

SOME LIKE IT HOT!

Reliable SRU Stack CEMS

David Inward
Area Manager, Endress & Hauser
SRU CEMS Specialist

Abstract

Continuously measuring stack emissions from the Sulfur Recovery Unit (SRU) is known as being notoriously difficult.

Since the properties of the tail gas are absolutely unique, it follows that applying conventional continuous emission monitoring (CEM) technology may not be the right approach.

Sulfur dioxide emission concentrations can fluctuate wildly, from low parts per million (< 100 ppmv) up to volume percent concentrations (> 10,000 ppmv) depending on whether the Sulfur Recovery Unit (SRU) is operating under steady-state or process upset conditions.

The likely presence of acidic aerosols (SO_3 / H_2SO_4) in the background gas means that any cooling of the flue gas can result in severe blockages in the sample system or fatal corrosion damage to sensitive optical parts.

The use of an emission monitoring technology incompatible with the application requirements will burden on-site technicians with frequent, unscheduled and difficult maintenance work. This burden on the maintenance team will inevitably result in a spiralling cost of ownership to keep the SRU CEMS system operational to ensure compliance and avoid potential penalties.

This paper provides a detailed examination of the nature of the application challenges; reviews reporting requirements in North America and assesses the most commonly applied gas analytical technologies for their suitability to both overcome the SRU CEMS application challenges and meet reporting requirements in full.

The paper examines the suitability of a hot extractive infra-red gas analysis technique, which whilst a long-established analytical method has until recently not been broadly applied in SRU CEMS.

A case study based around a project to replace SRU stack analyzers on two sulfur trains at a North American refinery will be shared.

Finally, a set of best practices drawn from the experiences gained from multiple installations will also be detailed.

SRU Stack Gas - Application Challenges

The basic design of the sulfur plant in a refinery is well understood.

Waste gases containing high vol.% concentrations of hydrogen sulfide (H_2S) are processed by the SRU to produce saleable elemental sulfur. Typically, a secondary tail gas treater unit (TGU) increases overall sulfur removal efficiency.

Prior to being emitted from the final stack, the tail gas exiting the sulfur unit passes through a thermal oxidizer (TOX) to destroy any residual reduced sulfur components due to the toxic nature of H_2S .

To ensure complete H_2S destruction efficiency, the TOX is operated at minimum 1200°F/650°C with a 2 vol.% excess of oxygen. Oxidation of trace reduced sulfur compounds results in an emission of sulfur dioxide (SO_2).

Sulfur removal efficiency varies greatly depending on the age and design of any given sulfur recovery unit. Furthermore, the SRU is prone to occasional process upsets.

SO_2 emission concentrations fluctuate both wildly and rapidly, from ppm concentrations during steady-state operation (< 100 ppmv) suddenly spiking up to volume percent concentrations ($> 10,000$ ppmv / 1 vol.%) during Tail Gas Unit (TGU) bypass or upset conditions.

A rapid spike in SO_2 concentrations in the stack gas brings with it an equivalent sudden increase in the acid dew point temperature of that gas.

When sampling the gas as the basis for measurement, allowing the sample gas to cool below its' acid dew point temperature may well result either in severe blockages in the sample system or fatal corrosive damage to sensitive optical parts.

To summarize the requirements of the continuous emission monitoring system, not only does the analytical task vary greatly and suddenly in nature, it is also fraught with danger in handling a sample gas that can be highly corrosive and highly prone to blockages.

Those dangers are present from the moment the sample gas is extracted out of the stack and remain until the sample gas is vented out of the gas analyzer.

Legislation Requirements – U.S.

Legislation in U.S. relevant for the sulfur recovery process differs fundamentally according to process type.

According 40CFR 60 Sub-Part J, petroleum refineries must comply with a normalized emission limit of 250 ppm sulfur dioxide (SO₂).

§ 60.105 Monitoring of emissions and operations.

(5) For Claus sulfur recovery plants with oxidation control systems or reduction control systems followed by incineration subject to [§ 60.104\(a\)\(2\)\(i\)](#), an instrument for continuously monitoring and recording the concentration (dry basis, zero percent excess air) of SO₂ emissions into the atmosphere. The monitor shall include an oxygen monitor for correcting the data for excess air.

§ 60.104 Standards for sulfur oxides.

No owner or operator subject to the provisions of this subpart shall:

Discharge or cause the discharge of any gases into the atmosphere from any Claus sulfur recovery plant containing in excess of:

(i) For an oxidation control system or a reduction control system followed by incineration, 250 ppm by volume (dry basis) of sulfur dioxide (SO₂) at zero percent excess air.

