Field Experience with a UV + TCD Analyzer and Application Specific Sample System for Amine Based Tail Gas Treating Units

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Abstract

The paper describes the development and subsequent field experience of a gas analyzer that utilizes a combination of UV and thermal conductivity detection principals for on-line process measurement of H_2S, COS and H_2 on amine based tail gas treating units (TGTU). The process requires measurement of H_2 (Hydrogen) and COS (Carbonyl Sulfide) to control and monitor the CoMo (Cobalt Molybdenum) catalytic reactor and the measurement of H_2S (Hydrogen Sulfide) to monitor the efficiency of the amine contactor.

The analyzer combines a non-dispersive ultraviolet (NDUV) optical bench with a thermal conductivity detector (TCD) for simultaneous measurement of H_2S, COS and H_2 from a sample point at the amine absorber overhead. The measurement has been performed over the years using various techniques and analyzers. The driving force in this development the request was significant reduction in cost, maintenance and improvement in safety.

The sample system was given special attention in this application. The toxicity of H_2S is well known and isolation from the process was a prime consideration during development.   Sample is taken from and spent sample returned to the process at a single point. It can be isolated from the process and back flushed with N2 so safety integrity is maintained during service intervention. After experiencing a major upset the sample system was revised to block the salts and particulate from entering the sample system.

Much was learned over the three years and the deployment of 60+ units. The paper sums this history, chronicles the lessons learned and improvement in the measurement(s).

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Introduction

Description of Amine Based Tail Gas Treating (TGT) PROCESS
  The Tail Gas Treater (TGT) is the basic unit operation for removing sulfur compounds from Claus SRU tail gas. There are several types of TGTs, including those that produce byproduct sulfates, but "closed loop" amine based TGTs, where the H_2S rich stream is recycled back to the front of the SRU, are the most prevalent. This paper is based on the experience for a SCOT tail gas treater but the analyzer and sample system has been applied to many variants of the amine based TGT.
The process consists of three basic steps:

- Catalytic hydrogenation and hydrolysis of all sulfur components (H_2S as well as SO_2 (Sulfur Dioxide), COS, CS_2 (Carbon Disulfide), sulfur vapor and sulfur liquid) in the Claus tail gas to H_2S. The catalyst is Cobalt Molybdenum and this stage is sometimes referred to as the "CoMo", reduction or SCOT reactor. Reduction of all the unreduced sulfur compounds to H_2S requires an excess of H_2 at the outlet of the CoMo SCOT reactor, hence the need for a H_2 analyzer. (1)

- H_2S is selectively absorbed from the tail gas by means of an amine solvent, after cooling. This stage is sometimes referred to as the (SCOT) absorber or contactor.

- Amine is regenerated (H_2S is desorbed from the solvent). The high concentration H_2S stream from the regenerator is recycled back to the inlet of the Claus SRU. The off-gas from the absorber is sent to the incinerator (operating permits are usually 250 ppm SO_2 with typical operation at 100 ppm SO_2 or below).
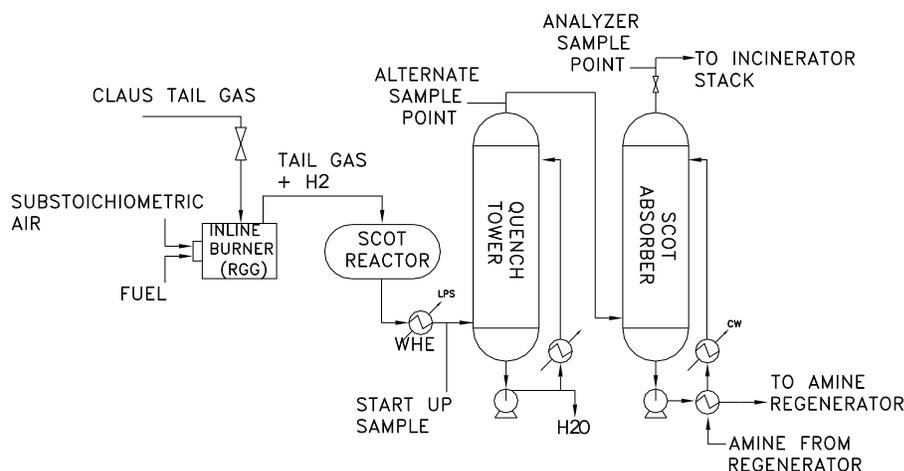
Figure 1 – Simplified Schematic of the SCOT Process, Where and How to Measure H$_2$S + H$_2$ in Tail Gas Treaters

There are two common sampling locations for the H$_2$S/Hydrogen analysis. One sample location is immediately after the CoMo reactor and Quench tower (before the absorber) so the H$_2$S measurement represents all of the sulfur compounds in the SRU tail gas. This serves as a fairly precise material balance (recovery efficiency measurement), which can be used as an optimization tool by the process engineer.

