

Accuracy Verification of Zolo**BOSS** Measurements

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The Zolo**BOSS**TM provides heretofore unavailable measurement capabilities for coal-fired boilers. The system simultaneously measures temperature and the concentrations of H₂O, O₂, CO, and CO₂ along multiple paths in the combustion zone and back-pass of the boiler. The instrument can be operated in open loop mode by the operator or integrated into a closed-loop combustion optimization system. The data that the system provides is used to balance and tune the combustion in a boiler in order to improve efficiency, reduce NO_x, minimize opacity events or better manage slagging thereby realizing significant return on investment (ROI) for the utility.

The measurement techniques employed by the Zolo**BOSS** are based on over 25 years of well-established and documented research on spectral absorption characteristics of specific constituents. The Zolo**BOSS** applies this technique, in a novel way, to the fossil-fired power applications to generate accurate and repeatable measurements. This paper discusses how the accuracy of these measurements is validated with simulated boiler conditions in our state-of-the-art laboratory and how Zolo Technologies' measurements compare to current industry measurement practices in the field.

Introduction

The Zolo**BOSS** provides unique information on the status of combustion constituents directly in the combustion zone of a boiler. Such information is novel in the power industry where, up until now, no instruments have been able to measure reliably or in real-time in the harsh furnace environment. The spectroscopic measurement principles used by the Zolo**BOSS** have been developed over the last 25 years by Stanford University along with numerous government and privately funded research institutions. Spectroscopy, and specifically, tunable diode laser absorption spectroscopy (TDLAS), the principle foundation of the Zolo**BOSS**, is now well proven and commercially available for a number of applications outside of the coal-fired boiler industry.

However, in understanding the application of spectroscopy to the coal-fired business, it is helpful to understand how Zolo**BOSS** generates data and how to judge the accuracy of the measurement data as conditions in the boiler are quite challenging. A separate white paper on TDLAS, which details the principles of the technology, is available for review.

Measurement Methodology

Initial Calibration

Since the Zolo**BOSS** system is based on well defined and verified spectral absorption characteristics, once it is installed in the field, it does not need to be re-calibrated unlike many types of analyzers which require frequent calibration using calibration gas standards. Instead, the system measures the ratio of the intensity of the transmitted beam passing through the sample to a reference beam, which is not absorbed by the sample. Species concentrations are then determined by solving the absorption equation (Beer's law). In order to utilize the equation, we must calibrate physical constants, the line strength S_0 , and the lower state energy level, E'' . These two values are unique for each measured species and absorption feature and they vary with temperature. Once these

constants are measured and validated in the laboratory, they remain fixed—they do not change or drift. Therefore, it is imperative to carefully determine these critical constants in a controlled laboratory environment. The absorption equation is complex however the essence of the equation is show below.

$$I_{\text{trans}}/I_{\text{ref}} = f(S_0, E'')$$

The line strength, S_0 , and the lower state energy level, E'' , are fundamental physical constants for a particular absorption feature. They describe how strongly the target species absorbs versus wavelength on a particular spectroscopic transition at a particular temperature. They are invariant. There are a number of external resources that provide values for S_0 and E'' for the absorption features that the Zolo**BOSS** system uses to measure species concentrations. The U.S. Government has compiled a spectroscopic database called HITRAN that lists values of S_0 and E'' for many transitions of many species. To further improve the accuracy of our measurements and supplement the HITRAN database, Zolo Technologies has contracted with Stanford University to independently measure S_0 and E'' and validate these constants. Finally, in addition to guidance from HITRAN and measurements by Stanford, we make our own measurements of S_0 and E'' in the calibration facility at Zolo Technologies. Only when measurements from these various sources agree, do we consider the fundamental spectroscopic constants to be known. Once they are known, these constants determine the “fingerprint” of absorption for specific constituents that can then be used to quantify their concentration and, most importantly, the system requires no further calibration.

Determining Temperature

The Zolo**BOSS** measures temperature by measuring the ratio of the integrated absorbance, i.e. line strength, S_0 , of at least two spectral features of the same species. Zolo Technologies uses H_2O as the target species, since it is omnipresent in combustion systems and it is a strong absorber. The spectral features are carefully chosen to exhibit line strengths that vary differently with changes in temperature. Different temperature dependencies require that the chosen spectral features have significantly different values of the lower state energy level, E'' . Comparing ratios eliminates the effect of all other common parameters for the two spectral features such as the mole fraction, pressure, and path length. The effect of differing line profiles for the two transitions disappears when integrating the features to obtain integrated absorbance values. The ratio is then a unique function of temperature. Two lines suffice to measure temperature, but the Zolo**BOSS** uses six spectral features in order to increase the accuracy of the measurement.

