

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

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## 1. Abstract

Accurate flare emissions analysis is essential for environmental compliance, from monitoring the disposal amount of downstream refinery units, to controlling the amount of emission to a minimum and efficient combustion control.

These analysis will also monitor the process conditions of the flare line if any rupture discs, safety valves, or safe-to-open valve outputs are activated during process shutdown to see what the heat value released in the flare will be when all outputs are activated simultaneously and a large volume of process gases at maximum pressure are directed towards the flare.

This paper highlights the critical roles of heating value, sulfur measurement and sampling system design to achieve reliable flare analysis performance.

Emphasizing their application under variable flare line process conditions. Special attention is given to the sampling system, where proper probe design, heating, filtration, and back-purging ensure representative and stable measurements. Practical insights show how errors in sampling or BTU and total sulfur analysis can impact emission reporting and downstream process control.

Of course, measuring the flow rate of the flare line is required for this application, but we will omit it due to the focus of this article on the analyzer.

## 2.Introduction

Refinery flares serve as critical safety devices designed to safely burn excess hydrocarbon gases during both routine operations and emergency process conditions. Proper operation of flares ensures that combustible gases are efficiently destroyed, minimizing the release of unburned hydrocarbons and reducing environmental impact. Also, by monitoring and minimizing it, huge economic savings can be achieved in the utility, feed and fuel costs of the refinery.

In recent years, environmental regulations have placed increasing emphasis on flare performance monitoring, particularly on ensuring adequate combustion efficiency and having minimal flaring.

Traditional air pollution monitoring systems, such as Continuous Emission Monitoring Systems (CEMS), continuous ambient emission monitoring system (CAMS) or Portable emission /ambient monitoring system (PEMS/PAMS) are used to measure individual pollutants like CO, SO<sub>2</sub>, NO<sub>x</sub>, CO<sub>2</sub>, O<sub>3</sub>, Particle matter (PM<sub>10</sub>/PM<sub>2.5</sub>) from combustion stacks. These systems are well-suited for fixed / portable exhaust/ambient sources where combustion takes place within a defined stack / ambient.

However, flare systems differ significantly because combustion occurs in open air, where it is not feasible to directly measure combustible components directly. Instead, monitoring focuses on measuring the heating value and total sulfur.

Accurate measurement of flare gas heating value is essential for ensuring proper combustion and compliance with regulations such as U.S. EPA 40 CFR Part 60 Subpart Ja and 40 CFR Part 63 Subpart CC, which define performance requirements for refinery flare operation. However, flare gas composition can vary dramatically depending on process conditions, particularly during startups, shutdowns, or upsets

These dynamic conditions make it challenging to obtain a representative, stable, and reliable sample for heating value and total sulfur analyzers.

Therefore, the design of a sampling system capable of handling variable flow, pressure, temperature, phase stability and composition is critical for reliable data acquisition.

Proper sample probe, sample conditioning, transport, disposal and analyzer selection directly influence measurement stability and repeatability.

A well-engineered sampling system must minimize lag time, prevent condensation or phase separation, and maintain consistent delivery of a representative sample to the analyzer. This paper explores the principles, challenges, and design strategies for effective flare gas sampling, heating value and total sulfur measurement.

Emphasis is placed on achieving repeatable and accurate results across varying process conditions to ensure compliance, reliability, and long-term operational stability.

### 3. Principles of Heating Value Measurement

The heating value expresses the total thermal energy released by complete combustion of a unit quantity of fuel. Two definitions apply:

- Higher Heating Value (HHV): heat released when all water produced during combustion condenses to liquid at reference temperature.
- Lower Heating Value (LHV): heat released when combustion products remain gaseous and water stays in vapor form.

And analyzers measure HV based on water vapor (LHV) and then calculate HHV, so we will only consider LHV here.

For a mixture with component mole fractions

$$\text{LHV}_{\text{mix}} = \sum (x_i \times \text{LHV}_i)$$

Example:

No	Gas Name	Vol%	Mol%	STD MJ/Mol	LHV MJ/Mol
1	CH <sub>4</sub>	64	0.64	0.802	0.51328
2	C <sub>2</sub> H <sub>6</sub>	11	0.11	1.432	0.15752
3	C <sub>2</sub> H <sub>4</sub>	2	0.02	1.333	0.02666
4	C <sub>3</sub> H <sub>8</sub>	4	0.04	2.046	0.08184
5	C <sub>3</sub> H <sub>6</sub>	3	0.03	1.884	0.05652
6	CH <sub>4</sub> H <sub>10</sub>	4	0.04	2.65	0.106
7	C <sub>5</sub> H <sub>12</sub>	3.5	0.035	3.257	0.113995
8	C <sub>6+</sub> (n-C <sub>6</sub> )	1	0.01	3.887	0.03887
9	N <sub>2</sub>	2	0.02	0	0
10	CO <sub>2</sub>	0.5	0.005	0	0
11	H <sub>2</sub>	5	0.05	0.242	0.0121
<b>Total</b>		<b>100</b>	<b>1</b>		<b>1.106785</b>

Given that C6+ usually contains heavy thrust compounds, we will divide it into heavier compounds to see the result.

No	Gas Name	Vol%	Mol%	STD MJ/Mol	LHV MJ/Mol
1	CH4	64	0.64	0.802	0.51328
2	C2H6	11	0.11	1.432	0.15752
3	C2H4	2	0.02	1.333	0.02666
4	C3H8	4	0.04	2.046	0.08184
5	C3H6	3	0.03	1.884	0.05652
6	CH4H10	4	0.04	2.65	0.106
7	C5H12	3.5	0.035	3.257	0.113995
8	n-C6	0.2	0.002	3.887	0.007774
9	n-C7	0.2	0.002	4.497	0.008994
10	n-C8	0.2	0.002	5.107	0.010214
11	n-C9	0.2	0.002	5.717	0.011434
12	n-C10	0.2	0.002	6.327	0.012654
13	N2	2	0.02	0	0
14	CO2	0.5	0.005	0	0
15	H2	5	0.05	0.242	0.0121
<b>Total</b>		<b>100</b>	<b>1</b>	<b>39.181</b>	<b>1.118985</b>

It can be seen that the result has changed significantly.

