Improving Refinery Flare Monitoring Through Optimized Heating Value Measurement and Sampling Design

Reza Modarres

MMR Constructor Inc.

16073 Airline Highway | Baton Rouge, LA 70817

KEYWORD

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ABSTRACT

Accurate flare gas analysis is a critical element in achieving environmental compliance and optimizing refinery operations. This paper evaluates the performance of analyzer systems under extreme process conditions, including emergency shutdowns and simultaneous relief events. The study focuses on the measurement principles of Lower Heating Value (LHV), Higher Heating Value (HHV), and total sulfur concentration under varying hydraulic and thermal conditions. Particular emphasis is placed on the sampling system, where probe design, heat tracing, and automated back-purging play essential roles in maintaining sample integrity and preventing plugging. The results demonstrate that a properly designed sampling and analysis system can significantly improve measurement reliability, reduce environmental emissions, and enhance combustion efficiency in flare systems.

INTRODUCTION

Refinery flares are critical safety systems designed to safely combust excess hydrocarbon gases during both routine operations and emergency process conditions. Efficient flare operation ensures near-complete destruction of combustible gases, thereby minimizing emissions of unburned hydrocarbons and volatile organic compounds (VOCs).

In addition to environmental considerations, effective flare monitoring provides measurable economic benefits by reducing utility consumption and improving the

recovery of potential fuel value. As a result, accurate monitoring of flare gas composition has become an essential requirement in modern refinery operations.

In recent years, environmental regulations have imposed increasingly stringent requirements on flare performance. In the United States, regulations such as EPA 40 CFR Part 60 Subpart Ja and 40 CFR Part 63 Subpart CC (Refinery Sector Rule) require continuous monitoring of combustion-related parameters to ensure a minimum destruction efficiency of 98%. Unlike conventional stack-based monitoring systems, such as Continuous Emission Monitoring Systems (CEMS) or ambient monitoring systems, flare systems involve open-air combustion, making direct measurement of exhaust gases impractical. Consequently, regulatory compliance relies on upstream measurements of flare vent gas properties, particularly net heating value (NHV) and total sulfur concentration.

Accurate measurement of flare gas properties presents significant technical challenges due to the highly dynamic nature of flare operation. Gas composition, flow rate, pressure, and temperature may vary considerably over short periods of time. During worst-case operating conditions, such as plant startups, emergency shutdowns (blowdowns), or process upsets, the flare system may experience large gas volumes, high velocities, liquid carryover, or cryogenic temperatures. These conditions make it difficult to obtain a representative and stable sample for analysis.

The reliability of flare gas measurement depends primarily on the performance of the sampling system. Proper design of the sampling probe, conditioning components, and transport lines is required to maintain sample integrity and minimize lag time. In practice, lag time is typically maintained within 1–2 minutes to ensure timely analyzer response. In addition, the system must prevent phase changes, such as condensation of heavy hydrocarbons, which can introduce significant measurement errors.

This paper presents the fundamental principles, design challenges, and practical solutions for flare gas sampling and measurement systems. Emphasis is placed on achieving accurate and repeatable measurements of heating value and total sulfur across a wide range of operating conditions, with the objective of improving environmental compliance, operational safety, and overall system reliability.

PRINCIPLES OF HEATING VALUE MEASUREMENT: LHV VS. HHV

The heating value of a fuel represents the total thermal energy released during the complete combustion of a unit quantity of gas. In flare gas analysis, two thermodynamic definitions are commonly used:

Higher Heating Value (HHV): The total heat released when combustion products are cooled to a reference temperature and the water formed during combustion is condensed to liquid, thereby releasing the latent heat of vaporization.

Lower Heating Value (LHV): The heat released when the water produced during combustion remains in the vapor phase.

In refinery flare applications, combustion occurs in the open atmosphere where water remains in the vapor phase. Therefore, flare monitoring regulations and engineering calculations are generally based on the LHV.

CALCULATION METHODOLOGY

For a multi-component gas mixture, the heating value is calculated as:

$$LHV_{mix} = \Sigma (x_i \times LHV_i) \quad (1)$$

Where xi is the mole fraction and LHV_i is the heating value of each component. The same approach applies to HHV calculations.

Two modeling approaches are typically considered:

- Simplified Model: Heavy hydrocarbons grouped as C6+.
- Detailed Model: Heavy hydrocarbons distributed from C6 to C10. (Table 1)

TABLE I. LHV and HHV calculation by basic formula (C6+ including C6...C10)

Gas Composition & Component Properties							Key Results	
Component	Input x	Used x	MW	LHV	HHV	x·MW	Mixture Molecular Weight	23.210
CH4	0.8108	0.8108	16.0430	0.8020	0.8900	13.0077	Specific Gravity	0.8013
C2H6	0.0352	0.0352	30.0700	1.4280	1.5600	1.0585	LHV (MJ/mol)	1.0234
C3H8	0.0150	0.0150	44.0970	2.0430	2.2200	0.6615	HHV (MJ/mol)	1.1235
n-C4H10	0.0100	0.0100	58.1240	2.6570	2.8770	0.5812	Wobbe Index (LHV)	1295.3
i-C4H10	0.0100	0.0100	58.1240	2.6570	2.8770	0.5812	Wobbe Index (HHV)	1421.9
n-C5H12	0.0100	0.0100	72.1510	3.2720	3.5090	0.7215	Gas Density @ std	0.0612
i-C5H12	0.0100	0.0100	72.1510	3.2720	3.5090	0.7215	Gas Density @ operating	0.0954
neo-C5H12	0.0050	0.0050	72.1510	3.2720	3.5090	0.3608	Calculated Z @ std	0.9958
n-C6H14	0.0050	0.0050	86.1780	3.8870	4.1630	0.4309	Calculated Z @ operating	0.9947
2-Methylpentane	0.0050	0.0050	86.1780	3.8870	4.1630	0.4309	Std Flow (scf/hr)	5,000,000.00
3-Methylpentane	0.0050	0.0050	86.1780	3.8870	4.1630	0.4309	Operating Flow (ACFM)	53,414.02
2,2-Dimethylbutane	0.0050	0.0050	86.1780	3.8870	4.1630	0.4309	Energy Rate (LHV, MMBtu/hr)	5,797.34
2,3-Dimethylbutane	0.0050	0.0050	86.1780	3.8870	4.1630	0.4309	Energy Rate (HHV, MMBtu/hr)	6,363.97
n-C7H16	0.0050	0.0050	100.2050	4.5020	4.8170	0.5010	Water content (ppmv)	1,000.000
n-C8H18	0.0020	0.0020	114.2320	5.1170	5.4710	0.2285	Water partial pressure (psia)	0.025
n-C9H20	0.0020	0.0020	128.2590	5.7320	6.1250	0.2565	Water dew point (°C)	-16.277
n-C10H22	0.0020	0.0020	142.2860	6.3470	6.7790	0.2846	Water dew point (°F)	2.701
C2H4	0.0010	0.0010	28.0540	1.3230	1.4110	0.0281	LHV (Btu/lb)	1.896E+04
C3H6	0.0010	0.0010	42.0810	1.9260	2.0580	0.0421	HHV (Btu/lb)	2.081E+04
CO2	0.0300	0.0300	44.0100	0.0000	0.0000	1.3203	LHV (Btu/scf @ std)	1,159.468
N2	0.0250	0.0250	28.0130	0.0000	0.0000	0.7003	HHV (Btu/scf @ std)	1,272.794
H2O	0.0010	0.0010	0.0000	0.0000	0.0000	0.0000	Z-Based Winter Screening	
H2	0.0000	0.0000	2.0160	0.2420	0.2860	0.0000	Winter Z Risk	Low winter phase-risk
TOTAL	FALSE	1.0000				23.2096	Screening Basis	30–40°F ambient basis

Small variations in heavy hydrocarbons significantly affect heating value due to their higher energy content. Therefore, condensation must be avoided in the sampling system to prevent measurement bias.

VALIDATION VIA SIMULATION

The analytical model was validated using Aspen HYSYS, where spreadsheet calculations were compared with results from a rigorous equation-of-state (EOS) model.

Volumetric Heating Value:

$$HV_v = HV_{mol} \times (P_{std} / (Z \times R \times T_{std})) \quad (2)$$

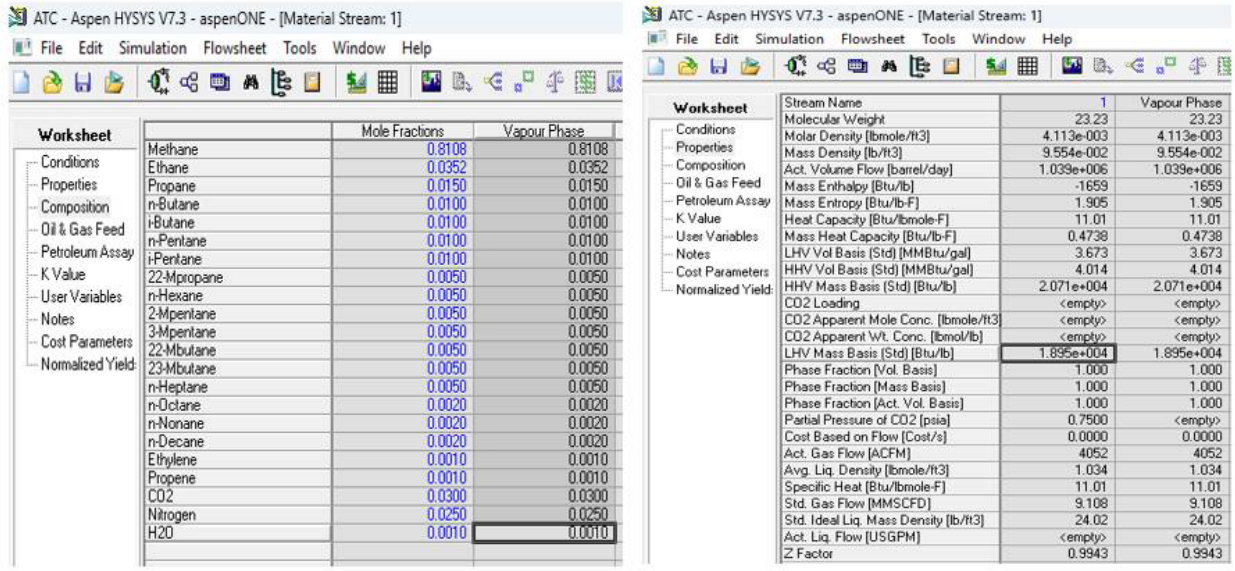
Mass-Based Heating Value:

$$HV_m = HV_{mol} / M_{mix} \quad (3)$$

Where HV_mol is the molar heating value, HV_v is the volumetric heating value, HV_m is the mass-based heating value, M_mix is the molecular weight of the gas mixture, Z is the compressibility factor, R is the universal gas constant, and T_std and P_std represent standard conditions.