A later version, 40 CFR 60 Sub-Part Ja includes a formula to establish a scalable SO₂ emission limit corresponding to differing concentrations of oxygen enrichment utilized in the Claus furnace to increase capacity (e.g. 441 ppm SO₂ for 43% enhanced oxygen). With O₂-enrichment, the concentration of SO₂ increases, due to removal of N₂, but the SO₂ mass emission remains relatively unchanged.

In contrast, onshore natural gas processing plants are required to report a “sulfur emission rate” expressed as a mass emission (lbs. SO₂ / hour). 40 CFR 60 Sub-Part OOOO (2011-2015) and 40 CFR 60 Sub-Part OOOOa (2015 onwards) both stipulate

§ 60.5407 What are the requirements for monitoring of emissions and operations from my sweetening unit affected facilities at onshore natural gas processing plants?

(b) Where compliance is achieved through the use of an oxidation control system or a reduction control system followed by a continually operated incineration device, you must install, calibrate, maintain, and operate monitoring devices and continuous emission monitors as follows:

A continuous monitoring system to measure the total sulfur emission rate (E) of SO₂ in the gases discharged to the atmosphere. The SO₂ emission rate must be expressed in terms of equivalent sulfur mass flow rates (kg/hr (lb/hr))

Emission Limit Value / Mass Emission Reporting

Normalized Emission Limit Values

An emission limit value expressed as a normalized concentration (units ppm/Nm³) requires correction of the raw measured pollutant concentration to dry basis (i.e. at 0. vol.% water vapor) and to a defined oxygen concentration (0.0 vol.% O₂ according 40 CFR 60 Sub-part J)

To meet a dry basis emission limit value, removing water vapor prior to measurement of sulfur dioxide (SO₂) and oxygen (O₂) concentrations seems logical.

However, the need to cool the sample gas as a means to condense out and remove the water vapor content is liable to trigger exactly those severe sampling issues (sampling blockages, acid corrosion) for which the SRU CEMS measurement is known.

The alternative is to keep the sample gas hot enough to keep the water vapor in the gaseous phase. Such a method demands that the water vapor (H₂O) concentration is measured as well as SO₂ and O₂ to enable compliance with the dry basis sulfur dioxide emission limit value.

Local reporting requirements may include requirements to additionally measure emissions of further components, most frequently carbon monoxide (CO), and oxides of nitrogen (NO+NO₂).

Mass Emission

In contrast, reporting the mass emission of sulfur dioxide (kg or lbs / hour) from sour gas processing requires a measurement made under wet conditions that can directly be combined with a (wet basis) flow measurement.

Beyond the flow measurement, there is no need to measure further components to qualify the SO₂ emission.

However, since greenhouse gases must also be reported as a mass emission, then there can be value in adding carbon dioxide (CO₂) as a measured component.

Summary

To be sufficiently flexible to be able to comply with the very different demands coming from reporting either against normalized emission limit values or a mass emission, the continuous emission monitoring system should have the following properties:

It should measure sulfur dioxide (SO₂) and any further pollutants (CO,NO,NO₂) in a wet condition.

To also measure carbon dioxide (CO₂) as a greenhouse gas will become increasingly relevant. It should also simultaneously measure reference gases, namely oxygen (O₂) and water vapor (H₂O).

Comparative CEMS Techniques

Cold Extractive Infrared

Cold extractive gas analysis by means of an infra-red photometer is the most broadly applied technology for conventional emission monitoring requirements.

The design base is to extract and transport the sample gas in a heated sample line before cooling the gas down to 36°F/2°C in a refrigerating cooler to condense out and remove the water vapor portion of the sample gas. The now dry sample gas flows through an infra-red photometer with an additional paramagnetic detector module present to measure oxygen.

This technology exactly fits the requirement to report a dry basis emission limit value.

However, as already emphasized, intentionally dropping the sample gas temperature below the dew point temperature to remove water is fraught with risk. Frequent maintenance can be expected as a minimum.

Dilution Sampling - Infrared / Ultraviolet Gas Analyzer

The dilution method coupled with infra-red (IR) and / or ultra-violet (UV) gas analyzer is another technology widely applied for the continuous measurement of emissions, especially in North America.

Applying a dilution method to monitoring SRU CEMS brings with it some challenges. Firstly that to avoid blockages of the dilution sample probe critical orifice, through which the respective flows of the sample gas and diluent gas need to be precisely controlled, it would be advisable to effectively pre-heat the very high volumes of diluent gas.

