Application Note

Determination of Total Sulfur in Aromatic Hydrocarbons and Related Chemicals by Ultraviolet Fluorescence according to ASTM D7183.

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

Keywords: ASTM D7183, ElemeNtS, Sulfur, UVF, Aromatic hydrocarbons

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.

ASTM D7183 is an established test method for the determination of total sulfur in aromatic hydrocarbons and related chemicals. This test method is applicable to samples with sulfur concentrations from 0.03 to 10 mg/kg. Halogens present in the specimen in concentrations greater than 10 % and nitrogen concentrations of 1500 mg/kg or greater can interfere. It uses combustion and UV fluorescence to quantify the sulfur concentration.

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.

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

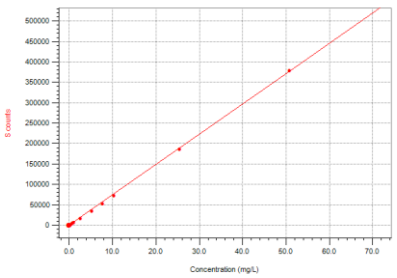
A stream of inert gas (helium or argon) takes the reaction products, after removal of the produced water vapor, into a reaction chamber. Here the SO_2 molecules are converted to excited SO_2^* by the absorption of energy of a UV lamp and emitting light (fluorescence) while it relaxes to a stable state.

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

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

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 ASTM D7183

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 for each. The ElemeNtS is linear in the entire method scope, but two calibration curves are created for optimal precision. The calibration curves easily meet the required R^2 of 0.99.

Table 1: 0-1 ppm calibration.

Calibration line 0-1 mg/L	
Concentration (mg/L)	**S counts**
0,00	100
0,05	327
0,10	541
0,25	1266
0,50	2523
0,75	3741
1,00	5029
Intercept	**65**
Slope	**4933**
R2	**0,9998**

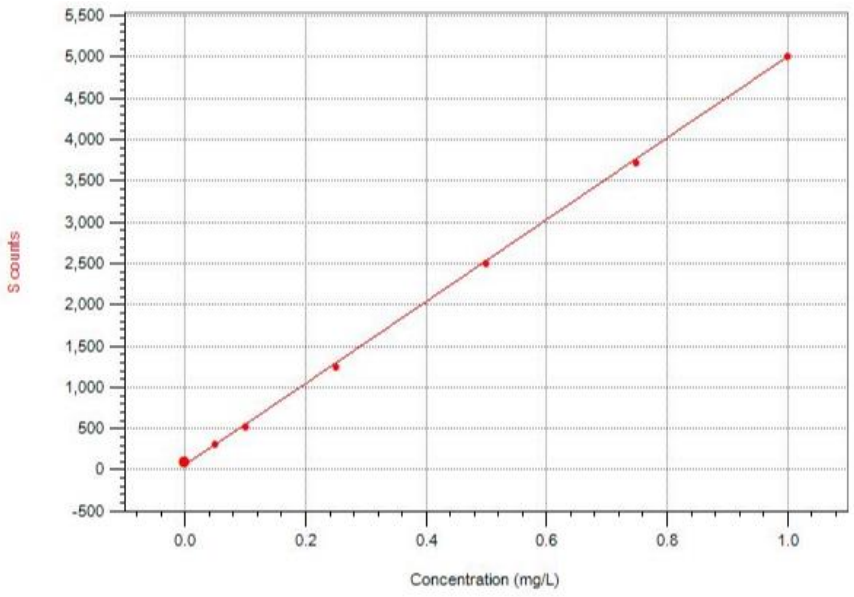


Figure 1: 0-1 ppm calibration curve.

