# A COMPREHENSIVE STABILITY STUDY ON THE XPLORER TOTAL SULFUR/TOTAL NITROGEN ANALYZERS

An elemental combustion analyzer is able to measure the amount of Total Nitrogen, and Total Sulfur by means of high-temperature combustion (approximately 1000 ˚C) in an oxygen-rich environment. In Trace Elemental combustion elements can be detected from trace level (µg/kg/ ppb level) up to 10.000 ppm/ mg/L (1%) there where the elemental analyzers for CHNSO are mainly designed for a high-level percentage measuring range.

By combusting sample material (Solid, Liquid or Gas), NO and $SO_2$ are formed which can be detected by a Pulsed UV-Fluorescence followed by a Chemiluminescence detector.

Our quartz combustion tube is constructed in such a way that it allows direct injection of the sample into the heated oxidation zone of the furnace and/or to accommodate the sample introduction using a quartz sample boat. The surface of the oxidation section of the combustion tube must be large enough to ensure complete oxidation of the sample. However, some elemental combustion analyzer manufacturers pack the quartz combustion tube with an oxidation catalyst to achieve this.

The XPLORER Series does not make use of oxidation catalyst: The unique construction of the Xplorer combustion tubes is designed in such a way, to always deliver sufficient oxidation power on samples that are difficult to combust.

More recently, ceramic material has been introduced as an alternative to fully quartz combustion tubes, for better protection of the tube when running samples containing high halogen concentrations (or other components which might attack the quartz material).

## Detection of Total Nitrogen – Chemiluminescence

When Nitrogen components are combusted in the high-temperature furnace, the following reaction takes place:

$R - N + O_2 \rightarrow NO + H_2O + CO_2$

After complete sample oxidation, the combustion gas is conditioned by removing water vapor and particles.

Ozone is added to the conditioned gas stream in the Chemiluminescence reaction chamber. Ozone reacts with Nitric Oxide (NO) to form Nitrogen Dioxide in an excited state ($NO_2$*). The emitted light is detected by a Photomultiplier Tube (PMT). The amount of detected emitted light corresponds with the amount of NO (Total Nitrogen) present in the sample.

**Detection:**

$NO + O_3 \rightarrow NO_2^* + O_2$

$NO_2^* \rightarrow NO_2 + h\nu_1$

## Detection of Total Sulfur – UV-Fluorescence

When organic Sulfur components are combusted in the high-temperature furnace, the following reaction takes place:

$R\text{-}S + O_2 \rightarrow SO_2 + H_2O + CO_2$

After complete sample oxidation, the combustion gas is conditioned by removing water vapor and particles.

The conditioned gas stream containing the Sulfur Dioxide ($SO_2$) molecules is transferred to the reaction chamber. The Xenon flashed UV lamp will excite the Sulfur Dioxide molecules to $SO_2$* at specific wavelengths and due to the unstable character of the $SO_2$* it will relax back to $SO_2$ instantly. The released energy will be emitted in the form of light and will be detected by the Photomultiplier Tube (PMT). The amount of light emitted equals the total amount of $SO_2$ (Total Sulfur) present in the sample.

**Detection:**

$SO_2 + h\nu 1 \rightarrow SO_2^*$

$SO_2^* \rightarrow SO_2 + h\nu_2$

*Xplorer TN/TS with Archie autosampler*

*Xplorer-V NS*

## Stability study setup

The following Xplorer elemental combustion analyzers have been used to perform the analysis of Total Nitrogen (CLD) and Total Sulfur (UV-F):

- Xplorer TN/TS — Horizontal furnace based setup
- Xplorer-V TN/TS — Vertical furnace based setup

All samples were introduced by direct liquid injection with either the Archie autosampler (combined with Horizontal Xplorer TN/TS) or the integrated liquid autosampler of the Xplorer-V. Basic standard method parameters were applied to the 3 sample matrices (see systems settings below). The samples were analyzed daily on the two systems for the duration of three months.

No calibration or re-calibration was applied to the setup during the 3 months stability study. Other than small minor maintenance tasks (replacing needles, replacing septum or refilling of solvents) no intervention was allowed to check potential drift or stability issues on the furnace, detectors and complete analyzer setup.

| **Sample Information** | | |
|---|---|---|
| **Sample Type** | Diesel, Petrol, Xylene based CRM Standards | |
| **Component** | Nitrogen, Sulfur | |
| **Concentration** | 0.1 – 100 mg/l | |
| **Methods Applicable*** **instrumentation complies with mentioned norms but is not limited by them* | ASTM D5453 | ASTM D4629 |
| | ASTM D6667 | ASTM D5762 |
| | ASTM D7183 | ASTM D6069 |
| | EN 20846 | ASTM D7184 |

## Summary

During a run time of 3 months, both analyzers showed excellent stability over the complete course. As mentioned, only minor maintenance actions were allowed (e.g. needle changes, septa and filters) both systems were running on their initial calibration lines during the course of the test.

