

TAKING ASTM D5453 ON-LINE DETERMINATION OF TOTAL SULFUR IN GASOLINE AND DIESEL

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ABSTRACT

ASTM method D5453 "Determination of Total Sulfur in Light Hydrocarbons, Motor Fuels and Oils by Ultraviolet Fluorescence" is a popular analytical method for determination of total sulfur in diesel and gasoline. ASTM methods undergo a rigorous series of inter-laboratory tests prior to publication. The analytical equipment used in such tests is laboratory equipment. Unfortunately some of the key analytical equipment and methodology specified in ASTM D5453 cannot or should not be used in the on-line environment. Given that it is not possible to exactly duplicate ASTM D5453 in the on-line environment one must precisely validate the analytical performance of on-line analytical instrumentation used for correlation. One must also consider that on-line analyzers must be designed for reliable unattended operation. It is essential that on-line analyzers be equipped with preventive maintenance tools such that reliable analytical results can be realized 24 hours/day, 7 days/week. This paper will discuss the methods used to validate an on-line version of ASTM D5453 and the preventive maintenance tools developed to ensure reliable operation.

INTRODUCTION

Measurement of total sulfur by ASTM D5453 requires that the sample (eg., gasoline or diesel) be fully combusted to CO₂, H₂O and SO₂. The concentration of SO₂ in the combusted sample is directly proportional to the total sulfur content of the gasoline or diesel. Measurement of the SO₂ concentration is accomplished by ultraviolet fluorescence (UVF). UVF involves irradiating the combusted sample with a specific wavelength, $h\nu_1$, of ultraviolet light. The SO₂ molecules, present in the combusted sample, temporarily absorb some of the UV light and achieve an excited state, SO₂*. The excited state molecules, SO₂*, quickly relax to their ground state and, in the process, emit light of slightly different wavelength, $h\nu_2$. The intensity of the emitted light is directly proportional to the SO₂ concentration. The intensity of the emitted light is measured with a photomultiplier tube (PMT).

Figure 1 is a simplified block diagram of an on-line analyzer that utilizes the measurement principles described in ASTM D5453-00.¹ The on-line analyzer does not comply with ASTM D5453 in the following ways:

- 1) ASTM D5453, being a laboratory technique, introduces sample to the combustion furnace by syringe or boat injection. In the on-line environment sample must be introduced via an automated liquid sample valve (LSV). The LSV must be operated and installed correctly to ensure a full accounting of all sulfur compounds.
- 2) ASTM D5453 also suggests that one use 100% oxygen as the oxidant in the combustion furnace. Given that most on-line instrumentation are installed in hazardous areas a safer approach is to use air as the oxidant instead of 100 % oxygen. In fact, the use of air provides a distinct advantage. In order to supply the same moles of oxygen, the air flow rate will necessarily be greater than the flow rate of oxygen, thus, sample dilution will be greater with air than with oxygen. The additional sample dilution can eliminate the need for drying systems at the outlet of the combustion furnace. The use of air does present one potential disadvantage. When using air the volumetric concentration of SO₂ at the UVF spectrometer is much lower than with oxygen as the oxidant. The additional sensitivity that is needed to accommodate an air oxidant is achieved, in part, through the use of a pulsed ultraviolet fluorescence spectrometer (PUVF).

These departures from ASTM D5453 require that the on-line method be fully validated to ensure a full accounting for sulfur compounds found in diesel, gasoline and their associated blend stocks.

Analytical techniques that involve sample combustion present a unique challenge to on-line analyzers. One must consider the consequences of combustion system failure. In the laboratory environment an instrument performing ASTM D5453 is frequently monitored by laboratory personnel, thus, combustion system failure can likely be detected early. In the on-line environment combustion system failure may not be detected until the failure has resulted in complete contamination of the analytical system with coke, soot and other products of incomplete combustion. If combustion system failure is allowed to reach this level then the time to repair the on-line instrument will reach an unacceptable level. A system for early detection of combustion system failure is needed for on-line versions of ASTM D5453.

