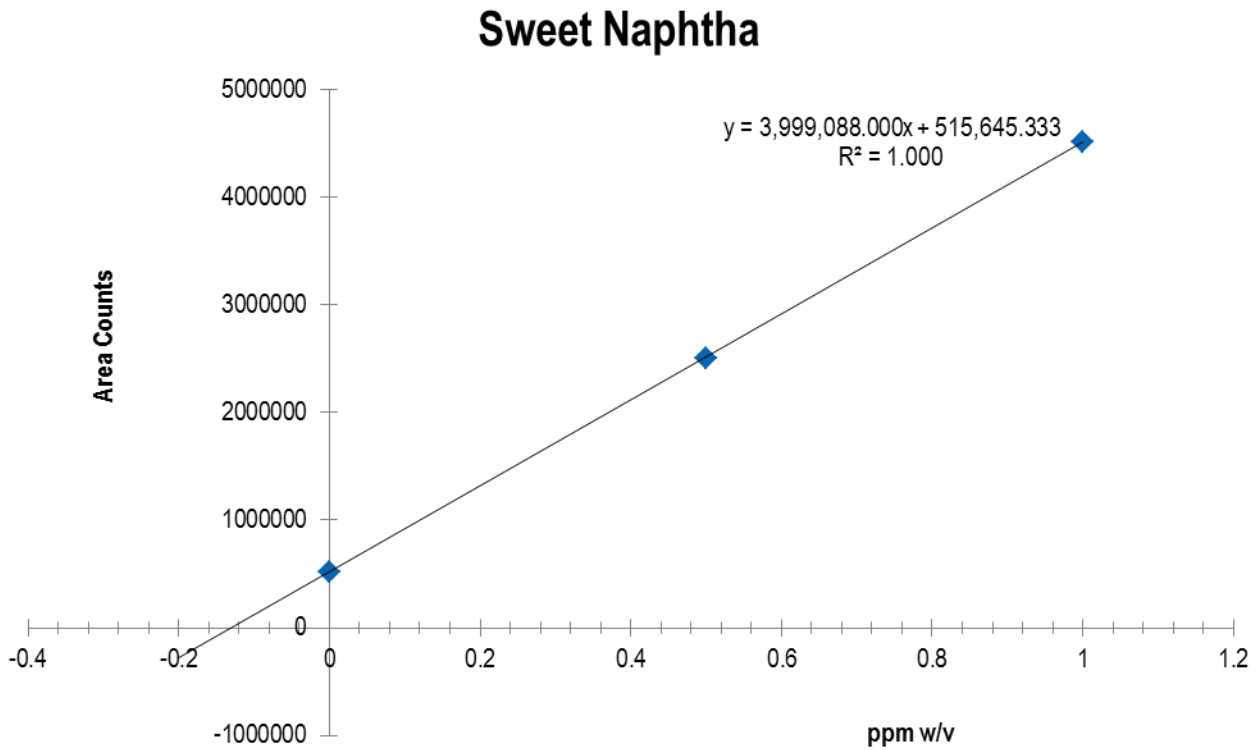
SLOPE =	5454182.8
INTERCEPT =	330805.1667
$C_{unk(ppm)}$ =	0.061