Therefore, it is emphasized that in calorific value analyzers, the sample should not be cooled or condensed under any circumstances, because heavy hydrocarbon compounds will have a great impact on the calorific value analysis result, and there will be a difference between the reality of the process and the analyzer result.

This measurement difference will be much more noticeable when the unit of measurement is based on volume or mass, especially in process conditions .

Calculating LHV based on volume and mass units:

$LHV_v = LHV_{mol} \times (P_{std} / ZRT_{std})$  , STD condition: T=288.15K , P=101.325kps

$LHV_v(C6+) = 46.79 \text{ MJ/m}^3$

$LHV_v(C6-C10) = 47.30 \text{ MJ/m}^3$

$LHV_m = LHV_{mol} / M_{mix}$  ,  $M_{mix}: 0.02 \text{ kg/mol}$

$LHV_m(C6+) = 55.34 \text{ MJ/kg}$

LHVm(C6-C10)= 55.95 MJ/Kg

The difference in the measurements between the two cases is about 0.5. Take this deviation and multiply it by your flow rate and your overall required heating value becomes exponentially different. This of course also depends on the actual components in the stream that are aa or above C7. This explanation is more visible when looking at actual process conditions.

(a flare flowmeter is also a requirement of the flare monitoring system).

Below are 2 Hysys simulations, both cases under process conditions, assuming that the entire sample is in the gas phase and no part of it has condensed.

Case1:C6+=N-C6

Worksheet		Mole Fractions	Vapour Phase
Conditions	Methane	0.6400	0.6400
Properties	Ethane	0.1100	0.1100
Composition	Propane	0.0400	0.0400
Oil & Gas Feed	Propene	0.0300	0.0300
Petroleum Assay	n-C14	0.0400	0.0400
K Value	n-Pentane	0.0350	0.0350
User Variables	n-Hexane	0.0100	0.0100
Notes	Hydrogen	0.0500	0.0500
Cost Parameters	CO2	0.0050	0.0050
Normalized Yield	Nitrogen	0.0200	0.0200
	Ethylene	0.0200	0.0200

Worksheet	Stream Name	1	Vapour Phase
Conditions	Molecular Weight	29.37	29.37
Properties	Molar Density [kgmole/m3]	3.340e-002	3.340e-002
Composition	Mass Density [kg/m3]	0.9808	0.9808
Oil & Gas Feed	Act. Volume Flow [m3/h]	1.336e+004	1.336e+004
Petroleum Assay	Mass Enthalpy [kJ/kg]	-2499	-2499
K Value	Mass Entropy [kJ/kg-C]	7.519	7.519
User Variables	Heat Capacity [kJ/kgmole-C]	70.16	70.16
Notes	Mass Heat Capacity [kJ/kg-C]	2.389	2.389
Cost Parameters	LHV Vol Basis (Std) [MJ/m3]	1.355e+006	1.355e+006
Normalized Yield	HHV Vol Basis (Std) [MJ/m3]	1.471e+006	1.471e+006
	HHV Mass Basis (Std) [kJ/kg]	5.009e+004	5.009e+004
	CO2 Loading	<empty>	<empty>
	CO2 Apparent Mole Conc. [kgmole/m3]	<empty>	<empty>
	CO2 Apparent Wt. Conc. [kgmol/kg]	<empty>	<empty>
	LHV Mass Basis (Std) [kJ/kg]	4.614e+004	4.614e+004
	Phase Fraction [Vol. Basis]	1.000	1.000
	Phase Fraction [Mass Basis]	4.614e+004 kJ/kg	1.000
	Phase Fraction [Act. Vol. Basis]	1.103e+004 kcal/kg	1.000
	Partial Pressure of CO2 [kPa]	1.984e+004 Btu/lb	<empty>
	Cost Based on Flow [Cost/ol]	0.0000	0.0000

Case2: C6+= n-C6 , n-C7 , n-C8 , n-C9 , n-C10

Worksheet	Mole Fractions	Vapour Phase
Conditions	Methane 0.6400	0.6400
Properties	Ethane 0.1100	0.1100
Composition	Propane 0.0400	0.0400
Oil & Gas Feed	Propene 0.0300	0.0300
Petroleum Assay	n-C14 0.0400	0.0400
K Value	n-Pentane 0.0350	0.0350
User Variables	n-Hexane 0.0020	0.0020
Notes	Hydrogen 0.0500	0.0500
Cost Parameters	CO2 0.0050	0.0050
Normalized Yield	Nitrogen 0.0200	0.0200
	Ethylene 0.0200	0.0200
	n-Heptane 0.0020	0.0020
	n-Octane 0.0020	0.0020
	n-Nonane 0.0020	0.0020
	n-Decane 0.0020	0.0020

Worksheet	Stream Name 1	Vapour Phase
Conditions	Molecular Weight 29.65	29.65
Properties	Molar Density [kgmole/m3] 3.340e-002	3.340e-002
Composition	Mass Density [kg/m3] 0.9902	0.9902
Oil & Gas Feed	Act. Volume Flow [m3/h] 1.336e+004	1.336e+004
Petroleum Assay	Mass Enthalpy [kJ/kg] -2487	-2487
K Value	Mass Entropy [kJ/kg-C] 7.479	7.479
User Variables	Heat Capacity [kJ/kgmole-C] 70.79	70.79
Notes	Mass Heat Capacity [kJ/kg-C] 2.388	2.388
Cost Parameters	LHV Vol Basis (Std) [MJ/m3] 1.367e+006	1.367e+006
Normalized Yield	HHV Vol Basis (Std) [MJ/m3] 1.484e+006	1.484e+006
	HHV Mass Basis (Std) [kJ/kg] 5.006e+004	5.006e+004
	CO2 Loading <empty>	<empty>
	CO2 Apparent Mole Conc. [kgmole/m3] <empty>	<empty>
	CO2 Apparent Wt. Conc. [kgmol/kg] <empty>	<empty>
	LHV Mass Basis (Std) [kJ/kg] 4.612e+004	4.612e+004
	Phase Fraction [Vol. Basis] 1.000	1.000
	Phase Fraction [Mass Basis] 4.612e+004 kJ/kg	1.000
	Phase Fraction [Act. Vol. Basis] 1.102e+004 kcal/kg	1.000
	Partial Pressure of CO2 [kPa] 1.983e+004 Btu/lb	<empty>
	Cost Based on Flow [Cost/s] 0.0000	0.0000
	Act. Gas Flow [ACT_m3/h] 1.336e+004	1.336e+004
	Avg. Liq. Density [kgmole/m3] 14.41	14.41
	Specific Heat [kJ/kgmole-C] 70.79	70.79
	Std. Gas Flow [STD_m3/h] 1.055e+004	1.055e+004
	Std. Ideal Liq. Mass Density [kg/m3] 427.2	427.2
	Act. Liq. Flow [m3/s] <empty>	<empty>
	Z Factor 0.9976	0.9976

