Continuous flare stack emission monitoring using the Thermo Scientific SOLA II Flare System

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Goal

The Thermo Scientific[™] SOLA II Flare System provides a solution for continuous and accurate determination of total sulfur in flare gas (high and low ranges). Sulfur emissions in process heaters and flares can be successfully monitored by petroleum refineries requiring compliance.

Total Sulfur Compliance Requirements for Flare Emissions

On June 1, 2012, the Environmental Protection Agency issued final amendments to the new source performance standards (NSPS) for process heaters and flares at petroleum refineries. For flares, the provisions apply to flares which commence construction, modification or reconstruction after June 24, 2008. Total sulfur measurement is now required to meet this regulation. All flares affected must be in compliance by November 17, 2015.

The SOLA II flare gas analyzer can be configured in a dual range per site requirements and is widely accepted. The SOLA II flare analyzer shares common spare parts with the liquid fuels version of the Thermo ScientificTM SOLA II, originally developed several years ago for the ultra low sulfur diesel requirements.

Principle of Operation

The SOLA II flare system is based on the field-proven SOLA II sulfur online analyzer that employs PUVF spectrometry for determination of total sulfur. To determine the total sulfur content of hydrocarbon samples by PUVF, all organically bound sulfur is converted to sulfur dioxide (SO₂) by sample combustion. Irradiation of SO₂ with ultraviolet light at a specific wavelength forms an excited form of SO₂. The excited SO₂ relaxes to its ground state by the emission of light or fluorescence. The intensity of the emitted light is directly proportional to the SO₂ concentration and thus the flare stack's total sulfur concentration.

The SOLA II flare is suitable for analyzing over a dynamic range of 10 ppm to 100% sulfur by volume using a single analyzer system. The SOLA II Flare utilizes two measuring ranges for all applications (Table 1). The end user sets the high measuring range requirement with the low measuring range fixed at 1% of the high range.



| | Low Range 1 | High Range 2 |
|--------------------------------|--|--|
| Total Sulfur | 0-3000 ppmv | 3000-300,000 ppmv |
| Repeatability & Linearity | ±1% of 3000 ppmv or better | ±1% of 300,000 ppmv or better |
| Valve Type | 10 port rotary valve | 6 port rotary valve |
| Sample Injection Volume | 100 ul | 1 ul |
| Range Switching Points | Low to high range at 10% 3300 ppmv | High to low range at 10% 2700 ppmv |
| Response During Flare Event | 2-4 min to fully achieve high response | 5-8 min to achieve recovery after a high sulfur flaring event |

Table 1: Thermo Scientific SOLA II Flare analyzer range configuration for a 30% measuring range.

To achieve the two independent measuring ranges and to maintain the $\pm 1\%$ of full scale linearity and repeatability for each range, a unique analytical arrangement is utilized. The PUVF detector uses dual PMT (photomultiplier tube) power supplies to set the detector sensitivity. Dual sample injection valves, with a 100:1 dilution ratio, are used to introduce the sample into the zero grade air carrier/



combustion gas. The software will automatically choose the appropriate measuring range (PMT setting and sample injection valve) based upon the sulfur level output at the moment. While monitoring the flare gas, the SOLA II Flare auto-ranges based upon the sulfur level being detected.

Using two sample injection volumes (low range 100 ul sample loop / high range 1 ul sample loop) to achieve the 100:1 dilution ratio allows approximately the same amount of sulfur to the detector when operating at the high end of both measuring ranges. This arrangement allows the SOLA II Flare to achieve an unmatched recovery time after a flaring event with high sulfur content. The recovery time is five to eight minutes from percent levels down to low ppm levels.

The excellent recovery time is important while measuring flaring events but is also critical for the required daily validations. Every 24-hour period, a high sulfur standard must be applied to the analyzer that is within 80-100% of the high measuring range. Daily validation time needs to be minimized – each validation gas is required to be analyzed for ten minutes. Depending upon the validation sequence selected, two to three protocol standards are required to achieve the four validation runs required for two measuring ranges.

Figure 1 indicates the typical valve configuration. Special ranges and configurations are available, along with single range total sulfur analysis to complement other analytical methods and applications that may be required for flare

gas analysis.

The key point to this valve arrangement is the three flows of clean air (zero grade air carrier/combustion gas). Clean Air Flow #1 is present in each SOLA II analyzer no matter the application. The purpose of this flow is to provide turbulence in the mixing chamber and add oxygen. This assures the sample is thoroughly mixed with the oxygen in the air prior to combustion in the pyrolyzer. Clean Air Flow #2 is continuously sweeping the low range 10-port sample injection valve. Clean Air Flow #3 is continuously sweeping the high range 6-port sample injection valve. In this configuration there are no dead legs in the flow of the analytical oven; where after a high sulfur event there could be bleed-off that would slow the recovery time.

The cumulative clean air flow passes through the detector; one sample injection valve is injecting at all times (each thirty seconds) based upon the level of sulfur being detected at that moment. This essentially provides a continuous flow of sample to the pyrolyzer where the hydrocarbons are combusted to water and carbon dioxide, and the sulfur compounds are combusted to SO₂. The combustion product then travels to the PUVF detector, which is programmed to operate on a 190 second rolling average and updated each second. This arrangement means even the shortest flaring events are detected and accurately reported.

