EVALUATION OF MCM HYGROMETER AND VALIDATION SYSTEM DURING

START UP OF PLATFORMER 4 AT SHELL BUKOM, SINGAPORE

APRIL 2005

Evaluation of an MCM moisture analyser and validation system during start up of Platformer 4 at Shell Bukom, April 2005.

OVERVIEW

Platformer start up requires an accurate knowledge of moisture levels in order too prevent over cracking, help optimise yields and prevent early catalyst damage. The presence of chloride and other contaminants during start up often affect the water content analysers which can quickly drift out of calibration tolerance before their next scheduled recalibration. MCM claim to have a faster, more robust technology that will give more reliable data.

OBJECTIVE OF THE EVALUATION

Shell can benefit from using faster validating instruments and employing validation methods that can quantify the changes in sensitivity, in order to provide more accurate data. It was agreed to compare the existing inline Panametrics hygrometer against MCM's technology, under real start up conditions of Platformer 4. MCM were invited to Shell Bukom to begin tests during the adjustment to normal operating condition when the 'platformate was to be run down to high octane Tk', this being the most critical point of the start up process.

MCM TECHNOLOGY

The MCM hygrometer uses a heated silicon sensor that the manufacturer claims to be very fast responding* and generally less prone to the effects of such contaminants due to a feature that dries the sensor within 30 seconds. It maintains a stable elevated operating temperature, maintaining traceability to its calibration data and claims to provide a degree of resistance to volatile contaminants by virtue of the sensor drying function, called 'push purge'.

**Interestingly, Shell's engineering and Design document also states the Silicon sensor technology to be faster and preferred to aluminum oxide or electrolytic (P2O5) when using this drying feature. See reference in appendix 1.*
(Dep 32.31.50.12-Gen)

MCM's VALIDATION METHODOLOGY

In order to validate any collected data, it was proposed to establish a validation system within the laboratory using calibrated hygrometers and a moisture source running continuously in equilibrium as a control system.

The MCM Portable Hygrometer to be tested on Plant gas was to be compared periodically with the 'master' Hygrometer monitoring both a 'dry' and 'wet' reference gas.

If the test instrument recorded consistent results, in comparison to the 'master' instrument, before and after the Plant testing, then it was reasonable to assume that there has been no significant contamination effect.

VALIDATION SYSTEM SET UP

The MCM validation system consisted of a mechanism to generate two continuous streams of clean reference gas using one of a pair of dry gas molecular sieve driers as a source and passing this gas through a manifold which branched into a moisture generator to provide a wetter 'span' gas. The wet and dry lines were established and left to run continuously through a calibrated transfer standard hygrometer, without disturbing them. In this way each stream, continuously monitored by the reference hygrometer, acted as a laboratory based 'datum' against which the portable unit under test could be compared before and after each field test, for any deterioration in zero or sensitivity.

Tests on the plant were performed using an intrinsically safe portable hygrometer from MCM (serial no. 5949) which was to be validated for zero and span stability before and after each test by routinely cross checking it against the validation system reference monitor (serial no.SA5183), installed in the Bukom Laboratory.

The data collected with the portable was compared against the plant analyser readings of the Panametrics, and any deviation recorded. See Graph A.

Testing on the 'Dry' Gas Reference

The system was left overnight to reach equilibrium within the sample system. The 'master' hygrometer reading was logged as below;

4 ppm[V] on dry gas - 'Master' Hygrometer Serial No. .: SA5183

The portable MCM instrument to be tested was put in series with the 'dry' gas supply at the outlet of the 'master' hygrometer and the readings noted as being 4ppm

SENSITIVITY (Span) TEST

Whilst a reading on 'dry' gas provides some useful data, a test of the analyser's sensitivity and time to equilibrium should be performed on a routine basis in order to confirm that it is able to respond adequately to a moisture change across the operating range to confirm it has sufficient sensitivity to raise an alarm when moisture exceeds a critical level.