Given that the concentration of heavy compounds is considered in the worst case, it seems that the measurement values for the two cases are approximately close. We will use this result in the following discussions of measurement method.

## 4. Sampling System Design and Considerations

Designing a reliable flare gas sampling system requires attention to **representativeness**, response time, contamination control, and system stability.

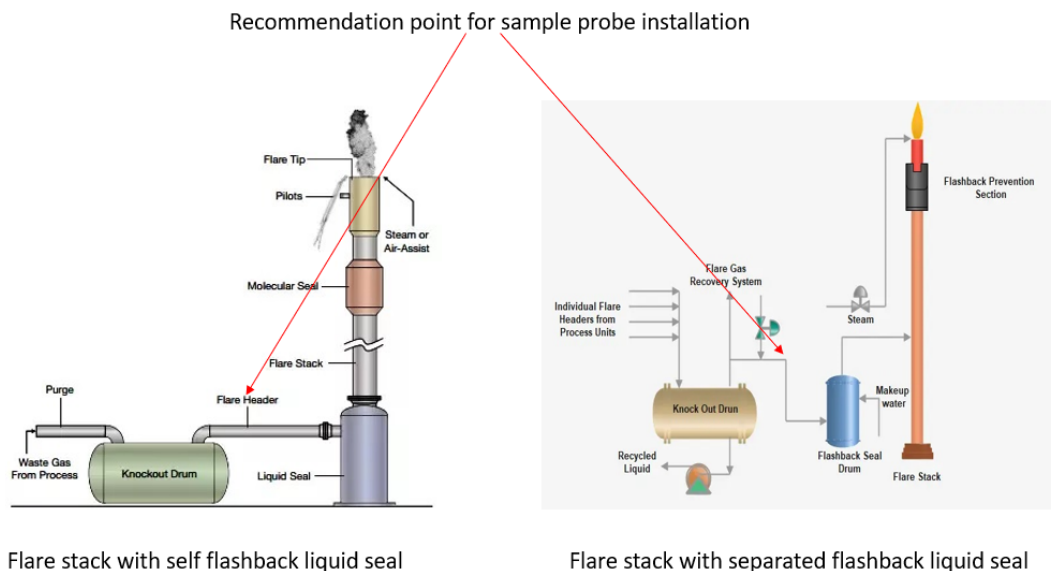
**Not sure what concept you were trying to capture in the above highlight, but we should find a word better suited for this sentence.**

Because flare gas conditions are highly variable and often contaminated, the system must maintain sample integrity from the tapping point to the analyzer under all operating scenarios.

### 4.1 Sampling Probe and Tapping Point

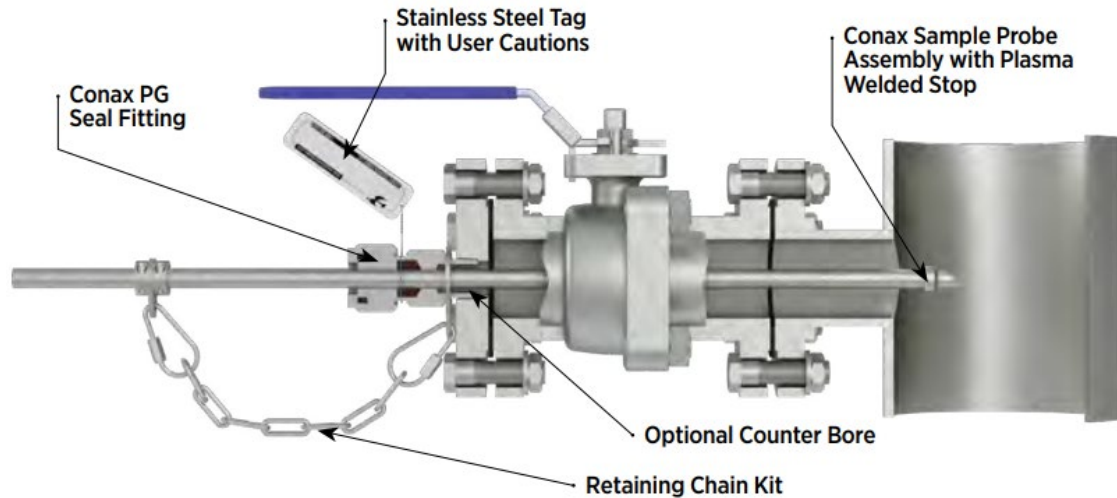
In refinery flare systems, the probe location is critical. It should be installed between the oil separator knockout drum and the water wash seal drum, where gas composition is stable and liquid content is minimal.

Of course, we have two types of water seal drums, which you can see in the figures below: The water seal drum is included in the flare, and the other model is separate. In the separate model, you might think that it is better to take the sample after the water seal drum because it is cleaner, but because the main role of the water seal drum is to act as a hydraulic flashback arrestor, for safety reasons, we are not allowed to sample after the water seal drum. **What is the reason this is not allowed, you stated because it's a flashback arrestor but what are the details behind why we cannot or should not measure from there?**



The role of the oil separator drum is very important and it functioning properly, has a direct impact on the performance of the flare and the analyzer monitoring it.





