

# **PERFORMANCE OF ENVIRONMENTAL MONITOR FOR TOTAL SULFUR AND HIGH HEATING VALUE OF REFINERY FLARE VENT GAS SYSTEMS**

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## **KEYWORDS**

UV fluorescence, Mass Spectrometry, Flare Emission Monitoring, High Heating Value, Total Sulfur Analysis

## **ABSTRACT**

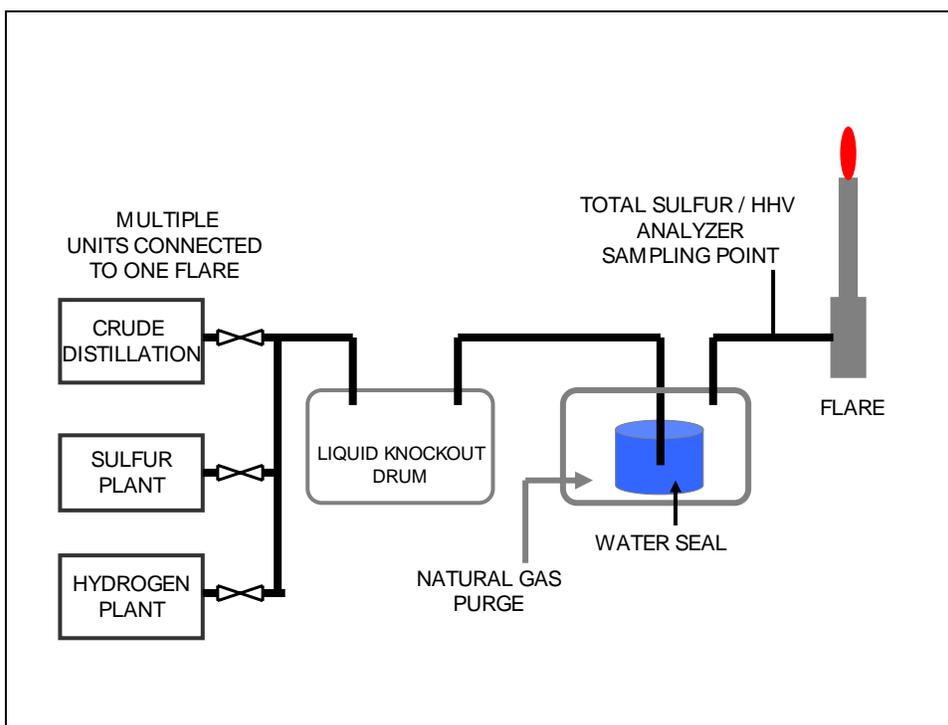
New environmental air regulations in California have required oil refineries to develop analytical systems to analyze the composition of flare vent gas streams for total sulfur and High Heating Value (HHV). Since a refinery can have multiple chemical processing units that are connected to a flare; the composition of its hydrocarbon stream can vary widely, depending on the units discharging to the flare. The sulfur concentration of the flare vent gas can vary from 1 – 150000 PPM and BTU values from 0 to 3000 BTU/FT<sup>3</sup>. This paper will discuss the method to extract and sample the process stream with minimal loss or adsorption of the analyte and provide the analytical figures of merit for the on-line total sulfur and HHV analysis. This data is representative of the first year of operation including SCAQMD certification data and daily performance data for five flare analytical systems.

## **INTRODUCTION**

The California Environmental Protection Agency regulation rule 1118 mandated by South Coast Air Quality Management District (SCAQMD) requires the monitoring of high heat value, total sulfur, and standard volumetric flow of vent gas directed to a refinery flare.

Refinery flares are designed to safely combust the vent gas. The combustion process generates air pollutants that affect the air quality which include oxides of nitrogen and sulfur. Total sulfur and high heating value analysis with the flow rate of the vent gas quantitatively measures the pollutants emitted into the air [1]. The performance and sampling requirement of the high heating value and total sulfur analysis are reported in this paper. The measurement of the volumetric flow is not discussed in this report.

Flare vent gases are produced in many different refining processes, such as, distillation, cracking, reforming, hydro treating, alkylation and hydrogen production as shown in **Figure 1**.



