TRUE TOTAL SULFUR ANALYSIS WITH NO-CT™ TECHNIQUE MEET THE NEW NITROGEN INTERFERENCE SOLUTION

Introduction

When analyzing Total Sulfur in Hydrocarbon Products or Derivatives, interference with high concentrations of Nitrogen-containing components might become troublesome. TE Instruments developed a new Nitrogen Oxide Correction Technology (NO-CT™) Solution for the analysis of true Total Sulfur values in samples that contain high quantities of Nitrogen.

Background

When using high-temperature oxidative sample combustion analyzers. The introduced Nitrogen containing components, present in a sample, are converted into Nitrogen Oxides (NO/NO_2). The Nitric oxide molecules interfere by absorbing and emitting light in the same wavelength range as SO_2 molecules do when using UV-Fluorescence detection techniques. This additional absorption and excitation of the nitric oxide molecules result in a false (positive) contribution to the measured amount of Total Sulfur.

In the ASTM 5453 19a (Standard Test Method for Determination of Total Sulfur in Light Hydrocarbons, Spark Ignition Engine Fuel, Diesel Engine Fuel and Engine Oil by UV-F), the contribution of Nitrogen to Sulfur was introduced with corrective suggestions. The contribution to Sulfur results may either be corrected by calculation, or by elimination of the NO molecules in the outlet gasses.

Preventing NO molecules to enter the Sulfur detector is frequently achieved by the elimination of the NO molecules. Elimination can be achieved by adding a gas flow of Ozone (O_3) to the flow path after the combustion, which when it reacts with NO forms NO_2 (NO_2 has no absorption in the UV-F detector). Since O_3 is an aggressive oxidator, it will damage the UV-F reaction cell over time. To add up: Dilution of outlet gasses with ozone has an impact on the limit of detection values and effecting the linearity of UV-F detectors.

The innovative Xplorer analyzers from TE Instruments and its UV-Fluorescence detection already have a reduced sensitivity for NO contribution when measuring Sulfur, but when true Sulfur numbers are required, the Xplorer analyzer can now be upgraded with the new Nitrogen Interference (NO-CT™) solution.

This new Nitrogen Interference solution corrects the NO interference and contribution in the Combustion Gas and calculates the true Sulfur results. With NO-CT™ no changes are applied to the gas flows, there is no impact on the UV-F detector, and LOD or Linearity is unaffected.

Effect of high Nitrogen on Sulfur

To demonstrate the effect of NO molecules on a UV-F Sulfur detector, a series of Nitrogen standards with increasing concentrations of Nitrogen, were measured on an Xplorer-TS analyzer. The following charts were recorded for 50, 100, 500, and 1000 ppm Nitrogen standards containing zero Sulfur:

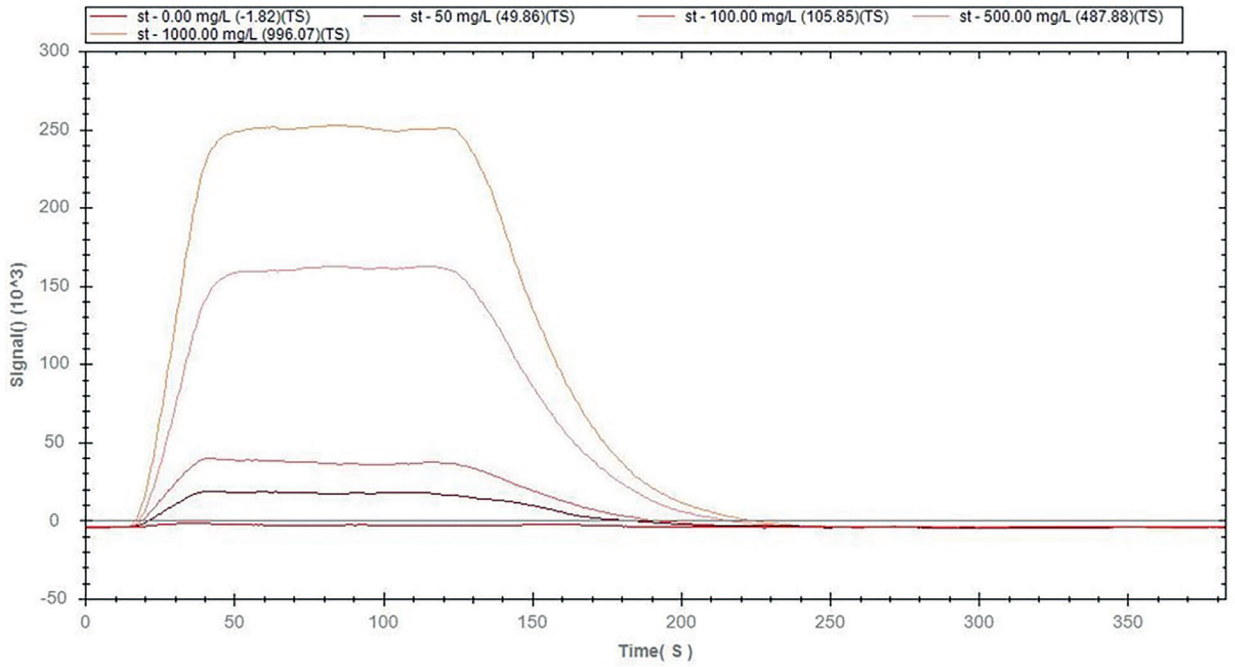

Figure 1: Overlay Chart of Sulfur detection on Xylene solvent with added 50, 100, 500, and 1000 ppm Nitrogen standard