Validating Measurement Accuracy

Even when the spectroscopic constants for all relevant transitions have been determined accurately, it is still possible to get an inaccurate value for concentration and temperature, especially in challenging, real-life applications, such as in a coal-fired boiler. Errors can be generated by incorrectly fitting the spectroscopic feature due to low signal to noise ratio, incorrectly calibrating the wavelength scale, incorrectly accounting for A/D offsets, background emissions offsets, systematic processing errors, window transmission loss, or simply high levels of noise. In order to account for these possible sources of error, accuracy verification tests are performed in the calibration facility

modeled as closely to boiler conditions as can be generated in the laboratory. To make the results of these laboratory verification experiments as realistic as possible, laser transmission noise is introduced with a frequency and amplitude that mimic, as closely as possible, the situation encountered in the boiler. This lab-generated transmission noise has a frequency content that extends to approximately 1 kHz, varies transmission from 100% down to 0.01% and significantly perturbs the wave front of the beam – much like the actual situation encountered in a typical boiler. Figure 1 shows temperature data from such a test.

The temperature is ramped from approximately 700 K to 1400 K, roughly the temperatures of the back-pass and the combustion zone of a coal-fired boiler, respectively. The discrete steps that the furnace takes at low temperature are due to the temperature control loop, which is tuned primarily for high temperature operation. As shown below, the Zolo**BOSS** measurements exactly follow the measured values of the tube furnace within our measurement specifications. The small discrepancy at high temperature has to do with window absorption that occurs only at high temperature leading to a slight measurement error. However, this error does not occur in a coal-fired boiler since the windows do not heat up to the level observed in the tube furnace.

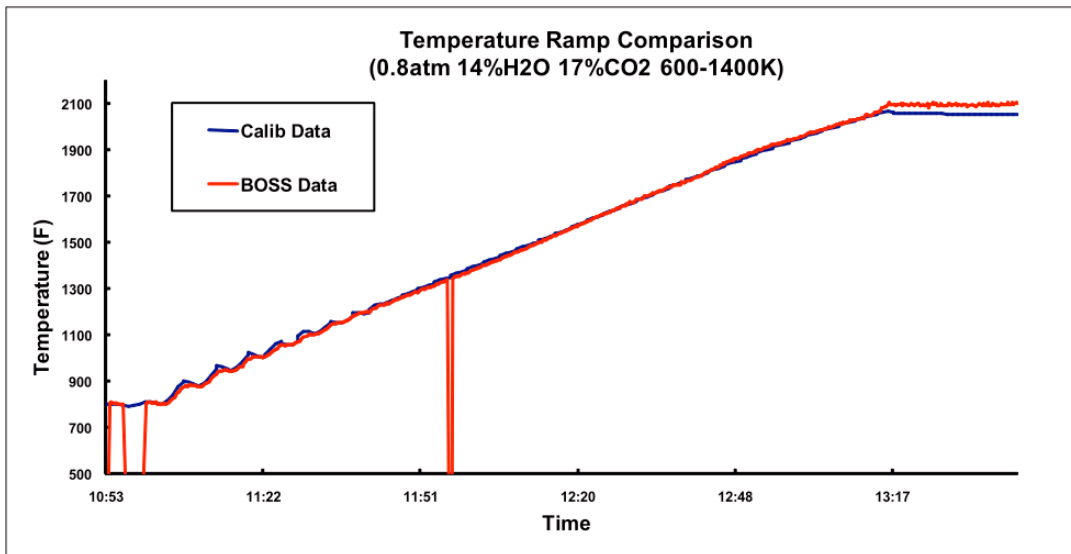


Figure 1: Temperature verification test. The Zolo**BOSS** measures temperature as gas approximating the mixture in a coal-fired boiler is ramped from 700 K to 1400 K.

Concentration accuracy is measured in similar validation tests as shown in Figure 2 for CO₂, Figure 3 for H₂O, and Figure 4 for O₂. In Figure 2, some data is shown in which CO₂ concentration is ramped repeatedly between 17.2% and approximately 13.2%. The Zolo**BOSS** responds accurately within stated specifications. (The response lag of the Zolo**BOSS** is a result of the residence time of the gas in the measurement cell and not the intrinsic response of the sensor). Figure 3 shows similar data for H₂O; in this case, the measured water concentration tracks the expected concentration over the large change in temperature shown in Figure 1 with a slight offset, but within our published specification. Similar tests for O₂ under back-pass conditions are shown in Figure 4. Results for CO are omitted here but will be published in an upcoming paper.