As it was not possible to remove the in line Panametrics hygrometer for direct validation it was suggested that the sensitivity of Bukom's existing validating instrument (the Shaw portable) could be assessed directly, as this normally is the instrument used to validate the inline Panametrics.

SPAN TEST with the MCM portable

The reading on the portable MCM was found to be 99 ppm, in agreement with the reference value of 99 ppm. See Table D.2

SPAN TEST with the SHAW portable

The Shaw portable read 8 ppm on dry gas after 10 minutes. When connected to the wet reference line stabilised at 100 ppm it settled to 16 ppm after 40 minutes, indicating a significant, 80% loss in sensitivity.

COMPARISON OF SENSITIVITY between Shaw and MCM

The Shaw was connected in series with the MCM portable in order to compare its speed of response and recovery by drawing ambient air through both analysers and then returning them both to dry gas.

The air was drawn through the Shaw and the MCM until the first instrument to respond went off scale to the wet side.

The MCM was reading 2 ppm on dry gas and responded to full scale (>1000 ppm) within 5 seconds at which point the dry gas at 2 ppm was reconnected to both instruments.

The Shaw read 6 ppm on a 2 ppm dry gas before wetting to ambient for 5 seconds. It rose up to 8 ppm by the time the dry gas was reconnected.

Subsequently the Shaw stayed at 8 ppm and the MCM recovered back to 2 ppm within 3 minutes. The Shaw was unable to reach stability within the 40 minutes of observation.

TEST – MCM Speed of Response

Initial response tests on MCM portable from 'wet' to 'dry' and then 'dry' to 'wet'.

From 99 to 4 ppm using sensor drying function, push purge took < 2minutes.
From 4 to 99 ppm took < 2 minutes.
From 99 to 4 ppm **without** push purge took 5 minutes.

MCM's claim of fast response and repeatability, even without the use of the push purge function, was readily demonstrated.

PLANT TESTS with MCM's portable hygrometer

It was agreed to leave the validation system and MCM portable analyser for the duration of Start up procedures. The MCM portable was re zeroed against the validation system prior to starting tests.

START UP PLANT TESTS - Panametrics v MCM - Graph A

During the field tests, the MCM portable hygrometers zero value was checked in the field by using one of the portable molecular sieve driers and a small nitrogen cylinder. The MCM portable was returned to the lab and checked against the validation system on both the dry gas (4ppm) and wet line (100 ppm) after each test. See graphs B and C and data in Table D.

The first validation tests confirmed a significant loss of sensitivity in the online Panametrics unit. It read 66 ppm in the sample stream against an actual value of 215 ppm on the portable, as validated by the lab system.

As the process temperature is raised when the online water reading is below 200 ppm it was of concern that the process was 'over cracking' because the decision to raise temperature had already been taken, based on the optimistically low reading of the Panametrics.

Graph A shows the difference in sensitivity between the MCM and the Panametrics throughout the trial. Note that the MCM is shown to be at least 3 times more sensitive under the same conditions of test.

VALIDATION ON SPAN GAS- Graph B

No adjustments were made to the MCM instrument until the last test of the 29th April, although in practice, for maximum precision, an adjustment could be performed after each test, if necessary, due to the fast settling time of the MCM technology.

The advantage of being able to adjust an instrument against a well defined span gas was clearly demonstrated when at one point the Panametrics and MCM were reading within 5ppm of each other. A validation check confirmed the displayed reading to be 36 ppm lower than true, highlighting the need for an adjustment. By checking zero and then applying a simple 3 ppm zero correction on the MCM, this reading rose by 21 ppm, putting the instrument within 1.5 degrees of the true value. A further span adjustment then brought it back to the correct value.

VALIDATION ON DRY GAS – Graph C

The importance of defining a stable zero point and being able to adjust an instrument against such a reference offers several practical benefits.

Without the use of a validation system and the subsequent ability to perform zero adjustment, the reading would have remained optimistically dry, as it did with the Panametrics, leading in this case, to prematurely increasing the process temperature, leading to over cracking.

