

### DETECTING LOW-LEVEL MOISTURE (WATER VAPOR) IN NATURAL GAS USING A TUNABLE DIODE LASER ABSORPTION SPECTROSCOPY (TDLAS) BASED ANALYZER

The measurement of water vapor in natural gas has long been of industrial importance, and has been addressed by a variety of analytical techniques over the years. Chief among these techniques have been quartz crystal microbalance (QCM) based analyzers. QCM technology is still the workhorse for production and pipeline applications, and the technique is considered to be both dependable and accurate. However, as with all chemical analyzers, sensor aging due to contamination presents a significant problem and increases long-term maintenance requirements for the analyzer. Sensor aging can be a problem with samples containing glycols or high levels of hydrogen sulfide (H<sub>2</sub>S).

Spectroscopic techniques are inherently free from many of the problems that can occur with physical-contact sensors. One spectroscopic technique that has gained acceptance for a variety of industrial measurements is tunable diode laser absorption spectroscopy (TDLAS). Industrial applications of TDLAS include combustion monitoring,

trace-species monitoring, and leak detection. A variety of different analytes have been addressed by this technique (e.g. CO, NO, CO<sub>2</sub>, NO<sub>2</sub>, CH<sub>4</sub>, NH<sub>3</sub>, O<sub>2</sub>, H<sub>2</sub>O, HCl, HF, and HBr).



AMETEK 5100/5100HD TDLAS analyzers

## TDLAS TECHNIQUE

In a conventional absorption spectroscopy experiment, light from an optical source is passed through a sample, which attenuates the optical power in proportion to the analyte concentration and the optical pathlength. The relative attenuation of the power is measured as the analytical signal. Specifically, the measurement is the ratio of the power measured with sample present to the power measured in the absence of sample (i.e. the background or blank). Measuring low concentrations of the sample material is limited by the noise present in the measurement of the background. This problem amounts to detecting a very small change in a large signal.

Measuring water vapor in natural gas at low concentrations is an application that requires higher sensitivity than can be achieved by conventional absorption spectroscopy. A variation on the absorption spectroscopy experiment, known as wavelength modulation spectroscopy (WMS), can provide a substantial increase in sensitivity over the

conventional approach. In WMS the wavelength of the optical source is modulated, so that a small region of the absorption spectrum of an analyte, containing a distinct absorption peak, is repetitively scanned. As the wavelength of the source scans through the spectral feature of interest, the relative attenuation of the source power is varied. By modulating the wavelength of the source, a time-varying signal (i.e. the optical power) is produced at the detector. A phase-sensitive detection scheme is used to detect the presence of, and quantify, the time-varying signal produced by the presence of the analyte species. In an ideal WMS experiment, the absence of analyte in the sample path results in no signal being detected. Thus, the ideal WMS experiment is considered a “zero-background” technique and transforms the absorption experiment (a ratiometric measurement) into a problem of detecting the presence of a small signal in the absence of any background.

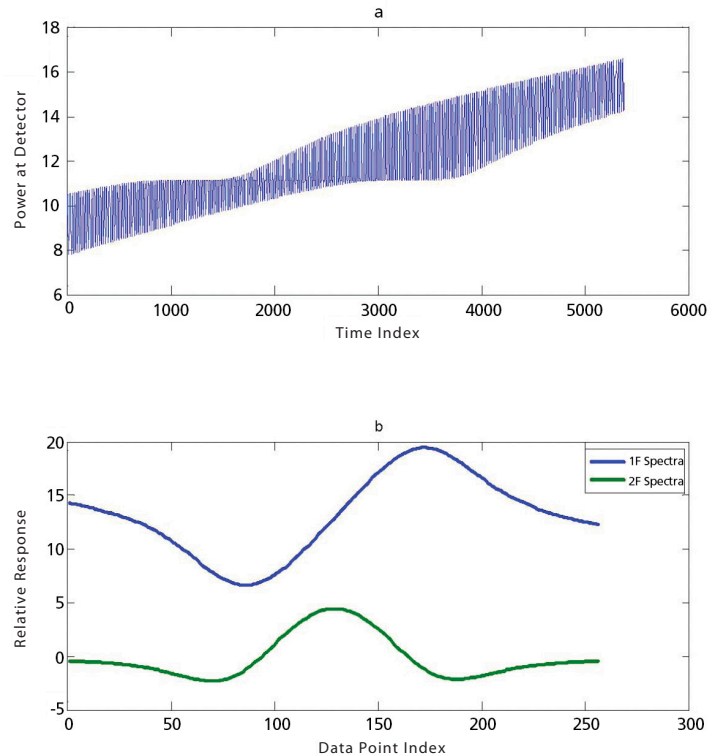
While it is possible to implement WMS with a number of source/monochromator technologies, the technique is most commonly implemented using tunable diode lasers as the source. Tunable diode lasers, with output wavelengths in the near-infrared (NIR) portion of the spectrum, can be operated at room temperatures, are small, possess high output radiance, have a long operational life, and can be modulated at high speeds. Further, the line widths of these lasers are much narrower than the individual absorption lines observed for gas phase molecules, giving the TDLAS technique extremely high resolution. While the output wavelength of the tunable diode laser is a function of both the junction temperature and the injection current, in practice a TDLAS spectrometer maintains the temperature of the laser at a constant value and the output wavelength of the device is controlled by the injection current. This arrangement enables the wavelength of the laser to be modulated at high frequencies. These attributes of tunable diode lasers make them ideal sources for spectroscopy and are responsible for the rapid growth of TDLAS instruments in recent years.

