



ANALYSIS OF TOTAL SULFUR ACCORDING TO ASTM D5453, WITH THE CONDITIONED SYRINGE INJECTION OPTION FOR THE VECTRA AUTOSAMPLER

Introduction:

At the beginning of 2024, TE Instruments (TEI) launched the Vectra autosampler, a new, automated solution for introducing liquid samples into the TEI combustion analyzers. This innovative autosampler incorporates advanced motion technology, offering an extended range of movements and setting the next stage for future developments in automated sample handling.

Initially, the Vectra autosampler supported two optional conditioned sample trays, allowing users to heat or cool sample vials based on their specific application needs. Now, with the newly developed syringe conditioning module, the Vectra sampler goes a step further by enabling precise heating and cooling of the syringe during liquid handling and sample analysis. This powerful feature significantly expands the system's versatility, especially for applications involving challenging or volatile sample matrices.



Vectra autosampler with conditioning block.



Syringe holder in conditioning position to warm or cool.

Background:

In modern analytical laboratories, automation is essential for increasing throughput, ensuring reproducibility, and minimizing human error. Among the most integral components of automated systems is the autosampler, which is responsible for the precise and accurate delivery of liquid samples to analytical instruments. Despite its routine use, proper liquid handling within an autosampler system is often underestimated — yet it plays a decisive role in data quality, instrument performance, and overall operational efficiency.

Accurate liquid handling ensures that the correct sample volume is aspirated and dispensed without contamination, evaporation, or carryover. This is particularly vital in high-sensitivity analyses such as combustion analysis, where even trace discrepancies can lead to false results, compromised calibrations, or costly reruns. Furthermore, improper handling can lead to needle blockages, increased wear on mechanical components, and irregular sample injections, ultimately impacting instrument uptime and maintenance costs.

One of the major challenges in handling low-boiling, volatile samples is ensuring proper aspiration and injection. Today, hydrocarbon-based samples with extremely low boiling points (25 degrees Celsius) are increasingly used in Total Sulfur, Nitrogen, or Halogen analysis. These samples present a significant risk of evaporating from the syringe before injection into the combustion analyzer — a scenario that was previously a barrier to their use.

At the other end of the spectrum, many waxy samples or heavy oils are solid at room temperature but become liquid when warmed. This makes them suitable for analysis when a conditioned sample tray is used to preheat the vials. A conditioned syringe ensures that the sample remains in a liquid state during transfer from the vial to the injection point or during cleaning cycles. Keeping the syringe heated not only maintains sample integrity but also extends the syringe's lifespan by reducing the risk of clogging.

This article explores the possibilities and benefits of using a conditioned syringe with the Vectra autosampler.

Vectra autosampler with conditioned syringe option:

The conditioned syringe module for the Vectra consists of two key components:

1. A conditioned parking station, used to thermally condition the syringe before and after injection.
2. A customized syringe injection head, featuring a specially designed heating and cooling buffer block.

During operation, the syringe—secured in a specialized holder—is placed in the conditioning block. Depending on the application requirements, it is either heated or cooled to a predefined setpoint. The system can accurately adjust the syringe temperature within a range of 10°C to 65°C.

Thanks to the precision-engineered buffer block around the syringe, the syringe reaches the temperature setpoint within 2 minutes and maintains the target temperature within $\pm 5^\circ\text{C}$ for 10 minutes. This ensures optimal temperature stability throughout the injection, washing cycles, and fully conditions the syringe for subsequent use.

This setup enhances process reliability and repeatability, particularly in temperature-sensitive applications where the sample's behavior must be tightly temperature-controlled.

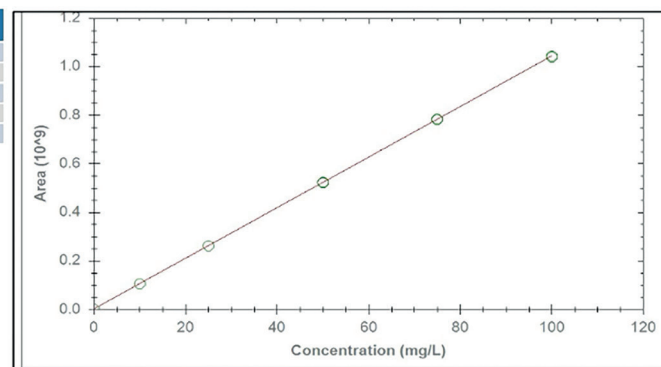
Experimental:

To confirm the principle of a conditioned syringe injection, we prepared an Xplorer Total Sulfur/ Total Nitrogen analyzer (TN/TS) with a Vectra Autosampler, 2 conditioned trays, and the syringe conditioning option.

