



The Xplorer-S with GBS autosampler is a reliable and safe solution for the analysis of Total Sulfur in gaseous hydrocarbons. Samples are taken from Tedlar™ gasbags at atmospheric pressure, eliminating the need to handle pressurized cylinders. This makes the transportation of samples safer and more convenient. The use of Tedlar™ gasbags is also cost-effective for low-pressure samples due to the inertness of the material. As a result, high priced protective coatings can be omitted for low concentration gaseous Sulfur samples.

In this application note, the GBS is used to enable the determination of Total Sulfur in Gaseous Hydrocarbons by UV-Fluorescence detection technique. Sulfur may be present in process feeds or finished products of the refinery. Sulfur-bearing materials in process feeds may lead to poisoning of process catalysts. Volatile sulfur compounds like thiols (mercaptans) and hydrogen sulfide (H₂S) are being removed through desulfurization to protect catalysts in the refining process. The amount of Sulfur in gaseous process feeds is monitored to determine the effectiveness of the desulfurization process. The amount of Sulfur in final products is determined for purposes of regulatory control.

Sample Information	
Sample Type	Gaseous Hydrocarbons
Component	Sulfur
Matrix	Gaseous Butane / Propane Mix
Concentration	10 mg/kg
Methods Applicable	ASTM D6667

Table 1 - Sample Information

Summary

The Xplorer-S elemental combustion analyzer, equipped with Liquids Introduction Module (Direct Injection), has been used to perform the analysis of Total Sulfur (UV-F) in Gaseous Hydrocarbon samples. Samples were automatically introduced by the GBS gas bag sampler using a 100 mL internal gas syringe. Calibration curves have been generated out of a single reference standard by injecting different sample volumes. According to the ASTM D6667, the maximum allowable difference or standard deviation is 1.2 mg/kg at the concentration level of 10 mg/kg sulfur.. The Xplorer-S provides accurate results with standard deviations well below the repeatability limits (*r*) as stated in the ASTM D6667.

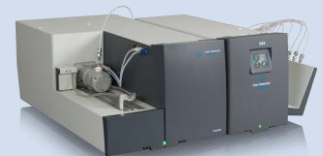
Results

Sample	Quantity (mL)	Concentration (mg/kg)	StDev (mg/kg)	RSD (%) n=5
Gaseous Butane / Propane Mix A	20	20.2	0.1	0.67
Gaseous Butane / Propane Mix B	100	9.0	0.03	0.29

Table 2 – Results for Total Sulfur Analysis - Repeatability limit is calculated by the formula $r = 0.1152(X)$

Solution

Xplorer-S GBS Autosampler



Liquids Module





Method

The GBS operates with a 100 mL internal gas syringe, which aspirates the sample from the assigned channel and ensures it is dispensed accurately into the Xplorer elemental combustion analyzer. Up to 10 Tedlar™ gas can be connected at the same time for sequential sample analysis by the Xplorer. The GBS autosampler can introduce any volume between 10 and 1000 mL. The required sample volume is set and adjusted easily through TEIS Software or the touch screen interface of the GBS. If for any reason a hydrocarbon spill is detected, the internal gas leakage sensor automatically warns the operator and aborts all activity.

System Description

Introduction – The internal gas syringe automatically aspirates a pre-defined sample volume from the selected channel and introduces it into the Xplorer-S. To avoid any cross contamination, the GBS is rinsed by carrier gas in between sample analyses.

Combustion - The Xplorer-S is fitted with a dual-zone furnace, which enhances combustion performances. The temperature is adjustable up to 1150 °C. The Collision Flow Tube has a secondary oxygen flow that collides with the oxidizing gas stream and replaces some of the depleted oxygen. Resulting in more oxidation power for samples which are difficult to oxidize.

Conditioning - Water vapor is removed from the gas stream by the Perma Pure gas dryer. Particles are blocked by a re-usable, cleanable filter, eliminating the need for expensive disposable PTFE fiber filters. Only the conditioned gas stream enters the Sulfur reaction chamber.

Detection - The amount of Total Sulfur is detected by a pulsed UV-Fluorescence detector. The integrated signal response from the detector is directly linear proportional to the concentration of Sulfur Dioxide (SO₂) in the sample. Samples can be reported easily or transferred into an available LIMS environment with TEIS software.

