DETERMINATION OF TOTAL SULFUR IN REFORMULATED GASOLINE BY UVF- A D5453 CORRELATION

- **Correlation between MultiTek® VNS and ASTM RFG PTP Program**
- **MultiTek® Performance Validation**
- **Excellent Sensitivity and Stability for Analysis of Sulfur in Gasoline**

Keywords:
MultiTek®, Total Sulfur, Gasoline, UVF, LOD, ASTM D5453

INTRODUCTION

Total Sulfur content in hydrocarbons by combustion and UV fluorescence 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. This application note deals with the total Sulfur content determination in gasoline according to the ASTM D5453 Standard Test Method[1]. Since sulfur is a ubiquitous element in hydrocarbon streams responsible for many undesirable effects like 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.

PRINCIPLE OF OPERATION

When hydrocarbon samples are introduced into a pyrotube at 1050ºC, sample components combust to form CO_2 and H_2O. Sulfur compounds are present in hydrocarbon mixtures and fossil fuels in a great variety of forms and chemical nature, however they also form combustion products as described in the general reaction equation (I).

$$R\text{-}S + O_2 \xrightarrow[1050°C]{} CO_2 + SO_2 + H_2O \quad (I)$$

Water in vapor or liquid phase can alter the measurement of sulfur and the combustion product must have the water removed before entering the reaction chamber where SO_2 molecules get excited and relaxed as per equations (II) and (III) below. A PMT set at the appropriate wavelength range will measure the emission signal of the sulfur species.

$$SO_2 + h\nu\ (190\text{-}230nm) \longrightarrow SO_2^* \quad (II)$$

$$SO_2^* \longrightarrow SO_2 + h\nu\ (230\text{-}450nm) \quad (III)$$

REFORMULATED GASOLINE (RFG) ANALYSIS

Samples were analyzed in the new Antek MultiTek® analyzer[2] in a vertical configuration equipped with an autosampler and UV Fluorescence detector. As a validation method, the MultiTek® performance was compared with the results from the ASTM Proficiency testing Program (PTP) on Reformulated Gasolines[3].

CALIBRATION

The MultiTek VNS analyzer was calibrated in the range from 0 to 25 mg/kg using dibenzothiophene (DBT) in toluene. The instrument paramaters utilized for the calibration and the RFG analysis are listed in Table 1. The sulfur calibration curve is shown in Figure 1. The resulting correlation coefficient was > 0.9999.

Calibration method		
• Inlet Ar flow	130	ml/min
• Inlet O2 flow	35	ml/min
• Main pyro O2 flow	450	ml/min
• Furnace temp	1050	°C
• Syringe volume	25	µl
• Sample size	15	µl
• Injection speed	1	µL/s
• PMT voltage	700	V

Table 1. Instrument Parameters

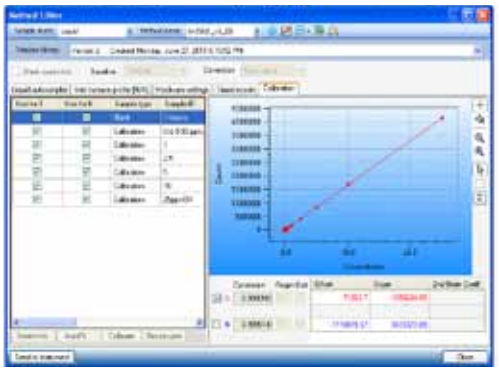

Figure 1. S Calibration for the 0 – 25 ppm range

Calibration data was used to determine the limit of detection (LOD), which is defined as 3σ. These data resulted in a LOD of 120 ppb sulfur for this application range.

RESULTS

A selected representation of the injection signal distribution can be observed in Figure 2. Samples were selected in an attempt to cover the whole concentration range of the samples analyzed. The results obtained for the last eleven ASTM ILS RFG reports are tabulated in Table 2. Figure 3 plots a correlation between MultiTek® results and the reported ILS robust mean for all the samples.

