SAMPLE CONDITIONING TECHNIQUES FOR SPECTROSCOPIC ANALYSIS OF OPAQUE PROCESSES

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ABSTRACT
Absorbance spectroscopy is widely utilized for online analysis of process streams. This technology has long provided substantial benefits including being solid state, requiring no consumables, and having a large dynamic range. Although extremely versatile, some complex stream compositions prevent the use of absorbance spectroscopy due to relatively high levels of opaque compounds. There are a variety of sample-conditioning techniques which can be employed to facilitate spectroscopic analysis in streams that otherwise could not be analyzed this way. This paper discusses three such techniques. The primary focus is on the implementation of an in-situ demister, a capillary separation column, and a headspace absorption tower. The design of each configuration is detailed, with particular emphasis on relevant applications for each approach. These sampling technologies provide a sample stream that is representative of the process with respect to the components of interest. They are also operable online in an industrial environment, and minimize service requirements and downtime. Future modifications for improvement are also discussed.

INTRODUCTION
In the analytical world, conditioning of a sample is always necessary to some degree. The sample conditioning methods employed and components installed are largely dependent upon both the type of analyzer and the parameters of the process.

In the case of spectroscopy there are a few standard rules for sample preparation.
- The phase of the sample must be homogenous, this means either 1 or 0 vapor fraction. Additionally, if the vapor fraction is 0, then the liquid phase must be miscible.
- The particle size, distribution, and load of the sample must be such that scattering is not present in the analysis.
- The sample must not be opaque in the relevant wavelengths of measurement.

**ABSORBANCE SPECTROSCOPY**

**BASIC THEORY**

Absorbance spectroscopy is based heavily on two equations of Beer-Lambert’s law relating absorbance to concentration (6).

The first notable equation is:

\[
A = \log(\frac{I_0}{I}) \tag{1}
\]

Where \( A \) = Absorbance  
\( I_0 \) = Light In  
\( I \) = Light Out

The second notable equation is:

\[
A = \varepsilon b c \tag{2}
\]

Where \( A \) = Absorbance  
\( \varepsilon \) = Molar absorptivity  
\( b \) = Path Length  
\( c \) = Concentration

Chemicals such as Hydrogen Sulfide, Sulfur Dioxide, Ammonia, Chlorine, Carbonyl Sulfide, Nitric Oxide, Nitrogen Dioxide, Benzene, Toluene, and Xylene all absorb light in the ultraviolet (UV) region of the electromagnetic spectrum and therefore can be measured using absorbance spectroscopy.

**IMPLEMENTATION OF THEORY**

**HARDWARE**

The “light flow” of the analyzer starts with a light source that generates electromagnetic radiation. Light source choices include Xenon, Tungsten, and Deuterium. The light source should be chosen based on which wavelengths will be of interest.
After generation, the light travels through a fiber optic cable until it reaches the sample path or flow cell. The flow cell is where the light is directed through the sample.

Physically, the flow cell is a cylindrical vessel with four connections. Two of the connections are intended for sample flow in and out. The other two connections allow light in and out.

After interacting with the sample, the unabsorbed light continues through another fiber optic cable to a concave holographic grating that separates the white light into its components. The light is then directed onto a diode array detector. The diode array can be thought of as 1024 individual detectors, each one measuring a different wavelength of light. The light intensity is measured at each diode and a spectrum is formed.

**MULTI-WAVELENGTH, MULTI-COMPONENT**

Diode array spectrometers measuring at multiple wavelengths offer a significant advantage over photometers measuring at one wavelength. Measurement at each wavelength from 200-800 nanometers allows for great selectivity and variability among applications. It also allows for one analyzer to measure multiple components simultaneously as can be seen mathematically in the following example (7).

