

MultiTek® Analysis of Sulfur in Diesel Engine Fuel and by Ultraviolet Fluorescence

- Rapid and Accurate Determination of Chemically Bound Sulfur
- Fully Automated Combustion System
- Sample Versatility
- MultiTek® Performance Verification

Keywords:

MultiTek®, Total Sulfur, Light Hydrocarbons, Spark Ignition Engine Fuel, Diesel Engine Fuel, Engine Oil, Ultraviolet Fluorescence, and ASTM D5453

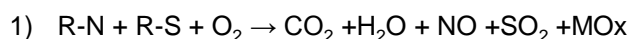


INTRODUCTION

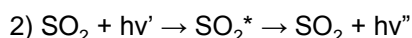
ASTM D5453 is an established test method for the determination of sulfur in liquid hydrocarbons. This test method is applicable to the determination of sulfur in liquid hydrocarbons containing less than 0.35% (m/m) halogen(s) and allows for a fairly rapid method for quantifying sulfur content in diesel (No. 2 Fuel Oil).

Reaction:

The principle operation for nitrogen and sulfur analysis begins with the complete, high temperature oxidation of the entire sample matrix as illustrated in equation (1). The sample is combusted with oxygen at a temperature of 1050°C. Oxidation products include CO₂, H₂O, NO, SO₂ and various other oxides (designated MO_x below). The combustion gases are routed through a membrane drying system to remove all water and then to the sulfur detector module(s) for quantification.



The SO₂ is exposed to ultraviolet light radiation of a specific wavelength as shown in equation (2). This radiation is released, in the form of sulfur fluorescence. The fluorescence is detected by a photomultiplier tube (PMT) and is proportional to the amount of sulfur in the original sample.



Sulfur calibration standards are analyzed to produce a calibration curve using horizontal and vertical configurations and the results are compared. Once the samples of a known concentration of sulfur content are analyzed, the MultiTek Software compares the unknown sample data to the calibration curve to generate and report the sulfur concentration.

Instrument Parameters:

Syringe Size (µl)	25
Sample Fill Volume (µl)	10
GFC1 – Ar/He (ml/min)	130
GFC2 – Pyro O ₂ (ml/min)	450
GFC3 – Ozone O ₂ (ml/min)	35
GFC4 – Carrier O ₂ (ml/min)	25
Furnace (°C)	1050
Cycle Time (mm:ss)	3:40
S-PMT High Voltage (V)	550

A calibration curve was composed using the standards shown in the table below. Each calibration sample was analyzed using five replicates and the regression recorded in order to plot counts vs. sample concentration. The calibration standards utilized vary from those recommended in the method (ASTM D5453), but nevertheless, enable the generation of consistent and accurate data, with the standards listed below.

VNS Calibration Standard Response

Calibration Standard Concentration (ng/μl):	Average Area Counts (n=5):
0	185556
5	2257451
10	4577769
15	6723538
20	9006332
25	11193399
40	17891266
60	27166373
80	36357537
100	45564622

The results shown above, along with the regression plot illustrated below were performed using the vertical sample introduction method