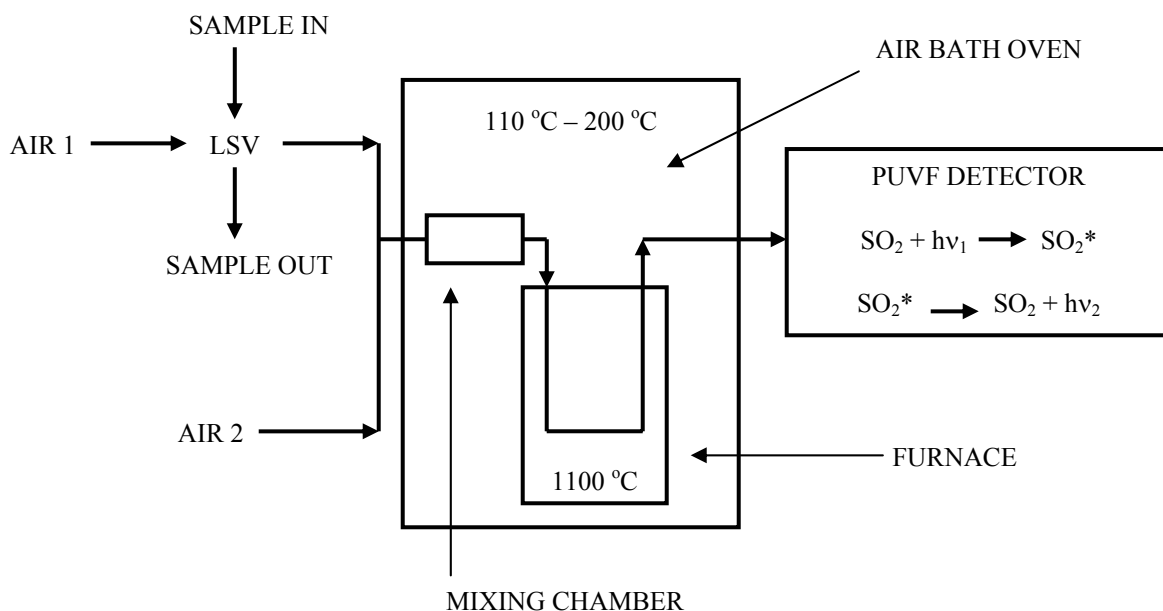


FIGURE 1 – ON-LINE ANALYZER FOR DETERMINATION OF TOTAL SULFUR IN GASOLINE AND DIESEL

VALIDATION OF TOTAL SULFUR IN GASOLINE DETERMINATIONS

As discussed, the use of a LSV and air as the oxidant has not been validated under ASTM D5453. In order to ensure the on-line method's analytical validity, gasoline range sulfur compounds must be accounted for. Gasoline is prepared from a wide variety of blend stocks. The most common blend stocks are isomerate, alkylate, reformat and fluid catalytic cracked (FCC), gasoline. In most cases it is the FCC gasoline that is the single largest contributor of sulfur to the gasoline pool.² Therefore, if one is interested to identify the types of sulfur compounds present in gasoline the FCC gasoline would be a good place to look.

FCC gasoline often contains a high concentration of thiophene, alkyl substituted thiophenes, benzothiophenes and alkyl substituted benzothiophenes. Many of these compounds have boiling points that are very near the end boiling point of gasoline (240 - 250 °C). In addition to several high boiling alkyl substituted benzothiophenes, untreated FCC gasoline may contain high boiling mercaptans (C₆ - C₁₀).^{3,4} Linear, high boiling mercaptans, where the mercaptan functional group (-SH), is relatively free to interact with metallic and other active surfaces, can be particularly difficult to transfer from the LSV to the combustion furnace.

Work by Golden and Fulton demonstrated that the highest sulfur concentration in FCC gasoline is present in fractions boiling at ≥ 220 °C.² These findings have a significant impact on sample introduction techniques. When performing total sulfur analyses one must consider that the majority of the analyte (sulfur) exists in the highest boiling fraction. This observation implies that the on-line total sulfur analyzer must be equipped with the means to totally vaporize all of the sample. As shown in Figure 1 the on-line analyzer is equipped with an adjustable set point air bath oven. The air bath oven allows manipulation of the LSV's temperature to ensure complete transfer of gasoline range sulfur

compounds to the combustion furnace. When working with gasoline samples one must ensure that sufficient sample backpressure is applied to maintain all gasoline components in the liquid phase.