From a reporting perspective, since water vapor is not removed, this meets the requirements to report a mass emission. However, since there is no water vapor measurement, it is not possible to report dry basis. Furthermore, the dilution technique means a second, separate oxygen analyzer is required.

Hot Extractive UV Gas Analyzer

The application of a hot extractive UV photometer is well known in sulfur unit process applications. A UV photometer is very capable of measuring sulfur dioxide (SO₂). The hot extractive sampling technique is a good fit in terms of addressing the critical application challenges and this method fits with reporting a mass emission.

However, the UV photometer is not able to measure water vapor, so is unable to report dry basis. The typical control temperature of the hot extractive UV photometer is 300°F/150°C which is not always sufficient to stay above worst case acid dew point temperatures during many SRU process upset situations.

Hot-Wet Extractive Infrared Gas Analyzer

The hot, extractive infra-red gas analyzer design base seems ideally suited for measuring the emissions at the SRU stack.

The hot extractive IR system comprises only three components,

- sample probe with integrated heated filter element
- heated sample line
- heated infra-red analyzer with integrated ejector pump.

Each element is typically maintained at 390°F/200°C, above the sample gas acid dew point temperature, which avoids both condensation of acidic species and deposition of solid sulfate salts.

The heated sample line connects directly to the hot extractive infra-red gas analyzer.

The hot extractive infra-red gas analyzer has a powerful multi-component capability. It can measure up to 10 infra-red active components, covering all gases typically required for the SRU stack gas application.

In addition to sulfur dioxide (SO₂), water vapor (H₂O), carbon monoxide (CO) and oxides of nitrogen (NO+NO₂) may need to be measured and reported.

The integration of a zirconium sensor to measure oxygen completes the measurement task and is an excellent fit with the “hot extractive” design base.

Since water vapor and oxygen are standard measured components, this analyzer is uniquely capable of reporting pollutants such as SO₂ both on a dry basis emission limit values (ppmv SO₂ dry basis at 0% O₂) and wet basis mass emissions (kg or lbs/hour).

Sulfur Removal Efficiency / Dual Sulfur Dioxide (SO₂) Range

One special aspect of the SRU CEMS measurement is the need to measure vastly different SO₂ concentrations corresponding to whether the process is operating normally or in TGU bypass mode.

The Beer-Lambert Law ($A = \epsilon \cdot c \cdot l$) expresses the relation between gas concentration and measuring cell length. To measure a low concentration of a target gas logically requires that the gas analyzer uses a long measuring cell and vice-versa.

The measuring cell length of the gas analyzer is selected to fit the typical measured target gas concentration. There is a limit on the capability to measure the target gas accurately when the concentration deviates significantly. A maximum measuring range ratio of 10:1 is a rough guide. So an analyzer ranged 0-300 ppmv SO₂ can't measure above 3000 ppmv SO₂.

So how to measure the vastly differing sulfur dioxide concentrations according to sudden changes in sulfur plant efficiency when the concentration may differ by a factor of 100 or more?!

This can normally only be addressed by two discrete measurement cells of differing lengths, inferring two dedicated SO₂ analyzers.

However, the hot, extractive infra-red gas analyzer offers an alternative solution thanks to its multi-component capability. It can utilize two different wavelengths at which SO₂ absorbs IR light. These are respectively of significantly differing absorption intensities, ideally fitting the two required SO₂ measuring ranges.

- 0-300 ppmv SO₂; measured at 7500 nm (normal process condition)
- 0-1.5 vol.% (15000 ppmv) SO₂; measured at 4000 nm (TGU bypass condition)

The analyzer effectively makes two simultaneous SO₂ measurements.