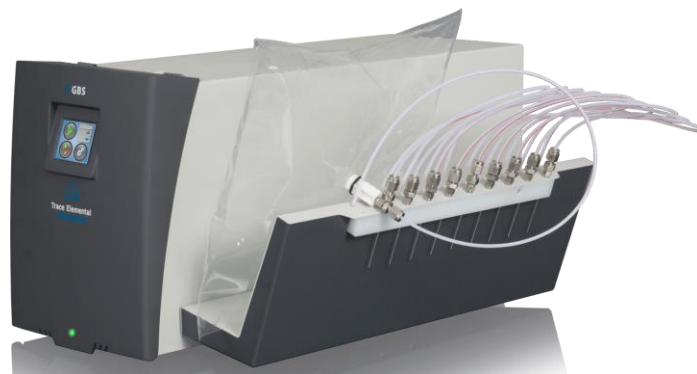


Figure 1 - GBS Autosampler with Tedlar Gas Bag

System Settings

Parameter	Setting
Oxygen Flow	300 mL/min
Argon Flow	200 mL/min
Oxygen Collision Flow	100 mL/min
Sample Introduction Speed	0.2 mL/sec
Furnace Temperature I	1000 °C
Furnace Temperature II	1000 °C
Liquids Module	500 °C
Internal System Temperature	30 °C

Table 3 - System settings for Gaseous Hydrocarbon Analysis using the GBS





Calibration

The GBS is capable of creating linear calibration curves out of a single reference standard by injecting different volumes. It is possible to use this method for creating calibration curves that go upwards as well as downwards. In this case, five different volumes of a 10 mg/kg Di Butyl Sulfide (DBS) in Gaseous Butane / Propane were analyzed to create the calibration curves. The tables below demonstrate how the calibration curves were created in TEIS Software, by injecting different volumes of the same reference standard. Notice that the same quantity of sample must be used for later analysis on the specific calibration curve. For the calibration curve of 10-50 mg/kg this is 20 mL, and for the calibration curve of 2-10 mg/kg this is 100 mL.

Volume injected	Set Quantity in Software after Analysis	Simulated Concentration
20 mL	20 mL	10 mg/kg
40 mL	20 mL	20 mg/kg
60 mL	20 mL	30 mg/kg
80 mL	20 mL	40 mg/kg
100 mL	20 mL	50 mg/kg

Table 4 - Calibration line: 2 – 10 mg/kg DBS in Gaseous Butane / Propane Mix

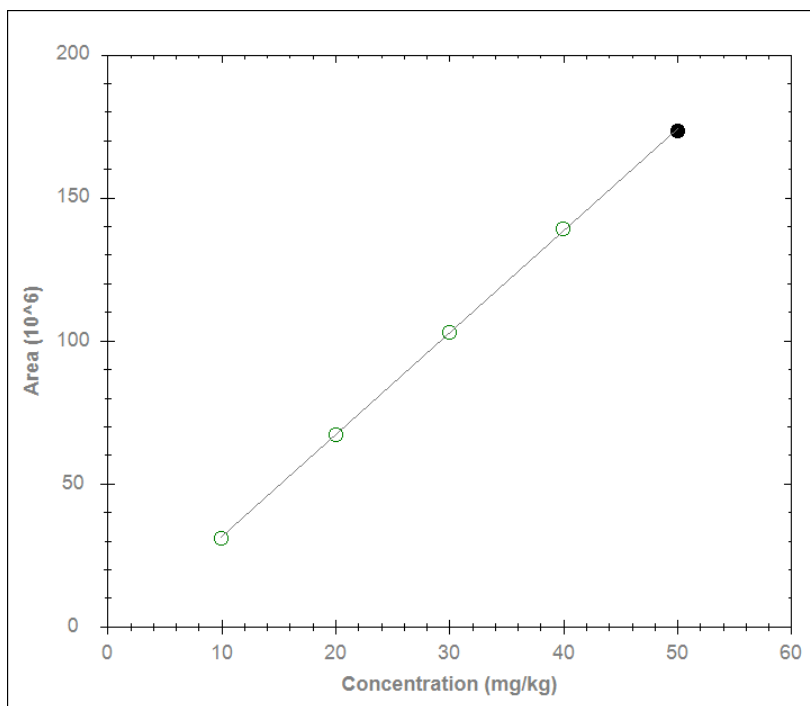


Figure 2 - Calibration line: 10 – 50 mg/kg DBS in Gasified Butane - 0.9999 r²

Volume injected	Set Quantity in Software after Analysis	Simulated Concentration
100 mL	100 mL	10 mg/kg
80 mL	100 mL	8 mg/kg
60 mL	100 mL	6 mg/kg
40 mL	100 mL	4 mg/kg
20 mL	100 mL	2 mg/kg