The data in table 1 was obtained from an on-line analyzer previously calibrated with a thiophene in iso-octane standard. Several standards were gravimetrically prepared using various sulfur compounds. Based on the gravimetric data the total sulfur content of each of these standards was calculated (see column labeled ppm S (w/w) calculated). Each of these gravimetrically prepared standards were then introduced to the on-line analyzer as an unknown and the result was recorded in the column labeled (ppm S (w/w) reported). There is good agreement between calculated and reported values for all samples. The results for samples prepared in benzene and toluene indicate no interference from aromatic matrices. It is striking to note the effect of air bath oven temperature (and consequently LSV temperature) on the analytical results for the sample containing 1-dodecanethiol, a C₁₂ mercaptan. The boiling point of 1-dodecanethiol, 266-283 °C, is slightly higher than the end point of most gasolines, 240-250 °C, therefore, it is not expected exist in significant concentrations in gasoline. However, since gasoline can contain many sulfur compounds and it is not practical to test the on-line analyzer for response to each compound then one attempts to select “bad actor” compounds for method validation. From an analytical point of view, 1-dodecanethiol can definitely be thought of as a “bad actor”. It is very high boiling and because it is a mercaptan it is prone to adsorption to tubing and other surfaces in the analyzer. Note the dramatic impact of LSV temperature on the analyses of a sample containing 96% 1-dodecanethiol as the only source of sulfur. Even with the use of inert tubing an oven temperature of 190 °C is needed to fully account for the total sulfur in samples containing 1-dodecanethiol.

TABLE 1 – CALCULATED VS. REPORTED VALUES FOR GASOLINE RANGE SULFUR COMPOUNDS

SOLVENT	SULFUR SOURCE	SULFUR COMPOUND BOILING POINT (°C)	OVEN TEMP (°C)	PPM S (W/W) CALCULATED	PPM S (W/W) REPORTED
ISO-OCTANE	TETRAHYDROTHIOPHENE	119	115	19.21	19.21
ISO-OCTANE	BENZOTHIOPHENE	221-222	115	20.28	20.70
ISO-OCTANE	METHYL DISULFIDE	109	115	33.24	32.26
ISO-OCTANE	1,2-PROPANEDITHIOL	152	115	15.58	15.62
ISO-OCTANE	1-HEPTANETHIOL	177	115	10.29	10.29
TOLUENE	BENZOTHIOPHENE	221-222	115	11.06	11.61
BENZENE	1-HEPTANETHIOL	177	115	12.92	12.53
TOLUENE	1-HEPTANETHIOL	177	115	10.14	10.19
ISO-OCTANE	1-DODECANETHIOL	266-283	115	61.85	<<10.00
ISO-OCTANE	1-DODECANETHIOL	266-283	190	61.85	61.00

The on-line determination of total sulfur in gasoline was further validated through comparison with an ASTM D5453 laboratory instrument. Table 2 lists the results obtained with the on-line analyzer and the ASTM laboratory instrument for five gasoline samples with varying sulfur concentrations. Note the results for gasoline 5, 141.0 vs. 143.4 ppm S (w/w). Gasoline 5 was originally run at an oven temperature of 120 °C. At 120 °C the mean reported value for gasoline 5 was 129.8 ppm S (w/w). Additionally, at 120 °C, the data for gasoline 5 was not evenly distributed about the mean, the data was gradually drifting upward. These observations indicate that at 120 °C the transfer of sulfur compounds from the LSV to the furnace was incomplete. When gasoline 5 was run at an oven temperature of 190

°C an even distribution of data about the mean and good agreement with the ASTM D5453 laboratory method, 141.0 vs. 143.4 ppm S (w/w), was observed.

TABLE 2 – ASTM D5453 LABORATORY INSTRUMENT VS. ON-LINE ANALYZER

SAMPLE	ASTM D5453 LABORATORY INST. PPM S (W/W)	ON-LINE ANALYZER PPM S (W/W)
GASOLINE 1	18.4	17.8
GASOLINE 2	4.8	4.0
GASOLINE 3	13.4	13.8
GASOLINE 4	12.3	12.6
GASOLINE 5	141.0	143.4

Long term measurement precision of the on-line analyzer was evaluated by running gasoline 2 for a period of 14 hours. The results of this 14 hour run are presented in Table 3.