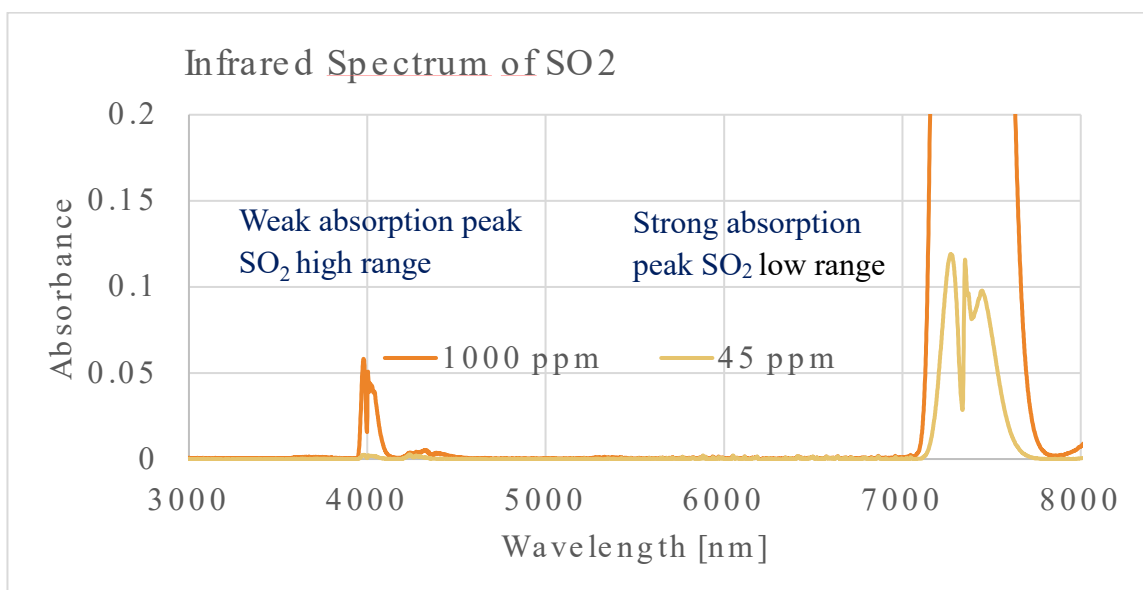


Figure 1 – SO₂ Infrared Absorption Spectrum

Case Study - SRU CEMS Project at a North American Refinery

The system design based around a hot extractive multi-component infra-red analyzer still needs careful consideration to achieve optimal performance.

A 2023 SRU CEMS project at a North American refinery offers a practical example of key application features and optimal system design. The refinery has two sulfur trains, with hot extractive infra-red analyzers supplied in 2008.

Process gas temperature was 1200°F / 650°C, maximum 1500°F / 815°C
Sample line length was approx. 100 feet (30 m)

Original Project Data (2008)

Standard System Design

- Unheated 3 ft / 1 metre sample probe tube (ANSI 4" 150# mounting flange)
- Sample probe with heated filter element & back-purge connection (inst.air)
- Heated sample line
- Heated diaphragm pump
- Heated flow-meter with low flow alarm
- Hot Extractive MCS 100 Infra-red Gas Analyzer

MCS 100 Infra-red Analyzer Measured Components	Measuring Range
Sulfur dioxide (SO ₂)	0-2. vol.% (20,000 ppmv)
Water vapor (H ₂ O)	0-40 vol.%
Oxygen (O ₂)	0-21 vol.%

Table 1 – MCS 100 Infra-red Analyser Configuration

Technical Meetings (2021/2022)

Discussions concerning problems with the aging of the on-site SRU CEMS systems started in fall of 2021.

The 2 x SRU CEMS systems were suffering with corrosion visible at the stack mounting flange (Figure 2) with acidic entrained liquids / aerosols clearly present in the extracted sample gas (Figure 3).

A back-purge function was regularly used to try to keep sample probe / sample filter clear of blockages / liquids. A steel wool sacrificial filter was placed in the probe to combat carryover of liquid acidics (weekly replacement necessary).

Regular maintenance of the heated sample diaphragm pump was also necessary. Corrosion products from the steel wool would enter the sample pump (Figure 4), reducing the life of the pump membranes (typically 6 months).

The hot extractive IR analyzer was still proving robust, but was no longer being manufactured and the availability of spares was an increasing concern.

The decision was therefore reached to replace the systems and to optimize system design to combat the prevalent maintenance issues.



