PROCESS APPLICATIONS OF A PHASE FLUOROMETRIC OXYGEN ANALYZER

Phil Harris
HariTec

Melvin Thweatt
Barben Analyzer Technology

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ABSTRACT

The operational characteristics, performance and applications of a phase fluorometric oxygen analyzer are presented. The analyzer measures the quenched fluorescence of an oxygen-sensitive ruthenium complex, which is embedded in a porous sol-gel or silicone matrix. The fluorescence lifetime is related to the oxygen concentration via the Stern-Volmer equations. The result is an extremely sensitive and specific fiber-optic oxygen sensor that is applicable to gas phase analysis as well as the measurement of dissolved oxygen in aqueous systems. Applications range from ppm oxygen measurements in hydrocarbon streams to ppb aqueous measurements to percent levels of oxygen in stack gas.

INTRODUCTION

Oxygen is the most prevalent element in the Earth's crust, is fundamental to life as we know it, and is one of the prerequisites for chemical combustion. The measurement of oxygen concentration is of value to many industrial process applications, as well as in environmental monitoring of both gases and liquids. This has resulted in oxygen being one of the most commonly measured chemical species, and understandably the measurement of oxygen represents a substantial component of the process analyzer market.

Oxygen is often used as a reactant in many chemical processes, and the amount of excess oxygen must often be carefully controlled. In some cases, such as in stack gas incineration, the control is "loose" in that assurance there is excess oxygen available for the incinerator to operate correctly is all that is needed. In other combustion applications, the measurement and control of the oxygen concentration is more precise, such as in power generation applications where proper oxygen control can reduce emissions of environmental pollutants such as NO_x [1]. Other applications, such as in sulfuric acid production, the measurement of oxygen at the inlet and outlet of a catalytic bed is a useful measure of catalytic activity.

In other applications, the very presence of oxygen is detrimental to upstream processes as oxygen may poison or otherwise destroy valuable catalysts. Heterogeneous catalysis involves the use of solid phase catalysts in contact with gas or liquid phase streams. Such reactions often use rare earth or noble metals, metal oxides or metal hydrides. It is well established that heterogenous catalytic gas phase reactions are characterized by marked reductions in performance due to poisoning by trace species such as oxygen. It is interesting to note that this has been known since as far back as the 1920's [2] but is still referenced to this date [3]. Many expensive materials such as platinum based catalysts are known to be de-activated by oxygen [4].

In aqueous systems, dissolved oxygen is a serious concern in many applications. In particular, dissolved oxygen in boiler feedwater will cause serious corrosion damage in steam systems by attaching to the walls of metal piping and other metallic equipment and forming oxides. This results in significant effort being placed on the reduction of dissolved oxygen concentrations and as such it becomes necessary to monitor the oxygen concentrations accurately, especially in higher temperature boilers. Other applications, such as water re-injection at natural gas and oil drilling sites, especially in off-shore applications, also require that the dissolved oxygen levels be monitored and controlled [5].

Given the wide range of applications and huge economic impact of oxygen measurement, it is understandable that numerous analytical techniques for oxygen analysis have been developed. In the gas phase, common techniques include:
- Galvanic or fuel cell sensors,
- Paramagnetic oxygen sensors, and
- High Temperature ceramic or zirconia sensors.

In recent years, spectroscopic sensors based on tunable diode lasers have been employed for gas phase analysis as well, both in-situ and ex-situ. In the liquid phase, the most common method of measuring dissolved oxygen is the Clark Cell.

Each of these sensor technologies has a range of applications, but also some limitations which make them better suited for particular applications and concentration ranges. The limitations and merits of different gas phase sensing techniques have been discussed in detail by Langridge [6] while the limitations of the Clark Cell have been discussed by Peterson and Gleeson [7]. In general, it may be summarized that:
1) Fuel cell sensors are often easily poisoned by reactive species such as sulfurs,
2) Paramagnetic and TDL analyzers are mostly suited for high concentration (percent level) oxygen measurements
3) Zirconia sensors are sensitive across a very wide dynamic range, but biased by the presence of combustibles in the gas stream, and
4) Clark Cells can require frequent calibration and are sensitive to environmental changes.

