



The analysis of Total Sulfur and Total Nitrogen in liquid hydrocarbons is a routine task at QC, Surveyor, and Refinery laboratories worldwide. These labs are often located at strategic positions, where lots of transshipment of petro (chemical) products takes place. These sites operate on a 24/7/365 basis. This makes it extremely important to have reliable instruments that deliver accurate results with maximum uptime. In this application note, TE Instruments introduces the XLS-30 liquid autosampler combined with the XPLOER-NS as a robust solution for these requirements.

## Sample Description

<b>Sample Type</b>	Liquid Hydrocarbons (boiling point <420 °C)
<b>Component</b>	Nitrogen / Sulfur
<b>Concentration</b>	0 – 100 mg/kg
<b>Methods Applicable</b>	ASTM D4629, ASTM D5453

## Summary

The XPLOER-NS elemental combustion analyzer, equipped with Liquids Introduction Module (Direct Injection), has been used to perform the analysis of Total Sulfur (UV-F) and Total Nitrogen (CLD) in Liquid Hydrocarbon matrices. All samples were introduced by the XLS-30 liquid autosampler and analyzed according to the fast method (3 minutes) and default method (6 minutes). Several round-robin samples have been analyzed to monitor the performance of the configuration according to the ASTM D5453 test method.

The results obtained are excellent, with standard deviations well below the repeatability limits (*r*), as stated in the ASTM D5453 for Total Sulfur and the ASTM D4629 for Total Nitrogen. Moreover, the results closely correspond to the mean concentrations of the related Inter Laboratory Studies (ILS) in which we participated.

## Solution

### XPLOER-NS

#### XLS-30

Liquid Autosampler



Liquid Introduction Module



Collision Flow Tube



## Results Default Method (6 minutes)

Sample n=5	Volume (µL)	Density (kg/L)	Conc. N (mg/kg)	RSD (%)	Conc. S - RR (mg/kg)	Conc. S (mg/kg)	RSD (%)
Fuel Ethanol	100	0.791	2.05	0.68	2.98	3.22	0.62
Biodiesel	100	0.843	3.91	0.62	5.80	5.86	0.25
FAME	100	0.885	1.37	1.48	0.46	0.35	3.97
Gasoil	100	0.832	108.59	0.20	N/A	7.04	0.23
Std. 10 ppm	100	0.864	10.15	0.36	N/A	10.18	0.39

Table 1 – Results for Default Method: Total Nitrogen and Total Sulfur Analysis in Liquid Hydrocarbons with the XLS-30

## Results Fast Method (3 minutes)

Sample n=5	Volume (µL)	Density (kg/L)	Conc. N (mg/kg)	RSD (%)	Conc. S - RR (mg/kg)	Conc. S (mg/kg)	RSD (%)
Fuel Ethanol	20	0.791	2.11	2.27	2.98	3.35	2.01
Biodiesel	20	0.843	3.72	0.50	5.80	5.64	0.61
FAME	20	0.885	1.33	6.05	0.46	0.41	9.82
Gasoil	20	0.832	102.56	0.35	N/A	6.80	0.81
Std. 10 ppm	20	0.864	10.01	0.30	N/A	10.17	0.44

Table 2 – Results for Fast Method: Total Nitrogen and Total Sulfur Analysis in Liquid Hydrocarbons with the XLS-30





## Method

The XLS-30 aspirates a pre-defined sample volume with high accuracy and volumetrically injects the sample material at a constant rate into the introduction module. The XLS-30 ensures uniform introduction of liquid samples into the direct injection- or boat module of the Xplorer Series. The XLS-30 forms a powerful combination with the elemental combustion solutions of TE Instruments in full compliance with, but not limited to, the following international test methods:

TN (CLD)	TS (UV-F)
ASTM D4629	ASTM D5453
ASTM D5762	ASTM D7183
ASTM D7184	EN ISO 20846
UOP 936	UOP 987 – Part A
UOP 981	

The fast method operates with 20 µL sample volume and is suitable for determination of concentrations >1 ppm. When ultra-sensitivity is required for trace level analysis (<1 ppm), a sampling volume of 100 µL is required. The larger sample volume improves the Limit of Detection and Limit of Quantification for trace level analysis.

