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LASIR^{TM}-R – THE NEW GENERATION RoHS-COMPLIANT GAS ANALYZERS BASED ON TUNABLE DIODE LASERS

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Abstract

The laser-based optical gas sensor using Tunable Diode Laser Absorption Spectroscopy (TDLAS) is rapidly gaining favor wherever high sensitivity, real-time measurement and freedom from interferences are required [1, 2], specifically for the measurement of HF in primary aluminum smelters and other process gases at various metal smelters. It eliminates the problems associated with extractive gas sampling techniques. A first generation of equipment designed by Unisearch Associates and based on the near-IR TDLAS appeared on the market in the mid-90s. It has since been improved significantly by employing fast scan measurement techniques. Now, the system is more compact, robust, easier to operate and calibrate, and it can be simply audited. The utilization of fast scan measurement techniques with the state-of-the-art high speed electronics and sophisticated software optimization algorithms not only provides enhanced stability and sensitivity but expands the dynamic range of the measurements to five orders of magnitude. This new generation RoHS-compliant instrument (Restriction of Hazardous Substances) is also very inexpensive compared to other gas analysis instruments. The technology has found applications in many industries that require fast, accurate measurement of trace emissions for both process control and environmental regulatory requirements. These include, but not limited to, HF emissions in aluminum smelters, NH_3 slip measurements for DeNOx scrubbers in the Power Industry, HCl and HF emissions monitoring in the Cement Industry and in Incinerators and for process control in Steel Smelting. This paper describes the new generation TDLAS-based gas analyzer and, as an example, its use in primary aluminum smelters.

Introduction

A basic TDLAS setup consists of a tunable diode laser light source, light transmitting optics, an optically accessible absorbing medium through which the light beam can be transmitted, receiving optics and detectors. The emission wavelength of the tunable diode laser is tuned over the characteristic absorption lines of a species in the gas in the path of the laser beam. This causes a reduction of the measured signal intensity, which can be measured by a detector and then used to determine the gas concentration. Most molecules are unsymmetrical and polyatomic. When the molecule becomes excited by absorbing near infrared energy, it increases its vibrational and/or rotational frequency. It is this tendency of the molecule to absorb energy that leads to spectroscopic identification of the molecule by the wavelength of absorption and the concentration of the molecule by how much of the energy is absorbed at that wavelength. Since the amount that a molecule vibrates or rotates at a specific wavelength will be dependent on its capability to absorb energy, it will behave differently at different temperatures and pressures. This alludes to the fact that both temperature and pressure compensations for line intensities are required for any spectroscopic measurement. Such compensations can be made either by measuring the property changes of the molecules directly (for simpler molecules) and applying a mathematical correction or by preparing a compensation database empirically (for complex molecules) with laboratory experiments performed under controlled operating environments.

The advantage of TDLAS over other techniques for concentration measurement is its ability to achieve fast, very low detection limits of the order of parts per billion with virtually no interference from the presence of other gas molecules.

The LasIR^{TM} is also widely being used by various aluminum smelters worldwide to measure gaseous hydrogen fluoride [3, 4]. Hydrogen fluoride (HF) is emitted during the aluminum smelting process. To avoid HF leakages in the work area, the electrolytic cells (pots) are hooded and the emitted gases are captured and vented through scrubbers. Hydrogen fluoride is a very toxic gas and represents a major health and safety hazard both for workers in the pot rooms and for neighboring environments. In addition, there is also an economic incentive to recovering this fluoride. The Tunable Diode Laser technology is presently used in over a hundred smelters in the world as an emissions monitoring device used to adjust emission control practices and equipment.

Description of Technology

The gas analyzing system consists of a tunable diode laser based analyzer and a small optical head that launches the laser light through a medium (that may contain the species of interest to be measured) and receives the transmitted laser light at the other end of the measurement medium. The analyzer itself can be located in a control room, as far as 1 km away from the measurement location. A fiber-optic cable and a coaxial cable link the analyzer to the optical head. Data are logged on to a compact flash disk built inside the TDLAS-based gas analyzer and/or an external PC via the Ethernet or RS232 outputs. Data is also transmitted to the plant database.