**FIGURE 1. TYPICAL REFINERY FLARE SYSTEM**

The different refinery processes produce vent gases with a high variability in composition. Vent gas can range from pure hydrogen to steam to a hydrocarbon fuel gas, with these gases containing multiple types of sulfur compounds. The varying composition creates analytical measurement problems do to density variation of the sample. To compensate for this variability the sample must be measured in a fixed volume or normalized by measuring the total composition.

The vent gas is only directed to the flare for combustion during emergency conditions to safely remove hot pressurized gases from a processing unit. These gases from the processing unit are directed to the flare through a low pressure path. The gases reaching the flare are at their dew point, and less than 10 psi, too low for typical sample conditioning system. To analyze a low

pressure sample a pump is require to pressurize the sample. The temperature of the sample must be controlled above the dew point at the higher pressure.

In this report Total Sulfur (TS) analysis of the flare gas was measured by UV fluorescence. This method has provided a fast and accurate sulfur measurement free from the sample matrix effects [2]. The UV fluorescence method combusts the sample in air to oxidize sulfur compounds to produce sulfur dioxide which is measured quantitatively [3]. Since the hydrocarbon sample is combusted to form carbon dioxide, water and sulfur dioxide, the measurement is independent of sample temperature and water. The sample is volumetrically injected into the sulfur analyzer to remove the effects of sample density. The vent gas can have a range of sulfur concentrations from parts per billion to percent levels. To measure sulfur over this wide range, the sample system must be designed minimize the adsorption of sulfur compounds that can bias results due to the loss of reactive sulfur compounds or contamination from sulfur carry over. The flare events require the analyzer system to rapidly monitor the changes in concentration. Response times needed to track the sulfur concentrations during a flare event require special coatings of the sample tubing and sample system devices to reduce sulfur adsorption.

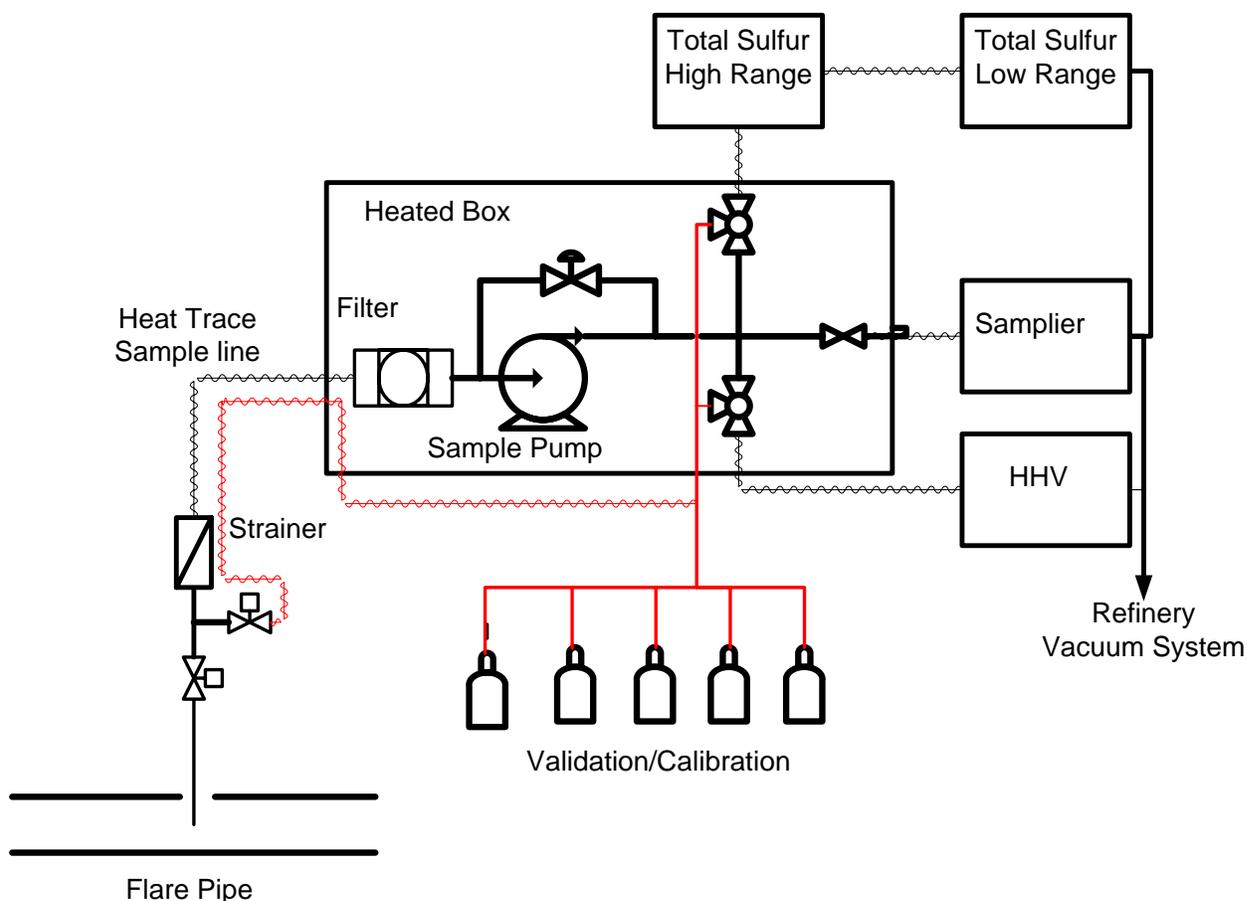
A High Heating Value (HHV) analysis of the vent gas is determined by analyzing the composition concentrations and by summing product of the mole fraction and there respective BTU values [4] to provide a composite BTU value for the stream. The chemical composition of the vent gas is determined by using mass spectrometry [5,6]