TABLE 3 – SUMMARY STATISTICS 14 HOUR RUN OF GASOLINE 2

STATISTIC	PPM S (W/W)
MEAN	4.01
MEDIAN	4.01
MODE	4.02
STANDARD DEVIATION	0.12
MAXIMUM	4.38
MINIMUM	3.60

VALIDATION OF TOTAL SULFUR IN DIESEL DETERMINATIONS

Examination the types and kinds of sulfur compounds present in diesel fuel reveals that diesel fuel contains many of the same substituted thiophenes and benzothiophenes found in FCC gasoline. In addition to these compounds, diesel fuel will contain very high boiling organic sulfur compounds, such as, 4,6-dimethyldibenzothiophene and other alkyl substituted dibenzothiophenes. There is good agreement in the literature that dibenzothiophenes with alkyl substitutions at the 4 and/or 6 positions are the most difficult sulfur compounds to remove by traditional hydrotreating.^{5,6} Generally mercaptans are removed quite easily by hydrotreating. The mercaptan functional group, SH, can readily orient itself in close proximity to hydrotreating catalyst, therefore, mercaptans are removed readily by hydrotreating. Indeed, the very characteristics that make the mercaptans difficult to handle in analytical instruments are responsible for their high reactivity in hydrotreating processes. On the other hand compounds such as 4,6-dimethyldibenzothiophene have a molecular structure that sterically hinders the sulfur from reaching the catalytic site (in the hydrotreater). Additionally, there is good agreement that hydrotreating of compounds, such as, 4-6-dimethyldibenzothiophene follow a uniquely different reaction pathway than compounds such as mercaptans.⁷ Because of their difficulty in removal by hydrotreating, dibenzothiophenes with alkyl substitutions at the 4 and/or 6 positions are referred to as “refractory sulfur”. The analytical implication is that low sulfur diesel can contain large concentrations of “refractory sulfur compounds”, therefore, the on-line analyzer must be shown to account fully for compounds such as 4,6-dimethyldibenzothiophene.

The data listed in Table 4 was obtained from various sulfur compounds dissolved in blank # 2 diesel fuel (certified to contain ≤ 1 ppm S (w/w)). As with the gasoline tests the on-line analyzer was previously calibrated with a thiophene in # 2 diesel standard. Each of the gravimetrically prepared samples were then run as unknown samples on the on-line analyzer. The expected result (based on gravimetric data) is listed in the column labeled “ppm S (w/w) calculated”. The result reported by the on-line analyzer is listed in the column labeled “ppm S (w/w) reported”. The results indicate that the on-line analyzer accurately accounts for the sulfur compounds found in hydrotreated diesel fuel.

TABLE 4 – CALCULATED VS. REPORTED VALUES FOR DIESEL RANGE SULFUR COMPOUNDS

SULFUR SOURCE	BOILING POINT (°C)	PPM S (W/W) CALCULATED	PPM S (W/W) REPORTED
t-BUTYLSULFIDE	151	21.12	21.46
n-BUTYLSULFIDE	185	50.00	48.83
BENZOTHIOPHENE	221	10.85	10.71
1-DODECANETHIOL	266-283	32.38	31.72
PHENYL SULFIDE	296	32.99	33.88
DIBENZOTHIOPHENE	333	24.08	23.40
4,6-DIMETHYLDIBENZOTHIOPHENE	>333	13.98	12.86

Further validation of the total sulfur in diesel analysis was accomplished by comparison of the on-line analyzer’s results with the results of a laboratory lead acetate colorimeter for two samples of heavy diesel fuel (end boiling point ≥ 400 °C). The results of this study are listed in Table 5.

TABLE 5 – LEAD ACETATE COLORIMETER VS. ON-LINE ANALYZER

SAMPLE	LEAD ACETATE COLORIMETER PPM S (W/W)	ON-LINE ANALYZER PPM S (W/W)
DIESEL 1	21.08	21.28
DIESEL 2	61.78	64.74

Long term measurement precision of the on-line analyzer was evaluated by running diesel 1 for a period of 16 hours and diesel 2 for a period of 52 hours. The results of these studies are presented in Table 6.

