Evaluation Test Report

Evaluation of:

MCM's heated Silicon Sensor Moisture Analyser
against
Aluminium Oxide
and Oscillating Crystal Moisture Analysers,
during
Molecular Sieve Test Runs
at
St Fergus, Scotland.

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1) Abstract

Methods for dehydrating natural gas using molecular sieves (mol sieve) are well established. Many strategies have been developed with the intention of extending mol sieve lifetime and preventing unplanned shut-downs of dehydration units. The amount of adsorbent required in such dehydration processes is determined by the water content in the feed, the end-of-run (EOR) water adsorption capacity of the mol sieve inventory and the minimum time required for regeneration of the mol sieve bed. When the capacity of the adsorbent falls below the level where all water in the feed can be adsorbed during the minimum adsorption time, then the adsorbent must be replaced.

Improving the speed of response and accuracy of moisture measurement within dehydration processes provides significant commercial benefit to production:

A: In cases where feed gas is unsaturated, the use of the adsorbent in gas plants can be maximised by improving the measuring accuracy of the feed inlet moisture. This helps prevent unplanned costly shut-downs, which in many cases can exceed the cost of mol sieve inventory.

B: Detecting moisture breakthrough on the beds as soon as possible reduces operating costs by optimising changeover and the regeneration schedule of those beds.

LNG plants often employ Aluminium Oxide probes on the mol sieve dryers, usually located both on the feed inlet and lower mol sieve beds. For a variety of reasons, these analysers suffer from drift, insensitivity and slow response (see Reference 9.1, pp17-20; T.K. Mehrhoff, General Electric Company – *Comparison of Moisture Analysers at Concentrations 1 to 15 ppm*).

Aluminium Oxide analysers are simple devices that provide no mechanism to automatically correct for drift. As a result these instruments produce unreliable data, often long before scheduled servicing is called up (see Reference 9.2, pp21-26; Saburo Hasegawa, National Bureau of Standards – *Performance Characteristics of a Thin-Film Aluminium Oxide Humidity Sensor*).

In order to boost confidence in the collected data, many production plants protect against the deficiencies of the Aluminium Oxide technology by also utilising an Oscillating Crystal analyser, which is generally considered to be more sensitive and responsive. Often, the Oscillating Crystal instrument is positioned at the common outlet of the mol sieve dryer. However, a "dual technology" approach such as this costs more to operate and support. If a faster, more accurate and reliable analyser could be identified, and the support overhead involved with dual technologies could be reduced to a single, more reliable system, then long-term cost savings could be achieved through common spares, training and validation (see Reference 9.3, pp27-28; *SEIC Terms of Reference* (*Rev 1 – March 13th, 2008*).

Shell's internal procedures already state that Silicon sensors are preferred over Aluminium Oxide technology (see Reference 9.4, pp29-31; *Design and Engineering Practice Document DEP 32.31.50.12-GEN – On-Line Process Stream Analysis – Analysers*). The goal of the evaluation was to confirm that MCM's heated Silicon Sensor was:

A: Inherently faster and more accurate than *either* of the currently installed systems.

B: Of commercial benefit to production plants using such dehydration processes.

1.1) Summary of Findings

A   All equipment was successfully installed at St Fergus and all three mol sieve beds were monitored to breakthrough, without any disruptions or delays. A full database of records on all channels was collected, at two minute intervals over the six week duration of the trials.

B   The Moisture Control & Measurement (MCM) heated Silicon Sensor technology was demonstrated to be more accurate and more sensitive than the Aluminium Oxide devices.

C   MCM's heated Silicon Sensor technology was demonstrated to be more accurate and three times more sensitive than the Oscillating Crystal devices

D   Following the two-month evaluation period, MCM's heated Silicon Sensor technology was shown to be reproducible and fast responding. Tests performed in Shell Global Solutions International (SGSI) laboratories quantified the response times to be, typically, within 5 minutes to a 95% confidence limit.

E   The MCM system that was configured as a "stand alone" unit demonstrated that on-site validation could be performed without interruption to the process, whilst also being configured as an intrinsically safe system.

F   ***As a result of points 1.1 A-E, the evaluation objectives as defined in the Shell Terms of Reference were considered to have been met.***

The below chart (Figure 1 – *Test Run Comparing MCM, Panametrics and Ametek*) demonstrates the information summarised above in points 1.1 A-F:
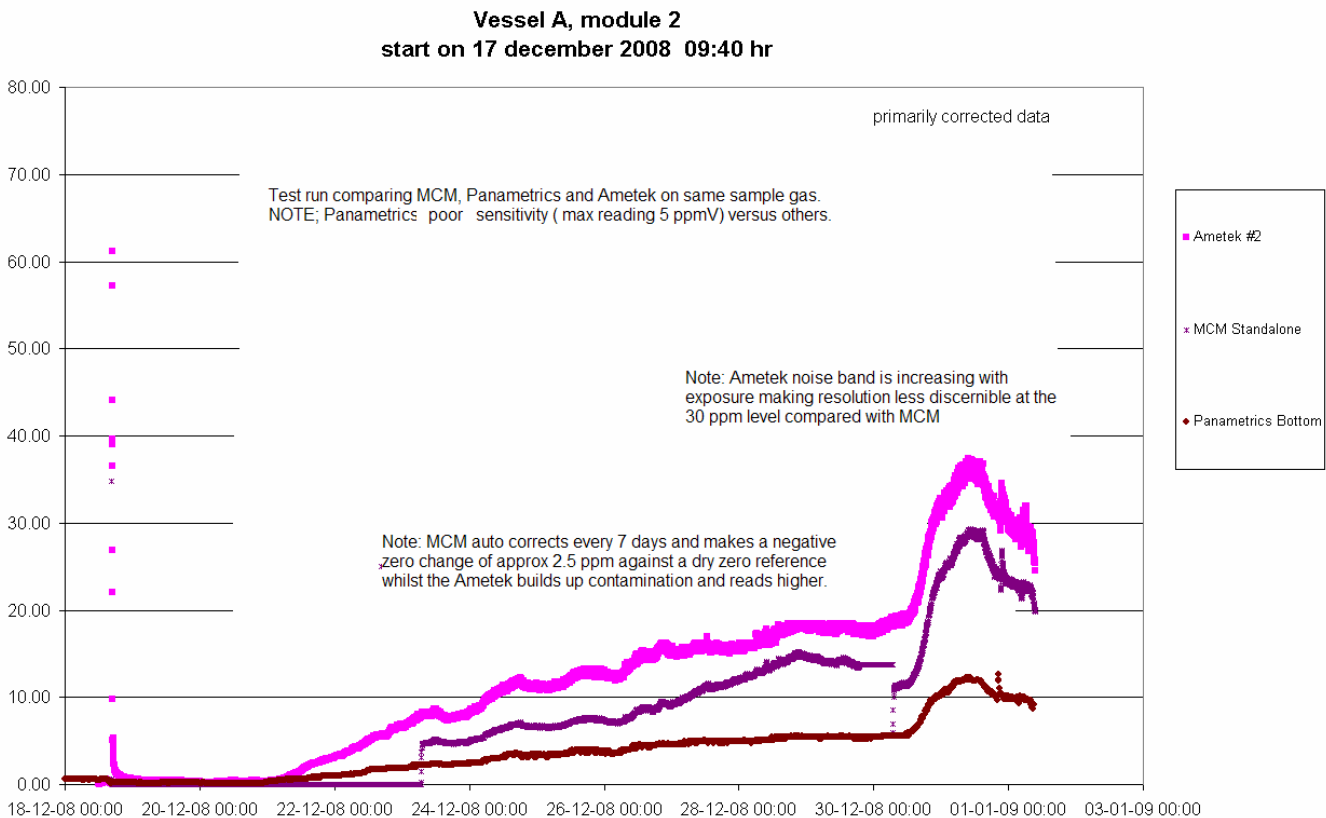

Figure 1 - *Test Run Comparing MCM, Panametrics and Ametek*

2) Background to the Trials

The existing Aluminium Oxide technology was considered unreliable and operators no longer based any plant changes on the data that these instruments provided, leaving them reliant on a single hygrometer using Oscillating Crystal technology (positioned at the common outlet).

There are multiple reports of unreliable performance, both within Shell and in the public domain, which confirm that Aluminium Oxide technology is unsuitable for measuring low moisture concentrations (see Reference 9.5, pp32-33; *Summary of Shell Experiences with Aluminium Oxide Moisture Sensors*).

The Oscillating Crystal analyser, installed on the common outlet, was deemed to be more reliable than the Aluminium Oxide devices and an annual cross-check was performed by SGSI in order to validate data.

For the purpose of the evaluation MCM supplied two (2) analyser systems, each featuring heated Silicon Sensor technology. This type of instrumentation had not been used previously at St Fergus and, as such, was put through a rigorous safety assessment by SGSI, who were ultimately responsible for the equipment.

SGSI prepared a Mobile Analyser Cabinet (MAC) that contained three (3) Oscillating Crystal (Ametek) instruments – monitoring inlet, bottom bed and outlet bed – and one (1) MCM transmitter system. The MCM system was installed in series with the Oscillating Crystal device monitoring the inlet (feed) gas (see Appendix 10.8, p49; *Process & Instrument Description Set-up*).

The Oscillating Crystal analysers were not intrinsically safe and, therefore, had to be enclosed in a purged cabinet to make them suitable for operation in a hazardous area. This setup made it impossible to access the units in order to perform any validation work during the trials, without first powering down the analysers.

As the validation of results is deemed to be a critical aspect when defining the absolute accuracy of the inlet feed gas, the second MCM system, configured in an identical manner to the first, was supplied as a "stand alone" unit. This system was manufactured to be intrinsically safe, which would allow periodic validations to be performed in the field, without interrupting measurements.

MCM's "stand alone" unit was installed in series with the Oscillating Crystal instrument that was monitoring the bottom bed. Each analyser produced a 4-20mA output, which was logged on a Yokogawa digital recorder that was also mounted within the MAC.

Both MCM systems were configured to automatically and periodically re-index themselves against a "dry" reference gas, once every seven days.

No user intervention was needed to operate either MCM system.

3)   Validation of Instrument Calibrations at SGSI

As all data was to be measured in concentration terms (ppmV), the MCM instrumentation was calibrated before and after the trials using a mass traceable ISO standard method – ISO6145-8 – Diffusion (see Appendix 10.1, pp34-35; *Initial Calibration Data by MCM*).

Parallel validations performed by SGSI, on each of the four MAC instruments, were based on a two temperature, two pressure saturated moisture vapour generator, whose output was mixed with "dry" gas to give predicted moisture concentrations. This was traceable to temperature.

As the MCM units were independently calibrated, within close tolerances on a mass traceable standard, it was possible to compare SGSI's generator output with MCM's traceable standard during the initial validation at SGSI in Amsterdam. Data from SGSI's validations were found to be in close agreement with the mass traceable calibrations performed on the MCM analysers (within 2 ppmV). No calibration factors had been applied by the vendor.

The spread of results for the Oscillating Crystal analysers was found to be 20 ppmV across the three systems. Calibration factors were then applied by SGSI in order to normalise them before use, based on SGSI's generated moisture values.

3.1)   Initial validation data from SGSI
(Comparison of MCM with Ametek on 12.11.2008)

In order to test the accuracy and sensitivity of each analyser, over the full operating range, each unit was tested against SGSI's moisture generator. Various moisture levels were used, ranging from a nominal "dry" value to a value over 45 ppmV. To investigate the hysteresis effect of each system, comparison runs were made from a "dry" starting condition, up to the "wet" level and then back down to "dry" again.

"Ametek 1" and "MCM1" were compared by placing them in series with the sample. Throughout the duration of the trials these two instruments monitored the same sample gas.

The below chart (Figure 2 – *SGSI Plots of Validation Data for MCM and Ameteks*) shows the relative performance of the MCM heated Silicon Sensor versus the three Ametek Oscilating Crystal systems.
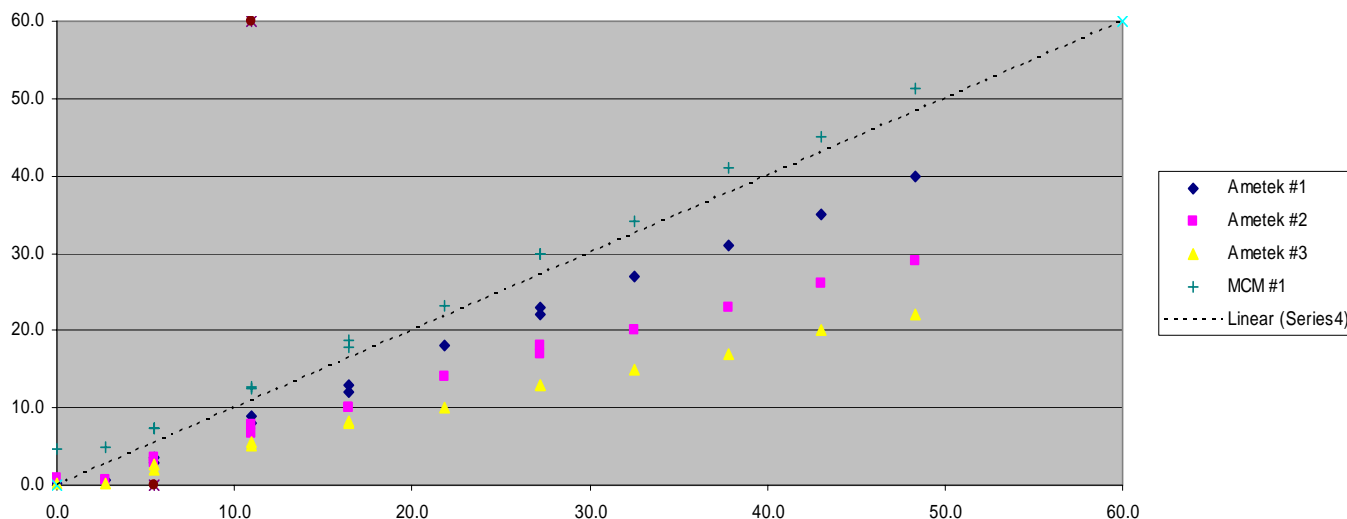
Figure 2 – *SGSI Plots of Validation Data for MCM and Ameteks*

Key: The dotted line represents the generated values

The diamond [♦], square [■] and triangle [▲] symbols refer to each of the Ametek analysers.

The cross symbol [✚] refers to the MCM analyser.

NB: Initial validation shows the MCM analyser to be in closest agreement with the SGSI generators. The MCM system also demonstrates closer linearity with the generated moisture levels than any of the Oscillating Crystal devices.

All three of the Ametek systems were seen to display a bias to the "dry" end of the scale, and each required calibration factors to be applied in order to correct the data. ***Comparing this large spread of results with the manufacturer's claim of 0.05 ppmv or 5% of the instrument reading (as per Ametek user manual, pp1-5) highlights the importance of verifying all performance claims prior to such testing.***

3.2) SGSI Validation Data

Generated Moisture ppmV	Ametek #1	Ametek #2	Ametek #3	MCM
	0.2	0.2	0.1	n/a
0.0	0.2	0.3	0.1	4.7*
5.5	3.6	3.5	2.6	7.3
11.0	8.9	7.8	5.5	12.5
21.8	18.0	14.0	10.0	23.3
32.5	27.0	20.0	15.0	34.1
43.1	35.0	26.0	20.0	45.1
48.3	40.0	29.0	22.0	51.3
27.2	23.0	18.0	13.0	29.9
2.8	0.6	0.6	0.3	4.8
5.5	3.0	2.8	2.1	7.3
11.0	8.1	6.8	5.2	12.7
16.4	13.0	10.0	8.0	18.8
27.2	22.0	17.0	13.0	30.0
37.8	31.0	23.0	17.0	41.0
16.4	12.0	10.0	8.2	17.9
0.0	0.2	0.9	0.2	4.7

* NB: The MCM analyser was seen to be reading 4.7 ppmV at the "dry" gas level, when it was expected that the "dry" gas value would have been near 0 ppmV. Upon investigation it was found that the MAC units were connected to water permeable PTFE sample lines, which were contributing water to the "dry" Nitrogen lines.

It is interesting to compare the repeatability of the instruments at the generated 5.5 ppmV and 11.0 ppmV levels, as the generator moves from the "dry" to "wet" levels and back to "dry" again. See extracted data below:

Generated Moisture ppmV	Ametek #1	Ametek #2	Ametek #3	MCM
5.5	3.6	3.5	2.6	7.3
5.5	3.0	2.8	2.1	7.3

Note the excellent repeatability of the MCM instrument (7.3 ppmV to 7.3 ppmV – within 0.0 ppmV at the 5.5 ppmV level). The repeatability of the Ametek analysers is 1.9 ppmV to 2.5 ppmV at best (data from Ametek 1).