Experimental Results



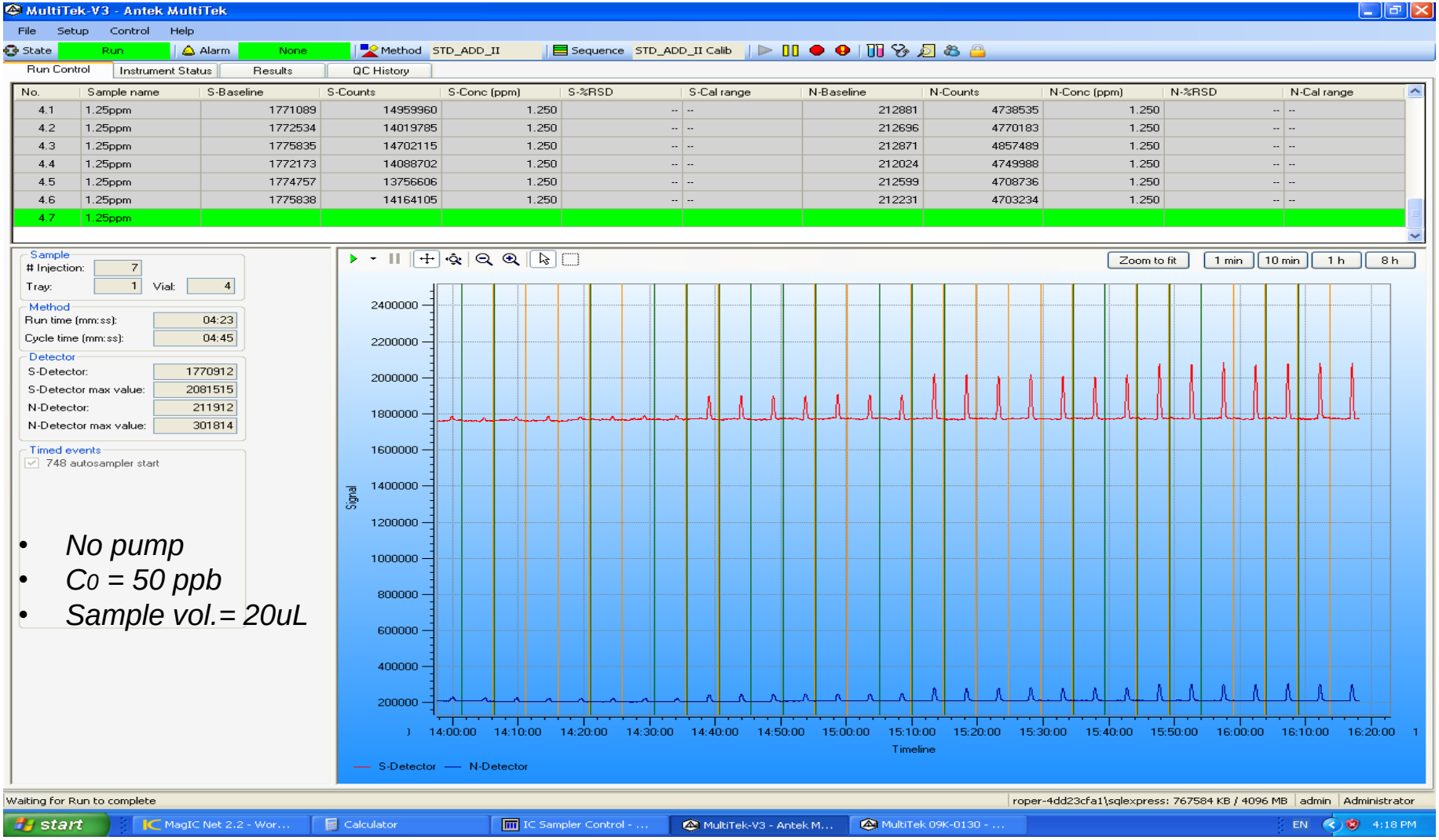
SLOPE =	3678571
INTERCEPT =	846774.8
$C_{unk(ppm)}$ =	0.230