Figure 2
Heavily Corroded
Stack Mounting Flange

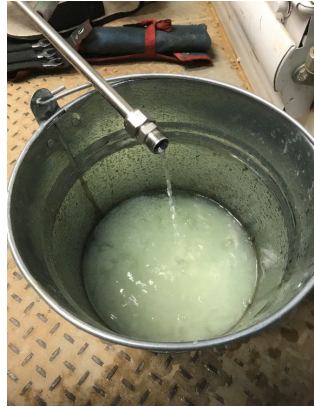
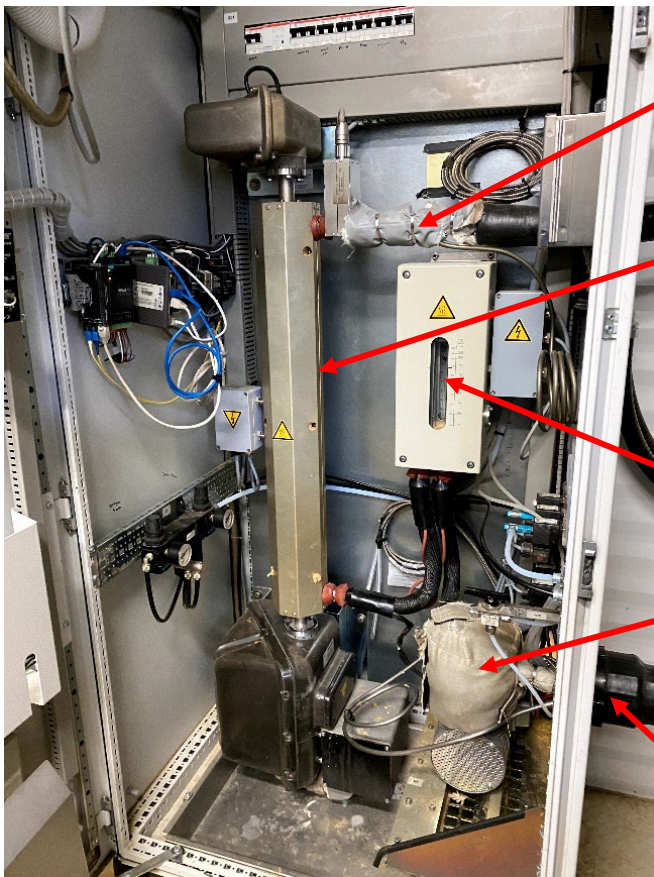


Figure 3
Corrosion Products On
Flushing Sample Probe



Figure 4
Solid Deposits Inside
Hot Sample Pump



5. Heated Sample Line Outlet

4. Heated Analyzer Measuring Cell
(Outlet Connection above)
(Inlet Connection below)

3. Heated Flow-Meter

2. Heated Sample Pump

1. Heated Sample Line Inlet

Figure 5 – Hot Extractive Infrared Gas Analyzer System
Previous Generation Design

New Hot Extractive Infrared Analyzer - 2023

Key considerations from the existing problems were

- Rapid cooling of the sample gas as it exited the stack (1200°F / 650°C) and passed through the unheated stack flange / sample probe flange connection.
- The back-purge using ambient air may have contributed an unwanted cooling of the sample gas.
- Corrosive attack of the sacrificial steel wool in the sample probe was creating sample problems further downstream.
- The system design contained too many interconnections (Figure 5). Each interconnection between heated elements is a potential cold spot.

New Design Concept (See Figure 7)

- Heated “transition piece” utilized at base of probe tube to address cold spot at stack flange / probe mounting flange (Figure 6).
- Back-purge excluded from system design (potentially cools sample gas).
- Change to a heated ejector (located downstream gas analyzer) as the basis to draw sample gas
- Heated sample line connected directly to analyzer inlet to minimize interconnections / avoid potential cold spots
- Worst case acid dew point temperature was calculated to be 390°F / 200°C. Keep all system elements heated at least 35°F/ 20°C above that temperature to avoid the threat of acidic liquids / aerosol formation.
- Use next generation MCS300P hot extractive IR analyzer (heated to 450°F/230°C)
- Dual SO₂ measuring ranges implemented to better fit application requirements
0-5000 ppmv SO₂ / 0-2.5 vol.% SO₂. H₂O 0-20 vol.%, O₂ 0-25 vol.%
- Keep a high sample flow rate to minimize residence time
- Ensure snug fit of heated sample line to sample probe / sample analyzer inlet connections (heating cable present at both ends!) during installation.



