PAC | Application Note

Determination of Total Volatile Sulfur in Gaseous Hydrocarbons and Liquefied Petroleum Gases by Ultraviolet Fluorescence according to ASTM D6667.

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

Keywords: ASTM D6667, ElemeNtS, Accura, Sulfur, UVF, LPG

INTRODUCTION

ASTM D6667 is an established test method for the determination of total volatile sulfur in gaseous hydrocarbons and liquefied petroleum gases (LPG). This test method is applicable to the analysis of natural, processed, and final product materials containing sulfur in the range of 1 to 100 mg/kg.

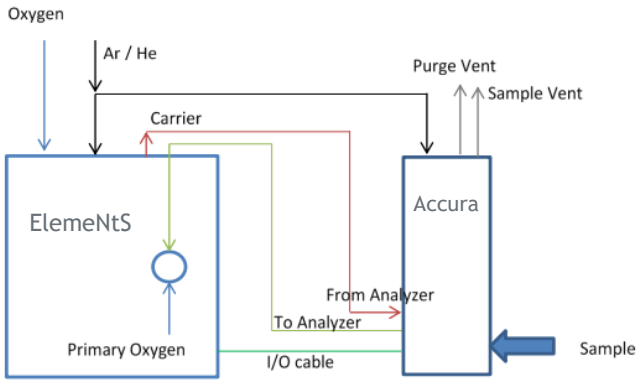
Sulfur could be present in LPG or gases, used for fuel purposes, through the production process as well as component of odorant. In both cases there is a need for measuring the total Sulfur content for regulatory compliance determination.

LPG or gases used as a feedstock for various processes should also be monitored for the sulfur content, as some process catalysts used in petroleum and chemical refining can be poisoned by sulfur bearing materials in these feedstocks.

SAMPLE INTRODUCTION

A gaseous hydrocarbon or LPG sample is introduced into the ElemeNtS by the automated Accura sampling device. The Accura has a vaporizer to convert the liquified gas (LPG) into a gas. After passing the vaporizer the gas (or vaporized LPG) enters a heated automated gas sampling valve. When the injection pulse is given (from the ElemeNtS software), the valve is switched, and the content of the sample loop transferred to the ElemeNtS with the carrier gas. An additional flow (controlled by a built-in Mass Flow controller) is added to ensure a sufficient flow.

For calibration purposes gases with a known concentration of Sulfur should be used. The calibration gases can be introduced into the ElemeNtS in the same way as samples are introduced, by directly connecting to the Accura.



MEASURING PRINCIPLE

The carrier gas coming from the Accura enters the 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.

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

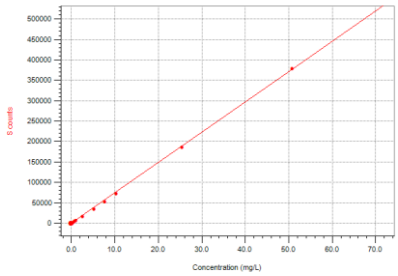
A stream of inert gas (helium or argon) takes the reaction products, after removal of the produced water vapor, into a reaction chamber. Here the SO_2 molecules are converted to excited SO_2^* by the absorption of energy of a UV lamp and emitting light (fluorescence) while it relaxes to a stable state.

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

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

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 recovery, response linearity, sample scope and repeatability, to validate its performance according to ASTM D6667

RECOVERY

Two samples were analyzed to determine the recovery in different sample streams. One sample is an LPG like sample, containing iso-butane, n-butane and propane mixture (liquid) with sulfur components. The other sample contains propylene with sulfur components.

Table 1: Recovery values of Propylene and LPG gas

Propylene		LPG	
Component	ppm mol S	Component	ppm mol S
Methyl mercaptan	8.6	Carbonylsulfide	14.9
Ethyl mercaptan	12.9	Dimethylsulfide	14.9
Carbonylsulfide	10.8	Ethylmercaptan	15.5
Dimethylsulfide	10.8	Hydrogensulfide	14.9
Hydrogensulfide	10.8	Methylmercaptan	15
Total S	**54**	**Total S**	**75**
Measured total S	**56**	**Measured total S**	**79**
R_{method}	**16.9**	**R_{method}**	**23.5**

LINEARITY

The linearity of response for the analyzer is verified by creating dynamic dilutions of a certified calibration gas (9,99 ppm mol SO_2). The dilutions are prepared by combining the calibration gas (sulfur compound in Helium) and dilution gas (pure Helium) using two separate mass flow controllers. Concentrations from ~ 10 ppm down to 100 ppb have been created and analyzed on the ElemeNtS system. Each dilution level is analyzed 10 times (2 series of 5 injections). A Calibration line has been created, with a linearity correlation > 0.9999 (Figure 2).

