

Reducing the Detection Limits for a Process Moisture Analyzer

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ABSTRACT

Piezoelectric moisture analyzers have been used in the process industry for over two decades. While this is an older technology for measuring moisture in gas phase samples, it is still one of the most reliable in the industry. The evolution of the quartz-crystal microbalance (QCM) has produced a new and substantially improved moisture analyzer, but the needs of industry continue to evolve. This paper describes modifications performed on an existing process moisture analyzer, which resulted in the lowering of the detection limit from 0.1 parts per million by volume (ppmv) to less than 0.01 ppmv.

INTRODUCTION

The performance requirements for process moisture analyzers are pushing the existing measurement technologies to their limits. Not only do these analyzers need to survive under a wide range of environmental conditions, but the need for lower detection limits is increasing. Detection limits of less than 10 parts per billion by volume (ppbv) water vapor – a value that was previously only achievable by laboratory grade instruments – are now being requested for process measurements. One example of these new requirements is in the natural gas processing industry. Specifically, there is a need to measure water vapor concentration below 100 ppbv in a natural gas stream that is entering a turbo-expander plant for the separation of the ethane and propane fractions. Because of the cryogenic conditions present in the turbo-expander separation process, even trace levels of water vapor will lead to ice formation on

expansion valves, and on turbine blades. If the plant operators catch the problem early, the result is down-time to remove the ice from the critical components. In the event that the problem goes undetected, ice formation on the turbine blades can lead to permanent damage, causing down time and a very expensive repair. At present, there are well in excess of 300 turbo expander facilities operating around the globe (1); as such, there is a large demand in the gas processing industry to detect water vapor at ultra-trace levels.

MOISTURE MEASUREMENT REQUIREMENTS OF THE TURBO-EXPANDER PROCESS

At a turbo-expander separation plant, the natural gas entering the facility must be dried, prior to undergoing the separation process. Drying of the gas is achieved by passing the gas stream through a bed of molecular sieve. At a typical facility, multiple molecular-sieve beds will be present, so that off-duty beds can be regenerated, without shutting the plant down. Typical molecular-sieve bed specifications are on the order of 0.1 ppmv water vapor at the outlet, with the nominal water vapor concentrations being below this value. Without the ability to accurately measure water vapor concentrations below 0.10 ppmv, the regeneration of the molecular sieve beds is performed on a timed cycle. The cycle time is set to a conservatively short duration, to prevent the possible breakthrough of water vapor into the turbo expander. Performing the regeneration in this fashion can be extremely expensive, because the plant must incur the cost of the regeneration more frequently that is required. With the ability to measure the water vapor concentration at the outlet of the molecular sieve beds, the plant operators can accurately observe the normal outlet conditions, and switch the active bed to regeneration as the leading edge of a breakthrough event is detected. By switching the beds based on a measurement of the breakthrough event, the plant operators can reduce the number of regeneration cycles performed; and hence, reduce the operating cost of the plant.

To regenerate molecular-sieve beds based on the detection of water vapor breakthrough, a process moisture analyzer with several key performance characteristics is required. First, since the critical value for switching the beds to regeneration is on the order of 0.1 ppmv, the analyzer must clearly be able to measure water vapor at this level. Specifically, the limit of quantization for the analyte (water vapor) must be below the critical switching point. As an added conservative measure, having the detection limit for the analyzer be a full order of magnitude below the switching point is desirable. Thus, the successful process moisture analyzer for this application must have a detection limit of 0.01 ppmv (10 ppbv). Additionally, the analyzer must respond fast enough to enable the plant operators to observe the breakthrough event and switch the bed to regeneration within a time span of only a few minutes. And finally, the instrument package must meet all applicable hazardous area requirements, and the extremes of ambient temperature that are present at these plants, which are located around the globe.

