PROCESS ANALYZER FOR CLEAN COAL
APPLICATIONS

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ABSTRACT
Coal is utilized as an energy source by two primary methods: burning in coal-fired electric generation plants and by coal gasification. The second method results in synthetic gas, known as syngas, which can further be converted into gasoline or diesel by the Fischer-Tropsch process (11). In the past twenty years, the clean coal initiative has forced the industry to invest billions in the development of coal cleaning processes and strategies. Sulfur is the main pollutant -- it must be removed, whether the coal is burned or gasified, to meet environmental standards (11). Various sulfur-cleaning technologies are available, from state of the art high-temperature syngas cleanup technology to the traditional sulfur recovery units. In both the flue gas (the combustion exhaust gas in coal-fired plants) and syngas, monitoring the concentration of the sulfur based components (H2S, SO2 and COS) is essential. Some measurements are due to an EPA requirement and others are part of the actual control of a process; for example, protecting an expensive catalyst from H2S in the Fischer-Tropsch reaction. UV spectroscopy techniques are used in the measurement of sulfur based components in various critical monitoring sites. The analysis technology needs to be in sync with process developments in order to assure environmentally friendly and economically sound use of coal. In the following paper, the measurement principles, applications and sampling systems for a variety of applications -- including an in-situ tail gas analyzer installed directly in the process stream measuring H2S and SO2 -- will be detailed.

INTRODUCTION
The United States holds one quarter of the world’s coal reserves, and utilizes 92% of them for power production – this means more than half of the electric power presently generated in the
USA is derived from coal. And this number may rise: alternative technologies besides coal fired burning are now being considered to convert coal into energy (1).

In the mid-1980s the majority of the pollution causing acid rain stemmed from coal-burning power plants (14). In 1985, the USA and Canada established The Clean Coal program to solve the acid rain situation. Today, power plants require that gases from the combustion of coal be cleaned, particularly of sulfur, before being released from stacks. This EPA compliance is best achieved by utilizing online analyzers instead of laboratory testing, because the analysis time is faster and allows for adjustments in real time.

**INSTRUMENTATION**

The Applied Analytics OMA-300 and TLG-837, both UV-VIS fiber-optics-diode-array process spectrophotometers, are used to measure the absorbance of the process sample (3,4,5,6,7).

The analyzers consist of four major sub units:

- a light source that generates electromagnetic radiation
- a sample area (flow cell or in-situ probe)
- a dispersion device that selects a range of wavelengths from the broad band radiation of the source (concave holographic grating)
- a diode array detector to measure the intensity of radiation at each wavelength

Light that is generated by the pulsed Xenon light source is transmitted through a fiber optics cable to a flow cell or probe, where the process gas absorbs light at a certain wavelength. The absorbance of the process gas in the flow cell is directly proportional to the concentration of the component to be measured (4). From the flow cell, the light travels through another fiber optics cable to the detector. The light is then dispersed by a holographic grating, resulting in a physical separation of the white light into its components. The light at each wavelength falls onto a different detector - the diode array contains 1024 detectors - and a spectrum (the light intensity or absorbance at each wavelength) is obtained. This process is rapid and requires no moving parts. See Figure 1.

**THE DETECTOR**

The detector is a high-resolution UV/VIS photodiode array. The diode array has a broad spectral response and high sensitivity in the ultraviolet range. The low dark current and large charge saturation enables signals to be obtained with a high signal-to-noise ratio. The detector’s aperture matches the fiber optics numerical aperture, maximizing light throughput.

**THE LIGHT SOURCE**

The light source is a very long-life, pulsed Xenon lamp. The radiant light is imaged onto the fiber tip with numerical aperture-matching optics, rather than a direct couple, for maximum light throughput, and to minimize pulse-to-pulse variation.
FIGURE 1. A DISPERSIVE BASED ANALYZER MEASURING SIMULTANEOUSLY FROM 190-800 NM AT 0.7 NM RESOLUTION

THE FLOW CELL

The gas or liquid stream interacts with light coming from the Xenon light source in a flow-through cell that is connected either directly to the process line or through a sampling system. Fiber optics are connected to the flow cell via a modular collimating lens unit. Flow cell lengths range from 1mm to 1000mm. The flow cell can be operated up to 300°C and at pressures as high as 206 bar (3000 psi). The flow cell design allows for very quick disassembly resulting in minimal downtime for routine maintenance.

