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TRACE S AND N IN HYDROCARBON MATRIXES BY COMBUSTION-UV FLUORESCENCE AND CHEMILUMINESCENCE.

- **OPTIMIZATION OF ANALYTICAL PARAMETERS.**

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INTRODUCTION

- ✓ Sulfur compounds in fossil fuels considered responsible for color degradation and gum formation in motor fuels.
- ✓ Contribute to enhance corrosion of tanks, vessels, reactors and pipe lines causing high maintenance efforts and costly downtimes.
- ✓ Trace nitrogen in naphtha and refinery streams important parameter for the optimization of refining catalytic processes since nitrogen containing compounds can irreversibly poison costly catalysts and affect the quality of final products.
- ✓ Combustion of hydrocarbons followed by UV-F[1] and Ozone CLD has become a preferred method to determine trace level amounts of sulfur and nitrogen in gases, liquids and solid samples[2].
- ✓ This procedure is fast, easy, reliable, selective, equimolar and wide DR.Complies with ten ASTM[3] and three European Standard Test methods.
- ✓ LOD as low as 10 and 15 µg/Kg, for S and N respectively has been determined and factors affecting this property are given special attention in this work.

INTRODUCTION

METHODOLOGY:

- Combustion of the sample in a pyrolytic tube held at a temperature of ca. 1050 °C.
- After the sample is combusted according to reaction (I), the gases are routed to a Nafion® membrane dryer for the total removal of the water formed in the combustion process[4].
- SO_2 and NO undergo reactions (II) – (IV) and the corresponding emitted energy is registered by two different PMT were the amplified signal is linearly proportional to the total concentration of both elements.

$$RS + RN + RH + O_2 \xrightarrow[1050\ ^oC]{} CO_2 + SO_2 + NO + H_2O \quad (I)$$

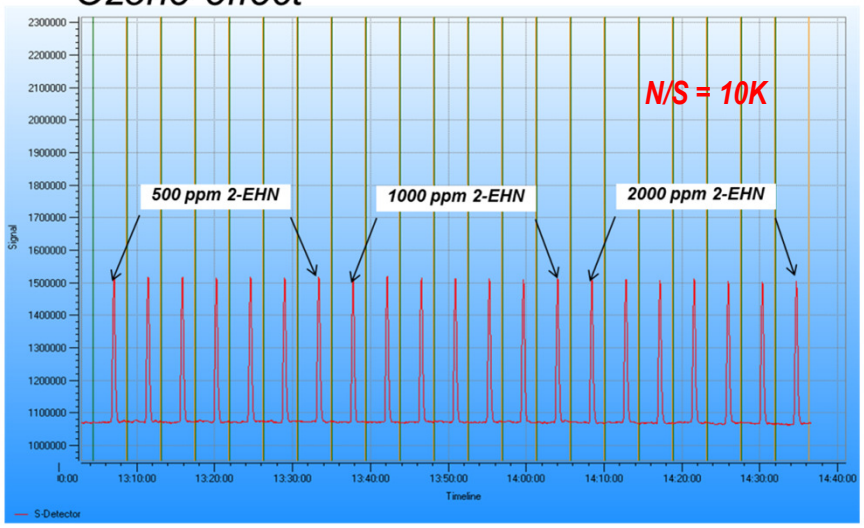
$$SO_2 + h\nu(190\text{-}230nm) \longrightarrow SO_2^* \longrightarrow SO_2 + h\nu''(240\text{-}450nm) \quad (II)$$