11.0	8.9	7.8	5.5	12.5
11.0	8.1	6.8	5.2	12.7

Again, the MCM instrument shows excellent repeatability (12.5 ppmV to 12.7 ppmV – within 0.2 ppmV at the 11 ppmV level). The repeatability of the Ametek analysers is 2.1 ppmV to 2.9 ppmV at best (data from Ametek 1).

3.3)   Observations During Initial Validation

During the validation run at SGSI it was observed that there was a 4 ppmV anomaly between the Oscillating Crystal and Silicon Sensor device, at the "dry" end of the scale (i.e.: using SGSI's "dry" nitrogen gas purge).

Upon investigation, it was found the fast loop sample system of the MAC unit incorporated PTFE tubing. Once the sample system had been modified, by replacing the PTFE with stainless steel, the anomaly disappeared.

3.4)   Test Run Data

The MCM and Ametek systems were connected to a "dry" nitrogen gas on 10.12.2008 – after 48 hours each unit was seen to be reading 0.1 ppmV. A full validation run was scheduled to be performed in the week commencing 02.03.2009.

4)   Test Results

4.1)   Speed of Response – Observations from Initial Tests at SGSI

A series of response speed tests were performed under controlled conditions at the SGSI research laboratory in Amsterdam. A portable MCM analyser utilising Silicon Sensor technology was compared with SGSI's existing MAC units, which relied on Ametek's Oscillating Crystal analysers. The collected data showed that the MCM had an inherently faster speed of response, both on "dry" to "wet" and "wet" to "dry" moisture excursions.

4.1.1) Initial Tests between Silicon Sensor and Oscillating Crystal Technology (Comparison of MCM with Ametek on 09.09.2008)

The Silicon Sensor and Oscillating Crystal analysers were connected, in series, to the same generated moisture levels.

Test 1   The analysers were connected to a nominal "dry" reference gas:

	Reading (ppmV)	T90% (minutes)
Ametek	3.3	>20
MCM	5.1	3

Test 2   The analysers were then connected to a wetter sample gas:

	Reading (ppmV)	T90% (minutes)
Ametek	19	>30
MCM	27	3

Test 3   The analysers were then connected to the original "dry" level (as per Test 1)

	Reading (ppmV)	T90% (minutes)
Ametek	3.7	>30
MCM	5.2	5

In each test the response time to 90% of the settled value was seen to be within 5 minutes for MCM's Silicon Sensor technology. This compared favourably with a T90 of approximately 30 minutes for Ametek's Oscillating crystal technology.

The differences in reading depending on the direction of the moisture excursion (i.e. "dry" to "wet" or "wet" to "dry") also demonstrates the reproducibility of both types of sensing technology – 3.3 ppmV to 3.7 ppmV "wet" to "dry" for Ametek, versus 5.1 ppmV to 5.2 ppmV "wet" to "dry" for MCM. This reproducibility was also demonstrated during the formal validation tests of 12.11.2008 (see Sections 3.1 & 3.2, pp4-5).

4.1.2) Test Runs at St Fergus

NB: The comments in this section refer to Appendix 10.4, pp39-46 – *Test Run on Vessel C, Module 2.*

- The largest moisture excursion can be seen on 07.12.2008 at 02.54 (line record 3324).

- MCM 1 reads 21.30 ppmV and is starting to move upwards at line record 3312.

- Ametek 1 reads 18.30ppmV and is starting to move upwards at line record 3324.

- MCM 1 starts to respond 24 minutes earlier than Ametek 1.

- MCM 1 reaches its peak value at line record 3377 (reading 67.17 ppmV).

- Ametek 1 reaches its peak value at line record 3378 (reading 47.90 ppmV).

- MCM 1 reaches the peak value two minutes before Ametek 1.

- Even at the beginning of the trial, MCM 1 displays significantly greater sensitivity than Ametek 1. This gap increases throughout the duration of the tests.

- MCM 1 recorded a moisture excursion of 45.87 ppmV (67.17-21.30 ppmV).

- Ametek 1 recorded a moisture excursion of 29.60 ppmV (47.90-18.30 ppmV).

4.2)   Stability

The short-term stability of MCM's Silicon Sensor can be observed in Appendix 10.6, pp49-53 – *MCM MicroView Hygrometer – Test Graphs & Supporting Letter*. Long-term stability data is provided by Brunei LNG, who have been monitoring "dry" gas with the same heated Silicon Sensor technology (calibrated over the same operating range as the instrumentation used in the St Fergus trials), for over six months under controlled laboratory conditions. Stability is recorded to be within 0.1 ppmV.

4.3)   Repeatability

The repeatability of both types of technology can be seen in the results of the initial tests at SGSI (see Section 4.1.1, p7) and in the test runs at St Fergus (see Section 4.1.2, p8 and Appendix 10.4, pp39-46 – *Test Run on Vessel C, Module 2*).

4.4)   Automatic Zero Correction

Throughout the test runs at St Fergus the automated zero correction (Auto-Zero) features on the MCM systems were configured to activate once every 7 days, for a period of 12 hours. This established a stable "dry" datum point, using an internal desiccant dryer installed on each system.

The Auto-Zero was designed to activate automatically on power recovery in the event of a power failure. Such an event was observed on the 18.12.2008 when a plant power failure occurred. The system worked correctly and initiated an Auto-Zero sequence, during which the last recorded output signal was "locked" until the process was complete. Upon completion of the Auto-Zero sequence the output signal was "unlocked" and the corrected value was seen to be displayed.

The Auto-Zero feature could also be initiated on demand, by interrupting power to the analyser as required. When the system returned from the Auto-Zero sequence it was quick to stabilise – records show a settling time of within four minutes.

The Auto-Zero feature therefore provides an automated and periodic validation, with automatic correction against a generated "dry" gas that can be readily manufactured on location.

5) End of Trial Validations

In order to verify the accuracy of all the analysers under test, a series of validations were performed immediately upon completion of the trials. This was done by cross comparison against a freshly calibrated portable hygrometer, with known uncertainties, which was placed in line with the MCM "stand alone" unit and the Ametek Oscillating Crystal analysers.

By changing the inlet sample lines, all analysers were assessed "in situ" against the calibrated portable hygrometer, using the same (conditioned) sample lines. Validation was witnessed by all parties. Once validation was completed, the portable hygrometer was sealed and returned to the calibration laboratory for revalidation against prime moisture generators, in order to establish if any shift in calibration had occurred.

Trial results clearly demonstrated that both the Oscillating Crystal and heated Silicon Sensor systems tracked moisture changes quickly and precisely.

The final validation results showed that the heated Silicon Sensor technology fell within 1 ppmV of true values when compared with the Oscillating Crystal analyser, which fell within 6 ppmV.

In comparison, data showed that the Aluminium Oxide instrument was somewhat insensitive. Validated data showed a true reading of 15 ppmV, versus 5 ppmV as displayed by the Aluminium Oxide instrument. It was concluded that the Aluminium Oxide probes had degraded over time, resulting in a loss of sensitivity. This conclusion is supported by independently published reports (see Reference 9.2, pp21-26; Saburo Hasegawa, National Bureau of Standards – *Performance Characteristics of a Thin-Film Aluminium Oxide Humidity Sensor*).

Absolute accuracy is critical in calculating the predicted lifetime of the mol sieve, and even a discrepancy of a few ppmV in moisture readings can have a serious influence.

For example, on a typical inlet gas with water content value of 33 ppmV, any analyser displaying just 1 ppmV dryer than true will over-predict the mol sieve change out time by 3% – consequently, a difference of 10 ppmV would equate to a 30% error in calculating the change out schedule.

In gas plants with an unsaturated inlet feed, inaccurate monitoring of the feed value leads to an increased risk of having to change out of the mol sieve inventory on an unscheduled basis, and therefore there is less chance of that change out coinciding with a planned shut down.

6) Observations

MCM's heated Silicon Sensor technology was demonstrated to be:

- Convenient to use, with minimal user intervention.

- Capable of automatically re-zeroing (Auto-Zero) in the event of power interruption. This feature could be inconvenient if the Auto-Zero process occurred during a water breakthrough. Consequently, a dual sensor system, in which sensors operate Auto-Zero "out of phase", would overcome this problem and both increase reliability and extend uptime.

- Flow independent, enabling sample system integrity to be checked on demand.

- Easily validated in the field, with minimal interruption (as the "stand alone" unit did not need to be powered down in order to work on it).

- Readily maintained, as dryers and components could be quickly changed (if needed) without the need to power down.

- Simple to upgrade. The systems could be upgraded from a simple transmitter configuration to a "stand alone" system, depending on the level of sophistication and / or level of safety required by each application.

7) Summary

7.1) Summary of Performance Tests

- The heated Silicon Sensor technology is fast responding (see Appendix 10.6, pp49-53 – *MCM MicroView Hygrometer – Test Graphs & Supporting Letter*)

- Under controlled conditions at SGSI, reproducibility of the MCM heated Silicon Sensor was demonstrated to be better than that of the Oscillating Crystal instrumentation (see Appendix 10.2, pp36-37 –*Initial Validation Data by SGSI*).

- Under controlled conditions at SGSI (and as recorded during subsequent test runs), the sensitivity of MCM's heated Silicon Sensor is greater than that of the Oscillating Crystal technology (see Appendix 10.4, pp39-46 – *Test Run on Vessel C, Module 2*.

- The absolute accuracy of MCM's heated Silicon Sensor is better than that of the Oscillating Crystal, as assessed at the end of all three test runs.

7.2) Summary of MCM Instrumentation

A picture of the MAC unit used by SGSI is shown in Figure 3 (p13), just prior to installation of MCM's heated Silicon Sensor Auto-Zero System.

The transmitter used in the Auro-Zero System is a compact device (housing electronics and the instrument's sensor) which can be configured to perform additional functions. In this particular case the transmitter was configured to automatically re-zero itself (Auto-Zero) against an internal "dry" gas. The "dry" gas was generated by a mol sieve desiccant dryer, which was mounted immediately behind the transmitter.

The construction shown was customised to fit into the MAC enclosure as a standard 19" diameter rack mounted system. As the MAC is a positive pressure purged cabinet, the MCM unit was not required to be certified intrinsically safe (however, if powered through appropriate Zener Barriers it is certified as Eex ia IIC T4).

The "stand alone" unit supplied by MCM used the same type of transmitter, but this system was built as an intrinsically safe unit, incorporating its own safe power supplies and sample system.

Figure 3 - The mobile analyser cabinet (MAC) used for water capacity test runs, with the MCM Auto-Zero transmitter unit prior to its installation (*Note the MAC's PTFE sample inlets*).
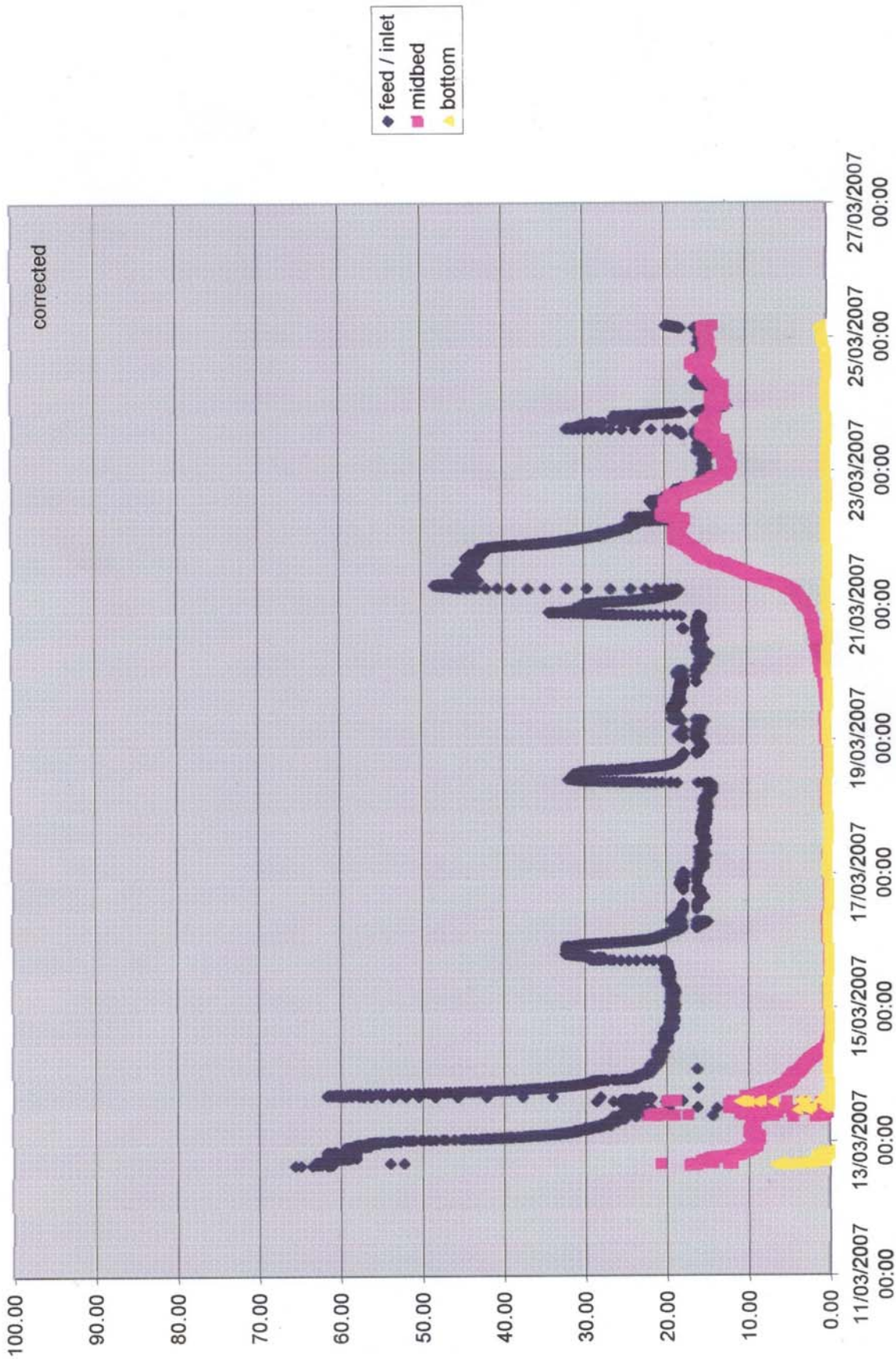
Figure 4 – Historic data collected during a performance test run of the dehydration unit at St Fergus

Notes:

- During a typical test run, the adsorption time is extended and the profile of water concentration at the mid-bed and bottom-bed probes is measured, as shown in Figure 2.

- The test run is usually terminated before a full breakthrough curve develops at the bottom probe, due to the water specification of the outlet stream.

8)   Conclusions

Logically, the operational lifetime of a dehydration unit can be predicted most accurately by adopting moisture monitoring technologies, which have the greatest accuracy and responsiveness. Regular performance test runs allow the dynamic capacity of the mol sieve bed to be calculated. By ascertaining the capacity of the mol sieve with greater accuracy, the inventory can be replaced during a planned shut down rather than through unplanned intervention. This saves the cost of lost production, whilst maximising the utility of the current inventory of mol sieve.

The use of moisture analysis systems such as the heated Silicon Sensor type, which can easily be validated in the field and that offer greater levels of response and accuracy, result in significant savings over slower, less accurate systems by means of providing production plants with more reliable moisture analysis data.

The ability of these Silicon Sensor hygrometers to respond quickly and with minimal hysteresis would make them suitable for monitoring both inlet and outlet conditions, reliably and with minimal intervention.

The adaptability of design, demonstrated by the vendor presenting two identical instruments configured for different safety ratings, means minimal loss of investment when upgrading equipment (for example upgrading a simple transmitter into an Auto-Zero system).

9) References

9.1) T.K. Mehrhoff, General Electric Company – *Comparison of Moisture Analysers at Concentrations 1 to 15 ppm*

9.2) Saburo Hasegawa, National Bureau of Standards – *Performance Characteristics of a Thin-Film Aluminium Oxide Humidity Sensor*

9.3) SEIC Terms of Reference (Rev 1 – March 13th, 2008)

9.4) Design and Engineering Practice Document DEP 32.31.50.12-GEN – *On-Line Process Stream Analysis – Analysers*

9.5) Summary of Shell Experiences with Aluminium Oxide Moisture Sensors

Comparison of continuous moisture monitors in the range 1 to 15 ppm

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Electrolytic, chilled mirror, and aluminum oxide dielectric hygrometers were evaluated by exposing them to known moisture levels in gaseous argon. The experiments were performed over a period of several months to determine the long-term hysteresis effects which may occur under continuous operation in the range of 1 to 15 ppm (parts per million). Air exposure effects were also examined. The results indicated hysteresis and drift problems in the case of the aluminum oxide dielectric hygrometers. The electrolytic hygrometer required a "recovery" period following exposure to high moisture levels. The chilled mirror hygrometer (with certain specified modifications) proved to be the most accurate and responsive in the 1- to 15-ppm test range.