An alternative analytical approach to the measurement of oxygen in many of the applications described above is therefore proposed. The method is based on the fluorescence of Ruthenium based dyes, which can be immobilized on the end of a sample probe and used for both gas phase and liquid phase applications. Phase fluorescence spectroscopy can have sensitivities as low as

parts per billions oxygen detection in aqueous streams, to parts per million in gas phases streams, and yet be used for accurate and reliable percent level measurements as well. The use of fluorescence spectroscopy for the measurement of oxygen provides many of the desired advantages of a reliable process gas analyzer. It is interference free, has minimal calibration drift and has proven long term stability and viability in a number of gas phase and liquid phase applications.

FLOURESCENCE OF RUTHENIUM COMPLEXES

Optical oxygen analyzers are intriguing and useful devices, since in general they are fast responding, employ no consumables or reagents, and are not easily poisoned. While absorption spectroscopy may be used to detect oxygen (reference), the absorption band is very weak and therefore it is difficult to get to low detection limits. An alternative method is based on the use of fluorescence based oxygen sensors. These sensors employ a fluorescence indicator whose luminosity is quenched by molecular oxygen; the decrease in intensity can be directly related to the oxygen partial pressure[8].

When employed as a sensor, the luminescent dye is integrated into a thin polymeric coating, which is then placed at the end of an optical fiber. The fiber optic may then be incorporated into a probe for measuring oxygen remotely. The fiber optic is used to both excite the dye, and to transport the subsequent emissions of the dye back to the photodetector. Such sensors have often been referred to as optodes – the optical analog of an electrode. One of the unique features of such sensors is their exceptional high specificity, exhibiting little or no interferences from common gases.

A general description of the fluorescence process and reaction kinetics is shown in Figure 1. In this figure, RuC represents a Ruthenium complex in its ground state, RuC* represents the excited state after absorbance, and RuC** represents a metastable intermediate state. Electrons in an atom or a molecule can absorb the energy from incident electromagnetic radiation and thereby get excited to an upper energy state (absorption). This upper energy state is unstable; therefore, electrons quickly find a way to return to the ground state. In this relaxation process, they may emit excess energy as photons. This relaxation process is known as fluorescence. Fluorescence takes place rapidly and generally occurs in about 10^{-5} s or less time from the time of excitation. When excitation and re-emission wavelengths are the same, the resulting emission is called resonance fluorescence and occurs in nanoseconds or microseconds.

Other than fluorescence, there are other mechanisms by which an excited atom or molecule can give up its excess energy and relax to its ground state. Internal conversion occurs in a series of non-radiative steps, in which the excess electronic energy is transformed to other forms of energy within the molecule. The molecule may also transfer energy to another molecule. If this energy transfer occurs before the original molecule could emit a photon, it is said that the fluorescence has been quenched. Obviously, if the fluorescence lifetime is very short there is little time or chance for quenching, but if the fluorescence lifetime is long there is more chance of quenching.