The other location is after the absorber (before the incinerator) to monitor the operation of the amine treatment section. Also, by comparing the H$_2$S measurement here to the SO$_2$ CEM's (Continuous Emission Monitor) value after the incinerator, the difference can be attributed to trace sulfur compounds including COS and CS$_2$ which is useful information for the process engineer and operations (or the COS and CS$_2$ can be measured by the UV analyzer). There are examples of TGTUs having H$_2$S measurements in both process locations with the H$_2$ measurement installed with the upstream analyzer.

The sample system considerations are not trivial. The strong preference from a simplicity standpoint is to locate the analyzer in either one of the positions described above because it means the sample system can consist of a custom heated probe, heated sample line and the heated cell. In applications requiring sampling before the quench tower (after the CoMo reactor) then the sample has to be conditioned with the addition of a sample chiller to eliminate potential water dew point issues. Note that the chiller is not required if the sample point is after the absorber.

There are two common reasons for choosing the sample point before the quench tower. First, with existing tail gas treaters the sample point may be located before the quench tower and changing the sample point is more costly than the addition of a sample chiller Second, in the case of Alon USA (who operate a 70,000 bpd refinery located in Big Spring, Texas, approximately 45 miles east of Midland, Texas), during the basic engineering phase the contractor expressed a desire to have the safety of being able to temporarily measure the H$_2$ before the quench tower / absorber during start up while the quench tower / absorber are being bypassed. It was desired to do this in addition to making the normal measurement of H$_2$S after the absorber when the SCOT unit is in full operation. This option prevents damage to the amine during the short interval of time the absorber is being bypassed. A simple manual switching system was designed, that can select either sample location, it back purges the unused sample leg with N$_2$ and uses a sample chiller to remove the water.

Analyzer Design

Based on previous experience of supplying UV analyzers to plants with SCOT units in their SRU, it seemed that there would be several advantages to a single (continuous) analyzer that was capable of measuring H_2, H_2S, COS and possibly SO_2. The primary advantage of combining these measurements is a cost savings in both the cost of the analyzer and also installation costs. Manufacturing costs are lower with elimination of duplicate items like micro-controllers, sample system, enclosures, power supplies, etc. Further cost savings can be realized during the installation because of the reduced number of sample lines, probes, electrical connections and also space savings.

The photometric portion of the analyzer was designed around a well-proven optical bench, which has been used for the measurement of these species in the past. The optical bench has been specifically designed to provide excellent baseline stability, exceptional linearity and high sensitivity. These performance specifications are desirable in applications where a single component is being measured at low concentrations with no interfering compounds present and especially when measuring multiple components with overlapping absorbance ranges. Further details on the design of this spectrometer and discussions on the advantages in comparison to other designs are available in References 2 and 3.
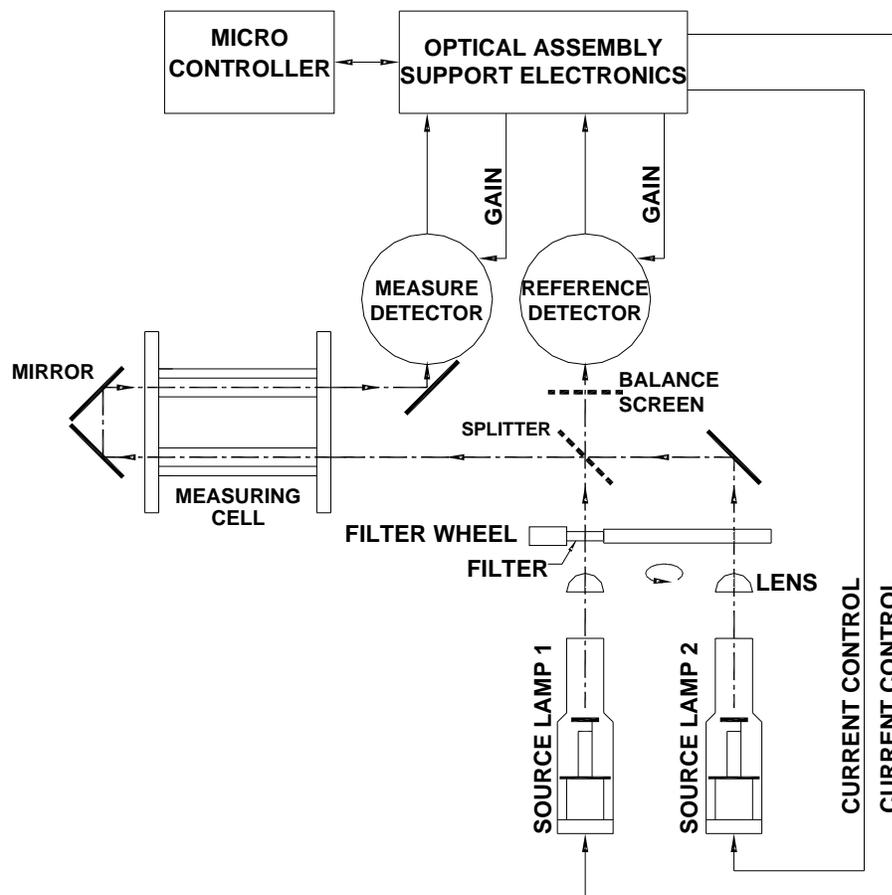