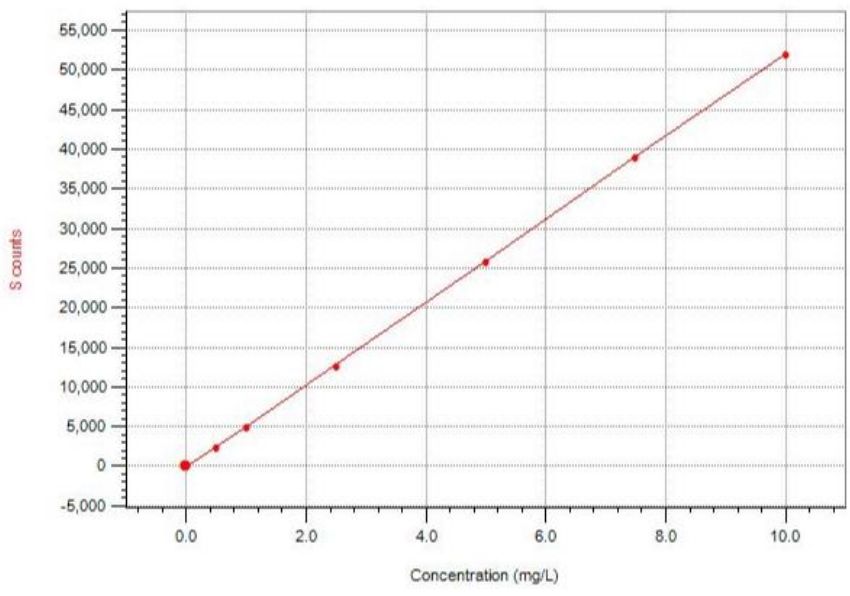


Figure 2: 0-10 ppm calibration curve.

Table 2: 0-10 ppm calibration.

Calibration line 0-10 mg/L	
Concentration (mg/L)	**S counts**
0,0	59
0,5	2516
1,0	4946
2,5	12714
5,0	25814
7,5	39063
10,0	52153
Intercept	**-166**
Slope	**5224**
R2	**0,9999**

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 to the scope of ASTM D7183.

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 0-1 mg/L calibration has a LOD of 18 parts per billion.