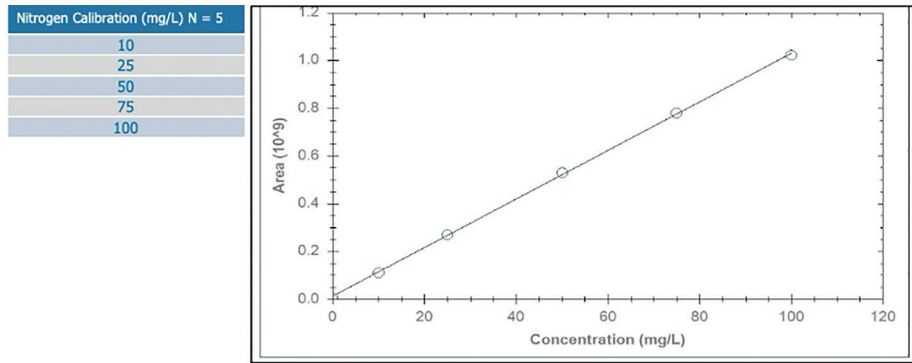
Prior to analysis of samples, the analyzer setup was calibrated with calibration samples (Number of injections, 5 times per concentration level). The standards used for calibrations were made out of Pyridine (N) and Thiophene (S) in Xylene and prepared by the Vectra liquids autosampler.

After running the calibration line, the system was calibrated with a coefficient (R^2) of 0.999994 for Total Sulfur.

Sulfur Calibration (mg/L) N = 5	
10	
25	
50	
75	
100	



Given that the analyzer was configured with a dual detector setup, including a CLD Nitrogen detector (Measuring Nitrogen as Nitrogen Oxide), a comparable calibration curve for Total Nitrogen was incorporated into the experimental procedure. This yielded a calibration line with a coefficient of determination (R^2) of 0.999798, indicating good linearity for Total Nitrogen.



A variety of different sample matrices were collected from renowned laboratories or commercially acquired. These samples were injected into the analyzer combination with and without the conditioned syringe option, to compare average concentrations and variations for RSD%.

The following Table shows the experimental matrix setup with variations:

Sample Matrix	Comment:	Syringe Temperature °C	Tray Temperature °C	Introduction Method
A - Pentane	Boiling point: 36 °C	10	15	Liquids module
B - Pentane		Not Conditioned	15	
A - Commercial Gasoline	Commercially available Gasoline	10	15	
B - Commercial Gasoline		Not Conditioned	15	
A - CRM Winter-Gasoline	Gasoline with a modifier that evaporates at 29 °C	10	15	
B - CRM Winter-Gasoline		Not Conditioned	15	
A - CRM Bio-Ethanol	Boiling point: 78 °C	10	15	
B - CRM Bio-Ethanol		Not Conditioned	15	
A - Palm Oil	Melting point 38 °C	65	60	Boat introduction (Liquids in boat injection)
B - Palm Oil		Not Conditioned	60	
A - Animal fat waste	Melting point 49 °C	65	60	
B - Animal fat waste		Not Conditioned	60	

Table 1: Overview of sample matrices and corresponding variations

For comparison, all samples were injected with and without the syringe conditioning option; in all cases, all sample vials were pre-conditioned in conditioned sample trays of the Vectra sampler prior to injection.

The room temperature while running this experiment was between 26 to 28 °C, this was the temperature for the injected samples without the Syringe Conditioning option.