MODIFYING A COMERCIAL QCM MOISTURE ANALYZER

A variety of moisture analyzers exist for the process industry. Typically, these instruments have been developed to meet hazardous location and environmental requirements. Meeting stringent hazardous area classification and environmental requirements often results in compromises against the instrument's performance. The performance requirements for moisture analyzers in other industries, notably the semiconductor industry (2), have been steadily increasing over the past decade. To meet these ever

increasing demands, the designs of the QCM-based moisture analyzers have evolved. Notable improvements to the basic instrument design have included the introduction of high-purity sample manifolds (3), and optimization of the sensor performance characteristics (4).

To enable a process QCM-based moisture analyzer to reach an detection limit of 0.01 ppmv, two primary modifications were required. These modifications were the addition of a zero-gas module, and the installation of a permeation-based moisture generator with an output of approximately 1 - 2 ppmv. Additionally, the instrument package also needed to have CENELEC Zone 1 certification, and it needed to operate over an ambient temperature range of -40 to $+60$ °C.

A flow-diagram for the modified instrument is shown in Figure 1. In the Figure, the portion of the flow manifold that is shown inside of the dotted rectangle (DV1 – DV3, and the dryer) are the additions required for this work. The remainder of the flow manifold is the normal configuration of the QCM-based analyzer. There are four separate sample paths in this analyzer manifold. The first is a simple bypass, which allows for an increased flowrate of sample gas (i.e. – opening the bypass valve (SV1) reduces the time required to equilibrate all portions of the sample system that exist upstream of the bypass valve). A capillary tube, located immediately downstream of SV1 (the coil shape in the Figure), limits the flow rate to approximately 1 standard liter per minute – the exact value of the bypass flow is a function of the inlet pressure to the analyzer. The remaining three flow paths are supplied with sample gas by the a proportional solenoid valve (PSV), which is used to regulate the flow of gas through the analyzer. Downstream of the PSV, the remaining three flow paths separate. One path goes directly through a capillary tube, and on to a three-way solenoid valve (SV2). The remaining two paths branch after the sample gas is passed through a dryer. The fourth flowpath contains a small moisture permeation tube. Thus, a portion of the flow through the analyzer is a bypass, a portion of the flow is passed directly to the QCM sensor assembly (the sample leg), the third portion is dried before passing to the QCM sensor (the dry reference leg), and the fourth flow path dries the gas and adds a controlled amount of water vapor to the stream (the “moisture generator” leg). The three-way solenoid valves (SV2 – SV4) are use to select the gas stream that is passed through the sensor, while the remaining two streams are passed to the vent. In normal operation of the analyzer, the analyzer continuously cycles between the sample and dry-reference gas streams. Essentially, this switching action modulates the water vapor concentration that the sensor is exposed to. As such, the resonant frequency of the sensor crystal is modulated, decreasing as the sensor is exposed to the water vapor in the sample stream, and increasing as the sensor is exposed to the dry reference gas. The water vapor concentration in the sample gas is measured as a function of the modulation amplitude. The role of the permeation device, the “moisture generator”, is to provide an on-board means to check the performance of the QCM sensor. In the “generator mode”, the QCM sensor is alternately exposed to the gas stream from the moisture generator and the dry reference stream.

The zero-gas module, shown inside of the dotted rectangle in Figure 1, is used to provide a dry gas stream at the inlet of the analyzer. Physically, the zero-gas module was installed external to the actual analyzer assembly, but within the explosion proof casting required for the CENELEC Zone 1 certification. Functionally, the zero-gas module is a very simple device, consisting of only three diaphragm valves and a dryer (an activated 3A molecular sieve device was used for this work). The diaphragm valves used in this device are UHP grade components; all surfaces are electropolished, and the gas connections are welded. Because of the high quality of the surfaces in these components, residual moisture retention is minimized; therefore, the assembly is capable of rapidly achieving a dry

condition, once the “zeroing cycle” has been initiated. Under normal operation of the analyzer, both DV1 and DV3 remain closed to protect the dryer, while DV2 is open to allow the flow of sample gas into the analyzer. To perform the “zeroing” operation, DV2 is closed, while both DV1 and DV3 are opened. Thus, the flow of sample gas is diverted through the dryer, providing a dry reference ($\ll 10$ ppbv) for the analyzer. By providing this dry reference gas as an external challenge to the analyzer, the zero-gas module enables the offsets present in the system (e.g. – electronic offsets, offsets caused by pressure differences in the different flow paths, and offsets caused by low-level outgassing of water vapor from upstream valving) to be measured. Normally, the magnitude of these offsets is relatively small, less than the equivalent of 0.1 ppmv (i.e. – the detection limit for the standard analyzer), so they are ignored. However, as the intention of this work was to design an analyzer system to have a detection limit of only 0.01 ppmv, these minor effects must be accurately determined and removed from the moisture measurement.