In the relaxation process, the molecule may relax directly to the ground state – or internal conversion may result in system crossing whereby the molecule gets into a stable state between the excited state and the ground state. Due to quantum mechanical considerations beyond the scope of this paper, this state is sometimes "forbidden" from radiative decay directly to the ground state. This results in long-lived "meta-stable" states with long fluorescence lifetimes, whereby the molecule undergoes the "forbidden" transition and give off a photon, but slowly. This can be particularly useful for measurement purposes, as the rate of decay can be increased by quenching with specific molecules that absorb the excess energy.
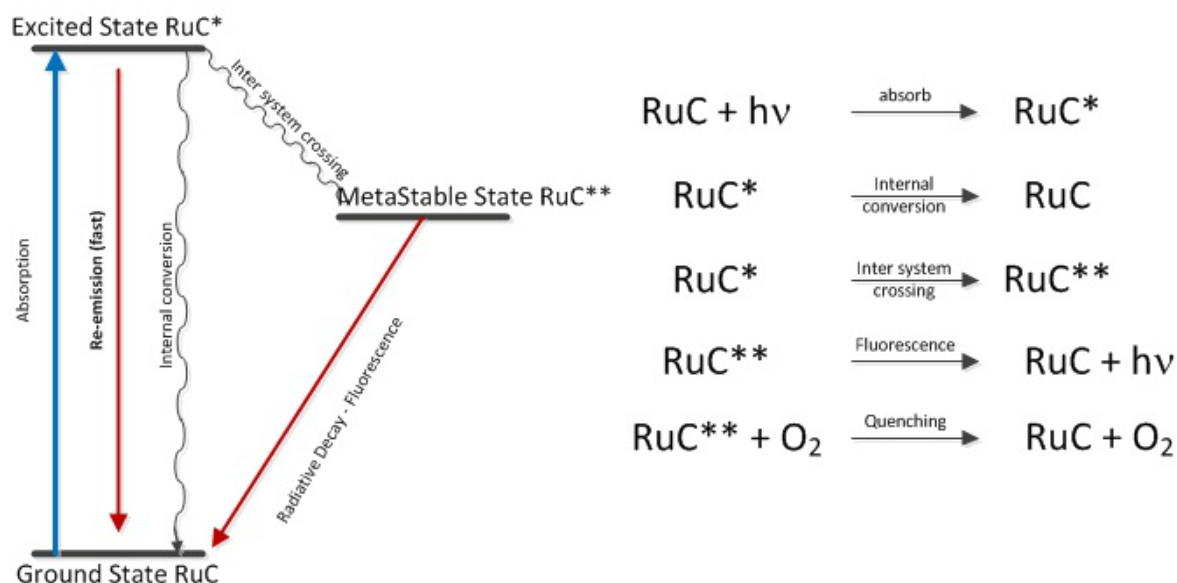

FIG. 1 – EXCITIATION, EMISSION AND KINETICS OF RUTHENIUM COMPLEX

The relative number of molecules that fluoresce is small because fluorescence requires structural features that slow the rate of the non-radiative relaxation and enhance the rate of fluorescence. In most molecules, these features are not there; therefore, they undergo non-radiative relaxation, and fluorescence does not occur. Ruthenium compounds and particularly organo-metal compounds, such as ruthenium diimine complexes, have been studied intently as potential fluorescent materials for oxygen analyzers [?]. Ruthenium and other similar transition metals (such as platinum) have 6 d-shell electrons that and can create strong ligand structures. The ruthenium atom acts as the co-ordination complex, with the organic functional groups (in this case imines) structured around the central ruthenium atom. One such structure which has been extensively tested as an oxygen sensitive fluorescent dye is tris(4,7 bis(4-propylphenyl)-1,10 phenanthroline)–ruthenium(II) perchlorate, the structure of which is shown in Figure 2 [8].

The first step of initiating the fluorescence process requires the molecule to absorb a photon to initiate the excitation process. Ideally, the wavelength of the photon will be chosen such that the molecular extinction coefficient (a measure of how strongly the molecule absorbs light) is large, and such that the excitation wavelength is quite different than the emission wavelength. In the case of the ruthenium complexes discussed herein, the situation is particularly beneficial for the design of a practical instrument. The molecules absorb strongly in the blue region of the

spectrum near 450 nanometers, and may be conveniently excited by a blue light emitting diode. Once excited, the emission spectrum of the metastable state is well separated from the exciting radiation, and occurs in the red near 600 nanometers as depicted in Figure 3 [8].
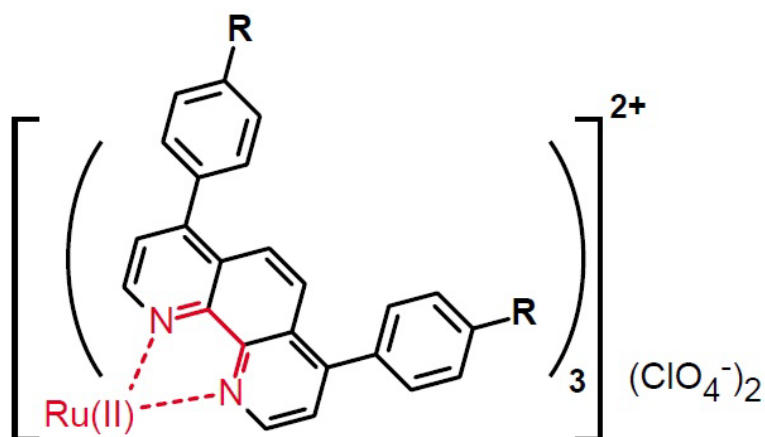

