PAC | Application Note

Determination of Sulfur content of Ethanol as blending component for petrol according to EN 15486

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

Keywords: EN 15486, ElemeNtS, Sulfur, UVF, Ethanol, Petrol

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.

EN 15486 is an established test method for the determination of total Sulfur in Ethanol containing 5 to 20 mg/kg Sulfur. Ethanol is used as a blending component for petrol, hence the need to determine the Sulfur content. Halogens interfere with this detection technique at concentrations above approximately 3500 mg/kg.

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.

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

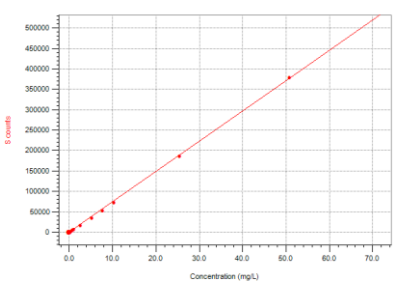
A stream of inert gas (helium or argon) takes the reaction products, after removal of the produced water vapor, into a reaction chamber. Here the SO_2 molecules are converted to excited SO_2^* by the absorption of energy of a UV lamp and emitting light (fluorescence) while it relaxes to a stable state.

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

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

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, level of detection (LOD), recovery and repeatability, to validate its performance according to EN 15486.

CALIBRATION

Calibration curves are composed using Dibenzothiophene (DBT) in Ethanol standards. Each calibration solution and blank is measured three times to determine the average net response for each. The ElemeNtS achieves a very good correlation factor of 0.9999, which easily exceeds the required factor of at least 0.995.

Table 1: Full range calibration.

Calibration line 0-20 mg/L	
Concentration (mg/L)	**S counts**
0	87
0.5	2,252
2.0	8,779
5.0	21,766
10	44,593
20	87,940

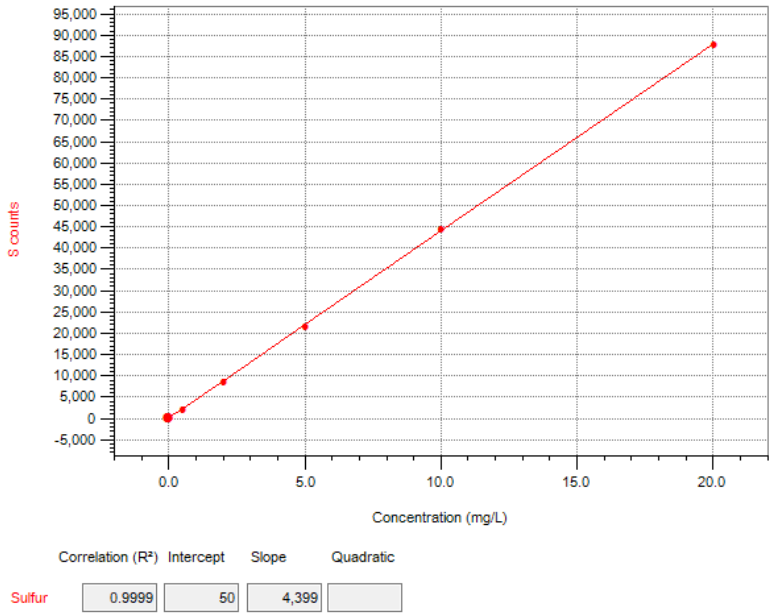


Figure 1: Full range calibration curve.

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 EN 15486.

With the IRIS software the ElemeNtS can be controlled and the results processed. Integrated into the IRIS software is a 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. The LOD based on the 0 - 20 mg/L calibration is 0.327 mg/L, easily complying to the demands of EN 15486

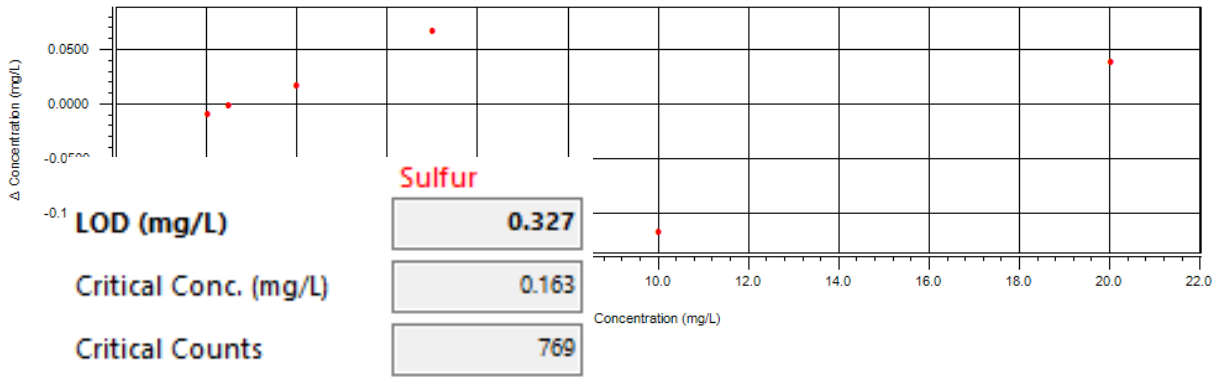


Figure 2: Residual plot with LOD according to ISO 11843.