The difference between spreadsheet calculations and simulation results was less than 1%, confirming the accuracy of the applied thermodynamic relationships. (Figure 1)

FIGURE 1: LHV and HHV calculation by Hysys (C6+ including C6...C10)

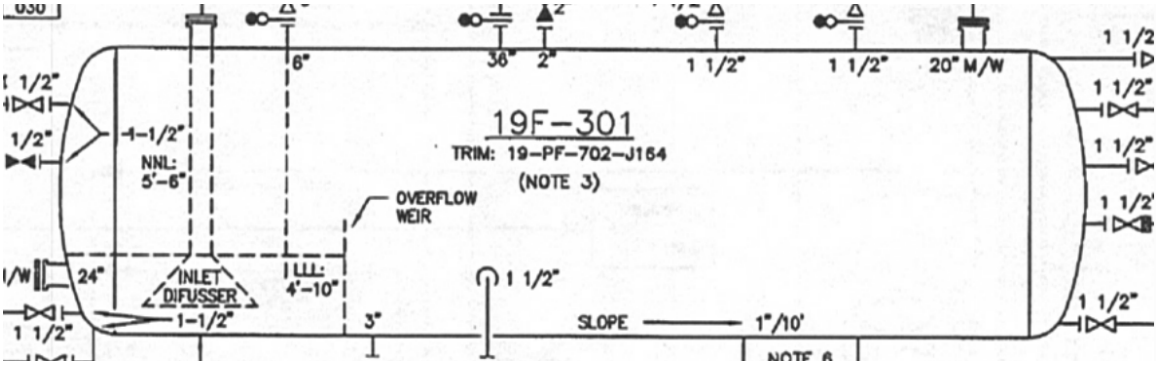


OPERATIONAL IMPLICATIONS

Beyond regulatory compliance, continuous LHV monitoring serves as a diagnostic tool for upstream process performance. In typical refinery configurations, Knock-Out (KO) drums and separators are designed to remove liquid hydrocarbons from the gas stream.

A sudden increase in measured heating value may indicate a carryover event or reduced separation efficiency upstream. Therefore, the flare analyzer can function as an indirect indicator of potential energy loss and equipment malfunction, providing actionable information for process optimization. (Figure 2)

FIGURE 2: Process Knock-out drum with diffuser and baffle



SAMPLING SYSTEM DESIGN AND CHALLENGES

The design of a flare gas sampling system must ensure that the extracted sample remains representative of the process stream under all operating conditions. This requires careful consideration of upstream separation performance, sampling location, probe design, and transport conditions.

Because flare systems operate under highly dynamic conditions-including startup, shutdown, and emergency relief events-the sampling system must be designed to maintain single-phase gas conditions, minimize lag time, and prevent contamination or plugging.

SAMPLING LOCATION AND UPSTREAM PROCESS CONDITIONS

Upstream of the sampling point, the flare gas passes through a knockout (KO) drum designed to remove entrained liquids prior to combustion. The KO drum typically incorporates internal elements such as diffusers and baffles to reduce gas velocity and promote phase separation. Liquid removal is primarily governed by gravitational settling and hydrocarbon dew point behavior, where heavy hydrocarbons and condensed water are separated from the gas stream.

In a properly designed process KO drum operating at flare header pressure, hydrocarbon components with dew points above approximately 130°F can be effectively removed. This significantly reduces the presence of heavy hydrocarbons in the flare gas, contributing to improved combustion performance, recovery of heavier fractions, and reduction of measurement uncertainty in the C6–C10+ range.

Under normal operating conditions, this process stabilizes the gas phase prior to sampling. However, during abnormal or emergency shutdown conditions, high flow rates and process disturbances may result in partial liquid carryover. Therefore, the sampling system must be designed with the expectation that complete separation is not always guaranteed.

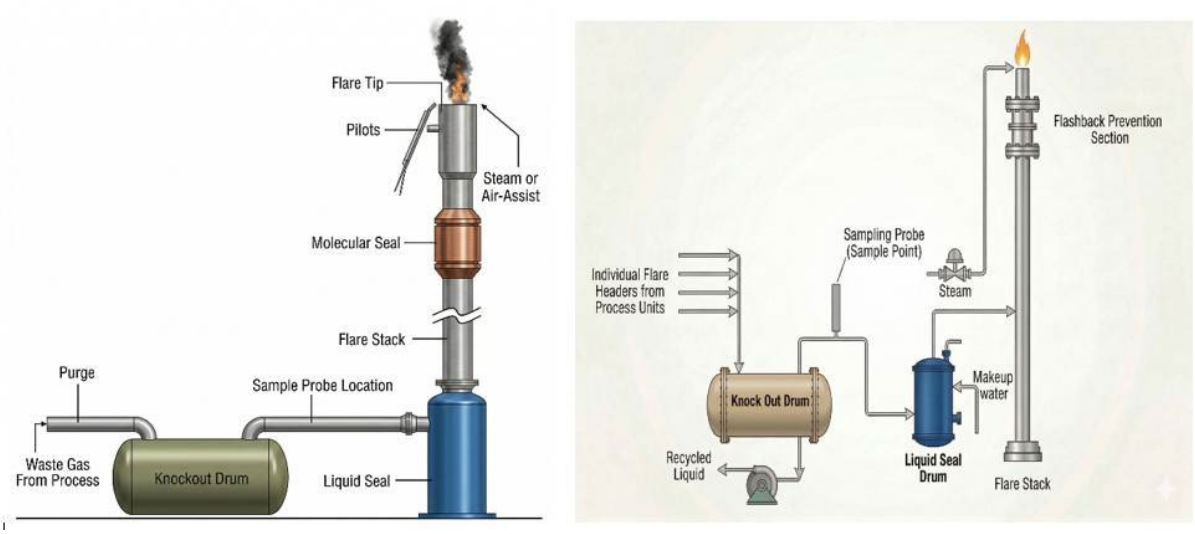
The effectiveness of the KO drum directly influences the composition of the sampled gas at the sampling point, particularly the presence of heavy hydrocarbons. Since these components significantly impact heating value calculations, maintaining consistent phase conditions upstream of the sampling point is critical.

In refinery flare systems, a water seal drum is commonly installed downstream of the KO drum relative to the sampling location, acting as a hydraulic barrier that prevents flame propagation into upstream process headers.

Safety Consideration: Although the gas may appear cleaner downstream of the water seal drum relative to the sampling point, sampling from this location is not permitted due to safety constraints. The water seal functions as a hydraulic flashback arrestor; therefore, extracting a sample downstream of this barrier may compromise protection against flame propagation into upstream process headers.

Accordingly, the preferred sampling location is between the KO drum and the water seal drum, where the gas is both relatively stable in composition and within the required safety boundary. (Figure 3)

FIGURE 3. Knock-out, Water-Seal and Sample tapping point location



SAMPLING PROBE DESIGN

The sampling probe installed at this location must be designed to obtain a representative gas sample while withstanding the mechanical and chemical challenges associated with flare service.

Proper probe placement is essential; the probe tip (stinger) should typically extend into the middle third of the pipe diameter to avoid the boundary layer near the pipe wall, where liquids, scale, and debris tend to accumulate.

Mechanical design shall account for dynamic flow conditions. During emergency or shutdown events, flare gas velocity can increase significantly, resulting in elevated wake frequency and flow-induced vibration. The probe must therefore be designed to prevent resonance and fatigue failure under high-velocity conditions.

Material selection is critical, particularly for sour service. All wetted components shall comply with NACE MR0175/ISO 15156. Depending on specific project conditions, corrosion-resistant alloys such as Monel, Hastelloy C-276, Inconel, or super duplex stainless steel may be considered to mitigate stress corrosion cracking and material degradation.

For applications involving total sulfur or reactive components, inert surface treatments such as SilcoNert (SilcoTek) or Sulfinert coatings are recommended to minimize adsorption effects.

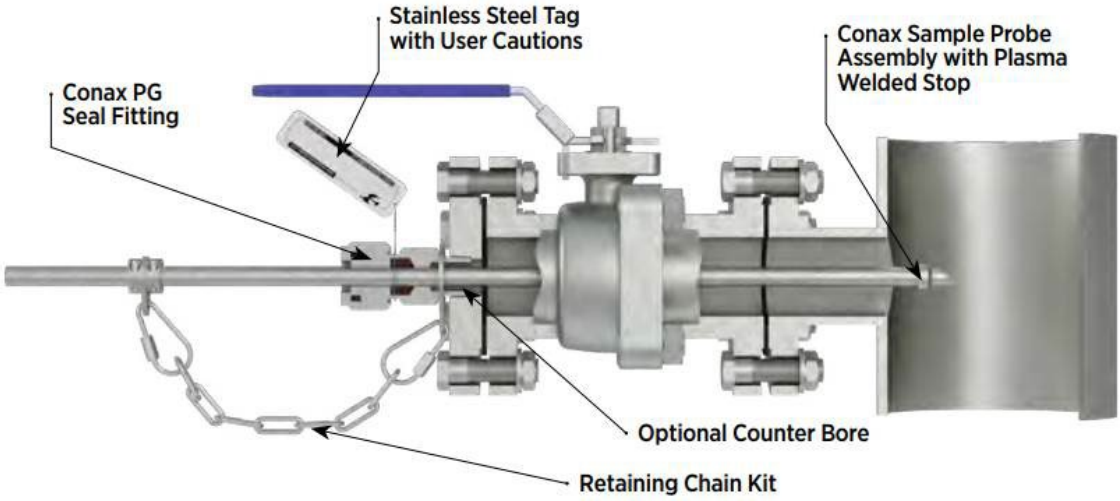
To maintain measurement integrity, the probe shall be fully heated and installed within an insulated system to prevent hydrocarbon or acid dew point condensation.

