Total Sulfur and Nitrogen Analysis Using a Multi-Layer Combustion Tube

Application Note

Combustion

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Abstract:

Crude oil is composed mainly of hydrocarbons mixed with a variation of nitrogen, sulfur and oxygen. The differences in the nitrogen, sulfur, and oxygen content can be attributed to where the crude oil originates. After drilling, crude oil is usually refined in order to create fuel, lubricants, etc. Due to the use of processing catalysts in the refining method, trace amounts of sulfur and nitrogen can be very detrimental. Thus, determining the nitrogen and sulfur content is very important. This application will examine total sulfur and nitrogen in light hydrocarbon samples using the NexiS combustion elemental analyzer complete with a new and novel multilayer combustion tube.

Introduction:

Nitrogen and Sulfur in petroleum products are tested for because if their presence is found in a product there is a risk of catalyst poisoning. It has been found that if there is even a trace amount of either of these elements; the refining process can be inhibited.

Reducing the sulfur content is vital for the protection of platinum based catalysts in naphtha reforming operations. Residual sulfur in fuel oils will influence emissions of sulfur dioxide resulting again in plant corrosion and atmospheric pollution if the residual level is too high. Trace sulfur is determined through combustion and Ultra Violet (UV) Fluorescence.

Nitrogen on the other hand, is detected using chemiluminescence. The nitrogen reacts with oxygen during combustion analysis. However, when the oxygen reacts with the nitrogen to create NO it also produces NO_2/NO_X. The NO is detected by chemiluminescence; the NO_2/NO_X is not. The NexiS Total Nitrogen/Sulfur Analyzer uses a Molybdenum (Moly) converter in order to convert the NO_2/NO_X to NO for better determination of total Nitrogen in the sample.

Using the NexiS Total Nitrogen/Sulfur Analyzer, the samples were combusted and carried through a multi-layer combustion tube. The layers in the combustion tube give a longer burn path, enabling better combustion and less “sooting”.

Experimental:

The NexiS Total Nitrogen/Sulfur Analyzer was set up with a solids module using a 25µl injection. The system was set to run for total Sulfur and total Nitrogen. Calibration standards were procured and transferred to two milliliter vials. The vials were placed on the 120 position autosampler configured on the NexiS. Next the experimental parameters were programmed into the NexiS software. Each calibration curve standard was then run four times each. Experimental parameters are listed in Table 1 below.

NexiS Total Nitrogen and Sulfur Analyzer	
Parameter	**Setting**
Argon Flow	100mL/min
Oxygen Primary Flow	250mL/min
Oxygen Turbo Flow	100mL/min
Ozonator Flow	100mL/min
Furnace 1 Temperature	850ºC
Furnace 2 Temperature	1000ºC
Moly Converter Temperature	320ºC
Injection Volume	25µL

Table 1: Experimental Parameters

After the experiments were run, the results were tabulated. The findings are listed in Tables 2 and 3, while graphics of the calibration curves and 50ppm samples are displayed in Figures 1 through 4.

Sulfur Calibration Curve			
Level (ppm)	**Average Result (ppm)**	**Avg. Area Count**	**%RSD**
1.0	-0.33	471.69	3.79
5.0	3.90	2342.73	0.89
10.0	8.95	4578.30	1.97
50.0	48.80	22207.95	1.08

Table 2: Sulfur Calibration Curve Results

Nitrogen Calibration Curve			
Level (ppm)	**Average Result (ppm)**	**Avg. Area Count**	**%RSD**
1.0	0.75	124.86	3.60
5.0	4.89	781.39	3.00
10.0	10.29	1639.11	0.71
50.0	49.96	7938.55	0.47

