PAC | Technical Note

Interference-free Determination of Total Sulfur by UV-Fluorescence in Fuels with High Levels of Nitrogen.

- Accurate sulfur determination in high nitrogen containing samples
- Easy, safe and robust nitrogen interference solution
- Excellent sensitivity, repeatability & linearity

Keywords: ElemeNtS, sulfur, UVF, diesel, cetane improver, nitrogen interference

INTRODUCTION

The analysis of total sulfur in ULSD samples by oxidative combustion followed by UVF detection can be hindered by interference from certain nitrogen components. This effect is caused by a cross-sensitivity to NO, which fluoresces in the same wavelength range as SO_2. Depending on the nitrogen content of the sample, this can lead to false positive sulfur results up to 1,7 mg/kg at 160 mg/kg nitrogen.

To increase the cetane index of diesel fuels, alkyl nitrates, more commonly 2-ethylhexyl nitrate (2-EHN), is added to the diesel. The relative high nitrogen concentration might cause a positive bias in the sulfur determination.

The Antek ElemeNtS total sulfur analyzer can efficiently reduce the interference of these type of compounds by means of a optimized sulfur detector without the need of software correction or added ozone supply.

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.

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

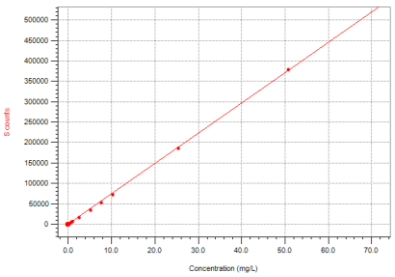
A stream of inert gas (helium or argon) takes the reaction products, after removal of the produced water vapor, into a reaction chamber. Here the SO_2 molecules are converted to excited SO_2^* by the absorption of energy of a UV lamp and emitting light (fluorescence) while it relaxes to a stable state.

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

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

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 concentration of standard mixtures versus integrated area.



EXPERIMENTAL CONDITIONS

Instrumentation

Tests are executed on a vertical ElemeNtS TS/TN configuration under standard operating conditions with and without an optimized sulfur detector. The optimization is based on a selective emission filter in front of the PMT (see figure 1A & 1B).

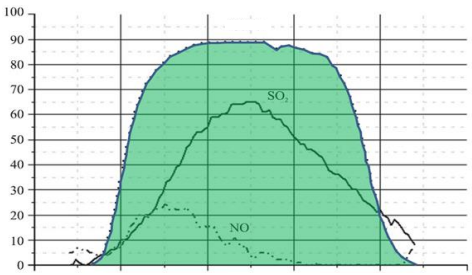


Figure 1A: Standard configuration using wide range emission filter (green band)

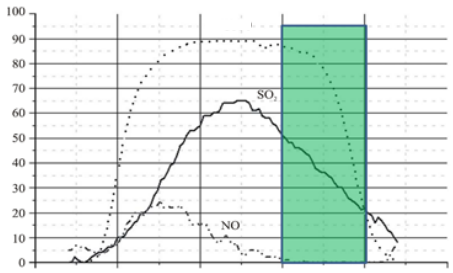


Figure 1B: Optimized configuration using narrow range emission filter (green band)

Calibration

Calibration curves (see figure 2A & 2B) are composed using tert-butyl-di-sulfide in o-xylene standards. Each calibration solution and blank (o-xylene) is measured five times. The average response of the blank injections is subtracted from each calibration standard response conform ASTM D5453.

