AN EVALUATION OF PERFORMANCE OF TRACE MOISTURE MEASUREMENT METHODS

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ABSTRACT

A group of 13 trace moisture instruments have been tested in a joint project by the UK National Physical Laboratory and BOC Edwards. The instruments were loaned to the project by collaborating instrument manufacturers and suppliers. The selection comprised several industrial-grade capacitive probes, plus other instruments of types for laboratory and/or process use, including a cavity ring-down spectrometer, a tuneable diode laser absorption spectrometer, electrolytic (P_2O_5) hygrometers and two condensation hygrometers. The tests included traceable calibration in terms of dew-point temperature down to -90 °C (nominally 100 parts per billion), repeated after approximately 12 months to evaluate long-term drift. Additionally, the instruments were tested for response to upward and downward changes in moisture content. Measurements were carried out in nitrogen and air, and each of the participating laboratories covered different but overlapping regions of the entire range. The more expensive "laboratory-grade" instruments performed broadly better than the industrial probes, but in several cases the capacitive probes performed quite adequately for common applications, albeit with some long-term drift in calibration. The tests clearly illustrated the effects of temperature changes on the measurement system as a whole. The study enables some general conclusions to be drawn for the different measurement methods and their suitability in different applications according to their likely accuracy, stability, responsiveness, and their functioning in ultra-dry conditions.

1. INTRODUCTION

Measurements of trace moisture are needed in a variety of different industrial sectors, including semiconductor manufacture, pure gas supply, atmospheric and climate research, aerospace, petrochemical processing, power generation, air filter and purifier manufacture, and supply of reference standards for other trace gases.

Trace moisture measurement is an area of advancing technology, and applications now require measurements of lower trace amounts of water vapour than ever before. Some measurement methods are now operated near their limits of applicability. Problems occur because, depending on type, trace moisture instruments can be prone to failure, drift, slow response, hysteresis and large calibration offsets. To help instrument users benefit from a more fully informed choice of measuring instrumentation, a study of performance of trace moisture measurement methods has been carried out by the UK National Physical Laboratory (NPL), and BOC Edwards (BOCE).

2. OVERVIEW OF STUDY

Instruments of the types listed in Table 1 were studied. All were commercially available (although the S2 spectrometer tested was an early production model). In what follows, particular products are not identified. However, the companies that collaborated by loaning instruments to the project (or by agreeing to the inclusion of instruments owned by the authors) are acknowledged at the end of this paper.

Table 1: Trace moisture instruments studied

Identification	Instrument type
S1	Cavity ringdown spectrometer
S2	Absorption spectrometer
C1 and C2	Condensation (frost-point) hygrometers
E1 and E2	Electrolytic (P_2O_5) hygrometers
P1 to P7	Capacitive probes (several types)

Calibrations of the instruments in terms of frost-point temperature were carried out against the NPL Low Frost-point Generator (LFG) [1]. Tests of response time, linearity and hysteresis, and response to moisture levels below 10 nmol/mol were carried out using the NPL Trace Water Vapour Facility (TWVF) [2]. Responses to temperature changes were tested using the BOCE UHP Mobile Laboratory [2]. The majority of instruments were scaled in units of frost-point temperature. The tests are reported in units of frost point or of amount fraction (nanomoles of water vapour per mole of sample gas – corresponding to parts per billion by volume) according to which facility was used.

The instruments were in general used in accordance with manufacturers' instructions with the slight exception that the back-pressure required to operate instrument internal mass-flow controllers was not in every case achievable in the laboratories. Care was taken to distinguish between the moisture- and temperature-sensitivity of the instruments being studied, and of the moisture generation and supply systems. Care was generally taken to treat instruments all similarly, although P4 and P5 were in fact exposed to ultra-dry (few ppb) conditions for several weeks longer than the other devices. All instruments were supplied with sample flow rates of 0.4 to 0.5 litres per minute, except for C2, E1 and E2, which received slightly lower flows. Where ideal rates of gas flow could not be supplied, or where insufficient gas pressure limited the measurements on certain instruments, this should be seen as a shortcoming of the study, not of these instruments. Ambient temperature was 21 °C ± 2 °C during calibrations, and 27 °C ± 2 °C during other tests (apart from where other temperatures are specified below). Measurements were carried out in air and nitrogen.