Given the potential for contamination and plugging, provisions for automated cleaning are necessary. Steam or nitrogen purging can be used for back-cleaning; however, purge systems must be properly controlled to avoid thermal or mechanical damage.

From an operational standpoint, retractable probe designs are strongly recommended. Although not strictly mandatory, they provide a critical maintenance advantage in flare systems where shutdown opportunities are limited.

Retractable (quill-type) probes, used in combination with appropriate isolation (e.g., double block and bleed), allow safe removal and maintenance while the flare header remains in service. (Figure 4)

FIGURE 4. Conax Retractable Sample probe



HEATED SAMPLE TRANSPORT AND PHASE PRESERVATION

Following extraction, the sample must be transported to the analyzer while preserving its chemical composition and phase integrity. Flare headers typically operate at low pressures (generally below 10 psig); therefore, a heated suction pump is required to maintain continuous flow and minimize transport lag time. The pump head shall be heated and constructed from corrosion-resistant materials, with appropriate pressure control to ensure stable operation.

To prevent condensation and selective loss of heavy hydrocarbons, the entire sample transport system shall be fully heated and insulated. The temperature setpoint of the heated bundle shall be maintained above the worst-case hydrocarbon dew point, typically with a design margin of at least 20%. In practical refinery applications, this often corresponds to operating temperatures in the range of approximately 120°C to 150°C (250°F to 300°F), depending on process conditions.

Maintaining a continuous thermal profile is critical. All connections—from the probe outlet to the analyzer inlet—must be free of cold spots. Even localized temperature drops at valves, fittings, or instrument connections can result in liquid dropout or sulfur adsorption, leading to measurement bias and potential data invalidation.

Independent temperature control is recommended for key sections of the system, including the probe, heated transport line, and pump head. PID temperature controllers shall be used to ensure stable operation and to avoid both underheating (which promotes condensation) and overheating (which may damage system components or coatings).

Material selection for the transport system is critical in sour and sulfur-containing services. All metallic components in contact with the sample shall comply with NACE MR0175/ISO 15156 to prevent sulfide stress cracking. For total sulfur measurement or reactive sulfur species, inert surface coatings such as SilcoNert (Sulfinert) are required to minimize adsorption effects and ensure accurate, real-time response.

For flare systems with a high likelihood of contamination or particulate carryover, the sample transport line diameter should be carefully selected. Based on project datasheets and operating experience, a minimum line size of 3/8 inch is recommended to reduce the risk of plugging and maintain reliable sample flow under transient conditions.

All installation accessories, including heat tracing, insulation systems, and electrical components, shall be suitable for the specified hazardous area classification. The sample line between the sampling system and the analyzer shall remain fully heated and protected to ensure consistent sample quality throughout the measurement system.

SAMPLING SYSTEM COMPONENTS AND CONTROL

CONDENSATE AND OIL SEPARATION

Due to potential process disturbances or upstream separation inefficiencies, the sample may contain entrained liquids upon entering the sampling system. Therefore, a heated condensate separator with an approximate capacity of 100 cc is required as a secondary protection stage. This unit shall be equipped with an automatic drain to a safe disposal point. Provision for nitrogen purging shall be included to enable periodic cleaning and prevent accumulation of heavy or sticky hydrocarbons.

HEATED HEAD DIAPHRAGM PUMP

Flare header pressures are typically low (often below 5 psig), and additional pressure losses within the sampling system further reduce available driving force. Therefore, a heated diaphragm pump is required to maintain continuous sample flow and ensure stable operating conditions at the analyzer inlet.

The pump head shall be heated to prevent condensation during compression. Both discharge pressure and temperature must be controlled, as an increase in pressure raises the hydrocarbon dew point. The sampling system temperature setpoint shall be selected accordingly to prevent condensation downstream of the pump.

In typical configurations, the pump head is installed inside the heated sampling system enclosure, while the electric motor remains outside with appropriate hazardous area protection. Alternatively, the pump head may be equipped with a dedicated heating system including a temperature sensor and controller. (Figure 5)

FIGURE 5. ADI (left and middle) and Buhler (right) Heated Sample Pump

MULTI-STAGE FILTRATION SYSTEM

A multi-stage filtration strategy is required to ensure reliable and contamination-free operation. The primary filtration stage, typically a sintered metal filter with a 20–50 µm rating, is installed near the sampling point.

Primary filtration elements installed near the sampling point shall be equipped with a cleaning facility, such as automated back-purging using steam or nitrogen, or designed to allow maintenance without system shutdown.

The secondary stage consists of a coalescing filter and/or membrane separator to remove fine liquid aerosols and oil mist. A final polishing filter (0.1–1 µm) shall be installed upstream of the analyzer to protect sensitive components.

Heated knockout pots with automatic drainage are required for handling high-density or sticky condensates. Differential pressure monitoring and automated purge sequences shall be provided to facilitate maintenance and prevent plugging.

FLOW AND PRESSURE CONTROL

Flow and pressure control are achieved using a combination of needle valves and back-pressure regulators. A bypass loop is implemented to maintain high velocity in the main transport line for fast response, while providing a reduced and stable flow to the analyzer.

SAFETY AND SYSTEM PROTECTION

The sampling system shall include safety components such as flame arrestors, non-return valves, pressure relief devices, and alarm switches for pressure, flow, and temperature.

All electrical and instrumentation components shall be suitable for the specified hazardous area classification (e.g., Class I, Division 1 or Division 2). Proper grounding and installation practices are required to ensure safe operation.

HEATING SYSTEM AND THERMAL STABILITY

Maintaining a single-phase gas condition throughout the sampling system is critical. Thermal energy shall be applied consistently across all sections, including the probe, heated transfer lines, sampling system enclosure, return lines, and disposal lines.

Temperature control must be stable and properly regulated to avoid both underheating (leading to condensation) and overheating. Excessive temperatures may cause polymerization of unsaturated hydrocarbons, resulting in fouling and plugging of the sampling system.

Proper insulation is required at all potential heat loss points, and temperature control systems shall be designed to maintain stable operation under varying ambient conditions.

SWITCHING AND CALIBRATION FACILITIES

The sampling system shall include provisions for automated switching between process sample, zero gas, and span gas. This is typically achieved using automated valve manifolds or modular switching systems.

These facilities enable validation of analyzer performance and verification of the entire sampling system, ensuring measurement accuracy and compliance with applicable performance requirements.

NITROGEN PURGE AND LOW-TEMPERATURE PROTECTION

The sampling system shall include a nitrogen purge capability for tubing and critical components. This function may be operated manually or automatically. In automatic mode, when the sampling system temperature drops below the minimum allowable limit, the process sample shall be isolated, and nitrogen shall be introduced at a controlled pressure and flow rate to purge the system.

This function is essential to prevent condensation, protect sensitive components, and maintain system readiness during abnormal or low-temperature conditions.

AUTOMATION, VALIDATION, AND SYSTEM INTERLOCKS

To ensure compliance with EPA Performance Specifications (PS-5/PS-7) and maintain high system availability, the sampling system shall incorporate automated control logic implemented within the PLC or DCS. This logic governs probe cleaning, analyzer validation, and system protection under abnormal conditions.

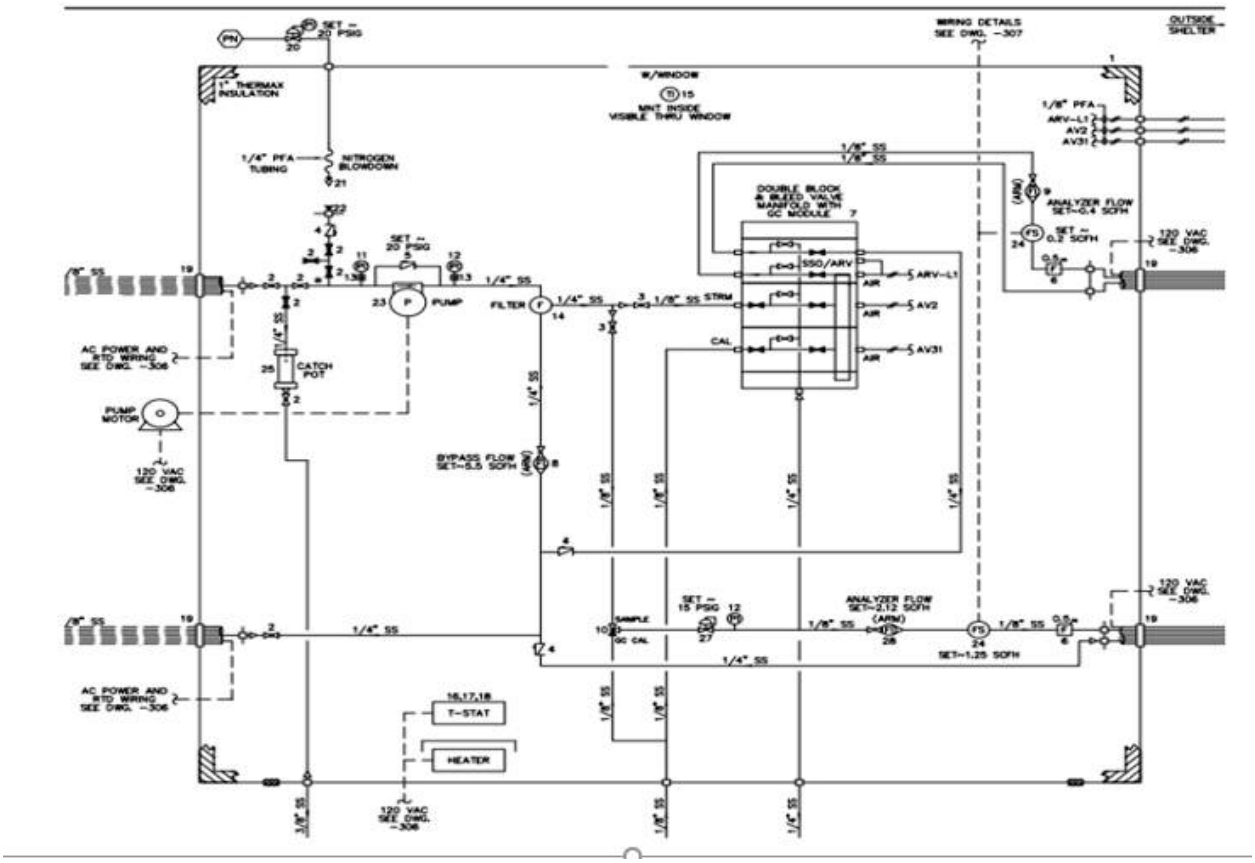
Automated Probe Back-Purge: The sampling system shall include an automated back-purge sequence to maintain probe and primary filter performance. This function is required to remove accumulated coke, scale, or particulates without prolonged interruption of analyzer operation. The sequence shall periodically isolate the analyzer, apply a short-duration high-pressure purge (using instrument air or nitrogen), and then

return the system to normal sampling conditions. A stabilization delay shall be included to ensure that the purge gas is fully cleared and the sample line is recharged with process gas before valid measurements resume.