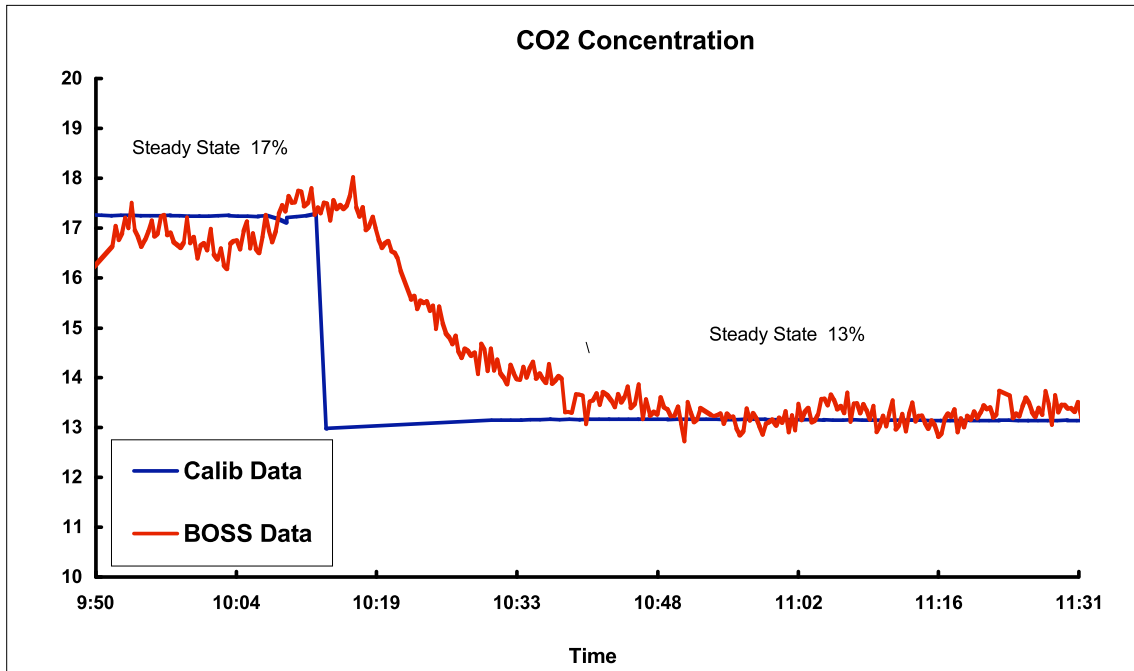


Figure 2: CO₂ concentration measurement validation testing. Testing was conducted at 800°F

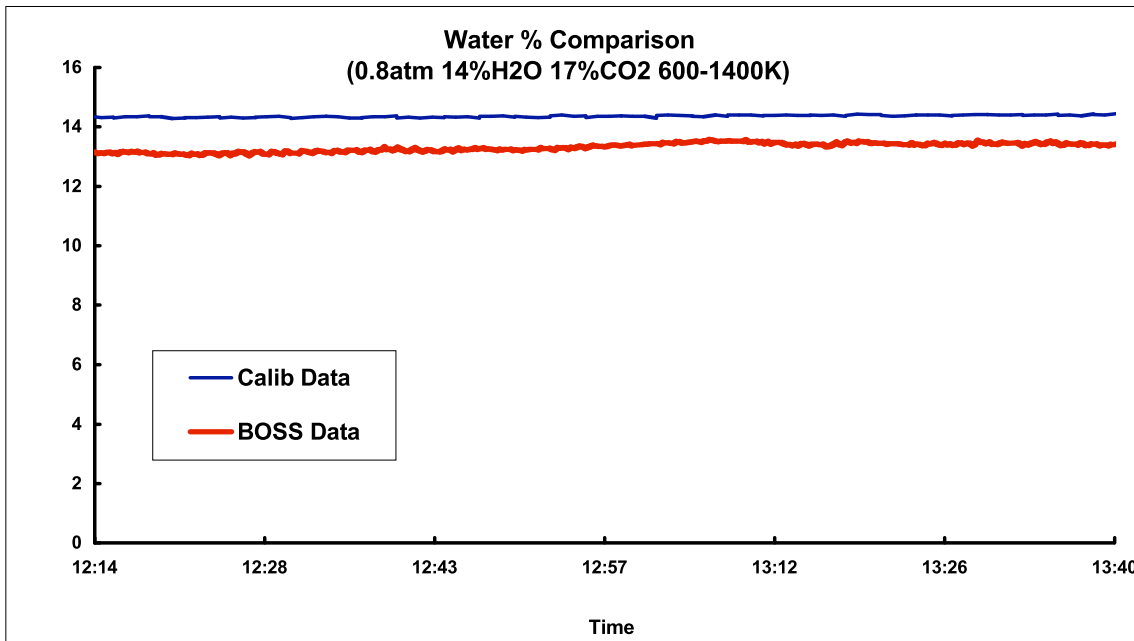


Figure 3: Water concentration validation testing over the temperature range shown in Figure 1.