The second modification of the analyzer package was to replace the standard permeation device, which is designed to deliver a moisture concentration of approximately 50 ppmv to the sensor assembly. Because the modified analyzer was to be used on very dry gas streams (typically $\ll 1$ ppmv), it was desirable to have the internal standard deliver a moisture concentration much closer to the normal working range of the analyzer. For simplicity, and availability of the required parts, a target concentration of 1 – 2 ppmv was selected for the permeation device.

The final modification from the standard configuration was to install the entire analyzer assembly (i.e. – the explosion proof casing containing the instrumentation) into a weather resistant enclosure. The enclosure was insulated; a small electric heater and a Vortec cooler were installed to control the internal temperature of the enclosure. This enclosure, with the associated heating and cooling capabilities, would enable the sample oven within the instrument package to remain at a constant temperature. The goal for this environmental packaging was to enable the instrument package to function in ambient temperatures from -40 to $+60$ °C.

EXPERIMENTAL

For all of the work performed in this study the QCM-based moisture analyzer was an AMETEK 3050 OLV (serial number 305A158). The instrument was received as a “standard product” by the authors, and was subsequently modified for this work. As such, the instrument was calibrated over a 0 – 2500 ppmv range, using a two-pressure standard moisture generator (5-7) with a dilution system – this piece of equipment is identified as the M3 calibrator at the authors’ facility. Within the two-pressure standard moisture generator, the system temperature is monitored with a pair of Hart Scientific 1504 thermometers. Pressure in the standard generator is monitored with a pair of Omega Engineering PX5500 precision pressure transducers. The total uncertainty for the system, with the final dilution step included, is approximately $\pm 1\%$ of the target value.

After performing the required modifications to the instrument hardware, the performance was measured for moisture concentrations less than 100 ppbv. To perform these tests a second calibration fixture was used. The “low-level” setup utilizes a set of permeation tubes for the moisture standards, with a variable dilution stage that was custom manufactured by Environics (serial number 2329). The dry diluent gas for this system is nitrogen, which is obtained as boil-off from the facility’s liquid nitrogen supply. Further drying of the gas was performed in two stages. The first stage was activated 3A molecular

sieve, which dries the nitrogen to less than 10 ppbv. The final stage in the drying process is a hot getter. The moisture content at the outlet of this drying system is less than 1 ppb. The uncertainty estimated for this system is approximately +/- 2 % of the target, or 1 ppbv (i.e. – the larger of the two uncertainty values is used).

All of the environmental testing for the instrument package was performed in-house, using an Envirotronics model WPH650-2-7.5 environmental chamber.

RESULTS AND DISCUSSION

All of the testing for this study was designed to evaluate the measurement performance of the QCM-based moisture analyzer, and its ability to function in extreme environmental conditions. The results of this testing are presented below, starting with the calibration of the analyzer, which was performed prior to the modifications performed for this study. Testing results for the modified analyzer include a study of the base-line noise characteristics, the response to external and internal moisture challenges, the response of the system to a moisture challenge at the detection limit, and the behavior of the system over a wide ambient temperature range.