Not all instruments were covered by all tests: E1 and the display unit of P7 failed and were repaired during the course of the study, and C2 was not available for calibration against the LFG. Due to intermittent availability, S1 was replaced after initial calibration by a similar instrument for the remainder of the reported tests.

3. CALIBRATIONS AND LONG-TERM STABILITY

Figures 1 to 6 below show graphs of calibration corrections determined by comparison against the NPL Low Frost-point Generator, for all types of instrument studied. The frost-point calibration range was from nominally –60 °C to below –95 °C (although measurements below –90 °C were outside the normal operating range of the LFG). The calibrations were repeated approximately 12 months later, to assess long-term stability of the instruments. The error bars indicate uncertainties at a coverage of $k = 2$ (95% confidence level). Where error bars are not shown, they are smaller than the data symbols. The instruments were not adjusted in the light of calibration results.

Initial results for spectrometers S1 and S2 and condensation hygrometer C1 showed only small deviations from reference values of less than 2 °C in frost-point temperature – often much less – throughout the range of calibration. The calibration corrections for two of the capacitive probes were determined to be less than ±7 °C in frost point. The other results for capacitive probes, and for both electrolytic instruments, had calibration corrections of up to 12 °C in parts of the range. (Both the

electrolytic instruments were only partially calibrated – one failed and was repaired, but also the laboratory had some difficulty providing the required sample gas pressure.)

The repeat calibration for C1 showed very little long-term drift. For the other devices, drift over the year varied between about zero and 15 °C in frost point. Notably, P4 and P5 were two of the same product, and the pattern of drift for the two was highly similar (although this might not reliably be the case). The replacement S1 final results were also very close to the initial calibration, although these were two different instruments.

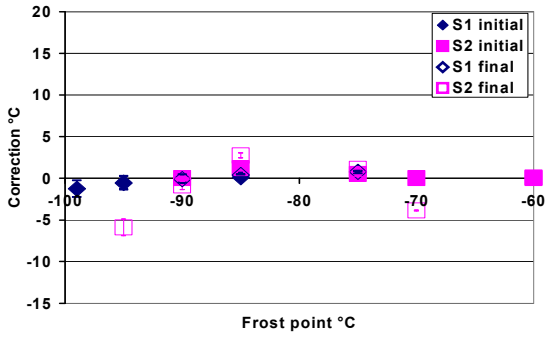

Figure 1: Initial and final calibrations of spectrometers S1 and S2 (S1 initial and S1 final were different instruments)