Validation and Calibration Sequence: The system shall provide automated validation capability to verify analyzer performance on a routine basis. This includes periodic zero and span checks using certified calibration gases. Calibration gas shall be introduced through the sampling system (preferably at the probe location) to validate the entire system response. The control system shall monitor analyzer response, compare measured values to certified references, and evaluate performance against predefined acceptance criteria. If measurement deviation exceeds acceptable limits, the system shall generate appropriate status flags (e.g., maintenance warning, questionable data, or out-of-control condition) in accordance with regulatory requirements. Following calibration, sufficient time shall be allowed for the system to return to stable process measurement conditions.

Safety and Fault Interlocks: The sampling system shall include automated interlocks to protect both the analyzer and the integrity of measurement data. Critical conditions requiring automatic response include: low temperature in the heated sample system, high liquid level in separators or filters, and low sample flow. Under such conditions, the system shall automatically isolate the analyzer and prevent invalid data from being reported until normal operating conditions are restored. (Figure 6)

FIGURE 6. Example of Heated Flare Sampling System for two parallel Analyzer



ANALYZER PANEL DESIGN, INSTALLATION, AND SAFETY

THERMAL PROTECTION

The enclosure shall be located and designed to minimize exposure to radiant heat from the flare system. In accordance with IEC 61285, double-wall stainless steel construction with appropriate insulation (e.g., mineral wool or ceramic fiber) shall be used. Reflective shielding may be required on the flare-facing side to reduce thermal load and improve system reliability.

CLIMATE CONTROL (HVAC)

Stable internal temperature is required to maintain analyzer performance. The enclosure temperature shall be controlled within the typical operating range of 20–35°C (±2°C). HVAC systems shall be sized for worst-case ambient and process heat loads. Redundant (duty/standby) cooling systems are recommended to ensure continuous operation and meet high availability requirements.

ENVIRONMENTAL SEALING

The enclosure shall meet appropriate ingress protection ratings (e.g., NEMA 4X / IP66). All cable and tubing entries shall utilize certified glands suitable for the hazardous area classification (e.g., Ex d or Ex e). Special attention shall be given to the heated sample bundle entry point to prevent thermal losses and internal condensation.

MAINTENANCE AND MONITORING

The enclosure shall be designed to allow safe monitoring and maintenance without compromising environmental or thermal integrity. Viewing windows and external indicators shall be provided to enable inspection of flow, pressure, and system status without opening the enclosure.

DISPOSAL AND VENTING SYSTEM

PRESSURE STABILITY

The analyzer outlet shall operate at or near atmospheric pressure to maintain measurement stability. If the disposal line is connected to a flare header with fluctuating pressure, appropriate pressure control devices (such as back-pressure regulators or eductor systems) shall be used to prevent pressure disturbances from affecting analyzer performance.

BACKFLOW PREVENTION

The disposal system shall include flame arrestors and high-integrity check valves to prevent reverse flow or flashback into the analyzer system. These components are essential for protecting both equipment and personnel.

PHASE CONTROL IN VENT LINES

The disposal line shall be heated and insulated to prevent condensation of acidic or sulfur-containing components. Cooling of the vent gas may result in corrosive condensate formation, leading to plugging or material degradation. For extended vent lines, provision for condensate collection and automatic drainage shall be included.

PRESSURE MANAGEMENT

Where disposal pressure exceeds analyzer outlet pressure, auxiliary systems such as nitrogen eductors or makeup gas systems shall be used to maintain a slight negative pressure and ensure stable flow conditions.

MAINTENANCE AND PURGING

Provision shall be made for purging the disposal system using inert gas (e.g., nitrogen) during shutdown or maintenance conditions. This prevents accumulation of reactive or corrosive species and maintains system integrity.

HEATING VALUE MEASUREMENT METHODS

It should be noted that flare systems are highly dependent on process-specific conditions, and the requirements presented in this section are intended as general engineering guidance. Due to the wide variation in process compositions, operating conditions, and project constraints, the final selection of the measurement method shall be determined by the project engineering team. Therefore, the methodologies described herein are not intended to be prescriptive for all applications, but rather to provide a technical basis for evaluation and comparison.

The heating value (HV) of flare gas represents the total thermal energy released during complete combustion and serves as a key parameter for both process monitoring and environmental compliance. In refinery and petrochemical applications, the Net Heating Value (NHV) is particularly important, as it directly influences flare combustion efficiency and operational safety.

According to environmental regulations (e.g., EPA 40 CFR § 63.670), maintaining a minimum heating value (typically around 270 Btu/scf) is essential to ensure stable combustion and to prevent the release of unburned hydrocarbons and hazardous compounds. As a result, heating value measurement is not only a monitoring function but also a control parameter used for assist gas injection and flare optimization.

Flare gas composition is inherently dynamic and can vary significantly across operating conditions. During normal operation, the stream typically consists of light hydrocarbons, while process upsets or emergency events may introduce heavier hydrocarbons, inert gases, hydrogen-rich streams, or sulfur-containing components. Therefore, the analyzer system must operate reliably across a wide range of compositions and transient conditions.

To meet these requirements, several analytical technologies have been developed and are widely used in industry. The most common methods for flare gas heating value determination include:

Gas Chromatography (GC)
Mass Spectrometry (MS)
Combustion-Based Calorimetry (Residual Oxygen/BTU Analyzer)
Optical-Sonic Methods

Each method offers specific advantages and limitations in terms of accuracy, response time, robustness, and maintenance requirements. The selection of an appropriate technology depends on process conditions, regulatory requirements, and system design constraints.

GAS CHROMATOGRAPHY (GC)

PRINCIPLE

Process Gas Chromatography (PGC) is the most widely used method for determining flare gas heating value. The technique separates the gas mixture into individual components using specialized columns and carrier gases (typically helium or hydrogen). Each component is quantified using a Thermal Conductivity Detector (TCD) or other suitable detectors, and the total heating value is calculated by summing the contribution of each component based on its molar fraction and known heating value.

ADVANTAGE

Gas chromatography is widely accepted as the regulatory gold standard due to its ability to provide detailed compositional analysis. This enables precise calculation of heating value as well as additional parameters such as hydrogen concentration, CO_2 content, and carbon footprint metrics.

The method provides high accuracy (typically within ±1% of full scale) when properly calibrated and offers flexibility for analyzing a wide range of hydrocarbon compositions.

LIMITATION AND PRACTICAL CONSIDERATIONS

Despite its accuracy, GC is inherently a batch process. Each analysis cycle typically ranges from 5 to 15 minutes depending on configuration. This introduces a response delay (T90) that must be considered when meeting regulatory reporting requirements such as 15-minute block averaging.

GC performance also depends on the predefined component list. If unexpected or undefined heavy hydrocarbons enter the system, they may not be correctly resolved, resulting in integration errors or delayed elution behavior.

To address heavy hydrocarbon behavior (C6+), many modern flare GC systems use a backflush-to-detector configuration. In this approach, heavier components are not fully separated into individual species but are grouped and reported as a composite fraction. This improves analysis speed and prevents column contamination, while introducing a controlled approximation in heating value calculation.

RESPONSE TO PROCESS CONDITIONS

Under upset or high-flow conditions, flare gas composition can change rapidly, including the introduction of heavier hydrocarbons or condensable components. Although upstream knockout drums are designed to remove bulk liquids, high-velocity events may still result in partial carryover.

Since C6+ fractions are often represented as grouped or surrogate components in GC calculations, the heating value may be slightly underestimated or simplified. However, in most refinery applications where heavy hydrocarbons remain below approximately 0.5%, this approximation is considered acceptable for both regulatory and operational purposes.

C6+ Representation and Measurement Uncertainty

Due to the wide variation in flare gas composition and operating conditions, it is not possible to define a fixed or universally applicable fraction of heavy hydrocarbons that remain in the gas phase versus those removed upstream. Therefore, flare gas analysis must adopt a conservative and flexible representation of heavy components.

In practical GC configurations, heavy hydrocarbons are typically grouped and reported as a composite fraction (e.g., C6+ or C9+), commonly implemented using a backflush-to-detector approach. In this method, heavier components are not individually resolved but are measured as a combined signal, ensuring that no fraction is excluded from the total heating value calculation.