Results showed that even a small correction in zero of 3 ppm lifted the span reading by 21 ppm up to 81 at the 96 ppm level. (Table E; 29.04 at 13.40)

In general, all hygrometers benefit from having their zero value checked before analysis, if they have been previously exposed to the effects of gas contaminants. It also provides an early indication of any build up of contamination and helps to quantify the effects of such contaminants.

However, in order to get best precision on the zero value the hygrometers must be allowed sufficient time to reach equilibrium.

In the case of MCM, the technology is proved to be very fast responding and able to stabilise within just a few minutes, making a zero adjustment in the field a viable proposition. For slower responding or de-sensitised instruments it can take many hours (even days) before equilibrium is established, which is impractical in a start up situation.

SUMMARY

The average speed of response to a settled value using the MCM analyser was found to be 3 minutes, whether starting from a wet or dry condition.

'The unique sensor drying feature proved particularly useful in significantly reducing sampling times and in removing some of the volatile contamination that accumulated by using the 'push purge' sensor drying feature.

It was possible to validate the MCM portable before a test, take a quick reading on plant, validate on a dry reference at the sample point, and perform a full validation in the laboratory, all within 30 minutes- a significant improvement in productivity and precision, over the existing equipment.

The portable Shaw meter was found to be both very slow and very insensitive having lost over 80 % of its sensitivity. When checked against the span gas it was reading too low, namely 20 ppm against a reference value of 101 ppm.

There was a benefit in determining the 'as found' condition of both plant and validating hygrometers - before they were to be used.

These tests confirmed MCM claim of having a faster, more stable and repeatable technology.

RECOMMENDATIONS

To review moisture testing procedures to include speed of response and sensitivity tests.

To adopt the demonstrably faster responding silicon sensor technology in conjunction with a laboratory based validation system, operating with traceability at atmospheric pressure, for future start ups.

To consider for future use, auto zeroing silicon sensor based systems that can self correct for zero shift.

Tests performed at Shell Bukom, Singapore during 27 and 28 April.