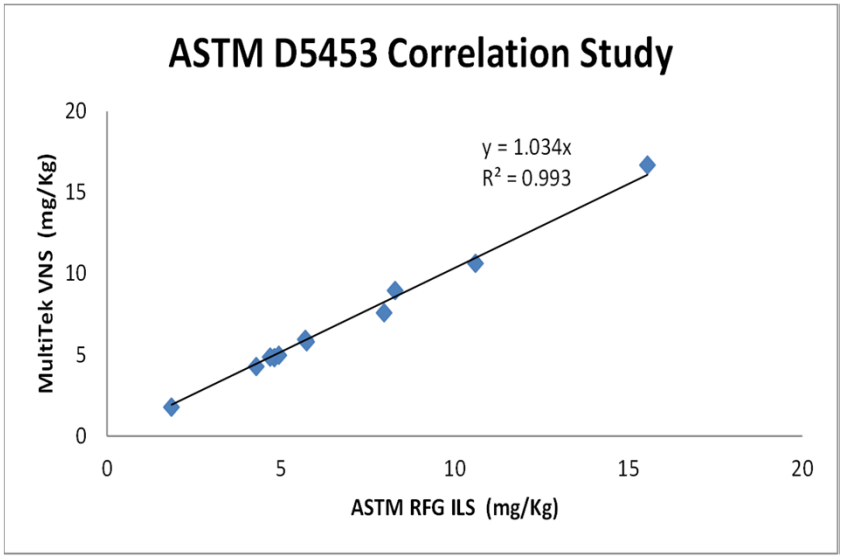
$$NO + O_3 \longrightarrow NO^*_2 \longrightarrow NO_2 + h\nu(vis\text{-}NIR) \quad (III)$$

Standardized Methods & Applications

ASTM D7359	ASTM D7183	EN 20846
ASTM D5453	ASTM D7184	UOP 971, 936
ASTM D6667	ASTM D7551	ENV 12260
ASTM D6069	ASTM D5176	DIN 38409
ASTM D4629	ASTM D5762	

Ozone effect





RESULTS AND DISCUSSION

- All experiments were performed in a MultiTek® VNS analyzer[4].
- Long term stability of the S content of a Ultra Low S Diesel sample with a minimal standard deviation over 420 repetitive injections.
- No soot formation was detected during the test.
- Calibration curve with: High linear regression, high repeatability and extremely high sensitivity.
- LOD values correspond to a signal to noise ratio of more than three times the experimental standard deviation value[5].

LIMIT OF DETECTION

- By definition LOD is defined as the minimum concentration that can be reliably distinguished from the blank signal i.e. with a certain degree of confidence. This degree of confidence varies but in general it is based on the standard deviation of the blank which is equivalent to the S/N ratio.

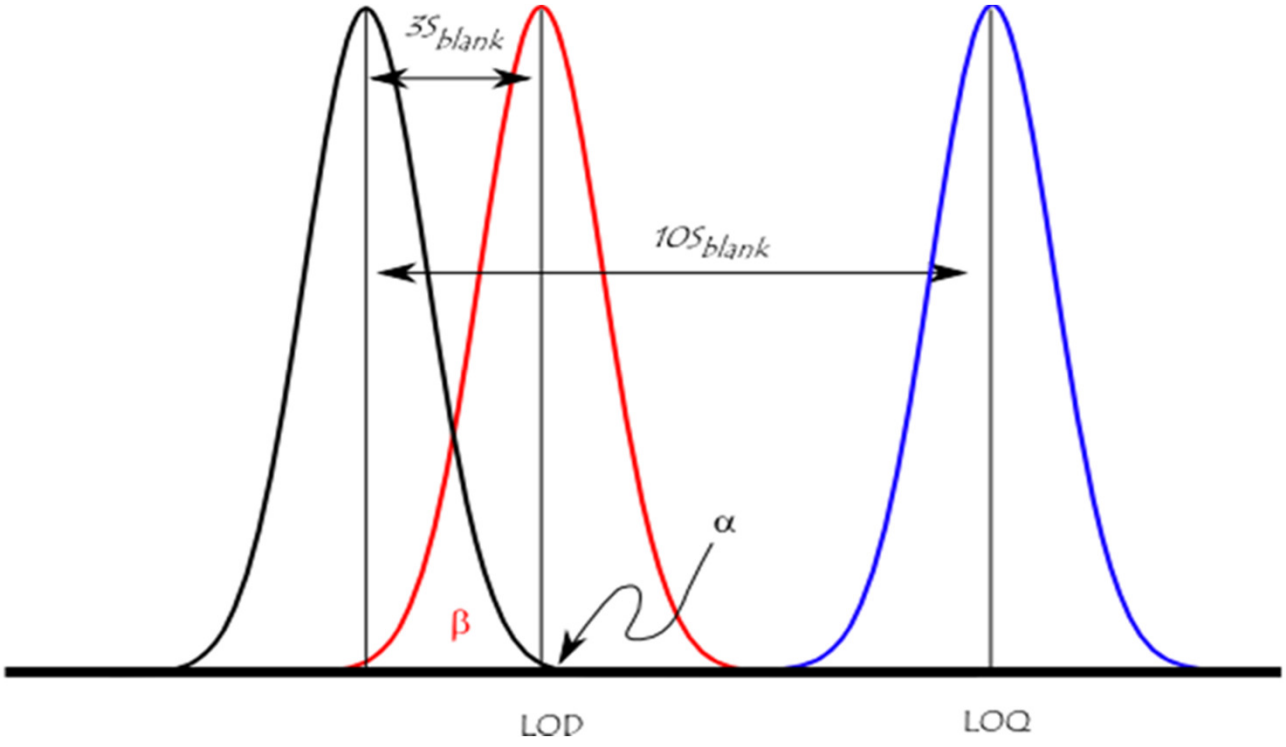
- The Limit of Quantitation however is the minimum concentration of a measurand that can be reliably determined by an analytical method and is generally considered to be equal to 10 times the Standard Deviation of the base line.