Figure 6 – Sample Probe Heated Transition Piece

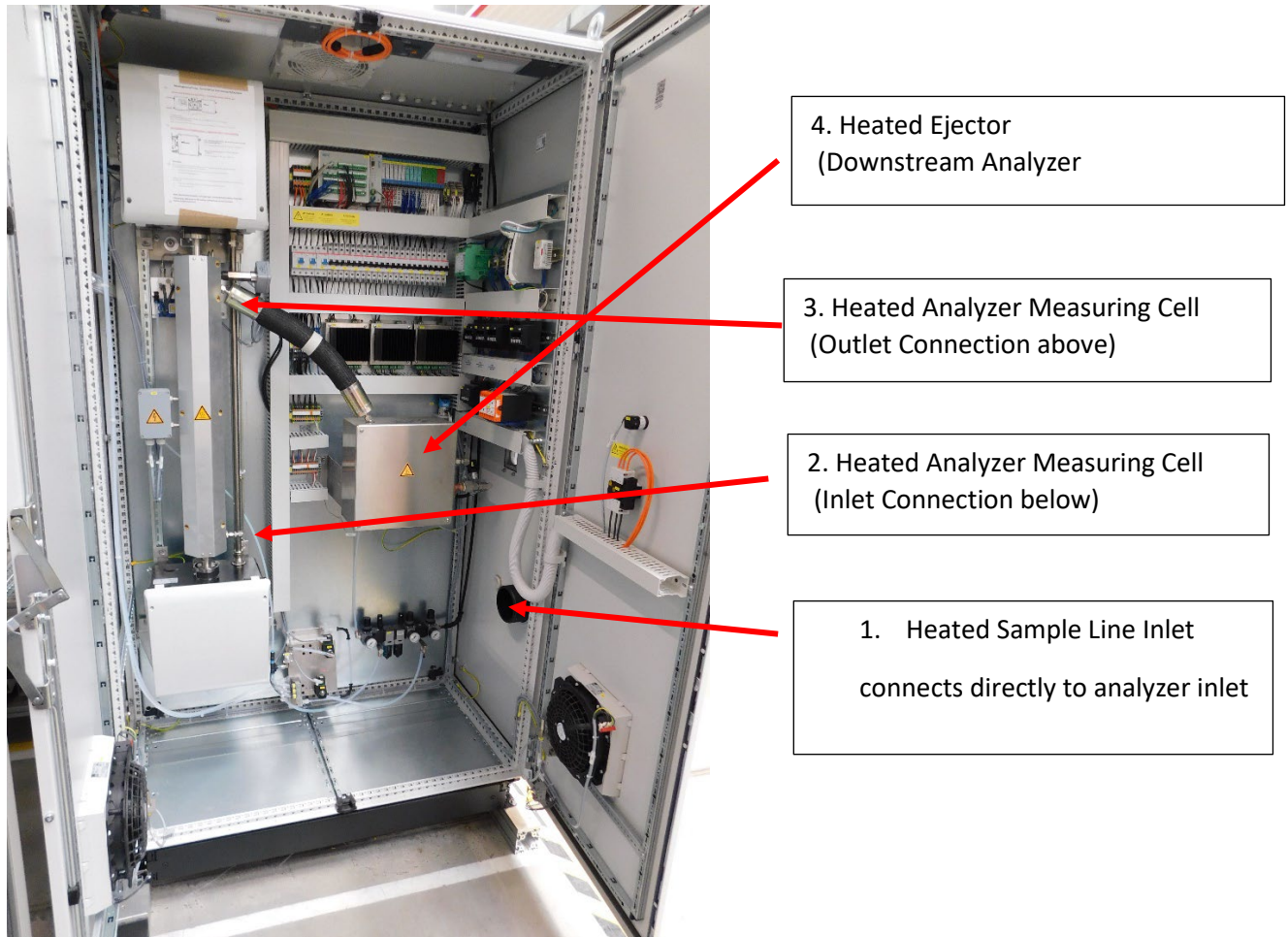


Figure 7 - New Hot Extractive Infrared Gas Analyzer – System Design

Current Status

The two new SRU CEMS hot extractive analysis systems were commissioned in Fall 2023.

The performance has shown high availability.

Maintenance is significantly reduced.

Across almost 2 years operation, the two hot extractive gas analysis systems on both SRU trains have proven capable of measuring SO₂ concentrations under all process conditions (steady-state & process upset) and can report dry basis at 0 vol.% oxygen thanks to the water vapor measurement.

This plant is also required to report an SO₂ mass emission (lbs/h SO₂)

Thermal Oxidizer Monitoring

The multicomponent capability of the hot extractive infrared analyzer offers additional potential benefits. An SRU CEMS trial on a European refinery resulted in control problems with the thermal oxidizer being identified by the SRU CEMS analyzer.

When observing emissions during TGU bypass, there seemed to be a clear relationship between spikes in SO₂ and an increase in CO emissions.

Initially, the SO₂ spikes (Figure 8 blue trendline) would result in the CO emission (Figure 8 orange trendline) dropping to zero ppmv. Then the subsequent rapid drop-off in SO₂ concentration would seem to trigger a CO emission spike.