Figure 2 – Dual Beam Multi-Wavelength Spectrophotometer

A cell length of 81 cm was used for the first installation measuring H_2S in the amine contactor overhead of the SCOT unit, where a full-scale measuring range of 0-500 ppm was required. Since that original installation, the most common full-scale measuring range for H_2S in contactor overhead applications is 0-1000 ppm, so a 40 cm cell length is often used.

Thermal Conductivity Sensor

The thermal conductivity sensor uses a Wheatstone bridge type circuit with matched heated-wire elements on both sides of the bridge. One of these heated elements is used as a reference and is sealed inside a compartment containing air while the other element is exposed to the sample gas. A constant voltage is supplied across the bridge and this controls the maximum temperature of the elements. The measuring element loses more heat than the reference element if the sample gas has a higher thermal conductivity than the reference air. Increased heat loss reduces the temperature and lowers the resistance of the measuring element. The reduction of measuring element resistance unbalances the bridge circuit, resulting in an increase in the bridge output voltage, which is read as increasing thermal conductivity of the sample gas. Both heated elements are located in a compartment behind a sintered stainless steel flame arrestor with sample gas flowing past the sintered disk and diffusing into the area around the elements as shown in Figure 3.
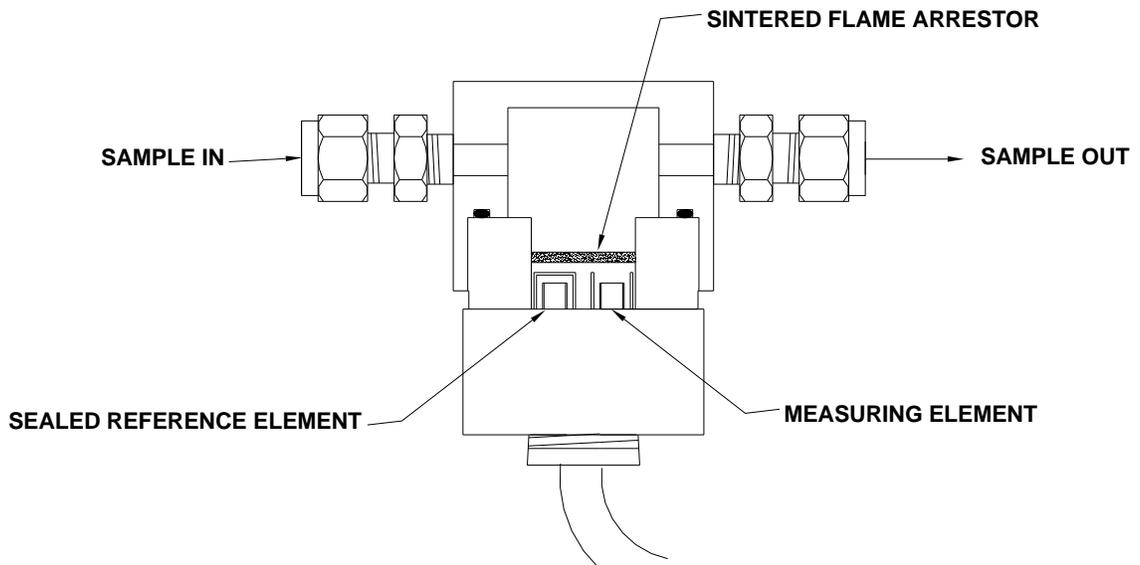