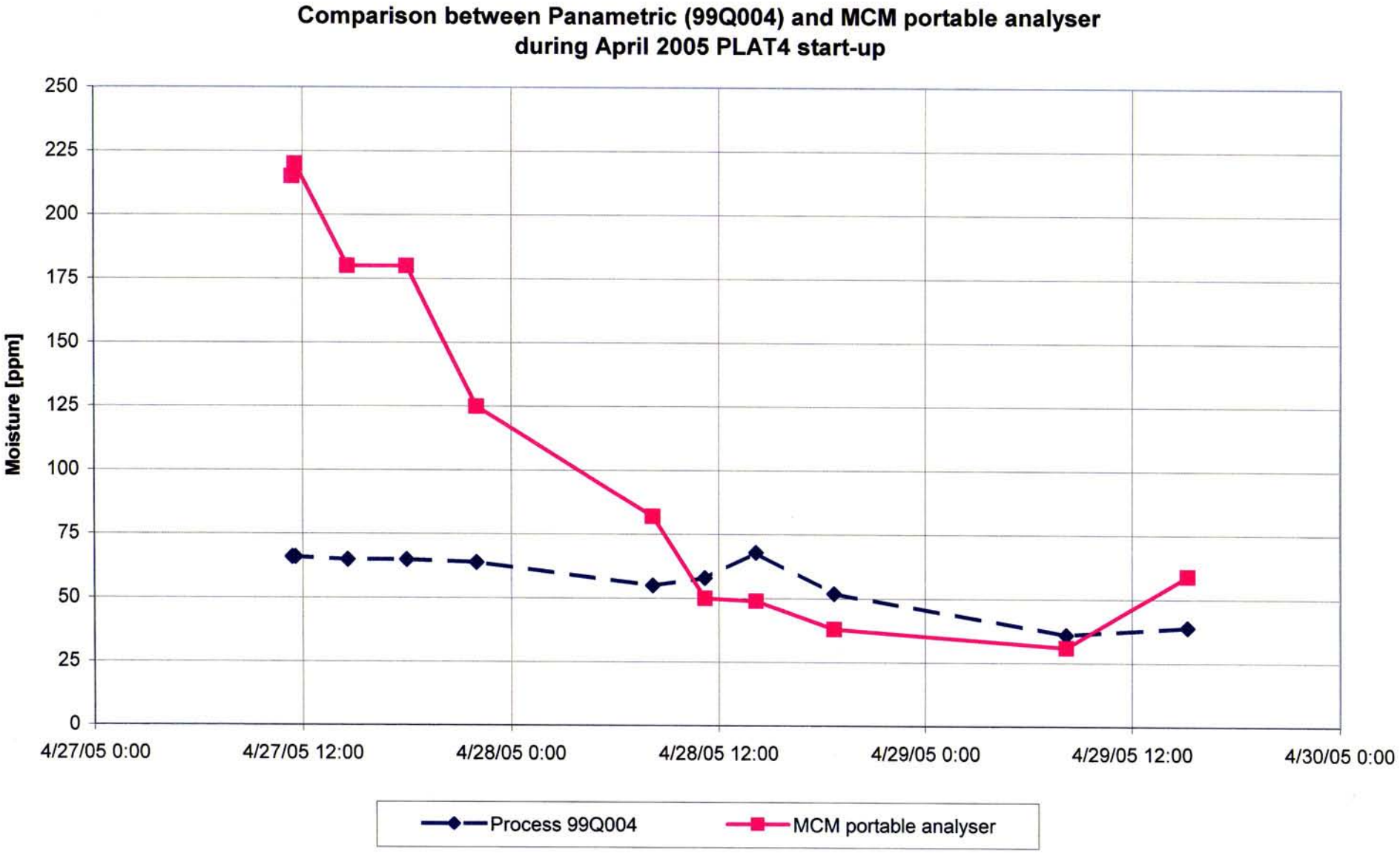
Validation and plant tests witnessed by;

Cyril Vernin	–Process Technologist, Shell Bukom
Tan Ker Kuan	
Lawrence Tang	
Patrick Leng	- QMI Engineer
Masroni	- Laboratory, Shell Bukom
R.Berka	- Export Manager MCM Ltd, UK
H.Stone	- Production Manager MCM Ltd, UK

