APPLICATION NOTE

TS

NEXIS VP

REPEATABILITY PERFORMANCE OF TOTAL SULFUR ANALYSIS IN GASOLINE AND DIESEL SAMPLES BY COMBUSTION UV-FLUORENSCENCE METHOD ACCORDING TO ASTM D5453 AND ISO 20846

INTRODUCTION

Instrument reliability, compliance, ease-of-use, stability and accuracy are key factors for customers to consider, when they need to select a Combustion Analyzer to report accurate total sulfur data to their (internal) customers. In the field of petroleum industry, the analysis of automotive fuels is most routine and drives laboratories to automation and fast reporting of precise data day-in-day-out. The use of round robin or proficiency testing data are also a tool to proof that the existing analyzer condition fits within the scope of the method and assure the reported data are within the confidence limits.

This Application Note shows the long-term performance of the NEXIS VP model Total Sulfur Analyzer for a set of gasoline and diesel fuel samples based on a 21-days trial to determine the precision of the obtained results in compliance to ASTM D5453, ISO 20846 methods and the TIER 3 program.

The obtained data from this test also indicate the stability of the instrument configuration without recalibration of the detector or perform any maintenance of the analyzer. This also can be supported with so-called Shewart plots generated through the instrument operating software (NEXIS LINK), which enables customers to optimize their QC operation.

Figure 1:
NEXIS VP analyzer with AS120 autosampler

EST & tHR analytical

PRINCIPLE OF OPERATION

A liquid fuel sample is directly injected, by a fully automated liquid sampler, into a pre-heated injection port connected to a vertical positioned dual zone high temperature combustion tube where the Sulfur containing components are vaporized and combusted. The released Sulfur is oxidized to sulfur dioxide (SO_2) in an oxygen rich atmosphere.

A stream of inert gas (Helium or Argon) is taking the reaction products, after removal of the produced water vapor by an effective semi-permeable membrane, into the reaction chamber. Here, the SO_2 molecules are converted to excited SO_2* under UV-Flash light and emitting light (fluorescence) while it relaxes to a stable state. A photomultiplier tube measures the emitted light signal.

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

$$SO_2 + h\nu_1 \;\rightarrow\; SO_2^* \qquad (1)$$

$$SO_2^* \;\rightarrow\; SO_2 + h\nu_2 \qquad (2)$$

The response signal is integrated to calculate the area counts. The Sulfur concentration of an unknown sample is calculated using the linear regression function of the of the concentration of standard mixtures versus integrated area.

INSTRUMENT SETTINGS

The following instrument configuration settings of the NEXIS VP model has been used for the calibration points and analysis of the samples. The analyzer operation and data handling are controlled by NEXIS LINK software.

Parameter	System Value
Argon carrier	75 mL/min
Oxygen primary flow	300 mL/min
Oxygen secondary flow	100 mL/min
Inlet temperature	500°C
Temperature furnace I	900°C
Temperature furnace II	1000°C
Sample volume	20 µL

Table 1:
NEXIS VP Total Sulfur Analyzer instruments settings

CALIBRATION

A Calibration curve of 0 – 25 ppm has been prepared using dibenzothiophene standards in xylene. Each calibration solution and blank is measured five times to determine the area counts for each.