TABLE 6 – DIESEL LONG TERM MEASUREMENT PRECISION

STATISTIC	DIESEL 1 16 HOUR RUN PPM S (W/W)	DIESEL 2 52 HOUR RUN PPM S (W/W)
MEAN	21.28	64.74
MEDIAN	21.28	64.74
MODE	21.27	64.74
STANDARD DEVIATION	0.10	0.22
MAXIMUM	21.62	65.58
MINIMUM	20.97	64.02

LINEARITY OF TOTAL SULFUR DETERMINATIONS

Linearity of total sulfur determinations was determined by collecting the mean (for a 10 minute run) raw detector counts for each of the samples listed in Table 7.

TABLE 7 – SAMPLES USED FOR DETERMINATION OF LINEARITY

SULFUR SOURCE	SOLVENT	CALCULATED SULFUR CONC. PPM S (W/W)	MEAN RAW DETECTOR COUNTS (LESS ZERO OFFSET)
DODECYLSULFIDE	# 2 DIESEL	1.70	0.005
2-METHYLBENZOTHIOPHENE	# 2 DIESEL	3.32	0.011
DIBENZOTHIOPHENE	# 2 DIESEL	4.90	0.020
n-BUTYLSULFIDE	# 2 DIESEL	15.00	0.065
n-BUTYLSULFIDE	# 2 DIESEL	25.00	0.104
SULFOLANE	p-XYLENE	36.24	0.150
DIBENZOTHIOPHENE	# 2 DIESEL	39.20	0.162
DIBENZOTHIOPHENE	# 2 DIESEL	49.00	0.218
2-METHYLBENZOTHIOPHENE	# 2 DIESEL	275.8	1.081
DIBENZOTHIOPHENE	# 2 DIESEL	392.0	1.575
THIOPHENE	# 2 DIESEL	2815	10.848

A plot of the data listed Table 7 is provided in Figure 2. The correlation coefficient of 0.9999 indicates excellent linearity from 1.70 - 2815 ppm S (w/w).