The flow cell path length is optimized for each application. When choosing the path length, one needs to consider that as path length increases, so does absorbance. This relationship can be utilized in order to provide high absorbance even when measuring very low concentrations. However, transmitting light in the low UV through a long flow cell can be a challenge. In order to measure in the 210 nm range using a long (1 meter) flow cell, the optics must be perfectly aligned and designed for maximum light throughput in the low UV.

UV ABSORBANCE SPECTROSCOPY

According to Beer-Lambert’s law, the absorbance at a specific wavelength is equal to the molar absorptivity of the specific molecule at a specific wavelength, multiplied by its concentration and path length (4). As a result, the absorbance of a component at a specific wavelength can be correlated to its concentration when the path length is held constant. Molar absorptivity for a specific component varies from wavelength to wavelength. Since this absorbance tends to also
differ from component to component, analysis of a large spectrum allows for simultaneous measurement of multiple components (6).

A correlation factor is determined between absorbance and concentration during the calibration process. The correlation factors at each wavelength depend on path length and the molar absorptivity of that specific molecule at that wavelength.

MULTI-WAVELENGTH, MULTI-COMPONENT ANALYSIS

The term multi-component analysis is used to describe procedures in which several components are determined simultaneously. A variety of powerful mathematical tools can be applied to the analysis of spectroscopic data (6,8,9,10).

Multi-wavelength and multi-component analyses are feasible with the use of full spectrum spectroscopy, since an entire (190-800 nm) high-resolution spectrum is measured and processed. The same analysis method is utilized in both single and multi-component applications.

ADDITIONAL ANALYZERS

In many applications, technologies other than the UV spectroscopy must be utilized in order to supply a complete solution to a measurement problem, specifically, CO, CO₂, H₂O and O₂. These can all be measured by other techniques, such as IR spectroscopy and tunable diode lasers.

INFRARED PHOTOMETER

An infrared photometer measures the light intensity at a specific wavelength. Light generated by a tungsten light source is transmitted thru a flow cell containing the fluid to be measured. A pyroelectric detector -- containing individual optical filters designed for the analytical wavelength associated with the component to be measured -- monitors the light levels on the other side of the flow cell. The analyzer can be a stand alone unit, where the signals are converted internally into absorbance and concentrations, or an integrated unit with the UV analyzer, where only a single controller is needed.

OXYGEN ANALYZER

The oxygen analyzer utilizes a tunable diode laser as a light source and detector, which measures light lost following the interaction with the sample gas molecules. The absorbance spectrum of oxygen consists of many sharp lines, where the intensity at each line provides information about the concentration of O₂ in the sample. The laser emits light at very narrow wavelengths and high light throughputs, allowing the measurement of single high absorption lines. Furthermore, tunable lasers can scan between very close wavelengths. Stable readings are produced when the measurement and the internal reference wavelength are in close proximity.
APPLICATIONS

COMBUSTION EFFICIENCY - OXYGEN AND CARBON MONOXIDE ANALYZERS

For coal fire plants, measuring and controlling the amount of oxygen is critical. The air-to-fuel ratio needs to be controlled in order to ensure complete combustion. This prevents carbon monoxide from being sent to the flare as well as carbon monoxide being present in the ash. Measurement and control of the air-to-fuel ratio also minimizes excess air usage, which results in an increased flow of flue gas and therefore heat loss (12). Analyzers are used to measure and control combustion efficiency by measuring carbon monoxide and oxygen.

To ensure complete combustion, the caloric value of the flue gas is an important property: measuring the caloric value allows for close control of the oxygen demand. The calorific value of a gas can be measured based on a measurement of residual oxygen after combustion.

