

## MATRIX EVALUATION ON THE XPLOERER-V WITH VECTRA AUTOSAMPLER ACCORDING TO ASTM5453

### Introduction:

At the beginning of 2024, TE Instruments introduced a new autosampler designed for the introduction of liquid sample materials for the Xplorer Total Sulfur (TS), Total Nitrogen (TN), and Total Halides (TX) elemental combustion analyzer series. The innovative Vectra model incorporates advanced movement principles, offering an expanded range of motion and paving the way for future enhancements in sample handling.

Initially, the Vectra was exclusively compatible with the Xplorer TN/TS/TX analyzers (horizontal version) and the XPREP C-IC. However, TE Instruments has extended the compatibility of the Vectra to include the Xplorer-V analyzer.

### Background:

In the classic Xplorer TN/TS, the furnace is positioned horizontally, and a separate liquids injection module is used for evaporation of sample material. This module is typically maintained at a temperature of 500 °C. It is recommended that the maximum boiling temperature for liquid samples is limited to 420 °C for the Xplorer TN/TS to prevent accumulation of sample material in the introduction module.

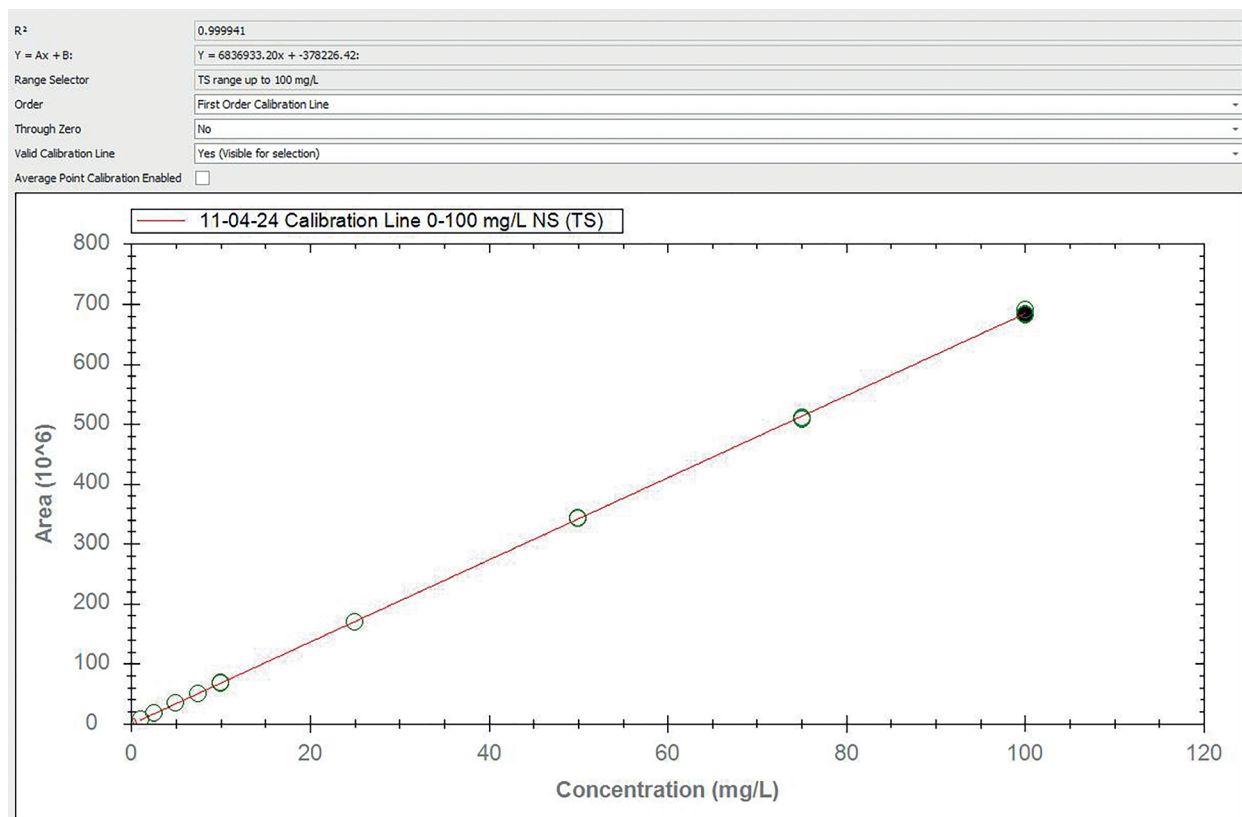
When samples with higher boiling ranges need to be injected on the Xplorer TN/TS, a boat inlet module should be utilized instead of the liquid injection module. With this boat inlet introduction, the sample is injected into a quartz cup filled with quartz wool. The cup is transferred into the high-temperature furnace with a pre-defined boat program. This method is advantageous for high boiling samples and complex matrices, as the introduction is precisely controlled by the speed of the cup movement, allowing for the measurement of samples with relatively high boiling points.

