

# TOTAL SULFUR AND TOTAL NITROGEN ANALYSIS - HORIZONTAL VERSUS VERTICAL FURNACE ARRANGEMENT

In the analytical market, there has always been an ongoing discussion about which furnace setup performs the best in combustion analyzers. Some analysts claim a horizontal furnace placed version gives you the best performance, others swear on a vertical furnace setup.

TE instruments has recently developed a new model analyzer, Xplorer-V, for the analysis of total sulfur and total nitrogen levels in hydrocarbon products with a boiling point between 25 and 520 °C. The Xplorer-V is equipped with (as the name suggests) a furnace that is placed vertically for the combustion of samples. The analyzer is equipped with a sulfur detector that uses UV-fluorescence and a nitrogen detector that is based on chemiluminescence.

The Xplorer-V was launched as an extension of the existing portfolio of the similar already available analyzer from TE Instruments, the Xplorer TNTS. The Xplorer TNTS is based on the same analyzer principles as the Xplorer-V, utilizes the same detectors but has one main difference; the furnace is placed horizontally for the benefit of a boat-inlet for solid applications.

## Horizontal VS Vertical:

During the development and introduction of the new Xplorer-V analyzer, a validation of the performance characteristics was performed and compared against the Xplorer TNTS. Both types of analyzers were simultaneously validated, and the results were used to look at biases in the performance between both analyzers.

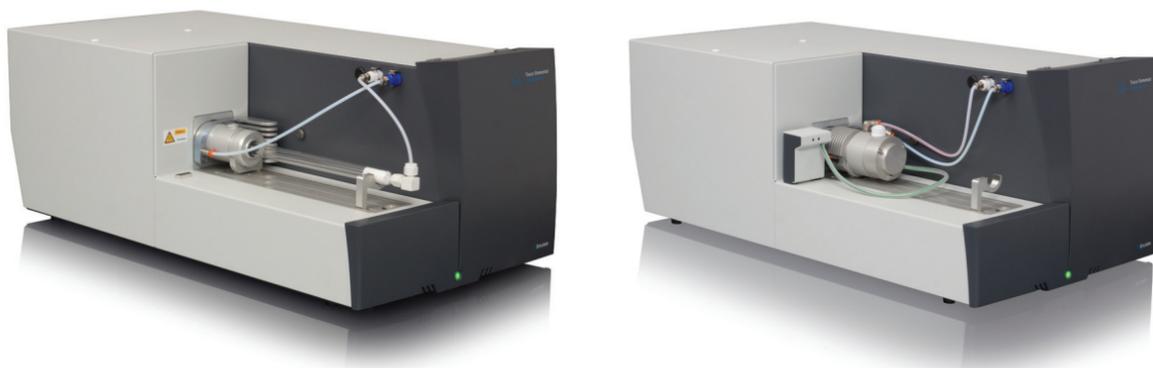
The Xplorer-V was expected to perform at least as well as the current analyzer Xplorer TNTS, in terms of repeatability and reproducibility. Changes in the design of the Xplorer-V analyzer, like the absence of a separate liquid inlet module and the vertically placed furnace, suggest it should be better able to measure components with a final boiling point of  $\geq 420$  °C without compromising repeatability (RSD) and/or recovery.

In the Xplorer TNTS the furnace is placed horizontal, and a separate liquids injection module is used to evaporate the sample. This liquids introduction module is set at a fixed temperature of 500 °C. Hence the maximum boiling temperature for liquid samples is set at 420 °C for the Xplorer TNTS to be safe and to prevent accumulation of sample material in the module.

In case samples need to be injected with higher boiling ranges on the Xplorer TNTS, a boat inlet module needs to be utilized instead of the liquids module introduction. With a boat inlet introduction, the sample is injected into a quartz cup filled with quartz wool. The cup is transferred into the high-temperature furnace at a pre-defined speed and depth. This method is great for high boiling samples and difficult matrices, as the introduction is nicely controlled by the speed of the cup movement. A minor drawback however, is the analysis time due to the cooling step at the end of the analysis. Sample analysis with a liquid introduction module tends to be around 3 to 6 minutes, while a boat introduction typically comes with an analysis time of approximately 5 to 9 minutes.