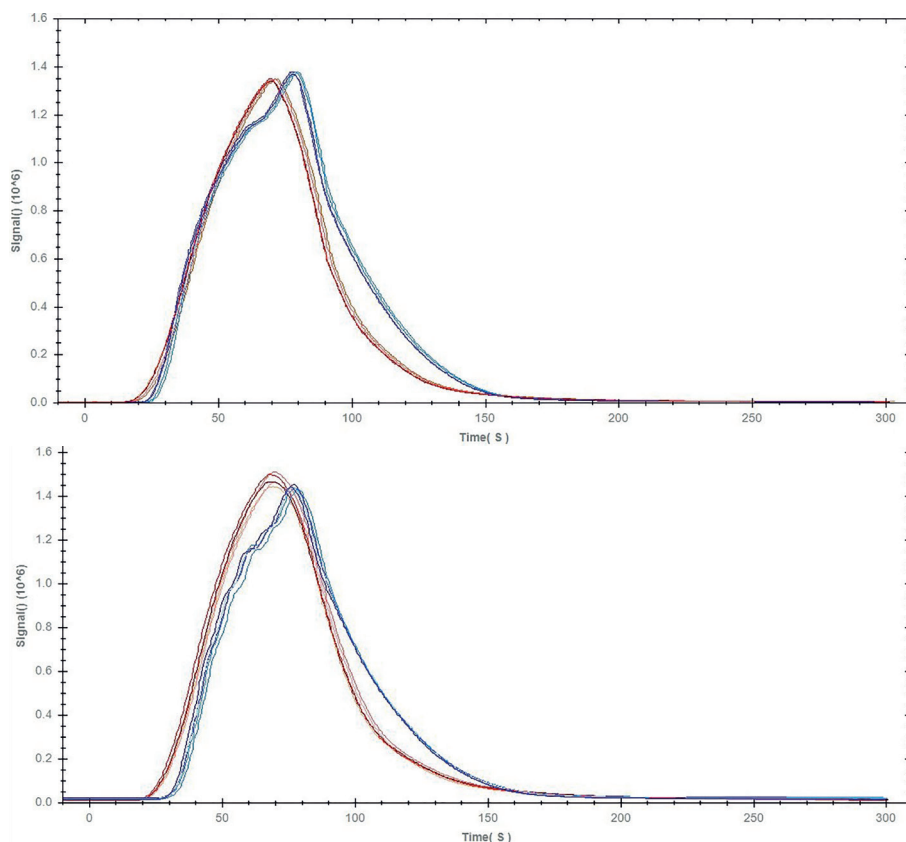
Each sample matrix was subjected to 10 repetitions of 50 µL as the injection volume. The average concentration and Relative Standard Deviation (RSD) were calculated and validated.

Results:

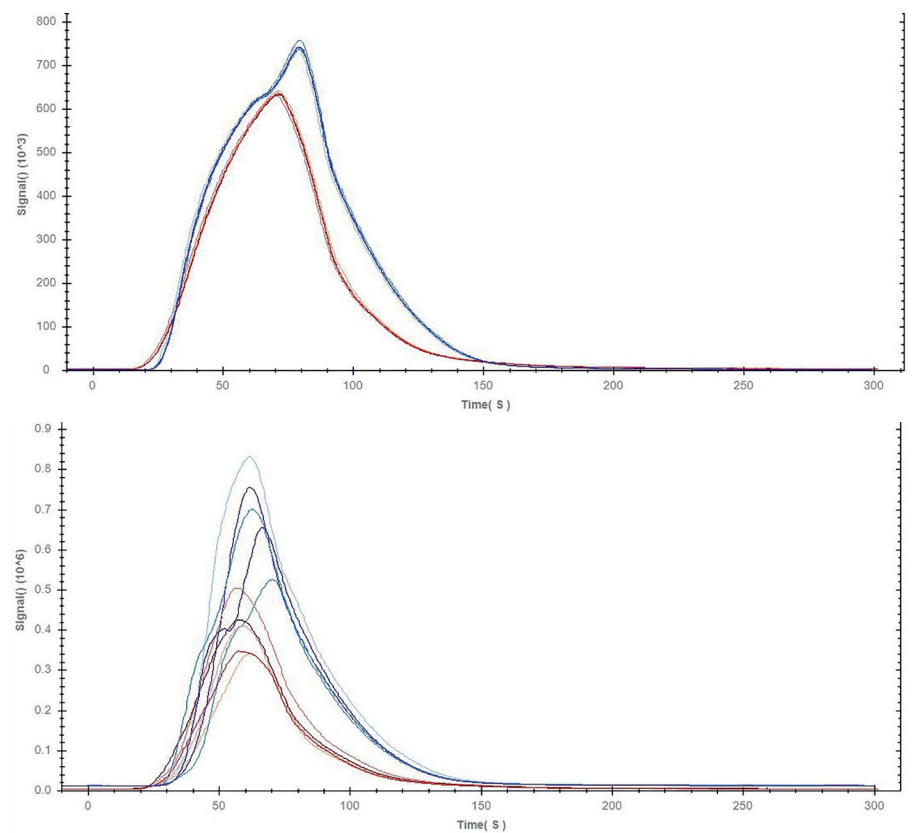
The following table shows the results of the experiment (all results with A are injections with the conditioned syringe option, and B are injections using the standard syringe configuration).