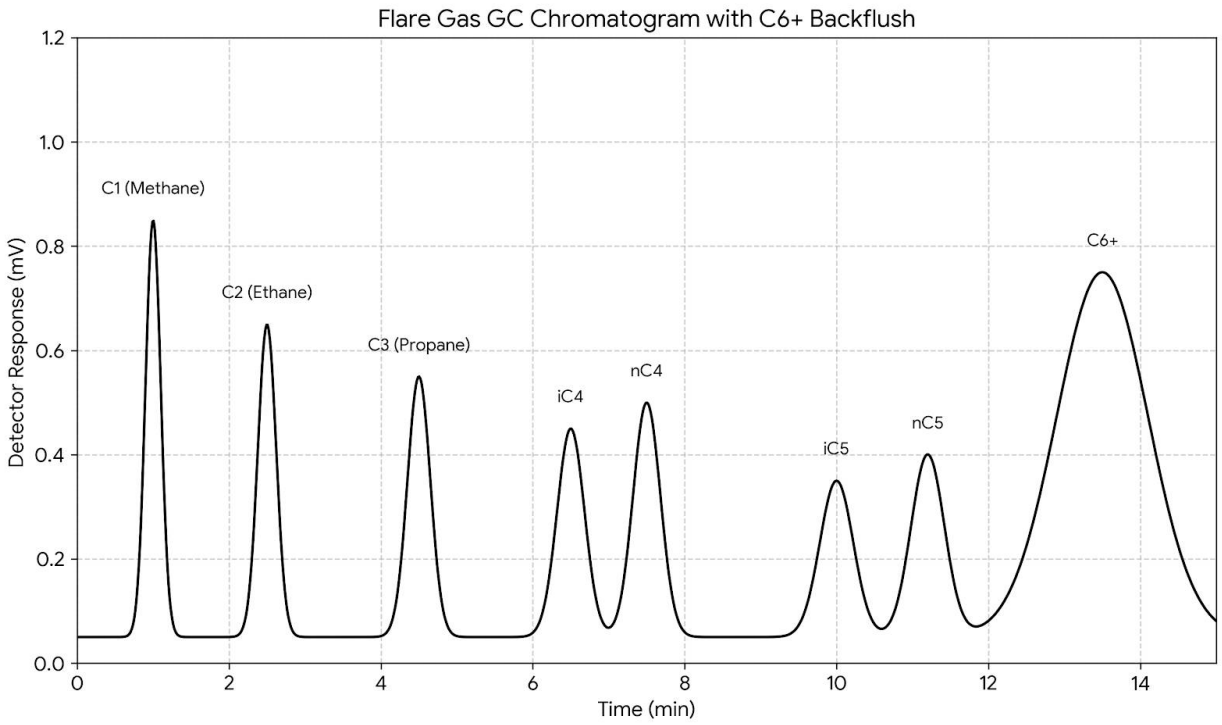
However, the accuracy of this representation depends on the calibration model used. Specifically, the definition of the C6+ fraction in the calibration gas-whether represented by a single component (e.g., n-hexane) or a mixture of heavier hydrocarbons (e.g., C6-C10)-introduces a measurable uncertainty. (Figure 7)

As demonstrated in the theoretical analysis, the choice of representation for the C6+ fraction can result in deviation in calculated heating value. While this deviation is generally small under typical refinery flare conditions, it becomes more significant during upset conditions with elevated heavy-end content.

Therefore, the selection and definition of the C6+ fraction must be aligned with both process conditions and calibration strategy to ensure accurate and consistent heating value determination.

This highlights the importance of consistency between analytical configuration, calibration methodology, and thermodynamic modeling when interpreting flare gas heating value results.

FIGURE 7. GC Chromatogram for C1-C6+

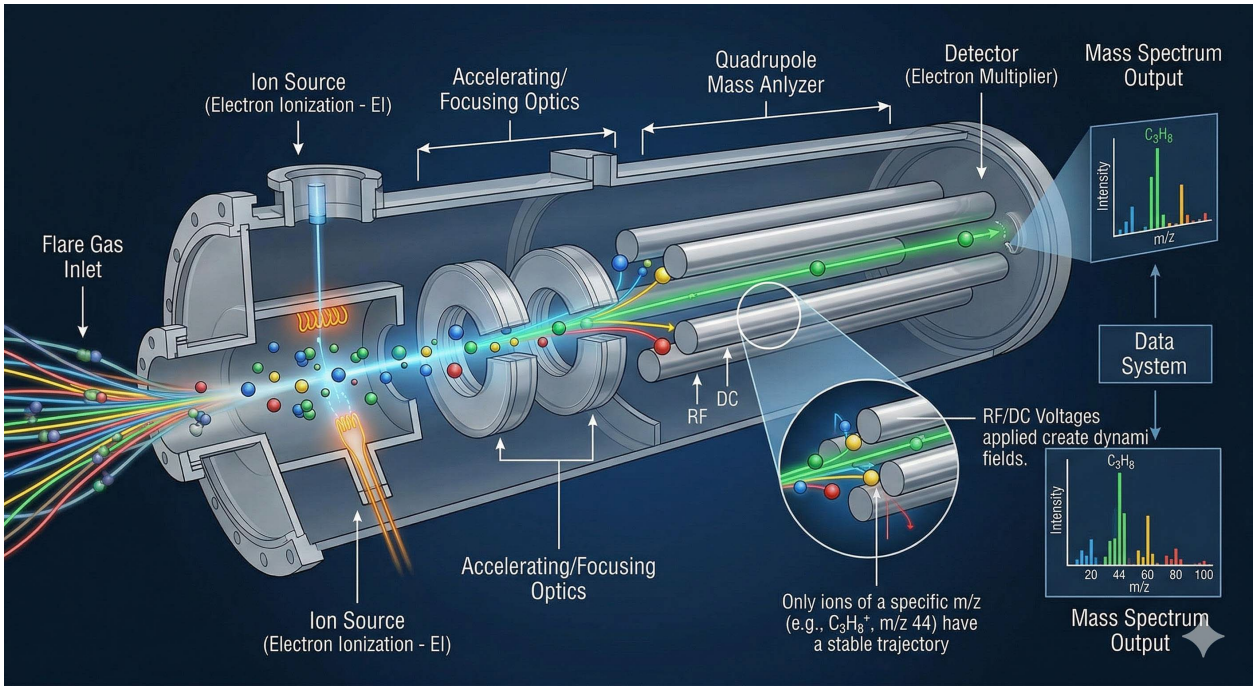


MASS SPECTROMETRY (MS)

PRINCIPLE

Process Mass Spectrometry (MS) determines gas composition by ionizing sample molecules in a high-vacuum chamber and separating the resulting ions based on their mass-to-charge ratio (m/z). Unlike gas chromatography, which performs a sequential separation, MS analyzes multiple components simultaneously using a magnetic or quadrupole field. The measured ion signals are processed using a deconvolution (matrix calculation) algorithm to determine the concentration of each component, which is then used to calculate the overall heating value (NHV). (Figure 8)

FIGURE 8. Mass Spectrophotometer Principal



ADVANTAGES

Mass spectrometry provides near real-time measurement, as it continuously analyzes the sample stream rather than operating in discrete cycles. This enables the system to capture rapid composition changes during transient flare conditions such as process upsets or blowdowns, where GC-based systems may miss short-duration peaks.

MS systems do not require carrier gases, simplifying infrastructure and reducing operating costs compared to GC systems that depend on high-purity helium or hydrogen.

The technique offers a wide dynamic range, allowing accurate measurement from low ppm levels up to high-percentage concentrations without detector saturation. This makes MS particularly suitable for flare systems that experience large composition swings.

In addition, the response of MS systems is highly linear across a broad measurement range, reducing the need for frequent multi-point calibrations.

LIMITATION AND PRACTICAL CONSIDERATIONS

One of the primary challenges in MS analysis is the fragmentation of heavier hydrocarbons. When large molecules (e.g., C6+) are ionized, they break into smaller fragments that overlap with signals from lighter components. This creates a complex

spectral pattern that requires advanced deconvolution algorithms, and the accuracy of the result depends strongly on the calibration model and spectral library.

Another key limitation is the requirement for stable vacuum operation. MS systems rely on a high-vacuum environment (typically on the order of 10^{-5} to 10^{-6} torr). The presence of condensable components or liquids can destabilize the vacuum system, degrade measurement accuracy, and potentially damage internal components. Therefore, strict phase control in the sampling system is essential.

Maintenance of MS systems is generally more specialized compared to GC. The ion source, vacuum pumps, and associated electronics require trained personnel and periodic servicing, which may increase lifecycle cost and operational complexity.

Fragmentation and Spectral Interference

A critical limitation in flare applications is mass spectral overlap. For example, hydrogen sulfide (H_2S) and oxygen (O_2) produce signals at similar mass ranges (m/z ~32–34), and heavier hydrocarbons (e.g., C6+ species) generate fragment ions that overlap with lighter hydrocarbons. In complex flare mixtures, this creates a background interference that can limit accuracy, particularly at low concentration levels.

As the number of overlapping species increases, the deconvolution problem becomes more complex, and uncertainty in calculated concentrations increases. This effect is especially significant when heavy hydrocarbons or unexpected species are present.

C6+ Representation and Measurement Approach

Unlike GC systems, MS does not use a physical backflush mechanism to manage heavy hydrocarbons. Instead, it relies on mathematical or virtual grouping methods to represent heavy-end fractions.

In this approach, heavier hydrocarbons are not individually resolved but are grouped into a composite fraction based on characteristic ion fragments. For example, the C6+ fraction may be represented using surrogate components such as n-hexane or a defined mixture (e.g., C6–C10) within the calibration model.

This ensures that no fraction is physically excluded from the measurement; however, the accuracy depends on how well the calibration model represents the actual process composition. Like GC, the definition of the heavy-end fraction introduces a level of uncertainty that must be considered in heating value calculations.

Performance and Application Considerations

While the absence of physical separation introduces dependency on modeling and calibration quality, the primary advantage of MS lies in its speed. The near real-time response enables rapid detection of composition changes and allows fast control actions, such as assist gas injection, to maintain flare performance within regulatory limits.

For dynamic flare applications where rapid response is critical, MS can provide superior operational performance compared to slower, batch-based techniques. However, this

advantage must be balanced against its sensitivity to spectral interference and the need for careful calibration and maintenance.

Therefore, MS is particularly well-suited for applications where fast response time is the primary requirement, and where the system is properly engineered to manage sampling conditions, calibration strategy, and spectral complexity.