Interpolating the areas on a calibration line gives an estimate of the added values of Nitrogen concentrations to the Sulfur values:

Sample	Additional Area counts in the UV-F detector	Estimated mg/L added concentration on Sulfur values
10 ppm sulfur + 50 ppm Nitrogen	2838601	0,11
10 ppm sulfur + 100 ppm Nitrogen	5562669	0,23
10 ppm sulfur + 500 ppm Nitrogen	20926227	1,30
10 ppm sulfur + 1000 ppm Nitrogen	32648538	2,60

Table 1: Added values of Nitrogen on Sulfur results.

NO-CT™

NO-CT™ is a correction technique, based on calculations in TEIS, the software package from TE Instruments for the control of the analyzers and interpretation of data. This software feature is available in TEIS 2 software packages from version 2.5.7 or higher and makes use of a combination of Sulfur measurement and a Nitrogen interference measurement.

Analyzers which contain both a UV-F detector and a CLD detector were already able to use this corrective technology but for systems without a CLD detector, the correction was not possible.

Standard	Concentration Total Sulfur (ppm)	Spiked Concentration Total Nitrogen (ppm)
1	10	0
2	10	100
3	10	500
4	10	1000

Table 2: Calibration Standards used for correction technology test.

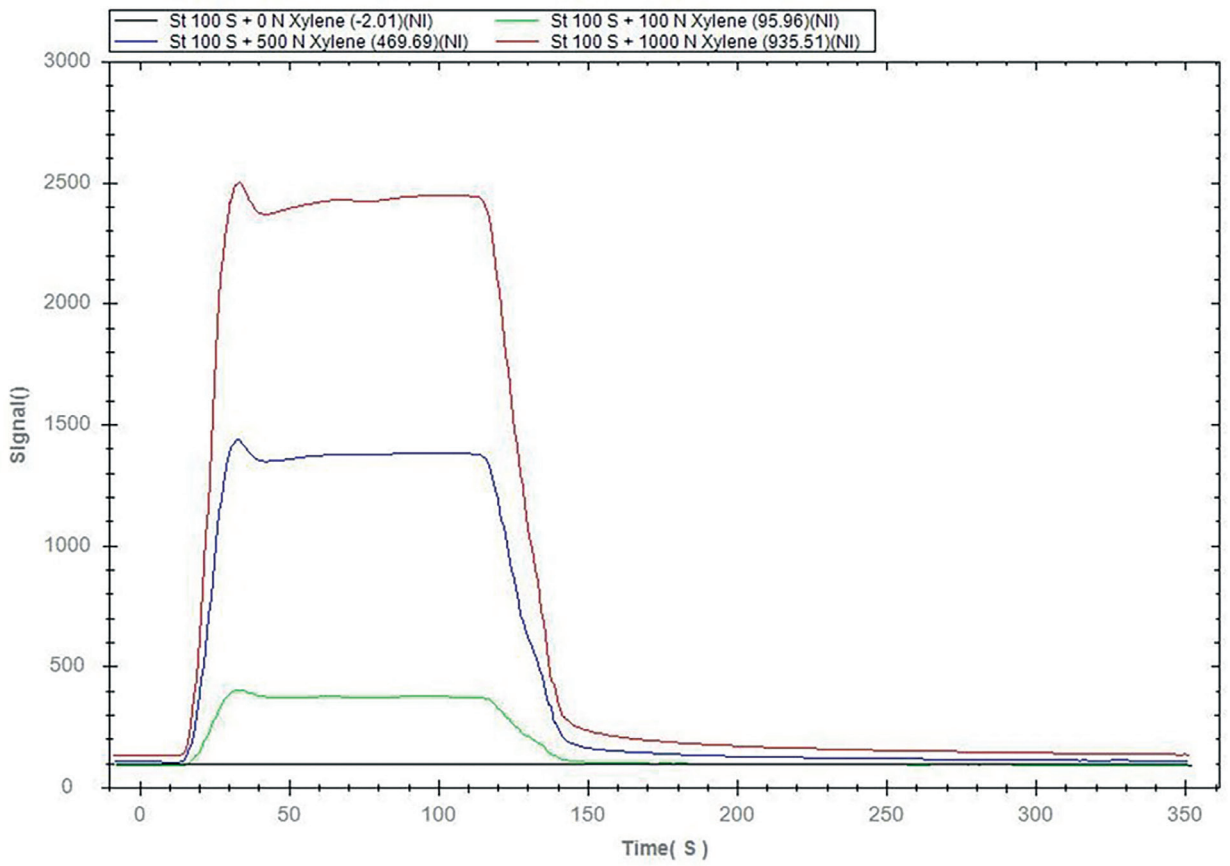

Figure 3: Overlay Chart of the NO-CT™ on 0, 100, 500, and 1000 ppm Nitrogen standards.