Figure 3 – Layout of Thermal Conductivity Sensor

Thermal conductivity sensors can be used to measure the composition of binary gas mixtures if the two components in the mixture have sufficiently different thermal conductivities. However, sample gas in the amine contactor overhead in a SCOT unit is not a binary gas mixture. A typical stream contains approximately 10% water vapor (H_2O), 10% carbon dioxide (CO_2), and 3% hydrogen, with most of the balance being nitrogen (N_2). There are small quantities of hydrogen sulfide, various hydrocarbons, carbonyl sulfide, and carbon monoxide, but these do not have a significant effect on the thermal conductivity of the mixture because their concentrations are low relative to the major constituents. It is still possible to make the hydrogen measurement by considering the sample gas to be a binary mixture, if the concentrations of water vapor and carbon dioxide are stable, or if the impact of their variation can be minimized. Water vapor concentration is a function of the

temperature and pressure in the amine contactor since the sample gas is essentially saturated with water in the contactor. Good control of the amine temperature and stream pressure will result in a relatively stable water vapor concentration. Carbon dioxide concentration is affected by changes in the composition of SRU plant feed and swings in SRU air demand. It can also vary with the duty cycle of the reducing gas generator (RGG) that is typically used to add hydrogen to the stream before the SCOT catalyst bed. Carbon dioxide concentration varies more than the water vapor, so it is desirable to operate the TC sensor under conditions that minimize the effect of changes in CO_2.

Experiments were carried out to determine the effects of sample pressure and sensor temperature on the thermal conductivities of gas mixtures containing nitrogen, hydrogen, carbon dioxide and water vapor. It was found that the effect of CO_2 variation on the mixture thermal conductivity could be minimized at TC sensor temperatures between 400°C and 600°C where the thermal conductivity of CO_2 is closer to that of nitrogen and air than it is at lower temperatures. Higher temperatures increase the effect of water vapor concentration changes, which is not an issue in applications with stable water vapor content. In applications with unstable water vapor concentration, or if the analyzer is switched between streams, it is possible to dry the sample gas to eliminate this issue. The output of the TC sensor is shown in Figure 4 at hydrogen concentrations of 0 to 10%. The output is very linear with only a very small non-linearity correction being required.
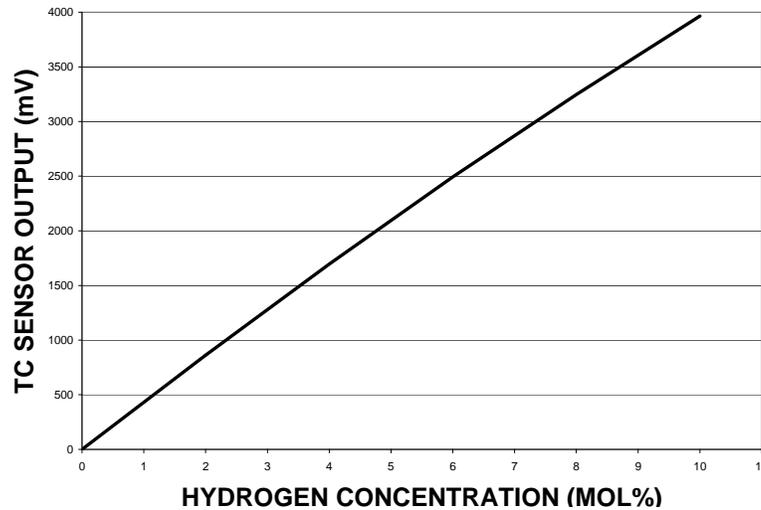

Figure 4 – Output of TC Sensor vs Hydrogen Concentration

After reviewing the data from these experiments, it was determined the hydrogen concentration of mixtures representative of SCOT contactor overhead sample gas could be calculated using the following equation:

$$H_2 = S_{H2}(M_S-M_0) + Q_{H2}(M_S-M_0)^2 - \alpha(P-P_0) - \beta[CO_2] - \gamma[H_2O] \qquad (1)$$

Where H_2 = Hydrogen concentration (mol %)
S_{H2} = TC sensor linear gain
Q_{H2}= TC sensor quadratic correction
M_S = TC sensor signal on sample gas (mV)
M_0 = TC sensor signal on zero gas (mV)
α = Pressure coefficient
P = Pressure reading (mmHg)
P_0 = Pressure reading during zero (mmHg)
β = Correction Factor for carbon dioxide
$[CO_2]$ = Carbon dioxide concentration in sample gas (mol %)
γ = Correction Factor for water vapor
$[H_2O]$ = Water vapor concentration in sample gas (mol %)

The tests were also used to select the supply voltage for the TC sensor that would result in the element operating temperature that offers the best combination of sensitivity to H_2 measurement over a 0 to 10% range and also minimize the effect of CO_2 concentration changes. Since water and CO_2 are not being measured, static concentration values are used in the software to correct the H_2 reading for their presence in the process gas.

