Analysis of Total Nitrogen (CLD) and Total Sulfur (UV-F) in renewable fuels: Aviation Fuel-HEFA and Diesel-HVO using the Xplorer-V

Introduction

HEFA (hydroprocessed Esters and Fatty Acids) and HVO (Hydrotreated Vegetable Oils) are renewable fuel products produced by treatment of vegetable oils, waste oils, or fats through a process that uses hydrogen (hydrogenation). In the first steps of this process, oxygen is removed by hydrodeoxygenation, followed by cracking and isomerization of the straight paraffinic molecules to chain lengths comparable with conventional fuels.

HEFA/ HVO are straight chain paraffinic hydrocarbons that are free of aromatics and oxygen, low in sulfur and have high cetane numbers. HEFA/ HVO offers a number of benefits over FAME (Fatty Acid Methyl Esters), such as reduced NOx and SOx emissions, better storage stability, and cold flow properties. HVO Properties are similar to biomass-to-liquid diesel fuels, hence HVO can directly be used in all diesel engines. HEFA products are more applicable for jet fuel replacement, as they resemble more with Kerosine composition. Commercially, blends of HVO with regular Diesel are also offered, in mixing ratios of 20%HVO/ 80%Diesel. The maximum blend ratio is for Air jet fuels is 50% with conventional jet fuels. (ASTM spec: D7566).

Solution

Xplorer-V Series

Sample Information	
Sample Type	HVO, HEFA, Kerosine, Diesel, blend/ mixtures.
Component	Nitrogen, Sulfur
Concentration	0.1 – 100 mg/l
Methods Applicable	ASTM D5453, ISO 20846

Summary

The Xplorer-V elemental combustion analyzer, has been used to perform the analysis of Total Nitrogen (CLD) and Total Sulfur (UV-F) in pure HVO/ HEFA products and blends commonly used in combination with conventional fuel products. All samples were introduced by direct liquid injection with the integrated liquid autosampler. The Xplorer-V provides repeatable results with standard deviations well below the stated repeatability limits *(r)* of the ASTM D5453 and ISO 20846. A Diesel round robin sample and Kerosine CRM standard were included in the sample queue to demonstrate high accuracy of analysis and as basis for the blending of sample material.

HEFA/ HVO seems like excellent clean candidates to use as alternative for conventional fuel material. Both HEFA and HVO sample material contained low levels of Nitrogen and Sulfur, or well below the detection limit of the Xplorer-V. As a reference, we injected a 10 ppb level of a standard to confirm the detection limit (see example peaks). Since the lower level of the calibration line for this study was aimed at 100 ppb, we reported this level as the limit of reporting.

To confirm the analytical applicability of HEFA and HVO were blended with the sample material of a Round robin Diesel and Kerosine CRM. The results out of the blends show a perfect recovery of the expected values according to the values of the non-blended conventional fuel and the analysis on the base products HEFA/ HVO.

Analysis of Total Nitrogen (CLD) and Total Sulfur (UV-F) in renewable fuels: Aviation Fuel-HEFA and Diesel-HVO using the Xplorer-V

Method

The Xplorer-V analyzer is a robust and reliable configuration for the analysis of Total Nitrogen and Total Sulfur in Hydrocarbon Products by liquid sample introduction with the integrated liquid autosampler. The setup is optimized for hydrocarbon sample analysis offering fast combined TN/TS analysis, top detection performances and smart operation features.

The analyzer can work with any sample volume between 5 and 200 µl, for this application a volume setting of 100 µl was used. Simultaneous Nitrogen and Sulfur analysis is possible by using the same sample volume for both elements.

The analyzer was calibrated in the ranges of 0.1 – 10 mg/L and 1-100 mg/L by volumetric dilution of Pyridine (N) and Dibutyl Sulfide (S) in Iso-octane solvent. All samples were directly injected and automatically matched, according their peak area counts, to the appropriate calibration line.

System Description

Introduction – The 26 position LS autosampler automatically introduces the sample into the Xpro-V inlet tube with a controlled injection rate. The Xpro-V inlet is specifically designed for the introduction and evaporation of samples with a maximum boiling level of 530 °C.