The measurement of Hydrogen Sulfide (H$_2$S) and Sulfur Dioxide (SO$_2$) is a typical multi-component application that has been historically done with a diode array spectrometer. They exhibit overlapping absorbance curves in the ultraviolet region and as a result cannot be measured by a single wavelength photometer. The following equations provide an oversimplified, basic understanding of how a diode array spectrometer solves for two components. In actuality, these equations are being solved at each wavelength specified within the wavelength range.

\[
\text{Log } \left( \frac{I_0}{I} \right)_{220\text{nm}} = b(\varepsilon_{H_2S-220\text{nm}} \times C_{H_2S} + \varepsilon_{SO_2-220\text{nm}} \times C_{SO_2})
\]

\[
\text{Log } \left( \frac{I_0}{I} \right)_{280\text{nm}} = b(\varepsilon_{H_2S-280\text{nm}} \times C_{H_2S} + \varepsilon_{SO_2-280\text{nm}} \times C_{SO_2})
\]

Where $I_0$ = Light In
$I$ = Light Out
$b$ = Path
\(\varepsilon_{H_2S-220\text{nm}}\) = H$_2$S extinction coefficient at 220 nanometers
$C_{H_2S}$ = H$_2$S concentration
\(\varepsilon_{SO_2-220\text{nm}}\) = SO$_2$ extinction coefficient at 220 nanometers
$C_{SO_2}$ = SO$_2$ concentration

Figure 1 is an illustration of H$_2$S + SO$_2$, as well as each in their analytically separated spectra using proprietary software.
FIGURE 1. H₂S AND SO₂ SPECTRA

ANALYZING OPAQUE PROCESSES

Most chemical processes are made up of several compounds. In a given process, one is interested in measuring the concentration of one or more of these compounds. There are countless different measurement techniques available, each having their own advantages and disadvantages. One of these techniques is absorbance spectroscopy (2).

A primary concern when using absorbance spectroscopy is the issue of absorbance dynamic range. There are two basic scenarios in which absorbance dynamic range will have an impact on the viability of absorbance spectroscopy as a measurement technique. In one case, the absorbance of the analyte is significantly lower than the absorbance of the total process matrix. This prevents accurate measurement of the analyte because variation in its absorbance will be indistinguishable from noise in the total process absorbance. In the other case, the total absorbance of the process stream is so great that essentially no light is transmitted through the sample. Since absorbance is a function of transmitted light, as seen in Equation 1, when no light is transmitted through the sample the absorbance increases rapidly. The maximum absorbance (or minimum transmittance) is ultimately governed by the performance (noise level) of the spectrometer used. While there are spectrometer solutions available with extremely low noise detectors, which can measure very small amounts of light accurately, they are typically not suited for industrial use. Also as performance increases, so does cost. These factors make the best choice a detector that possesses the best combination of performance, ruggedness, and price.

In both of the previous cases, the overarching issue is that of high process absorbance in the wavelength range of interest. Therefore, if a solution could be found that did not require high operation or capital costs, delicate electrical devices, or extensive operator training, it would be
ideal. The solution should permit the use of absorbance spectroscopy as the analytical technique in these high absorbance processes.

The solution is physical separation. In these high absorbance processes, one approach is to physically condition the sample stream such that high absorbing components of the matrix are separated from the component(s) of interest.

The first case study is a traditional tail gas application. The typical tail gas process stream contains considerable levels of elemental sulfur (in vapor phase), along with low percent levels of $\text{H}_2\text{S}$ and $\text{SO}_2$ (5). Sulfur vapor exhibits a significant absorbance curve in the low UV (200-300nm) wavelength range. This is also the range in which typical absorbance spectroscopy based $\text{H}_2\text{S}$ and $\text{SO}_2$ measurements are made. Through the implementation of an in-situ demister probe, the sulfur vapor can be condensed out of the process sample, allowing for the measurement of $\text{H}_2\text{S}$ and $\text{SO}_2$ in the low UV range.

The second case study is a gas process stream that contains mostly nitrogen, low percent levels of $\text{SO}_2$, and low PPM levels of $\text{H}_2\text{S}$. For this application it is necessary to measure both of these components. However, due to the large difference in concentration (and thus absorbance) between these two sulfur compounds, the $\text{H}_2\text{S}$ cannot be measured accurately using absorbance spectroscopy in an unconditioned process sample. Through the use of a capillary column, specially designed sampling system, and customized software, the $\text{H}_2\text{S}$ can be separated from the $\text{SO}_2$ temporarily. This allows for the measurement of the $\text{H}_2\text{S}$ concentration as it exits the column just before the $\text{SO}_2$. This can be referred to as a hybrid (GC-UV) measurement approach.