INTRODUCTION

Frequently, industrial process gases used in the manufacture of semiconductors and other sensitive electronic devices are required to be free of moisture, often to as low as a few parts per million (ppm). Low moisture level working areas are typically created by circulating an inert gas such as argon through a tightly sealed glove box through one or more gas purifiers. Construction of an inert atmosphere dry box has been described by Pack and Libowitz.[1] Every precaution must be taken to ensure that moisture entering the glove box is minimized. Low permeability elastomers (such as butyl rubber) are used in the construction of the gloves. Moisture hygrometers monitor the level of moisture to assure that the purifier is working properly and that materials introduced into the glove box do not significantly degrade the dry environment. At our facility, moisture monitors are calibrated at six-month intervals; but what occurs during the period between calibrations? Do the monitors read properly, or do they drift up or down? This report compares the performance of three different types of moisture monitoring devices in the range of 1 to 15 ppm. Experiments were conducted over periods of several months to monitor the long-term drift and hysteresis effects.

I. BACKGROUND

Moisture monitoring methods have been reviewed by Long.[2] For low-ppm levels, the most popular commercially available moisture monitors are electrolytic cells,[3-5] dielectrics of aluminum oxide,[6,7] and chilled mirror types.[2] A brief description of these three types is given below.

The electrolytic cell hygrometers consist of precious metal electrodes coated with a moisture absorbing desiccant (usually phosphorous pentoxide). The electrodes are typically wound in a spiral on the inner circumference of a small diameter glass tube through which the gas sample is passed at a known flow rate. The current in amperes (I_w) required to dissociate the absorbed water is related to the molar concentration of moisture (C_w) in the flowing gas stream by application of Faraday's law in Eq. (1)

$$I_w = 2C_w R_s F. \qquad (1)$$

where R_s is the flow rate through the electrolytic cell in mol/s and F is Faraday's constant $= 9.65 \times 10^4$ C/mol. A factor of 2 is required since two electrons are transferred for each molecule of water dissociated.

Aluminum oxide moisture monitors consist of an aluminum substrate which has been anodized to form a thin porous layer of aluminum oxide. A conductive metal coating is applied over the aluminum oxide, forming a capacitive element. The quantity of moisture within the porous aluminum oxide structure affects the impedance of the capacitor formed. This impedance is measured by the electronic readout section of the monitor and correlated with the moisture content of the surrounding gas to establish a calibration curve.

Chilled mirror moisture monitors consist of a reflective surface to which a platinum resistance thermometer is attached. Also in intimate contact with the mirror is a thermopile stack used to heat or cool the mirror as required. The sample gas is passed over the mirror while a phototransistor monitors the light reflected off the mirror from a light emitting diode. The mirror is chilled by the thermoelectric cooler until a decrease in reflected light, due to the formation of frost, is sensed by the phototransistor. The thermoelectric cooler then heats the mirror until the frost layer dissipates. At this point the chilling process is again initiated to reform the frost layer. Thus, the temperature of the mirror is regulated to the frost point of the sample gas by a hunting process controlled by a microprocessor in the electronic readout section of the instrument. Dew point and/or frost point can be converted to units of partial pressure using the Goff-Gratch[8] formulations.

The equation for the saturation vapor pressure (e_i, in mbars) over a planar surface of pure ice at a temperature T (in degrees Kelvin) is given below.

$$\log_{10} e_i = -9.09718(T_0/T - 1) - 3.56654 \log_{10}(T_0/T)$$
$$+ 0.876793(1 - T/T_0) + \log_{10} P_i. \qquad (2)$$

where T_0 is the ice point temperature (273.16 K) and P_i is the saturation vapor pressure of water/ice at the ice point temperature (6.1071 mbars).

Modifications to the chilled mirror hygrometer were

needed in order to reach very low frost points, i.e., -50 to -80 °C. It was necessary to chill the third stage of the thermopile stack using a super-cool 50% water, 50% antifreeze at temperatures between -10 and -15 °C. Additionally, a precooling water jacket was added to the inlet side of the sample flow line immediately before the point where the sample gas reaches the chilled mirror surface. The entire sensor unit was then insulated to minimize heat transfer from the atmosphere. A dry nitrogen flow tent was also added to the exterior to prevent formation of frost on the outer surfaces of the sensor housing.

If the chilled mirror hygrometer is operated continuously for more than four days, the indicated dew point will sometimes rise to a level slightly above that of the sample gas. This has been attributed to gradual changes in the surface texture of the frost layer and/or to contamination, and can be overcome by turning the hygrometer off and then on again, causing the instrument to initiate an internal mirror heating cycle followed by an electronics balance cycle. This technique was used successfully in our laboratory by installing an electrical program timer in the power cord line. The timer was programmed to turn off the power for 1 h after midnight and then to turn it back on again. After installing this timer, we had no further problems with frost point drift rise.

II. EXPERIMENTAL

Four different moisture monitors were examined. Two es of aluminum oxide moisture monitors were purchased from two different manufacturers (A and B). The unit from manufacturer A was ordered with an electronic readout unit and three aluminum oxide moisture probes. The unit from manufacturer B was ordered with an electronic readout unit and two aluminum oxide moisture probes. The electrolytic moisture monitor (purchased from manufacturer C) consisted of an electronic readout unit with a self-contained, replaceable, electrolytic cell. Sample and by-pass flow meters were also attached to the readout unit. The chilled mirror moisture monitor (purchased from manufacturer D) consisted of an electronic readout unit and a remote chilled mirror sensor on a 10-ft cable. The chilled mirror moisture monitor was modified to measure very low frost points as previously described.

All four monitors were initially calibrated using a two-pressure moisture generator similar to that described by Amdur and White.[9] The monitors were calibrated at five frost point levels: approximately -74 °C (1.4 ppm), -65 °C (5.3 ppm), -60 °C (10.7 ppm), -40 °C (126 ppm), and -20 °C (1019 ppm). All four monitors met a frost point tolerance of ± 2 °C at all points.

The initial calibration procedure was as follows: The sensors were placed on a stainless-steel manifold downstream of the moisture generator, and were exposed to dry -74 °C frost point) nitrogen for a period of two to three days. The -74 °C point was then read and noted. The two-pressure generator was then set to -65 °C frost point and 8 h later this point was read. Similarly, the -60 °C frost point was read 8 h later, followed by the -40 °C frost point 4 h later, and the -20 °C frost point 4 h after that. In the cases

of the electrolytic and the chilled mirror monitors, the above data were used to verify whether the instruments were within a ± 2 °C frost point calibration tolerance. In the case of the aluminum oxide moisture monitors, the above data were used to generate a calibration curve of instrument readout units versus frost point. All five aluminum oxide probe calibration curves agreed well with factory supplied calibration curves. Where readings below -74 °C frost point were encountered, the factory calibration points were used.

Following this initial calibration, the moisture sensors were placed on a stainless-steel manifold (Fig. 1) fed by a double dilution moisture generator. The double dilution generator is capable of operating continuously over a period of two months or longer, whereas the two-pressure generator is limited to approximately 12 days of continuous operation due to the formation of crystal blockage in the ice bed region. The dilution generator was fed by high-purity dry argon which was further purified to the 0.3-ppm moisture level by a zirconium–titanium–nickel alloy getter furnace purifier. Distilled water was used in the bubbler section of the generator. The rotameters were individually calibrated at their respective operating pressures with a calibrated Bubble-O-Meter. The manifold pressure was controlled via a vent bleed valve at the exit end point. The manifold pressure was maintained at 1290 ± 10 Torr and monitored at each reading with a calibrated Bourdon gauge. Flow rates were 300 to 400 cm^3/min for all monitors. On the electrolytic moisture monitor, the sample flow rate was set to 100 cm^3/min while the by-pass flow rate was set to 300 cm^3/min.

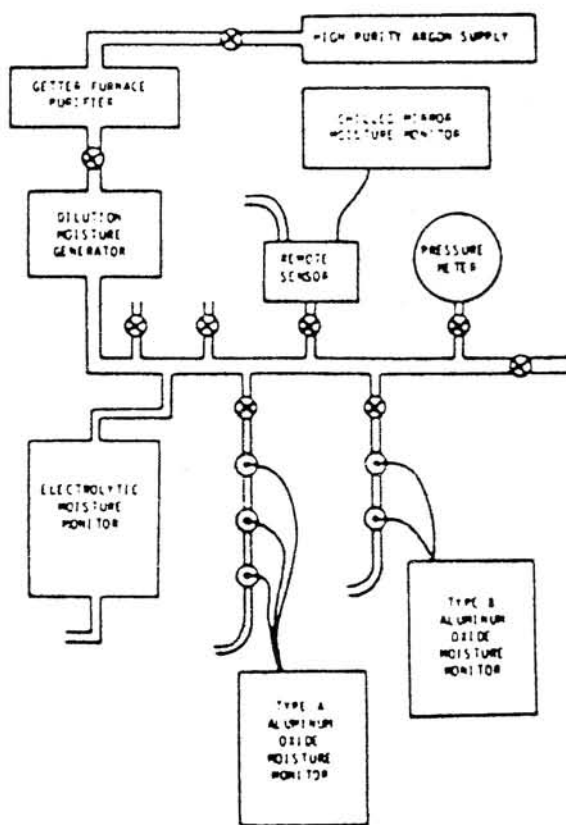Pressure for each moisture monitor sensor was ambient

FIG. 1. Manifold for evaluation of moisture monitors at the 1-20-ppm level.

... except in the case...electrolytic monitor which requires a pressurized sample. Inlet pressure for this monitor was approximately that of the manifold (1290 Torr). The aluminum oxide sensors were installed in special threaded stainless-steel (type 304) probe cells. These cells (a total of five) were connected to the main manifold as shown in Fig. 1. This arrangement of a single moisture generator feeding seven individual moisture sensors simultaneously afforded the ideal opportunity for the cross checking of monitor versus monitor and monitor versus standard.

Readings were taken at approximately 5 h intervals except near step changes of moisture level when readings were taken more frequently, and on weekends, holidays, and at night when readings were taken less frequently. A series of experiments were conducted over a time span of five months. The first experiment was to determine the response of the monitor going from a dry condition (< 1 ppm) to a more moist condition (~ 15 ppm). The dilution generator moisture level was held at less than 1 ppm for a period of three days and then raised to approximately 15 ppm in a single step change. The 15-ppm level was maintained for a period of 167 h. Figure 2 displays the readings obtained by the individual monitors (M) in parts per million divided by the reading of the standard (S) in parts per million at that same time. The ratio M/S is plotted against time in hours (time = 0 corresponds to the step change) The graph indicates that all of the monitors require at least 1 h to respond to the step change and that the readings stabilize after approximately 4 h. During the period from 20 to 167 h after the step change, all five of the aluminum oxide type sensors declined in sensitivity and, in fact, read low for the entire experiment. The chilled mirror and the electrolytic cell monitors stabilized near the standard value (M/S ≈ 1) and remained there for the duration of the experiment. The calibration tolerance of ± 2 °C frost point is also shown on the graph for reference. Please note that for purposes of clarity, overlapping data points of like symbols have been suppressed. This is also true for the second and third experiments.

The second experiment consisted of reducing the moisture level from a high 15-ppm moisture level to a low-moisture condition of 2 ppm in a single step change. The 2-ppm level was held for approximately eleven days. The results are plotted in Fig. 3. Time = 0 corresponds to the step change to 2 ppm. Monitor to standard values (M/S) are plotted against time as in the previous experiment. Within approximately four hours the chilled mirror and electrolytic cell monitors were reading within the calibration tolerance and maintained this level for the remainder of the experiment. The aluminum oxide sensors read correctly near the beginning of the experiment but drifted continually downward. At the end of the experiment (274 h after the step change), all five of the aluminum oxide sensors read well below the calibration tolerance interval. The aluminum oxide sensors from manufacturer B drifted downward more slowly than the aluminum oxide sensors form manufacturer A.

The third experiment consisted of exposing all of the moisture sensors to air for a period of two weeks. Following the air exposure all moisture sensors were returned to the system which was stabilized to 3-ppm moisture. This level

FIG. 2. Experiment 1, output of moisture monitors (M) in ppm compared to double dilution generator moisture standard (S) held at 15 ppm for 167 h starting at time zero. Moisture level below 1 ppm prior to experiment.

was maintained for a period of 53 days. Figure 4 shows the readings of the seven moisture sensors (M) divided by the reading of the standard moisture generator (S) in parts per million. Also shown is the calibration tolerance for the original calibration. The figure indicates that the aluminum oxide sensors from manufacturer A read within tolerance for the period 48 to 90 h. Prior to 48 h these sensors read high. After 90 h the sensors read low. There is an apparent long term drift of the readings which slowed down with time but did not actually stop decreasing in the 53-day period.

The aluminum oxide sensors from manufacturer B performed in a very similar manner; however, the rate of decline was decidedly slower. These sensors read within the calibra-
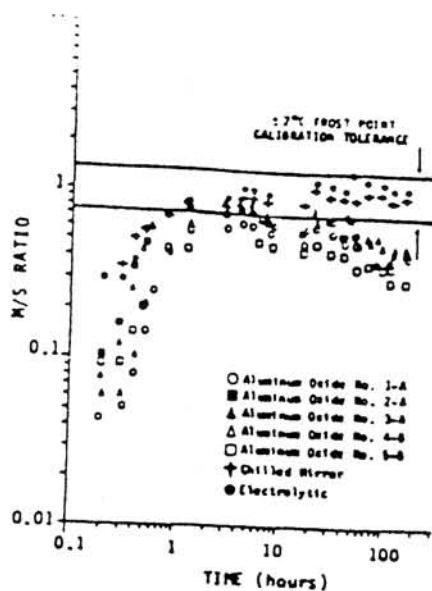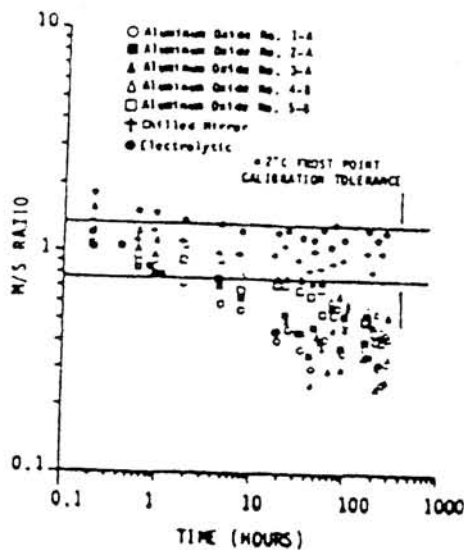

FIG. 3. Experiment 2, output of moisture monitors (M) in ppm compared to double dilution moisture standard (S) held at 2 ppm for 274 h starting at time zero. Moisture level was at 15 ppm prior to experiment.
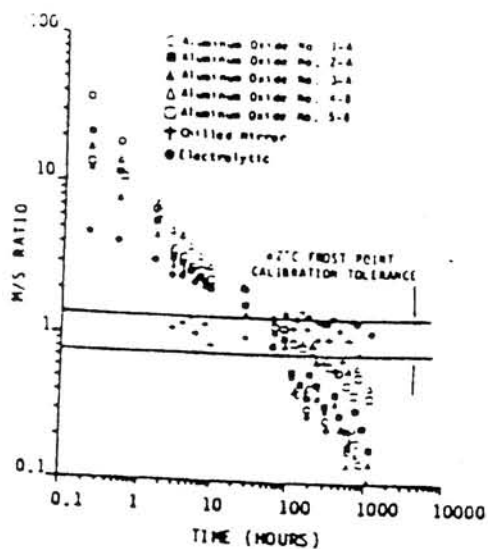
FIG. 4 Experiment 3, output of moisture monitors (M) compared to moisture in argon standard (S) held at 3 ppm for 1266 h starting at time 0. All moisture sensors were air exposed prior to the experiment.

tion tolerance for the period 65 to 210 h. Prior to 65 h the readings were high. After 210 h the readings were low.

The electrolytic sensor took approximately 80 h to recover from the air exposure, then read at or near calibration tolerance for the remainder of the experiment. The chilled mirror sensor required about 5 h to recover from the effects of air exposure, then read within or very near the tolerance for the remainder of the experiment.

III. DISCUSSION

Throughout these experiments a downward trend in the readings of the aluminum oxide sensors was apparent. Even in the first experiment where 15 ppm was approached from the low side, the aluminum oxide sensors declined in sensitivity after reaching a maximum approximately 10 to 20 h into the experiment. The third experiment indicated that this sensitivity could be restored (for a short time at least) by air exposure. This experiment, which lasted for 53 days, indicated that the downward drift for aluminum oxide sensors stored at low parts per million levels is a very significant problem for long term moisture monitoring applications. Hasegawa, in his evaluation of aluminum oxide humidity sensors,[6,7] observed hysteresis effects as well as a gradual decline in sensitivity over time. His evaluations were mainly in the range of 500 to 3000 ppm. Our evaluations in the range of 1 to 15 ppm indicate similar but more exaggerated effects in this lower ppm range.