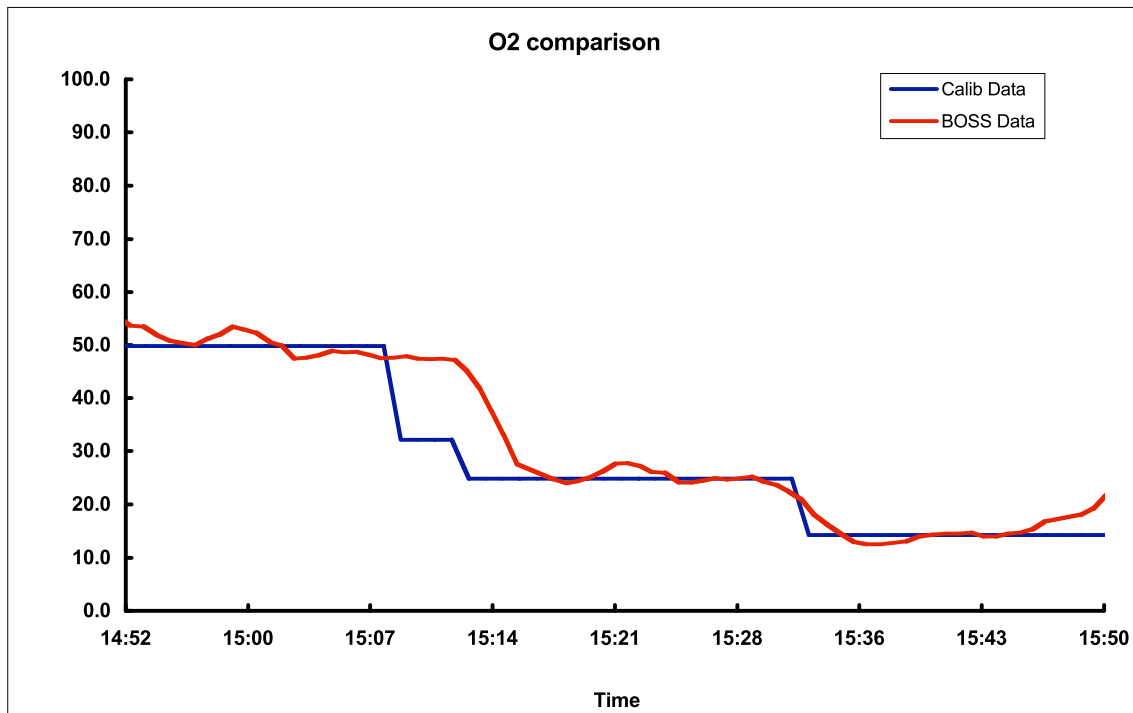


Figure 4: Zolo**BOSS** O₂ measurements versus calibration source under back-pass temperature conditions.

Calibration Validation Results

Testing on all constituents and temperature in the Zolo Technologies laboratory under simulated boiler conditions confirms the accuracy of the Zolo**BOSS** system to within the specifications below.

Constituents	Temperature Range °F	Accuracy	Minimum Detectable Limit	Maximum Detectable Limit	Long Term Repeatability
Temp	-	±5% of measured value (omv)	500 °F	3000 °F	±0.1% omv
O ₂	500 – 3000	±(0.2% abs + 5% omv)	0	0.15	±0.02%
H ₂ O	500 – 3000	±(0.1 + 5% omv)	0.001	0.3	±0.02%
CO	500 – 3000	±(500 ppm + 5% omv)	500 ppm	1	±100 ppm
CO ₂	500 – 800	±(0.15% + 5% omv)	0.003	1	±0.02%

Accuracy versus Repeatability

While it is important to verify the accuracy of the Zolo**BOSS** system through proper calibration and testing, it is just as important to note that the Zolo**BOSS** is extremely repeatable in its measurements. This is critical as the primary application of the Zolo**BOSS** is to provide temperature and constituent data in order to properly balance and optimize the combustion process. As a result, repeatable relative measurement data are of the utmost importance to the performance engineer, operator, or control system (such as a neural network), rather than absolute accuracy. Still, the Zolo**BOSS** has excellent relative *and* absolute accuracy.

Traditional measurement methods, such as HVT probes or zirconium oxide probes, typically exhibit a random measurement error for each reading and each device. Even with multiple points or probes, this random error can often mask small changes or trends in the combustion process. Conversely, the Zolo**BOSS** system uses the same laser and same signal processing on each path, which eliminate most of this random error. This results in significantly more consistent and repeatable measurements.