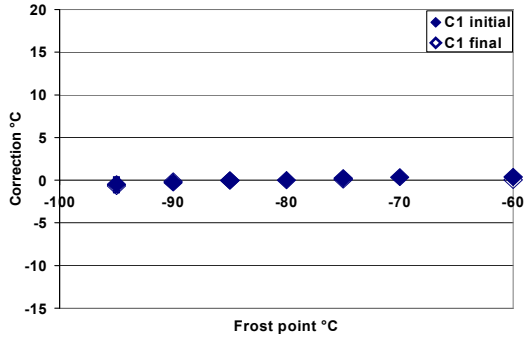

Figure 2: Initial and final calibrations of condensation hygrometer C1

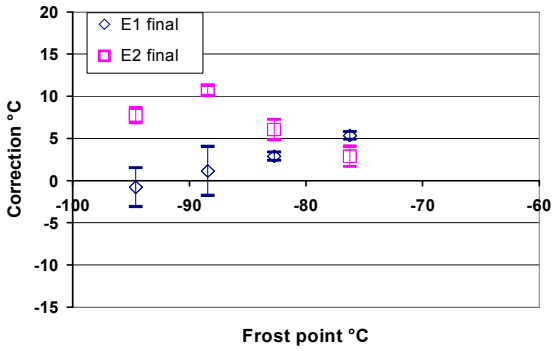

Figure 3: Final calibrations of electrolytic (P2O5) hygrometers E1 and E2

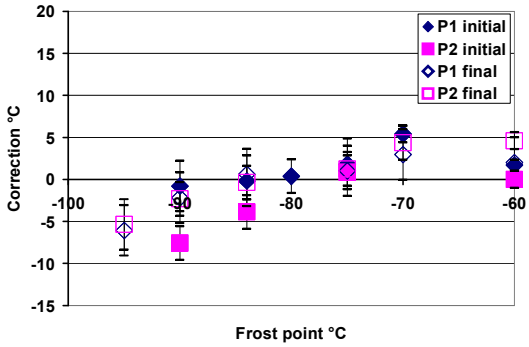

Figure 4: Initial and final calibrations of capacitive probes P1 and P2

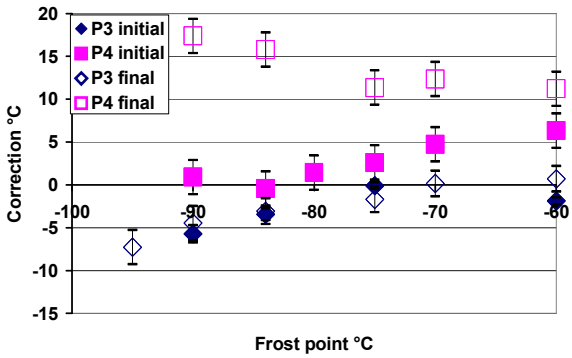

Figure 5: Initial and final calibrations of capacitive probes P3 and P4

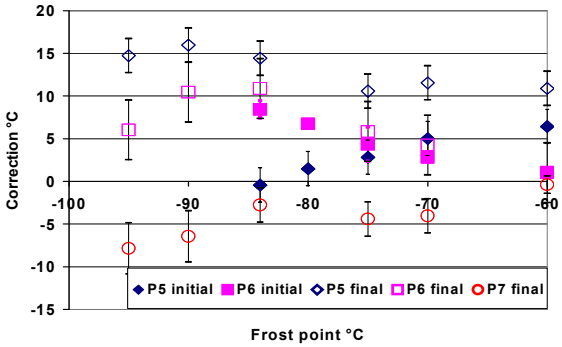

Figure 6: Initial and final calibrations of capacitive probes P5, P6 and final calibration of P7

4. TEMPERATURE RESPONSE

For a period of several weeks, the instruments were subjected to conditions of fluctuating laboratory temperature. This revealed the temperature-dependence of the trace moisture readings, as illustrated in Figure 7, which shows the variations in instrument responses to a nominally fixed applied condition of 115 nmol/mol over the ambient temperature variations shown as the dotted line in the upper portion of the graph. The coefficients of temperature sensitivity were determined for each instrument at various water vapour levels. (Some instruments greatly over-read near 2 nmol/mol – hence coefficients of several nmol/mol were seen.) Figure 8 shows an illustration of the variation of temperature sensitivity with measuring range for Spectrometer S1. Table 2 summarises the temperature sensitivities evaluated for all the instruments studied. It should be noted that these temperature coefficients are the combination of the temperature responses of the instruments with any underlying temperature response of the source and connecting pipework.

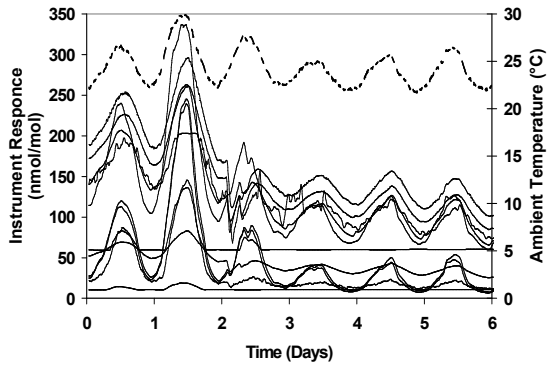

Figure 7: Response of full set of instruments at temperatures varying diurnally, in a range between 20 °C and 30 °C. (Dashed line is temperature.)