Phase-sensitive detection, normally employed in WMS, allows for the measurement of different multiples of the drive frequency used to modulate the output of the tunable diode laser. Most implementations of TDLAS technology have made use of the second harmonic signal for two main reasons. First, the second harmonic signal approximates the second derivative of the absorption spectrum, and as such removes sloping backgrounds and offsets that are the result of the less-than-ideal output characteristics of the tunable diode lasers. Secondly, the second harmonic spectra display a peak, which coincides with the peak in the absorbance spectrum.

Figure 1 illustrates the power envelope observed by the detector in a WMS experiment, and the spectra observed by demodulating the detector output at 1X and 2X the drive frequency for the laser. These are typically referred to as the 1F and 2F spectra. As observed in the figure, the 1F spectrum is a very close approximation to the derivative of the absorbance peak, and the 2F spectrum is a similar analog to the 2nd derivative of the absorbance peak. We detect the signal at the laser drive frequency 1F (so the spectra can be normalized without a separate measurement of the laser power) and calculate the 2F signal, which produces a zero baseline signal.

Another factor that can plague spectroscopic measurements is fouling of the optical surfaces. Normalization of the demodulated spectra to the total power received at the detector eliminates the effect of light attenuation due to buildup on the optical surfaces, which reduces the overall

throughput of the optical system. However, if the surfaces are significantly contaminated, causing excessive loss of received light at the detector, the analyzer will alarm the situation and invalidate the measurement.



**Figure 1.** a) Power envelope recorded by detector in a WMS experiment. b) “1F” and “2F” spectra obtained by demodulating the detector output (shown in “a”) by 1X and 2X the drive frequency for the laser

### Line broadening effects

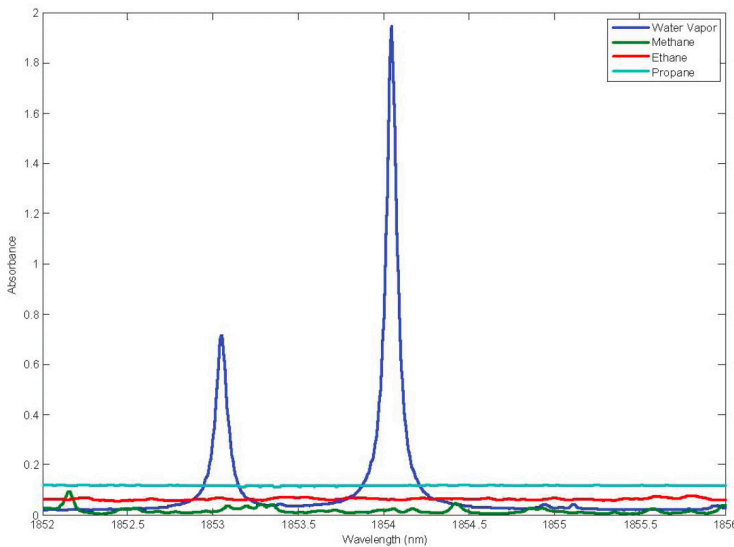
The amplitude of absorption profile and the harmonic signals decrease with increases in absorption profile width caused by collision broadening. Sample pressure and temperature influence this effect, and therefore are measured, and changes in absorption profile widths are compensated for by advanced algorithms.