**Note: Since heavy hydrocarbon compounds have a major impact on the calorific value of the measured gas, it is prohibited to consider any gas cooling instrument.**

**Of course, the use of a knockout pot is necessary to remove possible condensates when the process knockout drum is not working properly, or the process conditions are out of control in order to maintain the health of the analyzer system.**

Cleaning should be automated through steam or nitrogen purging. To manage high hydrocarbon or acid dew points, the probe should be fully heated with a temperature controller and installed in an insulated enclosure.

Given that good quality steam is available in the flare area, the best option for backwashing the probe is to use steam. It is essential to ventilate the probe for backwashing so that the pressure and temperature of the steam do not damage the probe components.

Because air contains oxygen, it is not recommended as a backflow fluid.

#### 4.2 Sample Transport line

After extraction, the sample must be transported and conditioned to maintain its chemical and physical integrity. Flare headers operate at low pressures (typically <10 psig), making a heated suction pump mandatory to ensure continuous flow. The pump must be corrosion-resistant, heated, and pressure-controlled.

Heated sample lines should be maintained above the dew points with PID temperature controllers. Materials must be NACE-certified, and Sulfur inert coating or Monel may be required for high sulfur content.

Heated bundle tube temperature setpoint calculations should be at least 20% higher than the hydrocarbon dew point under worst-case process conditions (shutdown).

It is essential to consider installation accessories with area protection class appropriate to the project conditions.

Sample transfer lines between the sampling system and analyzer must also be fully heated.

### 4.3 Sample Handling System

The sample handling system ensures that the gas extracted from the heated sample probe is delivered to the analyzer under stable conditions (pressure, flow and temperature) by the heated manifold tube. In this application, since the line pressure at the flare tapping point is less than 5 PSI, a heated sample pump is used to increase the pressure, maintain a constant flow, overcome the pressure drop of the system and the transfer line, and ensures sufficient velocity through the filters and bypass loops to minimize delay time.

Note that the pump outlet pressure and temperature must be controlled so that condensation of the sample does not occur in the sampling system. Calculation and control of the hydrocarbon dew point is required considering the pump outlet pressure and the sampling system temperature setpoint to avoid drop out of an analyte prior to measurement.

A particulate filter (typically 2–5  $\mu\text{m}$ ) is installed before the analyzer to protect sensitive optical or thermal sensors. The filter housing and lines are made of 316 SS NACE resist corrosion from  $\text{H}_2\text{S}$  and other sour components. Add in a point about Swageloks sour gas service cleaning? Add something in about Parker R-Max valves later if applicable.

Flow and pressure are controlled via a needle valve and backpressure regulator located downstream of the analyzer. A bypass loop allows high-velocity flow for fast response while maintaining a reduced, steady flow through the analyzer cell.

The system includes optional safety features such as a flame arrestor, check valves, and pressure relief to protect both the analyzer and operator during maintenance or abnormal flare backflow conditions or high flare pressures. Each component is designed for continuous operation in hazardous areas with appropriate electrical classification and grounding.

Usually, the head of these pumps is placed inside the sampling system and the electric motor with suitable protection class is coupled to the pump from outside the sampling system.

Or the pump head has an electric or steam heater with a temperature sensor and its own controller.

In the images below, you can see examples of Heated pumps.

4.4?



Two models of diaphragm pumps from ADI with the ability to install heads in heated sampling systems



Buhler diaphragm pump with head mounting capability in a heated sampling system using a flange coupling

A multi-stage filtration system is essential for extracting the sample from the point of collection to entry into the analyzer. The primary filter, made of sintered stainless steel with 10–50  $\mu\text{m}$  mesh, is installed at the probe tip and equipped with automatic back-purging using steam or nitrogen.

The secondary stage combines a coalescing filter and membrane separator to remove fine dust and oil mist. The final polishing filter (0.1–1  $\mu\text{m}$ ) may be used before the analyzer. Heated knockout pots with automatic drainage to safe disposal point and self-cleaning are required for sticky, high-density condensates.

Differential pressure gauges and automatic purge sequences are necessary for maintenance. The filtration design ensures reliable, continuous, and contamination-free operation under dynamic flare conditions.

The system includes optional safety features such as a flame arrestor, non-return valve, and pressure relief to protect both the analyzer and operator during maintenance or abnormal flare backflow conditions. Each component is designed for continuous operation in hazardous areas with appropriate electrical classification and grounding. Repeat

Non-intrusive monitoring of flow and pressure through sight windows or remote displays is essential, avoiding the need to open the enclosure. Automatic calibration systems with multi-port valves and NIST-traceable gases must be integrated for reliable and repeatable results.

#### 4.5 Analyzer Panel Design, Installation, and Safety Considerations

Analyzer shelter must comply with IEC 61285 for internal and external design, wiring, and safety. They must also be installed at a safe distance from the flare to minimize exposure to radiant heat. The enclosure walls should be double-layered and insulated with mineral wool or ceramic fiber, with reflective surfaces facing the flare.

HVAC systems are required to maintain internal temperatures between 20–35°C even when ambient temperatures exceed 55°C. Panels must be rated at least IP55/NEMA 4X with corrosion-resistant stainless-steel construction. Accessibility, viewing windows, and safe electrical entry are mandatory. Heated sample lines must be properly routed and sealed to avoid cold spots or condensation.

#### 4.6 Disposal Unit

The disposal or vent unit handles the analyzer outlet stream safely after measurement. In flare gas monitoring systems, the exhaust must never be released directly to the atmosphere due to flammable and toxic content.

The typical design connects the analyzer vent to the flare header or a local exhaust manifold via a dedicated disposal line equipped with a flame arrestor and check valve. This configuration ensures that any backflow from the flare header cannot reach the analyzer system.

Where routing to the flare header is impractical, a safe vent stack with sufficient height and dilution air may be used, provided it meets local environmental and safety regulations. A small nitrogen purge is sometimes added during analyzer standby or maintenance to keep the disposal line free from corrosive gas accumulation.

Proper drain traps or condensate collection points are provided at low spots in the disposal line to prevent liquid accumulation that could restrict flow or cause pressure fluctuation at the analyzer outlet.