The almost straight line decline of the aluminum oxide sensors on a logarithmic time scale indicates that the aluminum oxide sensors' rate of decline slows as time passes. If these sensors are kept in a dry atmosphere, they may eventually reach a point where their drift becomes slow enough to be tolerable. If this in fact does occur, then it may be possible to calibrate the aluminum oxide probes *in situ*, using a

chilled mirror hygrometer or some other verifiable transfer standard after the probes have stabilized. In this way the aluminum oxide sensors are never exposed to air or high-humidity conditions. A calibration system of this type using a chilled mirror hygrometer has been described by Gutierrez.[10]

The electrolytic moisture monitor provided reasonably accurate data, although it required a fairly long (~ 80 h) recovery period after being air exposed. This long recovery period is due to a residual background current which dissipates slowly. Baumann[5] has reported that a background current is frequently encountered with this type of cell, and that this background current can be compensated for most easily by determining the parts per million level at two different flow rates. For the electrolytic moisture monitor used in this study (which is calibrated for 100 cm^3/min), one would determine the readings at 100 and 200 cm^3/min and subtract the two to obtain a background corrected reading. This differential technique has been tried in our laboratory. It seems to work quite well. Our experience indicates that the time between the change in flow rate and reading the electrolytic hygrometer should be approximately 45 min. The data shown in Figs. 2, 3, and 4 were taken using the normal method of a constant 100-cm^3/s flow rather than the differential method. Had the differential method been used, the recovery period from air exposure seen in Fig. 4 would have been reduced considerably.

The modified chilled mirror moisture monitor provided accurate readings in the range tested. Its response was as good as, or better than, that of other moisture monitors tested. The chilled mirror monitor is also generally more expensive than either the electrolytic or aluminum oxide types, and the manufacturer states that the chilled mirror moisture monitor will be affected by condensable impurities in the sample gas.

ACKNOWLEDGMENTS

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PERFORMANCE CHARACTERISTICS OF A THIN-FILM
ALUMINUM OXIDE HUMIDITY SENSOR *

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Summary

A laboratory study was made of the performance of a miniature-size, thin-film aluminum oxide humidity sensor over a range of ambient temperatures from 0°C to 40°C and encompassing humidities from 40 to 78,000 parts per million by volume (ppm-v). Hysteresis and temperature effects of the sensors were obtained from tests performed at ambient temperatures 40°C, 25°C and 0°C and encompassing relative humidities from 19 to 98 percent. Information on short-term repeatability, sensitivity and storage effects was obtained from tests performed at an ambient temperature of 23°C and encompassing humidities from 40 to 6,000 ppm-v.

Introduction

There have bee numerous investigations [1-6] substantiating the deleterious effects of internal moisture on semiconductor devices. In view of the increasing number of incidents of integrated-circuit failures due to high internal water vapour content, rejection criteria are being implemented in MIL.STD.883 as Method 1018 on "Internal Water Vapour Content". Method 1018 specifies the use of a small humidity sensor within the package or the measurement of the humidity of the emitted gas on puncturing the package, with the latter measurement done primarily by mass spectrometry.

Although present efforts within the industry are leading to increased intralaboratory precision and interlaboratory correlation, there is still a great need for the development of test packages with known humidity which would be suitable for use as a transfer device for interlaboratory measurements. The development of a suitable transfer standard requires the use of a well-characterized humidity sensor, mass spectrometer and test package. This paper describes the study of a commercially available humidity sensor for possible use in the study of the behavior of water vapour inside experimental test packages.

Description of Sensor

The aluminum oxide sensor is a variable impedance device.[7-8] It consists essentially of an oxidized silicon-wafer base or substrate on top of which is a thin layer of aluminum with a porous surface of aluminum oxide. The latter is overlaid with a thin film of gold. The gold and aluminum serve as electrodes. Water vapour diffuses through the porous gold film to the oxide surface. On sorbing water vapour the oxide changes its impedance.

The sensor was attached to a TO-5 header using epoxy and air cured at room temperature. 0.0025cm (one-mil) gold wires were attached to the electrodes using an ultrasonic bonder.

Two groups of sensors were treated. The sensors designated by Series "A" were purchased in early 1979 and the "B" Series sensors were obtained from Rome Air Development Center in 1978.

The capacitance of the sensors was measured with an impedance bridge with an accuracy of 0.1 percent. A frequency of 770 Hz was used for the tests and the peak-to-peak voltage was less than 1 volt.

Test Procedure

The National Bureau of Standards two-pressure humidity generator[9] was used for these tests. Briefly, the humidity generator produces atmospheres of known humidity by saturating a gas stream at an elevated pressure and constant temperature and then expanding this gas into a test chamber which is in a separate temperature-controlled bath. The pressure in the test chamber is nominally at atmospheric pressure. The humidity of the gas in the test chamber is calculated from the measured values of the temperature and pressure in the saturator and in the test chamber. The uncertainty of the humidity of the gas produced by the generator does not exceed 0.3 percent of the value (volume ratio, ppm) over most of the range covered in this paper. The carrier gas used for these tests was air.

Seventeen sensors were tested simultaneously, nine sensors of the series "A" and eight of the series "B". To obtain general information on the operational characteristics such as shape of response curve, sensitivity, hysteresis and temperature coefficient, the first series of test was performed at ambient temperatures 25°C, 40°C and 0°C. The second series of runs was made at an ambient temperature of 23°C and at various humidities below 6000 ppm-v to obtain more detailed information on such factors as the sensor stability, storage effects, hysteresis and sensitivity. Between the first and second series of tests the sensors were baked in vacuum at a nominal absolute pressure of 0.7 Pa (5 millitorr) and a temperature of 100°C for a period of eight hours.

Each sensor was electrically connected to the measuring circuit through a selector switch and a shielded cable. Capacitance calibrations were made of the measuring circuit and used to adjust the output readings.

Results for First Series of Tests

A family of calibration curves (isotherms) is shown in Fig. 1 for sensor A5, which had a sensitivity close to the average of the sensors "A" Series and similarly in Fig. 2 for sensor B3. The output in picofarads has been plotted as a function of the logarithm of the volume ratio (parts per million by volume) for ambient temperature 40, 25 and 0°C.

The temperature coefficients for two sensors from each lot are given in Table 1. The two selected sensors are sensors which have the highest and lowest sensitivities for their respective lot. The coefficients express the percentage change in the volume ratio per degree Celsius change in ambient temperature for fixed capacitance. They can be used to estimate the error in the indicated volume ratio due to an uncertainty in, or a failure to account for, the ambient temperature. The coefficients are given for the temperature intervals 25 to 40°C and 25 to 0°C.

Fig.1 Family of Calibration Curves for a Typical 'A' Sensor

Table 1

Temperature Coefficient

Sensor	Volume ratio span	Mean temperature coefficient for temp. range 40 to 25°C 25 to 0°C (% of volume ratio per degree C)	
A1	57k to 10.2k	3.8	
A1	30k to 1.8k		5.4
A3	61k to 9.4k	4.3	
A3	29k to 1.9k		5.2
B4	40k to 6.4k	2.9	
B4	28k to 1.0k		5.4
B2	44k to 7.1k	3.7	
B2	27k to 1.5k		5.1
	average	3.7	5.3

Typical hysteresis loops at ambient temperatures 25 and 0°C are shown in fig. 3. Starting the calibration from the low humidity point of the isotherm, the volume ratio was increased in steps to the highest value and then reduced in steps to the initial point. At 40°C, the loop was not completed and therefore no hysteresis data were available. A summary of the average calibration cycle hysteresis for each sensor is given in Table 2. There is a significant difference in hysteresis between the "A" and "B" lot sensors with the "B" sensors exhibiting a larger hysteresis at both the 25 and 0°C calibrations.
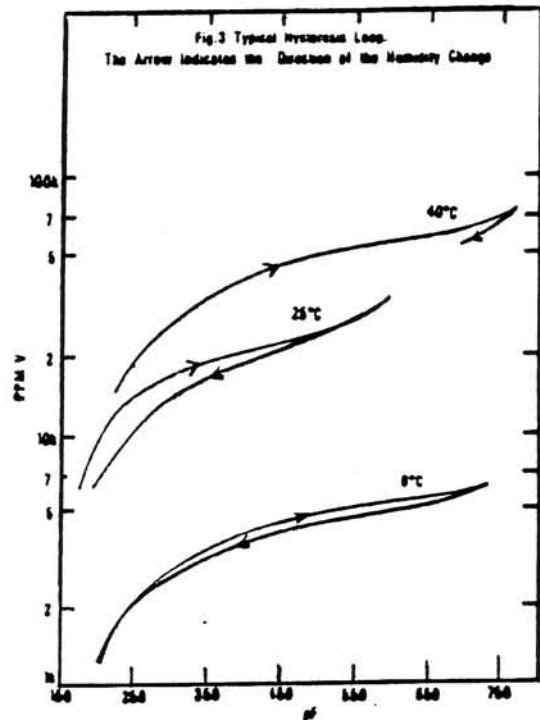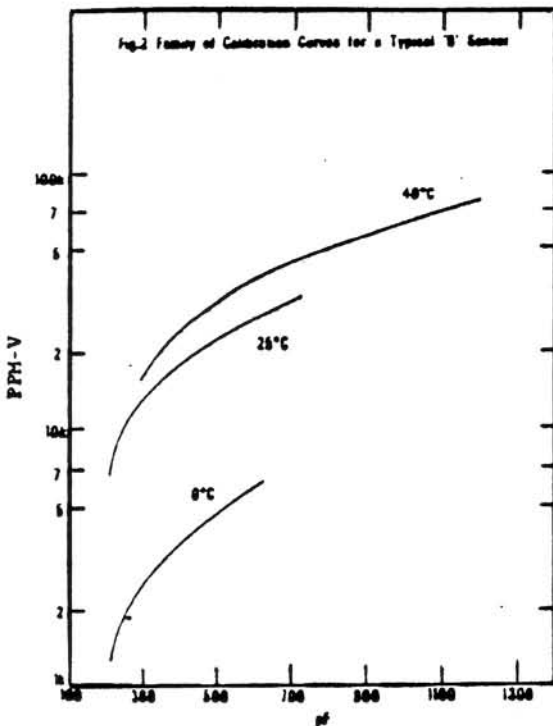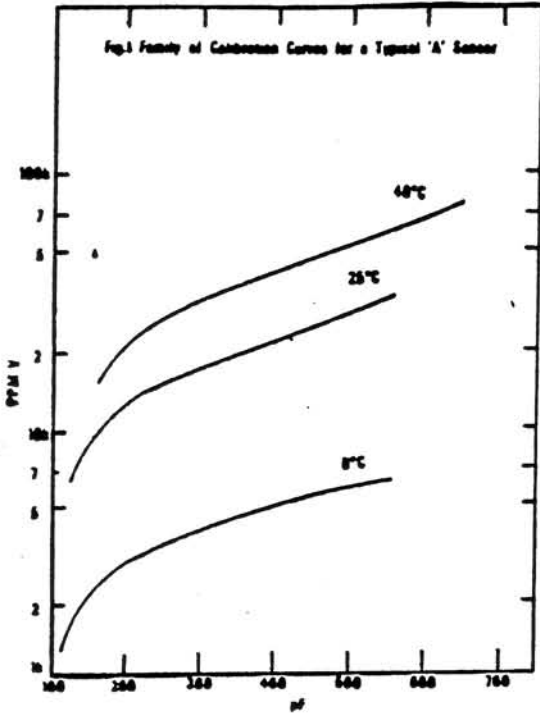

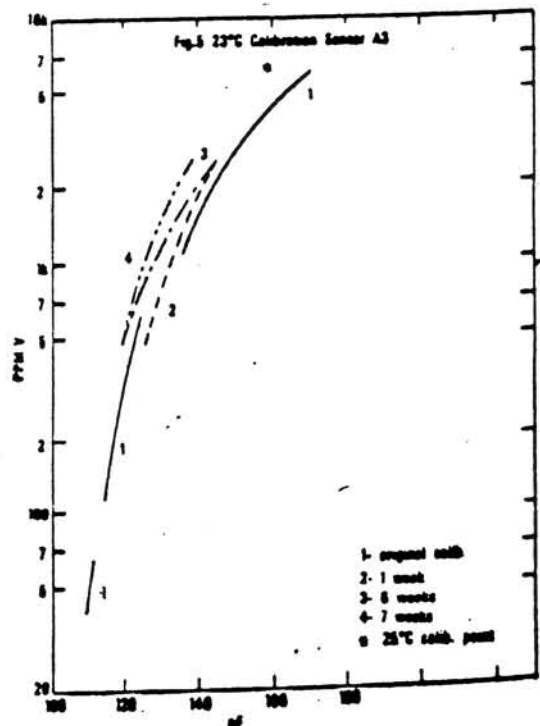Fig.2 Family of Calibration Curves for a Typical 'B' Sensor

Fig.3 Typical Hysteresis Loops.
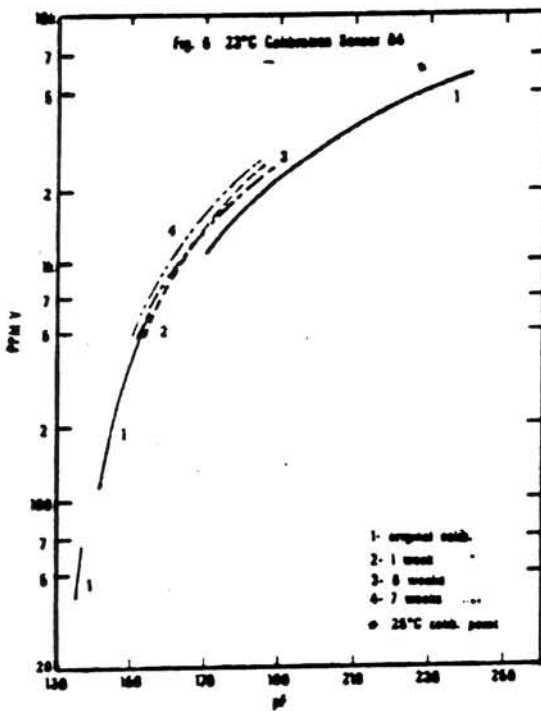The Arrow Indicates the Direction of the Humidity Change

Table 2

Average Hystersis for First Test Series

Ambient Temperature (°C)	Humidity Range (ppm-v)	Sensor Number									
		A1	A2	A3	A4	A5	A6	A7	A8	A9	Mean
		Average Hysteresis, ppm-v									
25	8000 to 30000	1600	1700	1100	600	800	700	600	800		990
0	1500 to 6000	220	240	530	400	380		410	250	400	350

		Sensor Number						
		B1	B2	B3	B4	B5	B7	B8
		Average Hysteresis, ppm-v						
25	8000 to 30000	2600	1800	3200	3700	3400	2800	3000
0	1500 to 6000	680	650	540	540	510	450	510

(Note: Mean column for B section: 25 row = 2900; 0 row = 550)

Results for Second Series of Tests

One of the factors which affect the sensitivity of a sensor is the number of available sites on which the water molecule can sorb on the surface. Since maximum sensitivity of the sensor was required for the investigation of test packages, the following procedure was used in an attempt to clean the sensor surface before beginning the second test series. The sensors were put in a vacuum chamber (approximate absolute pressure of 0.7 Pa) and baked at a temperature of 100°C for a period of 8 hours. After this bake-out procedure, the sensors were stored in air at moderate vacuum (absolute pressure of approximately 19kPa) for 3 weeks and then for 2 weeks at room humidity (not exceeding 50% RH) before starting the second series of tests.

The 23°C calibration curves for the sensors with the highest and lowest sensitivities from each of their respective lots are shown in Figs. 4-7. The "star" in Figs.4-7 indicate the 25°C calibration point of the sensor at 6000 ppm-v prior to the first bake-out. The curves labelled "1" (solid line), covering a humidity range of 40 to 6000 ppm-v, represents the initial calibration in this series of tests. Three consecutive days of testing were required to cover this range. The sensors were then stored at room humidities for one week before performing the first recalibration tests. The results for this recalibration are represented by curve "2" in Figs. 4-7.