## System Description

**Introduction** – The 30 position liquid autosampler automatically introduces the sample at controlled rate into the heated liquids module (500 °C). This module is specifically designed for the introduction of liquid samples with a final boiling point up to 420 °C.

**Combustion** - The XPLOERER-NS is fitted with a dual-zone furnace, which enhances combustion performances. The temperature is adjustable up to 1150 °C. The Collision Flow Tube has a secondary oxygen flow that collides with the oxidizing gas stream and replaces some of the depleted oxygen. Resulting in more oxidation power for samples which are difficult to oxidize.

**Conditioning** - Water vapor is removed from the gas stream by the Perma Pure gas dryer. Particles are blocked by a re-usable, cleanable filter, eliminating the need for expensive disposable PTFE fiber filters. Only the conditioned gas stream enters the Sulfur reaction chamber.

**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 XPLOERER-NS analyzes Total Sulfur and Total Nitrogen simultaneously. Valuable information about samples containing both Sulfur and Nitrogen is created during a single run.

## System Settings

Parameter	Setting
Oxygen Injection	300 mL/min
Argon Injection	100 mL/min
Oxygen Collision Flow	100 mL/min
Oxygen Ozonator Flow	50 mL/min
Furnace Temperature I	1000 °C
Furnace Temperature II	1000 °C
Liquids Module	500 °C
Injection Speed	1 µL/s

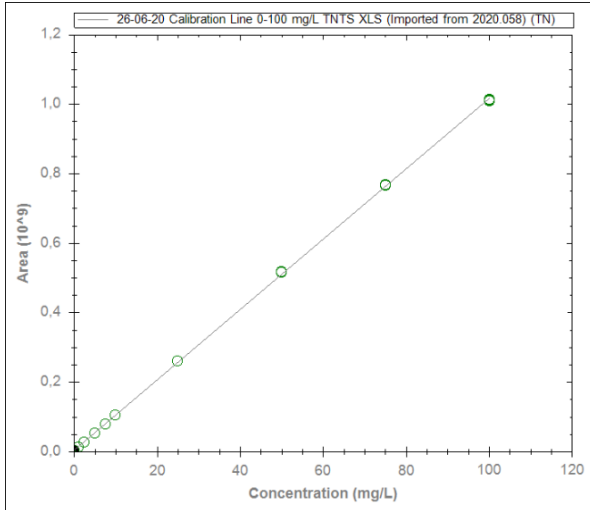
Table 3 - System settings for the Analysis of Total Nitrogen and Total Sulfur in Liquid Hydrocarbons