Prior to the combustion of samples, controlled sample evaporation is key to achieve the best result. In the case of the Xplorer TNTS, the boat inlet or liquids module handles this. For the Xplorer-V, the sample evaporation is controlled by a pre-combustion inlet which is placed inside the combustion tube. After evaporation of the sample, the material is carried into the hot zone of the combustion tube by the inert carrier gas. With the collision of oxygen gas, combustion of the sample takes place. In the Xplorer-V, the sample is injected into pre-combustion inlet where the sample fully evaporates under an inert gas stream at 650°C prior to entering the vertically placed combustion tube. In the combustion tube, the sample reacts with oxygen for full combustion. Due to this new design, hydrocarbons with a high boiling point have less tendency to deposit in the "colder" pre-combustion inlet. Together with the carrier gas flow the sample also enjoys the gravitational forces which assists the sample to flow into the hotter bottom part of the combustion tube.

As mentioned, both analyzers are combustion analyzers in which a small amount of sample, typically  $\leq 100$   $\mu$ L, is injected and combusted. The exhaust stream of this oxidation process is analyzed for the presence of sulfur dioxide and nitric oxide with the use of UV-fluorescence and chemiluminescence measuring principle.



Picture 1: Left - liquids introduction on Xplorer TNTS with liquids module, right - liquids introduction on Xplorer TNTS with boat inlet.

For the validation of the new analyzer, a side-by-side bias comparison is made between the Xplorer-V and the Xplorer TNTS.

During the validation and comparison, the following required and non-required parameters have been analyzed: Limit of Detection (LOD), repeatability, recovery, memory effect, and Linearity. In this condensed paper, we present the results for repeatability and recovery as main parameters for comparison. Other parameters reach out of the scope of the topic of this paper.

## Apparatus and method settings:

### Vertical combustion analyzer:

Xplorer-V N/S version with standard combustion tube inlet and Xpro-Vtm combustion tube. Liquid autosampler integrated in analyzer.



Picture 2: Xplorer-V TN/TS version

### Horizontal combustion analyzer:

Xplorer TNTS version with Xpro Combustion Tube with dual stage filters and liquids introduction Module with Archie Liquids autosampler.



Picture 3: Xplorer TNTS

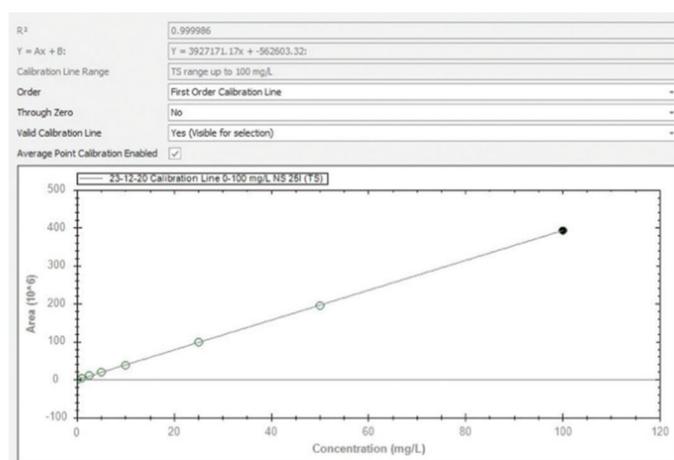
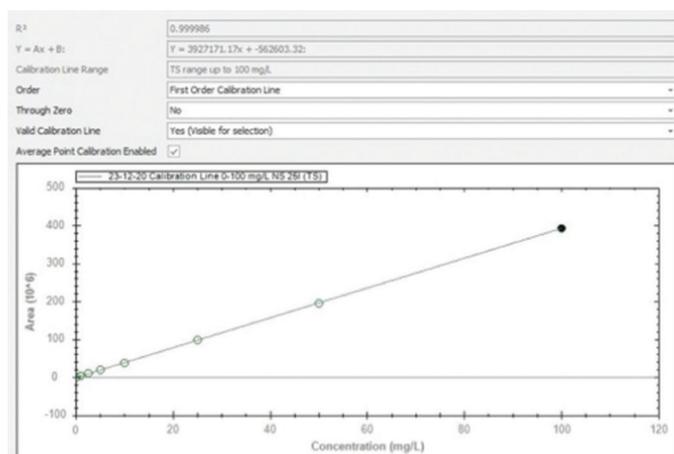
|                            | Xplorer-V TN/TS        | Xplorer TNTS |
|----------------------------|------------------------|--------------|
| <b>Temperatures (°C)</b>   | Inlet module           | 650          |
|                            | Zone 1                 | 650          |
|                            | Zone 2                 | 1000         |
| <b>Gas flows (ml/min)</b>  | Carrier                | 100          |
|                            | Oxygen                 | 400          |
| <b>Sample introduction</b> | Sample volume (µl)     | 100          |
|                            | Injection speed (µl/s) | 1,0          |