Calibration Methodology and Facility

To fully evaluate the results of the calibration testing, it is important to understand the calibration methodology, the testing facility, and its limitations. Zolo Technologies has developed a laboratory calibration facility that is routinely used to check the accuracy of measurements. Since it is a laboratory facility, complete control over the gas concentrations and temperature is achieved during the tests. Gas samples are prepared from NIST traceable gas mixtures and diluent gases (e.g. pure nitrogen or air), and calibrated mass flow controllers to introduce gas samples into a spectroscopic cell embedded inside a tube furnace to control temperature. Gas mixtures are created to mimic boiler conditions, to study cross-species spectroscopic interferences, or to measure the line strength function, $S(T)$, broadening parameters, or lower state energy level, E'' , of the spectroscopic features that we use to make measurements. The initial gas mixture and the effluent from the gas cell is analyzed for the species CO, CO₂ and O₂ using a Sick Maihak 710 analyzer. The water content is monitored using a chilled mirror hygrometer (EdgeTech DewMaster). To ensure accuracy, measurements are made both before and after the high temperature cell, since reactions can, and often do, occur at the high temperatures of the cell. For instance, the water gas shift reaction occurs at high temperature between CO and H₂O to form CO₂ and H₂. The progress of this reaction is measured using the Sick Maihak analyzer, which shows excellent agreement with equilibrium chemistry calculations using a package such as Chemkin or Cantera.

By comparing and confirming data at multiple points in the lab setup, the precise gas concentration and temperature are known. The temperature of the three-zone tube furnace is carefully controlled to eliminate any boundary effects so that the entire gas sample exists at uniform temperature and pressure inside the measurement region.

Limitations and Uncertainties

Uncertainties accrue due to uncertainty in the temperature of the tube (basically thermocouple measurement uncertainty), measurement of the pressure in the tube, measurement of the length of the tube, etc. However, as will be discussed below, the

propagation of most of these errors is prevented by measuring the actual conditions in the test cell using calibrated, third-party analyzers, pressure transducers, and thermocouples.

For instance, the quoted temperature accuracy of our tube furnace is given by the manufacturer as $\pm 5\text{ }^{\circ}\text{C}$ – too large to be used as an absolute standard for our purposes. Instead of relying on the oven set point, an array of S-type thermocouples is used to measure the actual gas temperature in the cell. S-type thermocouple measurement uncertainty is quoted to be $\pm 0.15\text{ }^{\circ}\text{C}$ up to 1100 K, and then increases linearly up to $\pm 3.0\text{ }^{\circ}\text{C}$ at 1450 K.

It should be noted that testing is limited by the softening temperature of the tube at temperatures above 1400 K (2060 $^{\circ}\text{F}$). In the boiler, temperatures routinely exceed 2500 $^{\circ}\text{F}$, and it should be noted that our measurement currently relies on an extrapolation of lower temperature data. This introduces some error in very high temperature measurements; however, this error is minimal relative to other sources of error.

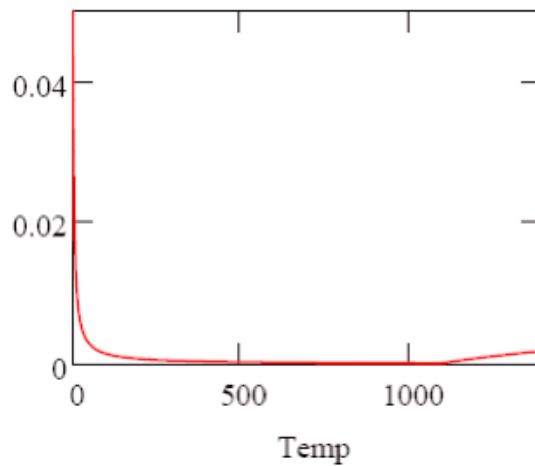


Figure 5: Relative temperature measurement uncertainty in calibration facility

Pressure Uncertainty

The calibration facility utilizes two sets of pressure sensors. One set measures at the inlet of the flow tube and the other measures at the outlet. The redundancy verifies that no leaks exist within the flow tube. The set consists of one pressure sensor to measure low pressure ($> 0.247\text{ atm}$) accurately and another to measure high pressures ($> 2.47\text{ atm}$) accurately. Figure 6 shows the accuracy specifications of both sensors.