The regulatory quality control (QC) requirements are daily calibration validation, system linearity, sample system bias and zero drift. The total sulfur and HHV daily validation measurement error must be less than 5% and 2.5% of full scale respectively. The TS and HHV system linearity errors must be less than 10% and 5% of each standard respectively. The sample system bias must be less than 5% for both systems. Zero drift measurement must be less than 2% for both systems. This paper will discuss the QC performance measure for five flare analyzer installations.

## Experimental

The flare analyzer pilot installation has been described in a previously submitted paper [7]. Five flare analyzer systems are evaluated. The flares are grouped into two ranges of total sulfur 0 - 1% (three flares - Group II) and 0 - 15% (two flares - Group I). The systems for both flares are identical except the sulfur analyzers range has different ranges. **Figure 2** shows a schematic of HHV and TS analyzer systems.

The vent gas is sampled in the middle 50% of the flare line with a Sulfinert® coated [8] angle cut probe [9]. The sample line connecting to the sample probe is split to allow the addition of a validation gas. After passing through a filter the sample line is connected to a heat traced tube bundle which contains both the sample and calibration lines. These samples lines are Sulfinert® coated and are routed to a heated sample pump box. The temperature of the tubing and pump box is maintained at 285 F. The temperature was selected to stay above the dew point of water at 50 psi.



**FIGURE 2. FLARE ANALYZER SYSTEM SCHEMATIC.**

The sample entering the pump box is filtered (5 um) and pressurized to 30 psi with a diaphragm pump. The pressurized sample is directed to both the high range TS analyzer, the HHV analyzer, and the gas sampler with heat trace sample lines. The sample lines and instrumentation used upstream of the TS and sampler are Sulfinert coated. The outlet of the analyzers and the sampler is discharged to the refinery vacuum system. The distance from the sample probe to the analyzer varies from 50 to 150 feet. The sample flows are 500 cc/min for TS, 500 cc/min for HHV and 1000 cc/min for the sampler. All flows are based on methane gas. The lag time to transport the sample from the probe to the analyzer varies for 22 to 65 seconds.