Experimental Results



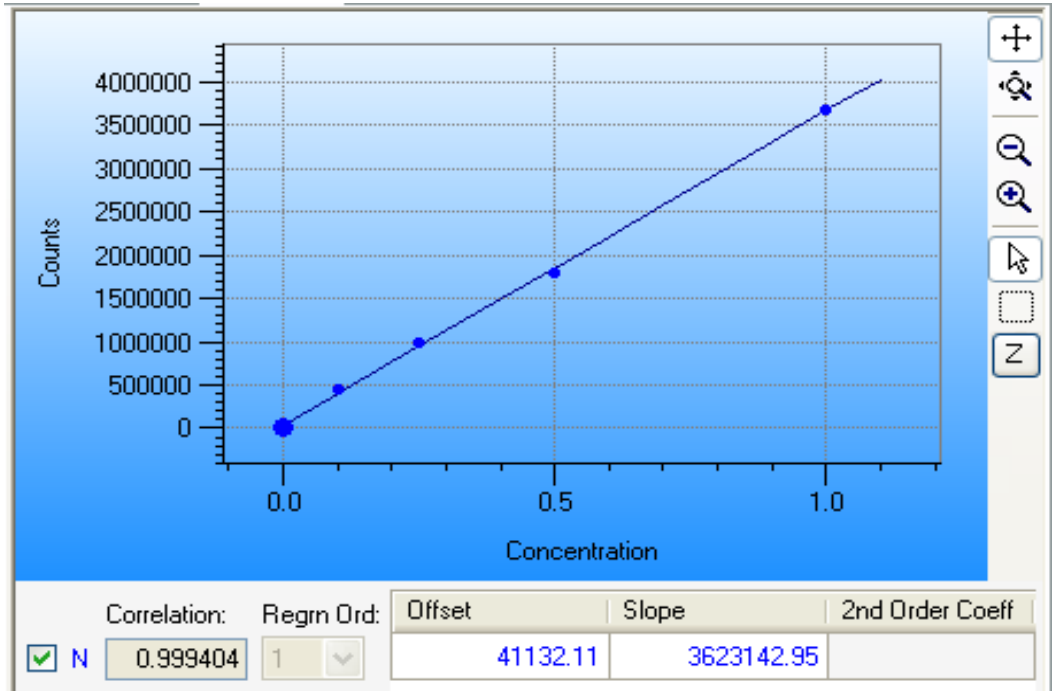
SLOPE =	3999088
INTERCEPT =	515645.33
$C_{unk(ppm)}$ =	0.129