The “standard” process moisture analyzer, used in this study, was calibrated for a moisture concentration range of 0 – 2500 ppmv. The final step in the calibration process was to validate the instrument’s performance over this same concentration range. The data in Figure 2 were recorded for the validation tests of the analyzer used in this study. In the figure the instrument’s responses are plotted against the challenge levels, which were 5.0, 10.0, 25.0, 100, 500, 1250, and 2277 ppmv. At each challenge level, there are two data points shown in the Figure: the points marked by an “o” are for the sensor’s normal operating mode, and the points marked by an “*” are for the “sensor saver” mode of operation. The “sensor saver” mode is used to reduce the contact time that the sensor is exposed to the process gas - for the remainder of the work performed in this study, the QCM sensor was used in the normal operating mode. The data in the figure are very linear; all of these data points were well within the +/- 10% specification for the analyzer. These data illustrate the response of the instrument over a wide range of moisture concentrations; however, the primary goal of this study was to reduce the detection limit of the analyzer to 0.01 ppmv (10 ppbv).

The most important performance characteristic for meeting a detection limit of 0.01 ppmv was the system noise level. A standard definition for the limit of detection is (8-9)

$$LOD = \mu_b + 3\sigma_b \quad (1)$$

Where μ_b is the value of the baseline signal, and σ_b is the standard deviation observed for the baseline measurements.

The base-line noise characteristics of the modified QCM analyzer were monitored over a period of several weeks. For this work, the system noise observed for the modified analyzer was treated as two separate components: the short-term random variations in the signal, and the longer-term base-line stability. Essentially, the short-term random variations are described as high-frequency noise (i.e. – the time-scale is minutes to hours), while the base-line stability is ultra-low frequency noise (i.e. – the time-

scale is days to weeks). Over short duration intervals 1 – 2 hours, the standard deviations observed for the base-line measurements were typically on the order of 1 ppbv. Long-term variations in the baseline (drift) were observed to exhibit a maximum value of approximately 5 ppbv in a 24 hour period; however, the typical level of variation was in the range of 1 – 3 ppbv in a 24 hour period. This long-term variation in the baseline is kept centered about 0 ppbv by using the zero-gas module to adjust the system offsets on a regular basis. If the maximum variation observed in the baseline (5 ppbv) is used as the value μ_b in Equation 1, then this expression yields the maximum level of uncertainty in the estimation of the detection limit. Combining the maximum drift rate of 5 ppbv per day with the observed short-term noise level of 1 ppbv, the detection limit was estimated to be 8 ppbv. This estimate is conservative, as the typical levels of base-line drift observed were about half of this value; thus, the typical performance of the analyzer would yield a detection limit on the order of 5 ppbv. Clearly, both of these values exceed the required detection limit of 10 ppbv for the turbo-expander application.

The next tests evaluated the performance of the analyzer on low-level moisture challenges, both from internal and external sources. Figure 3 is a plot of a moisture challenge provided by the internal permeation device, which is used for “on-line” calibration checks. These data were recorded for a 30 minute cycle, during which the sensor is exposed to the permeation device for a period of 27 minutes; the final 3 minutes in the cycle are provided for the system to “equilibrate” after the switch back to the sample gas. In these data the rapid response of the QCM sensor is clearly displayed. The sensor responds to the internal challenge within 2 minutes – the challenge was initiated at approximately the 6 minute mark in the Figure – and returns to a value of less than 0.01 ppmv within 10 minutes. Figure 4 is a plot of the analyzer’s response to external challenges of 60 and 90 ppbv. The analyzer was returned to a level of 0 ppbv between the two moisture challenges. The initial response of the analyzer is very rapid, but slows down as the readings approach the target level. Considering that the initial response is very rapid, the analyzer is very suitable to detect breakthrough events, such as the molecular-sieve bed failure in a turbo-expander separation plant. Further, these response characteristics are still impressive, as the original (i.e. – unmodified) analyzer is designed to have an detection limit of only 100 ppbv.