### The sample matrix

Isolating a specific absorption line for the analyte species enables the TDLAS technique to effectively remove most background effects from the measurement, and make relatively interference-free measurements of the analyte, even in complex sample matrices. However, this approach does have limitations. Specifically, TDLAS works well for

the measurement of small gas-phase molecules, but as the size of the molecule increases the absorption spectra do not exhibit the same high-resolution features, limiting the applicability of the technique. Larger molecules are generally not suitable for analysis by TDLAS, due to the lack of very narrow peaks in their absorption spectra. While this limitation does reduce the number of species that can be measured with TDLAS, it also can help to simplify background effects in the sample matrix. This is the case with the measurement of water in natural gas.

The principal component of natural gas is methane, which is usually present at concentrations greater than 85%. The other significant constituents of natural gas are ethane and propane, which are present in concentrations in the 0 to 10% range. In pipeline quality gas, water vapor is present at concentrations of less than a few hundred ppmv. Absorption spectra for water vapor, methane, ethane, and propane are shown in Figure 2; these data were recorded at room temperature (~20°C) and at a pressure of 1.0 atm.



**Figure 2.** Absorption spectra recorded for water vapor, methane, ethane, and propane. The concentration of water vapor is approximately 1% (v/v); all of the other compounds are 100% (v/v)

There are several key features in these data. First, the concentrations for the spectra of water vapor and the hydrocarbon components are quite different. The concentration of water vapor is approximately 1%, while the concentration of the hydrocarbons is 100%. It is clear that the hydrocarbons contribute almost no significant background to the measurement of water vapor at the 1854 nm line, which is used by the AMETEK TDLAS analyzers. The figure shows that only the methane has a very small spectral feature, which overlaps with the

absorption peak of water vapor at 1854 nm. The other species in the sample do not contribute any significant interference at 1854 nm. For measuring water vapor at low concentrations (i.e. less than 100 ppmv), even this small peak observed for methane must be compensated for adequately. With a simple analog instrument, compensating for this background can be problematic, especially when the concentration of methane in the sample gas is not constant. For this reason, finding a target wavelength with a minimum of background from methane has been a key requirement for many TDLAS instruments. However, because the AMETEK TDLAS analyzers record the spectrum of the sample around the water peak, it can adequately measure and compensate for the methane in the sample. Thus, the signal processing capabilities of the 5100 offer distinct performance advantages over simple analog implementations of the TDLAS technology.

### Built-in laser line lock functions

The AMETEK TDLAS analyzers use a sealed reference cell (containing moisture vapor in a buffer gas that does not absorb in the spectral range of interest) to verify the analyzer is outputting and locked in on the correct wavelength. The output wavelength of the tunable diode laser is a function of both the diode junction temperature and the injection current. The diode laser is maintained at a constant temperature and the laser output wavelength is controlled by the injection current. Laser wavelength can drift due to slight changes in the diode temperature. Even a very small wavelength error can result in much larger signal error in the derivative mode. The spectra of the moisture sample in the reference cell are monitored and any shift in the observed peak is used as a feedback signal for the temperature control of the tunable laser diode. The laser wavelength is locked on the water line, guaranteeing dependable results.

## SUMMARY

TDLAS is a sensitive tool for measuring low levels of moisture in the presence of interfering species, such as methane in natural gas. The signal-to-noise ratio is superior because the detection is carried out at frequencies far from the baseband noise. TDLAS is a dependable technique, especially with laser line lock.

## AMETEK 5100/5100HD TDLAS ANALYZERS

AMETEK's TDLAS-based moisture analyzers have a very robust methodology and incorporate several significant features compared to other laser-based units. The laser source and the detector are isolated from the process, and the optical surfaces are easy to service and clean.

The 5100 noise specifications are superior to equivalent competing models because of improved digital processing methodologies supported by increased precision derived from use of a reference cell. Any residual methane interference is directly measured and compensated for. If desired, methane concentration may be output in addition to water concentration.

Reliability, quick response to changing process conditions, built in laser line lock, and low installed cost are some of the features that natural gas customers have come to expect.

The 5100 analyzers embody these features and more:

- Built-in reference cell is used to line-lock the laser on a desired wavelength. Any minor shift in the observed spectrum is used as feedback to adjust the laser, ensuring the proper operating wavelength. Thus, there is a real-time confirmation that the laser is locked on the desired absorption line.
- The analyzer does not rely on older analog techniques; it is an all-digital implementation of the TDLAS technology
- Digital curve analysis techniques are more robust than a simple light intensity measurement
- Web browser-based user interface
- Suitable for outdoor installation (-20 to 50°C/-4 to 122°F)

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