Finally, the disposal system design should ensure near-atmospheric outlet pressure to avoid analyzer cell pressure effects and must maintain continuous venting during sample pump operation to keep the system in a steady-state of flow. **Is this to avoid overpressure and condensate?**

## 5. Analyzer Selection

### 5.1. Heating Value Measurement Techniques

Regarding the heating value (HV) represents the total energy released during complete combustion of the flare gas and serves as a key indicator to determine how much heat we are releasing to the environment or to monitor the status of a downstream process.

In Petro-refinery applications, the analyzer system must perform reliably across a wide range of compositions-from light hydrocarbon gases during normal operation to heavy, inert, or sulfur-rich mixtures during process upsets.

Four major analytical techniques are commonly used for flare gas heating value determination: Gas Chromatography (GC), Mass Spectrometry (MS), Residual Oxygen (BTU) Analyzer, and the Optical-Sonic Method.

#### 5.1.1 Gas Chromatograph (GC) Method

Principle:

Gas chromatography separates and quantifies individual gas components such as H<sub>2</sub>, CO, CO<sub>2</sub>, CH<sub>4</sub>, C<sub>2</sub>H<sub>6</sub>, C<sub>3</sub>H<sub>8</sub>, C<sub>4</sub>H<sub>10</sub>, C<sub>5</sub>H<sub>12</sub>, C<sub>6</sub>+ and heavier hydrocarbons.

The total heating value is then calculated using the standard combustion enthalpy of each component.

Advantages:

- High accuracy (typically  $\pm 1\%$ ) for well-defined gas mixtures.
- Provides complete compositional data, valuable for process diagnostics.
- Established and accepted by environmental regulatory agencies.

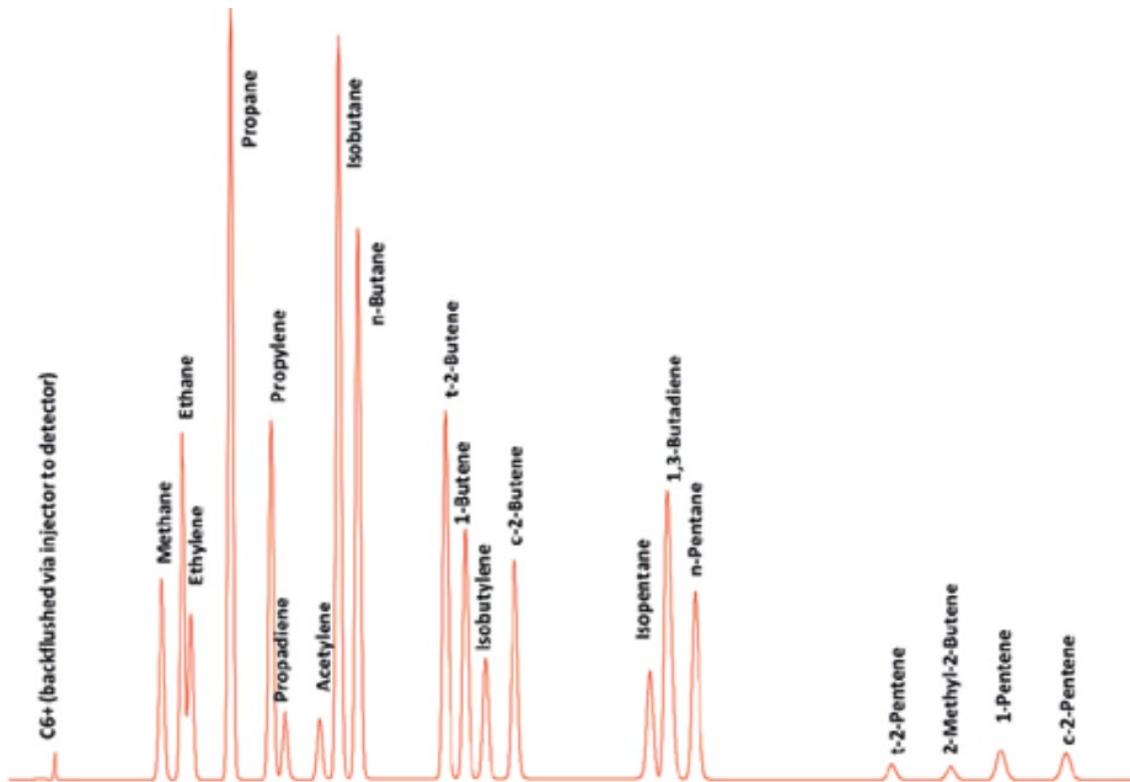
Limitations:

- Slow response (60–180 s) compared to real-time analyzers.
- Limited ability to follow rapid transients during shutdowns or upsets.
- It is only measurable for the defined components and if a new component is present in the sample, it will not be possible to measure it and may even have a negative effect on the measurement of other previously defined components.

This is more severe for C<sub>4</sub> and heavier compounds because these compounds have many chemical isomers.

-Limitation of measurement component definition, because if we want to define more than 10 components for measurement, the measurement cycle time may increase to half an hour, which practically does not make sense for an online analyzer.

**Note2:** Given that we expect C5 and heavier compounds to be removed in the knockout drum section (oil separator), we can expect a sample with a maximum hydrocarbon dewpoint of 55°C to be extracted from the flare line after the knockout drum, which means we will not have most of the heavy isomers in the sample and our C5+ will be less than 0.5% by volume in the worst case and will be measured as a total backflash to the detector. Therefore, with these conditions, we can expect stable and repeatable measurements from the GC even under abnormal process conditions.



