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Key Words

- Stack
- Flare
- Flare Header
- Emissions
- Environmental Regulations
- Sulfur Analyses
- Continuous
 Sulfur Analysis
- ASTM 5453
- ISO 20846
- BAAQMD
- SCAQMD Rule 1118
- EPA 40 CFR 60, Subpart J/Ja
- EPA 40 CFR Part 52

Continuous Flare Stack Emission Monitoring Using the Thermo Scientific SOLA II Flare System

Introduction

Increasing awareness of greenhouse gases and their impact on the global environment is resulting in regulations that dictate strict monitoring of flare stack sulfur dioxide (SO₂) emissions. In February 2008, California's South Coast Air Quality Management District (SCAQMD) mandated SO₂ emissions must be less than 0.5 tons per million barrels of crude oil produced by 2012.

Once set forth in California, environmental regulations of this nature tend to be adopted over time by other states. A case in point is the US Environmental Protection Agency (USEPA) Rule 40 CFR Part 52 for Billings/Laurel, Montana. Issued in April 2008 to assure attainment of SO₂ National Ambient Air Quality Standards (NAAQS), this ruling cites both the SCAQMD and the Bay Area Air Quality Management District (BAAQMD) as references for establishing standards regarding equipment performance, analytical methods and accuracy requirements. This ruling is an indication that tough flare stack emission regulations are likely to become the norm for the continental United States.

SO₂ flare emissions in Southern California are now covered by SCAQMD rule 1118, "Control of Emissions from Refinery Flares" that mandates continuous monitoring of these emissions. Section 3-I-ii of this rule specifically calls for the use of a total sulfur analyzer for continuous monitoring and subsequent recording of flare stack emissions.

The Thermo Scientific SOLA II Flare is a total sulfur analysis system and is the only method tested by the SCAQMD for the purpose of monitoring and recording SO₂ emissions. This continuous, online system has proven itself in rigorous field operations and is now enabling refiners to more easily comply with these tough regulations.



Thermo Scientific SOLA II Flare system

Wide Measuring Range Ensures Compliance

Typically, environmental agencies use a rolling average calculation for emission monitoring, including sulfur. The USEPA requires refineries to monitor and maintain a log of these emissions. It is anticipated that the agency will begin enforcing Rule 40 CFR 60, Subpart J/Ja nationwide, requiring several new flare measurements. To facilitate these measurements, refiners need a flare monitoring/ recording system that offers a wide measurement range from at least 10 ppm to 95% S by volume. There are two reasons why this range is important. For one, during periods of low emissions, refiners can confirm the exact amount of sulfur emitted to reduce the overall average. Secondly, during a flaring event, the range enables a refinery to confirm the duration of the event as well as the amount of sulfur emitted.



figure 1. Refinery with flare system



figure 2. A 33-minute run at 100% sulfur with a standard deviation of 812, indicating excellent repeatability.

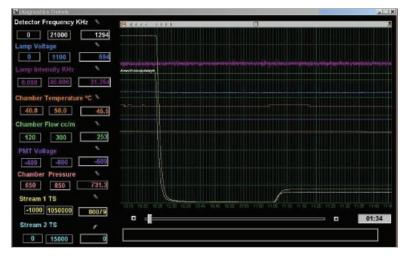


figure 3. Excellent response time for transition from 100% sulfur to 0 with a run backup to 8%.

Both improve the reporting accuracy of the emissions and enable the refinery to report actual sulfur emission quantities rather than engineering or worse case estimates.

The SOLA II Flare system is designed to measure this extremely wide range of total sulfur concentrations. It is a SCAQMD-accepted analytical method for use in all flare emission systems and has exceeded all analytical and operational expectations. With the high accuracy of this system, refiners can more precisely measure the extreme fluctuations like those found on the flare supporting the sulfur recovery unit (SRU). Its wide dynamic measuring range also ensures the SOLA II Flare will comply with any measuring range mandated by the USEPA today and in the future.

Proven Technology Facilitates Measurement

The SOLA II Flare is an adaptation of the Thermo Scientific SOLA II which was originally designed to monitor sulfur content in motor fuels and now has a worldwide installation base. The new single analyzer system incorporates the capabilities of two analyzers while maintaining excellent response time as well as accuracy across a wide analytical range.

The single analyzer system offers many advantages, including:

• A reduced footprint, yet it incorporates the same capabilities as a two-analyzer flare system; this consolidation minimizes space requirements inside of shelters, simplifies and lowers the cost of installation, and reduces overall operating costs.

- Two independent calibration ranges that allow for two widely varying independent measuring ranges (low range 10-10,000 ppm / high range 10,000 ppm – 95% S by volume); the software controls the automatic selection of the appropriate sample injection valve and and the photomultiplier tube (PMT) voltage to ensure the system is configured to accurately monitor the sulfur level occurring at that time.
- Dual PMT power supplies that provide the capability to set the sensitivity of the pulsed ultraviolet fluorescence (PUVF) detector; users have the flexibility to set the two widely varying independent measuring ranges and to have the appropriate measuring range automatically selected by the analyzer software.
- Dual sample injection valves that ensure precise control of the sample size being injected into the analytical system and ultimately to the PUVF detector; it is this dilution ration that allows approximately the same amount of sulfur to enter the detector regardless of which measuring range is in use and allows the analyzer to maintain the same repeatability for both measuring ranges; the dilution ration also minimizes the problematic memory effect when the analyzer is used to measure a variety of sulfur compounds.
- Utilization of less carrier and calibration gases along with less overall operational and maintenance costs, resulting in significant cost savings.
- A reduction in the sample conditioning system components needed for switching and control between the flare system and the analyzer which also reduces operational expenses.