Sample System Design

Development of the Heated Sample Probe
Sample gas from the absorber overhead in the SCOT process contains moderately high levels of H_2 and H_2S that make it undesirable to vent to atmosphere, even at the low flow rates required by an analyzer. The sample is typically saturated with water at a temperature between 40°C and 50°C, requiring heating of the probe and other sample handling components to prevent condensation. An aspirator was selected for the sample transport method to avoid moving parts and return the sample to the process. The sample return point was the preferred location for the aspirator to avoid the vent backpressure issues associated with long sample lines. A probe was developed that combined the sample and vent into a single sample point connection that included two ball valves for manual isolation of the sample and vent, a 25 mm (1") diameter membrane filter on the sample side, and an aspirator on the vent side. A heater is mounted on the top of the probe to allow all of the components including the sample and vent line connection fittings to be kept at a temperature higher than the water dew point. A flow schematic of the probe is shown in Figure 5. A Pt100 RTD in the probe is connected to the analyzer and used to provide probe temperature control. An internal temperature switch is used as a secondary over-temperature limit control. The heater is certified for use in Division 1 and Zone 1 hazardous areas.
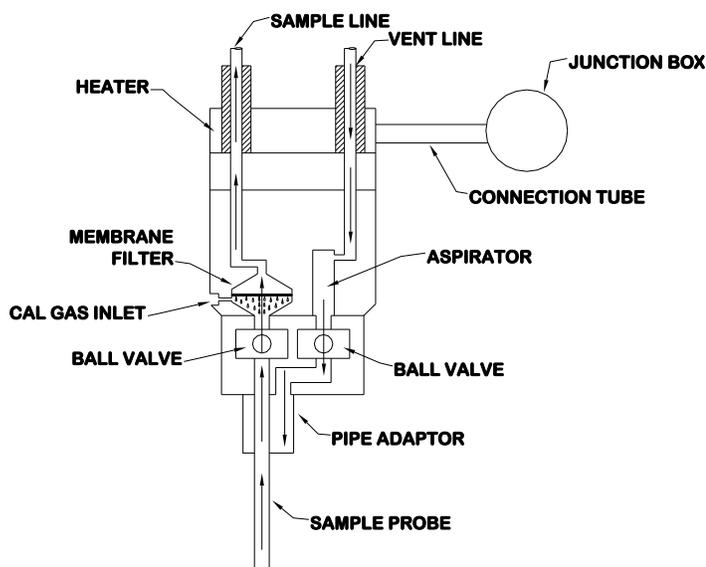
Figure 5 – Schematic of Heated Sample Probe

Installation at Big Spring, Texas Refinery

The Big Spring refinery has two SRUs, (one 60 t/d and one 75 t/d capacity), a SCOT tail gas treater follows both. "SRU one" was operating under a grandfather clause without a tail gas treater. The load to SRU two is relatively stable with load variations being handled by SRU one. The high load variations seen in SRU one made it a good location to evaluate the SCOT $H_2 + H_2S$ analyzer. The SCOT unit was constructed as a fast track project in 2004 with Ortloff Engineers and it was brought on-line in April 2005.

Installation

The analyzer included a heated sample switching system, which allowed temporary manual switching between the standard sample point at the amine absorber outlet and another sample point before the absorber and the quench tower. A sample dryer was used to remove the water vapor from the sample to avoid problems with the very high water content when sampling before the quench tower. The sample system schematic is shown in Figure 6.