Validation of SOLA II Flare Response

Passing the daily validations, without the need to manually oversee the analyzer, is the second most important

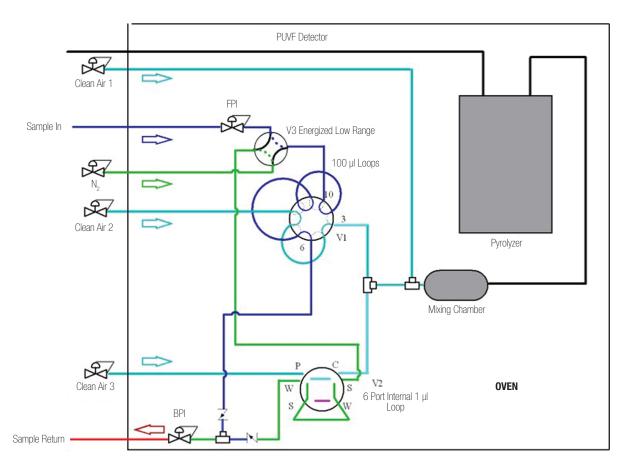


Figure 1: A typical valve configuration within the Thermo Scientifc SOLA II Flare Gas Analyzer.

aspect of the analyzer installation. The SOLA II Flare insures the validation parameters are tightly controlled. During the validation sequence the PLC or DAS takes control of the SOLA II Flare – no auto-ranging is allowed during the validation sequence. The PLC or DAS drives the validation by commanding the SOLA II analyzer to select the appropriate measuring range and drive the pneumatic output selecting the appropriate validation gas. Each validation gas is analyzed for 10 minutes.

Options of daily validation sequences using a 30% high range as an example are show in Tables 2 and 3.

| Daily Validation Option 1: | | |
|----------------------------|---------------------|----------------------|
| 10 min | Low Range/High Gas | 2,800-2,900 ppmv |
| 10 min | Low Range/Low Gas | Nitrogen |
| 10 min | High Range/High Gas | 280,000-290,000 ppmv |
| 10 min | High Range/Low Gas | Nitrogen |
| Return to Process | | |

Table 2: Option 1 requires a total of 40 minutes off-line to perform the validation sequence. Only two protocol cylinders are required.

| Daily Validation Option 2: | | | |
|----------------------------|--------------------------------------|----------------------|--|
| 10 min | Low Range/Low Gas | 175-200 ppmv | |
| 10 min | Low Range/High Gas | 2,800-2,900 ppmv | |
| 10 min | High Range/Low Gas | 2,800-2,900 ppmv | |
| 10 min | High Range/High Gas | 280,000-290,000 ppmv | |
| 5 min | N2 prior to returning to the process | | |

Table 3: Option 2 requires 45 minutes off-line to perform the validations sequence. Three protocol cylinders are required; the 2,800-2,900 ppmv cylinder is used for both ranges.

Quick Analytical Response of Sola II Flare

Figure 2 shows the SOLA II Flare being purposely over-ranged at 12:49 PM. By 12:57 PM (white line) the analyzer is lined-out on the new value of 166,439 ppmv.

Figure 3 shows an hydrogen sulfide sample running at 53% and then switched to nitrogen at 10:54 AM. At 10:55 AM, the analyzer picked-up the change. At 11:14 (end of chart) the analyzer is reading 52 ppmv.

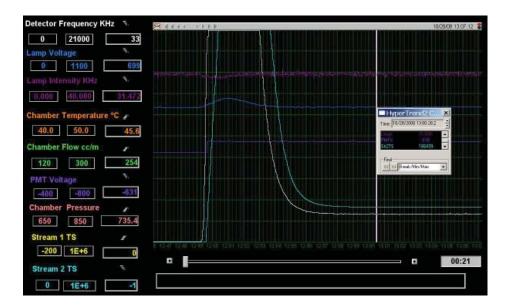


Figure 2: Representative data for the Thermo Scientific SOLA II Flare over-range.

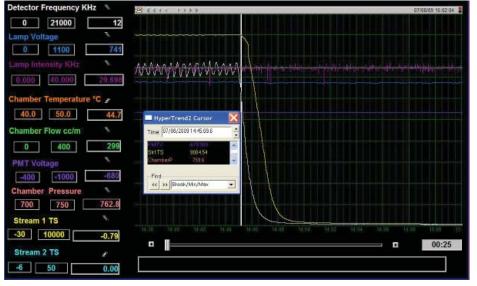


Figure 3: Representative data for a hydrogen sulfide sample.

Conclusion

The Thermo Scientific SOLA II Flare total sulfur gas analyzer (Figure 4) can meet compliance for flare monitoring regulations at low and high, total sulfur ranges and perform validation within an hour. The analyzer can respond within minutes of changing sulfur concentrations that may occur due to a flare event. This allows for quicker validation and reporting in case of a flare upset. The quick recovery of the PUVF detector minimizes any over reporting of sulfur that may occur with another detection system of slower response and recovery. Also the analyzer system has been ruggedized for HF sampling contaminants.



Figure 4: Thermo Scientifc SOLA II Flare Gas Analyzer.

The Thermo Scientific SOLA II Flare provides turnkey solutions for flare monitoring systems and is backed by years of trustworthy operation.

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