PROMETH2O

20IND06 PROMETH2O

Metrology for trace water in ultra-pure process gases

Calibration and Measurement: Ensuring Traceability in Industry

Ned Hawes - Qrometric UK

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EMPIR EURAMET

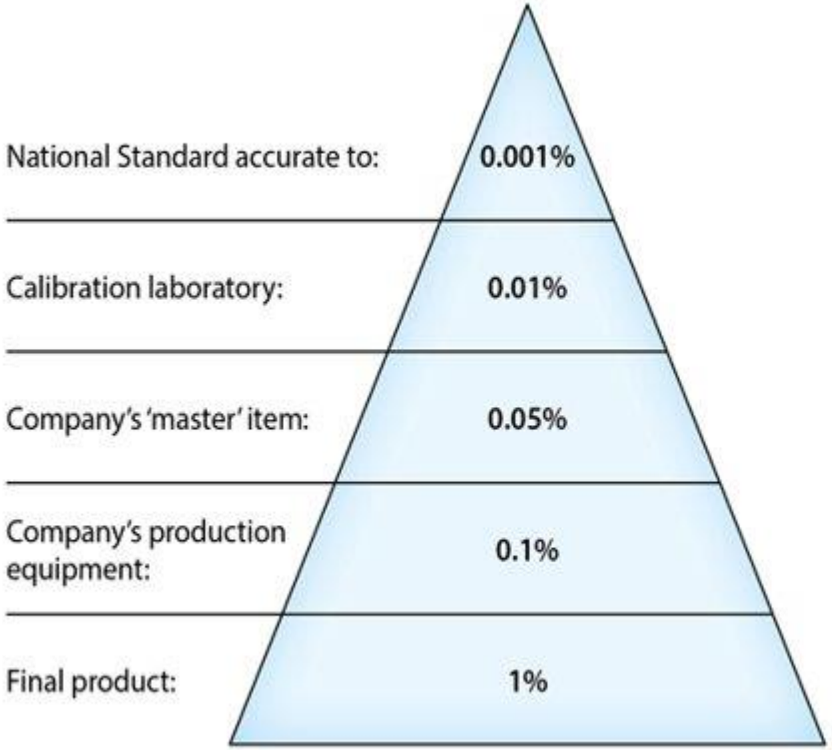
The EMPIR initiative is co-funded by the European Union's Horizon 2020 research and innovation programme and the EMPIR Participating States

Measurement Traceability

National Measurement Institute
Primary standard

Local laboratory
Transfer standard

User
Instrument



- Uncertainty accumulates at each step – typically due to long-term drift and irreproducibility of instruments/measurements
- This is why we need top-level standards with small uncertainty

PROMETH2O

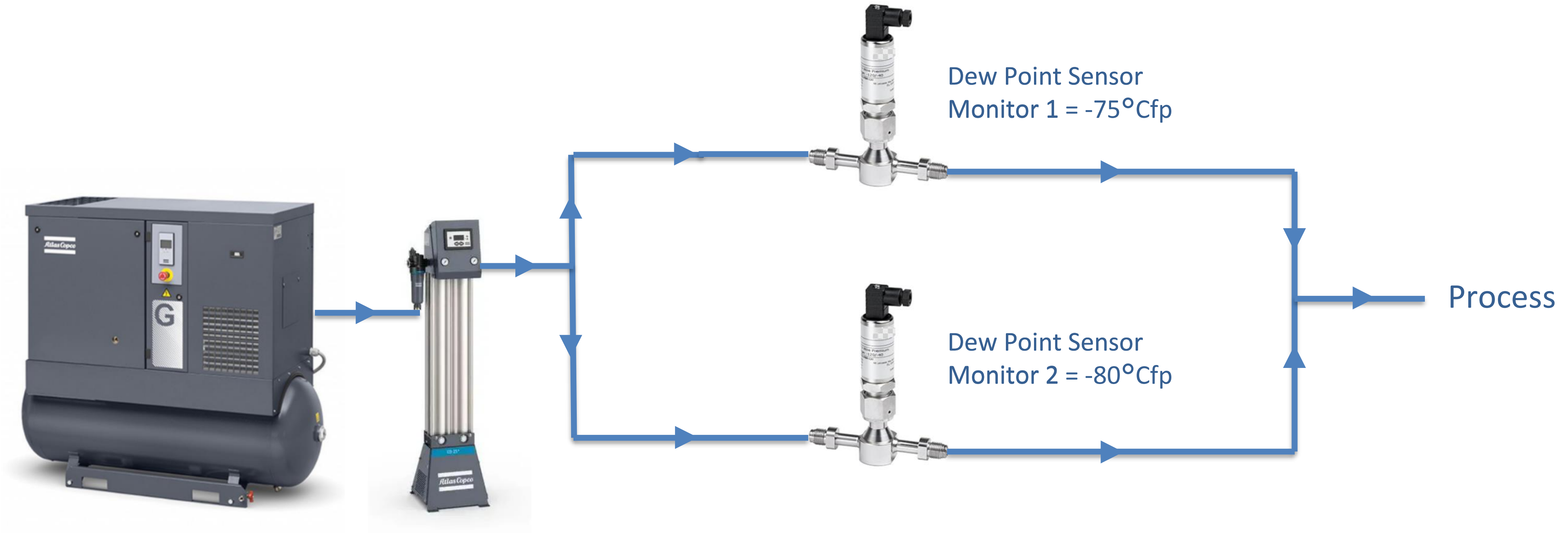
Highest level of trace water-vapour measurements