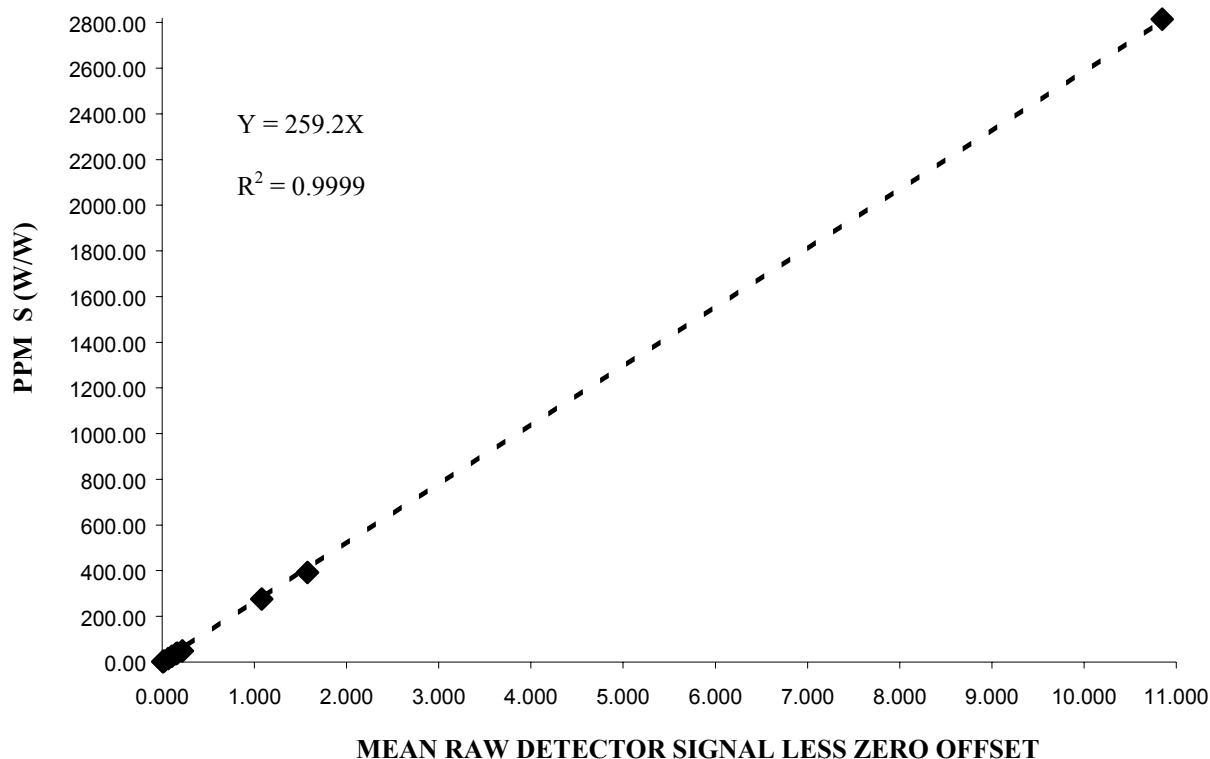
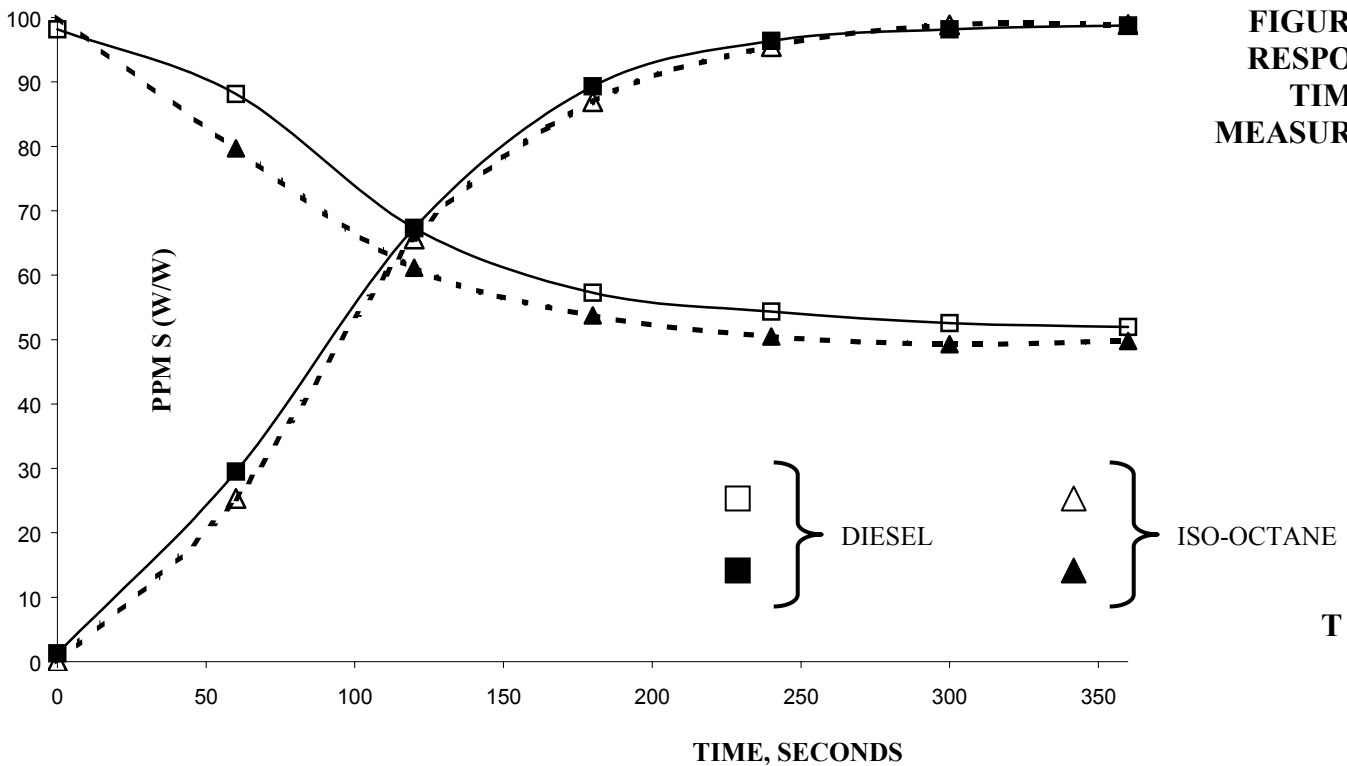