The quantification is based on Beer-Lambert Law that relates the absorption of light to the properties of the material through which the light is traveling. It states that when a radiation of frequency $I(v)$ passes through an absorbing medium, the intensity variation along the path of the beam is given by:

$$I(v) = I_o(v)\, e^{-\sigma(v)\, c\, l} \qquad [1]$$

where,

- $I(v)$ is the transmitted intensity of radiation after it has traversed a distance l through the medium, (in milliwatts)
- $I_o(v)$ is the initial intensity of the radiation, (in milliwatts)
- $\sigma(v)$ is the absorption cross-section of the absorbing species, (cm^2/# of molecules)
- C is the number density (concentration) of the absorbing species, and (in # of molecules/cm^3)
- l is the path length or the traverse distance through the medium (in cm).

Remote measurement of gases using TDLAS provides the concentration that actually represents a value averaged across the entire path. This gives *in situ* measurement an advantage over point sampling in which a probe is inserted to draw the gas out of the duct, especially when concentration gradients or heterogeneities exist. The path averaged value obtained from *in situ* sampling is better representative of the overall concentration within the process.

The use of a laser source coupled with a fiber-optic cable allows the light to be optically multiplexed to make simultaneous measurements of the species of interest at different locations. With the TDLAS-based gas analyzer, measurements can be made from 1 to up to 16 different locations with a single analyzer. In addition, multi-species can also be measured with the same analyzer where the absorption signals of the species lie relatively close to each other and within the tunable range of the laser. Measurement of gases in explosion-proof environment can easily be done by using optical heads that require no electrical components (with configurations that transmit and receive the optical signal via fiber-optic cables).

Unisearch has recently introduced a new generation of TDLAS-based gas analyzers that are RoHS-compliant and available in either rack-mount or table top models as standards. With the advent of high speed electronic data processing and measurement techniques, the costs of these types of TDLAS based analyzers are significantly reduced. The gas analyzers come in a compact form that makes them suitable for aluminum smelter environments. They are available in configurations from simple portable single-channel analyzers to systems capable of measuring up to 16 channels that can monitor both multiple locations or different gas species. All the measurement channels are independently controlled, which permits a single multi-channel analyzer to simultaneously measure gas levels in duct/stack, long-path ambient air, extractive sampling and any such combination. Each channel can handle very different gas levels with no interference with other channels. The possible measurement configurations are shown in Figure 1. The system can also be configured as a stand-alone portable gas analyzer with the optical head integrated with the electronics. This light-weight (< 5 kg), energy-efficient (consumes less than 20 W) model can be mounted on a tripod stand and, with the use of a retro-reflector array, allows measurement of various gases in an open-path mode to up to several hundreds of meters. A stand-alone, pre-configured and aligned probe model is also available that can be mounted at any stack/duct for short-term or long-term measurements.

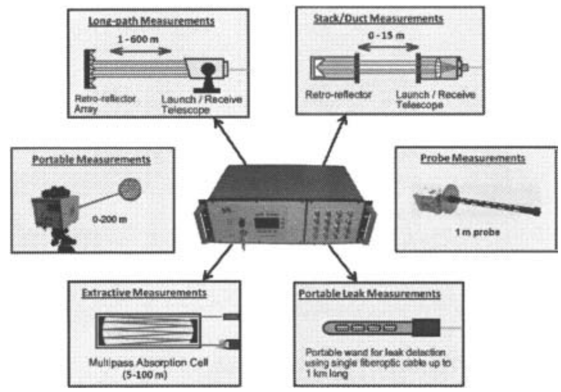

Figure 1. Schematic of TDLAS-based gas analyzer and the optical head configurations that can be connected to the analyzer by fiber-optic and coaxial cables. Portable stand-alone models are also shown.

The TDLAS-based gas analyzer consists of appropriate hardware and software that require no field calibration. This eliminates the requirement of having calibration gas cylinders available on site. For regulatory purposes, compact hand-held audit modules are provided that allow the user to periodically audit the system as a whole (analyzer and optical heads) when desired or use the periodic automated audit feature. Automated audit results can be stored and displayed on screen. Alternatively, where auditing is to be performed by flowing a known level of gas on the path of the optical beam, an optional add-on module is available that can be configured as an inline or a stand-alone offline audit assembly. Calibration, although not required, can also be performed with this add-on module where regulatory requirements have to be fulfilled. With the use of a TDLAS-based analyzer, fast, real-time, in-situ measurements of gas concentrations linear to five orders of magnitude (sub-ppm to percent levels) can be made under various industrial environments.