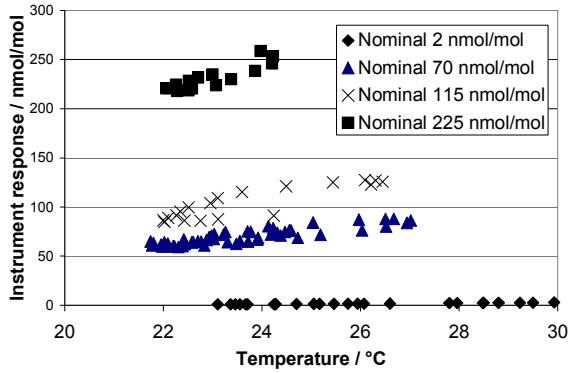

Figure 8: Example temperature response of one instrument (S1) at several moisture concentrations.

Table 2: Table showing the temperature sensitivities at different concentrations

		Temperature coefficient in (nmol/mol) / ^{o}C for instrument										
Nominal concentration nmol/mol	**Nominal Frost point °C**	**S1**	**S2**	**C1**	**C2**	**E1**	**E2**	**P2**	**P3**	**P4**	**P5**	**P7**
2	-110	0.3	-5.3	1	0.9	5.7	0.8	12.5	10.8	3.5	3.8	1
70	-92	5	-6	5.6	4.3	10.2	1.3	14.2	15.1	10.6	11.3	1
115	-89	9.1	2.2	9.2	6.8	11.9	2.1	13.4	14.9	9.2	10.2	3.1
225	-85	15.2	-4.9	15.6	9.9	22.4	18.4	19	31.4	24.5	22.7	5.8

5. RESPONSE TO STEP CHANGES

In most high purity applications, fast detection of step changes in moisture is of interest, particularly for upward changes. Figures 9 and 10 show time response to steps from nominally 300 nmol/mol to 850 nmol/mol, and back to 300 nmol/mol. The graphs show times taken to achieve 10% and 90% of these step changes. The interval between instrument readings was five minutes, except for C2 which had an automatic 20 minute averaging. The step changes were achieved by rapid flow switching, and were much quicker than the sampling time. Some instruments showed consistently fast responses (eg S1, C1, and C2), others were relatively slow (E1, P1, and P3), while the remainder showed

significant variation in response depending on whether the step change was positive or negative. For P7, only the 90% upward response and 10% downward response are shown (both conservative values), due to the output being set at a coarse resolution during this test. Operational constraints meant that the flow rates used for S2 were lower than recommended for the instrument, and so the response time data for S2 may not reflect its normal speed of response.

One common observation for all instruments was that the 10% response time was consistently as fast or faster for the negative step compared to the positive one. No conclusive explanation has been found for this unexpected effect. This could be connected with the thresholds for adsorption and desorption of water from pipework surfaces, or it could reflect the fact that the upward step is effectively a greater fractional change than the downward step. Further analysis of these results, and further study of this effect in a wider range would be desirable.

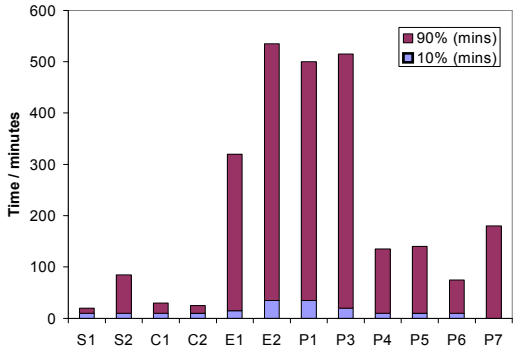

Figure 9: Response to upward step change from 300 nmol/mol to 850 nmol/mol.