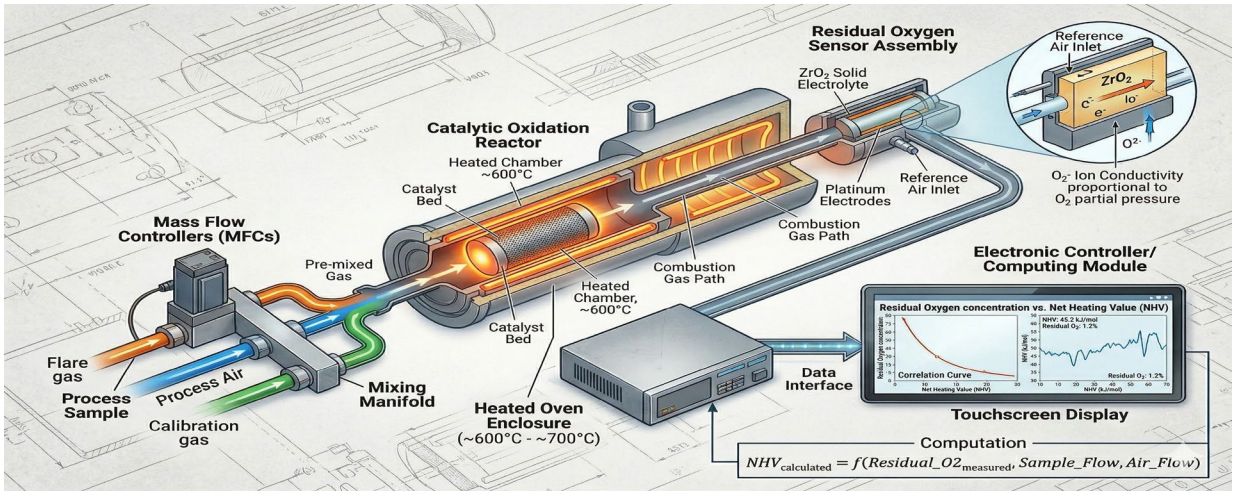
COMBUSTION-BASED CALORIMETRY (Residual Oxygen)

PRINCIPLE

Combustion-based calorimetry determines the Net Heating Value (NHV) by continuously mixing a representative flare gas sample with a controlled flow of combustion air and burning the mixture in a controlled furnace. A zirconium oxide (ZrO_2) sensor measures the residual oxygen concentration in the exhaust gas.

The NHV is calculated based on the principle that oxygen consumption is directly proportional to the heat released during combustion (calorimetric principle / Caldwell's rule). This approach provides a direct measurement of the overall 'burnability' of the gas mixture rather than relying on compositional analysis. (Figure 9)

FIGURE 9. Residual Oxygen Principal



Advantages

A primary advantage of this method is its fast response time. Since the analyzer operates in a continuous mode, it provides near real-time measurement (typically T90 of 5–15 seconds), making it highly suitable for dynamic flare conditions and automated assist gas control.

The system is relatively simple compared to GC or MS technologies, as it does not require carrier gases or high-vacuum systems. This results in lower capital cost, reduced infrastructure requirements, and simpler maintenance.

Additionally, the method inherently measures the total heating effect of the gas. Unlike compositional analyzers, it does not rely on predefined component lists and can respond to unknown or unexpected hydrocarbons entering the flare stream without requiring method reconfiguration.

LIMITATION AND PRACTICAL CONSIDERATIONS

Despite its simplicity, this method provides only a single aggregated heating value and does not offer compositional information. As a result, it cannot distinguish between individual hydrocarbon species or identify the presence of inert gases or specific sulfur compounds.

Sensor performance can be affected by contamination. High concentrations of sulfur compounds (e.g., H_2S) may degrade the ZrO_2 sensor over time or lead to corrosion

within the exhaust path. Proper material selection, periodic maintenance, and purge strategies are required to maintain reliability.

Hydrogen (H_2) Interference

One of the most critical limitations of combustion-based calorimetry is its sensitivity to hydrogen content. At elevated hydrogen concentrations (typically above 5–10%), measurement errors can become significant.

Hydrogen exhibits a higher flame speed and lower molecular weight compared to heavier hydrocarbons. This results in faster diffusion and localized combustion effects within the burner, which can distort the relationship between oxygen consumption and heat release.

In addition, hydrogen combustion produces a higher proportion of water vapor. Since residual oxygen sensors operate effectively in a wet gas environment, increased water vapor can alter the effective gas composition and introduce systematic bias in the measurement.

These combined effects typically result in an underestimation of heating value (false-low NHV) at elevated hydrogen concentrations. To mitigate this effect, some systems incorporate hydrogen compensation algorithms or auxiliary measurement channels; however, these solutions introduce additional complexity and potential uncertainty.

High Sulfur and Condensation Considerations

In applications with elevated sulfur content or heavy hydrocarbon presence, additional protective measures are required. The analyzer may operate in an intermittent injection mode, where purge cycles are used to prevent the accumulation of sulfur deposits or soot within the combustion chamber.

Furthermore, the entire analyzer system, including the sample inlet and combustion section, must be maintained at a temperature above the sulfur or hydrocarbon dew point (typically above ~150°C) to prevent condensation and solid deposition. Failure to maintain proper thermal conditions can result in plugging, corrosion, and measurement instability.

Performance Considerations

While combustion-based analyzers offer simplicity and fast response, their accuracy depends on stable combustion conditions and proper correction for interfering components. Therefore, they are best suited for applications where rapid response is prioritized and gas composition remains within a predictable range.

In highly variable flare systems, particularly those with significant hydrogen or sulfur content, careful evaluation is required to determine whether this method can meet the required accuracy and reliability for regulatory compliance and process control.

Why High H_2 Causes Errors in Calorimeters

The measurement error associated with hydrogen (H_2) in zirconium oxide–based calorimeters is primarily driven by combustion behavior and gas properties:

1. Diffusion and Flame Speed: Hydrogen has a significantly higher flame speed and lower molecular weight compared to methane or propane. In the burner, H_2 diffuses more rapidly into the flame front, causing localized combustion and distortion in oxygen consumption measurement.

2. Water Vapor Formation: Combustion of hydrogen produces a higher fraction of water vapor. Since zirconia sensors effectively measure oxygen in a wet gas basis, the increased H_2O content alters gas composition and results in a false-low NHV reading when hydrogen exceeds approximately 5–10%.

3. Compensation Requirement: To address this bias, modern analyzers may use hydrogen compensation factors or secondary measurement channels; however, these introduce additional complexity and uncertainty.

OPTICAL-SONIC (Hybrid Method)

PRINCIPLE

The optical–sonic method determines the Net Heating Value (NHV) by simultaneously measuring two independent physical properties of the gas: the speed of sound and optical characteristics. The speed of sound is primarily a function of molecular weight and thermodynamic properties, while the optical measurement is sensitive to molecular structure, particularly for hydrocarbon species.

A mathematical model combines these two measurements to estimate gas composition and corresponding heating value. This dual-parameter approach enables differentiation between gases with similar molecular weights but different chemical structures, such as distinguishing hydrogen-rich mixtures from hydrocarbon-based gases.

ADVANTAGES

One of the key advantages of the optical–sonic method is its extremely fast response time, typically in the sub-second to one-second range. This makes it highly suitable for real-time flare control applications, including rapid assist gas adjustment.

The method performs particularly well in hydrogen-rich environments, where traditional calorimetric techniques may introduce bias. Since hydrogen significantly affects the speed of sound, the analyzer can accurately capture its influence without requiring additional correction algorithms.

Operationally, the system is relatively simple. It does not require carrier gases, combustion air, or vacuum systems, resulting in lower utility requirements and reduced maintenance. The measurement is non-destructive, allowing the sample to be returned to the process if required.

LIMITATION AND PRACTICAL CONSIDERATIONS

The performance of the optical-sonic method depends strongly on maintaining a stable single-phase gas condition. If the gas temperature drops below the hydrocarbon dew point, condensation may occur within the measurement cell, leading to optical fouling and measurement drift.

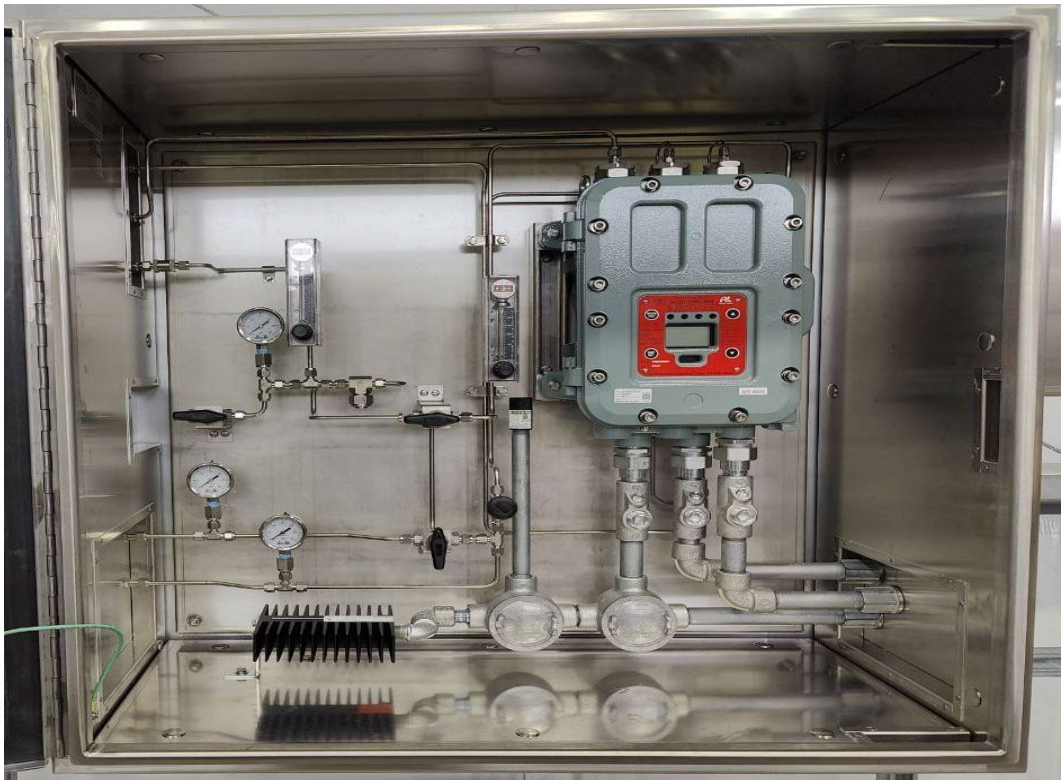
The method relies on predefined correlation models. If the actual gas composition deviates significantly from the calibration basis-particularly in the presence of unexpected heavy hydrocarbons-the accuracy of the heating value calculation may be reduced.