HF Gas Measurements as Process Control in Primary Aluminum Smelters

One of the primary requirements of a gas analyzer, especially when used as a Continuous Emissions Monitoring system, is the accuracy and linearity of the measurements. This data is concurrently important when a system is used for process control applications such as maintaining scrubber efficiency and improving work practices, as well as reducing emissions. Various test and certification agencies exist that are able to verify the functionality of such analyzers. One such certification agency is the well-recognized German TÜV. Approval requires the use of two essentially identical analyzers measuring the same gas. Laboratory and field (industrial plant) tests are conducted in order to verify the manufacturer-stated specifications. These include, among many other parameters, the linearity, accuracy, precision and the operation of the analyzer under various environmental conditions.

Figure 2 shows the linearity and accuracy of two TDLAS-based gas analyzers for low levels (0 to 2.5 ppm-m) of HF gas measurement. As can be seen from the plot, the measured HF gas levels were almost identical between the two analyzers.

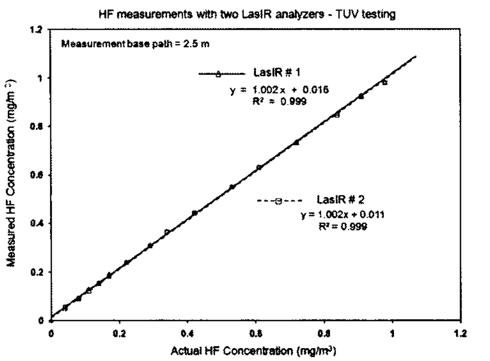

Figure 2. HF measurements with two TDLAS-based LasIR™ during TÜV certification.

In aluminum smelting process, aluminum metal is extracted from its oxide alumina, generally by an electrolytic process called the Hall-Héroult process. As such, aluminum smelters use enormous amounts of electricity and are often located very close to large power generating stations.

Primary aluminum is produced by the electrolytic reduction of alumina (Al_2O_3), dissolved in a mixture of molten cryolite (Na_3AlF_6) and AlF_3. Since HF is emitted during the process, the electrolytic cells (pots) are hooded and the emitted gases are captured and vented through scrubbers. Hydrogen fluoride is a very toxic gas and represents a major health and safety hazard both for workers in the pot rooms and for neighboring environments. In addition, there is also an economic incentive to recovering this fluoride. Dry scrubbing technology is used at most of the world's aluminum smelters. The hydrogen fluoride is chemisorbed directly on to the alumina from the hot exhaust gas. Fresh (primary) alumina is injected directly into the raw exhaust gas stream, which mixes and reacts with the alumina. Then the reacted alumina, as well as the particulate fluorides and other particulate materials, are removed from the exhaust gas stream by bag filtration. The alumina collected (secondary alumina), which contains almost all the fluorides and particulates emitted from the reduction process, is then fed to the pots. Thus, the entire process operates as a closed loop for the captured cell emissions. It has been found that manipulations in the feed of alumina to the dry scrubber altered the levels of HF emitted from the scrubber outlet that is usually vented to open air. Therefore, a continuous in-situ measurement is a useful tool to optimize the feed of alumina to the dry scrubbers, and/or the secondary alumina recycle rate.

An example of the control of alumina feed is shown in Figure 3, obtained from tests conducted at an installation site. The higher HF levels were produced by reducing the primary alumina feed to the scrubber. In just a few minutes, the levels rapidly rose from 0.47 mg/Nm³ to 0.8 mg/Nm³. A few minutes later, when the HF levels appeared to reach stable values, the recycle rate for injected secondary alumina was reduced. The concentration rose to almost 1.8 mg/Nm³. To evaluate the scrubbing response, all parameters were set to normal. Once all the alumina feeds were turned on, an exponential decay in HF emissions was observed.

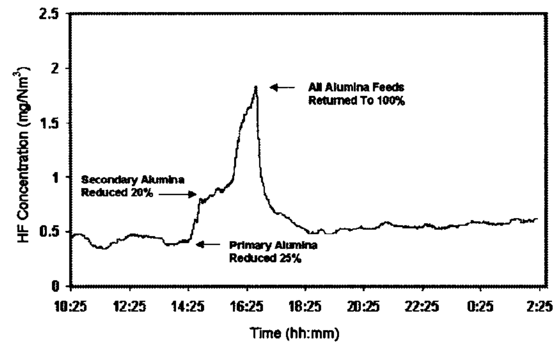

Figure 3. Variation in HF emissions as measured by a TDLAS-based gas analyzer as a function of alumina feed to the dry scrubber.

