Frozen Assets

Hygrometry is a complex science. The water molecule is small, polar and abundant in nature. It is also a universal solvent. Consequently, it interacts with many processes and takes time to reach equilibrium. To detect it, or more challengingly, measure it with precision, requires attention to detail in several disciplines including sample system construction and performance optimisation.

MCM, a specialist in moisture analysis since 1968, has developed moisture standards and measuring instruments for providing accurate and reliable moisture data to a variety of industries including petrochemical, refinery, process and air separation plants around the world.

Collecting reliable moisture data requires, as a minimum, fast response, stability and repeatability from a moisture analysing instrument. MCM utilises a unique, fast responding temperature controlled silicon sensor technology to address these fundamental requirements and has successfully applied it to gas phase sampling in a variety of industries, including LNG.

Measurement or trend?

Defining whether a determination should be trended or quantified is an important decision to make because it impacts the reliability of any data and the associated cost of supporting a measurement in the field. It is often much more costly, having defined tolerances on performance, to try to keep analysers within those tolerances, than it is to support a system that indicates a trend in the field.

However, defining performance tolerances in a plant environment has proven difficult in the past. Setting analyser tolerances is a complex problem involving many disciplines and interactions. It does not fit comfortably in any business model as it cannot be easily categorised or labelled as other, more static parameters can.

Richard Berka, Moisture Control & Measurement Ltd, UK, demonstrates the importance of *moisture analysis and hygrometry*.

Failure to define optimum tolerances brings with it performance issues, followed by increased maintenance and eventually re-engineering, or even replacement. These add on costs impact other departments such as maintenance, who then have to 'sort it out.'

In the LNG industry it is often necessary to monitor a trend during production and raise an alarm within set tolerances. This can be at the point of transfer, during custody transfer or during a dispute. As soon as a tolerance is quantified it calls for a measurement, and the instrumentation has to be calibrated against traceable standards.

Therefore, specifying tolerances on performance automatically implies a measurement and that in turn raises many, generally expensive, questions such as: how much calibration, validation, maintenance and intervention will be required in order to keep the analyser within these tolerances?

The answer to these questions will largely depend on the rate of degradation in performance, which is affected by contamination, and the level of tolerance put on the measurement. As contamination is a fact of life, good sample system design is a prerequisite.

Consider a common LNG problem: how to determine if a process gas is sufficiently dry enough to be transported without blocking the pipe and stopping a plant?

To use a simple analogy of trying to detect if one object is heavier than another, one can use a dead pan balance or a precision weighing instrument accurate to +/- 1 g, and thereby quickly identify which object is heavier. The pan balance determines a trend whilst the precision weighing instrument gives a measured value, defined by its calibration, against an external reference. Both serve a useful purpose. One gives a robust trend, the other more quantitative information, but which approach should be used when both trending and alarm capabilities are needed?

Generally, if a condition has any tolerance placed on it then a measuring instrument must be specified. It is the stability, repeatability and response speed characteristics that will define the analyser's ability to trend and provide accuracy.

Traceability

If a traceable audit is required, only the units of measure that give traceability should be used in the measurement. For example, if measuring water content in units of ppm, a concentration term, then traceability to mass is needed.

Similarly, if traceability is available only at atmospheric pressure, as in the case of water content measurement, then that measurement can only be made at atmospheric pressure and not at elevated pressures, which may be more convenient but offer no traceability back to national standards.

Defining the maintenance and intervention interval

Setting the intervention (service) interval for moisture analysers is a function of precision and reliability. The tolerances on accuracy or speed of response limits affect the service interval. In the presence of contamination, both response speed and precision will degrade, leading to loss of signal, attenuation, and ever slower response times. Therefore, the result of degradation is more and more unreliable performance between scheduled services until eventually a process problem occurs.

Validation

Having defined the tolerances on stability, repeatability and speed of response, and agreed on the route of traceability, the specifier must consider how these will be practically tested in order to establish a validation methodology. Without this the users face a significant increase in risk of failure and additional costs in keeping the system within the specified performance criteria.

Case study 1: impact of temperature in humidity analysis

The majority of humidity analysers used within the petrochemical and LNG industry use non temperature controlled aluminium oxide sensors. If no compensation or temperature control is applied to correct what can be significant discrepancies in temperature between calibration and operation, they give unreliable data.

Unreliable means expensive

Consider a glass of cold water. The external surface is detecting humidity as seen by the pick up of condensation with different sensitivities according to the gradient of surface temperature of the glass.

The sensitivity of the moisture detector (the glass) is directly related to its temperature. The colder the surface becomes the more water it picks up, and vice versa, as can be observed by the amount of condensation deposited on the surface. Without appropriate temperature control or compensation, a humidity sensor that is varying in temperature cannot give stable readings. The result is a biased reading depending on the discrepancy in temperature from its calibrated temperature, normally at 21 ˚C. The solution is to control the temperature of the sensor.

The temperature coefficient of commonly used aluminium oxide humidity sensors is well documented. It is typically 4% of indicated moisture per ˚C of temperature deviation from the instruments temperature during calibration. In hotter climates where ambient temperatures can be 40 ˚C, a non temperature controlled instrument using such sensors will systematically read lower than true by as much as 80%.