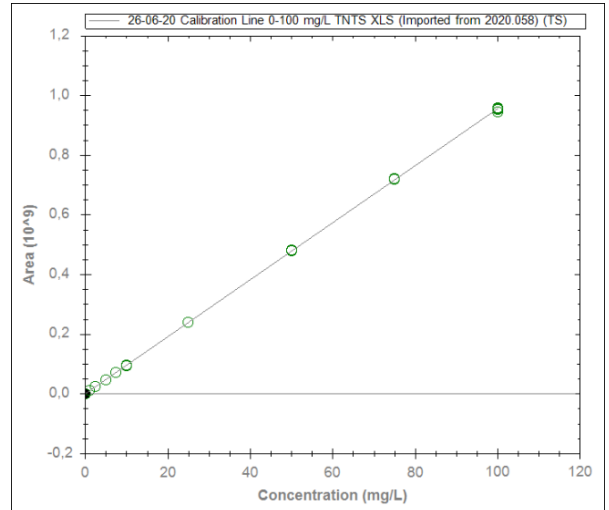


## Calibration

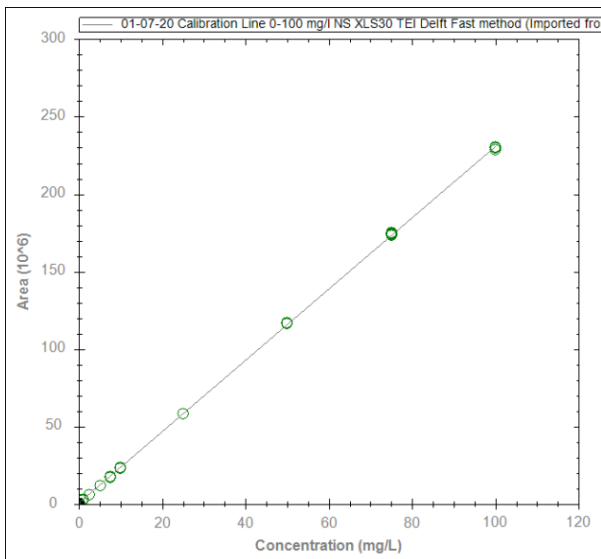
Calibration standards for both methods were made from DBS and Pyridine in Xylene following the ASTM guidelines. The Xplorer-NS was calibrated in the range of 0-100 mg/L. The calibration curves of both elements are demonstrated below.



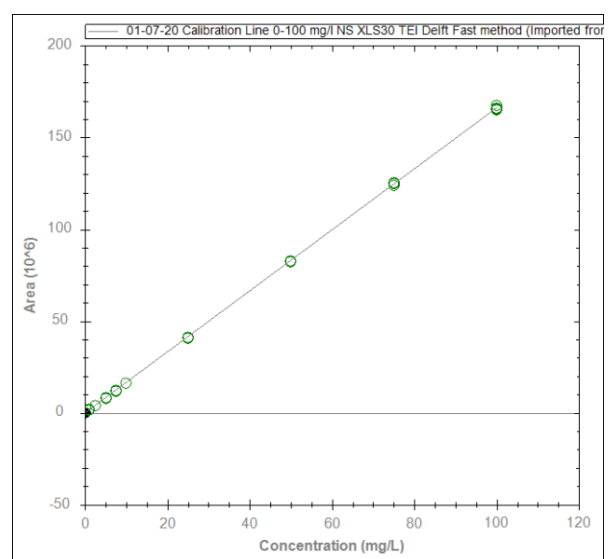
Cal. line TN Default: 0 – 100 mg/L,  $r^2$  0.9998