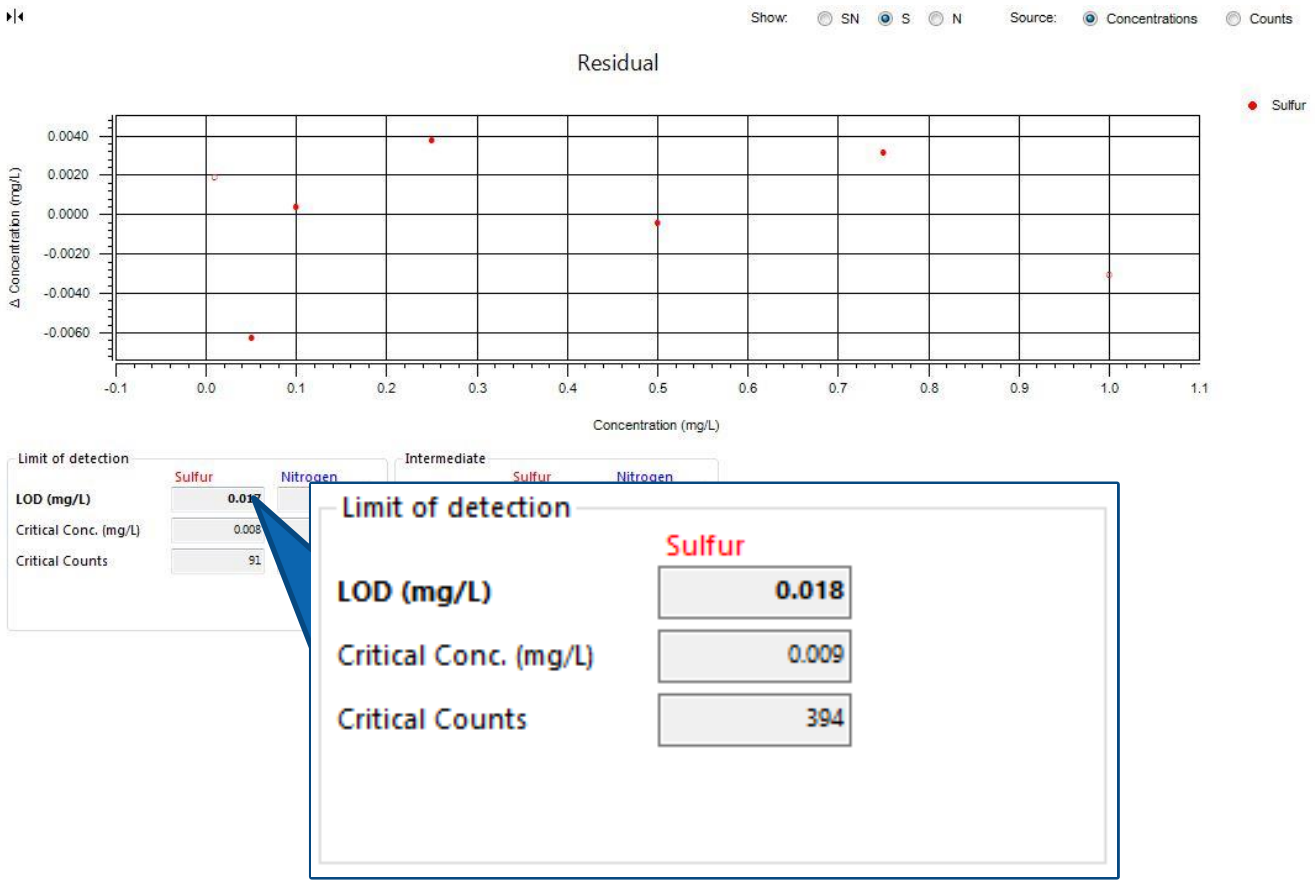


Figure 3: LOD-calculation according to ISO 11843

RECOVERY

Different samples are prepared to cover the scope of the method. All samples were prepared from high purity aromatics with known quantities of sulfur added. To obtain one result, each sample is measured five times, and the average detector response is calculated. The results are compared with the gravimetric data of the preparation of the samples. All sample results are within the ASTM D7183 specification limits for the corresponding gravimetric prepared values (table 3).

Table 3: Overview of sample results, compared with gravimetric prepared values and ASTM D7183 precision data.

Results recovery D7183						
Sample name	**Target conc. (mg/kg)**	**Blank corrected conc. (mg/kg)**	**R**	**LSL**	**USL**	**Recovery %**
Benzene I	**0,230**	**0,206**	0,20	0,140	0,320	89,7
Benzene II	**2,85**	**2,82**	0,84	2,52	3,28	98,9
Benzene III	**4,78**	**4,74**	0,84	4,42	5,18	99,2
Toluene I	**2,38**	**2,36**	0,48	2,08	2,52	99,0
Toluene II	**10,0**	**10,0**	1,90	9,15	10,85	100
p-Xylene I	**0,796**	**0,785**	0,30	0,676	0,944	98,6
p-Xylene I	**9,05**	**9,03**	0,93	8,68	9,52	99,8

The samples with a concentration lower than 1 mg/L are analyzed using the 0-1 mg/L calibration, the other samples were analyzed using the 0-10 mg/L calibration.