Qrometric
Industrial and scientific metrology

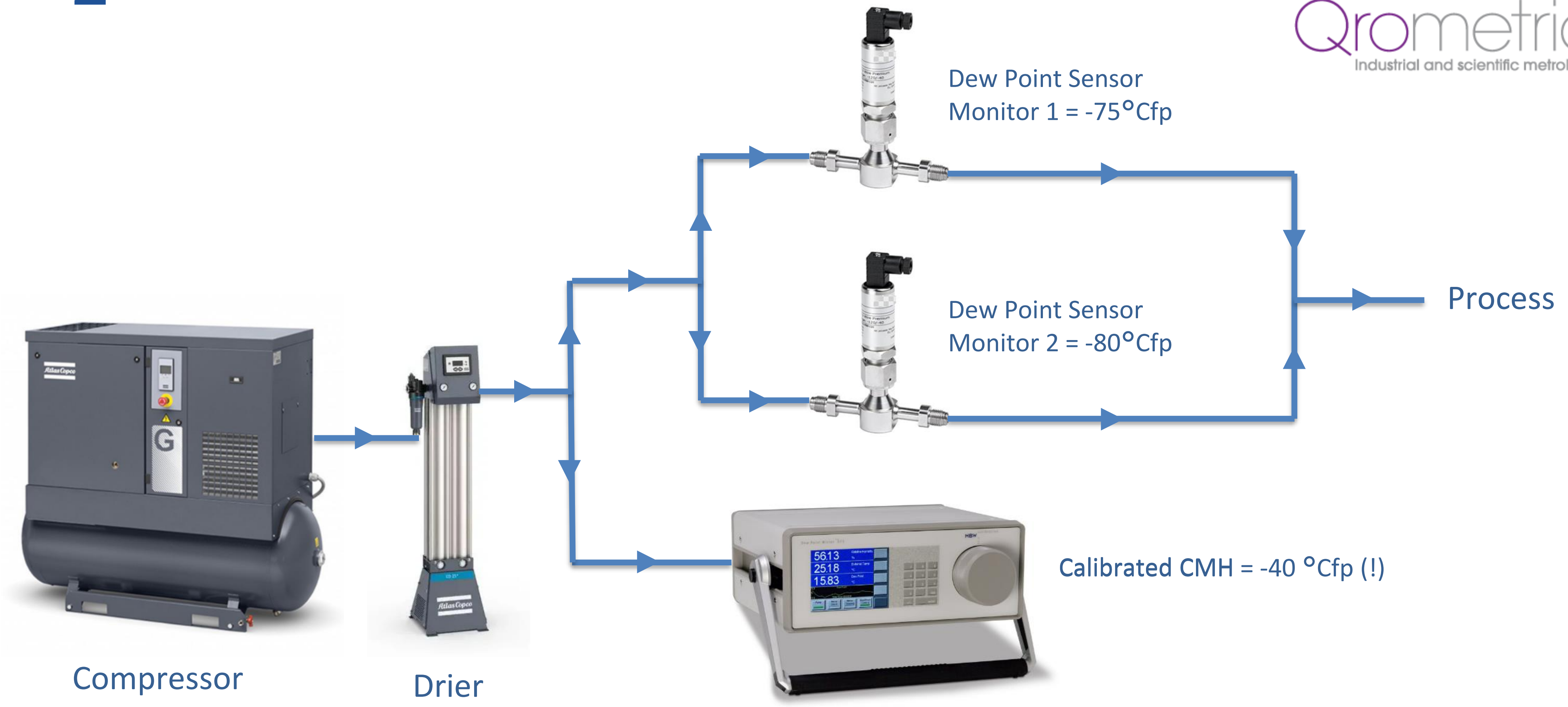
NPL
National Physical Laboratory

INRiM
ISTITUTO NAZIONALE
DI RICERCA METROLOGICA

Example 1 – measurement dew point of compressed air



Example 1 – Dew point measurements in compressed air



ProMetH2O – a long time coming!

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Industrial and scientific metrology

An evaluation of performance of trace moisture measurement methods
S.A. Bell, T. Gardiner, R.M. Gee, M. Stevens, K. Waterfield, A. Woolley,
Proceedings of TEMPMEKO 2004, Cavtat-Dubrovnik, Croatia, June 2004, 663-668.