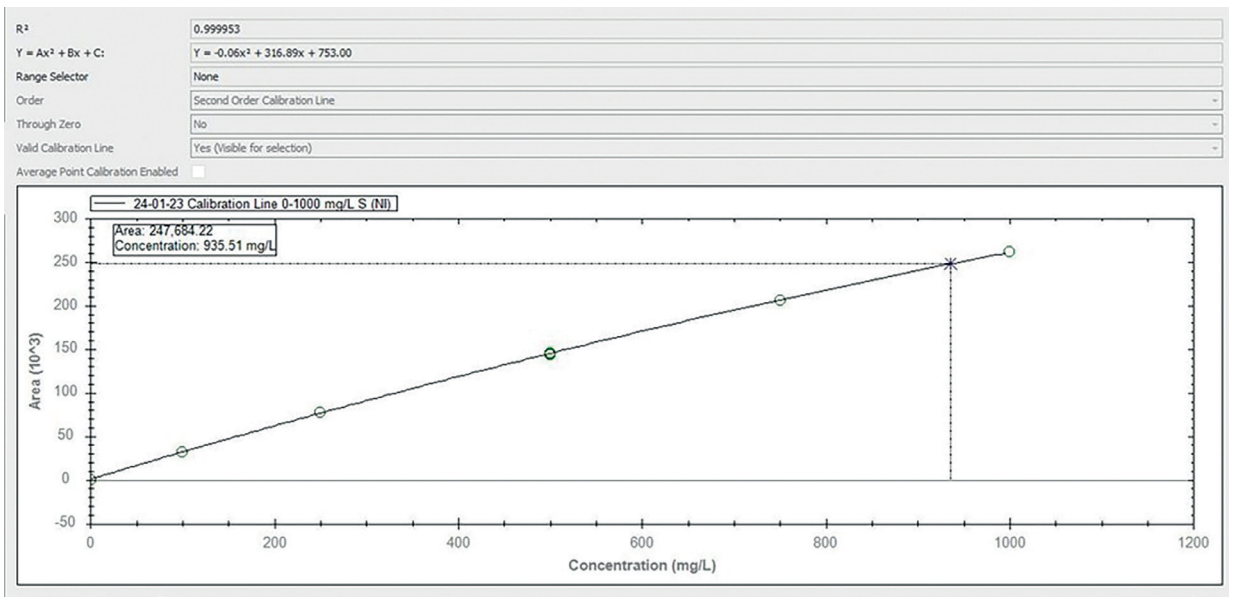

Figure 4: Calibration line of NO-CT™ 0 – 1000 ppm.

Standard	Measured Total Sulfur without NO-CT ™ (ppm)	Measured Total Sulfur with NO-CT ™ (ppm)
1	10,21	10,23
2	10,35	10,19
3	11,48	10,24
4	12,89	10,22

Table 3: Results of using NO-CT™

Parameter	Setting
Oxygen Flow	400 mL/min
Argon Flow	100 mL/min
Inlet cleaning time	10 seconds
Furnace Temperature I	800 °C
Furnace Temperature II	1050 °C
Internal System Temperature	31 °C
Injection Speed	1 µL/s
Injection Volume	100 µL

Table 4: System settings

TEI analyzers are currently available with the following detector setups:

1. Total Sulfur (UV-F)
2. Total Nitrogen (CLD)
3. Dual detector solution, Total Sulfur (UV-F) + Total Nitrogen (CLD)

Laboratories that are not interested in measuring Nitrogen, but do want to have True Sulfur results, were left out with the software-based Nitrogen correction. For this reason, TE Instruments developed a unique hardware solution for Xplorer-TS-only analyzers. This solution corrects for Nitrogen values at levels ranging from 10 ppm, up to 1000 ppm, without losing performance.

Before enabling the correction, users need to record a special calibration line that only contains Nitrogen. In most cases, a calibration line of up to 500 ppm of total Nitrogen will cover most of the interferences. The calibration line is stable up to 1 year from calibration and there is no need to recalibrate the sensor on a regular basis. After the calibration line is recorded it is simply a matter of turning the correction "ON" in the TEIS configuration.

Example data with NO-CT™

As a validation experiment using the correction technique, multiple standards were made using Dibutyl Sulfide (Sulfur) and Pyridine (Nitrogen) in a matrix of Xylene. The standards were spiked with increased amounts of Nitrogen.

After injection of the standards, the following overlay and calibration line and results were recorded.

Used Analyzer and Settings

Xplorer-V TS with the new NO-CT™. The new NO-CT™ can be added to existing systems with the following upgrade kit: KIT0176990 Xplorer-TS only NOCT Upgrade kit.

Author Contact Details

Sebastian Sanchez, TE Instruments

- **Voltaweg 22, 2627 BC Delft, The Netherlands**
- Tel: +31 (0) 15 879 55 59
- Email: sales@teinstruments.com
- Web: www.teinstruments.com