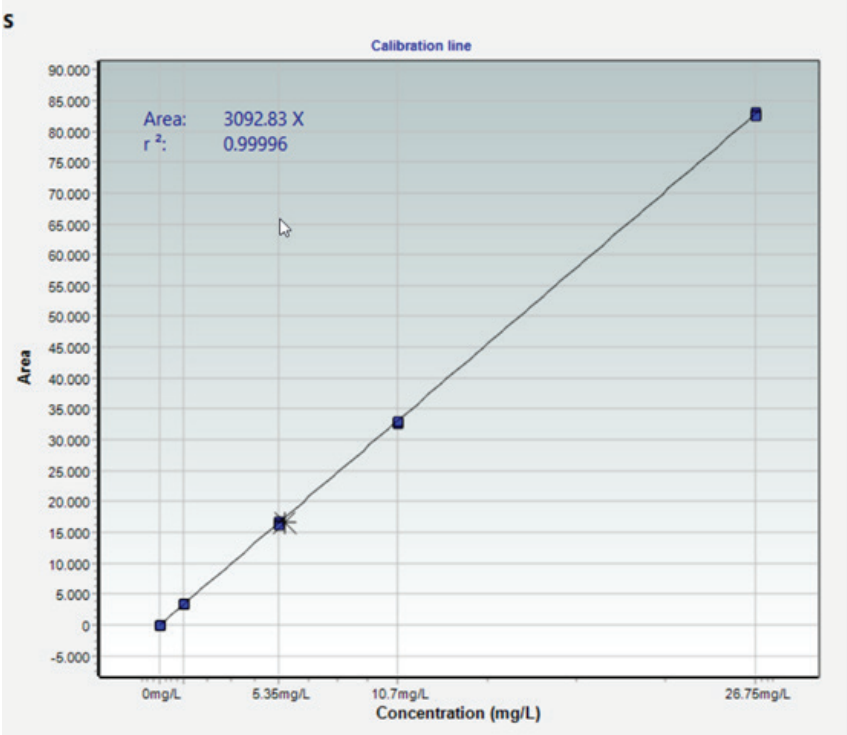

Figure 2:
Calibration curve 0 - 25 ppm S

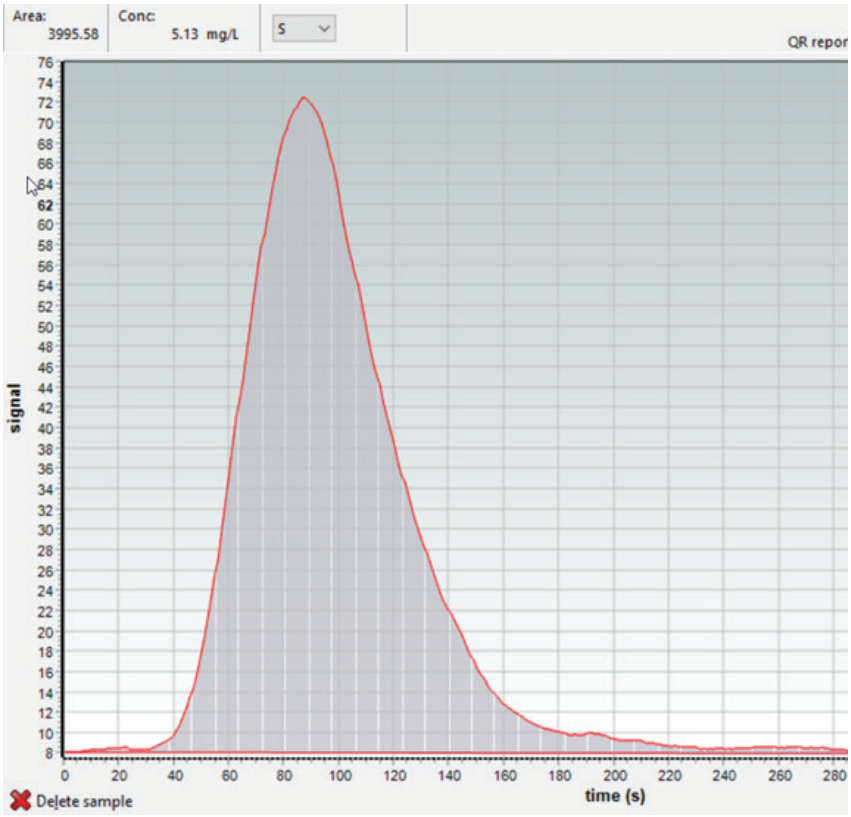

Figure 3:
Sample peak Reformulated Gasoline E95-E10

REPEATABILITY

Long-term repeatability for the NEXIS VP analyzer model is determined for 3 gasoline and 1 diesel fuel samples, which are analyzed as 5 replicates during 21 days, without any recalibration or maintenance of the NEXIS VP main analyzer. Also, a 10 ppm sulfur CRM has been analyzed every day as a QC sample to determine the accuracy of the test results.