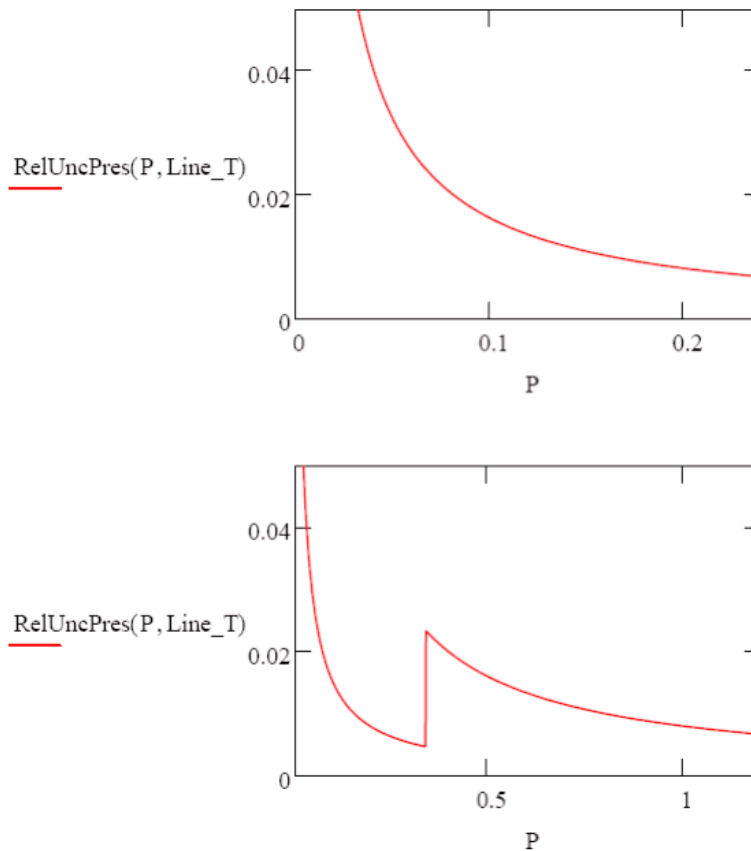


Figure 6: Relative pressure uncertainty of the pressure sensors

Uncertainty in the Path Length

We estimate that the path length is 44.83 cm \pm 0.635 cm. While this measurement seems straightforward; due to thermal expansion at high temperatures, the path length actually increases by 0.6% at 1400 K. This path length uncertainty is included in our error budget calculations.

Concentration Accuracy

The accuracy with which we can produce a target concentration of gas depends on the identity of the target constituents. This is because each gas is measured using a different analyzer. Accuracy of water concentration depends on the accuracy of the H₂O chilled mirror hygrometer and knowledge of the total pressure since the hygrometer reports dew point; not concentration. The accuracy of CO, CO₂, or O₂ mixtures depends on the accuracy of the Sick Maihak analyzer and, if H₂O is present in the mixture as well, the accuracy of the hygrometer (and pressure measurement). After compounding all possible sources of error, the final concentration uncertainty is dictated by the analyzer accuracy. In general, the error in CO, CO₂, and O₂ concentrations is \pm 0.02% absolute, \pm 0.2% absolute, and \pm 0.2% absolute.

That is, if the following gas mixture is delivered:

[CO] = 0.5%

[CO₂] = 14%

[O₂] = 3.0%

The expected delivered concentrations would be in the ranges shown below:

[CO]: 0.48% - 0.52%

[CO₂]: 13.8% - 14.2%

[O₂]: 2.8% - 3.2%

Water Concentration Accuracy

Figure 7a and 7b show the uncertainty in water concentration that is expected versus pressure. This curve results directly from the specifications of the chilled mirror hygrometer and the inaccuracy in the pressure sensors. Pressure is a variable in this case, because the hygrometer reports dew point and total pressure is required to change dew point to concentration.

Plot of Uncertainty of H₂O concentration at different pressures

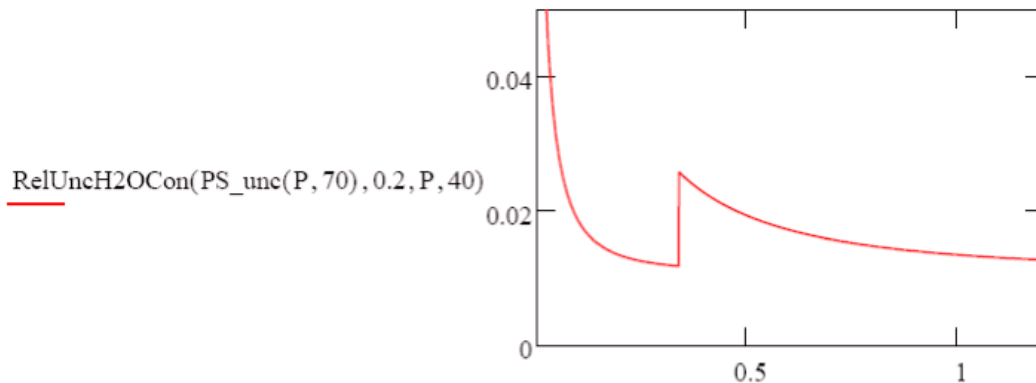


Figure 7a: Calculation of uncertainty in delivered H₂O concentration as a function of measured pressure and dew point.