Table 5 - Calibration line: 2 – 10 mg/kg DBS in Gasified Butane



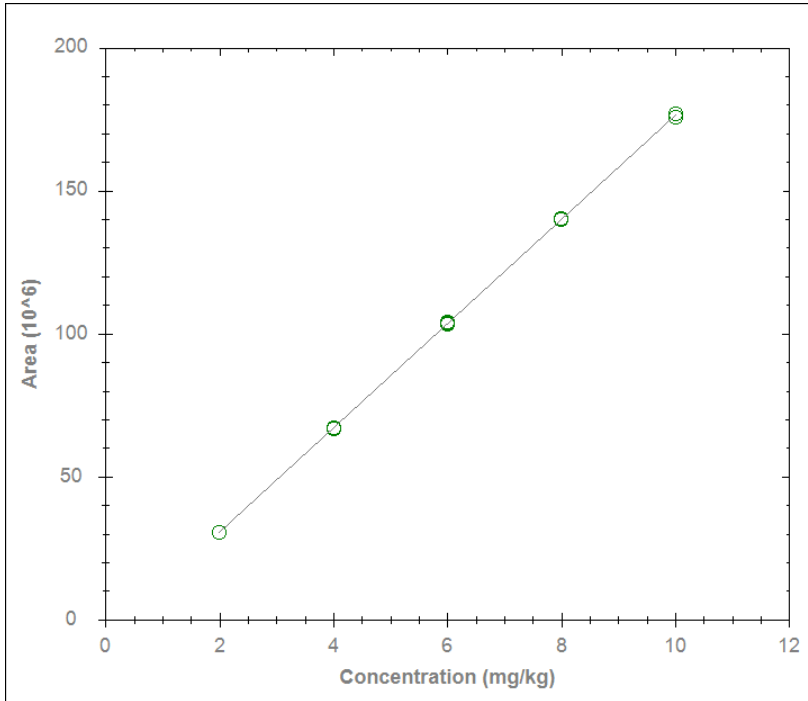
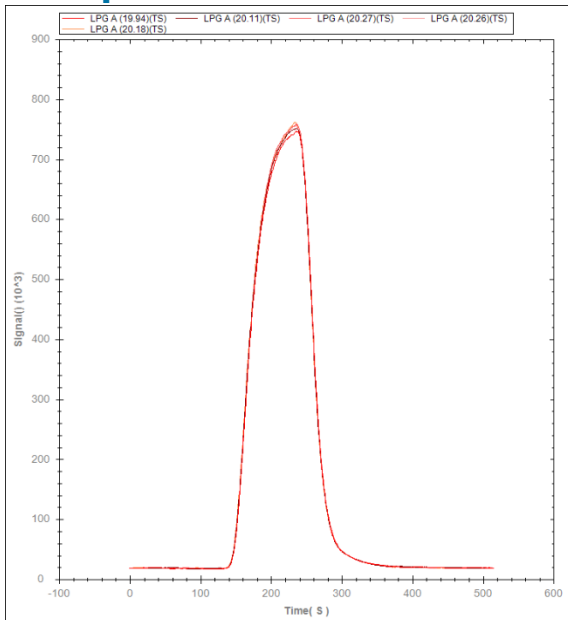
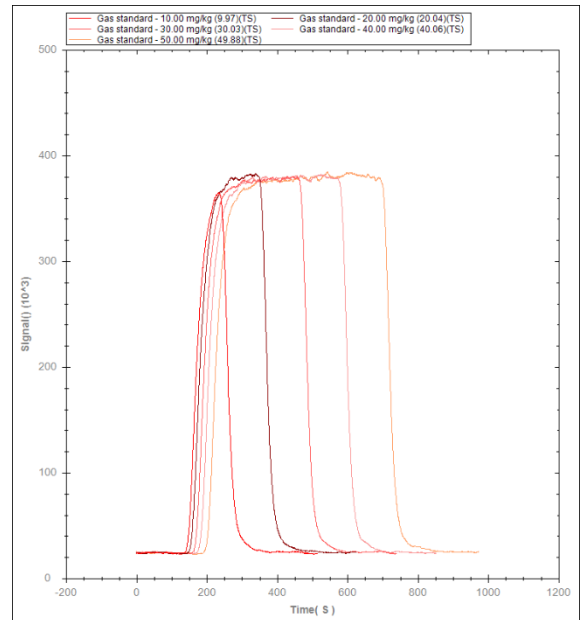


Figure 3 - Calibration line: 2 – 10 mg/kg DBS in Gasified Butane - 0.9999 r²

Example Peaks



Peak Overlay Gaseous Butane / Propane Mix A
Concentration: 20.2 mg/kg
Replicates: 5
RSD: 0.67%



Peak Overlay Different Standards
Calibration line 10 – 50 mg/kg