Fig.4 23°C Calibration Sensor A1

1- original calib.
2- 1 week
3- 6 weeks
4- 7 weeks
★ 25°C calib. point

Fig.5 23°C Calibration Sensor A3

1- original calib.
2- 1 week
3- 6 weeks
4- 7 weeks
★ 25°C calib. point

Fig. 6 23°C Calibration Sensor A4

ppm v

1- original calib.
2- 1 week
3- 6 weeks
4- 7 weeks
o 23°C calib. point

ppm v

1- original calib.
2- 1 week
3- 6 weeks
4- 7 weeks
o 23°C calib. point

Fig. 7 23°C Calibration Sensor B2

After the first calibration, the sensors were again heated to 100°C under vacuum for 8 hours to determine whether the drifting of the calibration curve was due to trapped water molecules on the sensor surface. After this rebaking, the sensors were stored in dried nitrogen atmosphere for a week before performing the second recalibration. The results for this second recalibration are represented by curve "3" in Figs. 4-7.

After the second recalibration, the sensors were stored for a week in a dried nitrogen atmosphere before performing the third recalibration. The results of the third recalibration are represented by curve "4" in Figs. 4-7. The numbers of weeks of elapsed time since the original calibration for each of the recalibration runs are also listed in Figs. 4-7.

Table 3

23°C Calibration Shifts

Sensor no.	Duration of Storage		
	1 week	6 weeks	7 weeks
	(average calibration shifts, percent of the indicated humidity)		
A1	23	56	76
A3	29	32	45
B4	19	15	22
B2	26	9	20
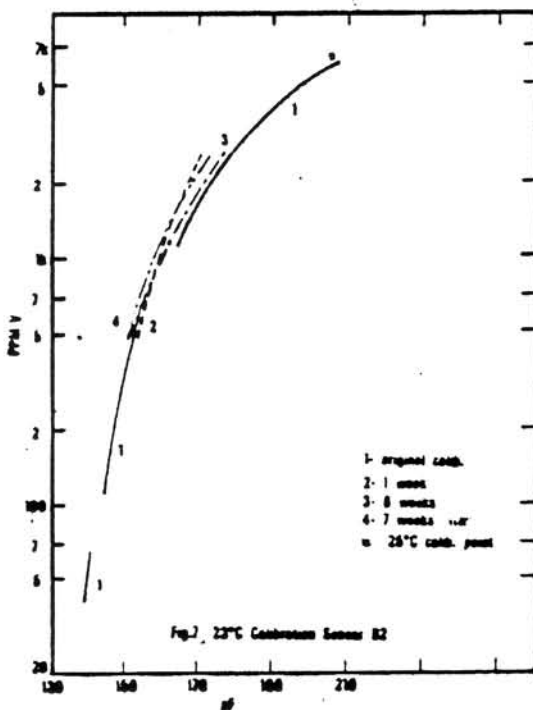
In general, the shift in the calibration was to give a lower capacitance reading for the same humidity which has the effect of indicating a lower humidity for the same capacitance reading. The average shifts in the calibration for the four sensors illustrated in Figs. 4-7 are given in Table 3. The average shifts are given in units of percentage change of the indicated volume ratio over the humidity span of 500 to 2500 ppm-v and were obtained by comparing the recalibration results with the original calibration. After storage for 1 week, there appears to be no significant difference in behavior between the two lots of sensors and the repeatability (more precisely, the lack of repeatability) is approximately 25 percent. However, after rebaking the sensors, the sensors in the "A" lot appear to have a significantly larger shift than those in the "B" lot. It should be emphasised that the values listed in Table 3 should not be used to compute the rate of shift of the sensor with duration of storage because the sensors were rebaked prior to the time when the reading listed under 6 weeks were taken. A comparison of the values listed under 1 week and the difference between the values listed under the 7 weeks and 6 weeks columns would indicate the effect of storage for a week under room humidity conditions as compared to a week storage in dried nitrogen atmosphere. The bake-out procedure did not produce a recovery of the original calibration characteristics of the sensor. The sensor shows a continual drift towards lower capacitance reading for a given humidity. Storage of the sensors in a dried nitrogen atmosphere did not stop this drifting of the calibration curve.

Table 4
Sensitivity, 23°C Calibration

Sensor	Calib. Curve	Humidity, ppm-v				
		2500	2000	1000	600	500
		Sensitivity, ppm-v / pF				
A1	Original	64	57	36	28	28
	1st recal.	59	62	47	33	29
	2nd recal.	46	50	40	29	25
	3rd recal.	52	67	56	41	36
A3	Original	145	129	81	68	66
	1st recal.	124	131	99	71	62
	2nd recal.	94	101	78	56	49
	3rd recal.	109	132	109	79	70
B2	Original	128	115	73	82	74
	1st recal.	126	144	115	83	73
	2nd recal.	96	101	77	55	48
	3rd recal.	90	111	93	68	59
B4	Original	73	66	42	48	48
	1st recal.	40	70	65	48	43
	2nd recal.	43	61	54	40	35
	3rd recal.	42	69	63	46	41

Table 4 is a compilation of the sensitivities of the four sensors illustrated in Figs. 4-7 and given in units of ppm-v / pF. The sensitivities were obtained by differentiating the calibration equations and solving the differentiated equations at capacitances corresponding to the indicated humidities. The calibration data for each sensor by means of a least squares regression to a second order polynominal. In Table 4, a smaller number indicates a more sensitive sensor. In general, the sensitivity of the sensor is increased after undergoing the bake-out procedure.

Due to the fact that these sensitivities are based on limited numbers of calibration points subject to various influences and errors, no great significance can be placed on individual values.
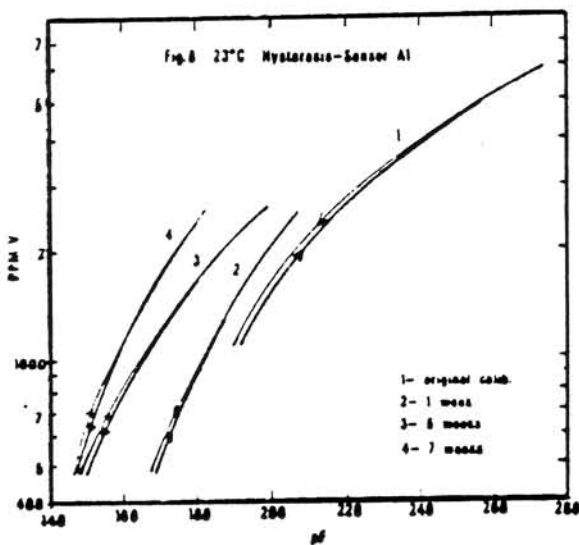
Fig. 8 shows the hysteresis loops for sensor A1 and it illustrates the type of hysteresis the sensor exhibits when the sensor is exposed to a maximum humidity of 6000 ppm-v at 23°C. A summary of the average hysteresis for each sensor is given in Table 5. The average hysteresis of the "B" sensors is approximately 50 percent smaller than the lot "A" sensors. Prior to subjecting the sensors to the bake-out procedure the sensors in the "B" lot had significantly larger hysteresis than the "A" lot sensors.

Table 5
Average Hysteresis for Original
Calibration Second Test Series

Humidity Range (ppm-v)	Sensor Number									
	A1	A2	A3	A4	A5	A6	A7	A8	A9	Mean
	Average Hysteresis, ppm-v									
1200 to 6000	130	150	160	110	100	130	180		130	130

Humidity Range (ppm-v)	Sensor Number								
	B1	B2	B3	B4	B5	B6	B7	B8	
	Average Hysteresis, ppm-v								
1200 to 6000	20	20	64	60	70	82	84	70	59

Conclusions and Discussions

The sensitivity of individual sensors varied by a factor of at least two. The variability of the sensors require individual calibration for each sensor. The sensors are also sensitive to ambient temperature and at temperatures near 25°C, the temperature coefficient is approximately 4 to 5 percent of the indicated volume ratio (ppm-v) per degree Celsius.

The sensor decreased in sensitivity with time and the procedure of baking the sensor at 100°C and under vacuum increased the sensor's sensitivity. Storing the sensor in dry nitrogen atmosphere did not stop the shift in calibration with time. The bake-out procedure reduced the hysteresis of the "B" lot sensor.

The response time characteristic was not investigated; however, it was found that the sensor took a much longer time to reach equilibrium when subjected to high humidity (40 and 25°C calibration) as compared to the conditions during the second test series. For the first test series performed at high water vapour content, the sensor exhibited a normal hysteresis curve, i.e. for a fixed humidity, the capacitance reading was larger for the descending curve than for the ascending curve. However, for the second test series, the hysteresis characteristic was reversed and the capacitance reading was larger for the ascending curve. Combined with the observations of faster response time at the low water vapour content, overall drifting of the sensor to lower capacitance and a shift in the calibration curve after an elapsed time of 1 day, it is surmised that this reversed hysteresis curve is a result of the sensor undergoing a shift in calibration after an elapsed time of less than an hour. After storage in a dry nitrogen atmosphere, the sensors still continued to drift towards lower capacitance.

Fig. 8 23°C Hysteresis-Sensor A1

1- original calib.
2- 1 week
3- 6 weeks
4- 7 weeks

However, the hysteresis curve returned to normal indicating a possible reduction in the rate of the calibration shift with storage in dry nitrogen atmosphere. Unfortunately, control sensors were not set aside during the bake-out procedure to test whether the procedure used to increase the sensor sensitivity was detrimental or beneficial for the over-all performance characteristic of the sensor.

The results of the test indicate that, although the sensitivity and hysteresis characteristics may be adequate, the drift in the calibration curve is too large for these sensors to be useful to study the behavior of water inside experimental test packages over extended time periods.

Reference

1. D.S. Peck and C.H. Zierdt, Jr., "Temperature - Humidity Acceleration of Metal-Electrolysis Failure in Semiconductor Devices", 11th Annual Proceedings Reliability Physics Symposium, April 1973.

2. H. Koelmans, "Metallization Corrosion in Silicon Devices by Moisture-Induced Electrolysis", 12th Annual Proceedings Reliability Physics Symposium, 1974.

3. A. Shumka and R.R. Piety, "Migrated-Gold Resistive Shorts in Microcircuits" 13th Annual Proceedings Reliability Physics Symposium, April 1975.

4. N. Sbar, "Bias-Humidity Performance of Encapsulated and Unencapsulated Ti-Pd-Au Thin Film conductors in an Environment Contaminated with Cl_2", Proceedings 26th Electronic Component Conference, 1976.

5. A. Der Marderosian and C.R. Murphy, "Humidity Threshold Variations for Dendrite Growth on Hybrid Substrates", 15th Annual Proceedings Reliability Physics Symposium, April 1977.

6. D. Stroehle, "On the Penetration of Gases and Water Vapour into Packages with Cavities and on Maximum Allowable Leak Rates", 15th Annual Proceedings Reliability Physics Symposium, April 1977.

7. M.G. Kovac, "A New Moisture Sensor for 'In-Situ' Monitoring of Sealed Packages", 15th Annual Proceedings Reliability Physics Symposium, 1977.

8. M.G. Kovac, "Performance Characteristics of Al_2O_3 Moisture Sensor Inside Sealed Hybrid Packages, Proceedings of the 1977 International Microelectronics Symposium, 1977.

9. S. Hasegawa and J.W. Little, "The NBS Two-Pressure Humidity Generator, Mark 2", J. Res. Nat. Bur. Stand. (U.S.), 8LA, No. 1, 81-88 (Jan.-Feb. 1977)

9.3) SEIC Terms of Reference (Rev 1 – March 13th, 2008)

TERMS OF REFERENCE
MCM moisture probes
Seek for alternatives

Revision 1 – March 13th, 2008

Purpose: On the LNG Mol sieve Bed Dryers 2 on-line moisture measurements are installed to assure no moisture breakthrough will occur and specification can be met (below 1 ppm). Historically within Shell Panametric Probes have mainly been selected to perform Dew Point measurements on Instrument Air Dryers but at several LNG sites a number of problems have been observed due to the timely response failure of these probes[1]. Correct absolute accuracy, live performance diagnostics and fast response-times are utmost important to guarantee reliable operations for the LNG production gas-industry. MCM silicon sensors have successfully been applied at several sites and so parallel tests may prove that the MCM sensors may be a promising alternative for this special application at a very low alarm setting from 0 to 0.5 ppmv which is unique for this industry.   Successful implementation of 24 units at MLNG[2] and 13 units at Sakhalin energy in Russia supports further investigation.

Justification: When the ultimate task of the installed moisture sensors can be achieved, i.e. a reliable timely early moisture break-through detection of the LNG Mol sieves dryers at the particular low moisture level it will not only offer the protection against freezing / blocking of the following refrigeration process but also the option for earlier LNG production after start-up / shut-down. Only a few hours would offer huge savings and certainly justifies additional tests to look for possible alternatives like MCM.

Scope: Sour treated natural gas, passing the mol sieve dryer beds having a moisture range usually below 1 ppm(v), at full operating pressure (50bar) and normal process temperature will be analyzed using the 3 different probes available:

- **Panametrics** (probes)
- **Ametek** (Crystal oscillation, based) located at the common outlet of the 3 molsieve dryers
- **MCM probe**
- **Portable- analysers** where available

The cross challenge will be on:

- **Accuracy**   (weight 30%)
  Using ISO6145-8 and ISO 6327

- **Response-time**   (weight 40%)
- MCM will make use of multiple diffusion cells (ISO 6145-8) which can be used to step change between different pre conditioned moisture levels to quickly assess dynamic performance changes.

Note: The MCM sensors are calibrated traceable to mass standards.
Dew Point calibrations are limited to –70°C traceable moisture standards.

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[1] GS.05.50868 Buhasa/ NLNG (20 failures out of 23)/ OP 01 300000, BLNG problems of accuracy
[2] STATUS & BEST PRACTICES AT JAN 2005 BY GSES

- To establish the reference for the applied sensor tests a 'zero' off-line measurement will be executed in advance at the QMI / Laboratory.

- Perform technical evaluation of all obtained data on Base Zero-signal and internal diagnostics

- The samples for the MCM test probes will be retrieved in parallel from the Panametrics / Ametek sample conditioning system while the existing sampling system should not be disturbed,

- All additional test equipment, cabinets, utilities should comply with the Ex zone and Safety requirements as valid for the location where they will be applied,

- Required for evaluation of in situ plant testing is the availability of trend recording, if feasible by means of standard PI- / DCS, during test-run where signal variation is expected to record dry down process and /or potential breakthrough

- Data loggers may be used as alternatives for signal recording

- Operator and QMI -assistance is required to assure that the gathered data will reliably been obtained (read-out can be trusted)

MANUAL

ON-LINE PROCESS STREAM ANALYSIS - ANALYSERS

DEP 32.31.50.12-Gen.

April 2003

DESIGN AND ENGINEERING PRACTICE

PREFACE

DEPs (Design and Engineering Practice) publications reflect the views, at the time of publication, of:

Shell Global Solutions International B.V. (Shell GSI)

and

Shell International Exploration and Production B.V. (SIEP)

and

Shell International Chemicals B.V. (SIC)

and

other Service Companies.

They are based on the experience acquired during their involvement with the design, construction, operation and maintenance of processing units and facilities, and they are supplemented with the experience of Group Operating companies. Where appropriate they are based on, or reference is made to, international, regional, national and industry standards.

The objective is to set the recommended standard for good design and engineering practice applied by Group companies operating an oil refinery, gas handling installation, chemical plant, oil and gas production facility, or any other such facility, and thereby to achieve maximum technical and economic benefit from standardization.

The information set forth in these publications is provided to users for their consideration and decision to implement. This is of particular importance where DEPs may not cover every requirement or diversity of condition at each locality. The system of DEPs is expected to be sufficiently flexible to allow individual operating companies to adapt the information set forth in DEPs to their own environment and requirements.

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All administrative queries should be directed to the DEP Administrator in Shell GSI.

2.5.8   H₂S measurement

For measurement of H_2S in ambient air, refer to DEP 32.30.20.11-Gen. For measurement of low concentration H_2S in process gas, the lead acetate paper coloration principle or PGC with flame photometric detector should be used. For higher concentrations (% range), UV spectrophotometer or PGC may be used.

2.5.9   KVP measurement

Where KVP is measured in order to obtain a correlation with RVP, an RVP analyser should be used directly.

2.5.10   Moisture measurements in gaseous products

a)   Dewpoint mirror techniques are absolute measurements. They are costly and are specifically suitable for higher moisture concentrations (0.05 % and higher). The technique shall not be used to measure water in natural gas, due to the difficulty in obtaining consistent results.

   NOTE: High hydrocarbon concentrations may interfere. Typically, the hydrocarbon dewpoint should not be higher than 10 °C above the water dewpoint.

b)   Karl-Fischer-type titration is an absolute measurement. Output shall be expressed in mg/m^3.

c)   Metal-oxide-type sensor measurements are relative measurements. The output shall be calibrated against a test gas mixture or against an absolute measurement. The output calibration is dependent on temperature and pressure. For accurate measurements the flow cell shall be kept at constant pressure and temperature. The characteristics of aluminium-oxide-type sensors are, in general, not stable and regular verification of the calibration factors is therefore required (a typical requirement is once per year, but this may vary depending on the application).

d) P_2O_5 (phosphorus pentoxide) sensors are theoretically absolute measurements. However, they shall be treated as a relative-type measurement and calibrated with a test mixture or against an absolute measurement. This analyser type shall not be used in process streams containing double-bonded hydrocarbons or those rich in hydrogen. The analyser is flow-sensitive.

e)   LiCl (lithium chloride) type sensors are applicable for Relative Humidity measurements. Their main application is in buildings, for use as a tool for climatic conditioning.

f)   Hygroscopically coated vibrating crystal-type moisture meters have the best accuracy. This type of meter should not be used for prolonged measurements of moisture concentrations in excess of 2000 cm^3/m^3.