Combustion – After passing the inlet and evaporation stage, the sample material reaches the Xpro-V combustion tube which is placed in a high-temperature dual zone furnace where the sample is oxidized completely. The temperature is adjustable up to 1150 °C . The special designed cleaning Flow valve in the analyzer, provides a secondary oxygen flow running through the XPro-V Inlet, which supplies additional oxygen gas resulting in more oxidation power for samples and to automatically clean the inlet after each analysis.

Conditioning - Water vapor is removed from the gas stream by the Perma Pure gas dryer. Particles are blocked by a simple disposable PFTE filter and last up to 10.000 injections. Only the conditioned gas stream enters the Nitrogen and Sulfur reaction chambers.

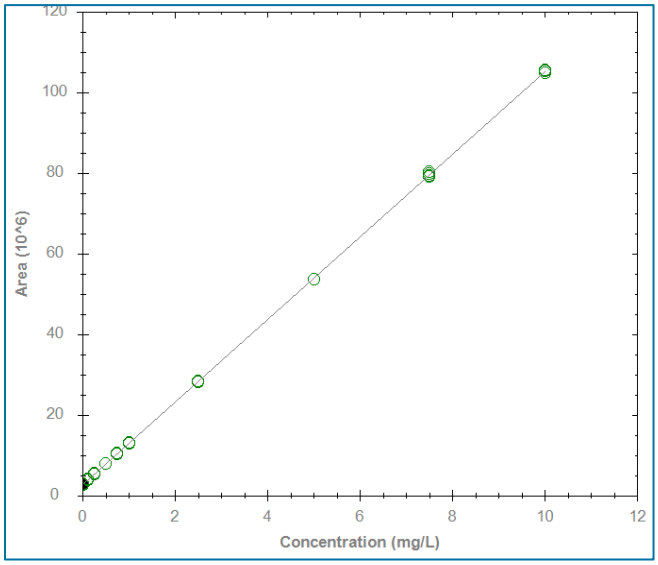
Detection – After conditioning, the amount of Total Sulfur is detected by pulsed UV-fluorescence and the amount of Total Nitrogen by the chemiluminescence detector. The Xplorer-V analyzes Total Sulfur and Total Nitrogen simultaneously. Valuable information about samples containing both Sulfur and Nitrogen is created during a single run.

Calibration

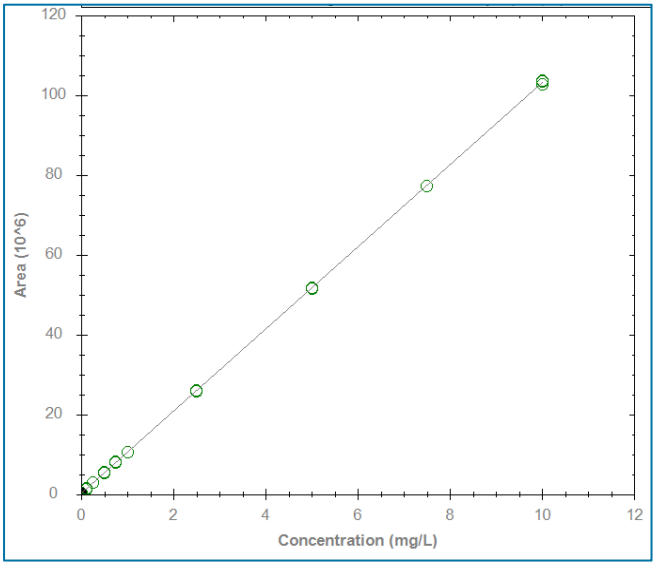
Standards used for calibration were made from Pyridine (N) and Dibutyl Sulfide (S) in Iso-Octane. The Xplorer-V is calibrated in the range 0.1-10 mg/L and 1-100 mg/L. All calibration points have been corrected for the average blank area count