The final evaluation was to measure a moisture challenge at the detection limit for the modified instrument. To perform this test the analyzer was run on dry gas for a period of several hours, prior to initiating the moisture challenge. Then, a challenge of 10 ppbv was initiated. The data recorded for this challenge are displayed in Figure 5. Because of the low-level of this challenge, the y-axis of Figure 5 has been labeled in ppbv, rather than the ppmv scales that were used for the higher-level challenges. Instrument readings recorded prior to the challenge are centered about 0 ppbv, with a standard deviation of 1 ppbv. The instrument responded rapidly at the lead-edge of the challenge, and reached a steady-state value after approximately 1 hour. These data are a clear demonstration that the detection limit of the modified analyzer was below the target value of 10 ppbv. However, because at other points during the evaluation of this analyzer the authors observed a maximum base-line drift of approximately 5 ppbv in a 24 hour period, the detection limit was assigned a value of 8 ppbv (see above).

The final set of tests performed for this study were designed to evaluate the ability of the instrument package to operate over a wide ambient temperature range. As such, the entire analyzer system was placed into an environmental chamber. For a one week interval, the analyzer system was exposed to a range of ambient temperatures from –70 to +60 °C. Data recorded for the environmental testing are given in Table I. Of these data, the most important information is the temperature of the sensor oven, which must be maintained at 60 +/- 0.1 C for proper operation of the analyzer. At all of the ambient

temperatures tested, the sample oven temperature was maintained within the specified range. Further, the duty cycle for the oven temperature control did not reach the limiting values (i.e. 0 and 100%), demonstrating the system was able to properly control the sample oven temperature at the ambient temperature extremes. The electronics temperature was measured inside of the analyzer, located in the explosion proof casting. Over the entire range of ambient temperatures tested, the temperature of the electronics was not sufficiently high to damage the electronics, which would occur for temperatures in excess of 70 °C. At low ambient temperatures, there was enough heat generated by the system to keep these same components above freezing. The instrument air pressure, shown in the second column of the Table, are simply the air pressures supplied to the Vortec cooler. For the low ambient temperatures, no instrument air was required, as the Vortec cooler was turned off. Although the instrument package was successfully tested down to – 70 °C, some components used on the exterior of the system were only rated to –40 °C. Thus, the ambient temperature rating for this system should not exceed the lower limit of – 40 °C.

SUMMARY

The present generation of process QCM-based moisture analyzers can be modified to provide enhanced sensitivity, and detection limits low enough to meet the demanding requirements of a turbo-expander separation plant. In addition to meeting the sensitivity requirements, these instrument systems can also be modified to meet the demanding ambient temperature and hazardous area requirements for installation at facilities around the globe. This work demonstrates that detection limits below 10 ppbv are achievable with only minor modifications of the standard analyzer.

REFERENCES

- 1) True, W.R., “Special Report: Worldwide Gas Processing”, Oil & Gas Journal, June 2000, 64-119.
- 2) “International Technology Roadmap for Semiconductors”, 1999 Edition, SEMI, Mountain View, California, 1999.
- 3) Simmermon, J.C., Dell, C.G., Peterson, D., Blakemore, C.B., Remaley, J.B., Golod, A., Bear, R.S., United States Patent, Number 5,616,827, 1997.
- 4) Bear R.S., “Redefining the Limits of the Quartz Crystal Microbalance for Low-Level Moisture Detection”, Papers and Abstracts from the Third International Symposium on Humidity & Moisture, London, England, 6 – 8 April 1998, 456 – 457.
- 5) Wiederhold, Pieter, “Calibration”, Water Vapor Measurement, 1st Edition, Marcel Dekker, Inc., New York, New York, 1997, 259-265.
- 6) Greenspan, L., “Functional Equations for the Enhancement Factors for CO₂-Free Moist Air”, Journal of Research of the National Bureau of Standards –A. Physics and Chemistry, Vol. 80A, No. 1, 1976.
- 7) Huang, P. H., “New Equations for Water Vapor Pressure in the Temperature Range –100 °C to 100 °C for Use With the 1997 NIST/ASME Steam Tables”, Papers and Abstracts from the Third International Symposium on Humidity & Moisture, London, England, 6 – 8 April 1998, 68-76.
- 8) Kaiser, H., *Anal. Chem.* **1970**, *42*, 26A.
- 9) IUPAC, *Spectrochim. Acta* **1978**, *33B*, 242.