   NOTE: At moisture concentrations in excess of 2000 cm^3/m^3, the hygroscopic layer on the crystal may be washed off.

g)   Measurement by conductivity of a hygroscopic salt-glycerol solution is fairly suitable for natural gas application as the sensor is relatively easy to rejuvenate, although this requires specialist attention.

h)   Silicon oxide type sensors are thermally stable and less hygroscopic than aluminium oxide type sensors. When equipped with a feature to momentarily heat the sensor, they burn off any hydrocarbon contaminants and 'left over' moisture from high loads, thus giving faster response and recovery. A silicon oxide type sensor is preferred to metal oxide and P_2O_5 sensors.

i)   Fibre-optic type sensors provide an in situ means of measurement and measure dew point from - 70 °C to 10 °C at pressures up to 250 bar and temperature from - 30 °C to 95 °C. It is a relative humidity measurement and converts results to ppmv, dew point.

9.5)   Summary of Shell Experiences with Aluminium Oxide Moisture Sensors

This reference cites documentation within the Shell I and E News Forum and is considered confidential.

This reference only provides an extract to demonstrate that these issues have been known and debated within Shell for some time.

A full transcript can be accessed by Shell employees by contacting GSES and GSEE News Forum, Telephone: +31(0)70 377 1833 Fax: +31(0)70 377 2004

INSTRUMENTATION and ELECTRICAL NEWS FORUM
Shell Global Solutions International B.V., The Hague

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EDITORIAL NOTE:

IENF I-1229   Dick Horst, Nigeria LNG Ltd

PANAMETRICS MOISTURE PROBE PROBLEMS

_____

Dear colleagues,

Here at NLNG - Nigeria we are faced with the following 2 problems concerning the Panametrics moisture probes that are applied for early break-through detection on the molsieve dryers and so we like to obtain experiences from other sites to see if these problems are limited to our site only.....

10) **Appendices**

10.1) Initial Calibration Data by MCM

Calibration Datasheet

Serial No.: 2375

Customer   SHELL (19"AZ) ST. FERGUS

Job No.: na

Date of Calibration: 14/11/08

Sensor No.:

Input Moisture (ppmV)	Capacitance (fF)	Input Moisture (ppmV)	Reading (ppmV)
'Dry'	82857438	'Dry'	<0.1
0.5	82904638	0.5	0.54
2.5	82989856	2.5	2.60
7.5	83250928	7.5	7.37
120.4	85194371	120.4	119.45
600.0	na	600.0	na
1000	na	1000	na
6000	na	6000	na

Date passed to Inspection   14/11/08

Signed _____

Calibration Datasheet

Serial No.:   2376

Customer   SHELL (ST, FERGUS) AZ

Job No.:   na

Date of Calibration: 14/11/08

Sensor No.:

Input Moisture (ppmV)	Capacitance (fF)	Input Moisture (ppmV)	Reading (ppmV)
'Dry'	95081547	'Dry'	<0.1
0.5	95149200	0.5	0.51
2.5	95295405	2.5	2.54
7.5	95738860	7.5	7.30
120.4	98839086	120.4	120.14
600.0	na	600.0	na
1000	na	1000	na
6000	na	6000	na

Date passed to Inspection   14/11/08

Signed   _____

10.2) Initial Validation Data by SGSI

Calibratie 12november 2008

d.d.	time	brooks (%) H2O/N2 25.7 liter	brooks (%) N2 1217 liter	liter	liter	dilution	temp bath °C	press bara	STFlash theoret. ppmV	verdund ppmV	Dewpoint theoret. ppmV	verdund ppmV
13/11/08	11:30	ref gas	Ref gas									
13/11/08	12:00	0	60	0.0	730	#DIV/0!	4.8	5.2			1572	0.0
13/11/08	16:50	10	60	2.6	730	285.1	4.8	5.2			1573	5.5
13/11/08	12:30	20	60	5.1	730	143.1	4.8	5.2			1573	11.0
13/11/08	13:30	40	60	10.3	730	72.0	4.8	5.2			1573	21.8
13/11/08	14:10	60	60	15.4	730	48.4	4.8	5.2			1573	32.5
13/11/08	14:45	80	60	20.6	730	36.5	4.8	5.2			1573	43.1
13/11/08	15:50	90	60	23.1	730	32.6	4.8	5.2			1573	48.3
13/11/08	16:15	50	60	12.9	730	57.8	4.8	5.2			1573	27.2
14/11/08	08:00	5	60	1.3	730	569.2	4.8	5.2			1573	2.8
14/11/08	09:00	10	60	2.6	730	285.1	4.8	5.2			1573	5.5
14/11/08	11:25	20	60	5.1	730	143.1	4.8	5.2			1573	11.0
14/11/08	11:40	30	60	7.7	730	95.7	4.8	5.2			1573	16.4
14/11/08	13:10	50	60	12.9	730	57.8	4.8	5.2			1573	27.2
14/11/08	15:30	70	60	18.0	730	41.6	4.8	5.2			1573	37.8
18/11/08	13:00	30	60	7.7	730	95.7	4.8	5.2			1573	16.4
18/11/08	17:00	0	60	0.0	730	0.0	4.8	5.2			1573	0.0
theoretisch												0
												60
27/11/2007	15:30	Aansluiting gemaakt met 10 liter calibratie bombe 31 ppmV H2O in CH4										31.0
		Bombe: 5702321 certifikaat geldig tot 02xx2006										
		direkt aangesloten op de MAC manifold					calibratie bombe ===>					

Ametek #1	Ametek #2	Ametek #3	MCM
0.2	0.2	0.1	n.a.
0.2	0.3	0.1	4.7*
3.6	3.5	2.6	7.3**
8.9	7.8	5.5	12.5
18.0	14.0	10.0	23.3
27	20.0	15	34.1
35.0	26.0	20.0	45.1
40.0	29.0	22.0	51.3
23.0	18.0	13.0	29.9
0.6	0.6	0.3	4.8
3.0	2.8	2.1	7.3**
8.1	6.8	5.2	12.7
13.0	10.0	8.0	18.8
22.0	17.0	13.0	30.0
31.0	23.0	17.0	41.0
12.0	10.0	8.2	17.9
0.2	0.9	0.2	4.7
0			
60			
19	23	16	

Note: The MCM reads 4.7 ppmV at the dry gas level (near 0 ppmV) because the systems were connected to water permeable PTFE sample lines, which made the dry Nitrogen gas wet on low flow. This negative bias was not detected by the Ameteks because they had corrected their zero value based on this false (wet) source. This resulted in the Ametek instruments displaying lower than true values.

Note: Compare the repeatability of the MCM when going from dry to wet and wet to dry with that of the Ameteks. It is much better!

Note: The MCM returns the same value on recovery from wet to dry as dry to wet (7.3ppmV)

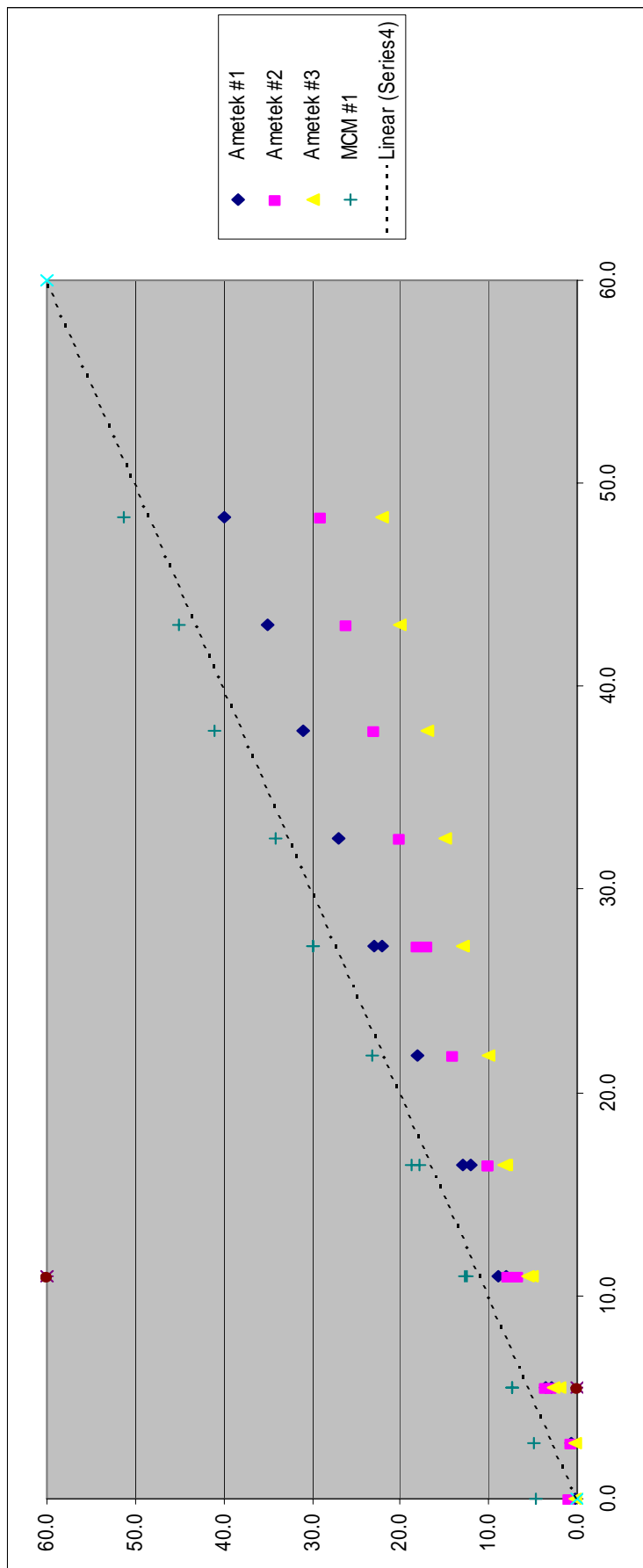Note: The poor agreement spread between all 3 Ameteks is biased to the dry and upto 15ppm lower.

Figure 5 – *Initial Validation Data by SGSI on 12.11.2008*

Note: The MCM demonstrates closer linearity with the generated moisture levels than the Ametek analysers.

10.3) Final Validation Results taken on site with a Portable Hygrometer

Recorded Monday 19.01.2009 at 13.16pm

Tests witnessed by C. Low of St Fergus and B. Manshande of SGSI.

Measurements displayed on instruments within the MAC enclosure:

Ametek Inlet	10.0 ppmV	MCM on inlet (in MAC)	21.4 ppmV
Ametek mid bed	4.3 ppmV		
Ametek outlet	<0.1 ppmV		

Validation with newly calibrated portable instrument (recorded at 14.00 Hrs)

MCM on inlet (in MAC)	21.2 ppmV
MCM Inlet (standalone)	20.4 ppmV
Ametek (inlet)	12.0 ppmV
Validation instrument	19.3 ppmV on the same gas.

On return to the laboratory, the validating portable hygrometer was assessed and found to be within 0.2 ppmV of declared values at 20 ppmV level, as recorded on the day.
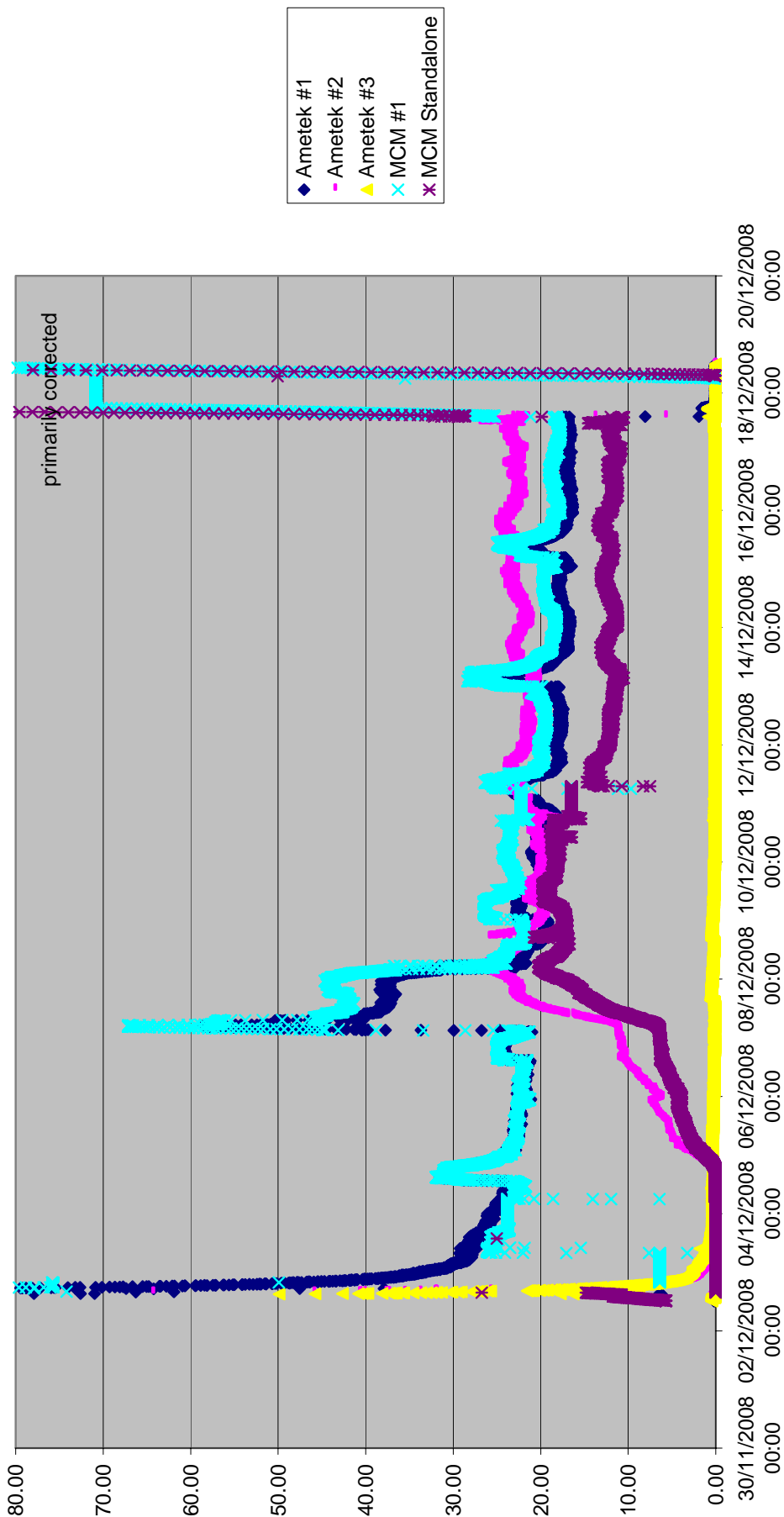
Conclusion

▪ Both of the MCM analysers read within 0.8 ppmV of each other at the 20 ppmV level.

▪ Both of the MCM analysers were validated to be within 1.9 ppmV of the reference instrument.

▪ The Ametek analyser read lower by 7.3 ppmV at the 20ppmV level.