- Experimental parameters that depend on the condition of the analyzer, The suitability of the analytical method and the quality of the standards used in the calibration step.

- In general the lower the repeatability value and the higher the signal to noise ratio the lower the LOD will be.

LIMIT OF DETECTION

Classical relationship between LOB, LOD and LOQ.



$$LOD = \mu b + KD \times \sigma b$$

Factors affecting the LOD

…… Common misconception: LOD is the smallest concentration that can be measured.

Instead it is the smallest concentration at which we can decide whether an analyte is present or not in the sample; i.e. it is the point where we can just distinguish a signal from the blank or the background.

LIMIT OF DETECTION

Alternatively :

$$LOD = LOB + 1.645 \times SD(lc) \quad (V)$$

$$LOB = \mu(blk) + 1.645 \times SD(blk) \quad (VI)$$

Where:

SD(lc)- SD of lowest concentration sample
μ(blk) – Average value of the blank

It is important to note at this point that the LOD values shown had been calculated according to Ambruster et. al[5] and based on the Limit of Blank(LOB) according to:

LOD at different degrees of confidence

S (ppbv)		N (ppbv)	
LOD[5]	3xσ	LOD[5]	3xσ
12.01	6.78	18.05	6.47
27.1	8.7	45.36	44.58
40.32	26.71	51.62	51.52
57.33	25.01	72.02	23.74
78.53	42.18	88.75	71.56
142.6	65.3	126.56	71.85

The fact that eq. (V) takes into account the variance of the blank and the variance of the lowest concentration sample, makes more stringent the LOD final value.