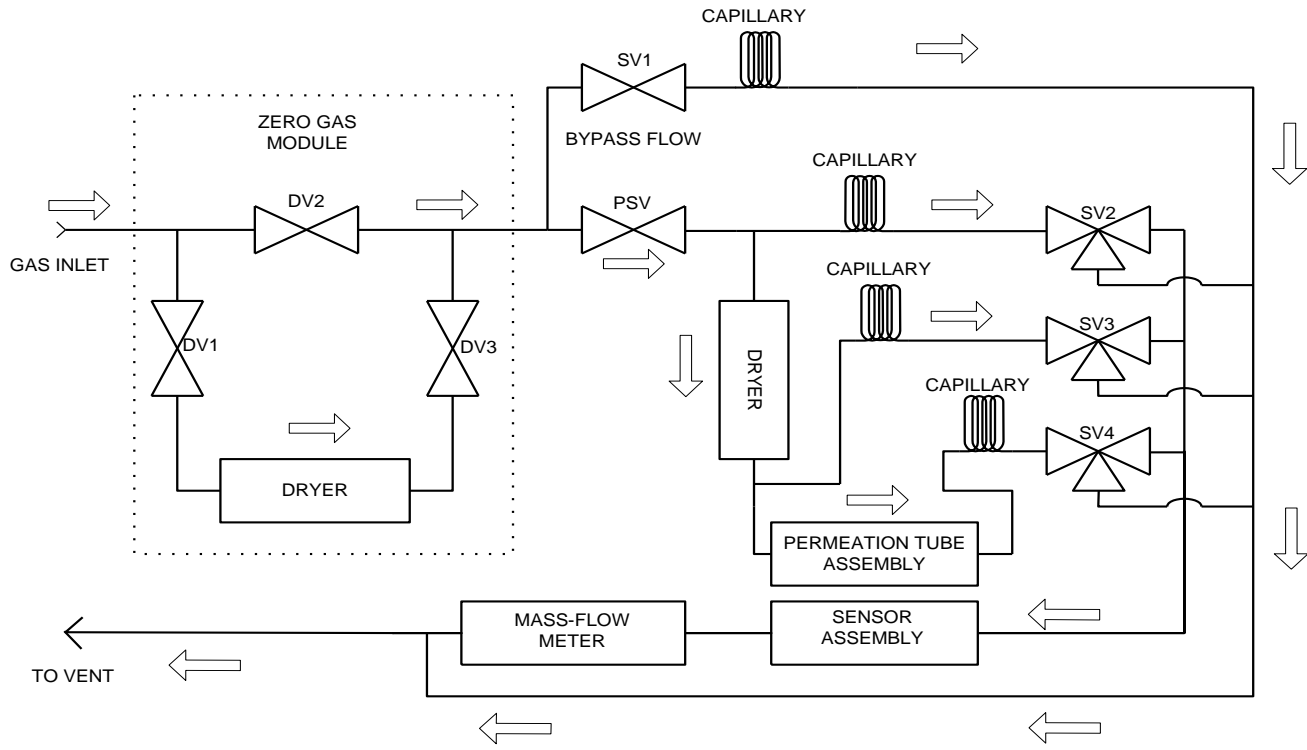


FIGURE 1 – FLOW SCHEMATIC OF THE MODIFIED QCM-BASED MOISTURE ANALYZER.