The final case study is a liquid crude oil process, which contains PPM levels of dissolved $\text{H}_2\text{S}$. Again, it is necessary to measure the concentration of this component. The liquid crude oil process is essentially opaque in the low UV region, preventing traditional absorbance spectroscopy measurement. In this case a desorption column is used to enrich an inert carrier gas with the component of interest. The carrier gas is then passed through the flow cell for analysis.

THE CLAUS PROCESS, TAIL GAS PROBE, AND Sulfur Vapor

THE CLAUS PROCESS

A critical step in refining crude oil and natural gas is the removal of naturally occurring hydrogen sulfide ($\text{H}_2\text{S}$) and other contaminating sulfur compounds. Typically, an amine unit is used to absorb $\text{H}_2\text{S}$ from fossil fuels. The Claus sulfur recovery process is the industry standard for turning the toxic $\text{H}_2\text{S}$-rich gas from the amine unit (also known as “sour” gas) into elemental sulfur.

In the reaction furnace, $\text{H}_2\text{S}$ is combusted with oxygen at a pressure of approximately 1.5 barg and a temperature of approximately 1000 $\text{C}$. The process reaction for the combustion is shown below:
\[ 3\text{H}_2\text{S} + \frac{3}{2}\text{O}_2 \rightarrow \text{SO}_2 + \text{H}_2\text{O} + 2\text{H}_2\text{S} \quad (5) \]

During the combustion reaction, approximately 70% of the \( \text{H}_2\text{S} \) in the sour gas is converted to elemental sulfur.

In an effort to remove additional sulfur, and hydrolyze any carbonyl sulfide (COS) and carbon disulfide (CS2) the gas is then sent through a series of three catalytic reactors at temperatures of approximately 305\( ^\circ \)C, 225\( ^\circ \)C, and 200\( ^\circ \)C, respectively. Commonly an \( \text{Al}_2\text{O}_3 \) (alumina) catalyst is used. The process reaction for the catalytic reactor is shown below:

\[ 2\text{H}_2\text{S} + \text{SO}_2 \rightarrow 2\text{H}_2\text{O} + 3\lambda\text{S}_\lambda \quad (6) \]

During the catalytic reactions, approximately 20%, 5%, and 3% of the \( \text{H}_2\text{S} \) is converted to elemental sulfur, respectively.

The Claus process as a whole is capable of achieving 98% conversion of \( \text{H}_2\text{S} \) to elemental sulfur(18).

The correct stoichiometric ratio of \( \text{H}_2\text{S} \) to \( \text{SO}_2 \) (2:1) is necessary for efficient conversion. As seen in the combustion reaction, maintaining this ratio requires constant adjustment of the oxygen flow. The efficiency of the Claus process thus hinges on accurate, continuous measurement of the concentration of \( \text{H}_2\text{S} \) and \( \text{SO}_2 \). Additionally, the monitoring instrument should be able to detect concentrations of CS2 and COS, as the presence of these components in the tail gas stream indicates potential problems with the catalyst bed.

**THE TAIL GAS PROBE DESIGN**

The Claus process is not without sampling challenges. Perhaps, the most troublesome is the presence of elemental sulfur. This issue is two fold. Not only can solidification of the sulfur cause plugging in sampling lines, but also any elemental sulfur remaining in the sample can cause inaccuracies in the \( \text{H}_2\text{S} \) and \( \text{SO}_2 \) readings. In an effort to eliminate these issues, a demister is generally used.

The probe is designed to draw a continuous sample for analysis. As the sample enters the probe, it passes the demister. The demister acts as a heat exchanger and cools the sample passing by it. As the sample cools, elemental sulfur condenses and returns to the process by gravity. After being measured and leaving the probe head, the sample is exhausted back in the process pipe (17).

In Figure 2, a schematic of the probe head is shown. The arrows signify flow direction. The red disk represents the sample path across which the measurement is taken. To be sure that the sample does not cool, the disk has steam running through it. The purple disk offers the aspirated motivation needed for sample flow. The teal disk is welded to the demister and is where the cooling steam enters and exits the probe.
FIGURE 2. SCHEMATIC OF PROBE HEAD

SPECTRA FROM THE TAIL GAS PROCESS

The TLG-837 is also equipped with a diode array spectrometer and is able to capture the unique spectral characteristics of gases typically found in the Claus process like H₂S (Figure 3), SO₂ (Figure 4), COS, and CS₂.