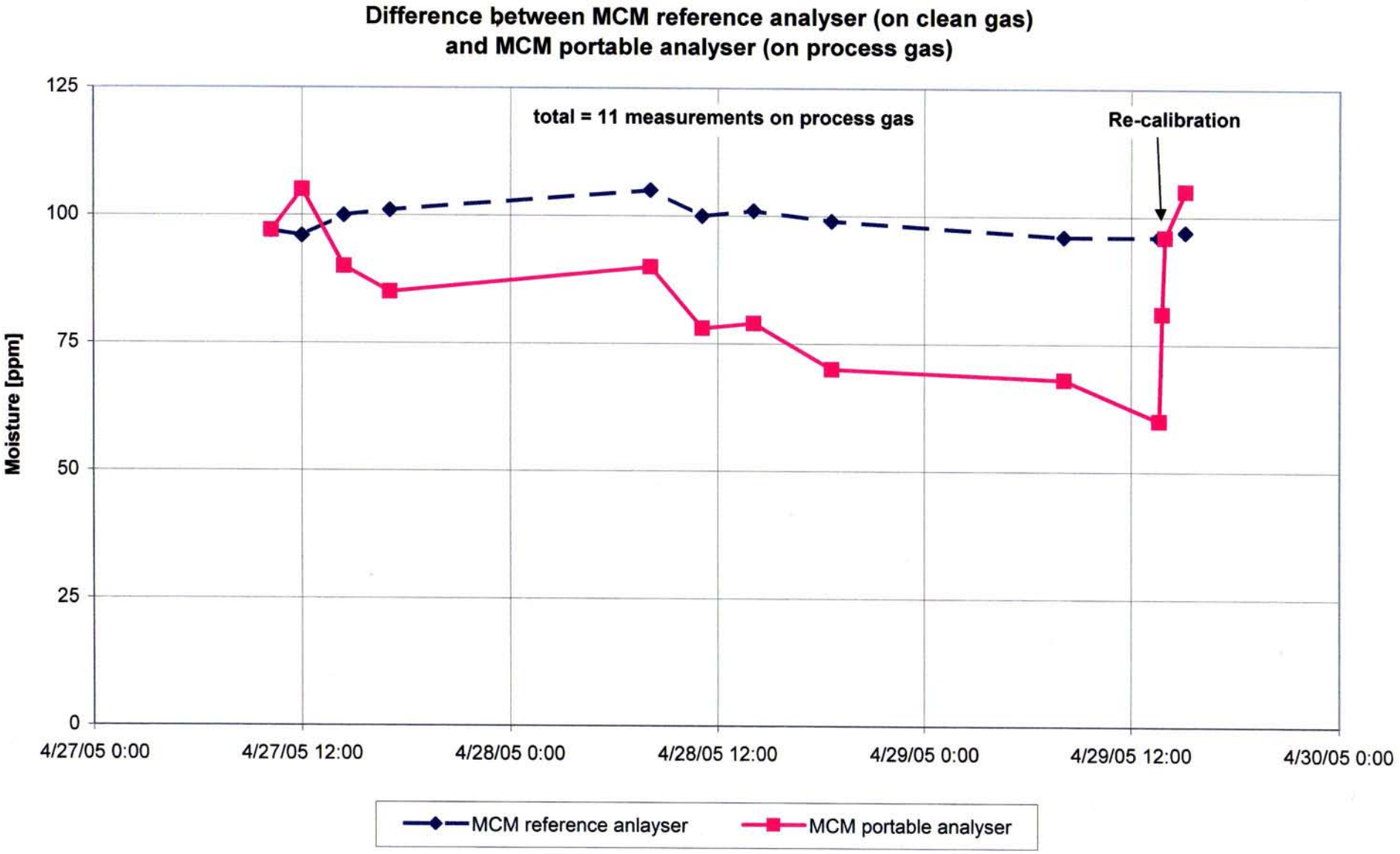
APPENDICES

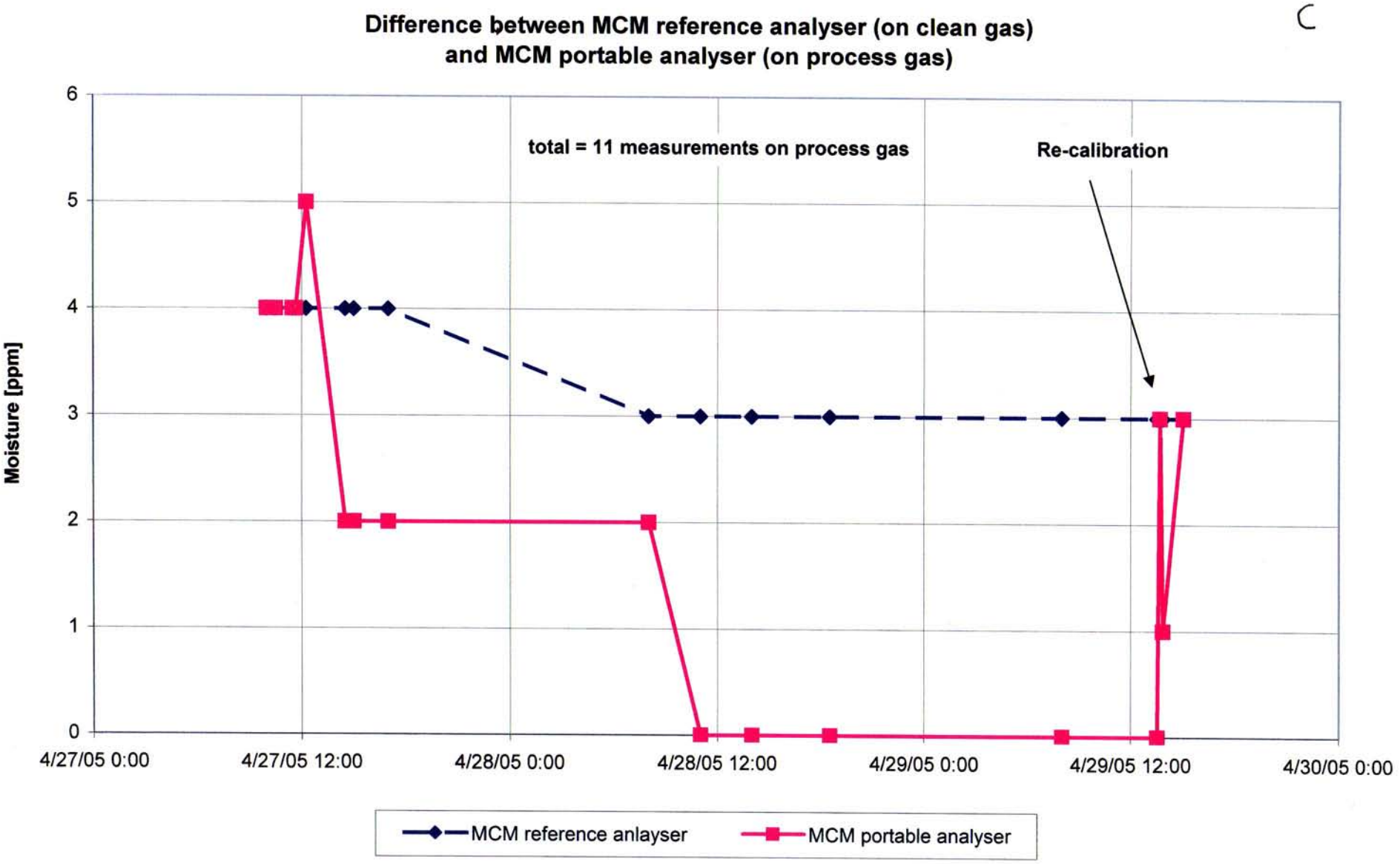
Graph A	Comparison between Panametrics and MCM portable during April 2005 PLAT 4 start up – PROCESS GAS
Graph B	Difference between MCM reference analyser (clean gas) and MCM portable (on process gas) – WET LEVEL
Graph C	Difference between MCM reference analyser (clean gas) and MCM portable (on process gas) – DRY LEVEL
Table D	MCM portable analyser testing during PLAT 4 start-up 1. Process measurement 2. Wet gas check 3. Dry gas check
Table E	Combined data set including validation data and adjustment values
F	Shell Dep 32.31.50.12- General (page 14 extract)

A


Comparison between Panametric (99Q004) and MCM portable analyser during April 2005 PLAT4 start-up
Moisture [ppm]
250
225
200
175
150
125
100
75
50
25
0
4/27/05 0:00
4/27/05 12:00
4/28/05 0:00
4/28/05 12:00
4/29/05 0:00
4/29/05 12:00
4/30/05 0:00
Process 99Q004
MCM portable analyser

B


Difference between MCM reference analyser (on clean gas)
and MCM portable analyser (on process gas)
total = 11 measurements on process gas
Re-calibration
Moisture [ppm]
125
100
75
50
25
0
4/27/05 0:00
4/27/05 12:00
4/28/05 0:00
4/28/05 12:00
4/29/05 0:00
4/29/05 12:00
4/30/05 0:00
MCM reference anlayser
MCM portable analyser


Difference between MCM reference analyser (on clean gas)
and MCM portable analyser (on process gas)
total = 11 measurements on process gas
Re-calibration
Moisture [ppm]
6
5
4
3
2
1
0
4/27/05 0:00
4/27/05 12:00
4/28/05 0:00
4/28/05 12:00
4/29/05 0:00
4/29/05 12:00
4/30/05 0:00
MCM reference anlayser
MCM portable analyser