However, a minor drawback is the increased analysis time due to the cooling step at the end of a boat introduction program. Sample analysis using a liquid introduction module typically takes approximately 3 to 6 minutes, while a boat introduction extends the analysis time to about 5 to 9 minutes. Controlled sample evaporation prior to the combustion is essential for achieving optimal results.

In the Xplorer-V configuration, the sample is injected vertically into the pre-combustion inlet, where it fully evaporates under an inert carrier gas stream at a higher temperature compared to the liquid module of a horizontal setup. The vertical placement of the furnace allows for a broader boiling point range of liquid sample material to be injected. While a classic horizontal liquid module typically can handle samples



Picture 1: Wide working area of the Xplorer-V with Vectra



with a maximum boiling point of 420 °C, the Xplorer-V can accommodate samples with a boiling point up to 650 °C.

Additionally, the automatic cleaning step is performed after each analysis, where the carrier gas is switched to oxygen via an automatic valve, enabling all residual condensates to be burned off and prepare the system for the next analysis.

For example, the analysis of biodiesel mixtures and pure B100/FAME samples is possible on the Xplorer-V with a direct liquid injection, where a conventional horizontal setup still require a boat introduction for B100/FAME samples.

### Xplorer-V and the Vectra autosampler:

Upon its introduction in 2021, the Xplorer-V featured an internally integrated liquid autosampler with a capacity for 26 sample positions. The sample injection principle was based on a "transfer tube" design which separates the needle from

Sulfur Calibration (mg/kg) N = 5

0.5
1.0
2.5
5.0
7.5
10
25
50
75
100

Overview 1: List of calibration standards and plotted calibration standards

the syringe, providing a cost-effective solution as the syringe has no direct contact with the sample, resulting in an annual replacement of the syringe. This integration results in a compact analyzer setup.

The new Vectra, which succeeds the Archie autosampler, operates on the direct syringe injection principle. With a substantial capacity of up to 150 sample positions for standard 2 mL vials, the Vectra has additional options for high-throughput laboratories.

Offering high-performance conditioned tray modules, with 50 sample positions each, the Vectra introduces both cooling and heating capabilities. Such thermal control options were previously unavailable on the Xplorer-V when used with its internal autosampler.

Combining the Vectra autosampler with the Xplorer-V analyzer results in a powerful synergy, leveraging the strength of both systems. To validate the performance of this combination, an extensive matrix evaluation study was conducted on a wide range of sample matrices, affirming the power of the setup. This paper presents an extract of the results from this research.

**Calibration:**

For calibration of the Xplorer-V with the Vectra autosampler, the following calibration samples were introduced into the analyzer combination (N = 5 per calibration level). This resulted in a calibration line with a coefficient (R<sup>2</sup>) of 0.999941 for Total Sulfur.

**Matrix evaluation:**

A wide variety of different sample matrices was collected from a renowned contract laboratory and injected into the Xplorer-V equipped with a Vectra autosampler over a period of five days. Each sample matrix was subjected to five repetitions daily, with the average concentration and Relative Standard Deviation (RSD) calculated and validated. The variation in Initial Boiling Points (IBP) and Final Boiling Points (FBP) effectively show a good representation of the variation in sample matrices. The average results for Total Sulfur are reported in mg/kg.

**System performance:**

For verification of the repeatability and system performance, 3 matrices were selected to inject over an extended period of time:

- Gasoline
- Diesel
- B100/ FAME

The three sample matrices were injected in triplicate into the Xplorer-V and Vectra combination. Especially the B100/ FAME samples are notoriously heavy on cleanliness and have a high impact on system performance. This matrix may contain higher salts and Glycerin concentrations, which take a high toll on the needle of the syringe and the quartz combustion tube of the analyzer.