The analyzer was commissioned and after operating for some time, it was determined that the service life of the membrane filter in the probe could be increased by periodically switching between sample points while back flushing the idle probe with nitrogen. This back flushing seemed to be effective in temporarily removing particulate from the filter element. The probe was redesigned to allow the installation of a larger diameter membrane filter (approximately 55 mm diameter), which should result in higher sample flow rate and longer intervals before service is required. A small diameter flat element fiber filter was also added to reduce particulate loading on the membrane filter.
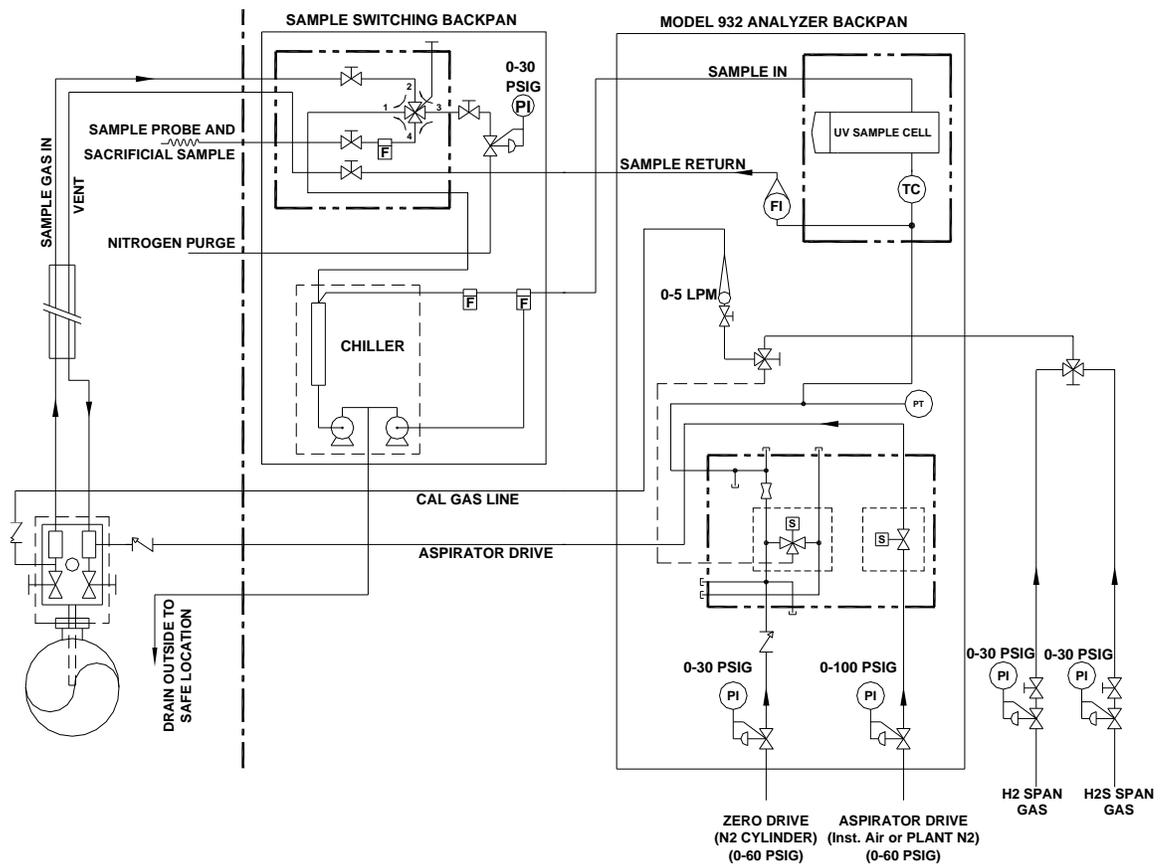
Figure 6 – Schematic of Analyzer Sample System

The redesigned heated probe was installed at the Big Spring refinery in September 2006 and operated for over 3 months without back-flushing. The probe seemed to be working properly at the end of this testing, but the flow rate had dropped from over 5 L/min (10 scfh) to about 2.5 L/min (5 scfh). The probe was disassembled and the inspection showed that the fiber filter had a 6 mm (1/4") thick coating of what appeared to be sulfur as shown in Figure 7. It is thought that this sulfur deposited on the filter during a process upset when SO_2 breaking through the CoMo catalyst bed required that the absorber amine solution be replaced. The membrane filter was still fairly clean, in spite of the sulfur deposit on the fiber filter. A spare fiber filter was not available at the time, so the sulfur coating was scraped off and a new membrane filter was installed. Removal of this sulfur coating restored the flow rate to a normal value of 5 L/min.

