PAC | Application Note

Determination of Sulfur content in Automotive fuels using Ultraviolet Fluorescence method according to ISO 20846

- Rapid and Accurate Determination of Sulfur
- Fully Automated Combustion system
- Excellent Sensitivity, Repeatability & Linearity

Keywords: ISO 20846, ElemeNtS, Sulfur, UVF, Automotive fuels

INTRODUCTION

Sulfur is a natural present element in many hydrocarbon streams, responsible for many undesirable effects such as catalyst poisoning, detrimental product quality and ecosystem pollution. There is a need to quantify and monitor its content in every step of the industry´s technical operations.

Analysis of total Sulfur content in hydrocarbons by combustion and UV fluorescence detection has been established as the preferred method to characterize feedstock, intermediate streams and finished hydrocarbon products due to its sensitivity, linearity, dynamic range and ruggedness.

ISO 20846 is an established test method for the determination of total Sulfur in automotive fuels containing 3 to 500 mg/kg Sulfur. These fuels include motor gasolines with up to 3.7% Oxygen content, diesel fuels with up to 30% FAME and synthetic fuels. For HVO and GTL the method is applicable to a range of 3 to 45 mg/kg Sulfur.

MEASURING PRINCIPLE

A hydrocarbon liquid sample is directly injected, by a fully automated liquid sampler, into a high temperature, dual temperature zone combustion tube where the Sulfur components are vaporized and combusted. The released Sulfur is oxidized to Sulfur Dioxide (SO_2) in an Oxygen rich atmosphere.

$$R - S + O_2 \xrightarrow{1050°C} CO_2 + SO_2 + H_2O$$

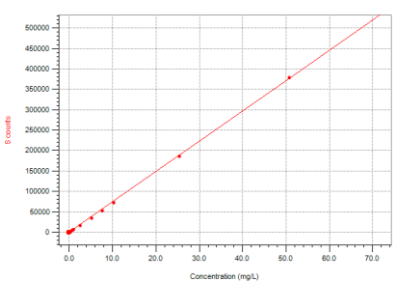
A stream of inert gas (Helium or Argon) takes the reaction products, after removal of the produced water vapor, into a reaction chamber. Here the SO_2 molecules are converted to excited SO_2^* by the absorption of energy of a UV lamp and emitting light (fluorescence) while it relaxes to a stable state.

$$SO_2 + hv \rightarrow SO_2^*$$

$$SO_2^* \rightarrow SO_2 + hv$$

A Photomultiplier tube measures the emitted light signal.

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



VALIDATION

The system and methodology of the **Antek ElemeNtS** total Sulfur analyzer is thoroughly tested for response linearity, sample scope, limit of detection (LOD), recovery and repeatability, to validate its performance according to ISO 20846.

CALIBRATION

Calibration curves are composed using dibenzothiophene in iso-octane standards. Each calibration solution and blank (iso-octane) is measured five times to determine the average net response. The ElemeNtS shows a linear correlation over the entire concentration range covered in this method. Dedicated calibration curves covering a smaller range can be constructed to improve precision. The calibration curves easily meet the required R^2 of 0.995.

Table 1: Full range calibration.

Calibration line 0-500 mg/L	
Concentration (mg/L)	**S counts**
0	414
0.5	3,117
1.0	5,834
2.5	14,319
5.0	28,222
10	56,573
25	143,306
50	290,223
100	585,471
250	1,451,572
500	2,907,776

