

MultiTek® Cetane Improver impact on the S content of Ultra Low Sulfur Diesel (ULSD) by UV-Fluorescence

- **Determination of Cetane Improvers high N content bias on sulfur analysis**
- **Double path pyrotube for complete combustion of low sulfur sample matrices**
- **Excellent linearity, sensitivity and repeatability**
- **Comparative study of CI kit and direct analysis.**

Keywords:

MultiTek®, Cetane Improver, Ultra Low Sulfur Diesel, Combustion Analysis, UV-Fluorescence, Ozone.

INTRODUCTION

The analysis of total sulfur in ULSD samples by oxidative combustion followed by UV-Fluorescence can be hindered by interferences from certain species like Nitric oxide that can fluoresce in the same region where sulfur dioxide does. When an ULSD sample is injected into a pyrolytic tube in the presence of excess oxygen sample is combusted and the sulfur compounds decompose according to the general equation (1). The amount of sulfur is determined according to the standard method ASTM D5453.

The operation parameters for the analysis are listed in Table 1.



Water formed in the combustion process strongly quenches the SO_2^* fluorescence signal so combustion gases are routed through a membrane drying system to remove the water before reaction (2) takes place. UVF is linear and equimolar with a dynamic range higher than 10^3 .



If nitrogen is present in the ULSD, nitric oxide is formed in the combustion stage producing NO^* excited which can also fluoresce in the same region creating false positives.

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

MultiTek by means of a Cetane Improver kit can efficiently reduce the interference of these type of compounds.

EXPERIMENTAL CONDITIONS

Instrumentation

Antek MultiTek Vertical configuration with Low Level Sulfur detection comprising a double path pyrolytic tube.



Figure 1. MultiTek Vertical Configuration with Liquid Autosampler

• Instrument Parameters

Table 1. Hardware parameters

Sample Volume (µL)	50
GFC 1- Ar carrier (ml/min)	130
GFC 2- Pyro O ₂ (ml/min)	450
GFC 3- Ozone O ₂ (ml/min)	35
GFC 4- Carrier O ₂ (ml/min)	25
GFC 5- Auxiliary O ₂ (ml/min)	25
Furnace (°C)	1050
Sulfur voltage (V)	700

Other ways to eliminate this interference is to be oxidize the NO to NO₂ prior to the excitation with the UV energy. NO₂ does not fluoresce in the same region as SO₂ does causing no bias in the analysis.

• Calibration Curve

Calibration was performed with Toluene standards with DBT as the source of Sulfur. Method ASTM D5453 was followed and it is shown in Figure 2.

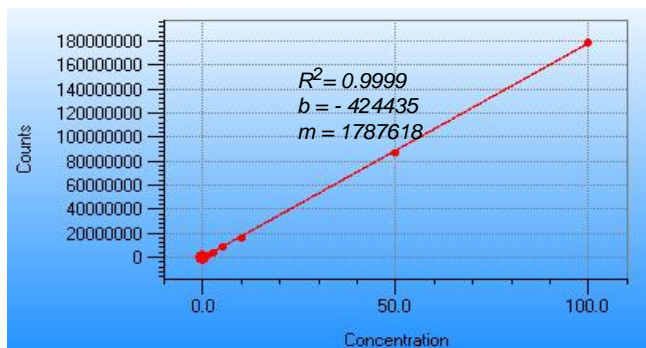
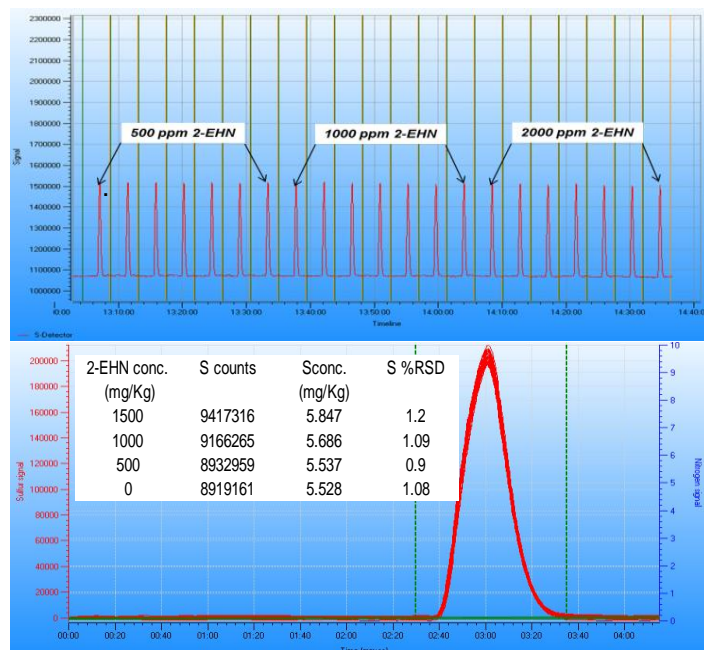


Figure 2. S Calibration plot

• Experimental Results

The dispersion of the sulfur signal can be seen below when ULSD samples were additivated with 2-ethyl hexyl nitrate up to 1500 ppm. This addition corresponds to the conventional maximum quantities presently used by the refiners.



CONCLUSION

The MultiTek Elemental Analyzer demonstrates the ability to accurately determine the total sulfur content in Ultra Low Sulfur Diesel (ULSD) samples doped with alkyl nitrate used to boost the cetane index without bias. The analysis allows the user to monitor and optimize the ULSD analysis and to assist the engineers to more effectively maximize the diesel production without seriously affecting the quality of the final products.

The Antek MultiTek is the only instrument on the market that combines sulfur, nitrogen, and halides analysis all in one. Compact, powerful, automated, and able to analyze gas, liquid, or solid samples, it's the perfect solution to today's increasing demand worldwide for fast, accurate detection and analysis of contaminants, and corrosive elements. Because MultiTek® delivers precise results with high sensitivity and unmatched versatility, it's a valuable process optimization tool that will deliver faster ROI and a better bottom line.