RECOVERY and BIAS

Two samples were gravimetrically prepared to contain typical concentrations of Sulfur. One sample contained the Sulfur as Dibenzothiophene (DBT), whilst the other contained it as Sulfuric acid. Each sample is measured three times to obtain one result. The resulting area is calculated to a corresponding concentration using the calibration curve. The results are compared to the actual concentration. All the results were within the EN 15486 reproducibility limits.

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

Results recovery / bias EN 15486					
Sample name	**Target concentration (mg/kg)**	**Result concentration (mg/kg)**	**Difference**	**EN 15486 R/√2**	**Recovery %**
Sulfuric Acid	**11.1**	**10.8**	0.29	2.44	97.4
DBT	**10.0**	**10.1**	0.08	2.31	100.8

Recovery values for both organic and inorganic Sulfur in Ethanol matrices are acceptable and well within the requirements of the test method. This is important due to the fact that Sulfur in inorganic form is typically found in Ethanol.

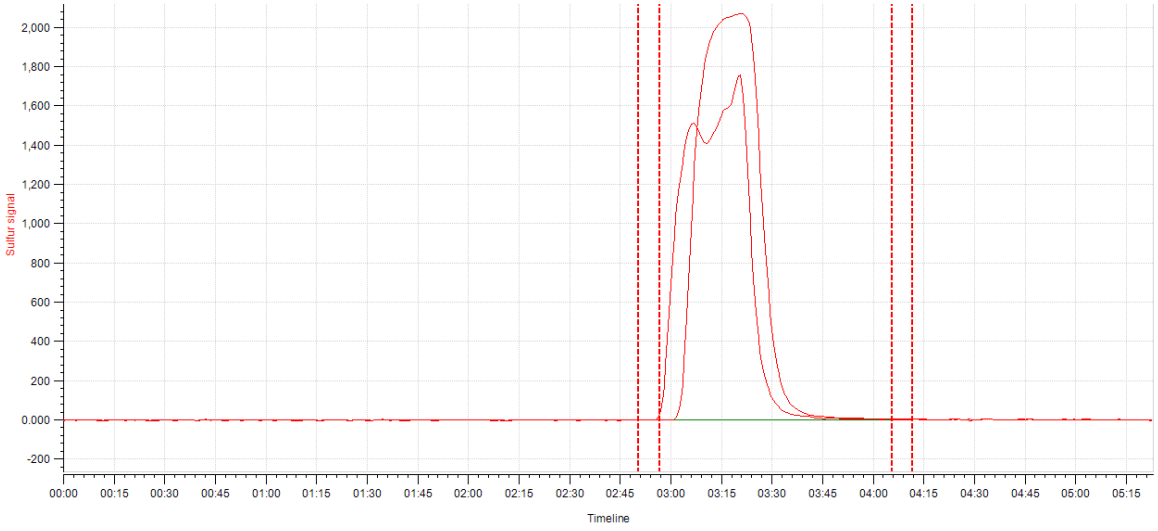


Figure 3: Overlay of sample containing Dibenzothiophene and Sulfuric Acid

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 requires 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 a sample. Repeatability standard deviation of total Sulfur is well within the precision statement of EN 15486.

Table 3: Repeatability values of two samples compared with the EN 15486 precision statement.

Repeatability sulfur (mg/kg)	
Run	**Ethanol**
1	9.972
2	10.073
3	10.167
4	10.085
5	10.067
6	10.103
7	10.084
8	10.173
9	10.035
10	10.118
Average	**10.088**
Standard deviation (SD)	
Measurement	**0.056**
Method SD (r/2.77)	**0.163**
Relative standard deviation (RSD)	
Measurement	**0.6%**
Method RSD	**1.6%**

CONCLUSION

These results demonstrate that the ElemeNtS analyzer is a powerful tool for the determination of total Sulfur in Ethanol used as a blending stock for petrol. The Antek ElemeNtS has very good linearity, very low LOD and excellent precision and repeatability.

The **Antek ElemeNtS** total Sulfur analyzer is meeting the EN 15486 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.