▪ Neither of the MCM analysers demonstrated any significant degradation during the trial. However, the Ametek analyser *did* display a loss of sensitivity during the trial.
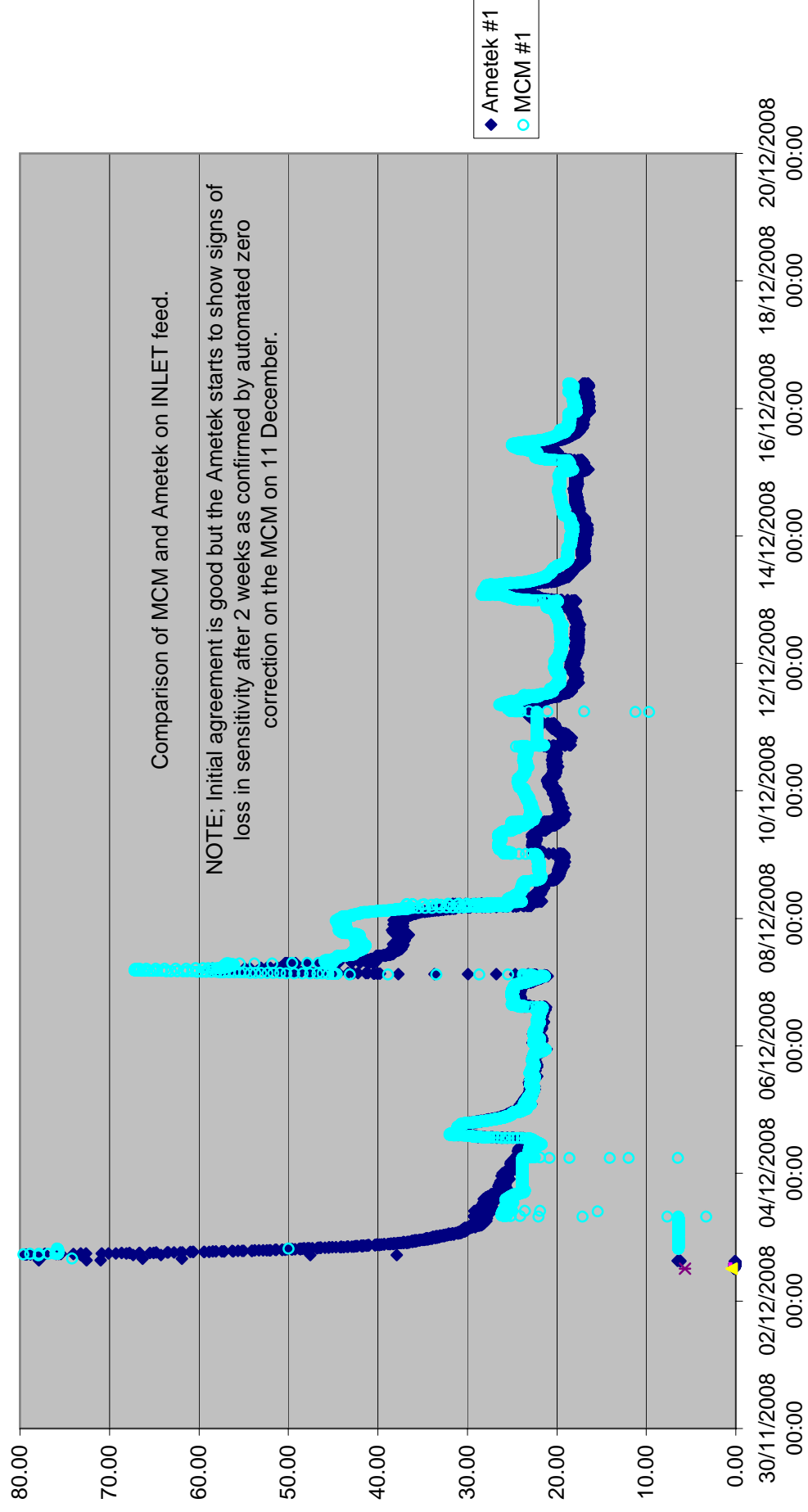
Subsequent final validation data performed at SGSI labs confirmed a loss of sensitivity in the Ametek analyser (see Appendix 10.5, pp47-48; *SGSI Final Validation Data*).

10.4) Test Run on Vessel C, Module 2 (overview graph)

**Vessel C, module 2
start 29 november 2008, 18:50 hr**

primarily corrected

Legend:
- Ametek #1
- Ametek #2
- Ametek #3
- MCM #1
- MCM Standalone

Vessel C, module 2
start 29 november 2008, 18:50 hr

Comparison of MCM and Ametek on INLET feed.

NOTE; Initial agreement is good but the Ametek starts to show signs of loss in sensitivity after 2 weeks as confirmed by automated zero correction on the MCM on 11 December.

Ametek #1
MCM #1

Vessel C, module 2
start 29 november 2008, 18:50 hr

Comparison of lower bed analysers showing possible impact of contaminants on Ametek 2.

The MCM unit automatically re zeros every 7 days and undergoes a 2.5ppm downward correction

Ametek #2
MCM Standalone

80.00
70.00
60.00
50.00
40.00
30.00
20.00
10.00
0.00

30/11/2008 02/12/2008 04/12/2008 06/12/2008 08/12/2008 10/12/2008 12/12/2008 14/12/2008 16/12/2008 18/12/2008 20/12/2008
00:00 00:00 00:00 00:00 00:00 00:00 00:00 00:00 00:00 00:00 00:00

Vessel C, module 2
start 29 november 2008, 18:50 hr

Magnification shows MCM is more precise and exhibits less noise than the oscillating crystal.

(approximately 3 x better repeatability)

Ametek #2
MCM Standalone

Vessel A, module 2
start on 17 december 2008 09:40 hr

Comparison of MCM 1 and MCM 2.

NOTE; MCM 2 does not exceed the inlet values.
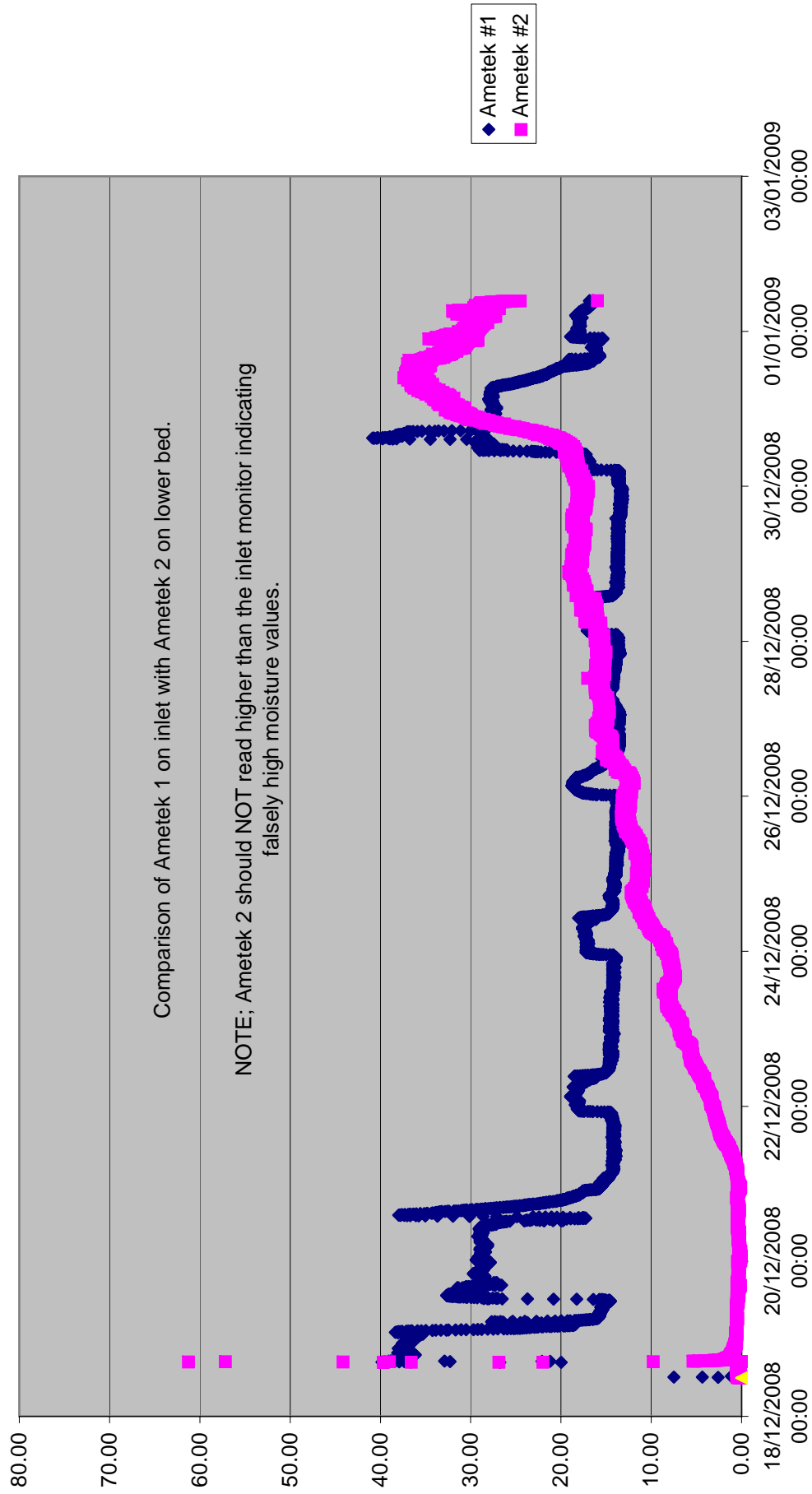
Legend:
- Ametek #1
- Ametek #2
- Ametek #3
- MCM #1
- MCM Standalone

Vessel A, module 2
start on 17 december 2008 09:40 hr

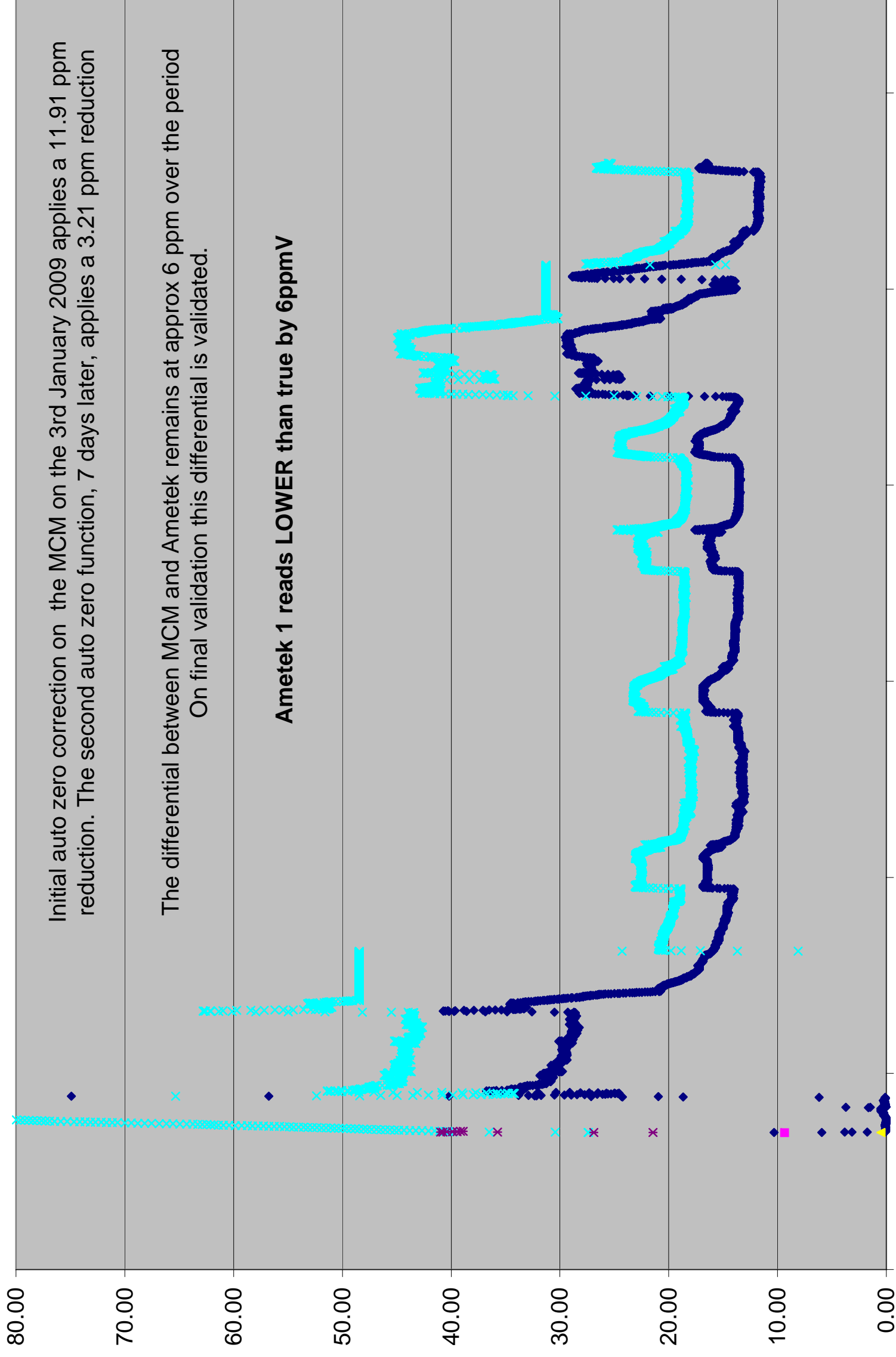Comparison of inlet analysers sensitivity (Ametek 1 v MCM 1)

MCM min to max spread 30.51ppm
Ametek min to MAX spread 20.45ppm

Ametek #1
MCM #1

Vessel A, module 2
start on 17 december 2008 09:40 hr

Comparison of Ametek 1 on inlet with Ametek 2 on lower bed.

NOTE; Ametek 2 should NOT read higher than the inlet monitor indicating
falsely high moisture values.

Ametek #1
Ametek #2

Vessel B, module 2
srtart 30 december 2008 08:44 hr

Initial auto zero correction on the MCM on the 3rd January 2009 applies a 11.91 ppm reduction. The second auto zero function, 7 days later, applies a 3.21 ppm reduction

The differential between MCM and Ametek remains at approx 6 ppm over the period
On final validation this differential is validated.

Ametek 1 reads LOWER than true by 6ppmV

Legend:
- Ametek #1
- Ametek #2
- Ametek #3
- MCM #1
- MCM Standalone

Calibratie   23 februari 2009

d.d.	time	brooks (%) H2O/N2 25.7 liter	brooks (%) N2 1217 liter	liter	liter	dilution	STFlash theoret. ppm	verdund ppm	temp bath °C	press bara	Dewpoint theoret. ppmV	verdund ppmV
23/02/09	09:00	ref gas	refgas									0
23/02/09	11:00	30	60	7.7	730	95.7			4.8	5.2	1572	16.4
23/02/09	13:00	20	60	5.1	730	143.1			4.8	5.2	1573	11.0
23/02/09	16:20	10	60	2.6	730	285.1			4.8	5.2	1573	5.5
24/02/09	10:00	40	60	10.3	730	72.0			4.8	5.2	1573	21.8
24/02/09	15:00	60	60	15.4	730	48.4			4.8	5.2	1573	32.5
24/02/09	17:00	50	60	12.9	730	57.8			4.8	5.2	1573	27.2
25/02/09	15:50	80	60	20.6	730	36.5			4.8	5.2	1573	43.1
25/02/09	16:15	90	60	23.1	730	32.6			4.8	5.2	1573	48.3
26/02/09	08:00	20	60	5.1	730	143.1			4.8	5.2	1573	11.0
theoretisch												0
												60
04/04/2009	15:30											