For the evaluation of the data, Tier 3 regulations for the calculation of system stability were applied to all the results, more information can be found in ASTM 7039. In the document, an R factor is calculated according to systematic standard deviation and averages, which results in maximal allowed limits for both accuracy and precision.

See section "results" for more in-depth information concerning the outcome of the study.

## Calibration

Standards used for calibration were made from Pyridine (N) and Dibutyl Sulfide (S) in Iso-Octane. The Xplorer analyzers are 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.

## Results

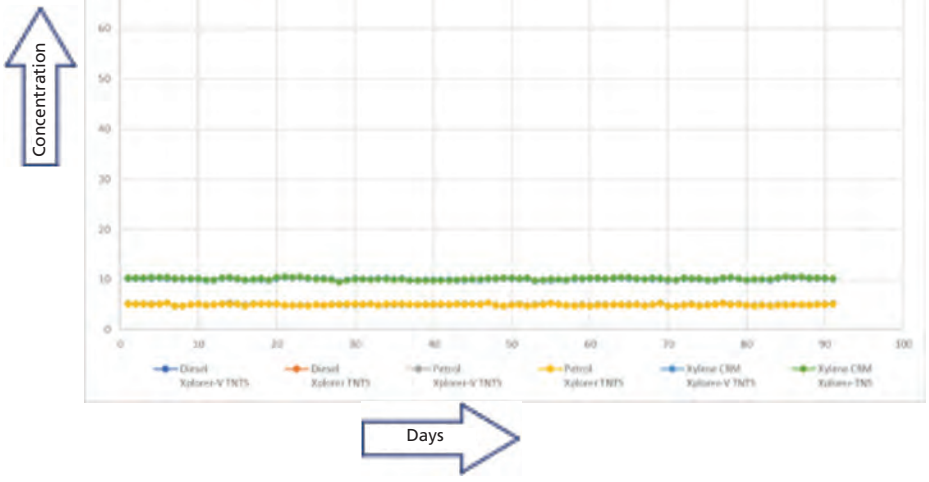
*Sulfur: Overview graph of the 90 day run*


*Sulfur: Calculated final Tier 3 results for precision and accuracy on Sulfur, 90 day run*

| Precision | Diesel Xplorer-V TNTS | Diesel Xplorer TNTS | Petrol Xplorer-V TNTS | Petrol Xplorer TNTS | Xylene CRM Xplorer-V TNTS | Xylene CRM Xplorer-TNS |
|---|---|---|---|---|---|---|
| Average | 5,72 | 5,79 | 5,07 | 5,03 | 10,08 | 10,08 |
| Standard deviation | 0,093 | 0,15 | 0,100 | 0,105 | 0,122 | 0,175 |
| RSD | 1,627 | 2,50 | 1,966 | 2,086 | 1,213 | 1,734 |
| Max standard deviation 1.5*(rASTM D7039)/2,77 | **0,694** | **0,70** | **0,650** | **0,648** | **0,942** | **0,943** |
| rASTM D7039 | 1,282 | 1,29 | 1,201 | 1,196 | 1,740 | 1,741 |
| **Final Result:** | **PASS** | **PASS** | **PASS** | **PASS** | **PASS** | **PASS** |

| Accuracy | Diesel Xplorer-V TNTS | Diesel Xplorer TNTS | Petrol Xplorer-V TNTS | Petrol Xplorer TNTS | Xylene CRM Xplorer-V TNTS | Xylene CRM Xplorer TNTS |
|---|---|---|---|---|---|---|
| Target value | 5,72 | 5,79 | 5,07 | 5,04 | 10,08 | 10,09 |
| standard deviation | 0,09 | 0,15 | 0,10 | 0,11 | 0,12 | 0,18 |
| Max standard deviation 1.5*(rASTM D7039)/2,77 | **0,694** | **0,699** | **0,650** | **0,648** | **0,943** | **0,943** |
| r of ARV | 1,28 | 1,29 | 1,20 | 1,20 | 1,74 | 1,74 |
| Max allowed Δ from target | 0,52 | 0,52 | 0,49 | 0,49 | 0,71 | 0,71 |
| **Final result** | **PASS** | **PASS** | **PASS** | **PASS** | **PASS** | **PASS** |