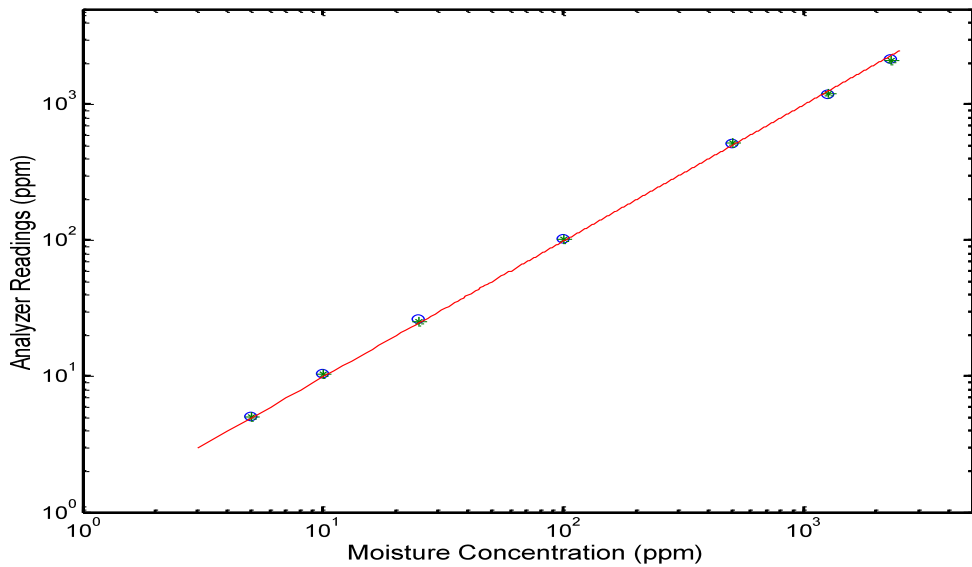


FIGURE 2 – RESULTS OF CALIBRATION FOR THE UNMODIFIED QCM ANALYZER. DATA RECORDED FOR THE NORMAL SENSOR MODE ARE INDICATED BY THE “O”, AND THE DATA FOR THE SENSOR SAVER MODE ARE SHOWN AS “*”.

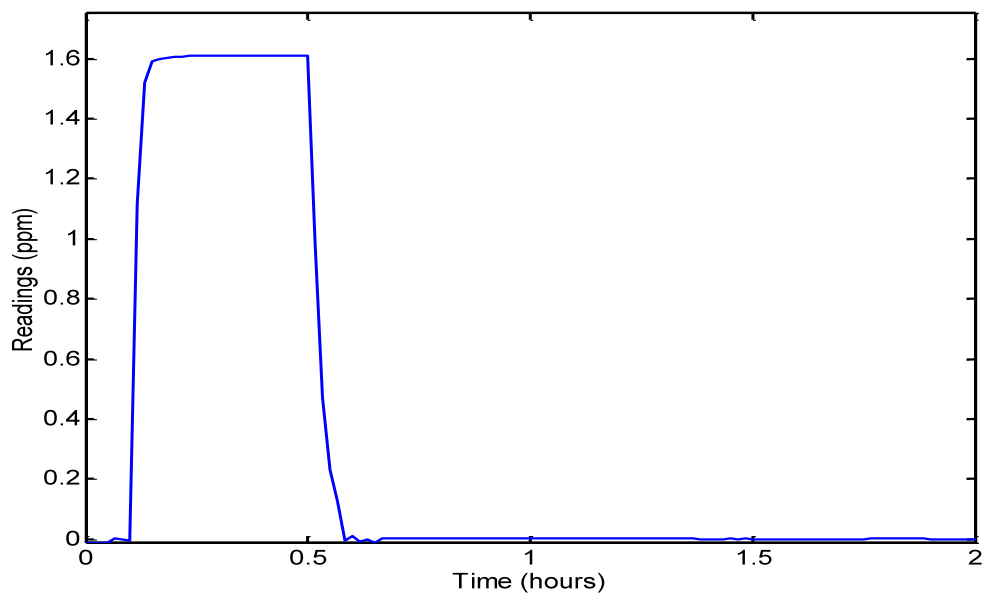


FIGURE 3 – RESPONSE OF THE MODIFIED ANALYZER TO A MOISTURE CHALLENGE PROVIDED BY THE INTERNAL PERMEATION DEVICE.