The large dynamic range of the sulfur measurement from low ppm to percent levels requires the use of a dual analyzers. The dual range system consists of two Thermo-Fisher Sola II sulfur analyzers. The sample is directed to the high range analyzer first. If the sulfur concentration is below the lower limit of the high range analyzer, the sample is also directed to low range analyzer for analysis. If the sulfur concentration measured at the high range analyzer is above the low range analyzer full scale the low range analyzer is switched to measure nitrogen as the sample. This minimized the sulfur contamination of the low range instrument with high concentrations of sulfur compounds. The flares were grouped into two sulfur ranges. Group 1 flares have a sulfur concentration of 0 to 150000 ppm sulfur. Group I TS analyzer's high range

analyzer was calibrated to 2000 - 150000 ppm S and the low range analyzer was calibrated 0 - 2500 ppm Sulfur. Group II flares the TS analyzers has a the high range analyzer is calibrated to 100 - 10000 ppm S and the low range analyzer was calibrated 0 - 200 ppm Sulfur. Each sulfur analyzer operates over the range from full scale to 1% full scale which is within the performance of each total sulfur analyzer. An overlap of the concentrations used to minimize measurement gaps when the reported sulfur measurement switches between instruments.

The daily validation requirement of the TS analyzers is the measurement of a zero gas (0-20% full scale) and a span gas (80-100% full scale). The sulfur compound used for the daily validation is Carbonyl Sulfide. The high oxidation potential of Carbonyl Sulfide compared to sulfur compounds typically found in vent gas provides confidence that all of the sulfur compounds will be oxidized to sulfur dioxide and detected by the TS analyzer. The group I TS analyzer daily validation is performed for 300, 2200 and 130000 ppm Carbonyl Sulfide in methane. The group II TS analyzer daily validation is performed for 30, 160 and 8700 ppm Carbonyl Sulfide in methane. The balance gas methane was selected as a leak detection gas, since there are no area Carbonyl Sulfide specific detectors available.

The HHV measurement is based on the chemical composition of the vent gas and the sum of the high heating values of each component concentration. The HHV value calculation is based on ASTM D3588-98, the chemical composition of the vent gas is determined with a non-scanning mass spectrometer. The mass spectrometer used is an Applied Instrument Technologies INC. MGA 1200EC. The instrument is setup to measure the composition defined in **Table I**. The composition was determined by measuring the flare vent gas over three years prior to the instrument installation.

**TABLE I. THE FLARE VENT GAS CHEMICAL COMPONENT AND CONCENTRATION RANGE.**

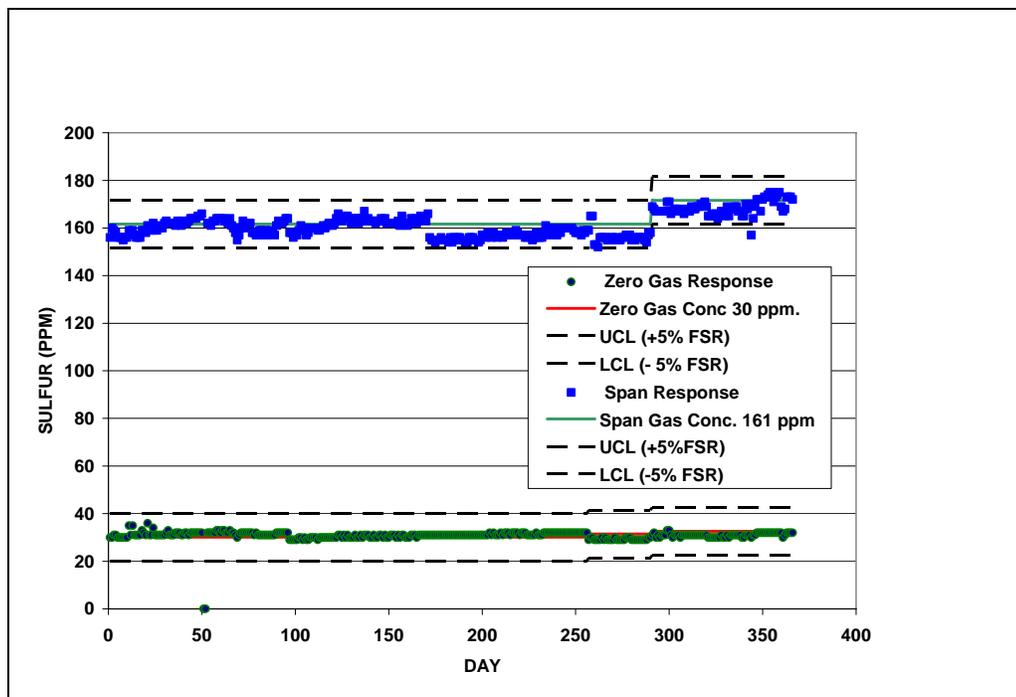
Compound	Minimum Volume %	Maximum Volume %	Median Volume %
Hydrogen	0	98	32
Methane	0	97	20
Ethane	0	26	3.5
Ethylene	0	25	0.3
Propane	0	45	2.0
Propylene	0	95	1.0
C4's (Butane/Isobutane)	0	75	0.7
C5+	0	13	0.2
Nitrogen	0	98	5.0
Oxygen	0	22	0
Carbon Monoxide	0	10	0
Carbon Dioxide	0	40	0.2
Water	0	100	6.0