Plot of Uncertainty of H₂O concentration at different dew points ^P

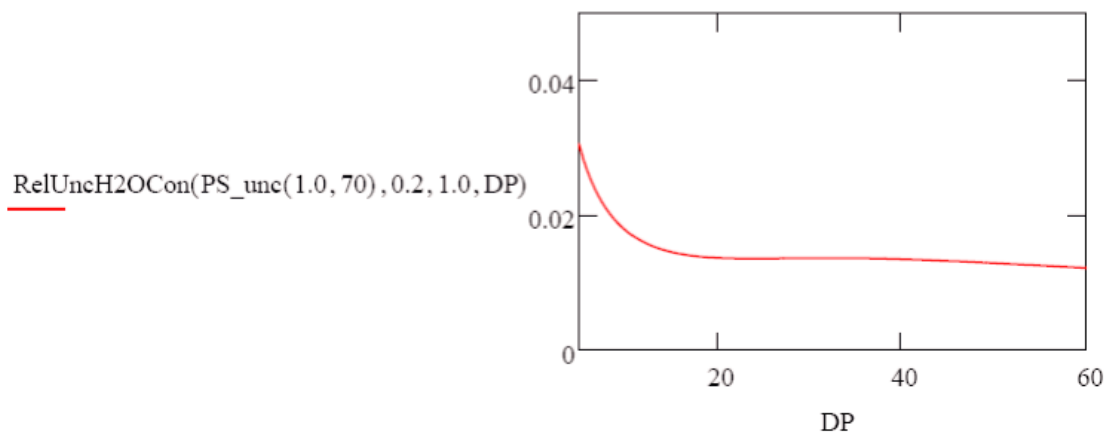


Figure 7b: Calculation of uncertainty in delivered H₂O concentration as a function of measured pressure and dew point.

The result of this error analysis is generally that desired water concentrations in the 5% – 15% range with a relative accuracy of $\pm 2\%$ can be produced. Thus, if the range concentration is 15%, the delivered water concentration will vary between 14.7% and 15.3%.

Comparison With Industry Measurements

While the accuracy of the Zolo**BOSS** measurements has been proven in boiler-simulated laboratory conditions, the system is designed to operate in the real boiler conditions found in an operating coal-fired power plant. To understand how the Zolo**BOSS** system translates from laboratory to field, a discussion and comparison to current measurement practices is warranted.

Currently, the accepted measurement method in a boiler is gas extraction with a high velocity thermocouple (HVT) probe. It is well known that sample extraction from an ongoing reaction zone, such as the fireball, leads to significant errors in concentration measurements. In particular, the sample cannot be quenched quickly enough to prevent further reaction in the probe before measurements are completed (without condensing water). This is especially true when using HVT in the combustion zone versus obtaining data further downstream from the combustion zone or even in the back-pass where combustion is completed. Using an HVT probe to obtain temperature measurements often leads to measurement uncertainties due to issues of heat transfer, radiation effects and difficulties of proper and repeatable sampling practices. Even experienced practitioners of HVT testing concede that HVT probes will under-report temperature, in some cases by several hundred degrees. While they strive to minimize these problems, they can not be completely eliminated. These challenges with current HVT practices create a need for a better measurement device to measure accurately where it counts—in the combustion zone.

In addition to the obstacles facing accurate HVT measurements, differences in the measurement acquisition methods hinder a direct comparison of HVT information with Zolo**BOSS** data. For example, the HVT data is obtained at specific *points* across the boiler. As a result, there can be significant time delays as the data is acquired via HVT across the entire boiler for each point; HVT only captures the constituent concentration at a single point in time; or the test probe can miss pockets of high concentrations or temperature across the boiler. Obtaining data in the middle of large furnaces can be impossible since HVT probes may not be sufficiently long. Also, while care is usually exercised to attain a steady-state condition during the HVT test period, it is very difficult to achieve in practice.

In contrast, the Zolo**BOSS** system obtains measurement data in real-time, for all constituents, based on a *path-average* across the boiler. This method captures all of the information across the boiler length and eliminates the impact of any operational changes that may occur during data acquisition. Meanwhile, a two-dimensional tomography grid offered by the Zolo**BOSS** system can also provide derived discrete point data across the measurement plane.

Temperature Field Testing Results

Despite differences and limitations, it is still instructive to compare HVT data with data from the Zolo**BOSS**. Indeed, if sufficient care is taken and the HVT temperature measurements are made in exactly the same location as our Zolo**BOSS** temperature measurements, it is possible to make a comparison of data.

Zolo Technologies has completed numerous measurement campaigns and the results show agreement between the Zolo**BOSS**-measured temperature and HVT measurements. As an example, January 2008, Zolo Technologies conducted a test to compare the two methods of obtaining temperature data. An HVT probe was inserted into a Zolo**BOSS** path opening (Path 1 in this case) and temperature data was obtained as the probe was traversed across the boiler. No HVT measurements could be obtained in the center of the boiler due to limited probe length and the high temperatures encountered would melt the probe. For the analysis, it was assumed that temperatures in the center of the boiler would be the same as the farthest point reached with the HVT probe in order to calculate an average over the traversed path so as to compare to the Zolo**BOSS** path average. This is somewhat conservative, but if temperatures were higher in the center this would only reduce the differences observed between HVT and Zolo**BOSS**. These HVT results were then compared to Zolo**BOSS** data in two ways. First, path 1 average obtained immediately prior to and following the HVT test (the Zolo**BOSS** system was removed on Path 1 in order to accommodate the HVT probe test) and second, an average of all of the remaining paths within the combustion zone (paths 2–9) during the HVT test period. Figure 8 shows individual HVT probe measurements, the average of those HVT values and the Zolo**BOSS** averages.