Table 3: Nitrogen Calibration Curve Results

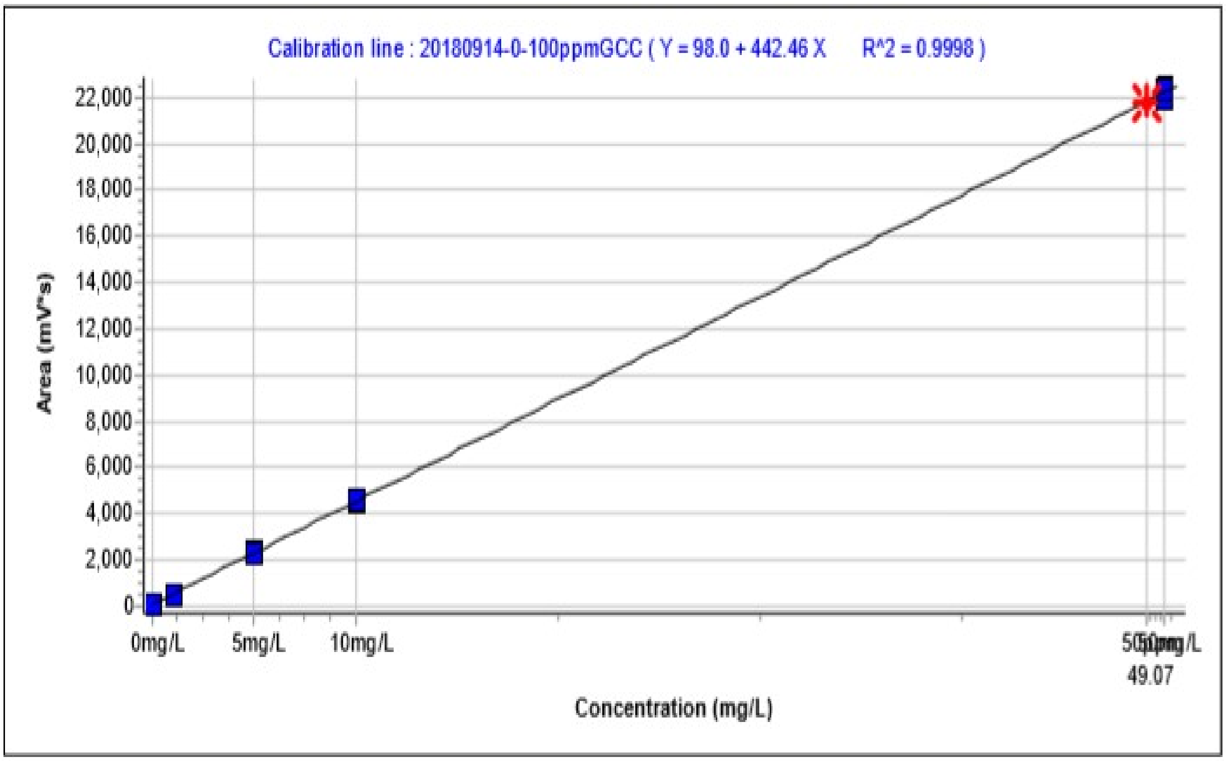

Figure 1: Sulfur Calibration Curve

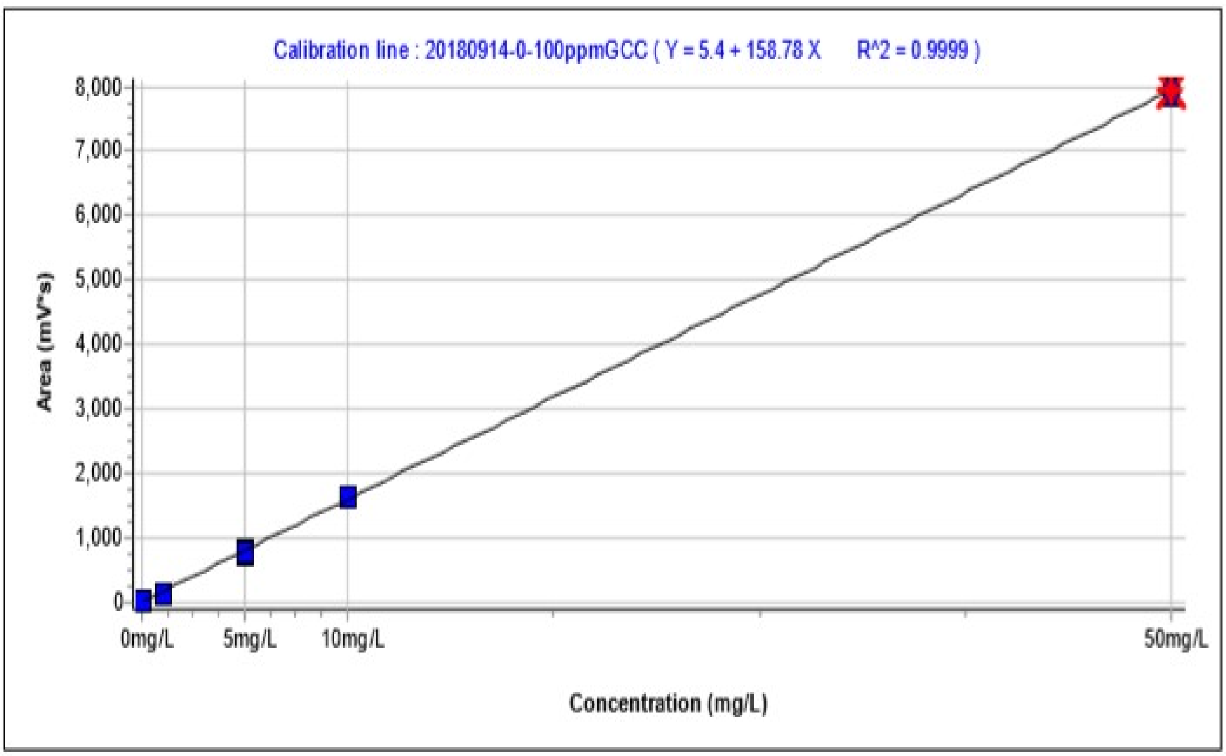

Figure 1: Nitrogen Calibration Curve

Signal	: Sulphur	**50ppm**	
Area	: 22327.93	**Concentration**	: **49.07mg/L**
Sample amount	: 25µL	Method	: TNTS_NexiS_Boat_AS120_lubrizol
Sample position	: 5	Analysis date	: 9/14/2018 1:53:34 PM
Dilution factor	: 1.000	Sample type	: calibration
Density	: 1.000	Comment	:
Tolerance	: 0.00		