Based on this composition the maximum HHV value measured was 2500 BTU. The Analyzer was ranged to 3000 Btu. The chemical composition of the vent gas is measured by simultaneously measuring the ion signal on 15 Faraday plate detectors and calculated by solving a set of simultaneous equations as defined in ASTM D2650-10. The ASTM method defines the selection of mass used in the calculation.

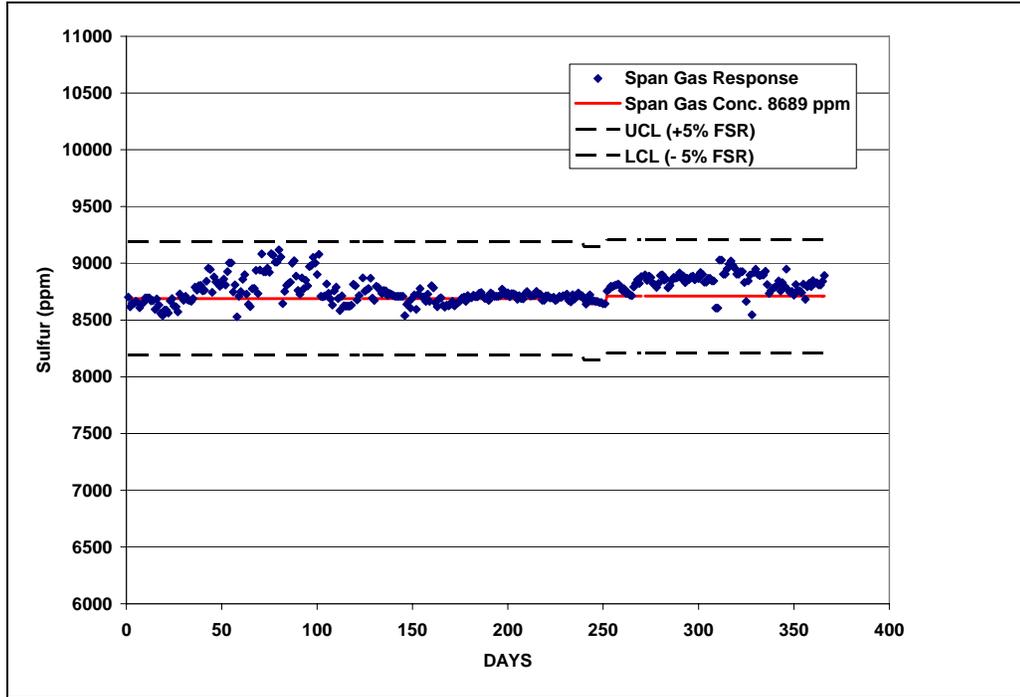
The daily validation requirement of the HHV analyzer is the measurement of a zero gas (0-20% full scale) and a span gas (80-100% full scale). The zero gas used for the daily validation is hydrogen which has a HHV value of 324 BTU. The span gas used for validation is propane with a HHV of 2516 BTU.