*Nitrogen: Overview graph of the 90 day run*



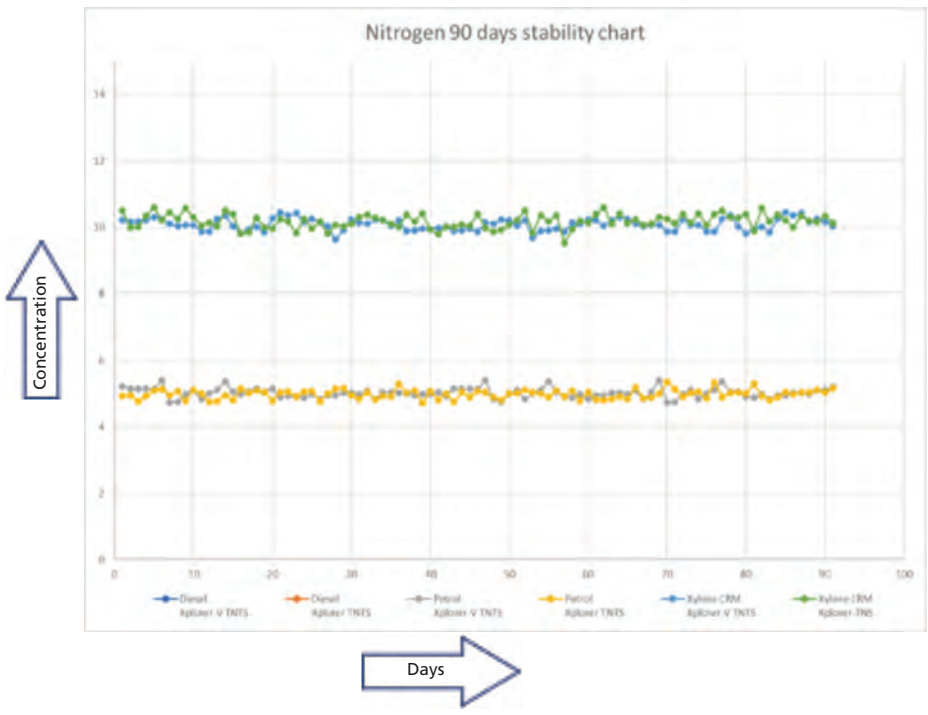

*Nitrogen: Calculated final Tier 3 results for precision and accuracy on Nitrogen, 90 day run.*

| Precission | Diesel Xplorer-V | Diesel Xplorer TNTS | Petrol Xplorer-V | Petrol Xplorer TNTS | Xylene CRM Xplorer-V | Xylene CRM Xplorer-TNS |
|---|---|---|---|---|---|---|
| Average | 87,87 | 89,42 | 5,02 | 4,98 | 10,08 | 10,18 |
| Standard deviation | 0,981 | 1,26 | 0,148 | 0,138 | 0,175 | 0,212 |
| RSD | 1,116 | 1,41 | 2,948 | 2,759 | 1,734 | 2,082 |
| Max standard deviation 1.5*(rASTM D7039)/2,77 | **3,034** | **3,06** | **0,647** | **0,644** | **0,943** | **0,947** |
| rASTM D7039 | 5,604 | 5,66 | 1,195 | 1,190 | 1,741 | 1,749 |
| **Final Result:** | **PASS** | **PASS** | **PASS** | **PASS** | **PASS** | **PASS** |

| Accuracy | Diesel Xplorer-V TNTS | Diesel Xplorer TNTS | Petrol Xplorer-V TNTS | Petrol Xplorer TNTS | Xylene CRM Xplorer-V TNTS | Xylene CRM Xplorer TNTS |
|---|---|---|---|---|---|---|
| Target value | 87,87 | 89,40 | 5,02 | 4,99 | 10,08 | 10,18 |
| standard deviation | 0,98 | 1,26 | 0,15 | 0,14 | 0,17 | 0,21 |
| Max standard deviation 1.5*(rASTM D7039)/2,77 | **3,035** | **3,063** | **0,647** | **0,645** | **0,943** | **0,947** |
| r of ARV | 5,60 | 5,66 | 1,19 | 1,19 | 1,74 | 1,75 |
| Max allowed Δ from target | 2,28 | 2,30 | 0,49 | 0,48 | 0,71 | 0,71 |
| **Final result** | **PASS** | **PASS** | **PASS** | **PASS** | **PASS** | **PASS** |

**For more information please visit www.teinstruments.com**

*Nitrogen: Overview graph of the 90 day run, zoomed in on lower levels*

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