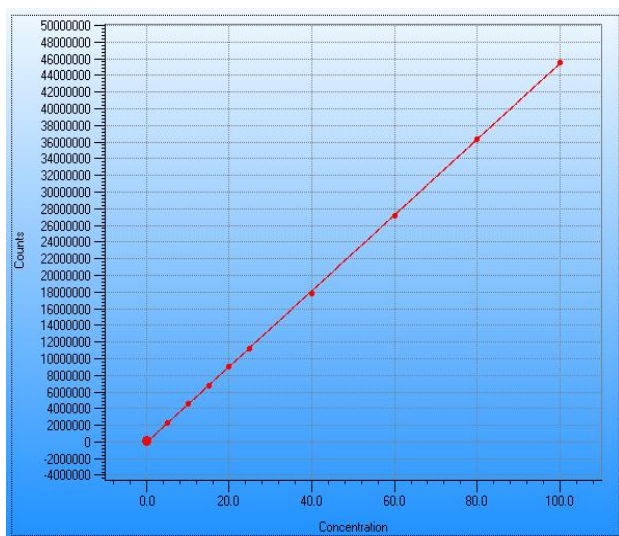


Figure 1: VS Calibration Plot
Correlation = 0.999961

Sample ID:	Sulfur Conc. (ppm):	%RSD (n = 10):	Area Counts (n = 10):
ULSD1005	5.1	3.8	2305415
ULSD1008	5.1	1.7	2291326
ULSD1110	6.4	1.5	3042043
ULSD1111	6.4	3.0	2977580
ULSD1211	6.4	3.3	2966302
ULSD1201	10.3	2.0	4642886
ULSD 1202	10.1	3.8	4574726

Several samples from ASTM Proficiency Test Programs were analyzed and compared statistically, by utilization of two instrument configurations (horizontal boat-inlet and vertical injection). The objective was to analyze a sample set with known concentration ranges, against data generated from a large laboratory test bed. Each sample concentration was then compared to the robust mean and standard deviation of the ASTM PTP.

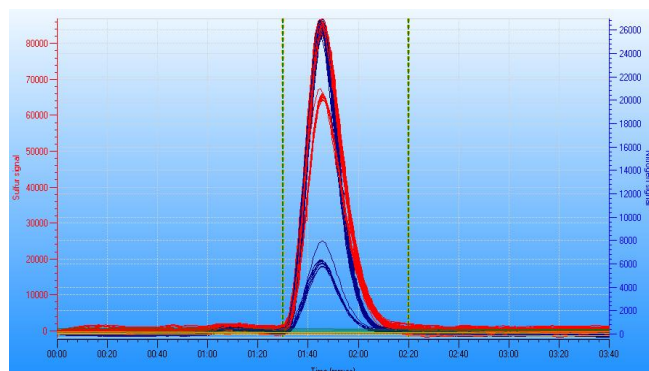


Figure 2: VS Sample Injection Overlays

The image above shows the sample injection overlays for the 7 samples analyzed, performed with 10 replicate injections for each of the samples. The percent RSD can be found in the table value listed above.

The horizontal configuration typically allows for more flexibility for analyzing samples in different phases (gasses, liquids, and solids). For this application, a calibration procedure identical to the procedure used for the vertical injection configuration was performed to establish accuracy and precision of both configurations. The chart shown below provides the standard response per concentration which is followed by the calibration plot.

HNS Calibration Standard Response

Calibration Standard Concentration (ng/μl):	Average Area Counts (n=5):
0	1415781
5.0	5199618
10.0	9994303
15.0	15012945
20.0	19810964
25.0	25095114
40.0	40073926
60.0	60259376
80.0	80547816
100.0	102172019