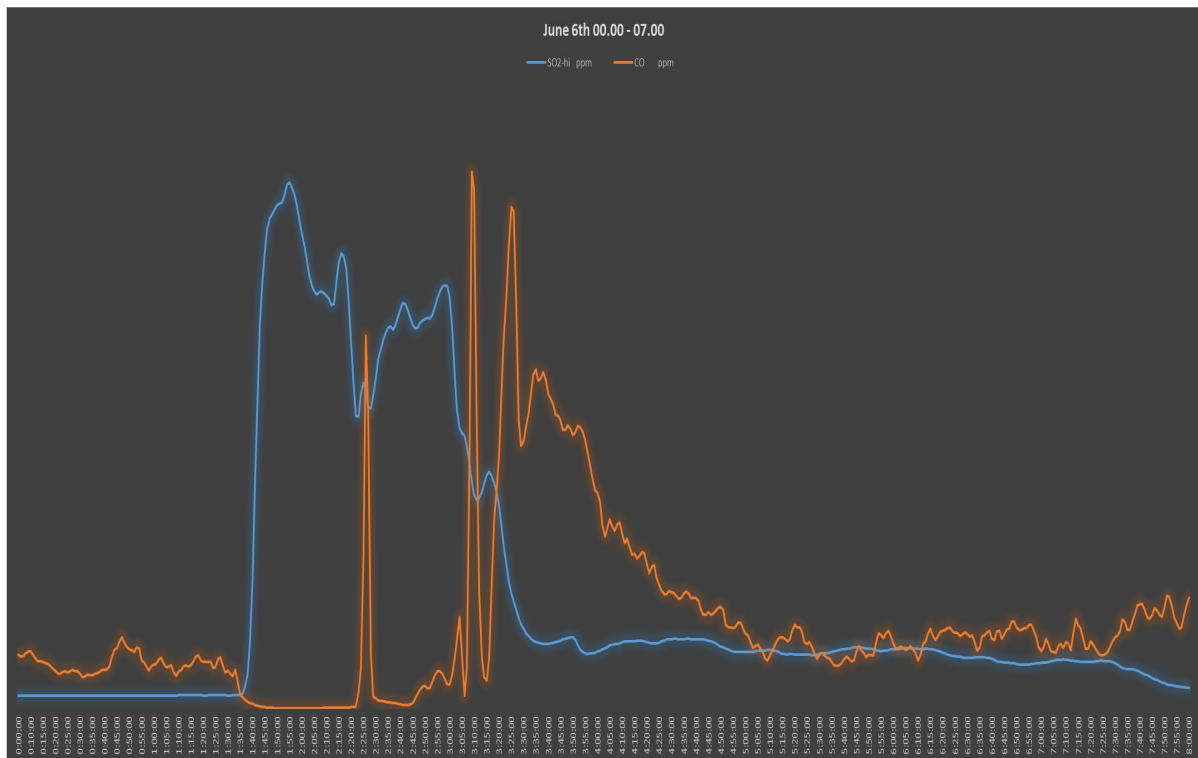


Figure 8 - Relation Between SO₂ Spikes (Blue Trendline) & CO Emission (Orange Trendline)

Looking more deeply into data during the TGU bypass established a cause. This was proven by additionally looking into temperature data during such events (Figure 9).