The collected data shows consistent long-term performance with 534 injections for B100/FAME samples over more than 100 days, achieved without re-calibrating the system.

Commercial Gasoline and Diesel are subject to maximum Sulfur levels as stipulated by US EPA Tier III and EU Euro 5 regulations. These kinds of matrices are typically analyzed in large quantities by various laboratories.

The following graph (see graph 1) illustrates the performance over approximately 350 injections for commercially available Gasoline and Diesel samples. The results, expressed in mg/kg, were obtained without re-calibrating the system.

**Used system setup:**

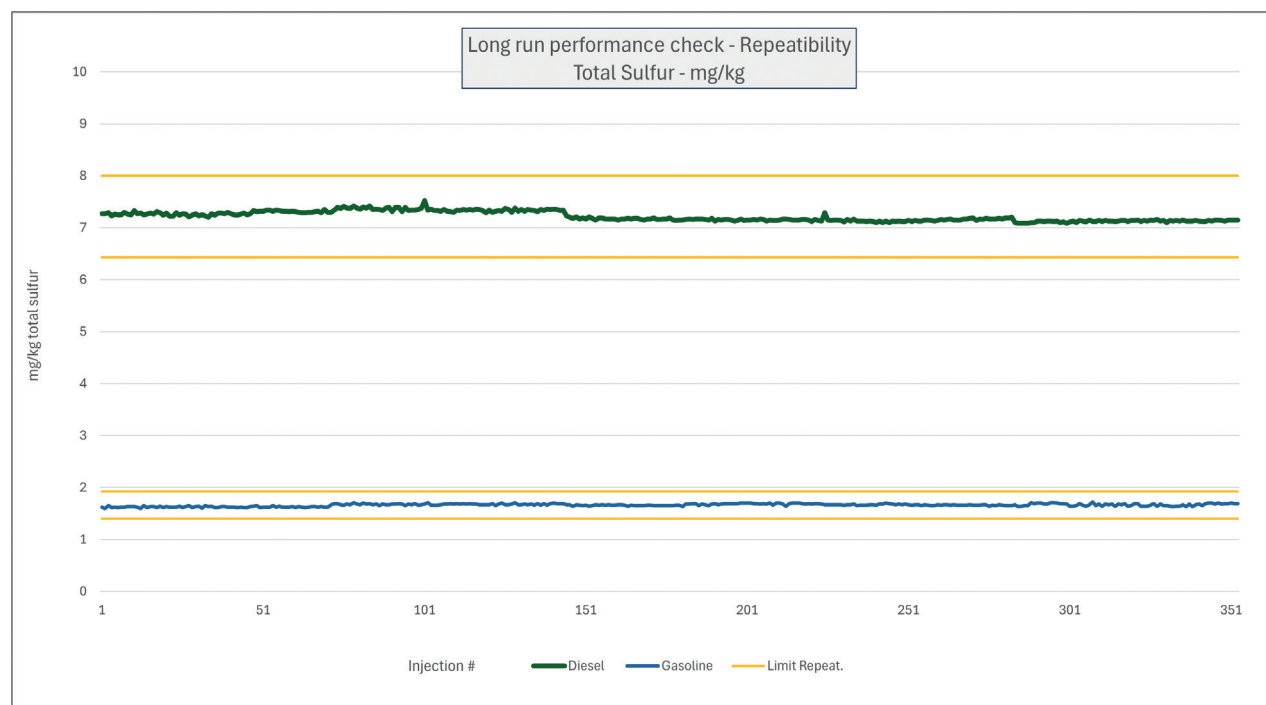
For the validation study, the combination of Xplorer-V with the Vectra autosampler was utilized. TE Instruments developed a special adapter bracket to seamlessly integrate the Vectra autosampler with the Xplorer-V. Maintaining the Xplorer-V as the smallest and most compact analyzer for combined analyses of Total Sulfur and Total Nitrogen on the market.

The system holds three sample trays, each with 50 sample positions for 2 ml vials. Additionally, two optional sample trays with temperature conditioning (heating/ cooling) can be included to enhance the configuration.

A notable feature of the Vectra is its capability for automatic syringe switching. The system can mount three syringe holders,

Table 1: Overview of sample matrices results and day to day average/RSD.