Because the measurement is based on physical properties, the system is sensitive to variations in pressure and temperature. Therefore, strict control of operating conditions upstream of the analyzer is required to ensure reliable performance.

Performance Considerations

The optical-sonic method is best suited for relatively clean and stable flare gas streams, especially those with high hydrogen content and limited heavy hydrocarbon presence. It is often implemented as a fast-response control analyzer, complementing more accurate but slower technologies such as gas chromatography. (Figure 10)

FIGURE 10. MMR OHC800 Flare gas system



Sulfur Measurement Overview (H_2S and Total Sulfur)

Accurate measurement of sulfur species in flare gas is essential for environmental compliance, process monitoring, and equipment protection. In refinery and petrochemical applications, sulfur measurements are primarily used to estimate potential SO_2 emissions, assess combustion performance, and evaluate corrosion risk and acid dew point conditions.

Regulatory Context and Terminology:

Under EPA 40 CFR Part 60 Subpart Ja, the distinction between different sulfur species is critical for compliance.

Hydrogen Sulfide (H_2S) is the primary toxic and corrosive sulfur compound and is typically subject to concentration limits (e.g., 162 ppmv as a 3-hour rolling average in refinery fuel gas systems).

Total Sulfur (TS) includes H_2S as well as organic sulfur compounds such as mercaptans, sulfides, and disulfides. Since all sulfur-containing compounds are ultimately converted to SO_2 during combustion, total sulfur measurement is required in applications where non-H_2S sulfur species are present in significant quantities.

In many refinery flare systems, particularly those associated with sour gas sources such as amine treating units or sour water strippers, Total Sulfur monitoring is mandatory unless it can be demonstrated that H_2S represents more than 90% of the total sulfur content.

Measurement Challenges in Flare Systems:

Flare gas composition is highly dynamic and can vary significantly during normal operation, process upsets, and emergency conditions. As a result, sulfur concentration can span several orders of magnitude, ranging from a few parts per million to several percent levels.

This wide dynamic range introduces one of the most critical engineering challenges in sulfur measurement: detector saturation. During upset conditions, rapid increases in sulfur concentration can exceed the operating range of the analyzer, leading to signal clipping, delayed recovery, or measurement bias.

Therefore, the selected analytical method must not only provide accuracy and repeatability under steady-state conditions, but also maintain reliable performance across extreme concentration swings. This includes considerations such as dynamic range, response time, recovery behavior, and resistance to contamination

Measurement Scope:

Depending on regulatory requirements and process conditions, sulfur measurement systems may be configured for selective (H_2S) or total sulfur measurement depending on regulatory requirements and process variability. The selection of the appropriate measurement technique must consider both the chemical composition of the flare gas and the required level of regulatory compliance.

Gas Chromatography (GC) for Sulfur Measurement

Principle

Gas chromatography separates sulfur-containing species such as hydrogen sulfide (H_2S), carbonyl sulfide (COS), mercaptans, sulfides, and disulfides using specialized columns and carrier gases. Each compound is detected and quantified individually, allowing total sulfur (TS) to be calculated as the sum of all measured sulfur components.

Detector Selection

The performance of sulfur GC systems is strongly dependent on detector type and configuration.

Flame Photometric Detector (FPD)

FPD provides extremely high sensitivity, particularly in the ppb to low ppm range. It is well suited for applications where H_2S is the dominant sulfur species and very low detection limits are required. However, the response is inherently non-linear, and detector saturation can occur at elevated sulfur concentrations, limiting its applicability in wide-range flare systems.

Thermal Conductivity Detector (TCD / HTCD)

High-temperature TCD (HTCD) systems offer a broader dynamic range and more linear response compared to FPD. These systems can measure sulfur concentrations from ppm levels up to percent levels without detector saturation. Although less sensitive at very low concentrations, HTCD-based GC is generally preferred for flare applications where large concentration swings are expected and robustness is required.

Advantages

A key advantage of GC-based sulfur measurement is speciation. Individual sulfur compounds can be identified and quantified, providing valuable diagnostic insight into process behavior (e.g., distinguishing H_2S from organic sulfur species during upset conditions).

GC systems can be configured for multi-stream operation, allowing multiple flare headers or process streams to be analyzed using a single analyzer platform.

In addition, GC-based systems do not require combustion air, simplifying system design compared to combustion-based sulfur analyzers.

Limitations and Practical Considerations

GC-based sulfur measurement is inherently a summation approach. The calculated total sulfur depends on the defined component list and calibration model. If an unexpected or unmeasured sulfur species enters the system, it may not be detected, resulting in underestimation of total sulfur.

The method is also subject to cycle-time limitations. Typical analysis times range from approximately 3 to 8 minutes, meaning that rapid transient sulfur spikes may not be fully captured.

High sulfur concentrations and complex mixtures can introduce matrix effects, including peak overlap and the need for advanced chromatographic techniques such as heart-cutting to maintain separation performance.

Analytical Coverage and Species Limitation

A practical limitation of GC-based sulfur measurement is the restricted number of sulfur species that can be included in the analytical configuration. Due to constraints in cycle time and column design, it is not feasible to program and resolve a large number of sulfur compounds, particularly heavier mercaptans and complex sulfur species.

As a result, some sulfur-containing components may not be individually measured or included in the calibration model, leading to potential underestimation of total sulfur.

Application Context and Relevance

In typical refinery flare applications, this limitation is often less critical because hydrogen sulfide (H_2S) is the dominant sulfur species and the contribution of complex organic sulfur compounds is relatively small.

However, in applications such as natural gas custody transfer, where accurate total sulfur speciation is required, this limitation becomes more significant and must be carefully considered.

Performance Considerations

While GC provides detailed and accurate sulfur speciation, its performance depends on proper selection of detector type, calibration strategy, and column configuration. For flare gas monitoring, HTCD-based systems are generally more robust for wide-range applications, while FPD-based systems are preferred where ultra-low detection limits are required.

Mass Spectrometry (MS) for Sulfur Measurement

Principle

Mass spectrometry identifies sulfur-containing compounds based on their molecular mass and ion fragmentation patterns. In principle, MS can detect key sulfur species such as hydrogen sulfide (H_2S) and sulfur dioxide (SO_2), and can be integrated into broader gas analysis systems.

For total sulfur (TS) measurement, MS systems typically require an external thermal oxidizer (furnace) to convert all sulfur species into SO_2 prior to analysis. This

requirement increases system complexity and reduces one of the inherent advantages of MS, namely direct and simplified measurement.

Limitations and Critical Considerations

The primary limitation of MS for sulfur measurement is spectral interference caused by mass overlap and fragmentation, particularly in complex flare gas mixtures.

Mass Overlap and Fragmentation Effects

Hydrogen sulfide (H_2S) with a molecular weight of 34 can overlap with oxygen-related signals due to isotopes and fragment ions. This creates ambiguity in signal interpretation and requires advanced deconvolution algorithms to resolve.

Similarly, sulfur dioxide (SO_2) at m/z 64 can overlap with fragments from heavier hydrocarbons. In flare gas systems, where hydrocarbon composition is highly variable, this results in a dynamic spectral background that complicates accurate sulfur quantification.

Matrix and Background Effects

The presence of heavy hydrocarbons introduces additional spectral fragments, increasing background noise and reducing the accuracy of low-level sulfur measurements. As the number of overlapping species increases, the uncertainty in deconvolution results also increases.

This limitation becomes particularly critical when attempting to measure sulfur at low ppm levels required for regulatory compliance.

Adsorption and Memory Effects

Sulfur compounds, especially H_2S, can adsorb onto internal surfaces within the MS vacuum system. This can lead to signal lag, memory effects, and delayed recovery following transient events, reducing measurement reliability during dynamic flare operation.

Total Sulfur Limitation

Without an external combustion or oxidation system, MS does not provide true total sulfur measurement. Adding a furnace introduces complexity comparable to ultraviolet fluorescence systems, while still retaining the inherent spectral and adsorption limitations of MS.

Performance Considerations

Mass spectrometry offers fast response and can provide a general sulfur trend, typically within seconds. This makes it useful for qualitative monitoring or integration with multi-component gas analysis platforms.

However, due to spectral interference, adsorption effects, and calibration dependency, MS is generally not suitable for accurate, low-level sulfur measurement in applications requiring regulatory compliance.

Conclusion

Despite its advantages in general gas analysis, mass spectrometry is typically not recommended as a primary method for sulfur measurement in refinery flare systems. The combination of spectral interference, adsorption effects, and calibration complexity makes it less reliable than dedicated sulfur measurement technologies for compliance-driven applications.

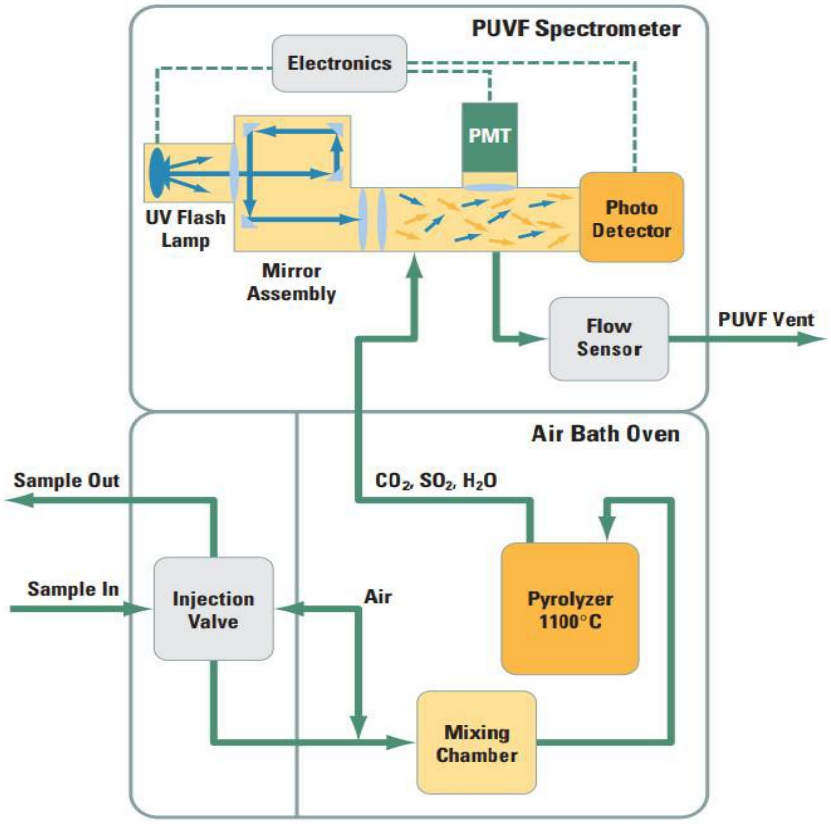
Ultraviolet Fluorescence (UVF) with Thermal Oxidation

Principle

Ultraviolet fluorescence (UVF) is a two-stage analytical method used for total sulfur measurement. In the first stage, the sample is mixed with combustion air and passed through a high-temperature furnace (typically 900–1100°C), where all sulfur-containing compounds—such as hydrogen sulfide (H_2S), carbonyl sulfide (COS), mercaptans, sulfides, and disulfides—are quantitatively converted to sulfur dioxide (SO_2).