Table 2: Response values

Dilution X	SO_2	Average Area
	ppm mol S	counts
Blank	-	35
Blank	-	-32
100	0.100	347
100	0.100	350
50	0.200	809
50	0.200	758
20	0.500	1902
20	0.500	2008
10	0.999	3775
10	0.999	3979
5	1.998	7867
5	1.998	7889
2	4.995	19757
2	4.995	19712
1	9.990	39437
1	9.990	39429

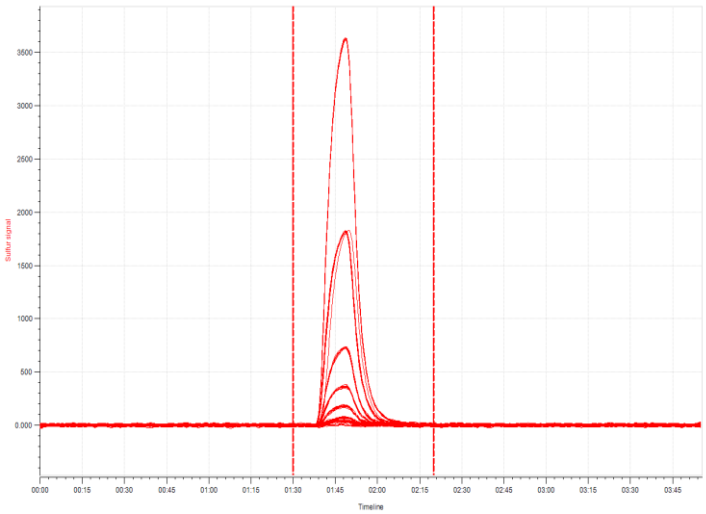


Figure 1: Overlay Calibration Gas dilutions

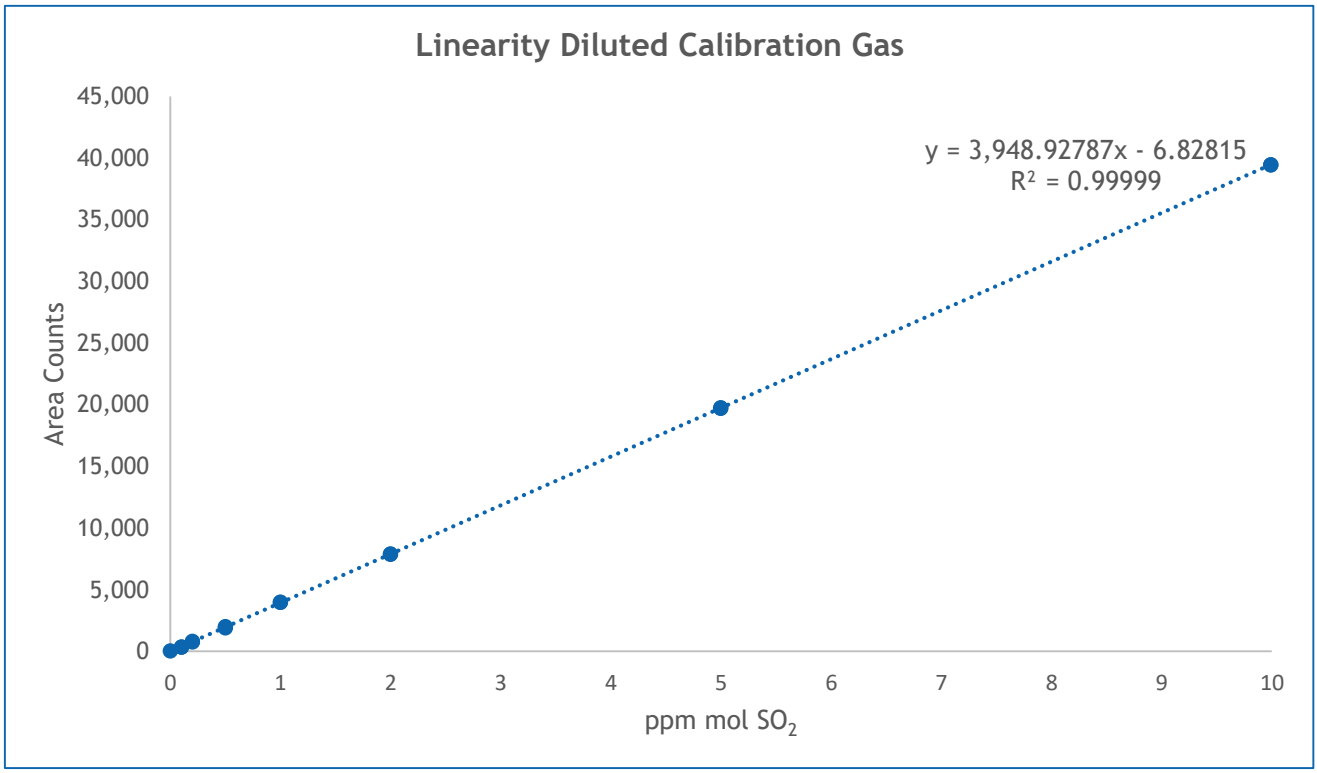


Figure 2: Linearity plot 0 to 10 ppm

DETECTABILITY

Detection limit of the ElemeNtS system in combination with the Accura sample injection, is calculated according to ISO 11483. A series of dilutions is prepared as described under “linearity”. An overlay of the injections at low level (< 1 ppm) is depicted in figure 3. The linearity correlation of the diluted calibration gas at this low level is still > 0.999. The calculated LOD according ISO11483 is 0,029 ppm mol (= ~0,03 mg/kg in LPG), which is much better than the desired detection limit (1 mg/kg).

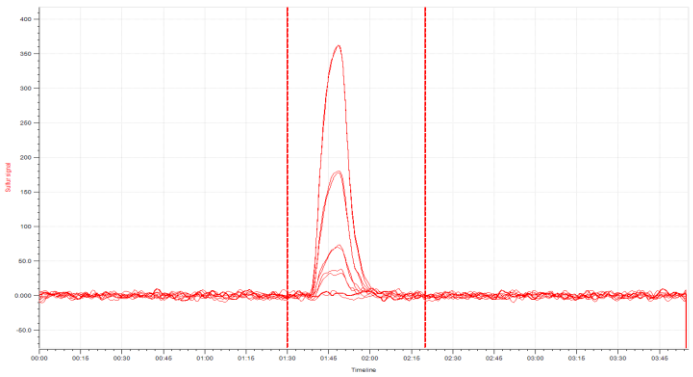


Figure 3: Overlay of blank, 100 ppb, 200 ppb, 500 ppb and 1000 ppb.

Table 3: Response values

Dilution X	SO_2	Average Area
	ppm mol S	counts
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Blank	-	-32
100	0.100	347
100	0.100	350
50	0.200	809
50	0.200	758
20	0.500	1902
20	0.500	2008
10	0.999	3975