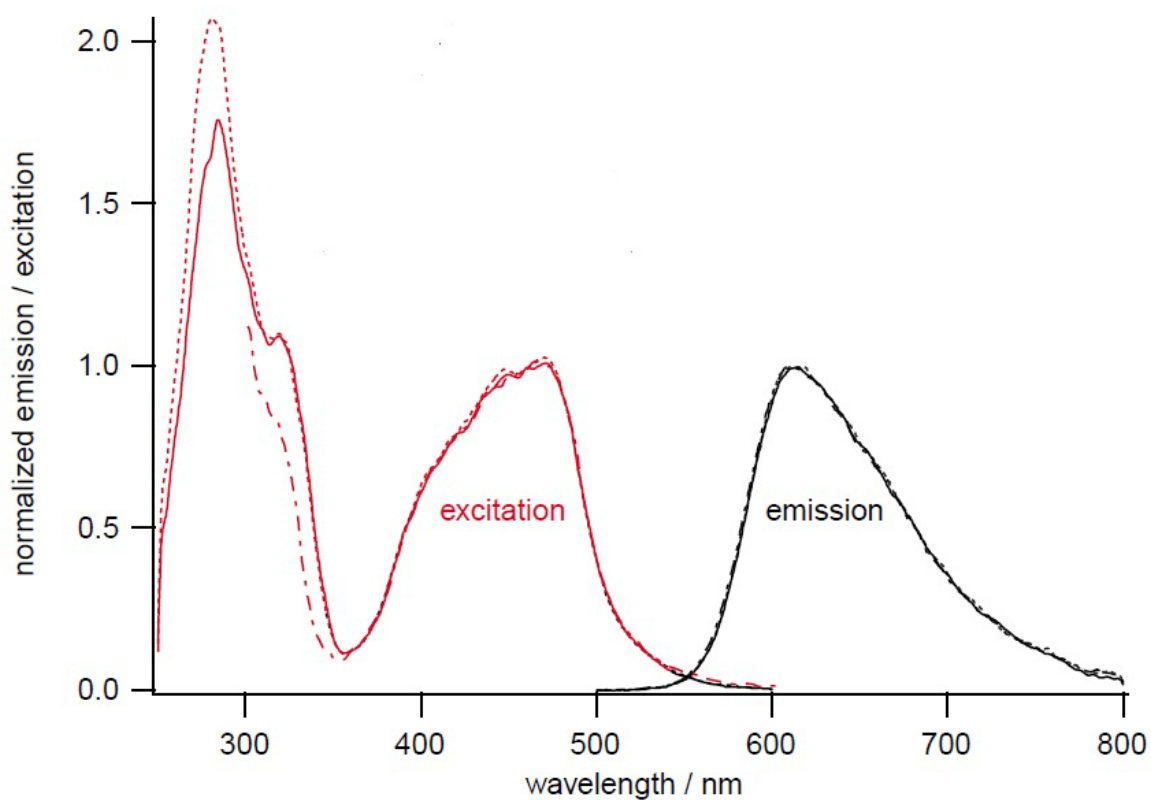**FIG. 2 – STRUCTURE OF RUTHENIUM DIIMINE DYES**

FIG. 3 – EXCITATION AND EMISSION SPECTRA

Fluorescence quenching may be used to measure the concentration of the quench gas. The fluorescent molecule absorbs a photon, and is raised to an excited state. In the absence of any quench gas, the excited state molecule may emit a photon (which occurs at a rate k_f) or underdo some non-radiative decay (rate k_d). If there is a quench gas present (such as oxygen), an additional process can occur whereby non-radiative decay rates are increased by quenching. In this case, the rate of the quenching reaction is $k_Q*[O_2]$, where k_Q is the quenching reaction rate constant and $[O_2]$ is the oxygen concentration. It is these competing reactions that give rise to the Stern Volmer equation, which is used to describe the changes in quantum efficiency of the reaction (Φ_f), as well as the change in luminous intensity with oxygen concentration (I_f), and also fluorescence lifetime (τ)[9].