Sample Matrix	Average Total Sulfur mg/L	%RSD	Average Total Nitrogen mg/L	%RSD
A - Pentane	6.61	1.82	7.63	1.75
B - Pentane	2.31	>5	3.58	>5
A - Commercial Gasoline	13.1	2.75	14.4	2.25
B - Commercial Gasoline	11.7	>5	14.3	>5
A - CRM Winter-gasoline	16.3	0.67	22.3	0.79
B - CRM Winter-gasoline	15.5	1.89	20.2	2.0
A - CRM Bio-Ethanol	11.4	0.47	11.2	0.50
B - CRM Bio-Ethanol	10.8	0.59	11.3	0.82
A - Palm Oil	3.46	1.40	7.56	0.74
B - Palm Oil	3.52	1.85	6.73	0.90
A - Animal fat waste	7.47	1.32	19.9	1.14
B - Animal fat waste	6.93	1.62	15.2	1.39

Table 2: Overview of concentrations and variation results of the experiment



Graph 1: Comparison overlay of injections of CRM Winter-gasoline with conditioned syringe (top) and without conditioned syringe (bottom). Red plot lines represent Total Sulfur graphs, Blue plot lines represent Total Nitrogen graphs.



Graph 2: Comparison overlay of injections of Pentane with conditioned syringe (top) and without conditioned syringe (bottom). The Red plot lines represent Total Sulfur graphs, Blue plot lines represent Total Nitrogen graphs.

Conclusion:

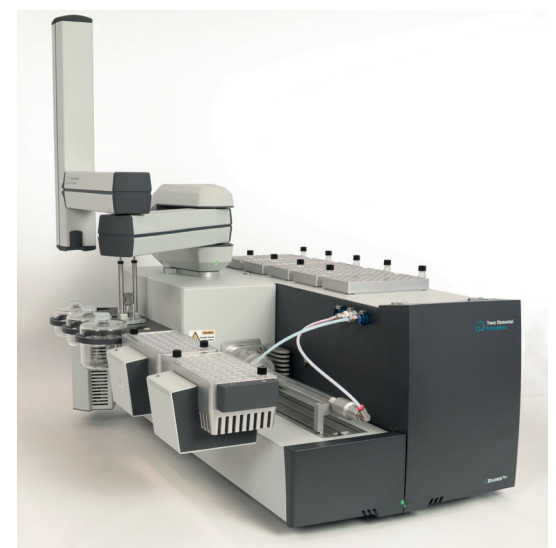
The comparative analysis of a syringe conditioned injection or without, across various fuel and bio-based matrices, reveals that incorporating syringe conditioning significantly improves both measurement precision and, in many cases, accuracy.

Across nearly all samples, a conditioned syringe resulted in lower %RSD values for both Total Sulfur and Total Nitrogen, indicating improved repeatability. The difference was particularly pronounced in the Pentane matrix; an injection without cooling results in extremely high variability (%RSD >5% for Total Sulfur and Total Nitrogen), compared to injection with the conditioned option (%RSD of 1.82% and 1.75%, respectively). This suggests a strong dependency on syringe conditioning in volatile or low-concentration matrices.

Overall, the inclusion of syringe conditioning enhances analytical reliability, reduces uncertainty, and is recommended as a standard practice, particularly for sensitive or variable matrices.

Used system setup:

For the validation study, the combination of the Xplorer TN/TS with the Vectra autosampler was utilized. This setup holds multiple sample trays, each with 50 sample positions for 2 ml vials. Additionally, two optional sample trays with temperature conditioning (heating or cooling) can be included, and a syringe conditioning option, to enhance the configuration.



Xplorer TN/TS with Vectra autosampler, 2 conditioned trays, and syringe conditioning

Analyzer Parameters	Setting
Oxygen flow	400 mL/min
Argon Flow	100 mL/min
Furnace Temperature I	Liquids module: 1000 °C Boat introduction 750 °C
Furnace Temperature II	1050 °C
Injection Speed	1 µL/S
Injection Volume	50 µL

Table 3: System settings of the Xplorer TN/TS

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