## Calibration

For calibration of the analyzers we made calibration lines with dissolved Pyridine in Xylene (Total N) and dissolved Thiophene in Xylene (Total S) according to the following dilution scheme:

|             | Concentration Total N (ppm) | Concentration Total S (ppm) |
|-------------|-----------------------------|-----------------------------|
| Standard 1  | 0                           | 0                           |
| Standard 2  | 1                           | 1                           |
| Standard 3  | 2.5                         | 2.5                         |
| Standard 4  | 5.0                         | 5.0                         |
| Standard 5  | 7.5                         | 7.5                         |
| Standard 6  | 10                          | 10                          |
| Standard 7  | 25                          | 25                          |
| Standard 8  | 50                          | 50                          |
| Standard 9  | 75                          | 75                          |
| Standard 10 | 100                         | 100                         |

The results of the calibration are presented in the 2 graphs below:



## Results:

A range of 8 different sample matrices ranging from low boiling to high boiling hydrocarbon liquids and material originated from biobased products like Biodiesel and FAME have been injected on both analyzer systems.

Each sample was injected from 10 individual vials. The results from both the nitrogen and the sulfur results are displayed in table 1 and table 2. As mentioned, the focus of this study was to check the reproducibility and accuracy of the different samples to compare the performance.

Table 1 Sulfur results:

| Sample (N = 10)     | boiling point (°C) | Horizontal (mg/kg) | RSD (%) | Vertical (mg/kg) | RSD (%) |
|---------------------|--------------------|--------------------|---------|------------------|---------|
| Diesel              | 150 - 380          | 5,60               | 0,75    | 5,80             | 0,69    |
| Gasoline            | 100 - 400          | 4,01               | 0,55    | 4,03             | 1,12    |
| CRM 100 mg/kg       | 140                | 101,29             | 0,70    | 99,81            | 0,14    |
| CRM 10 mg/kg        | 140                | 9,98               | 0,47    | 10,00            | 0,36    |
| Biodiesel           | 350                | 0,42               | 3,20    | 0,38             | 3,71    |
| Bio Ethanol         | 65                 | 2,20               | 2,56    | 2,71             | 2,71    |
| Fame                | 430                | 7,62               | 1,66    | 7,46             | 1,35    |
| Crude oil (Diluted) | 260 - 280          | 26,42              | 0,19    | 26,90            | 2,09    |
| VGO (Diluted)       | 425 - 510          | 151,81             | 0,32    | 150,17           | 0,70    |