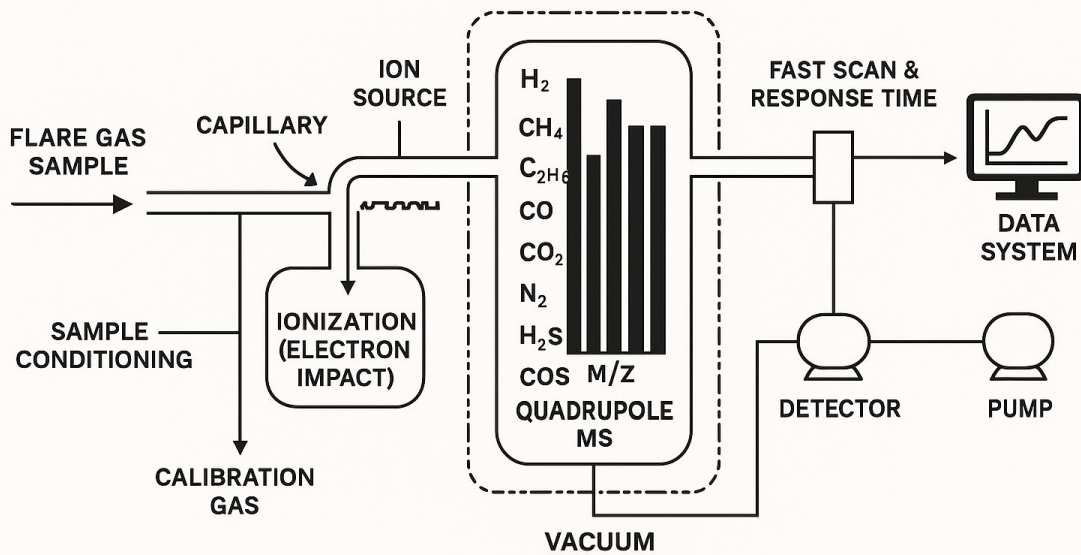
Chromatogram of C1-C6+ analysis with C4, C5 isomers. Of course, CO<sub>2</sub>, N<sub>2</sub>, H<sub>2</sub> analysis should also be added to this analysis, which of course will have a cycle time of at least 20 minutes.

### 5.1.2 Mass Spectrometer (MS) Method

Principle:

Mass spectrometry identifies gas components based on their mass-to-charge ( $m/z$ ) ratio. The analyzer measures ionized species in a vacuum chamber, quantifies their partial pressures, and calculates the heating value from the resulting composition in near real time.

#### MASS SPECTROMETER PRINCIPLE FOR FLARE COMPONENTS MEASUREMENT



Advantages:

- Extremely fast response (1–5 s) for each component, so total cycle time for 15 measurement components at worst case are 60 Sec.
- Excellent for dynamic or upset conditions; provides continuous trend data.
- Handles complex or varying compositions, including inert or non-hydrocarbon gases.
- Requires minimal carrier gas and no columns, reducing consumable use.
- High repeatability when properly calibrated and maintained.
- No dependence on measurement range or detector saturation.

Limitations:

- High capital cost and complex operation.
- Requires continuous vacuum integrity and periodic tuning.
- Sensitive to moisture and particulates; needs high-quality sample conditioning.

Best Application:

Real-time flare monitoring in refineries and petrochemical plants where gas composition changes rapidly or frequent process upsets occur.

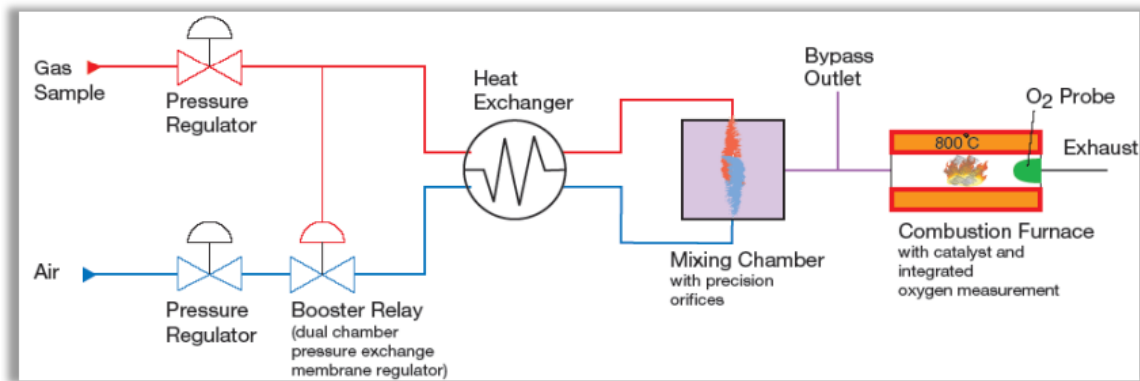
Considering the explanations given in Note 2, if we ignore its complexity and cost, we can say that this is the best option for analyzing the calorific value of flare gas.

### 5.1.3 Residual Oxygen (BTU) Analyzer – Combustion Method

Principle:

This indirect method determines heating value by measuring residual oxygen concentration after controlled combustion of the flare gas with a known air stream.

The analyzer computes BTU based on oxygen consumption relative to stoichiometric combustion.



Advantages:

- Simple and robust continuous measurement.
- Fast response (5–15 s).
- Less complex than GC or MS; suitable for field environments.
- Directly reflects combustion quality (BTU-to-air ratio).
- Operates reliably under low-pressure or variable-flow conditions with a heated suction pump.

Limitations:

- Provides heating value only (no compositional breakdown).
- Accuracy depends on stable combustion and proper calibration.
- Requires clean gas to prevent burner or sensor fouling.
- Needs periodic validation under high-sulfur or wet gas conditions.

-For samples containing hydrogen with a concentration of more than 10%, it has a measurement error.

Best Application:

Continuous flare performance monitoring where simplicity, reliability, and low maintenance are more critical than full compositional analysis.

**Note3: For cases where the amount of sulfur in the sample is more than 0.1% by volume and there is a possibility of condensation or solid sulfur particles in the sample, sampling in this analyzer is not continuous and is injection with cycle time.**