LIMIT OF DETECTION

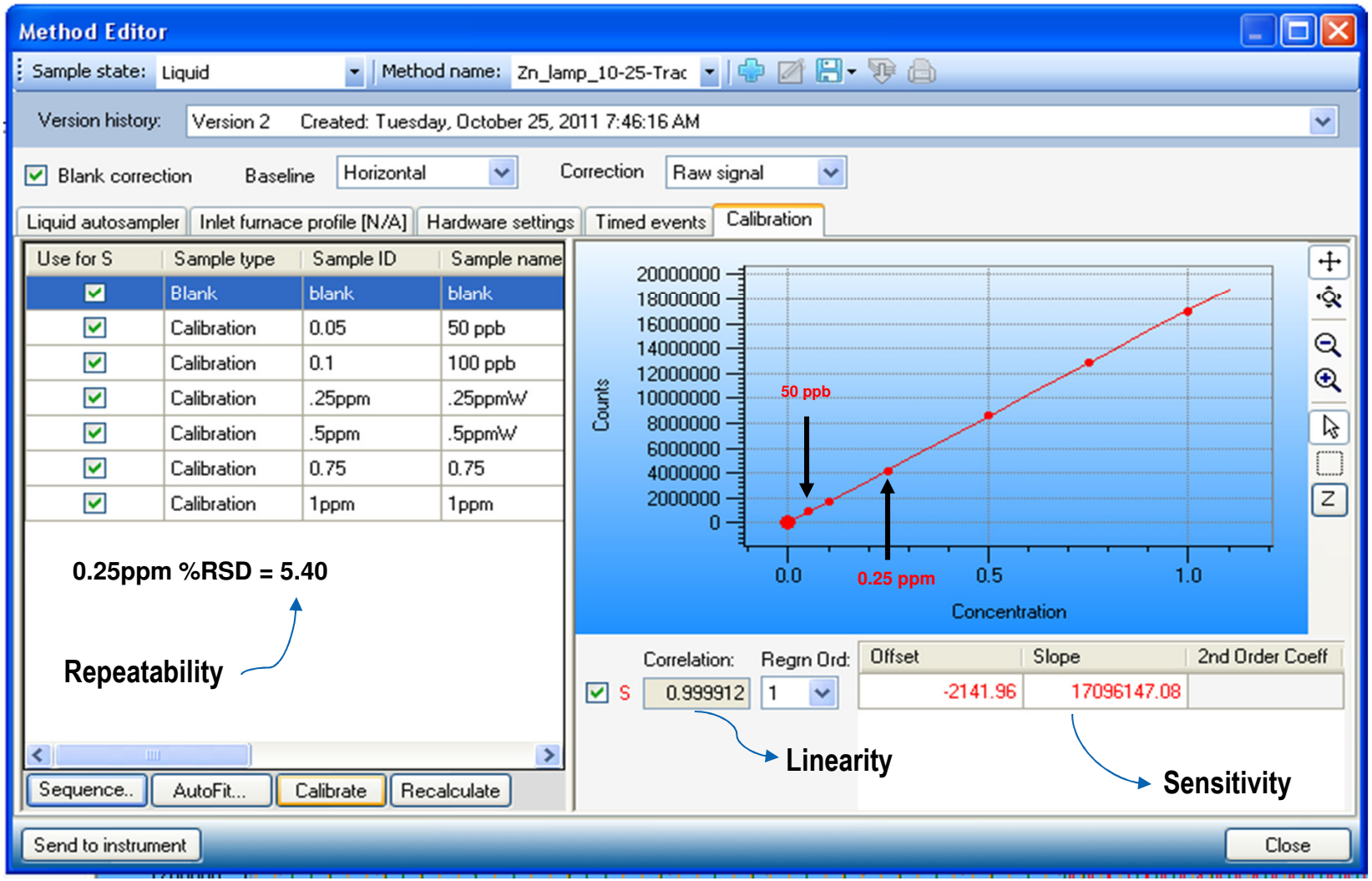


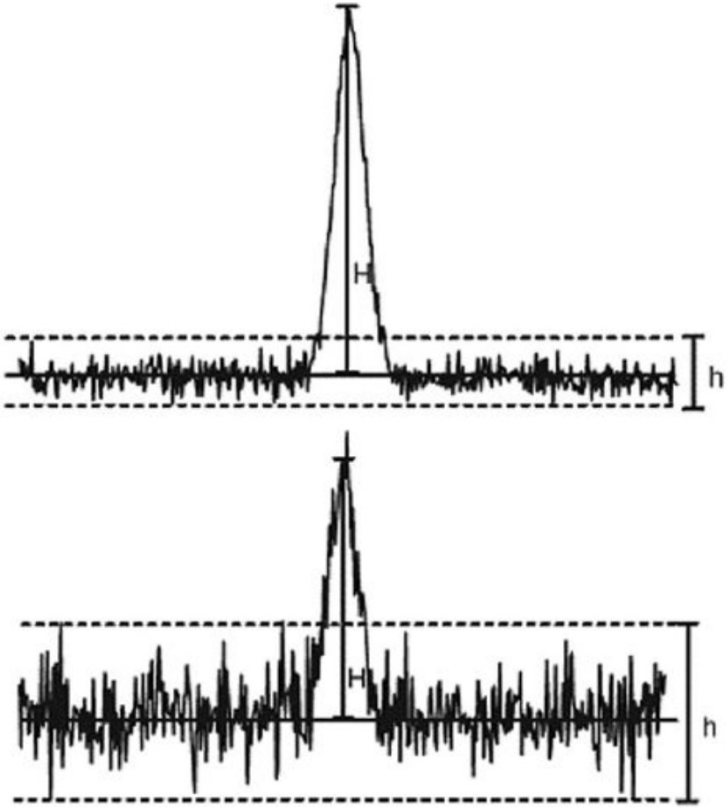
Figure 2. MT VNS analyzer Calibration parameters