10	0.999	3979

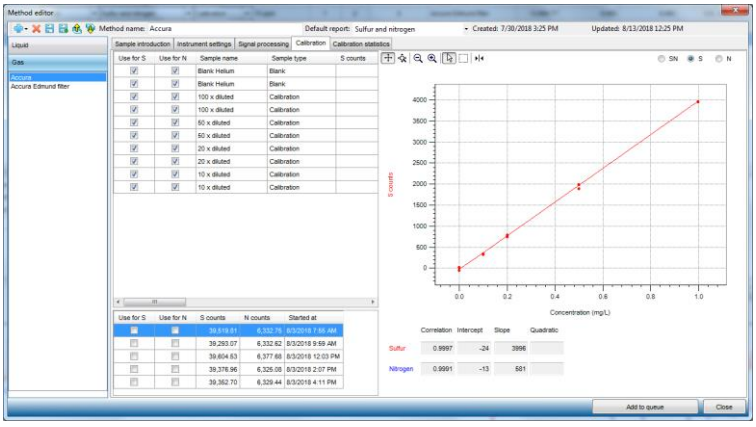

Figure 4: Calibration calculation in IRIS Software

Figure 5: Calibration statistics (LOD) calculation in IRIS Software according ISO 11483

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 two reference samples. Repeatability standard deviation of total sulfur is well within the precision statement of ASTM D6667.

Table 4: Repeatability values of LPG and Propylene reference material

Run	LPG	Propylene
	ppm mol S	ppm mol S
1	79.6	56.2
2	79.4	56.3
3	79.7	56.6
4	79.7	56.4
5	79.4	56.2
6	79.5	56.6
7	79.5	56.5
8	79.7	56.5
9	79.8	56.6
10	79.4	56.5
Average	**79.6**	**56.4**
Standard deviation (SD)		
Measurement	0.2	0.2
Method SD (r_{D6667}/2.77)	2.1	2.3
Relative standard deviation (RSD)		
Measurement	0.19%	0.26%
Method RSD (r_{D6667}/2.77)/mean	2.6%	4.1%

CONCLUSION

These results demonstrate that the ElemeNtS analyzer, in combination with the Accura automatic sample introduction, is a powerful tool for the determination of sulfur in Gaseous Hydrocarbons and Liquefied Petroleum, based on the exceptional calibration linearity, low limit of detection, excellent repeatability and recovery.
The **Antek ElemeNtS** total Sulfur analyzer in combination with the **Accura** is meeting the ASTM D6667 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.