A number of installations use TDLAS-based systems to monitor scrubber efficiency. In a typical installation, a single controller is used to monitor the HF concentrations at both the inlet and the outlet of the scrubbers. Figure 4 shows a plot of such measurements at a newly installed scrubber. Measurements were made in an in-situ mode. This plot shows that the new scrubber was able to remove more than 99.8% of the H. This information also allows the scrubber operator to maintain the desired reduction of fluoride emissions from aluminum smelting by adjusting the alumina feed rate (and the secondary alumina recycle rate) to the dry scrubber to optimize the capture efficiency of the gaseous fluoride byproducts. The measurement also indicates to the operator the surface adsorption inefficiencies that arise from losses of scrubber material such as bags either breaking or leaking, or saturation of the reactive material.

Also of importance is the accuracy and reliability of the measurements when made under an industrial environment. The gas temperature, pressure, humidity and operating environmental parameters can constantly change as a function of time. In order to validate the measurements, a continuous 5-day comparison study of the HF gas data was made between those reported by a TDLAS-based gas analyzer and the standard wet chemical method. Results are shown in Figure 5. Apart from the response time where the gas analyzer shows sharper peaks, the results were virtually the same.

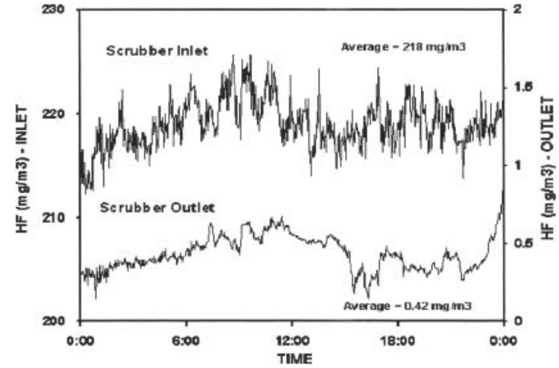

Figure 4. HF measurements at the inlet and the outlet of a dry scrubber; the scrubber efficiency is determined to be better than 99.8%.

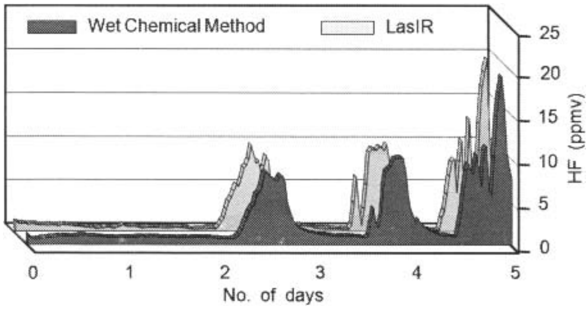

Figure 5. HF measurements at the inlet and the outlet of a dry scrubber. The scrubber efficiency is determined to be better than 99.8%.

Figure 6 shows the measurement of HF gas in the exhaust manifold of a single pre-baked anode electrolytic cell. The measurements were made in a path length of 0.5 meter and approximately 1 meter away from the end of the pot. Periodic reproducibility as a result of automated alumina feed and other related processes can easily be seen on the expanded plot.

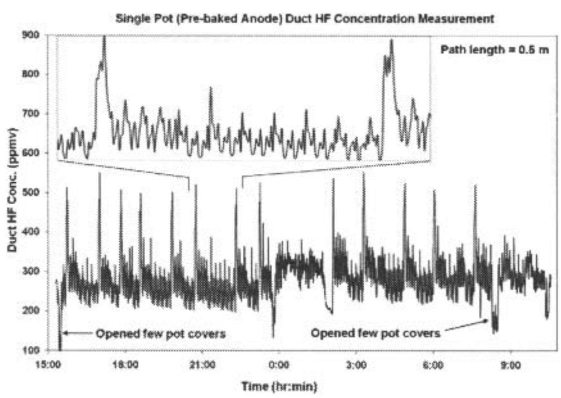

Figure 6. HF off-gas measurement from a single pot 1 meter away from the pot end.