FIGURE 2 – LINEARITY OF TOTAL SULFUR DETERMINATIONS

RESPONSE TIME OF TOTAL SULFUR DETERMINATIONS

Response time, for total sulfur in gasoline measurements, was measured by switching samples of dissimilar sulfur concentrations at the sample inlet to the on-line analyzer. The first response time test was conducted with blank iso-octane 0.0 ppm S (w/w) and 99.6 ppm S (w/w), thiophene in iso-octane. The second response time test was conducted with a sample of 99.6 ppm S (w/w) and 49.8 ppm S (w/w), both samples contained thiophene as the sulfur source and iso-octane as the solvent. In each case 90% of the new value was acquired in approximately 200 seconds. The test results are summarized in Figure 3.

Response time, for total sulfur in diesel measurements, was measured by switching samples of dissimilar sulfur concentrations at the sample inlet to the on-line analyzer. The first response time test was conducted with blank # 2 diesel and 99.6 ppm S (w/w), thiophene in # 2 diesel. The second response time test was conducted with a sample of 99.6 ppm S (w/w) and 49.8 ppm S (w/w), both samples contained thiophene as the sulfur source and # 2 diesel as the solvent. In each case 90% of the new value was acquired in approximately 270 seconds. The test results are summarized in Figure 3.



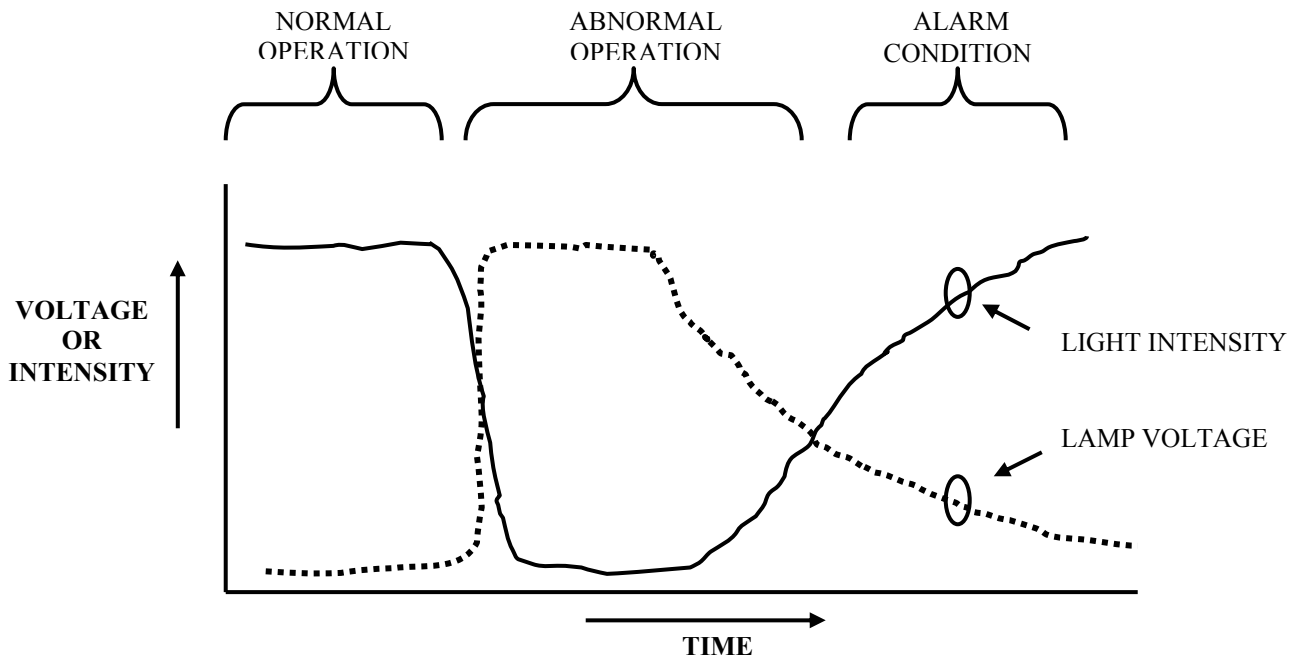
**FIGURE 3 -
RESPONSE
TIME
MEASUREMENTS**