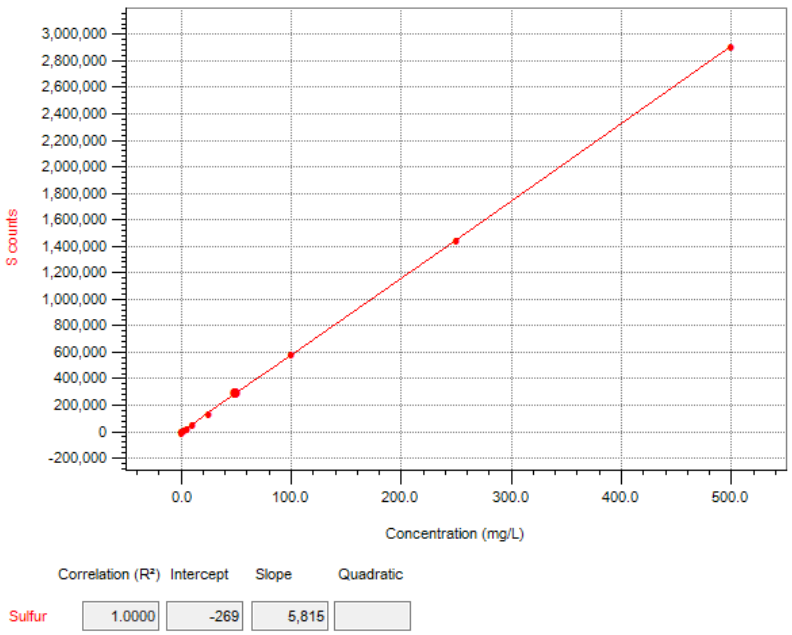


Figure 1: Full range calibration curve.

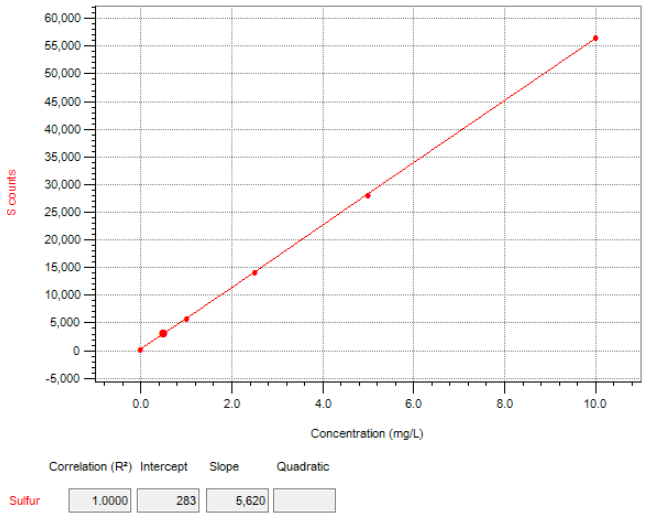


Figure 2: 0-10 ppm calibration curve.

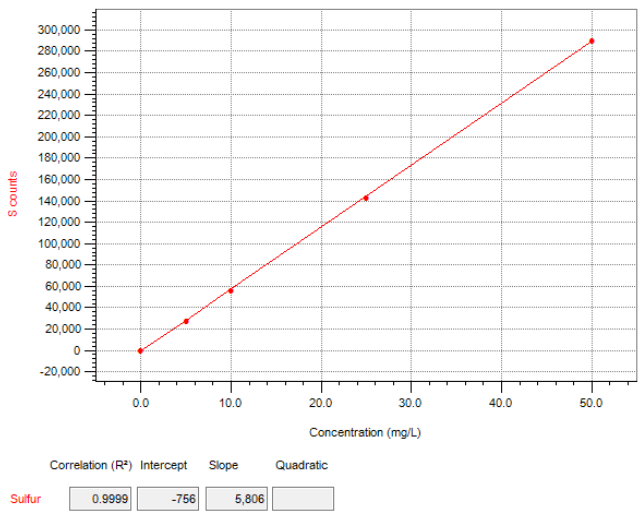


Figure 3: 0-50 ppm calibration curve.

LIMIT OF DETECTION (LOD)

The ElemeNtS is a very sensitive instrument, capable of detecting Sulfur concentrations as low as 20 parts per billion. This very low limit of detection means that the ElemeNtS conforms easily to the scope of ISO 20846.

With the IRIS software the ElemeNtS can be controlled and the results processed. Integrated into the IRIS software is an LOD-calculation according to ISO 11843, making it easy to check the sensitivity of the ElemeNtS. The LOD-calculation is based on a particular calibration on the device. A calibration between 0 and 1 mg/L was performed, resulting in an LOD of 18 parts per billion.