MCM portable analyser testing during PLAT4 start-up

D

1. Process measurement

	Source	Measurement
	Process 99Q004 [ppm]	MCM portable analyser [ppm]
4/27/05 11:25	66	215
4/27/05 11:35	66	220
4/27/05 14:35	65	180
4/27/05 18:00	65	180
4/27/05 22:00	64	125
4/28/05 8:10	55	82
4/28/05 11:10	58	50
4/28/05 14:10	68	49
4/28/05 18:40	52	38
4/29/05 8:10	36	31
4/29/05 15:10	39	59

2. Wet gas check

	Source	Measurement
	MCM reference anlayser	MCM portable analyser
4/27/05 10:15	97	97
4/27/05 12:00	96	105
4/27/05 14:25	100	90
4/27/05 17:05	101	85
4/28/05 8:05	105	90
4/28/05 11:05	100	78
4/28/05 14:05	101	79
4/28/05 18:35	99	70
4/29/05 8:05	96	68
4/29/05 13:35	96	60
4/29/05 13:45	96	81
4/29/05 13:55	96	96
4/29/05 15:05	97	105

3. Dry gas check

	Source	Measurement
	MCM reference anlayser	MCM portable analyser
4/27/05 10:00	4	4
4/27/05 10:30	4	4
4/27/05 11:30	4	4
4/27/05 11:40	4	4
4/27/05 12:15	4	5
4/27/05 14:30	4	2
4/27/05 15:00	4	2
4/27/05 17:00	4	2
4/28/05 8:00	3	2
4/28/05 11:00	3	0
4/28/05 14:00	3	0
4/28/05 18:30	3	0
4/29/05 8:00	3	0

4/29/05 13:30	3	0
4/29/05 13:40	3	3
4/29/05 13:50	3	1
4/29/05 15:00	3	3

MCM portable analyser testing during PLAT4 start-up

E

	Source		Measurement	
	Process 99Q004 [ppm]	MCM reference anlayser [pmm]	MCM portable analyser [ppm]	
4/27/05 10:00		4	4	
4/27/05 10:15		97	97	
4/27/05 10:30		4	4	
4/27/05 11:25	66		215	
4/27/05 11:30		4	4	
4/27/05 11:35	66		220	
4/27/05 11:40		4	4	
4/27/05 12:00		96	105	
4/27/05 12:15		4	5	
4/27/05 14:25		100	90	
4/27/05 14:30		4	2	
4/27/05 14:35	65		180	
4/27/05 15:00		4	2	
4/27/05 17:00		4	2	
4/27/05 17:05		101	85	
4/27/05 18:00	65		180	
4/27/05 22:00	64		125	
4/28/05 8:00		3	2	
4/28/05 8:05		105	90	
4/28/05 8:10	55		82	
4/28/05 11:00		3	0	
4/28/05 11:05		100	78	
4/28/05 11:10	58		50	
4/28/05 14:00		3	0	
4/28/05 14:05		101	79	
4/28/05 14:10	68		49	
4/28/05 18:30		3	0	
4/28/05 18:35		99	70	
4/28/05 18:40	52		38	
4/29/05 8:00		3	0	
4/29/05 8:05		96	68	
4/29/05 8:10	36		31	
4/29/05 13:30		3	0	
4/29/05 13:35		96	60	
4/29/05 13:40		3	3	(zero re-adjusted)
4/29/05 13:45		96	81	
4/29/05 13:50		3	1	(gain re-adjusted)
4/29/05 13:55		96	96	
4/29/05 15:00		3	3	
4/29/05 15:05		97	105	
4/29/05 15:10	39		59	

MANUAL

ON-LINE PROCESS STREAM ANALYSIS - ANALYSERS

DEP 32.31.50.12-Gen.

April 2003

DESIGN AND ENGINEERING PRACTICE

2.5.8 H_2S 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.