FIGURE 3. H₂S SPECTRA
FIGURE 4. SO₂ SPECTRA

TRENDS/PROCESS DATA

The concentrations of H₂S and SO₂, as well the mathematically derived Air-Demand signal, are used for control of air entering the Claus Process. If the process is too rich with air, then higher SO₂ readings will result. If the process is air deprived then higher H₂S readings will result. Therefore, the H₂S and SO₂ should show an opposite trend. This is illustrated in Figure 5.

FIGURE 5. TAIL GAS TREND GRAPH (H₂S IN GREEN, SO₂ IN BLACK, AIR DEMAND SIGNAL IN RED).
CAPILLARY COLUMN (GC-UV)

In this application, the customer required a measurement of both H₂S and SO₂ concentrations in an air background. When the concentrations of these two chemicals are similar, they can be measured simultaneously with one UV absorbance based analyzer by utilizing multi-component analysis since the necessary spectroscopic parameters are similar (wavelength range, required light source intensity). A detailed discussion of this approach is presented in a prior section of this paper.

However, in this particular case the two concentration ranges are substantially different (SO₂: 0-6600 PPM; H₂S: 0-30 PPM). Here, the SO₂ concentration is so much greater than the H₂S that its absorbance completely obscures that of the H₂S. This complication arises in any application in which there are two or more components, which absorb light in the same wavelength range and are present in significantly different concentrations. A visual illustration of this is provided in Figure 6.

![Figure 6. 30 PPM H₂S AND 6000 PPM SO₂](image)

**FIGURE 6. 30 PPM H₂S AND 6000 PPM SO₂**

This shows an absorbance curve of 30 PPM H₂S, and 6600 PPM SO₂. Both of these curves are observed with the same path length and cell pressure. The system parameters (light level and calibration method) that are required to accurately measure the SO₂ cannot be used to measure H₂S at the required concentration. Utilization of a gas chromatography (GC) column can circumvent this limitation of absorbance spectroscopy.
To provide a measurement solution for this application, a hybridized GC-UV technique is used. This technique takes advantage of the strengths of both the chromatography column and full spectrum UV absorbance measurement. The basic layout of such a system is presented in Figure 7.

![FIGURE 7. GC-UV SAMPLING SYSTEM (VALVES SHOWN IN INJECTION MODE)](image)

In this design, a small sample volume is passed through a capillary column prior to insertion into the measurement cell. This separation is carried out using a GC column that was specifically chosen due to its ability to effectively separate H$_2$S from SO$_2$. In normal operation, a carrier gas continuously flows through the column. An injection valve is actuated periodically to introduce a small volume of process gas into the column. This results in a discrete measurement cycle made up of a brief injection period, and a longer elution period during which carrier gas motivates the process injection through the column (14).

Unlike a typical gas chromatograph, the GC-UV system uses the absorbance of the component for quantification. The absorbance (as an array of absorbance versus wavelength) is measured several times during the elution period of the H$_2$S. Due to this measurement approach, the capillary column does not need to provide complete sample separation. Since the absorbance measurement is made at many wavelengths simultaneously, the analyzer still carries out multi-component analysis, thus preventing interference from trace amounts of other sulfur compounds (16).

Ultimately this hybridized GC-UV technique provides concentration measurements for low-level components in streams that could not otherwise be analyzed using UV absorbance. The system utilizes a field proven, highly selective UV absorbance measurement device and an industry-
proven chromatography column. The results from this device are similar to those produced by a classical gas chromatograph, with one important difference: they are based on the measurements of a multi-wavelength spectrometer, rather than a single point detector. When these results are analyzed in real time using specialized GC-UV software, the system becomes a highly selective and sensitive online process analyzer.

HEADSPACE

In petroleum refining, it is necessary to monitor the concentration of specific volatile compounds in liquid crude oil. In one particular case, there was a need to continuously measure the concentration of H₂S dissolved in a crude oil process. In order to carry out this measurement, absorbance spectroscopy was used in conjunction with a continuous flow headspace sampling system.

As stated previously, in this application it is not practical to carry out an absorbance analysis of the liquid process directly. This is illustrated in Figure 10.