Ametek #1	Ametek #2	Ametek #3	MCM		Ametek #1 calibratie factor	Ametek #2 calibratie factor	Ametek #3 calibratie factor	MCM
					0.3377	0.4736	0.3550	
0.2	0.2	0.1	0.4					
5.2	7.9	5.7	14.2					
3.2	5.1	3.7	9.1					
1.1	2.1	5.5	4.4					
7.5	11.0	8.1	21.5					
11.0	15.0	11.0	32.5					
9.4	13.0	10.0	27.2					
15	20.0	15.0	44.1					
16.0	23.0	17.0	50.4					
3.9	6.0	4.4	10.0					
0								
60								
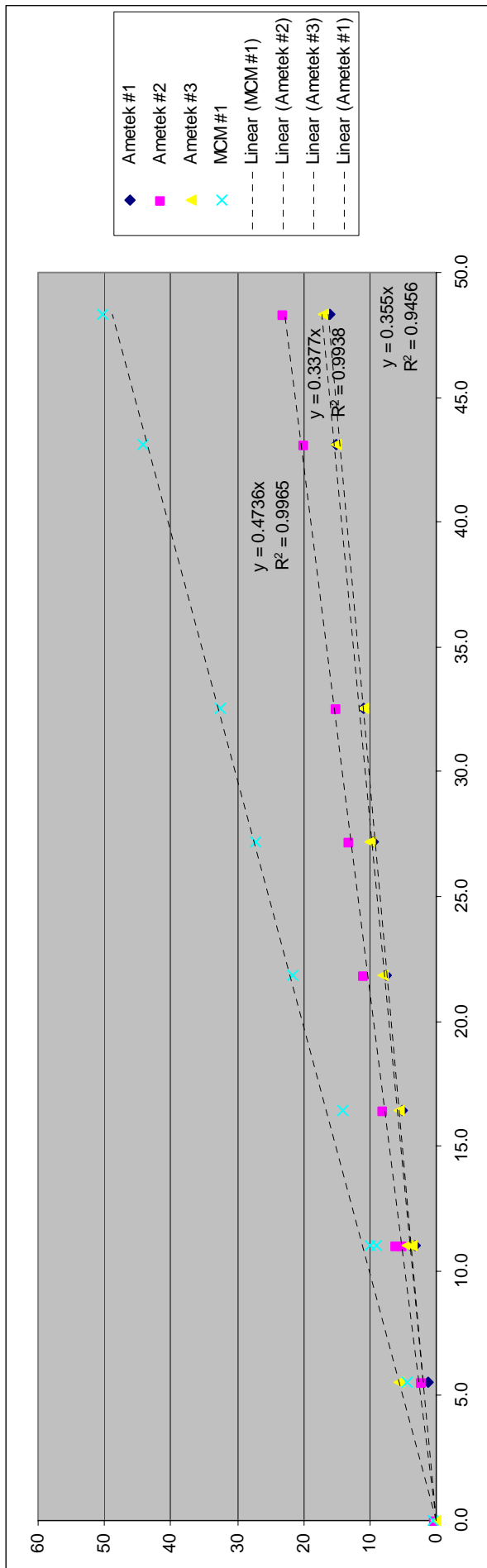
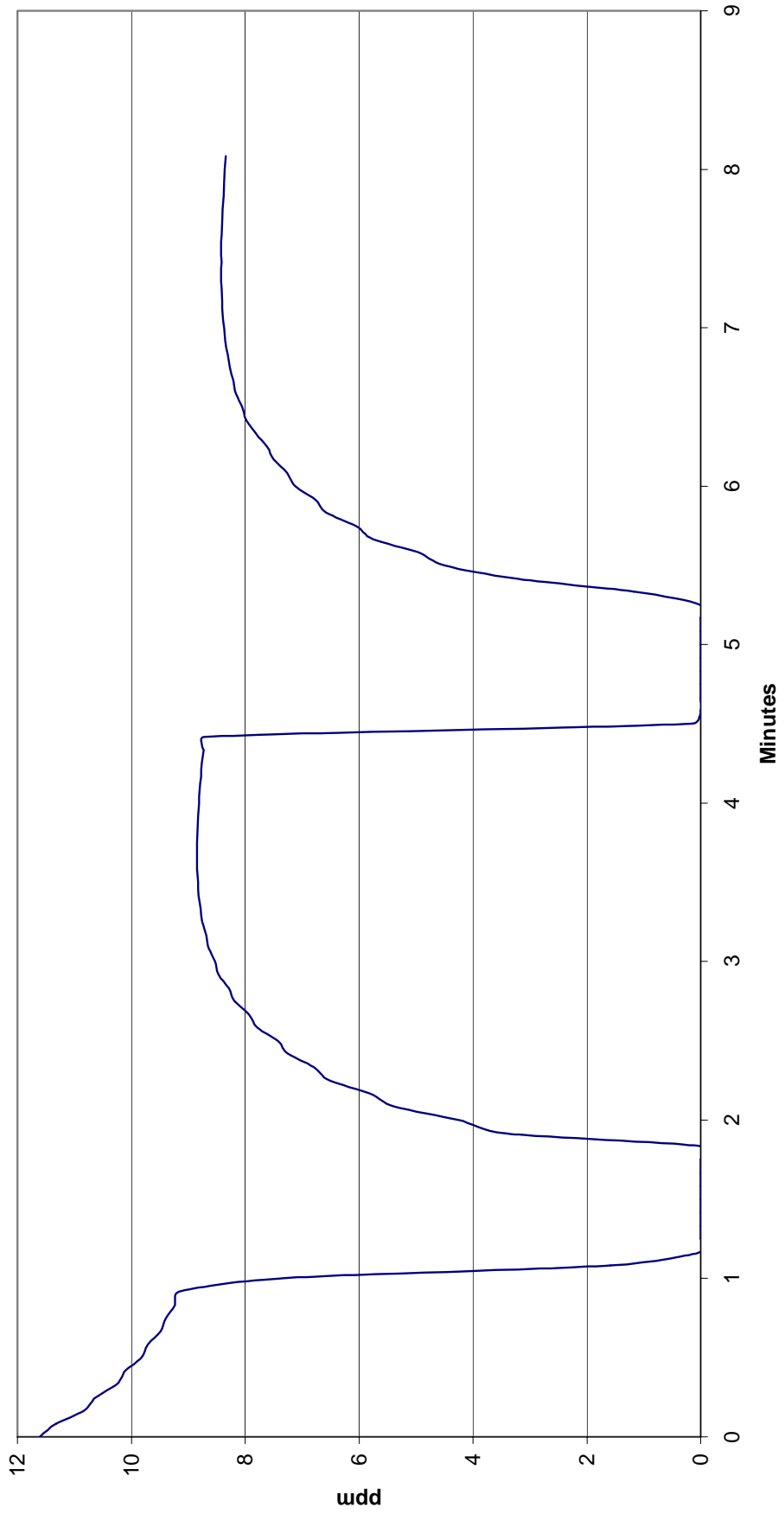Figure 6 – *SGSI Final Validation Data*

Test 1. Connecting to a cylinder from a dry start, showing time to equilibrium
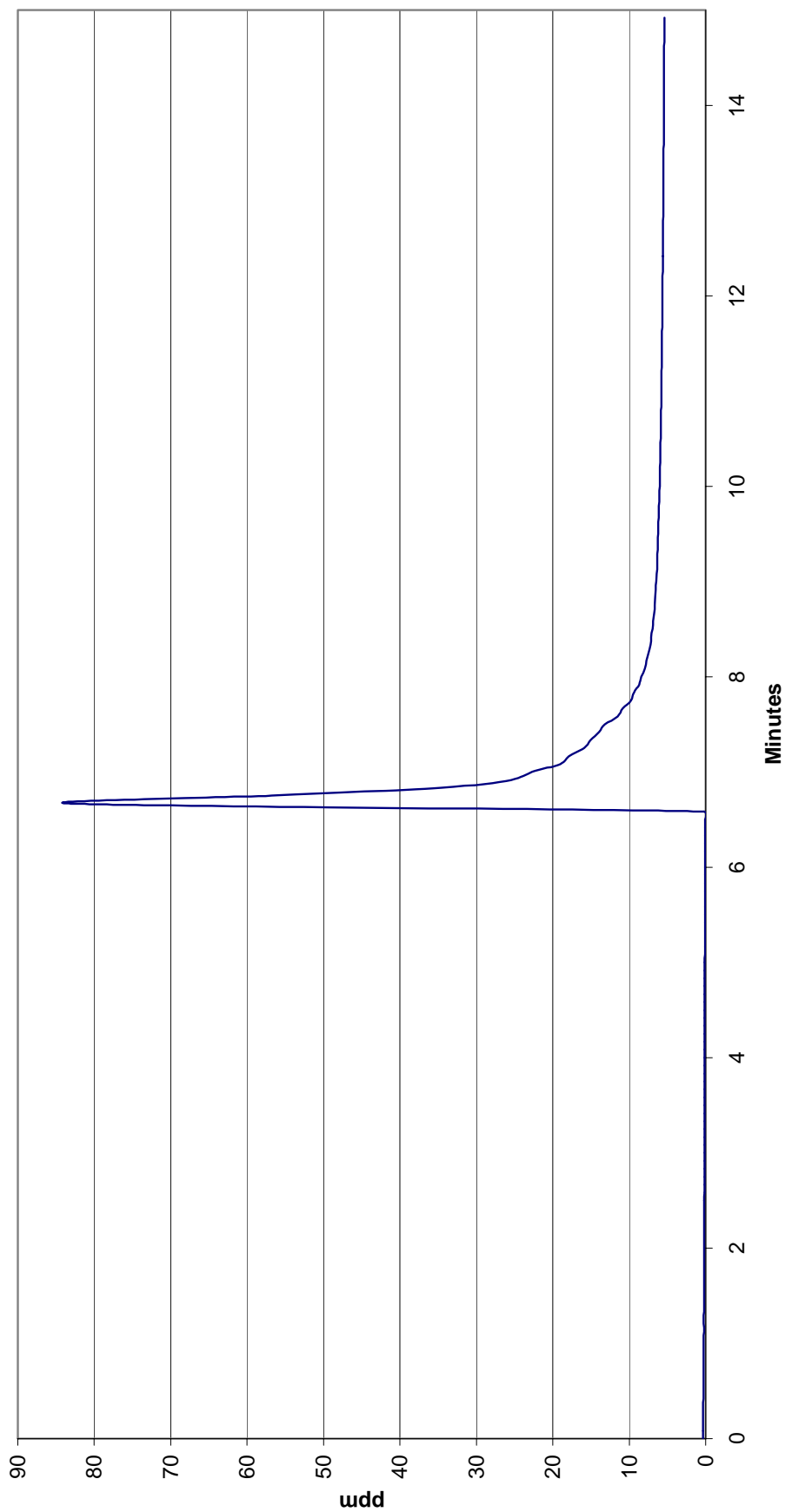
Test 2. Change from cylinder (5ppm) back to dry gas
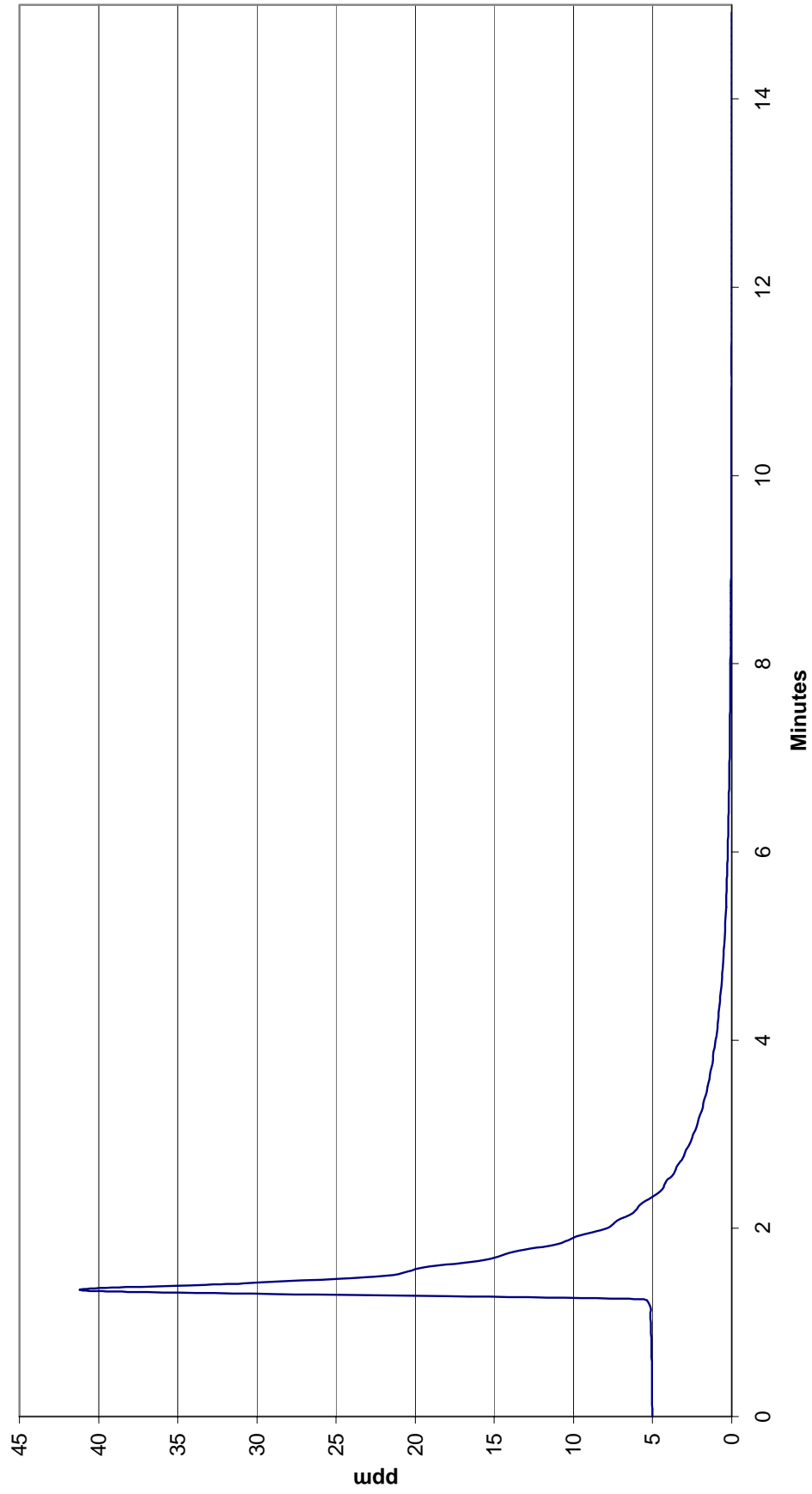
Test 3. Profile showing sensor dry down and recovery to wet (8.5 ppmV) repeating the sensor drying function to validate recovery and confirm response speed

I attach the print out of some of the logged data on the Microview for your information.

Test 1
With the analyser on dry purge gas reading less than 0.1 ppm it was connected to a cylinder and observed to settle down to equilibrium reading 5 ppm within 2 minutes.
Note the instruments sensitivity as ambient air is introduced momentarily into the analyser during changeover from cylinder line to purge gas, which the analyser detected easily.

Test 2
The same cylinder gas line at 5 ppm was then changed to a dry purge line and the instrument was allowed to reach equilibrium. It did so within 3 minutes and settled to less than 0.1 ppmV.

Test 3
This is the most indicative test of MCM's advantages.
It shows the sensor being dried down automatically to remove hysteresis and then recovered to equilibrium within 2 minutes. The process of checking the reading was then repeated by manually activating the sensor heating to 130 degrees Celsius and repeating the recovery cycle.

Observations
By comparison the MCM responds quicker and settles back to dry much faster than alternative instruments based on aluminium oxide or electrolytic sensors.

The MCM sensor drying feature removed hysteresis making the reading very reproducible.

By recovering to the same condition after disturbing the sensor temperature, the MCM technology demonstrates that no contaminants have accumulated on the sensor surface and clearly indicates if the sensor has lost any sensitivity or response speed.

Such features are of practical advantage in production because they tell operators if the readings are potentially contaminated or if the sensor has lost sensitivity, which could result in a failure to see an alarm condition, leading to a plant upset. It also provides improved quality control because potential contamination issues can be detected and appropriate action taken before the next formal recalibration period.

Summary

The MCM's typical response time is less than 3 minutes to 95% confidence in both directions, that is too say; from wet to dry, as well as dry to wet!

A typical MCM test takes 3 minutes @ a flow of 0.5 l/min which means that less than 2 litres of gas are consumed in total.

In comparison to slower technologies, which can take many hours to dry down before being ready to test, the productivity advantage and cost savings in wasted gas become obvious.

By introducing temperature control for improved stability and traceability and applying the

sensor dry down function for removing hysteresis, the MCM approach gives overall better precision and potentially longer sensor life in service.

I hope these records demonstrate how such a practical and easy to use technology offers fast reliable data that translates into improved Productivity and quality Control.

If you have any questions please do not hesitate to contact me.

Best regards

Richard Berka, MCM

10.7)   Process & Instrument Description Set-up

Three sample point connections are located at the sample probes located in the mole sieve bed (top, mid-bed and bottom). The connections are located at a T-junction just at the exit of the sample tube and will be going towards the Panametric analysers. Additional sample points are located at the feed of each dryer and at the outlet of each reactor. The common outlet of the three dryers is continuously monitored by St Fergus. The sample points of interest are schematically shown in Figure 1. The sampling systems used are described in Appendix C.

Schematic overview dryer operation St. Fergus
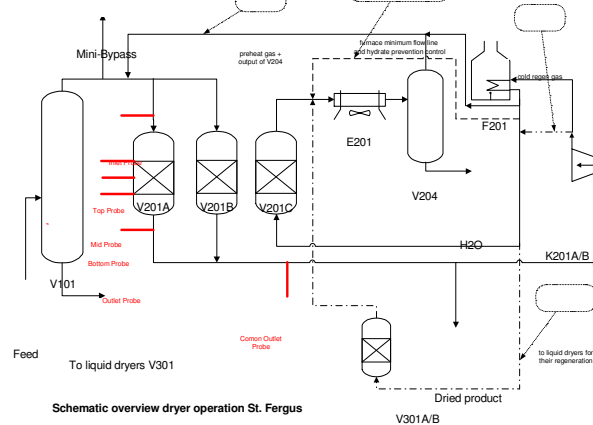
Persons present at, or involved with, the evaluation process include:

Shell St Fergus:

Kah Loong Choong

Calvin Lo

SGSI

Choon Ming Yap

Bernard Manshande

Ruud Herold

Kees Smit

MCM

Bruce Wallis

Richard Berka

Howard Stone

Witnessed and signed as a factual account of events:

For MCM:

Sign _____

Print _____

Date ____ / ____ / ____

For Shell St Fergus:

Sign _____

Print _____

Date ____ / ____ / ____

For SGSI:

Sign _____

Print _____

Date ____ / ____ / ____