In the second stage, the generated SO_2 is exposed to ultraviolet (UV) radiation, causing the molecules to emit fluorescence at a characteristic wavelength. The intensity of this emitted light is directly proportional to the sulfur concentration, allowing accurate determination of total sulfur. (Figure 11)

FIGURE 11. SOLAII-UVF Total sulfur analyzer



Regulatory Alignment

UV fluorescence is widely recognized as a reference method for total sulfur measurement and is aligned with EPA requirements (e.g., 40 CFR Part 60 Subpart Ja). Because all sulfur species are converted to a single measurable form (SO_2), the method inherently captures both H_2S and non-H_2S sulfur compounds, eliminating the risk of underreporting due to unknown or unmeasured species.

Advantages

The primary advantage of UVF is its ability to provide a true total sulfur measurement. Since all sulfur compounds are converted to SO_2, the method does not depend on predefined component lists or calibration assumptions for individual species.

UV analyzers offer a wide dynamic range, typically covering concentrations from low ppm levels up to percent levels with appropriate configuration. This makes them well suited for flare gas applications, where sulfur concentrations can vary significantly during process upsets.

The method provides stable and repeatable measurements, as it is less sensitive to compositional variability compared to GC or MS systems. In addition, the response time (typically 5–15 seconds) is sufficient to meet regulatory reporting requirements, including 15-minute averaging under dynamic flare conditions.

Limitations and Critical Considerations

The accuracy of the UVF method depends on complete conversion of sulfur compounds in the furnace. Any deviation in furnace temperature, residence time, or air-to-fuel ratio may result in incomplete oxidation, leading to underestimation of total sulfur.

Interfering species can also affect measurement accuracy. Compounds such as nitric oxide (NO) or certain aromatic hydrocarbons may produce signals in similar wavelength regions, requiring the use of internal scrubbers or optical filters to remove these interferences.

The method requires supporting utilities, including a stable supply of combustion air (or oxygen) and, in some configurations, fuel gas for burner stabilization. Proper system design is essential to ensure reliable operation under varying process conditions.

Performance Considerations

UV fluorescence is particularly well suited for applications where accurate and reliable total sulfur measurement is required for regulatory compliance. Its ability to handle unknown or variable sulfur compositions, combined with a wide dynamic range, makes it one of the most robust techniques for flare gas monitoring.

Conclusion

For refinery and petrochemical flare systems, UV fluorescence is generally considered the preferred method for total sulfur measurement. Its capability to convert all sulfur species into a single measurable component, combined with stable performance under dynamic conditions, provides a high level of confidence for compliance monitoring and reporting.

Lead Acetate Tape

Principle

The lead acetate tape method is a colorimetric technique used for measuring hydrogen sulfide (H_2S). The sample gas is exposed to a continuously moving tape impregnated with lead acetate. When H_2S is present, it reacts to form lead sulfide (PbS), which darkens the tape. An optical sensor measures the rate of change in darkness, which is directly proportional to the H_2S concentration.

Total Sulfur Configuration

To extend this method for total sulfur (TS) measurement, a thermal conversion stage is required. The sample is mixed with hydrogen and passed through a high-temperature furnace (~900°C), where organic sulfur compounds are converted to H_2S. The converted H_2S is then measured using the tape system.

Limitations and Operational Risks

While the method is highly sensitive at low concentrations, it presents significant operational challenges in refinery flare applications.

Heavy Hydrocarbon (C_3+) Interference: In flare gas streams containing propane or heavier hydrocarbons, the hydrogen-based furnace can promote cracking reactions, leading to soot formation. This can foul the furnace, contaminate the tape, and result in measurement drift or system failure.

Range Limitations: Lead acetate systems are typically configured for specific measurement ranges. Switching between low-level and high-level measurements requires different optical configurations and cannot be easily adjusted in the field.

Consumables and Waste Handling: The method requires continuous consumption of tape rolls and hydrogen gas. Used tape is classified as hazardous waste due to lead content and must be disposed of according to environmental regulations.

Performance Considerations

Although the lead acetate method provides high sensitivity for H_2S detection, its susceptibility to fouling, maintenance requirements, and operational limitations make it less suitable for modern flare gas applications, particularly under conditions involving heavy hydrocarbons or wide concentration variability.

Conclusion

For refinery flare monitoring under EPA 40 CFR Part 60 Subpart Ja, ultraviolet fluorescence (UVF) with thermal oxidation is generally considered the most robust and reliable method for total sulfur measurement.

Its ability to convert all sulfur species into a single measurable component (SO_2), combined with a wide dynamic range and stable performance under transient conditions, provides a high level of confidence for compliance monitoring.

While gas chromatography offers valuable speciation capabilities, and other methods such as lead acetate or mass spectrometry may be applicable in specific scenarios, these techniques present limitations in dynamic flare environments.

Therefore, the selection of sulfur measurement technology should be based on a balance between measurement accuracy, dynamic response, operational reliability, and process-specific constraints.

SYSTEM INTEGRATION AND CONTROL LOGIC

Integrated Analyzer System (IAS)

The successful monitoring of refinery flare gas requires the integration of multiple analytical technologies within a unified, climate-controlled environment.

The Integrated Analyzer System (IAS) is designed to manage the complete sample lifecycle, from extraction and conditioning to measurement and data validation. The objective is to ensure that the physical gas sample is converted into a reliable and legally defensible digital record for regulatory reporting.

Unified Sampling and Flow Architecture

To minimize lag time and simplify maintenance, a single high-flow suction loop is used to transport flare gas from the process header to the analyzer shelter.

Within the shelter, the sample stream is divided into multiple slipstreams, each dedicated to a specific measurement function:

Sulfur Measurement Stream: Directed to UV Fluorescence or GC-based sulfur analyzers

Heating Value Stream: Directed to calorimetric analyzers for fast control response or GC/MS for compositional analysis

Common Return Line: All bypass and excess sample flows are collected and returned through a heated manifold to a low-pressure flare point or a safe disposal system

This architecture ensures consistent sample conditions across all analyzers while maintaining high system responsiveness.

Control System and Data Acquisition (DAS)

The IAS is controlled by a Programmable Logic Controller (PLC) or a dedicated Data Acquisition System (DAS). The control system performs several critical functions:

Averaging: The system calculates 15-minute block averages for both Net Heating Value (NHV) and Total Sulfur, in accordance with EPA requirements (e.g., 40 CFR § 60.107a and § 63.670).

Validation (Calibration Cycles): Automated daily Zero and Span checks are performed. If analyzer drift exceeds predefined thresholds (e.g., >10%), the system flags the data as invalid or requires maintenance action.

Assist Gas Control: If the measured NHV drops below the regulatory threshold (typically ~270 Btu/scf), the control system automatically sends a signal to inject assist gas (natural gas) into the flare header to maintain combustion stability.

Safety Integration and Hazard Management

Given that flare gas contains flammable and toxic components (e.g., H_2S), the IAS must incorporate multiple layers of safety protection:

Gas Detection Systems: Continuous H_2S and LEL monitoring within the analyzer shelter

Emergency Shutdown Logic: Automatic shutdown of sample pumps and activation of purge systems in case of hazardous conditions

Purge and Ventilation: Continuous or on-demand purging of the enclosure to maintain safe operating conditions

System-Level Considerations

The effectiveness of the IAS depends on the coordinated operation of all subsystems, including sampling, heating, analysis, and control.

Any failure in sample integrity (e.g., condensation), analyzer performance (e.g., saturation), or control logic can directly impact regulatory compliance.

Therefore, system integration must be treated as a critical engineering function, rather than a simple combination of individual components.

CONCLUSION: THE STRATEGIC VALUE OF FLARE MONITORING

Process Integrity and Upstream Reliability

The success of any flare monitoring strategy begins with proper upstream separation, particularly the performance of the Knock-Out (KO) Drum. As the primary barrier between the process and the flare header, the KO Drum plays a key role in ensuring sample integrity.

A properly functioning KO Drum prevents liquid carryover that can damage sampling systems and analyzers. Without effective upstream separation, measurement errors may occur, leading to inaccurate reporting, false compliance violations, and potential operational risks.

Economic Impact: Fuel Loss vs. Emission Cost

Flare monitoring provides both environmental and economic value. While analyzers do not physically recover gas, they quantify energy losses associated with flaring events.

For example, a continuous flaring rate can represent significant financial loss when translated into fuel value. In addition, regulatory frameworks such as methane emission reduction programs impose financial penalties for emissions, making accurate monitoring essential for cost control.

Environmental and Operational Synergy

Modern flare monitoring systems support both environmental protection and process reliability.

Maintaining sufficient Net Heating Value (NHV) ensures complete combustion and reduces the release of toxic compounds such as H_2S. At the same time, high-speed analyzers provide early detection of process upsets, enabling operators to identify and resolve upstream issues before they escalate.

Final Remarks

Flare monitoring systems should be considered strategic engineering assets rather than simple compliance tools. By integrating robust sampling design, appropriate analytical methods, and reliable control logic, refineries can achieve a balanced approach to environmental responsibility, operational safety, and economic efficiency.

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