Day	Gasoline E95-E10	Gasoline E95-E10 Reformulated	Gasoline E95-E5	Diesel B7	CRM 10 ppm
1	2.71	5.24	4.21	7.41	10.30
2	2.80	5.36	4.25	7.32	9.73
3	2.73	5.35	4.33	7.46	9.85
4	2.80	5.34	4.23	7.48	9.82
5	2.74	5.19	4.23	7.20	9.75
6	2.72	5.16	4.16	7.24	9.97
7	2.69	5.23	4.17	7.30	10.75
8	2.71	5.16	4.06	7.14	9.44
9	2.70	5.01	3.99	7.09	9.42
10	2.70	5.12	4.06	7.10	9.28
11	2.75	5.14	4.16	7.10	9.41
12	2.63	5.06	3.97	7.26	9.80
13	2.61	4.90	3.96	7.03	9.54
14	2.72	5.16	4.13	7.29	9.61
15	2.62	5.07	4.24	7.18	9.63
16	2.68	5.00	4.07	7.04	9.78
17	2.68	5.07	4.08	7.09	9.84
18	2.57	5.15	4.04	7.15	9.78
19	2.63	5.04	4.01	7.15	9.94
20	2.58	5.03	4.07	7.12	9.72
21	2.69	5.16	4.12	7.13	9.73
Average	2.69	5.14	4.12	7.20	9.72
SD	0.0632	0.1199	0.1027	0.1316	0.2310
RSD (%)	2.4%	2.3%	2.5%	1.8%	2.4%

Table 2:
Total Sulfur data for a set of gasoline and diesel samples during 21 days

STABILITY TEST

Shewart plots will be generated through NEXIS LINK software and below example shows the stability performance of a gasoline sample which data fits within the 2-sigma (2s) confidence limits.

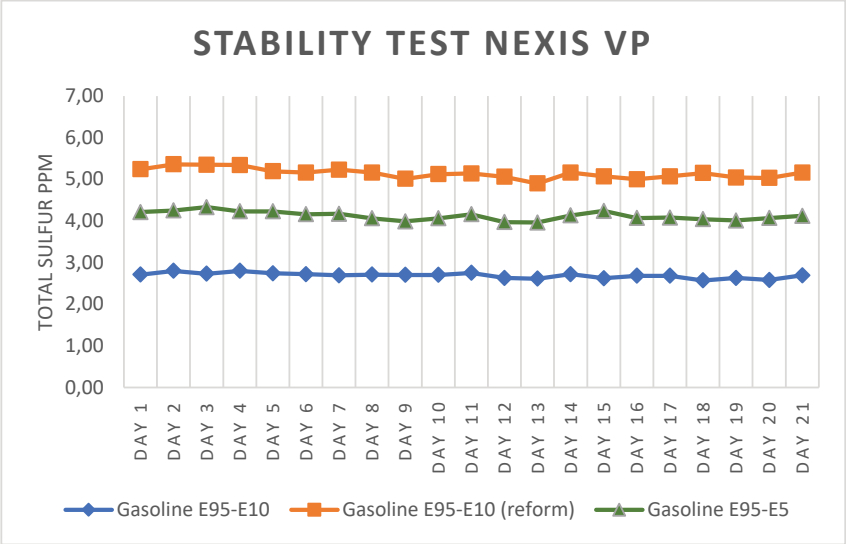

Figure 4:
Quality Control chart (Shewart plot)

DISCUSSION

The obtained results as presented in this Note shows the NEXIS VP analyzer as most suitable instrument for obtain accurate Total Sulfur data in automotive fuel products, such as blended gasoline and diesel samples, and fully meet the ASTM D5453, ISO 20846 and TIER 3 requirements. It shows an exceptional instrument stability with enhanced repeatability and precision within the precision statement of the above methods. The NEXIS LINK operating software, enables customers to optimize and customize their quality control process and ensure fast and easy recognition of eventually reported outliners which require further actions to optimize the refinery or blending process.

CONTACT INFO

E-mail: **sales.tshr@estanalytical.com**
E-mail (US only): **sales@estanalytical.com**
Our website: **www.estanalytical.com**

Visit our website to find your local TSHR distributor

EST analytical & tSHR

YOUR PARTNER IN COMBUSTION ELEMENTAL ANALYSIS