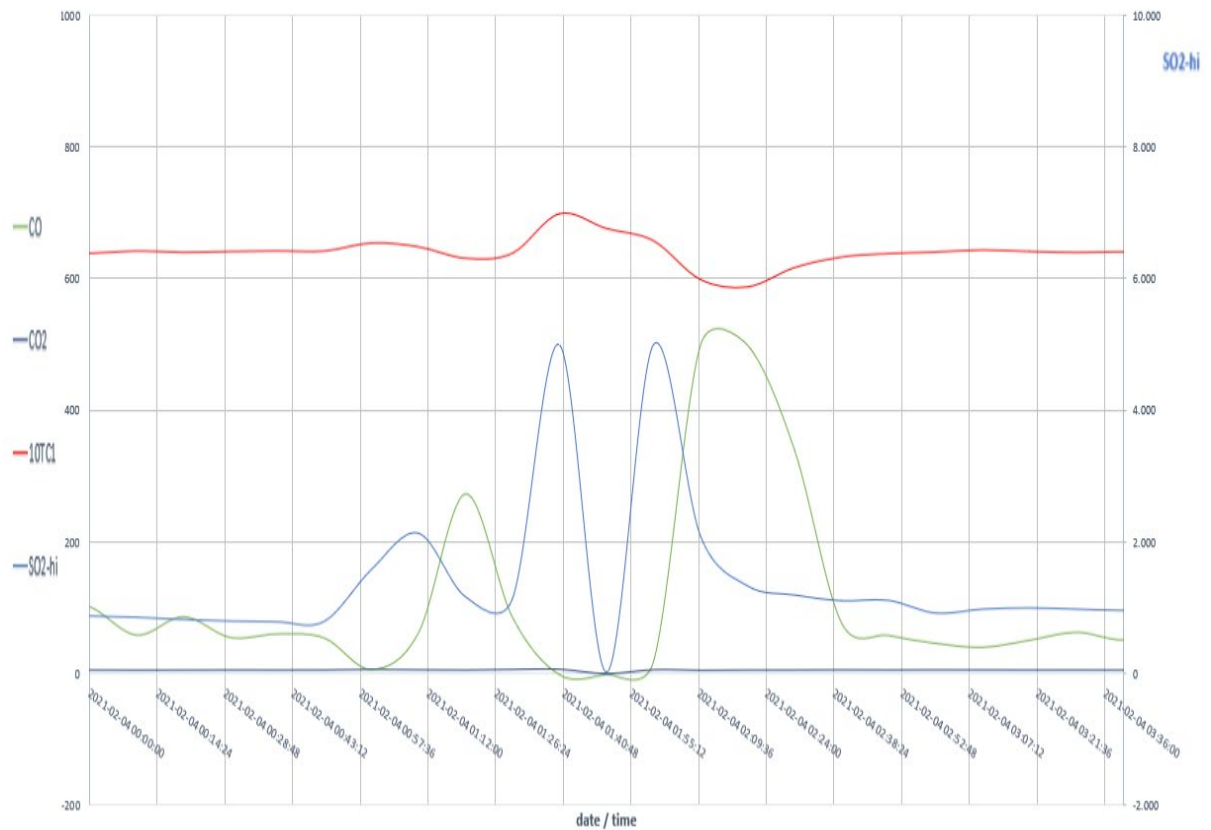


Figure 9 –Relation Between SO₂ , CO (Units ppmv) and Temperature (in°C)

Combustion of higher H₂S concentrations in the thermal oxidizer, seen as an increase in the SO₂ emission concentration (Figure 9 blue trendline) was driving a significant temperature increase (Figure 9 Red trendline), which resulted in more efficient CO combustion and a reduced CO emission concentration (Figure 9 green trendline).

As the H₂S concentration rapidly dropped away, the accompanying reduction in thermal oxidizer temperature led to inefficient CO combustion.

Cost Of Ownership - Experiences

Refinery in Europe (Commissioned 2021)

Performance Summary

- After 4 years operation only maintenance performed during annual service visit.
- Spares consumption is significantly lower than previous hot extractive UV analysis system.

Refinery in North America (Commissioned Fall 2023)

Performance Summary

- 2 x SRU CEMS systems approaching 2 years operation
- No IR light source replaced as yet
- Simplification of system design, especially the change from heated diaphragm pump to heated ejector has significantly reduced maintenance requirements.

SRU CEMS – Engineering Best Practices

- Keep the SRU CEMS analysis system heated above the acid dew point
- Calculate worst-case acid dew point as the basis for defining temperature set-points (ideally 35°F/20°C above worst case dew-point).
- Ensure thermal integrity in both system design & installation work – no cold spots!
- Use sampling concept based on simplicity. Minimal sampling components, minimal interconnections to overcome risk of cold spots.
- Reduce system residence time by means of high system flow-rate (5-6 litres/minute). Residence time for sample system with 100ft sample line - 8 seconds, residence time for sample system with 300 feet sample line - 24 seconds
- Use a heated ejector as the basis for drawing sample gas. No moving parts, negative sample pressure in measuring cell.
- Avoid stream-switching to a common analyzer
- Measure all components on a single multi-component analyzer.
- Utilize dual range SO₂ measuring ranges to optimize performance in both steady-state and TGU bypass process condition.

Summary

The acute problems associated with the SRU CEMS measurement are all related to allowing the sample gas to cool below the acid dew point temperature.

To report SO₂ as an emission limit value (250 ppmv dry basis at 0 vol.% O₂) from the sulfur recovery unit of a petroleum refinery according 40 CFR 60 Sub-Part J, it is necessary to measure oxygen (O₂) and water vapor (H₂O) in addition to SO₂ if the measurement is made under raw conditions (without prior water removal).

Local emission limit values for CO, NO, NO₂ (NO_x) may also be added.

Local regulation may demand SO₂ be reported as a mass emission (for example exceedance during process upsets).

Requirements to report the mass emission of greenhouse gases such as carbon dioxide and methane will grow in significance in future.

A single hot extractive multi-component infra-red gas analyzer is capable of meeting all of these reporting needs as the basis to demonstrate compliance.

The hot extractive infra-red gas analysis system is particularly well suited to overcome the unique threats of the SRU CEMS application.

This is done by keeping the analysis system heated above the acid dew point temperature, ensuring thermal integrity and minimizing residence time.

The result is a reliable SRU CEMS measurement with demonstrable low cost of ownership.