In one example, slow responding moisture analysers were blamed for failing to detect a moisture ingress problem in the main feed line to the compressors of an LNG train. This failure to detect the moisture buildup caused a chiller stage to freeze, leading to a controlled shutdown, loss of production and rescheduled shipments.

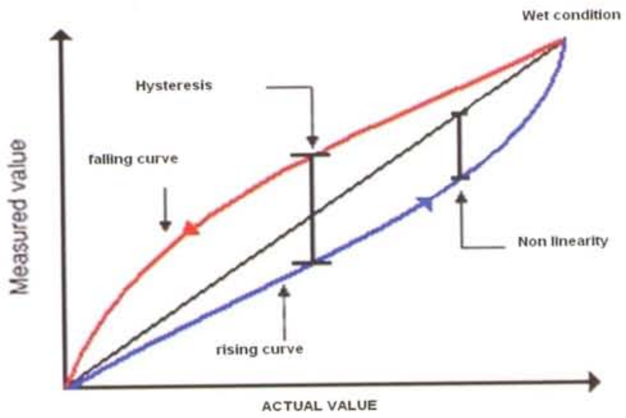

Figure 1. Effect of Hysteresis on moisture measurement.

Upon investigation the cause was identified as being due to a desensitised, slow responding analyser system. Recovery and loss of revenue costs were estimated to exceed US$ 200 000. Thus, badly specified humidity analysis equipment resulted in lost production that affected yield, shipments and ultimately, profitability. Had the instrument specification been better defined and appropriate validation checks put in place, the problem could have been avoided.

A review of maintenance procedure highlighted the need for more frequent instrument validation and closer involvement between the process and maintenance groups in better defining what these monitoring systems should be doing. The portable instruments used to cross check readings were insensitive and slow, attenuating any moisture readings to the point that they read drier than true in the sampling times allowed. As the location was prone to high variances in ambient temperature, the validating instruments were unstable. Thus, on a true 10 ppm, an instrument calibrated to read correctly at 21 ˚C only read 2 ppm at 40 ˚C and was consequently believed to be in specification.

When the analyser was sent to the site laboratory for revalidation it again read the correct value because it was (again) operating at its original calibration temperature of 21 ˚C, some 19˚ cooler than during its field test. The lab reported no fault with the analyser and technicians spent a few more days trying to understand what had caused the intermittent process problem. The analyser's certificate of calibration was to ISO9001 and the analysers were declared to be in good order on revalidation, but the pipe was still frozen.

Data was unreliable because no one took account of the temperature difference between the calibration and operation. No mechanism was in place to check the slow and insensitive nature of contaminated instruments.

Case study 2: the impact of hysteresis on validation.

In a recent LNG application there was a periodic requirement to validate a non temperature controlled inline moisture analyser monitoring LNG with a portable instrument, to establish whether the installed online system was reading within acceptable tolerances.

The application problem

The inline moisture measuring system approached measurement from a normally dry condition whilst any portable instrument would start its measurement from the much wetter condition than the measured value. This causes a significant

Figure 2. Comparative response and hysteresis of different hygrometers.

discrepancy in readings between the two analysers; a common validation problem.

The combined difference in approach, with one analyser approaching the reading from a wetter condition (Figure 1, the red line) and the other from the dry (the blue line), resulted in a discrepancy of +/-500% between readings despite each analyser being within acceptable calibration tolerances.

The comparison of several calibrated hygrometers in Figure 2 shows hysteresis, slow response and insensitivity when cycled through known moisture changes at -60, -40 and -20 ambient and then back through -20, -40, -60 and -70 dewpoint.

This demonstrates how hysteresis effects and slow analyser responses can make it practically difficult to validate moisture readings at the levels of interest for LNG, using traditional (aluminium oxide) based humidity analysers. The yellow line was the only temperature controlled silicon sensor device and the only one to track closely with the moisture levels generated.

For example, asking for 1% accuracy on a reading may seem reasonable at 1000 ppm, but when measuring at 5 ppm, it becomes almost impossible to work within a +/- 50 ppb tolerance. This makes compliance expensive and high maintenance.

Conclusion

Speed, sensitivity and repeatability are the basis of good measurement and a good starting point for specifying performance. Based upon a temperature controlled silicon sensor, MCM technology is fully capable of meeting these criteria.

With a significantly faster responding than aluminium oxide, electrolytics or oscillating crystal technologies, the silicon sensor also demonstrates superior stability and repeatability characteristics.

MCM's typical response time from off scale 'wet' to 1 ppmV in less than 2 min is unrivalled in humidity analysis and remains the benchmark within the industry.

The patented sensor drying function Push Purge® is an invaluable feature unique to MCM that speeds up sensor dry down by rapidly heating the sensor to 130 °C. This ability to index the instrument from a dry position every time significantly improves the repeatability of readings by eliminating hysteresis. Such technology features ensure that users have the choice to make more frequent measurements for improved productivity whilst maintaining high confidence in the reliability of data.