## Results and Discussion

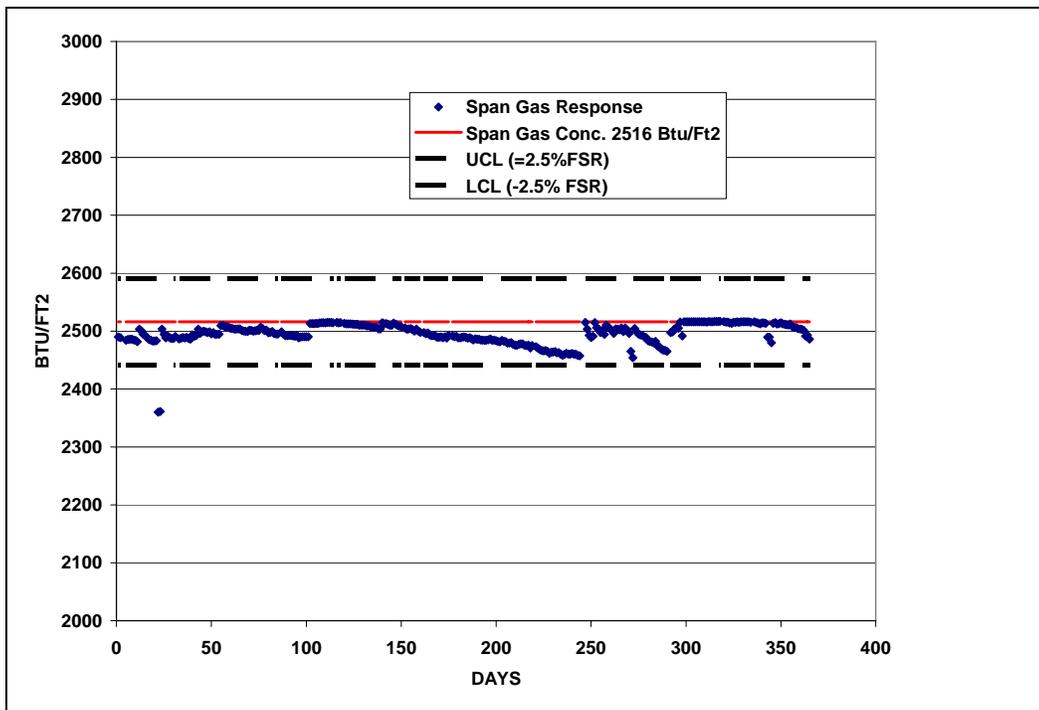
The performance of the flare measurement systems is measured by the daily calibration error, calibration drift, linearity error, and the system bias. The calculations for these performance measurements are defined by the California Environmental Protection Agency [10]. The daily calibration error is defined as the absolute value of the difference between the calibration gas concentration and the actual response divided by the full range response (FSR) shown as a percent. Two standards are used to measure the calibration error; a zero gas (0-20% FSR) and span gas (90-100% FSR) on both sulfur analyzers. **Figures 3 - 5** also show that the calibration error measurement for a group II flare system for the high range sulfur analyzer, low range sulfur analyzer and the high heating value analyzer.



**FIGURE 3. GROUP II LOW RANGE SULFUR ANALYZER CALIBRATION ERROR FOR 365 DAYS.**



**FIGURE 4. GROUP II HIGH RANGE SULFUR ANALYZER CALIBRATION ERROR FOR 365 DAYS.**



**FIGURE 5. HIGH HEATING VALUE ANALYZER CALIBRATION ERROR.**

The regulatory requirements for calibration error are 5% for the sulfur analyzer and 2.5% for the high heating value analyzer. The **Figures 3-5** show the instruments were recalibrated when the error approached the regulatory limit. The recalibration of the analyzer varied from weekly to 3 months. This is observed in the **Figure 3-5** where step changes occurred in the data.

The calibration drift is a measure of the performance over a period of time, The calibration drift is the sum of the absolute value of the average difference between the instrument response and calibration gas concentration and the absolute value of the 95% confidence limit divided by the full scale range shown as a percent. **Table II.** shows the calibration drift of all 5 flare systems over a year of operation. The performance of these systems meet the regulatory requires, but required daily monitoring and weekly to monthly recalibration. During this one year period all system there annual and biannual maintenance performed as defined by the instrument manufacturer.