Figure 7 – Sulfur on Particulate Filter After Process Upset

Data

Figure 8 shows some data from the analyzer recorded as one minute averages. Hydrogen sulfide concentration (ppm) at the absorber outlet and SCOT catalyst bed outlet temperature (°C) are plotted on the primary Y axis. The secondary Y axis shows the H_2 concentration at the absorber outlet (%), the COS concentration (ppm) at the absorber outlet, and the SO_2 concentration in the SRU tail gas which was measured by the SRU Air Demand analyzer. The first section of data shows normal, stable operation, with the H_2 between 2 and 3%, the COS at close to 0 ppm, and the H_2S at 100 ppm. During this same period, the SO_2 concentration in the tail gas is about 0.2% and the SCOT catalyst outlet temperature is just below 300°C. An upset occurs in the SRU at about 19:00, which drives the SO_2 concentration up above the 1% full-scale. The flow is switched to bypass around the SCOT unit in order to protect the amine from SO_2 breaking through the SCOT reactor (sometimes determined by a drop in pH of the water in the quench tower). Once the flow is bypassed, the analyzer is basically offline while the flow is in bypass mode. The temperature of the SCOT reactor drops during the period that the flow is bypassing the SCOT unit. SRU operation begins to stabilize at approximately 04:30 and after the SO_2 concentration drops down close to zero, the flow is switched back to the SCOT catalyst bed. The outlet temperature of the SCOT reactor rises when heated by the hot gas stream from the reducing gas generator (RGG) and the hydrogenation reactions. Readings from the analyzer show that the process quickly returns to normal operating conditions once the reactor temperature stabilizes. Normally there is no COS being read by the analyzer at the absorber outlet. The brief rise in the COS to just over 5 ppm occurred when the sample point was temporarily switched to before the quench tower. This COS reading of 5 ppm is consistent with the equilibrium concentration typically seen from fully active catalyst (in this case about 1.5 years old).
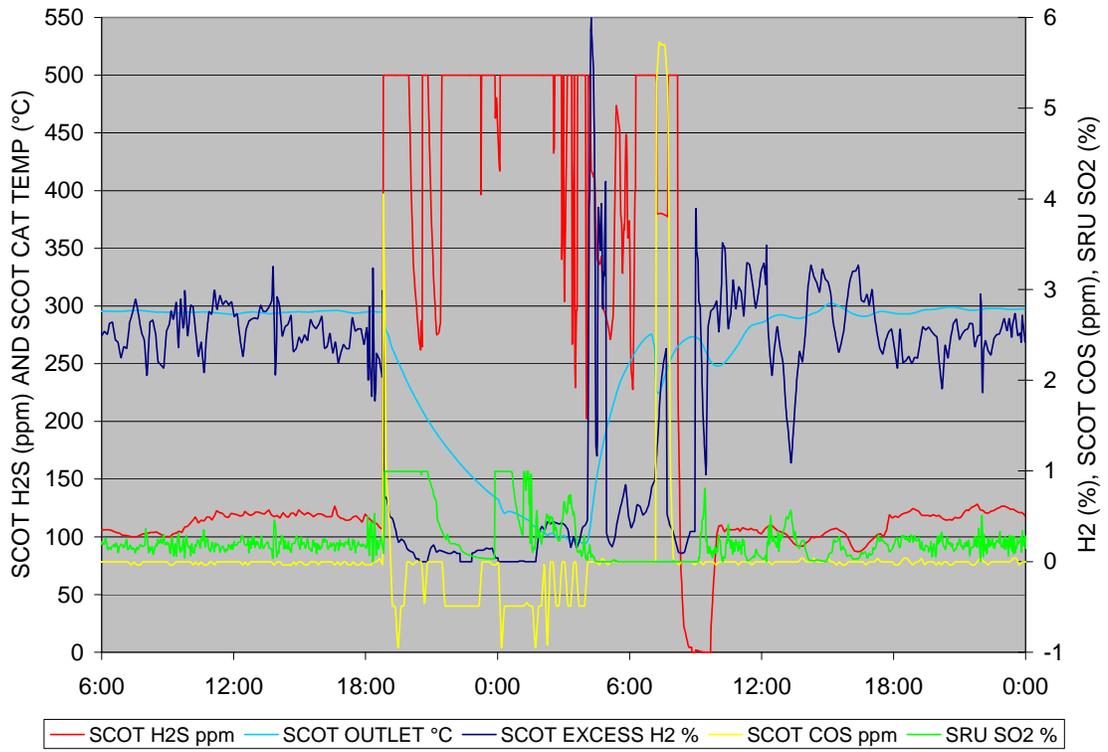
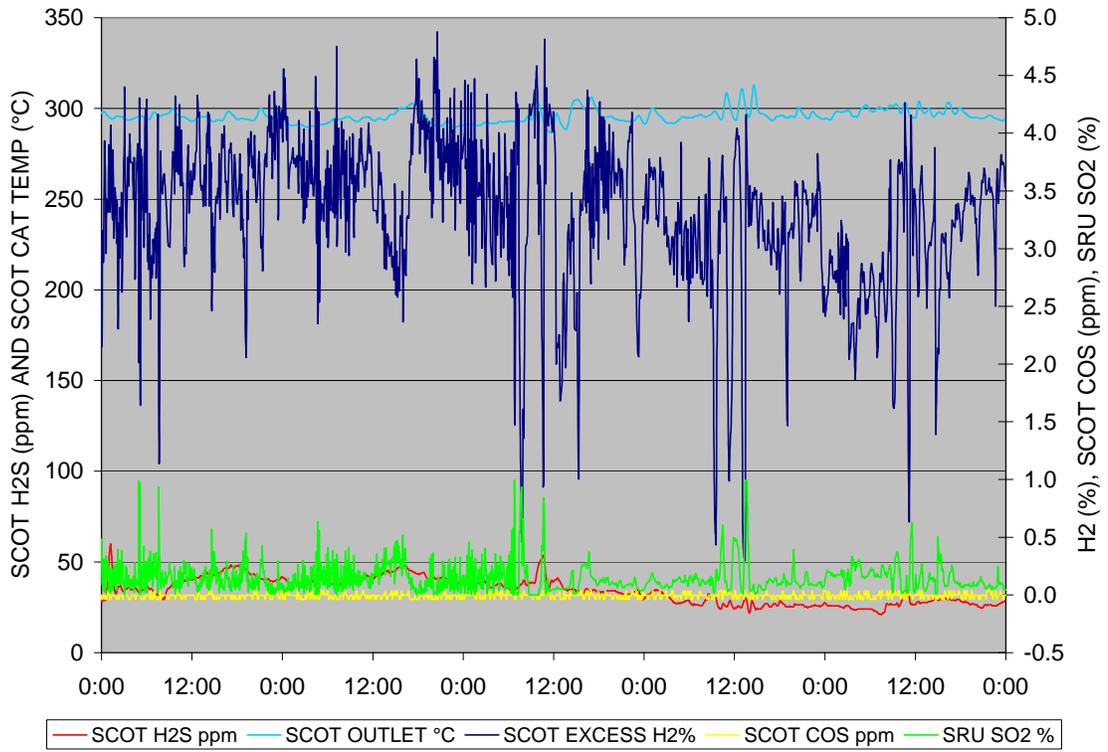**Figure 8 – Data from Process upset in SRU/TGT**