Calibration Standards mg/L	Mean Area TN - 100 µL (n=5)	Mean Area TS - 100 µL (n=5)
Blank	-	-
0.10	3938225	1370839
0.25	5400454	2912696
0.50	7874347	5438341
0.75	10392309	7982544
1.00	12943147	10526248
2.50	28141899	25794556
5.00	53658003	51522374
7.50	79578072	77194065
10.00	105296803	103341780

Table 1: Calibration line TN/TS 0.1-10 mg/L



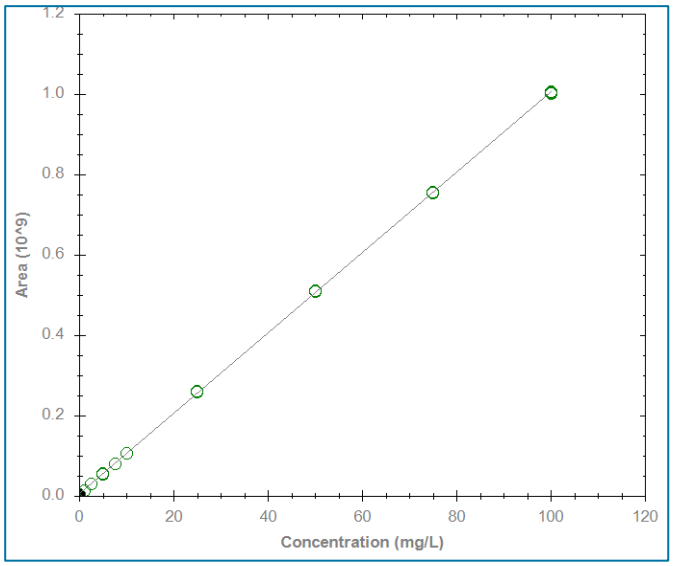
Calibration line TN 0.1 – 10 mg/L, r^2 = 0.99996



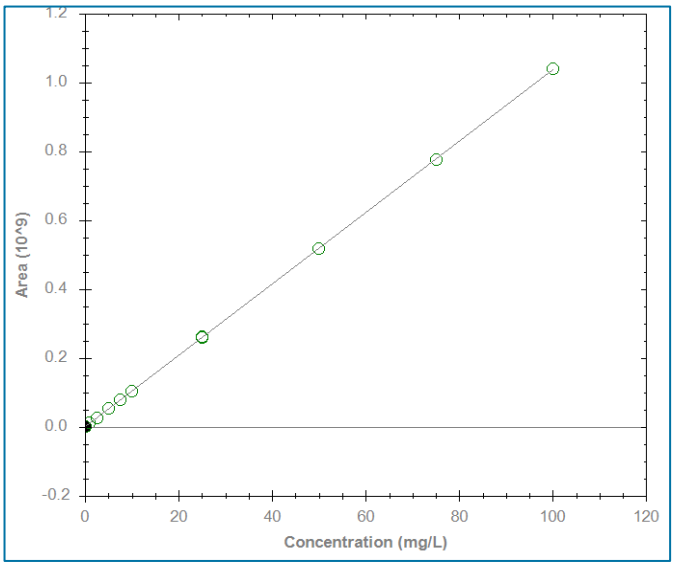
Calibration line TN 0.1 – 10 mg/L, r^2 = 0.99998

Calibration Standards mg/L	Mean Area TN -100 µL (n=5)	Mean Area TS - 100 µL (n=5)
Blank	-	-
1.00	13043244	10467256
2.50	28225461	25947773
5.00	53756844	51814100
7.50	79412688	77783137
10.0	105494774	104190741
25.0	258416263	259795886
50.0	508755512	516979281
75.0	754290212	775320179
100.0	1002618937	1039748202

Table 2: Calibration line TN/TS 1-100 mg/L



Calibration line TN 1.0 – 100 mg/L, r^2 = 0.99996



Calibration line TN 1.0 – 100 mg/L, r^2 = 0.99999

Analysis of Total Nitrogen (CLD) and Total Sulfur (UV-F) in renewable fuels: Aviation Fuel-HEFA and Diesel-HVO using the Xplorer-V