**TABLE II. CALIBRATION DRIFT MEASURED OVER ONE YEAR.**

Flare System	Low Range Sulfur	High Range Sulfur	HHV
1.) Group I	3.4	4.7	1.0
2.) Group I	4.0	0.7	0.9
3.) Group II	4.5	4.9	2.4
4.) Group II	0.2	0.9	1.3
5.) Group II	0.8	0.3	.0.8

The analyzer systems are required to meet a linearity performance of 10% error. The error measures the difference between the instrument response and the certified gas standard concentration divided by the certified gas standard concentration shown as a percent. The linearity error is shown in **Table III.**

Sample system bias is a measure of the amount of instrument response change by passing the sample through the sample system. The sample system bias is the difference in instrument response between introducing the gas standard at the instrument and at the sample probe divided by the full scale range shown as a percent. The bias is measured at two ranges 0-20% FSR and 80-100% FSR to determine if the bias is dependent on the concentration of the analyte. Both gas standards are injected at the probe and directly to the instrument to determine the sample system bias. **Table IV** shows the sample system bias for the 5 analyzer systems.

The final measurement of the system performance is the zero drift. The zero drift measures the ability to remove the sample from the system and the reproducibility of the baseline measurement. The measurement is made by introducing nitrogen at the sample probe for 30 min and recording the response. This is repeated every 2 hours for 24 hours. The zero drift is the sum of the absolute value of the average difference between the instrument response between successive cycles and the absolute value of the 95% confidence limit divided by the full scale range shown as a percent. **Table V** show the zero drift measurements of the 5 flare systems.

**TABLE III. LINEARITY ERROR MEASURED OVER THREE LEVELS OF INSTRUMENT RANGE.**

Flare System	Analyzer Type	Linearity Error Percent (<10%)		
		10-30% FSR	40-60% FSR	80-100% FSR
1.) Group I	High Range Sulfur	-5.21	-1.3	-2.6
	Low Range Sulfur	-6.9	-8.4	0.15
	High Heating Value	2.0	-0.4	0.1
2.) Group I	High Range Sulfur	-5.0	-5.8	-3.3
	Low Range Sulfur	-0.9	-4.2	2.5
	High Heating Value	0.7	3.7	1.3
3.) Group II	High Range Sulfur	3.2	0.8	.6
	Low Range Sulfur	2.0	5.1	1.2
	High Heating Value	0.04	0.06	0.5
4.) Group II	High Range Sulfur	4.1	1.9	3.4
	Low Range Sulfur	6.0	9.0	5.8
	High Heating Value	0.09	0.2	.6
5.) Group II	High Range Sulfur	4.7	1.4	1.3
	Low Range Sulfur	0.7	0.3	0.8
	High Heating Value	0.6	1.1	1.0

**TABLE IV. SAMPLE SYSTEM BIAS.**

Flare System	Analyzer Type	Sample System Bias	
		0-20% FSR	80-100% FSR
1.) Group I	High Range Sulfur	0.05	2.6
	Low Range Sulfur	0.08	0.36
	High Heating Value	0.0	0.04
2.) Group I	High Range Sulfur	0.03	1.1
	Low Range Sulfur	0.6	1.04
	High Heating Value	0.0	0.4
3.) Group II	High Range Sulfur	0.01	0.40
	Low Range Sulfur	0.0	0.1
	High Heating Value	0.0	0.1
4.) Group II	High Range Sulfur	0.02	0.77
	Low Range Sulfur	0	1.5
	High Heating Value	0	0.2
5.) Group II	High Range Sulfur	0.0	2.1
	Low Range Sulfur	0.5	0.5
	High Heating Value	0.0	0.03

**TABLE V. ZERO DRIFT MEASUREMENT OF 5 FLARE SYSTEMS.**

Flare System	Low Range Sulfur	High Range Sulfur	HHV
1.) Group I	0.004	0.005	0.013
2.) Group I	0.10	0.002	0.06
3.) Group II	0.0	0.014	0.012
4.) Group II	0.0	0.1	0.86
5.) Group II	0.0	0.02	0.02

## **CONCLUSIONS**

The above performance results show the analyzer systems meet the regulatory requirements. The data shows the importance of stable instrumentation, heated sample system and Sulfinert coated sample lines for all tubing in contact with sulfur compounds that are connected for sulfur analysis.

## **ACKNOWLEDGEMENTS**

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