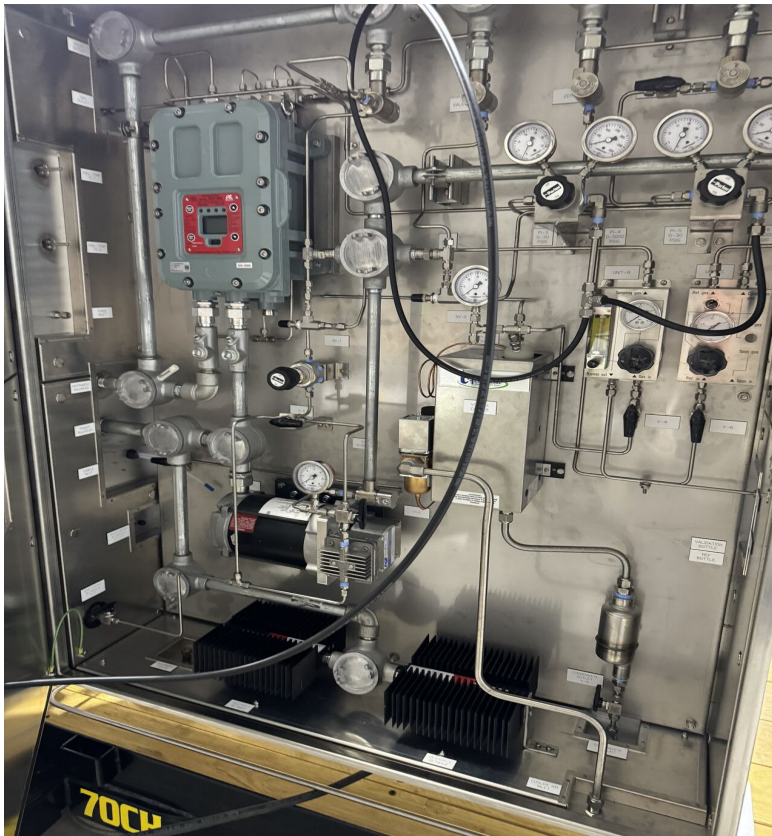
#### 5.1.4 Optic-Sonic Method (e.g., Riken Keiki OHC-800)

Principle:

The optic-sonic (or optical-acoustic) method simultaneously measures two physical properties of the gas:

1. Speed of sound – related to the molar mass and adiabatic constant of the gas.
2. Infrared absorption – related to molecular bond energy and composition.

By combining these two parameters through an empirical correlation, the analyzer calculates the Lower Heating Value (LHV) directly and in real time.



Advantages:

- Fast response (1–2 s) with no moving parts.
- Provides direct, continuous heating value measurement without combustion or vacuum

systems.

- Suitable for highly variable and mixed-composition gases.
- Minimal maintenance; robust against vibration and ambient temperature changes.
- Compact design allows installation close to the flare header.
- Low utility consumption.

Limitations:

- Requires accurate temperature and pressure compensation.
- Calibration must be verified periodically against a reference gas or GC value.
- Measures LHV only (not HHV).
- **The cell analyzer does not have any heating system, so the limit for samples with hydrocarbon dewpoints is greater than 30°C (provided that the analyzer box temperature is controlled at this setpoint).**

Best Application:

Real-time flare monitoring where rapid response and low maintenance are required — especially suitable for on-line control of flare combustion systems without heavy hydrocarbon in sample composition

## 5.2 Total Sulfur and H<sub>2</sub>S Measurement Techniques

Accurate measurement of total sulfur (TS) and hydrogen sulfide (H<sub>2</sub>S) in flare gas is essential for verifying compliance with EPA 40 CFR Part 60 Subpart Ja and related environmental performance standards. These measurements are used to determine potential SO<sub>2</sub> emissions, assess combustion efficiency, and evaluate the corrosivity and acid dew point of the flare gas stream.

Since the composition and flow of flare gas change significantly under the influence of process disturbances, the selected analytical method must be stable and, while being accurate and repeatable, avoid the problem of detector saturation.

### 5.2.1 Gas Chromatography (GC) Method

Principle: Gas chromatography separates individual sulfur species (H<sub>2</sub>S, COS, CS<sub>2</sub>, mercaptans, etc.) and quantifies them using specific sulfur detectors such as the Flame Photometric Detector (FPD) or Thermal conductivity Detector (TCD/MTCD/HTCD). The total sulfur concentration is calculated as the sum of the detected individual compounds.

Of course, FPD is suitable for measuring impurities and is not at all suitable for measuring in the flare line, but high-precision TCD (HTCD) is better for this purpose, although it has a lower range limit, usually around 20ppm.

Advantages:

- Provides detailed speciation of sulfur compounds, useful for process diagnostics.
- Compatible with analyzers already used for hydrocarbon and heating value measurement.

- Good laboratory or validation tool for stable streams.

Limitations:

- Cannot measure true total sulfur if unknown or uncalibrated sulfur compounds are present.
- Detectors are highly range-dependent and can saturate during process upsets.
- Requires stable sampling conditions and frequent calibration.
- Slow response (typically 3–5 minutes).

Conclusion: GC methods are suited for stable or laboratory applications but not for continuous flare gas monitoring where composition and flow are unpredictable.

### **5.2.2 Mass Spectrometry (MS) Method (Reject Method)**

Principle: Mass spectrometry analyzes gas molecules based on their mass-to-charge ratio ( $m/z$ ). With appropriate calibration, it can detect and quantify multiple sulfur compounds such as  $H_2S$ ,  $COS$ , and  $SO_2$  simultaneously with hydrocarbon components.

**Important point: Unfortunately, it cannot measure mercaptans and definitely requires a furnace to measure total sulfur.**

Advantages:

- Fast response (1–5 seconds).
- Capable of real-time multi-component analysis.
- No physical separation step — suitable for dynamic flare conditions.
- Allows integration with heating value analysis in the same analyzer.