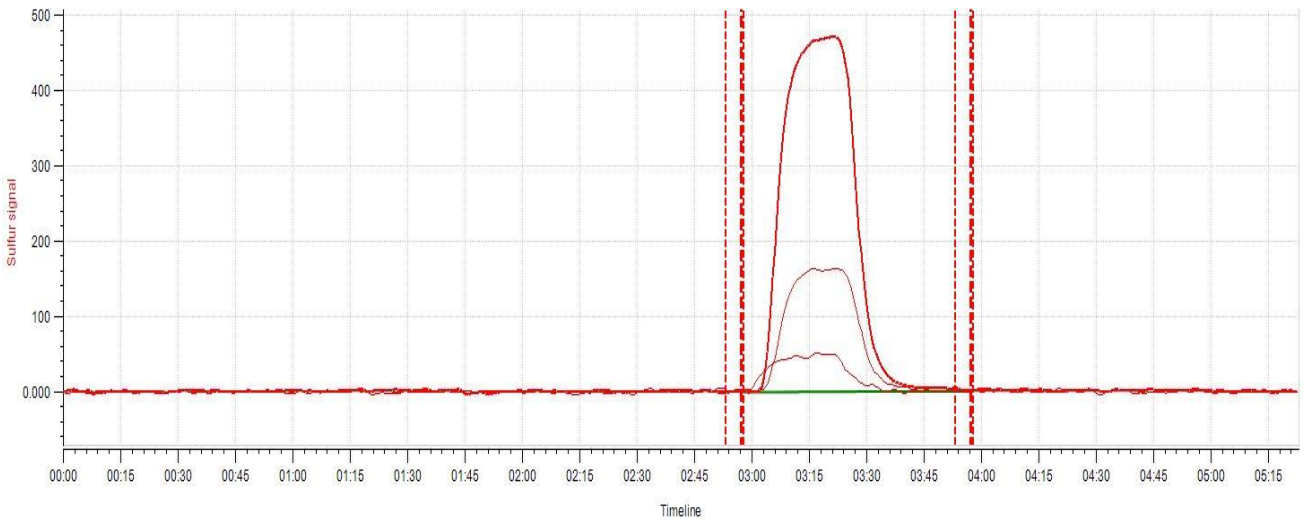


Figure 4: Overlay of three different samples

REPEATABILITY

Area (concentration) is the primary measurements 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 seven gravimetrically prepared samples. Repeatability standard deviation of Total Sulfur is well within the precision statement of ASTM D7183.

Table 4: Repeatability values of 7 reference samples compared with precision statement of ASTM D7183.

Repeatability sulfur (mg/kg)							
Run	**Benzene I**	**Benzene II**	**Benzene III**	**Toluene I**	**Toluene II**	**p-Xylene I**	**p-Xylene II**
1	0,232	2,90	4,72	2,26	9,98	0,847	8,95
2	0,239	2,90	4,71	2,22	9,96	0,839	8,95
3	0,257	2,90	4,73	2,26	9,99	0,865	8,96
4	0,242	2,91	4,75	2,26	10,00	0,851	8,98
5	0,248	2,89	4,72	2,23	9,99	0,837	8,97
6	0,249	2,90	4,73	2,22	10,00	0,866	8,96
7	0,260	2,91	4,75	2,23	10,01	0,836	8,96
8	0,249	2,92	4,74	2,24	10,02	0,846	8,99
9	0,252	2,88	4,72	2,26	9,99	0,847	8,97
10	0,245	2,96	4,76	2,25	10,01	0,843	8,97
Average	**0,247**	**2,91**	**4,73**	**2,24**	**9,99**	**0,848**	**8,968**
Standard deviation (SD)							
Measurement	**0,008**	**0,022**	**0,016**	**0,016**	**0,016**	**0,011**	**0,013**
Method SD (r D7183/2.77)	**0,018**	0,069	0,069	0,090	0,116	**0,018**	**0,097**
Relative standard deviation (RSD)							
Measurement	**3,41%**	**0,74%**	**0,34%**	**0,70%**	**0,16%**	**1,26%**	**0,15%**
Method RSD (r D7183/2.77)	**7,30%**	**2,36%**	**1,45%**	**4,02%**	**1,16%**	**2,13%**	**1,09%**

CONCLUSION

These results demonstrate that the Elements analyzer is a powerful tool for the determination of total Sulfur in Aromatic Hydrocarbons, like Xylene, based on the exceptional calibration linearity, low limit of detection, excellent repeatability and recovery.
The **Antek ElemeNtS** total Sulfur analyzer is meeting the ASTM D7183 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.