$$\Phi_f^0 = \frac{k_f}{k_f + k_d} = \frac{k_f}{\frac{1}{\tau_0}} = k_f \tau_0 \qquad \text{In absence of quencher}$$

$$\Phi_f = \frac{k_f}{k_f + k_d + k_q[Q]} = \frac{k_f}{\frac{1}{\tau_0} + k_q[Q]} \qquad \text{In presence of quencher}$$

$$\frac{\Phi_f^0}{\Phi_f} = \frac{\frac{k_f}{\frac{1}{\tau_0}}}{\frac{k_f}{\frac{1}{\tau_0} + k_q[Q]}} = 1 + k_q \tau_0 [Q] \qquad \text{Dividing these equations}$$

$$\frac{\Phi_f^0}{\Phi_f} = \frac{I_f^0}{I_f} = \frac{\tau_0}{\tau} = 1 + k_q \tau_0 [Q] \quad \textit{Stern-Volmer Equation}$$

FIG. 4 – DERIVATION OF THE STERN-VOLMER EQUATION

From the Stern Volmer equation, it is apparent that the ratio of the initial intensity (with no oxygen present) to the intensity measured with oxygen present is directly proportional to the oxygen concentration, and thus that the measurement of fluorescence quenching is a linear measurement of oxygen content in a gas or liquid phase stream. Similarly, it is seen that the

measurement of the fluorescent lifetime, τ, and comparison to the zero oxygen case, τ_0, provides a linear means to measure oxygen concentrations (Figure 5).
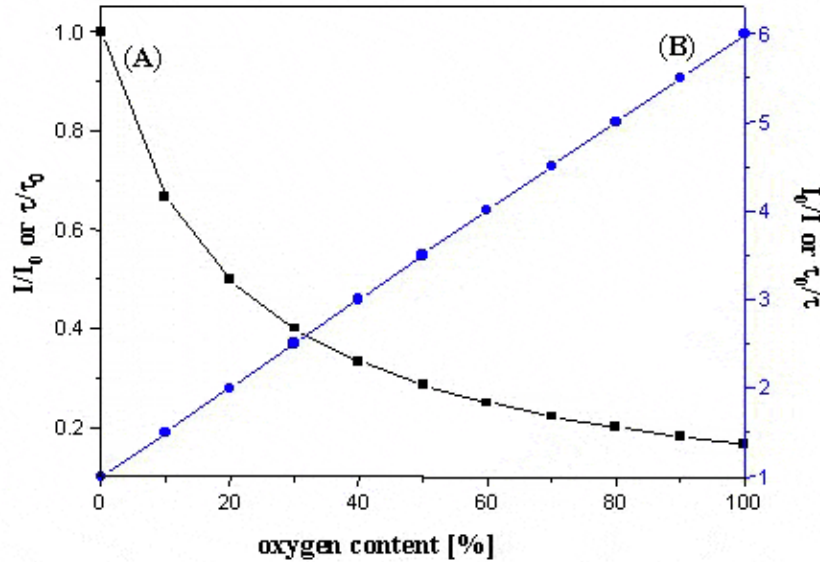

FIG. 5 – FLUORESCENCE WITH RESPECT TO OXYGEN CONTENT
(A) Luminescence decrease in the presence of oxygen. (B) Stern-Volmer plot.

Much has been published [10,11] on optical oxygen sensors based on intensity quenching of the fluorescence. It has, however, been established that these sensors have significant drawbacks for industrial use. The intensity measurement is subject to bias due to drift in the light source or detector gain, to changes in optical path, and drift due to degradation of the luminescent dye itself. These effects can be minimized by operating the sensor in the time domain rather than the intensity domain [12]. The lifetime, τ, is an intrinsic property of the fluorophore, which, unlike intensity, is virtually independent of external perturbations. The lifetime is reduced in the presence of oxygen in a manner which follows the Stern Volmer equation. The lifetime is monitored using a phase fluorometry technique where the oxygen sensitive phase difference is measured between the modulated fluorescence signal and a modulated reference signal. The effect of oxygen on the decay lifetime is shown in Figure 6.