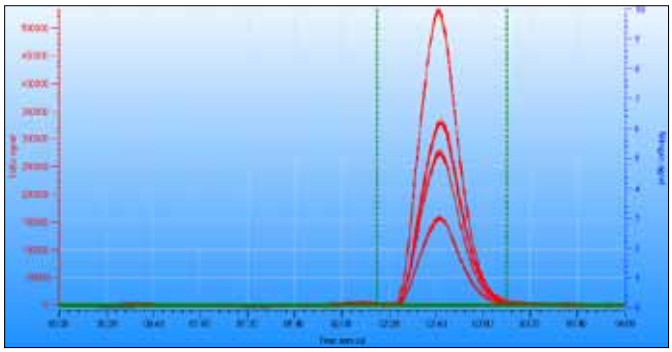

Figure 2. Sulfur results for 4 RFG samples (10 injections each)

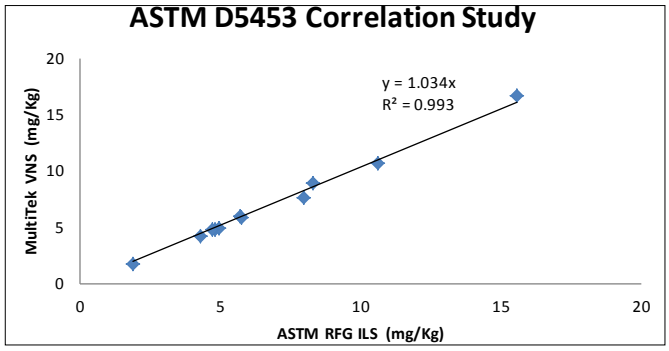

Figure 3. D5453 Correlation curve

Sample ID	ASTM RFG ILS S Different Mean (mg/Kg)	Robust ILS SD	# Labs	MultiTek® S (mg/kg) 10 injections	MultiTek® SD
RFG1006	4.8	0.64	93	4.8	0.06
RFG1008	4.9	0.54	94	5.0	0.08
RFG1009	4.7	0.73	96	4.0	0.03
RFG1010	15.5	1.35	91	16.7	0.07
RFG1011	5.7	0.66	92	5.9	0.26
RFG1012	5.7	0.65	93	5.8	0.10
RFG1101	8.0	0.93	88	7.6	0.31
RFG1102	8.3	0.93	92	8.9	0.34
RFG1103	10.6	1.17	95	10.6	0.10
RFG1104	1.9	0.46	87	1.8	0.04
RFG1105	4.3	0.68	95	4.3	0.12

Table 2. Comparison of ASTM ILS and Multitek® results

REPEATABILITY

The MultiTek® analyzer has proven to be a very stable and reliable instrument. Figure 4 shows the stability test on the MultiTek® system: a 10 ppm sulfur sample exhibits excellent stability to ensure product quality and process monitoring.

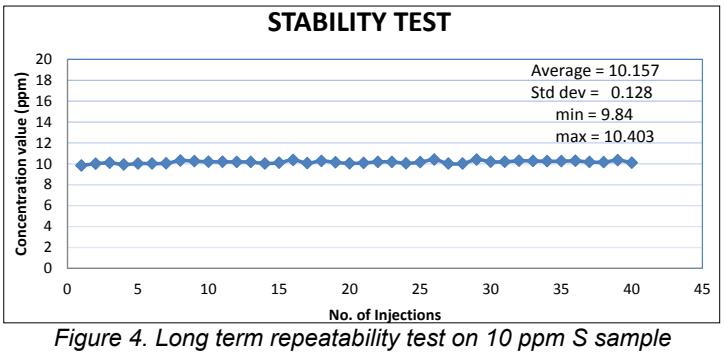

Figure 4. Long term repeatability test on 10 ppm S sample

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CONCLUSION

These results demonstrate that the MultiTek® analyzer is a powerful tool for the determination of sulfur to ensure the final product quality of gasoline based on the exceptional calibration linearity, low limit of detection, excellent repeatability and extremely stable response.

References:

1. ASTM Annual Book of Standards Vol. 05.03 2011; 2. MultiTek Technical Manual; 3. ASTM Committee D2. Proficiency Testing Program RFG Monthly Report

Antek's MultiTek® is the only instrument on the market that combines testing for sulfur, nitrogen, and halides all in one. Compact, powerful, automated, and multi-configurable,its the perfect solution to todays increasing demand worldwide for fast, accurate detection and analysis of unwanted chemicals, pollutants, contaminants, and corrosive elements. Because MultiTek® delivers precise results with high sensitivity and unmatched versatility, its a valuable process optimization tool that will deliver faster ROI and a better bottom line.