General product group:	Matrix:	IBP	FBP	Day 1		Day 2		Day 3		Day 4		Day 5	
				Average (mg/kg)	RSD (%)	Average (mg/kg)	RSD (%)	Average (mg/kg)	RSD (%)	Average (mg/kg)	RSD (%)	Average (mg/kg)	RSD (%)
Calibration CRM	CRM In Xylene	135	139	10.0	0.3	9.9	0.4	9.9	0.4	10.0	0.5	9.9	0.1
Solvents/ general chemicals	Iso Hexane	55	65	0.2	2.6	0.1	4.7	0.2	4.6	0.2	1.9	0.2	3.8
	Methyl tertiary-butyl ether	50	60	2.0	0.5	1.9	1.1	2.0	0.6	2.0	0.5	2.0	0.2
	Tertiary Amyl Methyl Ether	70	105	21.7	0.3	21.4	0.2	21.5	0.1	21.2	0.1	21.4	0.1
	Benzene	79	82	0.2	1.1	0.0	2.0	0.1	3.4	0.2	3.4	0.2	3.6
	Toluene	108	113	0.2	1.2	0.0	5.8	0.1	4.5	0.2	1.4	0.2	3.2
	IsoOctane	98	102	0.4	0.6	0.2	2.3	0.3	1.5	0.4	1.0	0.3	2.0
	Isomere Solvent additive	90	150	0.8	2.8	0.7	2.8	0.9	0.9	0.9	2.2	0.8	5.2
	Int. Process product C5-C6	80	220	7.1	1.2	6.9	0.4	7.0	0.2	6.9	0.9	7.1	0.8
Intermed. aromatic solution	40	140	0.1	5.0	0.0	5.0	0.1	4.7	0.1	4.8	0.1	5.3	
Gasoline and Diesel:	Gasoline/ derivative A	35	200	5.4	0.4	5.4	0.3	5.4	0.4	5.4	0.2	5.4	0.3
	- Pure Gasoline	35	190	3.1	0.6	3.0	0.5	3.1	0.2	3.1	0.4	3.1	0.6
-Derivates or blends	Gasoline/ derivative C	70	160	0.3	2.2	0.2	1.6	0.3	2.5	0.3	1.3	0.3	0.6
-Additives	Gasoline/ derivative D	70	210	6.9	0.2	6.8	0.2	7.3	0.3	6.8	0.1	6.9	0.1
	Gasoline/ derivative E	70	210	8.2	0.2	8.0	0.2	8.3	0.2	8.0	0.2	8.1	0.3
	Gasoline additive	35	65	8.7	0.9	8.6	0.6	9.3	0.5	8.8	0.4	8.8	3.2
	Diesel additive/ modifier	145	205	2.7	0.3	2.6	0.4	2.7	0.2	2.7	0.2	2.7	0.3
	Diesel blend	165	360	1.9	0.6	1.8	0.5	1.9	0.3	1.9	0.7	1.9	0.4
Naphtha	Medium Naphtha	70	170	0.3	0.9	0.2	1.4	0.3	1.6	0.3	1.5	0.3	1.9
	Heavy Naphtha	60	160	5.0	0.8	4.8	0.7	5.0	0.3	4.9	0.2	5.0	0.4
Synthetic/ New generation Fuels	Synthetic Fuel A	35	160	10.8	0.2	10.6	0.5	10.9	0.1	10.7	0.2	10.8	0.5
	Synthetic Fuel B	166	330	15.1	0.2	14.9	0.2	15.2	0.2	14.9	0.2	15.0	0.1
	Synthetic Fuel C	35	160	14.1	0.2	13.8	0.2	14.1	0.1	13.9	0.4	14.0	0.2



Graph 1: Long run on Commercial Gasoline and Diesel samples

allowing for automatic syringe switching. This option improves system robustness and workflow as follows:

- Automatic switching to different syringe volumes without operator intervention
- Automatic switching to a new syringe acting as a redundant option

Typically, injection volumes of 50 µL gave the best repeatability, results, and peak forms for all the tested matrices. All matrices were injected with a single uniform system method offering a robust solution for analysts operating the analyzer.

Table 2: System settings

Parameter	Setting
Oxygen Flow	400 mL/min
Argon Flow	50 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	50 µL



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