Results

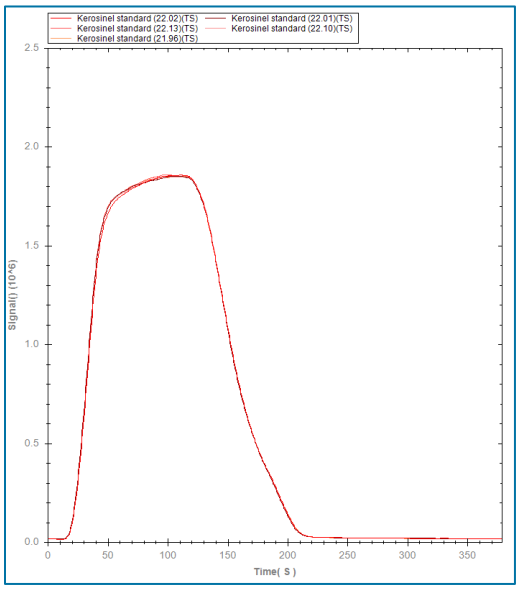
Nitrogen:

Sample	Expected value(mg/l)	Total Nitrogen (mg/l)	RSD (%) n=10
Kerosine CRM	0.36	0.34	2.35
Diesel RR	85.20	84.95	0.92
HEFA	n.a.	0.54	3.80
HVO	n.a.	2.59	0.72
HEFA/ Kerosine 50/50 V%	0.44	0.41	2.09
HVO/ Diesel 20/80 V%	68.48	68.49	1.34

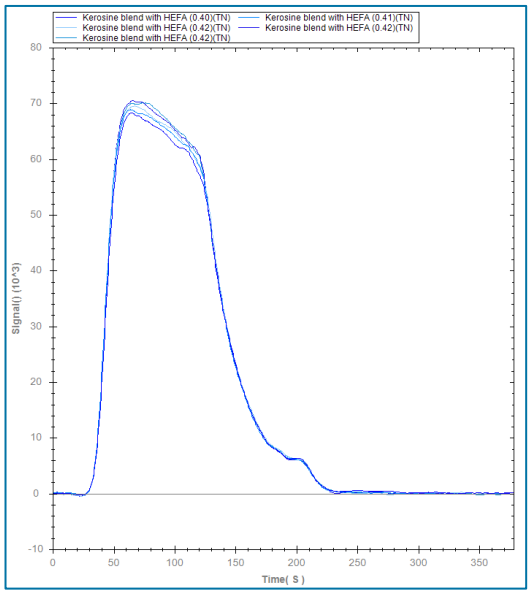
Sulfur:

Sample	Expected value (mg/l)	Total Sulfur (mg/l)	RSD (%) n=10
Kerosine CRM	22.10	22.05	0.20
Diesel RR	5.80	5.66	0.40
HEFA	n.a.	<0.10	n.a.
HVO	n.a.	0.14	1.15
HEFA/ Kerosine 50/50 V%	11.05	10.97	0.54
HVO/ Diesel 20/80 V%	4.67	4.59	1.61