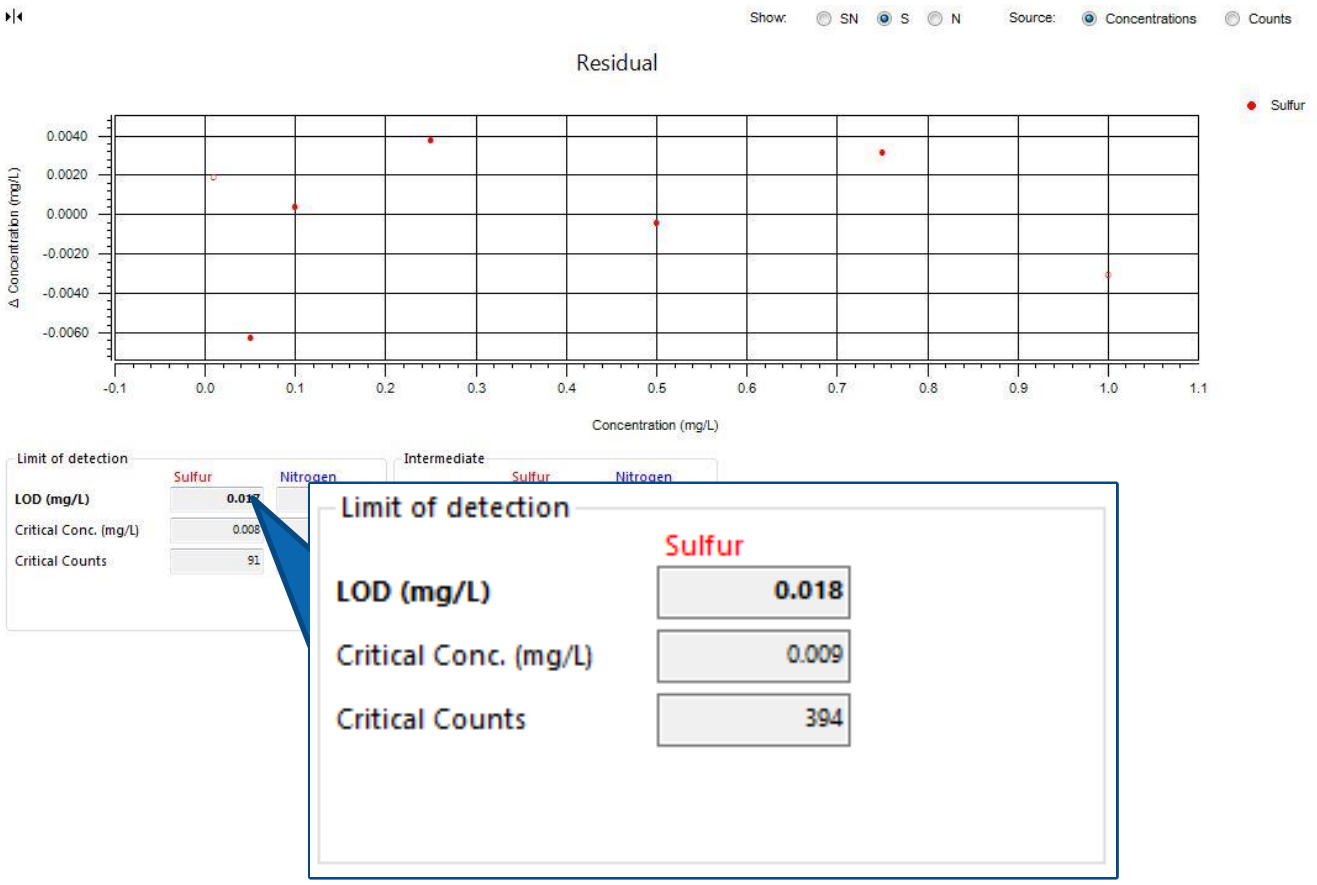


Figure 4: LOD-calculation according to ISO 11843

RECOVERY and BIAS

Different samples were selected to cover the scope of the method. Each sample is measured three times to obtain one result. The resulting area is calculated to a corresponding concentration using the applicable calibration line. The results are compared to the consensus values obtained during a Proficiency Testing Program (PTP). All the results were within the ISO 20846 reproducibility limits.

Table 2: Overview of sample results, compared with consensus values.

Results recovery / bias ISO 20846					
Sample name	**Part #**	**Target concentration (ppm)**	**Result concentration (ppm)**	**Difference**	**ISO 20846 R/√2**
Gasoline enhanced	00.02.733	**4.42**	**4.25**	0.17	1.23
Diesel B7	00.02.735	**9.64**	**9.86**	0.22	1.56
Heating Oil	00.02.737	**29.4**	**28.4**	1.0	3.1
Jet Fuel	00.02.736	**168**	**168**	0	14
Jet Fuel	00.02.732	**507**	**492**	15	40

The samples used here are also delivered with a new ElemeNtS system or can be ordered using the part number.