Measurements of changes in the decay lifetime are best made by sinusoidal modulation of the excitation intensity and observation of the resultant sinusoidal fluorescence signal. When there is no oxygen present, the output fluorescent signal is delayed substantially from the input signal, since the decay lifetime is long. As the oxygen concentration increases, the oxygen quenches the fluorescence and the delay is reduced. The delay appears as a phase shift (Φ) between the excitation and emission signal (Figure 7).
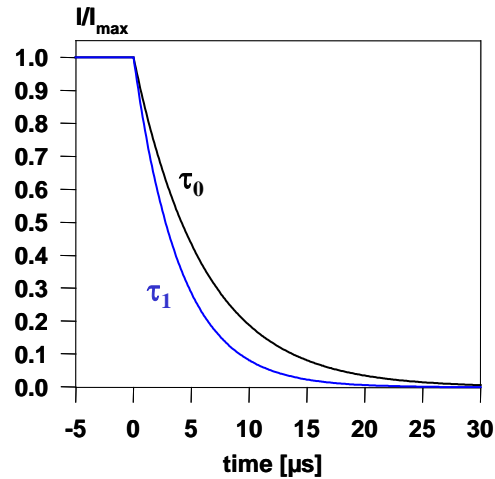
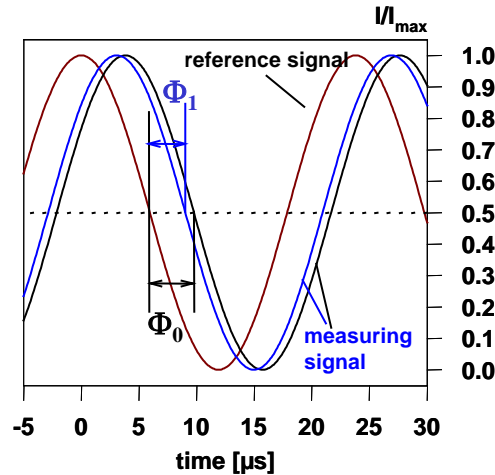**FIG. 6 - EFFECT OF OXYGEN ON FLUORESCENCE LIFETIME**

FIG. 7 - SINUSOIDAL MODULATION AND THE PHASE SHIFTED OUTPUT

APPLICATION OF FLUORESCENT OXYGEN PROBES

The Ruthenium complex can easily be coated on the terminal end of an optical fiber. The fiber is used to transfer light from a blue LED to the coating, which is absorbed and populates the excited states. The excited state decays back to ground state at a rate proportional to the oxygen concentration, and emits red photons. Some of these photons are captured by the fiber optic and transported back the spectrometer, where they are detected by a photomultiplier tube. The phase shift between the excitation source and the fluorescent signal is measured and the oxygen concentration calculated.

The result is a simple and reliable system for the measurement of oxygen in gas and liquid phase streams. It is not easily poisoned, can operate at elevated temperatures, and can be used over a wide range of applications, many of which are just now being explored.

Wellsite water re-injection

Production of oil and gas is usually accompanied by the production of water. This produced water may be natural to the formation, or be injected water in an effort to stimulate production. As exploited reservoirs mature, the production of water increases. Produced water is often the largest single fluid stream in exploration and production processes. Such waters are often re-injected into the reservoir in an effort to maintain reservoir pressure and enhance oil recovery.

Prior to re-injection, the water must be treated to meet a number of different requirements, not the least of which is low dissolved oxygen content – often less than 10 ppb. This low dissolved oxygen content is required to minimize corrosion of the steel pipes throughout the re-injection facility. Furthermore, higher levels of oxygen in the water supports the life of aerobic bacteria which can cause increased sulfur deposition in the reservoir itself, dramatically reducing porosity and production.

Phase fluorescence oxygen measurements can be made in the single digit ppb range in aqueous solutions, and have tremendous stability and drift characteristics. The method has been implemented in a number of off-shore production platforms.