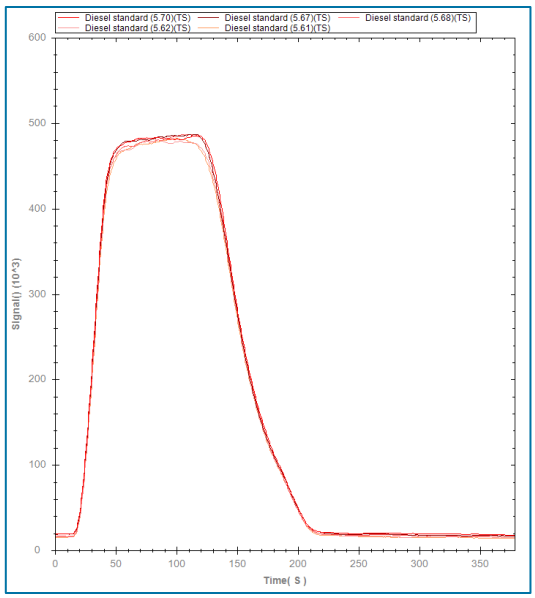
Example Peaks



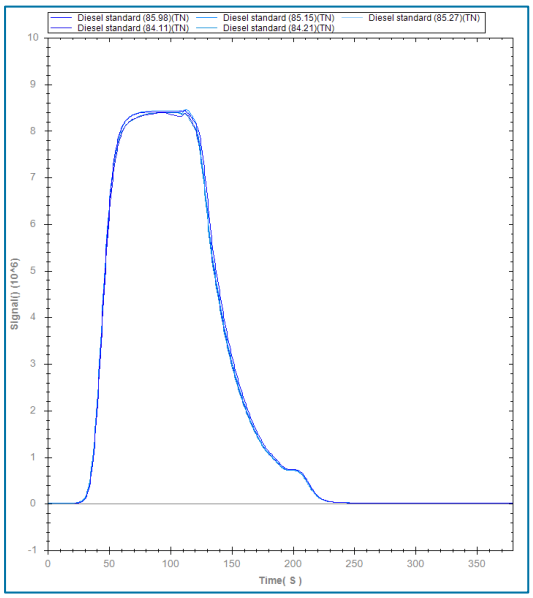
Kerosine/ HEFA blend – Peak Overlay
TS Signal
Replicates: 10
RSD: 0.54%



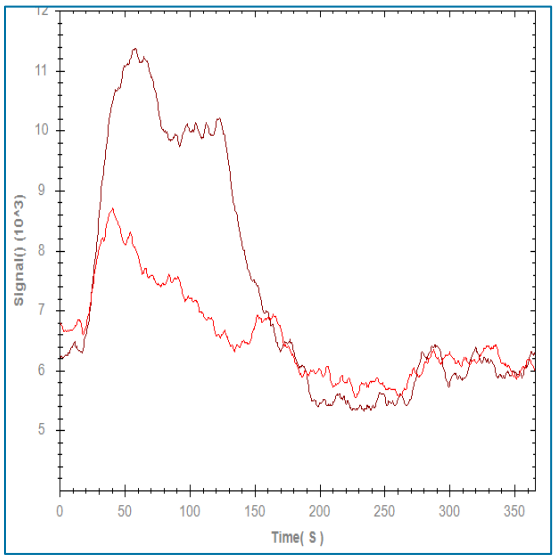
Kerosine/ HEFA blend – Peak Overlay
TN Signal
Replicates: 10
RSD: 2.09%



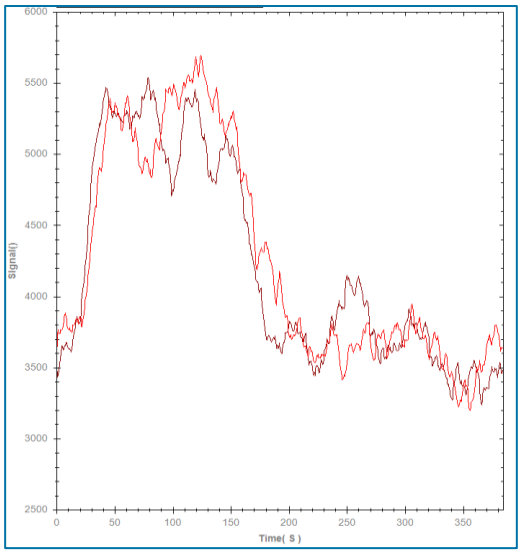
Diesel/ HVO blend – Peak Overlay
TS Signal
Replicates: 10
RSD: 1.61%



Diesel/ HVO blend – Peak Overlay
TN Signal
Replicates: 10
RSD: 1.34%



10 ppb compared to a blank – Peak Overlay
TS Signal



HEFA compared to a blank – Peak Overlay
TN Signal

System Settings

Parameter	Setting
Oxygen Flow	400 mL/min
Argon Flow	100 mL/min
Oxygen cleaning time	60 seconds
Furnace Temperature I	800 °C
Furnace Temperature II	1050 °C
Internal System Temperature	32 °C
Injection Speed	1 µL/s
Injection Volume	100 µL