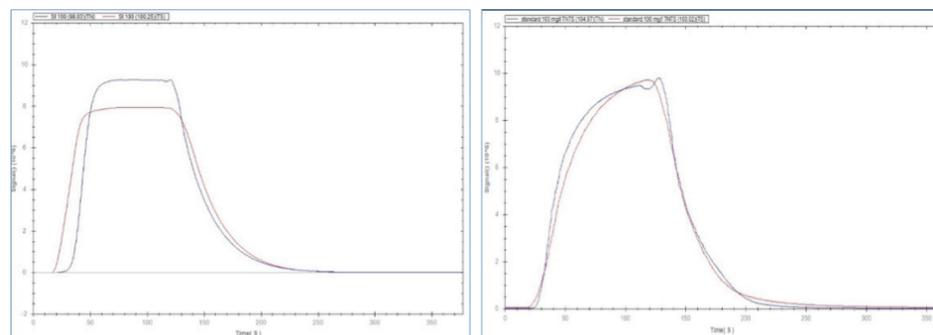
Table 2 Nitrogen results:

| Sample (N = 10)     | boiling point (°C) * | Horizontal (mg/kg) | RSD (%) | Vertical (mg/kg) | RSD (%) |
|---------------------|----------------------|--------------------|---------|------------------|---------|
| Diesel              | 150 - 380            | 91,24              | 0,62    | 92,01            | 0,22    |
| Gasoline            | 100 - 400            | 6,51               | 1,43    | 6,61             | 1,68    |
| CRM 100 mg/kg       | 140                  | 101,82             | 0,32    | 100,48           | 0,25    |
| CRM 10 mg/kg        | 140                  | 10,08              | 0,39    | 10,26            | 0,40    |
| Biodiesel           | 350                  | 1,73               | 3,29    | 1,88             | 2,86    |
| Bio Ethanol         | 65                   | 1,93               | 2,82    | 1,92             | 1,43    |
| Fame                | 430                  | 16,88              | 0,82    | 17,13            | 0,96    |
| Crude oil (Diluted) | 260 - 280            | 2,91               | 1,90    | 3,14             | 2,08    |
| VGO (Diluted)       | 425 - 510            | 58,10              | 0,84    | 59,56            | 1,03    |

\*For some samples, typical boiling ranges are reported, the exact boiling values were not available during time of reporting.

A vertically placed furnace gives a different peak shape compared to horizontal analyzer units. Peaks seem to reach an equilibrium in a faster way once reaching the detector chambers after combustion and keeps a steadily filled detector room. This is different compared to the peak behavior, which is seen in the Xplorer TNTS analyzer.

To show the difference, below two recordings are presented from a Xplorer-V compared to the Xplorer TNTS. The flat spot you see in the left picture is not because we reached a detector max. It is because we get a continuous supply of analytes in the detector chambers and already reached an equilibrium.



Picture 4: peak comparison of a 100 ppm CRM standard for Nitrogen and Sulfur, left Xplorer V, right Xplorer TNTS

Last notice on the results: The crude oil samples and VGO samples needed a small dilution to compensate for viscosity and to prevent coagulation of the material. Further on, for the VGO samples and crude oil, the boat introduction was required on the Xplorer TNTS to prevent accumulation or blocking of the sample material on the inlet.

## Conclusion:

From the tests run on both analyzer systems, it is hard to appoint a clear winner in our laboratories. Some samples run a little better on the vertical system, some on the horizontal system. In both situations, it is clearly seen that all different materials can be run on either one of these systems. It seems like it all comes back again to personal preferences and experience or situation-dependant.

If we were to put a sticker on both systems, we suggest the following:

- Use a vertical analyzer system for performing daily analysis on liquid and gasses (+ LPG) for samples ranging from a broad range of matrices, simple and steady with guaranteed high uptimes.
- Use a horizontal analyzer for performing analysis on liquids, solids, and gas (+LPG) with samples from a broad range of matrices but respecting boiling ranges from the samples. The Xplorer TNTS analyzer is more flexible because different liquid autosamplers are available, and solids can also be introduced with a dedicated autosampler.

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