DEFINITIONS

The caloric value (CV) of fuel is the amount of heat released by a specified quantity once it has combusted. The specific gravity of a fuel is the ratio of the density of the fuel to the density of air (SG = Density of Fuel Gas/Density of Air).

The Wobbe Index of a gas is defined as the calorific value divided by the square root of the specific gravity (13).

MEASUREMENT PRINCIPLE

A known flow rate of sample gas flows through a density meter to determine the density and specific gravity of the sample gas. The analyzer mixes the fuel gas with air in a heated combustion chamber for complete combustion. The gas exiting the combustion chamber is monitored with an oxygen analyzer to determine oxygen concentration. Measuring the remaining oxygen provides an accurate measure of the combustion air demand. The combustion air demand correlates to the Wobbe Index.

CONTINUOUS EMISSIONS MONITORING SYSTEMS (CEMS)

The EPA has strict regulation concerning the monitoring and reporting of pollutants emitted to the air (12). Several technologies are now available for coal stack gas monitoring; these online monitors can vary with respect to analytical methods and sampling technique, each with its own advantages and disadvantages. Parameters such as reliability, maintenance requirements and
sample integrity should be considered when choosing the technology to be used. Samples can be extracted for measurement or measured in-situ (12).

Flue gas contains carbon dioxide (CO₂), carbon monoxide (CO), sulfur dioxide (SO₂), excess oxygen (O₂), nitrogen oxides (NOₓ), nitrogen (N₂), and water vapor.

In a typical treatment process, the gas is sent to a unit that removes the ash particulates. It then moves to a de-NOₓ unit that removes nitrogen oxides, followed by a desulphurization unit to remove sulfur compounds. Prior to being released to the atmosphere, the EPA requires that these components be measured and reported. Continuous verification of analysis is also EPA specified (12).

CEMS ANALYZERS

The components to be measured are: CO₂, CO, NO, NO₂, SO₂ and O₂. An integrated system measures NO₂, NO and SO₂ with one full spectrum UV analyzer, the CO and CO₂ with two infrared non dispersive sensors, and the O₂ with a tunable diode laser. Moisture monitoring is often also integrated into the CEM system. The system is simple and easy to maintain because one UV analyzer is used for the measurement of three of the major components. Also, since all the sensors are integrated into one system, only one control unit is required. This simplification makes this a truly integrated system.

The CEMS sampling is done with a close coupled system measuring the hot wet sample. No dilutions and drying are necessary as long as the flow is kept hot to prevent condensation in the flow cell.

SAMPLING SYSTEMS

There are essentially two different sampling system techniques: in-situ, or extractive. An in-situ system is designed to measure directly in the process stream. Extractive systems are designed to remove a sample from the process line for measurement. There are significant advantages and disadvantages to both approaches (16).

THE IN-SITU APPROACH

Direct measurement of the process stream can have some distinct advantages. Since the sample is not being transported, there is no need for sample lines. This results in high sample integrity and fast response times. There are also some drawbacks to this approach. Verification by calibration gases can be difficult or impossible in some cases. The measuring device is subject to the stream conditions, notably heat, pressure and corrosive substances. Service can also be quite difficult to carry out, as removal from the process stream is often required.
THE EXTRACTIVE APPROACH

Using an extractive sampling system brings with it some considerable advantages as well. Calibration gases can be introduced easily in such a system. Where necessary, the sample can be heated, cooled, dried or further conditioned to achieve the desired sample state. The system can be designed for ease of service and without interaction with the process. As noted above, there are also drawbacks to the extractive approach. Most notable is the need for sample lines that transport the sample for the extraction point to the analyzer. In some cases these can be quite long, leading to significant sample lag time. Often these lines must be temperature controlled and specially coated to ensure that sample integrity is maintained during transport.

THE CLOSE COUPLED APPROACH

A close coupled system delivers the positive attributes of the other two techniques, while eliminating their negative aspects. Close coupled systems use a sample extraction probe for sample acquisition. Figures 2 and 3 show the close coupled system. The need for sample lines is removed by mounting the sampling system directly on the process line. This essentially eliminates sample lag and minimizes the need for specially treated tubing, thus maintaining excellent sample integrity. This also allows for measurement of the sample “as is,” further securing sample integrity. Since the system is not in situ, introduction of calibration gases is not a problem. Also, service and maintenance are relatively easy since the system is setup much like a traditional extractive system.