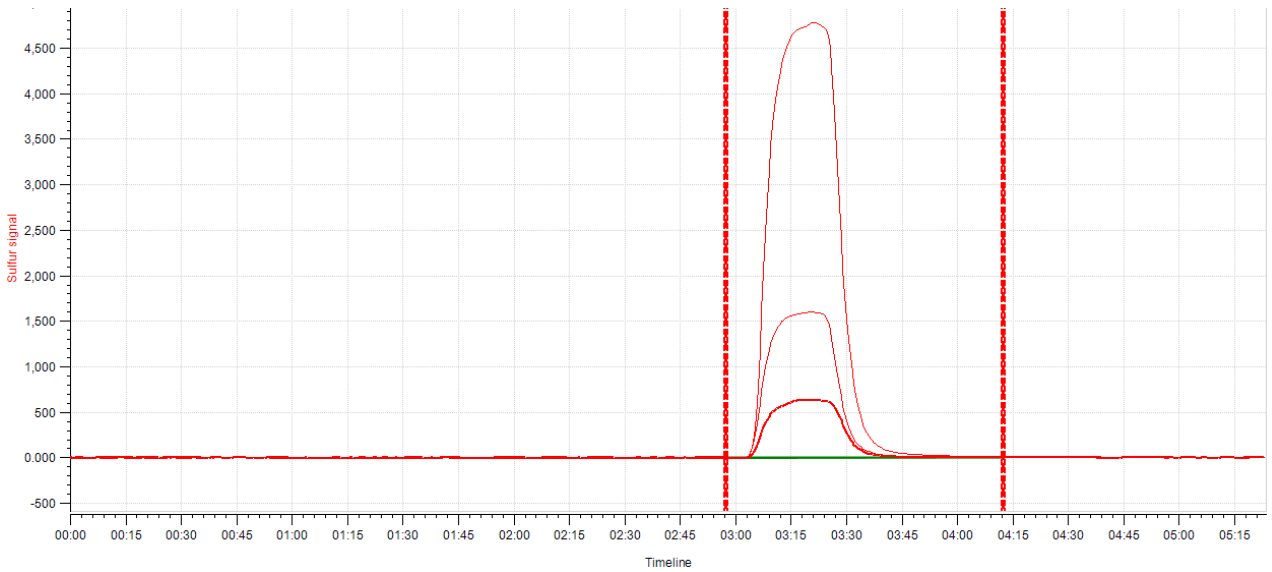


Figure 5: Overlay of three different samples

REPEATABILITY

Area (concentration) is the primary measurement in total Sulfur analysis. The precision in which it is measured ultimately determines the validity of the generated quantitative data. Area precision require that all parameters (temperatures, pressure, flow, injection) are controlled to exact tolerances. Furthermore, the inertness of the flow path can considerably affect area precision, especially for active Sulfur components at low levels.
Concentration repeatability for the ElemeNtS total Sulfur analyzer is measured for 10 consecutive runs for two samples. Repeatability standard deviation of total Sulfur is well within the precision statement of ISO 20846.

Table 3: Repeatability values of two samples compared with the ISO 20846 precision statement.

Repeatability Sulfur (mg/kg)		
Run	**Enhanced gasoline**	**Diesel B7**
1	4.173	9.743
2	4.264	9.916
3	4.265	9.880
4	4.222	9.873
5	4.242	9.916
6	4.313	9.796
7	4.163	9.845
8	4.364	9.846
9	4.225	9.895
10	4.308	9.929
Average	**4.254**	**9.864**
Standard deviation (SD)		
Measurement	**0.060**	**0.056**
Method SD (r/2.77)	**0.223**	**0.395**
Relative standard deviation (RSD)		
Measurement	**1.4%**	**0.6%**
Method RSD	**5.2%**	**4.0%**

CONCLUSION

These results demonstrate that the Elements analyzer is a powerful tool for the determination of total Sulfur in automotive fuel such as diesel and gasoline. The Antek ElemeNtS has very good linearity, very low LOD and excellent precision and repeatability.

The **Antek ElemeNtS** total Sulfur analyzer is meeting the ISO 20846 requirements.

Antek's lab instruments provide reliable, precise elemental analysis for total nitrogen and sulfur, speciated nitrogen and sulfur, fluoride, chloride, and bromide. Antek products are recognized by global regulating bodies, leading scientific research institutions, and process laboratories as the instrument of choice for selective multi-element detection.