Cal. line TS Default: 0 – 100 mg/L,  $r^2$  0.9999



Cal. Line TN Fast: 0 – 100 mg/L,  $r^2$  0.9998

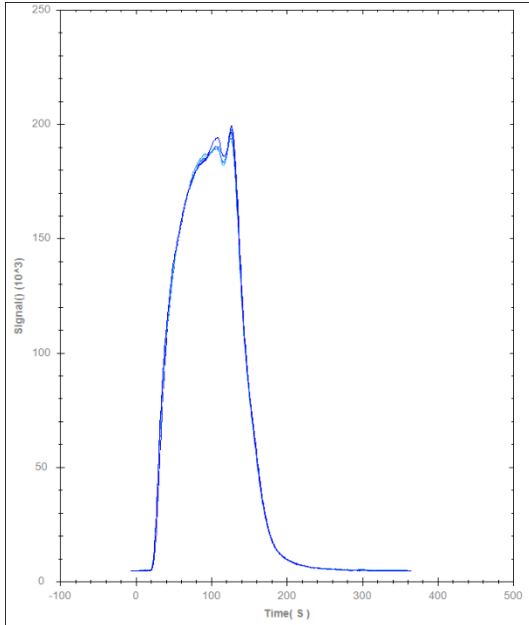


Cal. line TS Fast: 0 – 100 mg/L,  $r^2$  0.9999

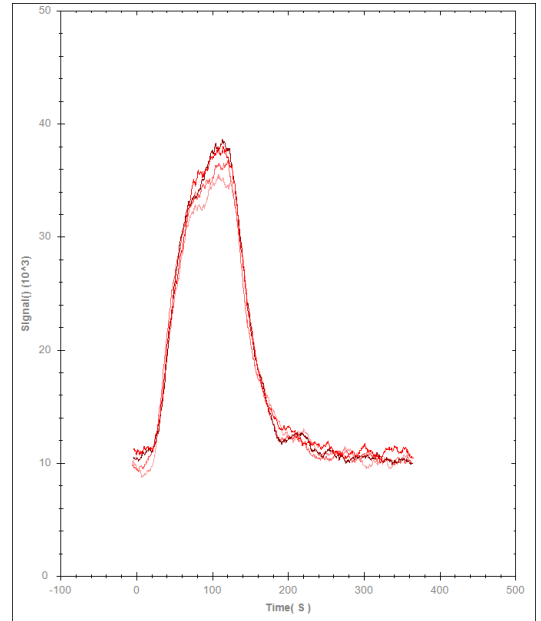




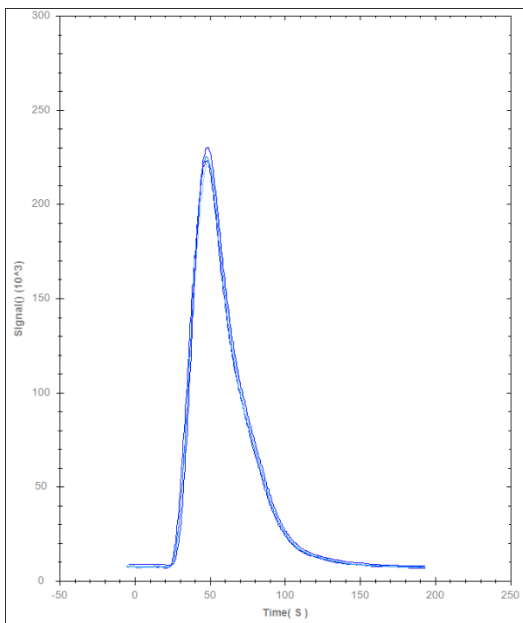
## Example Peaks



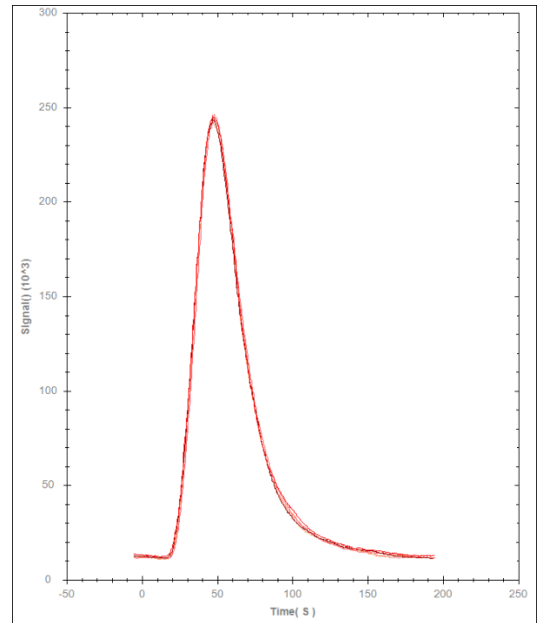
**Fuel Ethanol – Default Method – TN Peak Overlay**  
Concentration: 2.05 mg/kg  
Replicates 5 – RSD 0.68%



**FAME – Default Method - TS Peak Overlay**  
Concentration: 0.35 mg/kg  
Replicates: 5 – RSD: 3.97%



**Biodiesel – Fast Method – TN Peak Overlay**  
Concentration: 3.72 mg/kg  
Replicates 5 – RSD: 0.50%



**Gasoil – Fast Method – TS Peak Overlay**  
Concentration: 6.80 mg/kg  
Replicates 5 – RSD: 0.81%