Natural gas transmission

Oxygen in natural gas pipelines is problematic in that it contributes to pipeline corrosion, often with catastrophic results. The measurement has often been made using conventional membrane sensors (Clark Cells and Fuel Cells). However, such cells are easily poisoned by H_2S and may require a sample system to prevent water or hydrocarbon dewpoint issues. Certainly, an H_2S scrubber is required to prevent poisoning, and the scrubber may become saturated and ineffective.

Due to issues with the reliability of such cells, alternative technologies such as paramagnetic oxygen or tunable diode lasers have been considered. However, such devices are not sufficiently sensitive at the low parts per million of oxygen where the measurement must be made.

Phase fluorescence oxygen sensors have been employed extensive for this application. The sensor is not damaged, degraded or poison by H_2S, condensates or any other component of the natural gas stream. It performs very reliably on the 0 to 100 ppm range required, and needs little or no sample conditioning in front of it. Furthermore, the sensor recovers quickly from high oxygen levels, and responds quickly to changes in stream composition.

Vapor recovery units / Nitrogen blanketing

Increased environmental awareness and concern over greenhouse gas emissions has resulted in efforts to capture fugitive releases which may, in the past, have been released to the environment. Vapor recovery units are used to capture volatile hydrocarbons which may be emitted from a number of storage or hydrocarbon recovery operations. Such systems operate at low pressures and thus, oxygen ingress into the recovered stream from the ambient air is often a possibility.

Such ingress is problematic, in that the presence of oxygen mixed with the hydrocarbons increases the risk of fire or explosion.

A similar situation occurs in storage tanks containing hydrocarbons or other combustible or explosive materials. In such cases, the head space of the storage vessel is often purged with an inert gas such as nitrogen or carbon dioxide to minimize the risk of combustion. Oxygen ingress into the system represents a hazardous situation which needs to be monitored.

Again, technologies such as paramagnetic oxygen sensors or tunable lasers often do not have sufficient sensitivity to achieve the low limits of detection desired. Fuel cells or Clark cells are easily poisoned by sour components of the vapors, and thus are unreliable. Phase fluorescent oxygen analyzers are able to meet or exceed the required detection limits, are not easily poisoned and provide long-term stable and accurate analysis of oxygen ingress.

 Stack gas analysis

Oxygen in stack gas is an important measurement in many emissions monitoring systems. Often, stack gas effluent concentrations must be normalized to a given oxygen concentration. Such analysis can be performed on either a hot/wet or a cold/dry basis. Hot wet analysis is commonly performed using a zirconia oxygen sensor, which may be biased by the presence of combustibles in the stream and whose accuracy and response speed can be impacted by high concentrations of sulfur dioxide.

Recently, a Petrobras refinery was experiencing plugging and fouling issues while measuring oxygen in a sulfur recovery unit (SRU) stack. These issues were primarily associated with the presence of sulfur dioxide concentrations in excess of 1%. The system required a lot of maintenance, and complex and expensive sample conditioning to guarantee its functionality. The facility chose to test a phase fluorescence oxygen analyzer on this stack in an effort to provide a more accurate and reliable oxygen measurement. Prior to installing the sensor, the facility concluded that the system showed the following potential benefits [13]:
Easy Installation,
High Precision and Accuracy,
Easy Calibration,
High Reliability, and
Robustness.

The system was installed on the SRU stack simply by introducing the oxygen probe into one branch of a Swaglok tee fitting in the SO_2 analyzer oven. After three months of testing, the facility concluded, "The analyzer has far surpassed the expectations, and given the severe conditions. It is noteworthy since the mose significant difference (sic. from other oxygen analyzers) is the ease of installation without the use of complex and expensive sample conditioning".

The internal report goes on to state, "Although tested in a single condition, in the chimney of the sulfur recovery unit … we believe that this technique of on-line measurement of oxygen has much to offer".

CONCLUSIONS

There exist a number of compounds which fluoresce, and whose fluorescence may be quenched by oxygen. Some of these, particularly Ruthenium Diimines, can be used to provide sensitive measurements of oxygen concentration from the low parts per billion through to percent levels of oxygen. While measurements of the fluorescence intensity have been used to make oxygen measurements, it has been shown that the measurement of the fluorescence lifetime provides a more accurate, stable and reliable oxygen measurement for process applications. Applications for the technology abound and are under continued investigation

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