Experimental Results



- *No pump*
- *C_0 = 50 ppb*
- *Sample vol.= 20uL*

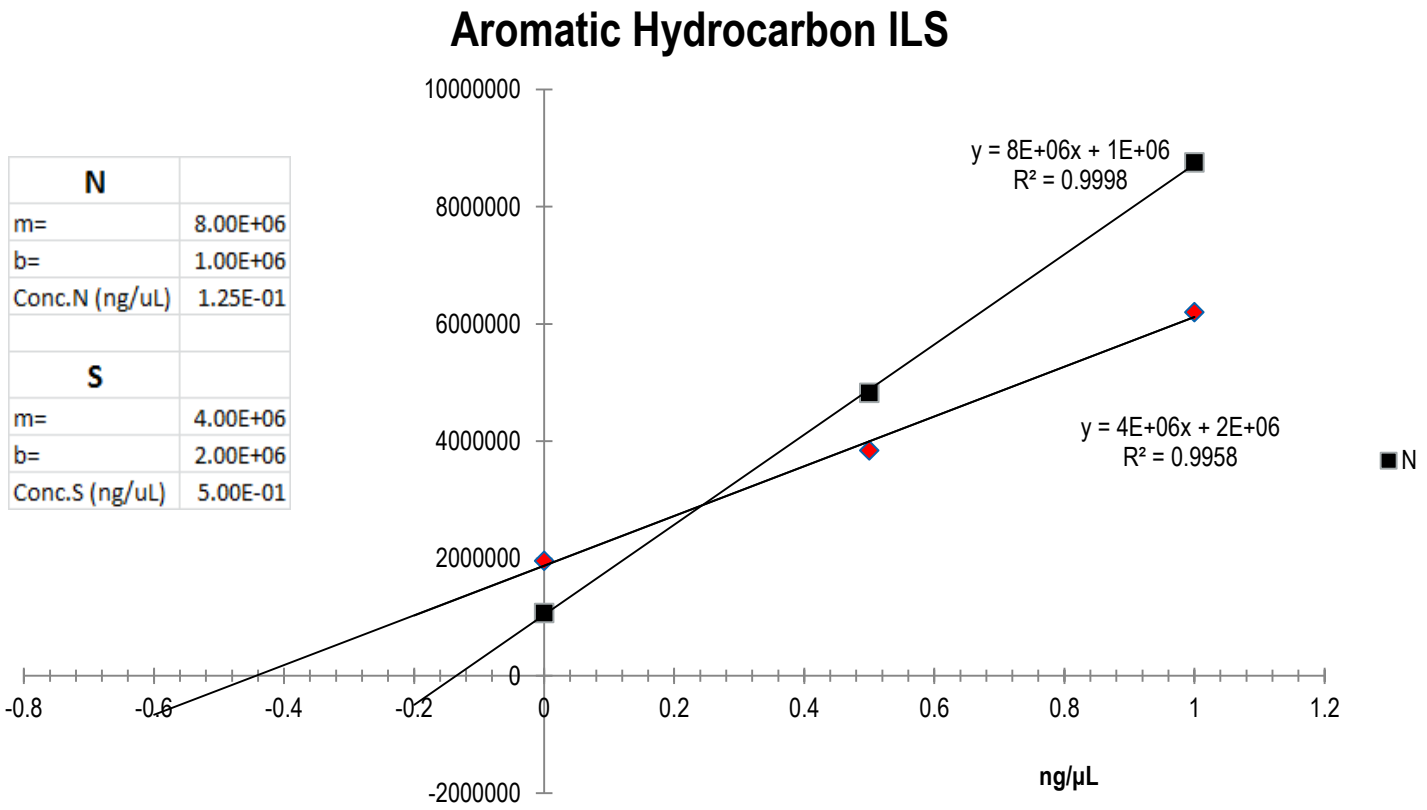
Experimental Results



Timestamp	Sample ID	Result ID	Method	Sequence	User	S-Cou	S-Cou	S-Conc (ppm)	S-%RS	S-Cal range	N-Counts	N-Coun	N-Conc (ppm)	N-%RSD
1/4/2012 8:2...	Reformate_Co...	7cac2a66...	N_Mod_E...	N_Trace	admin	0	--	0.000	0.00	Unkn...	840105	--	0.221	1.63
1/4/2012 7:5...	Charge_Conoco	32c27fee-...	N_Mod_E...	N_Trace	admin	0	--	0.000	0.00	Unkn...	471066	--	0.119	16.33
1/3/2012 6:2...	Std 1.00 ppm...	3c6ce462...	N_Mod_E...	@N_Mod_E...	admin	0	--	1.000	0.00	--	3680960	--	1.000	1.72
1/3/2012 6:1...	Std 0.50 ppm...	bcd804f4-...	N_Mod_E...	@N_Mod_E...	admin	0	--	0.500	0.00	--	1788676	--	0.500	1.57
1/3/2012 5:5...	Std 0.25 ppm...	e66b4cdb...	N_Mod_E...	@N_Mod_E...	admin	0	--	0.250	0.00	--	990127	--	0.250	2.13
1/3/2012 5:3...	0.1	8e521a00...	N_Mod_E...	@N_Mod_E...	admin	0	--	0.100	0.00	--	448712	--	0.100	2.56
1/3/2012 5:0...	Toluene	f08bcd74-...	N_Mod_E...	@N_Mod_E...	admin	0	--	0.000	0.00	--	0	--	0.000	6.80

Experimental Results

N	
m=	8.00E+06
b=	1.00E+06
Conc.N (ng/uL)	1.25E-01
S	
m=	4.00E+06
b=	2.00E+06
Conc.S (ng/uL)	5.00E-01



Conclusions

- Standard addition methods have proven suitable for analyzing trace level nitrogen samples.
  - Easy to set up in a MultiTek® system
  - Provides a good alternative
- 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 savings
  - Increasing quality of final products.

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