The HVT temperature data reported 10 – 40 °F below the Zolo**BOSS** measurements, well within the prescribed accuracy of both instruments. This test confirms that the Zolo**BOSS** readings are comparable to traditional methods in a boiler under real operating conditions. Not surprisingly, the HVT reads low, despite being operated with standard radiance shielding and the great care taken to verify that adequate gas flow rates were maintained across the flow tip to balance inevitable radiance losses.

ZoloBOSS vs. HVT Test Results	
Path 1 (°F)	
HVT average	2421
ZoloBOSS multi-path average	2461
ZoloBOSS path average	2431
Δ ZoloBOSS multi-path vs. HVT)	41
Δ ZoloBOSS path average vs. HVT)	10

Table 1: Temperature field test results

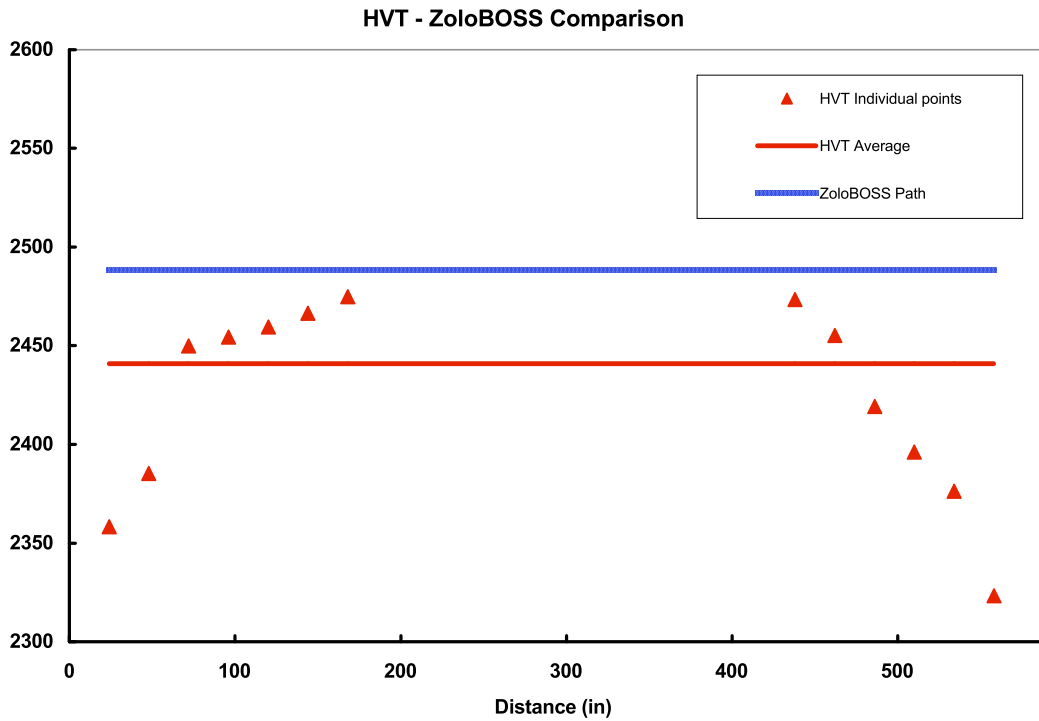


Figure 8: HVT measurements on a coal-fired boiler compared to ZoloBOSS measurements in the same location. HVT measurements were not possible in the middle section of the boiler where it was sufficiently hot (>2500 °F) that the probe started to melt.

Conclusion

The Zolo**BOSS** is a TDLAS based sensor in which accuracy is predicated on fundamental physical constants. Zolo Technologies has determined and verified these physical constants and their specific behavior in boiler-like conditions using their custom developed high-temperature laboratory set-up. In addition, Zolo Technologies has conducted side-by-side measurements with extractive HVT probes to measure temperature in actual boiler conditions with consistent results.

The Zolo**BOSS** measures, simultaneously, temperature and the concentrations of H₂O, O₂, CO, and CO₂ along multiple paths in the combustion zone and back-pass of the boiler. Together, multiple paths generate real-time concentration maps, which can be used open loop mode by the performance engineer or unit operator, or fully integrated into a closed loop combustion optimization system such as a neural network. This novel data aids operators in diagnosing, balancing, and tuning combustion to better manage slagging, minimize opacity events, reduce NO_x, and improve efficiency.

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