PREVENTIVE MAINTENANCE TOOLS

Many analytical techniques targeted at determination of total sulfur in fuels require complete combustion of the sample. Following combustion the resulting SO₂ can be detected using any one of several detectors, including: PUVF, electrochemical or flame photometric. Alternatively, hydrogen reduction then chemiluminescence or colorimetric detectors may follow the oxidative combustion process. Should the combustion system fail with any of these analytical techniques then the analyzer will likely be severely contaminated with carbon, soot and other products of incomplete combustion. Combustion system failure with an on-line analyzer may result in severe contamination because the condition may be undetected for several hours. Several hours to days of analyzer down time may be required to render the analyzer operational following contamination by carbon and soot.

Should sample be introduced to a combustion system where there the temperature is insufficient to support combustion then soot and carbon formation can be expected. This condition is easily prevented through interlocks that interrupt sample injection in the event of insufficient combustion system temperature. The on-line analyzer described herein will not allow sample injection until the oven and furnace are within +/- 5 °C of their respective set points.

Products of incomplete combustion will also be formed should the oxygen concentration be insufficient to support complete combustion. Additionally, conditions such as a leaking sample valve may introduce excessive sample thereby exceeding the combustion capacity of the furnace. If either of these conditions can be detected prior to the formation of coke and soot then one can dramatically reduce analyzer downtime. The on-line analyzer's PUVF spectrometer is equipped with a feedback circuit that automatically adjusts lamp voltage to maintain a constant UV light intensity. The heart of this feedback circuit is a photo detector that senses UV light intensity. Products of incomplete combustion include olefins, aromatics and un-combusted fuel, all will absorb or attenuate UV light.^{8,9,10} The presence of these organic compounds in the PUVF cell severely attenuate the UV light reaching the photo detector. The attenuation of UV light to the photo detector causes the feedback circuit to apply additional lamp voltage at a rapid rate. The rate of lamp voltage adjustment is monitored and should this rate exceed a preset limit an alarm is activated to indicate combustion system failure. Upon activation of the "combustion system failure alarm" sample flow to the LSV is automatically replaced with air to arrest further contamination of the analytical system. This "combustion system failure alarm" has been found to detect combustion system failure prior to the formation of visible carbon and soot thus dramatically reducing analyzer downtime. Figure 4 is a graphical depiction of the combustion system alarm. Note that the "combustion system failure alarm" is a latching alarm, this is done to encourage the operator to correct the condition that caused the alarm.



- NORMAL OPERATION:** LAMP VOLTAGE ADJUSTMENTS OCCUR AT A SLOW RATE TO MAINTAIN CONSTANT LAMP INTENSITY.
- ABNORMAL OPERATION:** PRODUCTS OF INCOMPLETE COMBUSTION ATTENUATE UV LIGHT TO PHOTODIODE. A RAPID INCREASE IN THE RATE OF LAMP VOLTAGE ADJUSTMENT IS OBSERVED.
- ALARM CONDITION:** LATCHING "COMBUSTION SYSTEM FAILURE ALARM" IS ACTIVATED. SAMPLE FLOW TO THE LSV IS REPLACED WITH AIR AND PRODUCTS OF INCOMPLETE COMBUSTION ARE FLUSHED FROM PUVF CELL.

FIGURE 4 – GRAPHICAL DESCRIPTION OF COMBUSTION SYSTEM FAILURE ALARM

CONCLUSION

An on-line analyzer for determination of total sulfur in fuels by pulsed ultraviolet fluorescence was shown to provide excellent correlation to ASTM D5453-00 laboratory instrumentation. The on-line analyzer was shown to account fully for the organic sulfur compounds expected to be found in hydrotreated diesel and gasoline. Measurement precision, linearity and response time was also demonstrated for the on-line method. A unique system for detection of combustion system failure was described. The system is capable of detecting combustion system failure prior to the formation of visible carbon or soot thereby preventing excessive analyzer downtime.

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