FIGURE 2. CLOSE COUPLED SAMPLING SYSTEM LAYOUT AND MOUNTING
Flue gas desulfurization units or scrubbers are used to remove sulfur from the flue gas. An analyzer is used to monitor the sulfur content of the flue gas before and after the desulfurization unit, examining the performance of the scrubbers. The same analyzer with stream and analysis method switching (different wavelength ranges) is used, continuously providing sulfur levels. Figure 4 shows the absorbance spectra of SO$_2$ at two concentration levels. It can be seen that at % levels the absorbance is very high at the 280nm peak (fully saturating the detector), so it must be measured on the side of the peak, where the detector is not saturated. For the low concentration it is better to measure at the peak, since it is where the absorbance is highest.

Utilization of multiple analysis methods allows for the use of one analyzer, where each method is optimized for a specific concentration range. Since a full spectrum UV analyzer is used, the SO$_2$, NO, and NO$_2$ can be measured simultaneously with a single instrument.

After the sulfur removal from the main flue gas stream, an acid gas stream rich in H$_2$S remains. This stream is sent to a sulfur recovery unit where H$_2$S is converted to elemental sulfur. Controlling the Claus sulfur recovery process is very important for high conversion efficiency (7).
FIGURE 4. SO₂ ABSORBANCE SPECTRA AT 500 PPM AND 1%

SULFUR RECOVERY

The Claus sulfur recovery process is commonly utilized for the removal of sulfur compounds from sour gas (7). The process is optimized when the correct stoichiometric ratio of H₂S to SO₂ is achieved. The efficiency of the recovery process depends on accurate measurements of the H₂S to SO₂ ratio. To obtain this accuracy, other stream components such as CS₂, COS, and sulfur vapor need to be taken into account.

THE SULFUR RECOVERY PROCESS REACTIONS:

3H₂S + 3/2 O₂ → SO₂ + H₂O +2H₂S  Reaction Furnace   (1)
2H₂S + SO₂ → 2H₂O + 3/xSx  Catalytic Converters   (2)

PROCESS CONTROL

Typically, the H₂S to SO₂ ratio should be 2:1 for efficient conversion. The feedback control parameter (air-demand) is equal to 2[SO₂]-[H₂S] and the process is optimized when the air-demand equals zero. Other similar processes require different ratios; the full-spectrum analyzer
allows for wide concentration dynamic range and therefore can easily be applied to the control of other possible ratios. The control formula is a user-defined parameter.

THE ANALYZER

The analyzer’s design adheres to the principle of no moving parts and no sample lines in sulfur recovery applications (7). The same diode array analyzer is utilized here, but an in-situ probe is used in place of the typical flow cell.

DEMISTER “COLD FINGER” PROBE

A patent-pending demister (“cold finger”) probe is used for in-situ measurements (7). The setup requires very low maintenance, benefiting from the innovative in-situ probe (See Figures 5 and 6). The probe is designed to draw a continuous sample into its body, and remove the sulfur vapor. This is done by a “cold finger” which condenses the sulfur out of the gas in a controlled manner, and an aspirator which draws the sample through the sample chamber and returns it to the process line.

The probe is constructed from three concentric tubes. The outer tube, called the “sample chamber”, is 1.5" in diameter. This tube passes down through a ball valve into the process line, where its angled tip helps draw the process gas into the chamber. The cold finger tube located inside the sample chamber is kept much cooler than the process gas. This causes most of the sulfur to condense and drip back into the process, creating a sample stream that is free of sulfur vapor. Cooled air is constantly fed to the bottom of the cold finger through a smaller internal tube and is exhausted out the opposite side. These three tubes are welded to the first section of the probe’s head, a 1” thick disk made using 316 stainless steel. Above this is a second disk, which contains an air-driven aspirator. This provides a vacuum, which draws the process gas into the sample chamber, past the cold finger and up through an integrated flow cell at the top of the probe head. The aspirator then pulls the sample down through a waste tube, where it is exhausted back into the process.