Modern cells fitted with hooding to capture the emissions are usually operated at a slight pressure. Process interventions such as the manual alumina feed, changing of anodes or metal tapping and suppression of anode effects, all require opening of the hoods. Such interventions and any leakage in the pot hooding itself result in the emission of HF into the pot room, which is ultimately vented through the roof of the pot room. By measuring the HF emissions in the pot room and correlating their occurrence with specific pot tending activities, improved work practices can be developed and better control of current efficiency can be achieved. Figure 7 shows the levels in a pot room measured with a gas analyzing system. The sampling time was 5 seconds and the path length was 400 meters.

There are several processes where the gas level changes over a wide range of magnitude. This can be as a result of a specific step in the process or the process as a whole. In order to verify the dynamic linearity of the analyzer, tests were made in an industrial environment where provisions of controlled variations in the injected HF levels existed. The HF gas level was varied from 0% to up to 50%. In the set up used, the levels of HF could not be increased beyond 50.5%. The results are shown in Figure 8 and indicate that the measurements are linear over the entire measured range. Such systems become increasingly useful in industries such as nuclear material processing plants.

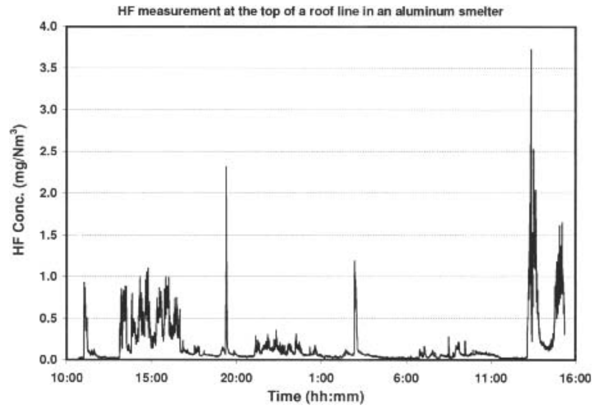

Figure 7. Measurement of HF at the top of a pot room of an aluminum smelter.

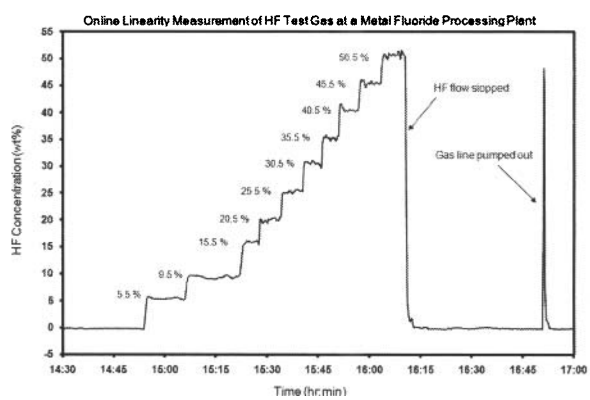

Figure 8. Linearity measurement of HF from 0% to 50%.

Conclusion

The Tunable Diode Laser based gas analyzer is being used as a tool for making in-situ measurements of emissions and flue gases in various industries. An example of its use specific to, and not limited to, aluminum smelters has been provided. Tunable Diode Laser Absorption Spectroscopy affords the most interference-free analytic method for measuring gas concentrations where fast and accurate response is desired. Such systems are particularly well suited to process control applications. These are small in size, can be designed as calibration-free, rugged and virtually maintenance-free, making it easy to install and operate. The use of fiber-optic cables permits the instrument to be located in an environmentally suitable area, remote from the actual measurement location. In addition, optical multiplexing permits measurements at a number of locations with a single instrument, making the systems very cost effective. Measurement of gases in explosion-proof areas can easily be done. The data is used for the control and optimization of various process related parameters. This leads to energy efficiency, reduction in production time and improvement of the quality of the products.

The technology has found applications in many industries that require fast, accurate measurement of trace emissions for both process control and environmental regulatory requirements. These include NH_3 slip measurements for DeNOx scrubbers in the power industry, HCl and HF emissions monitoring in the cement industry and in incinerators, off gas remediation of H_2S in wastewater treatment and nickel smelters, deuterated water leakages in nuclear power plants and for process control in steel smelting, to mention just a few.

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