The SOLA II Flare system is continuously monitoring via a 30-second injection period and offers many advantages to gas chromatograph (GC) users, including:

- Continuous monitoring versus step monitoring; a process GC's analysis cycle can take several minutes causing a blind period, during which an unmeasured flare event can occur; since the SOLA II Flare is an online analyzer, there are no blind periods.
- Use of less calibration gases; while a process GC is matrix dependent and requires complex calibration mixtures to properly calibrate the required matrix, the SOLA II Flare system uses one gas which results in annual savings from \$15,000 to \$60,000 depending on the type of gases required by the GC.
- Acceptance as an analytical method by the SCAQMD; the SOLA II Flare system is a proven analysis method that utilizes a robust analytical platform.
- An accurate, wide analytical range along with fast high-tolow range response time; by accurately measuring low

sulfur emissions, the SOLA II Flare system enables actual emission data to be reported rather than engineering "worse case" estimates and reduces the overall average as well as the aggregate value.

• A simplified design that lowers overall cost and increases instrument reliability.

Its wide dynamic measuring range also ensures the SOLA II Flare will comply with any measuring range mandated by the USEPA today and in the future.

This reliability along with the instrument's functionality, including the dynamic measurement range of 10 ppm to 950,000 ppm, enable users to achieve reliable sulfur emission monitoring.

Turnkey Solution Spans from Design to Installation

Thermo Fisher Scientific has entered into a non-exclusive agreement with Mangan Engineering, Inc., the systems integrator that designed and developed the first SCAQMDcompliant continuous emission monitoring system (CEMS), to provide a turnkey flare emission monitoring solution. During the development phase of SCAQMD's Rule 1118, Mangan Engineering was selected to work in conjunction with the major refinery chosen to host the flare measurement system pilot program. The test site chose to use the SOLA II Flare based on the results achieved during laboratory testing as well as its proven track record as a sulfur analyzer.

Based on this experience and several subsequent installations, Mangan has become well versed on the SOLA II Flare and is adept at specifying and designing the associated safety and control systems, the sample handling system, and the utilities to optimize cost, performance and maintainability. In addition to providing this turnkey solution, both companies offer technical support and contract services for their respective portion of the installation to ensure implementation within the time frame specified by USEPA.

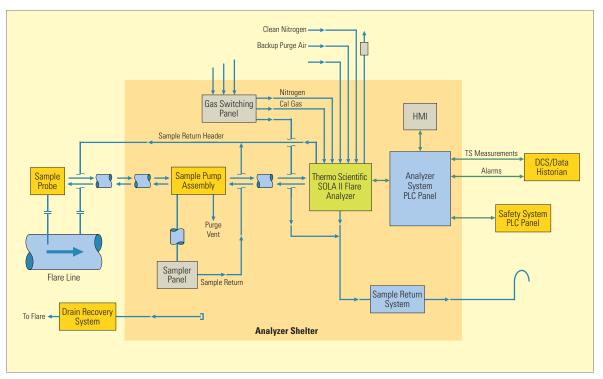


figure 4. SOLA II Flare in the flare system monitoring block diagram designed by Mangan Engineering

SOLA II Flare System Principle of Operation

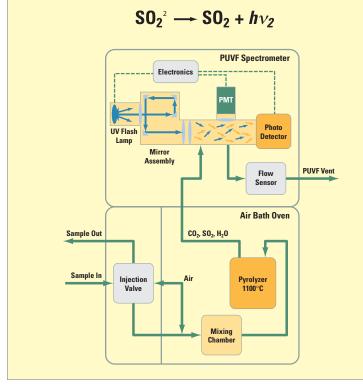
The SOLA II Flare system is based on the field-proven Thermo Scientific SOLA II sulfur online analyzer that employs PUVF spectrometry for determination of total sulfur. To determine the total sulfur content of hydrocarbon samples by PUVF, all organically bound sulfur is converted to sulfur dioxide (SO₂) by sample combustion. Irradiation of SO₂ with a specific wavelength of ultraviolet light forms an electronically excited form of SO₂. The electronically 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 SO_2 concentration and thus the flare stack's total sulfur concentration. The SOLA II contains all

apparatus necessary for sample combustion and total sulfur measurement by PUVF.

The SOLA II Flare is a proven system that offers outstanding performance and reliability along with lower installation, startup and maintenance costs. The flexibility of the dynamic measurement range coupled with its rapid response, accuracy and fewer maintenance requirements enable refiners to cost-effectively fulfill current environmental regulatory requirements as well as adapt to future regulatory changes without significant additional capital expenditures.

SOLA II is an Online Adaptation of the Well-Accepted:

 ASTM D5453
 "Determination of Total Sulfur in Light Hydrocarbons, Motor Fuels and Oils by Ultraviolet Fluorescence"



 $SO_2 + hv_1 \longrightarrow SO_2^{\dagger}$

figure 5. SOLA II Flare system employs PUVF spectrometry for total sulfur determination.

 ISO 20846
 "Petroleum Products – Determination of Sulfur Content of Automotive Fuels – Ultraviolet Fluorescence"

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