All air/gas connections in the head are ¼” tube fittings. These accommodate the aspirator air in, cold finger air in and out and calibration gas in. The integrated flow cell has fiber optic connections on each side. The system periodically washes and zeros itself. Calibration gases can be introduced into the probe at any time for data verifications, although recalibration or spanning is not required, since it is a solid-state analyzer.
FIGURE 5. SCHEMATIC DIAGRAM OF THE PATENT-PENDING “COLD-FINGER” PROBE (PATENT-PENDING)

FIGURE 6. TAIL GAS PROBE AND FIBER OPTICS GOING BACK TO THE ANALYZER (PATENT-PENDING)
TAIL GAS ANALYZER - UV ABSORBANCE SPECTRA

The concentrations of up to five components are measured: H₂S and SO₂ for process control, COS and CS₂ for catalyst efficiency and sulfur vapor for signal compensation (7). Each one of these components has unique UV absorbance spectra. Figures 7 and 8 show the absorbance spectra of H₂S and SO₂ at different concentration levels. Figure 8 shows the total signal of a mix of 1% H₂S and 1% SO₂ and the individual signals. The absorbance spectra of the individual components are superimposed to give the total absorbance spectrum of the process sample. Figure 9 shows a typical tail gas stream spectrum. To de-convolute the signals of each of the components, a full-spectrum, multi-component algorithm is used.

![Figure 7. Absorbance Spectra of SO₂%](image1)

**FIGURE 7. ABSORBANCE SPECTRA OF SO₂%**

![Figure 8. Total Signal Absorbance of a Mix of 1% H₂S and 1% SO₂ and the Individual Absorbance Signals](image2)

**FIGURE 8. TOTAL SIGNAL ABSORBANCE OF A MIX OF 1% H₂S AND 1% SO₂ AND THE INDIVIDUAL ABSORBANCE SIGNALS.**
DENOX PROCESS

Nitrogen oxides are found to be related to the formation of ground level air pollution (2). Several different processes to reduce the amount of NO\textsubscript{X} (nitrogen oxides) have been developed and employed worldwide. Regardless of the technique, all of these processes share two common factors: the need to control ammonia slip at low PPM levels, and the need to measure NO and NO\textsubscript{2} (16).

SELECTIVE CATALYTIC REDUCTION (SCR) PROCESS

Ammonia is injected upstream from a catalyst located in the flue gas stream. Nitrogen oxides are reduced to nitrogen and water; effective reduction levels are in the range of 80-90%. Ammonia is used as the reducing agent. After vaporization into a carrier gas, a controlled amount of ammonia is injected into the flue gas. The NO\textsubscript{X} and NH\textsubscript{3} reaction takes place on a catalytic bed.

SELECTIVE NON-CATALYTIC REDUCTION (SCR) PROCESS

Aqueous urea solution is used as the reducing agent. The reaction is a homogeneous gas phase reaction that does not involve catalysis. Key parameters for NO\textsubscript{X} reduction efficiency are temperature, residence time, unit configuration and limited amounts of ammonia slip.
A UV analyzer is used to measure all three gases -- NH$_3$, NO and NO$_2$ -- simultaneously. Measurement ranges are 0-10 PPM ammonia and 0-500 PPM NO$_X$. All three are measured in the low UV, taking advantage of the structural features of their absorbance spectra. Figures 10, 11, and 12 show the absorbance spectra of NH$_3$, NO, and NO$_2$ respectively.

**FIGURE 10. UV ABSORBANCE SPECTRA: NH$_3$**

**FIGURE 11. UV ABSORBANCE SPECTRA: NO**
COAL GASIFICATION AND THE FISCHER-TROPSCH REACTION

Developed in Germany during the 1920s, Fischer-Tropsch (FT) is an indirect process where coal is converted into a synthetic gas, which then is converted into liquid fuels (11).