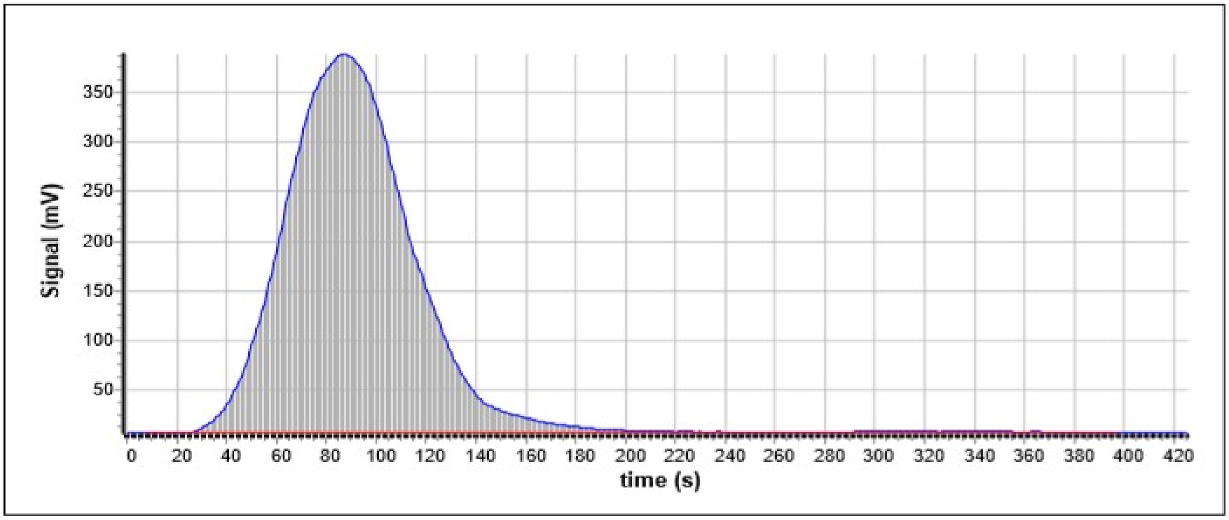

Figure 3: 50pppm Sulfur Results Graph

Signal	: Nitrogen	**50ppm**	
Area	: 7938.55	**Concentration**	: **49.96mg/L**
Sample amount	: 25µL	Method	: TNTS_NexiS_Boat_AS120_lubrizol
Sample position	: 5	Analysis date	: 9/14/2018 1:53:34 PM
Dilution factor	: 1.000	Sample type	: calibration
Density	: 1.000	Comment	:
Tolerance	: 0.00		

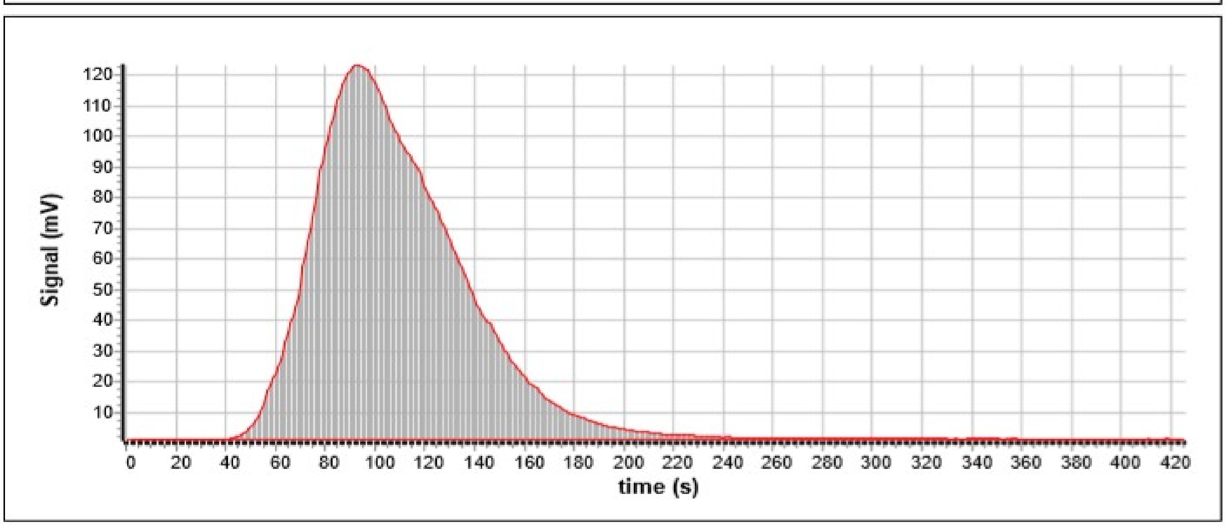

Figure 4: 50pppm Nitrogen Results Graph

Conclusions:

The NexiS Total Nitrogen and Sulfur analyzer with its 120 position autosampler provided excellent data for mid-level Sulfur and Nitrogen samples in compliance with ASTM Methods D5453 and D5762. Both calibration curves had excellent linearity of 0.9998 or better while the percent relative standard deviation for the standards was less than 3.8%. The multi-layer combustion tube provided a more efficient ignition of the samples resulting in shorter combustion times. The NexiS proved to be an outstanding sampling and analysis system for both Nitrogen and Sulfur by combustion.

References:

1. Standard Test Method for Nitrogen in Liquid Hydrocarbons, Petroleum and Petroleum Products by Boat-Inlet Chemiluminescence, ASTM Method D5762-18, 2018.
2. Standard Test Method for Determinationof Total Sulfur in Light Hydrocarbons, Spark Ignition Engine Fuel, Diesel Engine Fuel, and Engine Oil by Ultraviolet Fluorescence. ASTM Method D5453-16, 2016.

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