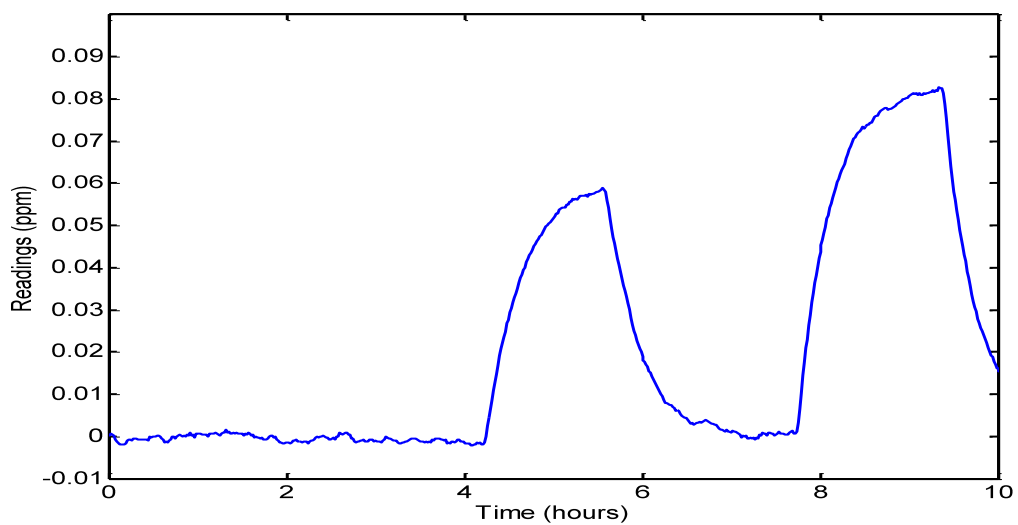


FIGURE 4 – RESPONSE OF THE MODIFIED ANALYZER TO CHALLENGES OF 60 AND 90 PPBV.

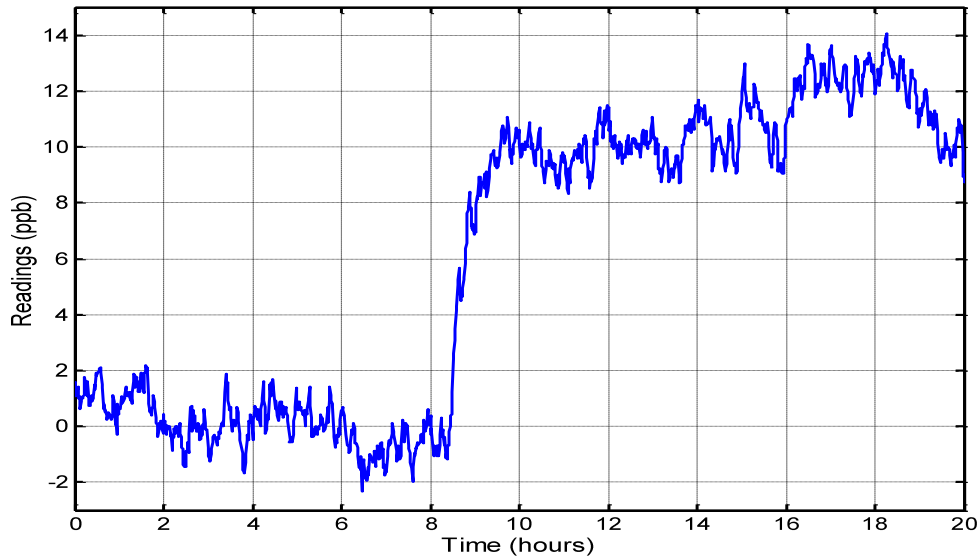


FIGURE 5 – RESPONSE OF THE MODIFIED ANALYZER TO A 10 PART PER BILLION CHALLENGE.

TABLE I – ENVIRONMENTAL TEST DATA FOR THE MODIFIED ANALYZER SYSTEM.

Ambient Temperature (°C)	Instrument Air Pressure (psig)	Electronics Temperature (°C)	Sensor Oven Temperature (°C)	Duty Cycle for Sensor Oven (%)
-70	N/A	1.0	59.9	79.6
-50	N/A	1.0	59.9	75.2
-30	N/A	24.5	60.0	46.5
0	90	44.1	59.9	25.1
20	90	45.1	60.0	23.5
25	90	52.9	60.0	12.5
60	90	59.8	60.0	6.6