Factors affecting the LOD

S/N @ 125ppb	Repeatability %RSD @ 125ppb	LOD (ppbv)[5]	Linearity (R^2)	Slope (m)
4.5	22.12	78.53	> 0.999	8.2xE05
6.32	14.25	74.09	> 0.999	4.3xE06
8.01	12.49	57.3	> 0.999	5.0xE06
8.90	11.23	40.32	> 0.999	5.1xE06
54.4	1.84(0.5pm)	28.40	> 0.999	7.0xE06
10.76	14.76	12.01	> 0.999	2.6xE05

Factors affecting the LOD

…….It is well known to practicing analytical chemists that as concentration of the analyte decreases, the precision, as expressed in the relative standard deviation, gets worse.



Factors affecting the LOD

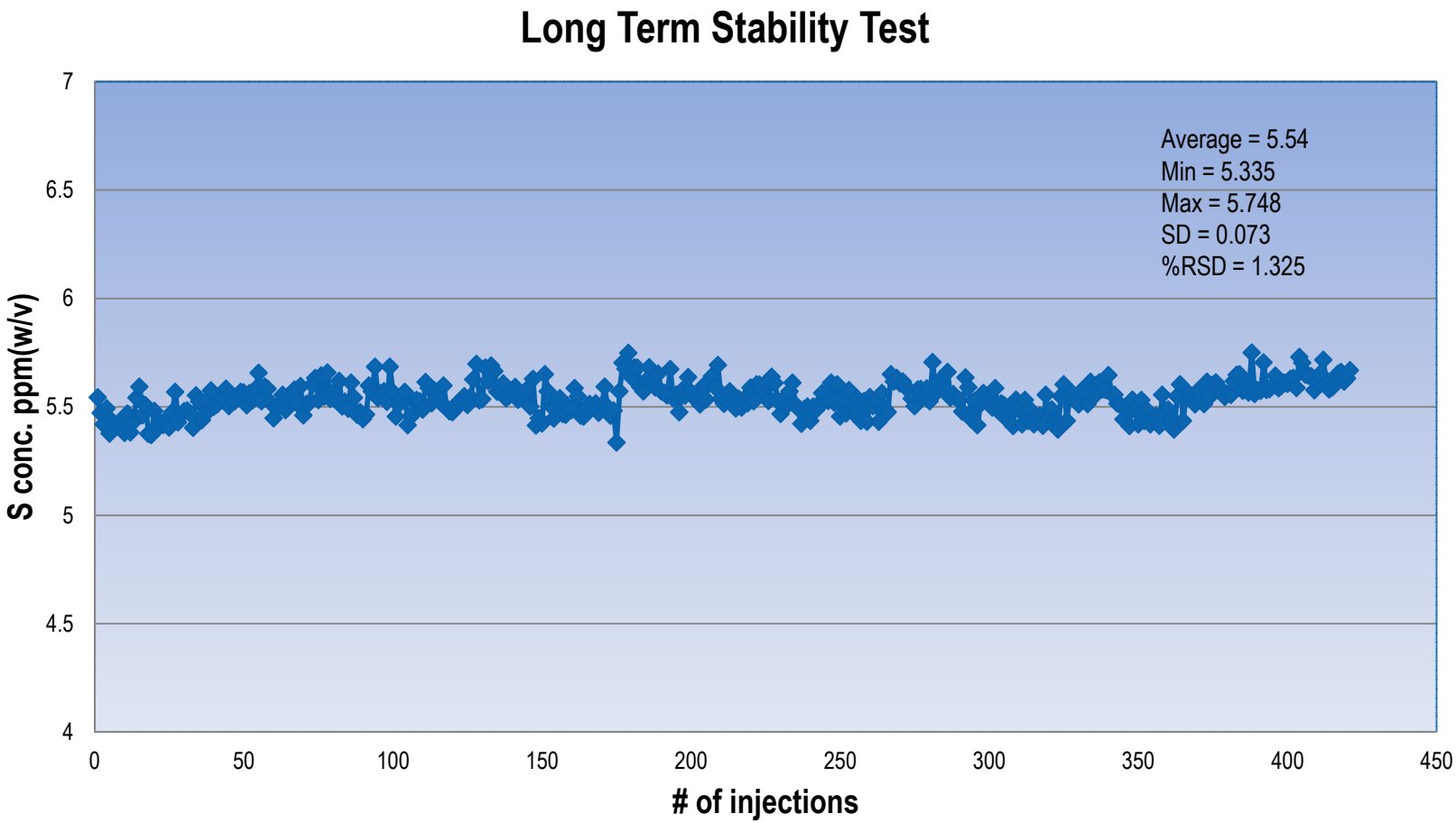
LOD (3xσ) (ppbv)	Slope (m)	Offset (b)	S/N @ 125ppb	$\mu_{(Blank)}$	SD (Blank)	%RSD (Blank)	R^2
10.98	5.1E+06	390616	3.5(70ppb)	262242	27910	10.64	0.9984
12.59	5.0E+06	308865	6.6	23880	44764	18.74	0.9984
13.07	0.5E+06	338442	9.05	272100	19264	7.08	0.9995
16.87(2)	6.3E+06	533898	4.2(70ppb)	448797	63974	14.25	0.9993
20.02	1.2E+06	71578	2.5(0.05ppm)	67015	9623	14.36	0.9999
26.27	1.2E+06	121897	5.80	151789	17408	11.47	0.9991
26.71	5.2E+06	459026	8.90	302318	98074	32.44	0.999
29.51	17E+06	357598	11.95	291684	188370	64.58	0.9996
42.18	0.8E+06	38681	4.52	18613	18240	98.0	0.9998
44.6(2)	0.5E+06	41772	10.9	58093	9388	16.16	0.9999
48.54	1.1E+06	102018	7.92	355919	38761	32.23	0.9998
58.90	0.4E+06	58886	14(0.05ppm)	43942	12021	27.36	0.9996
61.63	6.4E+06	356571	3.3(70ppb)	1083393	159283	14.70	0.9995
69.20	7.5E+06	1039348	10.54	334523	138139	41.29	0.9992