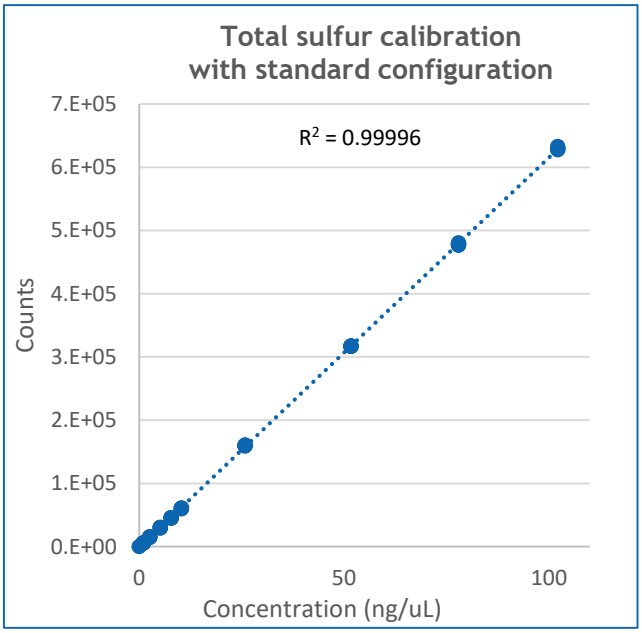


Figure 2A: Calibration curve using standard configuration

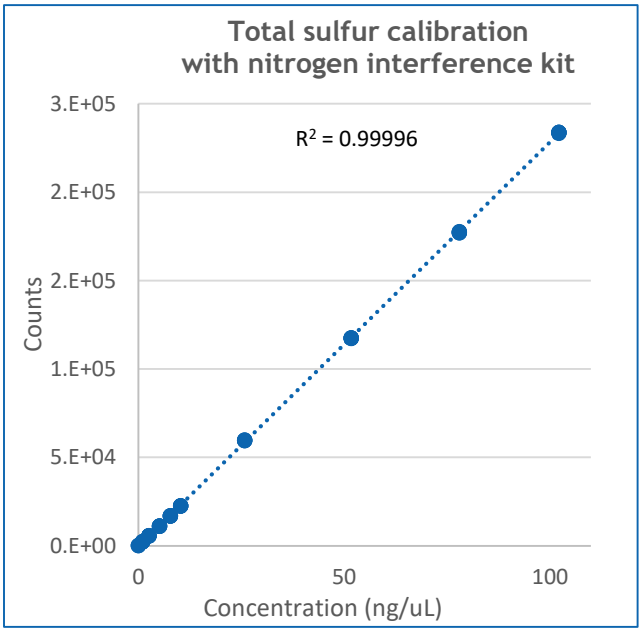


Figure 2B: Calibration curve using nitrogen interference kit

RESULTS AND DISCUSSION

The results for total sulfur of an ultra low sulfur diesel (ULSD) spiked with 2-ethylhexyl nitrate with and without the use of a nitrogen interference kit are summarized in table 1. The samples were analyzed in both configurations to show the interfering effect of nitrogen containing additives used to boost the cetane index as well as show the efficiency of the nitrogen interference kit used in the ElemeNtS instrument. The corresponding total sulfur analysis are shown in figures 3A & 3B.

	Standard configuration		With nitrogen interference kit	
2-EHN concentration (mg/kg)	Concentration S (mg/kg)	RSD (%)	Concentration S (mg/kg)	RSD (%)
0	10.18	0.35	**10.04**	0.70
642	10.49	0.36	**10.21**	0.36
1283	10.77	0.30	**10.28**	0.22
1926	10.98	0.28	**10.35**	0.37
2550	11.15	0.29	**10.35**	0.33
3209	11.39	0.25	**10.41**	0.27

Table 1: Total sulfur results of an ultra low sulfur diesel spiked with 2-ethylhexyl nitrate with and without the use of the nitrogen interference kit.

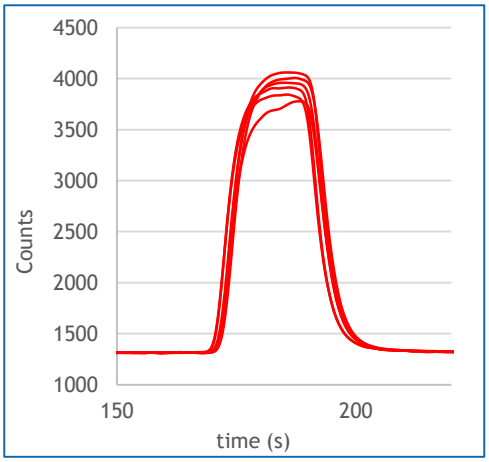


Figure 3A: overlay TS results with increasing N-content in a standard configuration

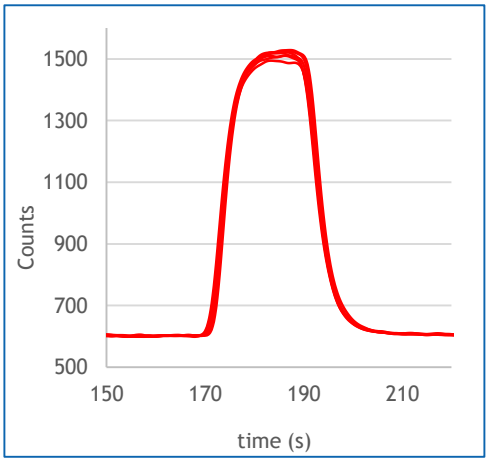


Figure 3B: overlay TS results with increasing N-content with improved sulfur detector

When analyzing diesel fuels containing higher total nitrogen quantities caused by addition of performance improving agents (e.g. cetane improver), the advantage of the improved sulfur detector is clearly visible. Depending on the nitrogen content, more or less significant difference between the two configurations occur. The precisely selected bandpass filter used in the nitrogen interference kit only focuses on the UV-fluorescence of SO_2 resulting in an accurate total sulfur content.

When using the optimized sulfur detector for minimal nitrogen interference, according to ISO-11843 the calculated LOD increases only by a factor of two.

CONCLUSION

The ElemeNtS elemental analyzer with optimized sulfur detector guarantees the correct results when measuring sulfur traces in presence of high nitrogen quantities. The instrument demonstrates the ability to accurately determine the total sulfur content in ultra low sulfur diesel (ULSD) samples doped with an alkyl nitrate used to boost the cetane index without bias with excellent stability and precision. This is especially important in quality control of diesel fuels and related matrices containing additives.

The nitrogen interference kit can be ordered under part number 38.00.550

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.