In the coal gasification process, coal is converted into gas by adding steam to powdered coal at high temperature and pressure, creating syngas. The products are hydrogen, carbon monoxide, carbon dioxide and hydrogen sulfide. The hydrogen sulfides are removed by scrubbers. The regeneration stream containing H₂S is sent to the sulfur recovery plant, where the H₂S is converted to elemental sulfur. The clean gas is then sent to the Fischer Tropsch reactors (11).

Oxygen flow is controlled so that only partial combustion to CO with minimal amounts of CO₂ is achieved. The coal then reacts with water to produce more CO and hydrogen. The water gas shift reaction is important since the FT reaction requires a 2:1 ratio of hydrogen to CO. This reaction adjusts the ratio. Finally, the FT reaction, where CO and hydrogen react over a catalyst, creates various hydrocarbon compounds.

\[
\begin{align*}
C + \frac{1}{2} O_2 & \leftrightarrow CO & \text{Partial Oxidation} \\
C + H_2O & \leftrightarrow CO + H_2 & \text{Hydrolysis Reaction} \\
CO + H_2O & \leftrightarrow CO_2 + H_2 & \text{Water Gas Shift Reaction} \\
n CO + 2n H_2 & \rightarrow (–CH_2–)_n + H_2O & \text{Fischer-Tropsch Reaction}
\end{align*}
\]

In the Fischer Tropsch reaction, hydrocarbons such as methane are produced by reacting syngas over a catalyst, creating natural gas and transportation fuels. Before the syngas goes into the FT
reaction it must have very low sulfur content due both to environmental regulations and because sulfur compounds will poison the expensive catalyst (15).

Measurement and control of oxygen is essential to ensure that the combustion is partial and CO₂ is not created. It is also important to monitor the CO and CO₂ concentrations, in order to keep the correct stoichiometric ratio of hydrogen to CO for the FT reaction. Due to the sensitivity of the catalyst to H₂S, the sulfur contents of the stream must be monitored prior to being in contact with the catalyst.

The oxygen is measured with a tunable diode laser. The CO and CO₂ are measured by non-dispersive IR. Again, when required, an integrated analyzer system is used with a single controller and sampling system. The H₂S is measured before and after the scrubbers by a UV analyzer configured with multiple analysis methods, allowing for accurate measurement of both high and low H₂S concentrations with a single device.

A system that is equipped with this H₂S analyzer is currently being setup at GreatPoint Energy. ‘By adding this catalyst to the system, GreatPoint Energy is able to reduce the operating temperature in the gasifier while directly promoting the reactions that yield methane. Under these mild “catalytic” conditions, less expensive reactor components can be utilized, pipeline grade methane is produced, and very low-cost carbon sources (such as lignites, sub-bituminous coals, petroleum coke and biomass) can be used as feedstock’. (13)

Another advantage of the full spectrum analyzer is that it can easily operate on various coal fed stocks with different sulfur levels without any adjustments.

**CONCLUSIONS**

For verification and reporting of pollutants to the EPA (CEMS), for controlling processes that clean or convert gas to a usable fuel or raw material, or for protecting expensive catalysts from sulfur poisoning, analyzers are an essential component of the process. The analyzers need to function continuously and reliably. The measurement needs to be of high quality both from an analytical and sampling perspective. This can be achieved by using a minimal number and type of technologies for analytical measurements; preventing and correcting for interferences from other components in the stream by measuring and analyzing a full spectrum; sampling the stream in the least intrusive manner by not altering the stream with dilutions, drying, cooling, or reducing pressure, while still allowing for verification of readings by span and zero gas.

Various technologies are available for online measurement of chemical concentrations in industrial application. Here we described a system based on a full spectrum UV diode array with no moving parts, integrated IR photometers, and a TDL oxygen analyzer. The use of such a system allows for relatively simple sampling of the wet and hot stream by a close coupled sampling system. Span and zero gas can easily be introduced into the integrated system. The analyzer’s technologies are in sync with process developments to assure environmentally friendly and economically sound use of coal.
REFERENCES