Current LOD values

Date	LOD (3xσ) (ppbv)	Slope (m)	Offset (b)	S/N @ 125ppb	$\mu_{(Blank)}$	SD (Blank)	%RSD (Blank)	Linearity R^2
11/12/2013	20.7	3.70E+06	150274	9.52	147785	26558	18.01	0.9989
11/20/2013	20.8	3.95E+06	235437	6.57	236312	27105	11.47	0.9994
11/22/2013	28.7	3.80E+06	264376	6.59	291684	24514	8.90	0.9996
12/03/2013	23.3	1.73E+06	231368	21.9	190903	26876	14.08	0.9970
12/05/2013	22.3	1.70E+06	230039	6.35	198083	40622	8.65	0.9990
1/15/2014	19.98*	3.94E+06	120324	6.45	37601	43727	116.3	0.998
1/16/2014	23.04*	4.31E+06	195913	8.54	54009	80426	148.91	0.991
1/17/2014	20.64*	2.64E+06	64433	2.69	67271	17245	25.64	0.9998

*_ LLS/Small PMT

Long Term Stability



CONCLUSIONS

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 12 and 6.5 ppbv for S and N respectively at a signal to noise ratio higher than 3σ[5].
Although it has been proven that the described techniques are equimolar in response for unknown samples the magnitude of any matrix effect can be readily reduced by standard addition analysis.
Results show excellent stability and no major differences when analyzing samples for S in samples with high N content.

Sulfur Base line stability and standard deviation of injections are affected by:

- Lamp condition(stability, intensity, alignment.)
- Band pass Excitation Filter quality
- PMT condition
- Vibrations
- Light and gas leaks
- Contamination Risks

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