![Crude Oil Absorbance Spectrum](image)

**FIGURE 10. CRUDE OIL ABSORBANCE SPECTRUM**

The absorbance of the liquid crude oil process is fully saturated throughout the H₂S measurement region, and thus prevents direct measurement.

Instead, a headspace desorption column is employed to enrich a carrier gas with the H₂S. After enrichment, the carrier gas flows into a flow cell where its absorbance spectrum is measured. By sampling the component of interest in this way, it can be measured using absorbance spectroscopy despite the high opacity of the original process stream.
Desorption (stripping) towers have long been used in chemical processing. These towers permit volatile compounds dissolved in a liquid stream to be transferred into a carrier (or stripper) gas. There are two basic types of desorption towers: plate and packed. These two differ in their internal design, however the basic principle is the same. By passing the carrier gas over a very high surface area of the liquid, mass transfer occurs at a high rate. This enriches the carrier gas with the volatile compounds present in the liquid. The column design, packing material used, and column temperature govern the mass transfer rate of volatiles from the liquid to the gas (16).

For this application, maximum mass transfer is desired since a greater concentration of the analyte in the carrier gas results in high absorbance signal and better analyzer performance. Thus the primary objective for tower design is to maximize the mass transfer rate of the volatile analyte. There are essentially three parameters that affect this rate: column dimensions, packing material, and column temperature. Although the flow rates of both the carrier gas and process liquid also influence the final quantity of analyte absorbed by the carrier gas, these are highly adjustable, and thus are set after construction (15).

Tower height and diameter are major factors when designing a desorption tower. Since the mass transfer rate is partially dependent on total surface area inside the tower, increasing its interior dimensions also increases the mass transfer rate of the system. It is important to note that these two parameters are strongly constrained by practical considerations. In reality this system must fit into an enclosure and/or analyzer shelter, which limits the maximum height and diameter of the column to a few feet and inches, respectively. In this particular headspace sampling system, the column chosen was two feet in height, and two inches in diameter. While quite small compared to its industrial scale chemical processing cousins, this desorption tower provides an excellent mass transfer rate despite its scale (15).

In a plate tower, the interior volume of the column is filled with a series of shallow plates. Plate towers offer some considerable advantages for large scale stripping columns, but are not economical for smaller scale operations (16). Packed towers differ from plate towers in that they are filled with an organized (or random) volume of specially designed packing material. In the case of small diameter columns, random packing is the most economical choice. In the case of this headspace sampling system, randomly packed 316 stainless steel Pall rings were selected. Randomly packed Pall rings are inexpensive and cause a minimal pressure drop compared to other options (16).

Another major factor to consider when designing a headspace sampling system is tower temperature. In order to facilitate maximum mass transfer of the volatile analyte, it is beneficial to increase the temperature of the column above ambient. Since the boiling point of the analyte in many cases is much lower than that of the bulk liquid, increasing the temperature increases the proportion of the dissolved analyte that moves into the gas (15). Thus the headspace sampling system incorporates heaters on the tower to bring the temperature closer to the boiling point of the analyte. Figure 11 illustrates a typical system for this application.
FIGURE 11. TYPICAL HEADSPACE SAMPLING SYSTEM

This system is made up of a UV diode array spectrometer, industrial computer, and all other electronics necessary to facilitate the absorbance measurement. The headspace sampling system is made up of a desorption tower, carrier gas and process liquid flow meters, and the necessary valves and regulators to control the system. The third and final major component is the measurement system is the flow cell, where the carrier gas absorbance is measured for analysis.

CONCLUSION

UV absorbance spectroscopy provides some distinct benefits in an industrial setting. The multi-wavelength nature of the analysis allows for component de-convolution. The measurement sample can be hot and contain water, therefore relatively little filtration is required. There are no moving parts and no consumables required for analysis. The measurement itself is very fast, allowing for fast response times. Given the benefits the approach provides, it is relatively inexpensive compared to other industrial analytical techniques. In many scenarios it is an attractive choice for process analysis.

As has been demonstrated however, there are many real world applications that cannot be analyzed directly using UV absorbance. This has led to the development of the sample conditioning techniques presented in this paper. Each accomplishes the task of converting an opaque process sample into an appropriately transparent one, thus permitting the quantitative analysis of specific process components. Furthermore, these systems accomplish this conversion continuously and automatically, making them effective online process analyzers.
REFERENCES