Figure 9 – Data Showing Effect of SO₂ Excursions

Although several hydrogenation and hydrolysis reactions are carried out in the SCOT reactor, the hydrogenation of SO_2 consumes a large portion of the hydrogen because it has a higher concentration than other sulfur species (with the exception of H_2S) and because 3 moles of H_2 are required for each mole of SO_2 as shown in Equation 2.

$$SO_2 + 3H_2 \rightarrow H_2S + 2H_2O \hspace{4cm} (2)$$

Sulfur vapor and liquid can also consume significant quantities of hydrogen, but their concentrations do not typically vary as much as SO_2. Stable operation of the SRU and good control over the SO_2 concentration / SRU trim air are critical for successful operation of a SCOT TGT. This effect is shown in Figure 9, where excursions in SO_2 concentration in the reactor feed result in sharp drops in H_2 measured in the absorber overhead. The reactor outlet temperature increases with SO_2 concentration because the reaction in Equation 2 is exothermic. Excess H_2 was on manual control, but was at a sufficient level during stable operation to maintain the excess during upsets.

Conclusions

Good control and measurement of excess H_2 is important to provide stable operation of an amine based TGT. The sample can be taken at the top of the quench or absorber column where the H_2 value is essentially the same and, depending on the sample point, the H_2S measurement is used for different purposes. A process analyzer has been developed that combines these measurements along with optional measurement of COS.

The analyzer was field tested for over a year on "SCOT one" unit at a refinery in Big Spring, Texas. Feedback from this testing was used to improve the design of the sample system, resulting in a system that operated reliably in a variety of conditions including process upsets. While collecting data and investigating the performance improvements in the heated probe design, it was decided to incorporate the probe modifications into the upgrade on "SCOT two" and for all subsequent TGTU applications. There are now some 65 analyzers in service.

There is a significant safety component to this application, in particular if the sample point is before the absorber where H_2S is ~2.5%. Technicians are more likely to maintain an analyzer with a simple and positive method to isolate the analyzer and where the sample system is specific to the application.

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