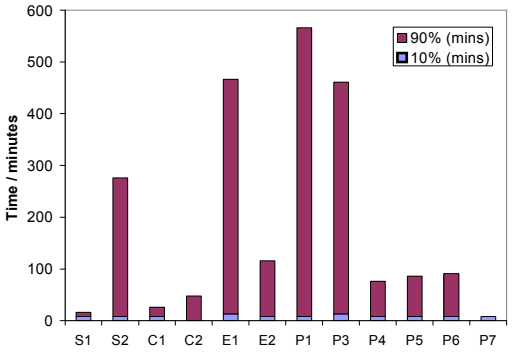

Figure 10: Response to downward step change from 850 nmol/mol to 300 nmol/mol

6. LINEARITY AND HYSTERESIS

The linearity and hysteresis of the instruments were evaluated by exposing them to dry (<10 nmol/mol) conditions and then stepping the concentration up through a series of fixed levels starting at 30 nmol /mol and going up to 850 nmol/mol, then down through the same levels back to dry conditions. Each concentration level was maintained for at least 24 hours before stepping to the next.

The results of these tests are summarised in Table 3. This table shows the hysteresis and linearity parameters for the various sensors. The hysteresis parameter is the difference in instrument response to 300 nmol/mol on the downward and upward steps, expressed as a fraction of the average of the two readings. The linearity parameter is the R^2 value for a linear regression fit to the complete set of instrument readings from 30 nmol/mol to 850 nmol/mol and back again.

The results from Table 3 show that certain instruments (C1, C2 and S1) showed excellent linearity and little hysteresis over the range, while the capacitive probes, in general, showed good linearity but variable hysteresis, and both electrolytic probes showed similar levels of hysteresis and non-linearity.

Table 3 : Hysteresis and linearity parameters for trace water vapour sensors between 30 and 850 nmol/mol

Instrument	S1	S2	C1	C2	E1	E2	P1	P3	P4	P5	P7
Hysteresis (at 300 nmol/mol)	0.017	0.282	0.009	0.034	0.217	0.200	0.082	0.139	0.270	0.391	0.007
Linearity (R^2)	0.9998	0.9829	0.9993	0.9985	0.9513	0.9614	0.9641	0.9877	0.9894	0.9817	0.9875

7. RESPONSE BELOW 10 NMOL/MOL

Some of the instruments studied were either not specified (S2, C1, P1, and P6) or not configured (P7) to operate down to 10 nmol/mol. For the others, which were nominally intended to work below this range, response to (and recovery from) a very dry condition was tested. It was found that most of the instruments were unresponsive to sample gas at 30 nmol/mol after being conditioned at below 5 nmol/mol. Some of those unresponsive to this upward change were able to follow a downward change from 30 nmol/mol to 5 nmol/mol when approached from above (100 nmol/mol.). Instruments of all types exhibited this mixture of responsive and unresponsive behaviour some or all of the time, except for S1 which appeared consistently responsive in this range.

8. CONCLUSIONS

The performance of the instruments varied greatly, with the more expensive "laboratory" instruments generally showing smaller calibration errors and less long-term drift. Across the full set of tests, condensation hygrometers C1 and C2, and spectrometer S1 performed best overall. But fast response and ability to tolerate very dry conditions were not exclusive to the more expensive devices. In some cases the "industrial" capacitive probes responded well.

With the exception of S2, C1 and C2 (which were resident in the authors' laboratories) the instruments were supplied expressly for performance testing. The instruments were generally studied in near-ideal conditions (apart for some exposure to very dry gas). Therefore users can realistically expect that in less ideal conditions, instrument performance would be easily as variable as found in this study, and quite possibly worse. In addition, users should also expect their own sampling and moisture generation systems to significantly affect the accuracy, stability and reproducibility of trace moisture measurements.

ACKNOWLEDGEMENTS

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