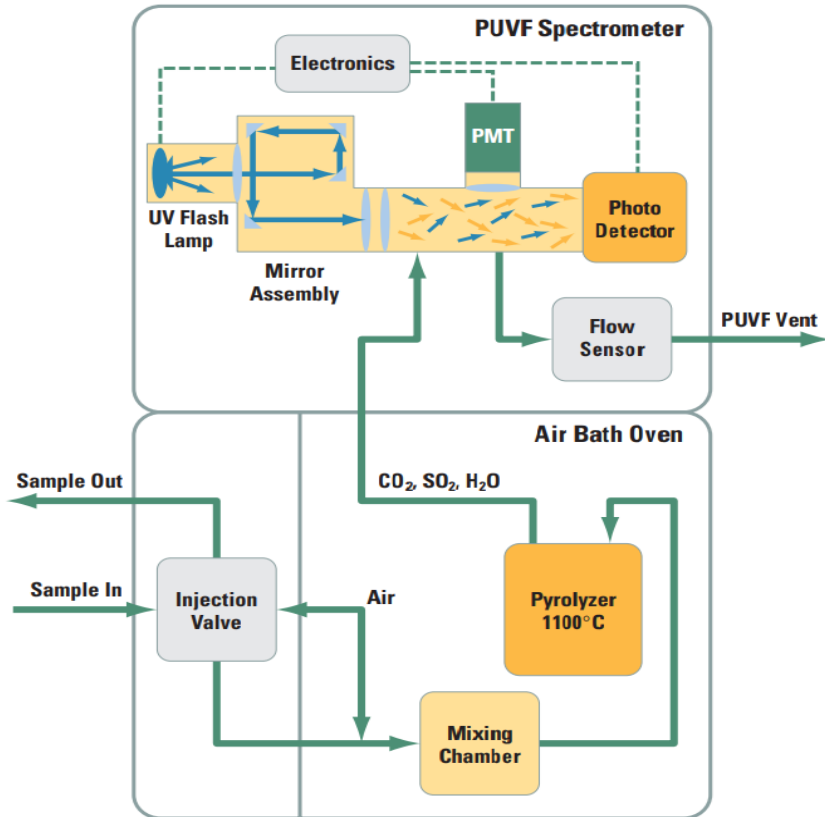
Limitations:

- Accuracy depends on calibration stability and knowledge of target compounds.
- May not detect unknown or heavy organosulfur compounds.
- Sensitive to moisture, particulate, and corrosion — requires high-quality conditioning.

Conclusion: MS analyzers provide valuable trend and variation detection for total sulfur by using furnace to convert all sulfur components to  $SO_2$ , but cannot fully replace certified total sulfur analyzers in regulatory applications.

### **5.2.3 Ultraviolet Fluorescence (UVF) Method**

Principle: All sulfur compounds are thermally oxidized to  $SO_2$  in a high-temperature converter. The resulting  $SO_2$  is then measured by ultraviolet fluorescence detection, which quantifies total sulfur concentration directly.



Advantages:

- Provides true total sulfur measurement, independent of compound type or number.
- Fast and continuous operation (response typically 5–15 seconds).
- High accuracy and wide dynamic range (ppm to %).
- Accepted method under 40 CFR Part 60 for continuous emission and flare monitoring.

Limitations:

- Requires a stable oxidation furnace for complete sulfur conversion.
- Needs heated sampling and conditioning to prevent condensation and adsorption.
- Requires periodic converter temperature verification and calibration.

Conclusion: The UV fluorescence method offers the most accurate and robust measurement of total sulfur in flare gas systems, provided that the oxidation furnace and sample conditioning are properly designed and maintained.

#### 5.2.4 Lead Acetate Tape Method

Principle: The sample gas passes over a lead acetate-impregnated tape, which darkens proportionally to the concentration of sulfur compounds (mainly  $H_2S$ ). The degree of darkening is measured optically and converted to concentration.

Advantages:

- Detects H<sub>2</sub>S and total reduced sulfur without depending on the number or type of sulfur compounds.
- Simple and low-cost system with minimal electronics.
- Provides continuous indication and alarm functionality.

Limitations:

- Produces hazardous lead waste, requiring regulated disposal.
- Similar to the UV method, this method also requires a furnace to convert all sulfur compounds to H<sub>2</sub>S to measure total sulfur.

However, it requires continuous hydrogen for conversion in the furnace, and its furnace has not had good feedback from consumers for some time for sample compounds containing C3 and heavy trace elements.

- Tape replacement and humidity sensitivity increase maintenance needs.
- Not approved as a primary method for regulatory sulfur measurement.

In summary, for refinery flare monitoring and compliance under 40 CFR Part 60, the UV Fluorescence (SO<sub>2</sub> conversion) and mass spectrophotometer analyzers provides the most accurate, stable, and regulation-approved method for total sulfur and H<sub>2</sub>S measurement.

## 6. Conclusion

Effective flare gas monitoring is not only a regulatory requirement but also an economic and operational opportunity. A properly designed analyzer system enables refineries to measure, control, and optimize flare performance, achieving both environmental compliance and process efficiency.

### 6.1 Meeting User Needs

End users in refineries expect analyzer systems that are reliable, accurate, and integrated with process control systems. These systems must provide real-time insight into heating value, sulfur content, and flare performance, enabling engineers to diagnose upstream process abnormalities and reduce unplanned flaring.

One of the most important items that is perhaps less considered is the knockout drum, a process that removes condensate, sediment, and heavy hydrocarbons. In fact, the correct operation of this item ensures the correct operation of all components of the sampling system and correct measurement of the analyzer. Of course, the entire system must be designed based on the worst-case conditions.

## 6.2 Economic Importance of Flare Monitoring

Beyond environmental compliance, flare monitoring delivers measurable economic benefits. Each cubic meter of flare gas represents potential fuel or feedstock loss. For example, 10 m<sup>3</sup>/min of methane corresponds to approximately 35.8 MJ/m<sup>3</sup>, or 358 MJ/min ( $\approx$ 5967 kWh/h). At \$0.08 per kWh, this equals about \$477 per hour, or roughly \$11,000 per day—over \$4 million per year. Preventing or reducing unnecessary flaring through monitoring thus provides substantial cost savings alongside emission reduce.

## 6.3 Environmental and Operational Synergy

Accurate flare monitoring contributes to emission reduction, early detection of process upsets, and verification of combustion efficiency ( $NHVCz \geq 270$  BTU/scf) as required by EPA regulations. Continuous measurement supports environmental responsibility and operational profitability simultaneously.

## 6.4 Final Remarks

Flare monitoring systems should be regarded not only as environmental compliance tools but also as economic performance assets. Combining accurate measurement, intelligent integration, and proactive maintenance allows refineries to achieve sustainable operation, regulatory assurance, and significant cost savings.

## 6.5 MMR Process Analytics.

At MMR's Integration and Analytical Center, we can provide one stop shop Engineering, Procurement and Construction for your Flare, CEM's and other Analytical measurement needs. We can select the best measurement method for your application, design commission and install an entire system around it; backed with a 1 year workmanship and functionality warrantee along with the MMR service the industry knows so well.

## References

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