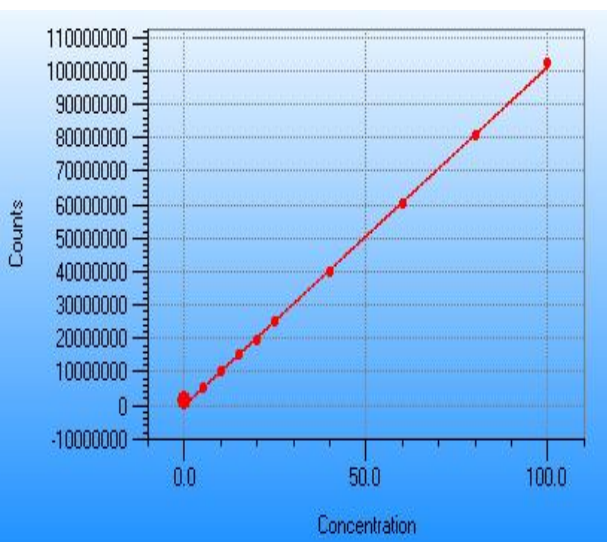


Figure 3: HS Calibration Plot
Correlation = 0.999833

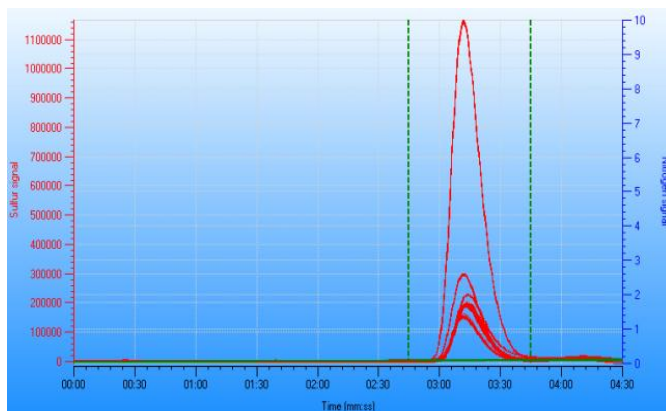


Figure 4: HS Sample Overlays

The chart below shows an accumulation of sample data obtained from the horizontal configuration, percent deviation, and area counts.

Sample ID:	Sulfur Conc. (ppm):	%RSD (n = 10):	Area Counts (n = 10):
ULSD1005	5.1	2.0	4860189
ULSD1008	5.0	2.6	4756979
ULSD1110	6.4	2.0	6253329
ULSD1111	6.3	0.9	6247316
ULSD1211	6.2	1.4	6109635
ULSD1201	9.9	0.4	9616157
ULSD1202	9.9	0.8	9623263

The results obtained from each analyzer were then gathered and evaluated by comparison of the data for each sample, against the robust mean of the ASTM Proficiency Test Program.

Sample ID:	ASTM Robust Mean:	Vertical Configuration n Lab Result:	Horizontal Configuration Lab Result:	ASTM Robust Standard Dev.	Vertical Z-score:	Horizontal Z-score
ULSD1005	4.8	5.1	5.1	0.4	0.8	0.8
ULSD1008	4.7	5.1	5.0	0.4	1.0	0.8
ULSD1110	6.1	6.6	6.3	0.4	1.3	0.5
ULSD1111	6.1	6.4	6.3	0.4	0.8	0.5
ULSD1112	6.1	6.4	6.2	0.5	0.6	0.2
ULSD1201	10.0	10.3	9.9	0.6	0.5	-0.2
ULSD1202	9.9	10.1	9.9	0.6	0.3	0.0

Correlation of Test Data:

Overall, the sample matrix shows excellent stability through replicate injections and the accuracy, based on the ASTM data pool is very accurate. The sample concentrations trend slightly less than those obtained with the vertical/direct sample introduction. This may possibly be attributed to sample loss from the horizontal introduction method.

Statistics

The z-score column reports each lab's deviation in units of standard deviations. The z-score is the ratio of the deviation to the standard deviation. A z-score greater than 2.0, or less than negative 2.0 should cause a laboratory to review their test data for a possible systemic error. Z-scores outside the range of ± 2.0 should occur only about one instance in twenty, if a laboratory has the average capability of completing the test method. Laboratories should strive to obtain z-score values close to zero. The duplicate laboratory results, obtained from the designated ASTM ULSD programs, were averaged and subtracted from the robust mean for the respective cycle of testing. The value obtained is then divided by the robust standard deviation to yield the z-score as demonstrated below:

$$(\text{Lab Res.} - \text{Mean}_{(\text{ASTM Robust})}) \div \text{Standard Dev.}_{(\text{ASTM Robust})} = \text{Z-score}_{(\text{Lab})}$$

$$\text{ASTM ULSD1202 z-score}_{(\text{Horizontal})} = (9.9 - 9.9) \div 0.6 = 0.0$$

CONCLUSION

The analysis of diesel fuel can be analyzed at low levels using a horizontal or vertical sulfur configuration. The variation of data is statistically insignificant with a diesel sample matrix.

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.