AN EVALUATION OF PERFORMANCE OF TRACE MOISTURE MEASUREMENT METHODS

S.A. Bell [1], T. Gardiner [1], R.M. Gee[1], M. Stevens [1], K. Waterfield [2], A. Woolley [1]

[1] National Physical Laboratory, Teddington, United Kingdom
[2] BOC Edwards, Crawley, United Kingdom

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 deviations of the readings from "true values". 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.

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. 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.

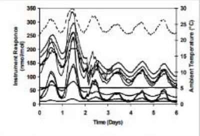


Figure 7: Response of full set of instruments at temperatures varying diurnally, in a range between 20 °C and 30°C.

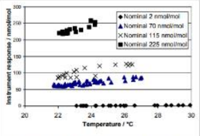


Figure 8: Example temperature response of one instrument (S1) at several moisture concentrations.

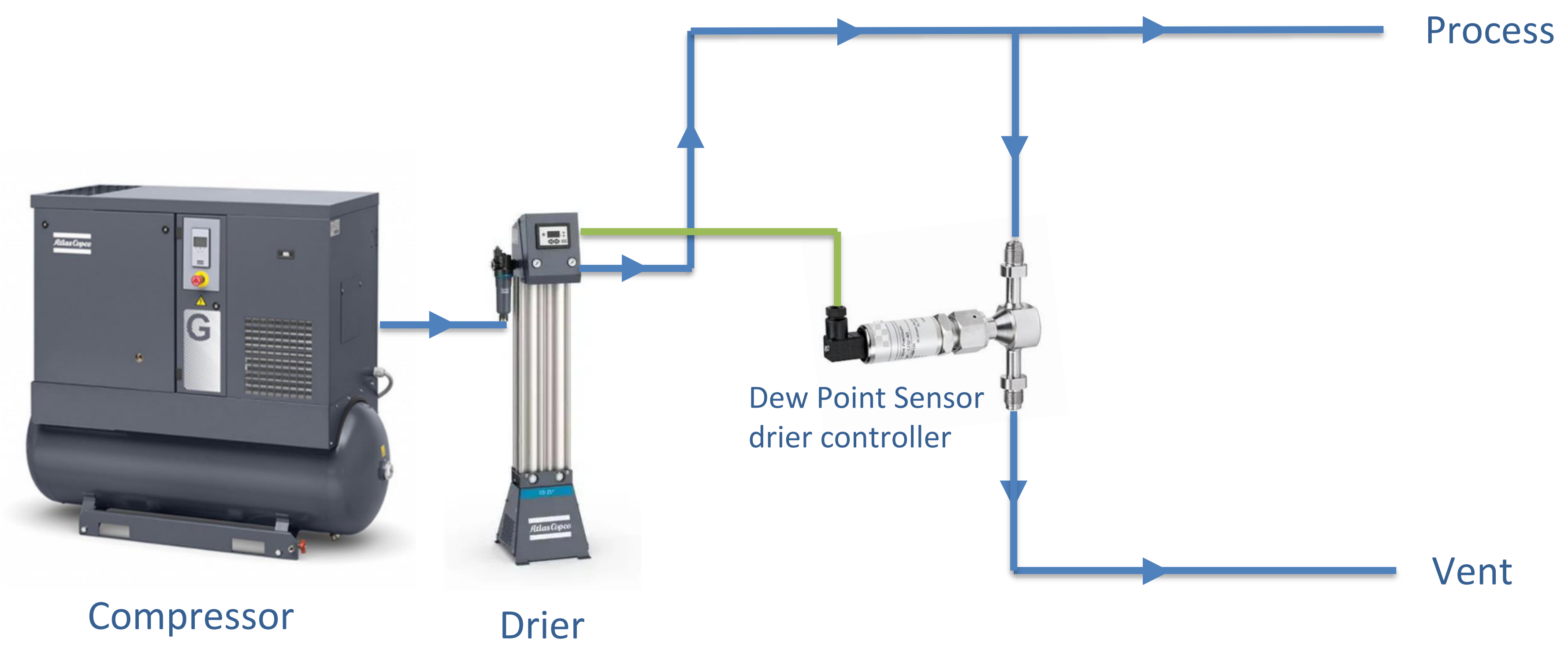
Table 2: Table showing the temperature sensitivities at different concentrations

	Temperature coefficient in (nmol/mol) / °C for instrument										
Nominal concentration (nmol/mol)	**S1**	**S2**	**C1**	**C2**	**E1**	**E2**	**P2**	**P3**	**P4**	**P5**	**P7**
2	0.3	-5.3	1	0.9	5.7	0.8	12.5	10.8	3.5	3.8	1
70	5	-6	5.6	4.3	10.2	1.3	14.2	15.1	10.6	11.3	1
115	9.1	2.2	9.2	6.8	11.9	2.1	13.4	14.9	9.2	10.2	3.1
225	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 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.

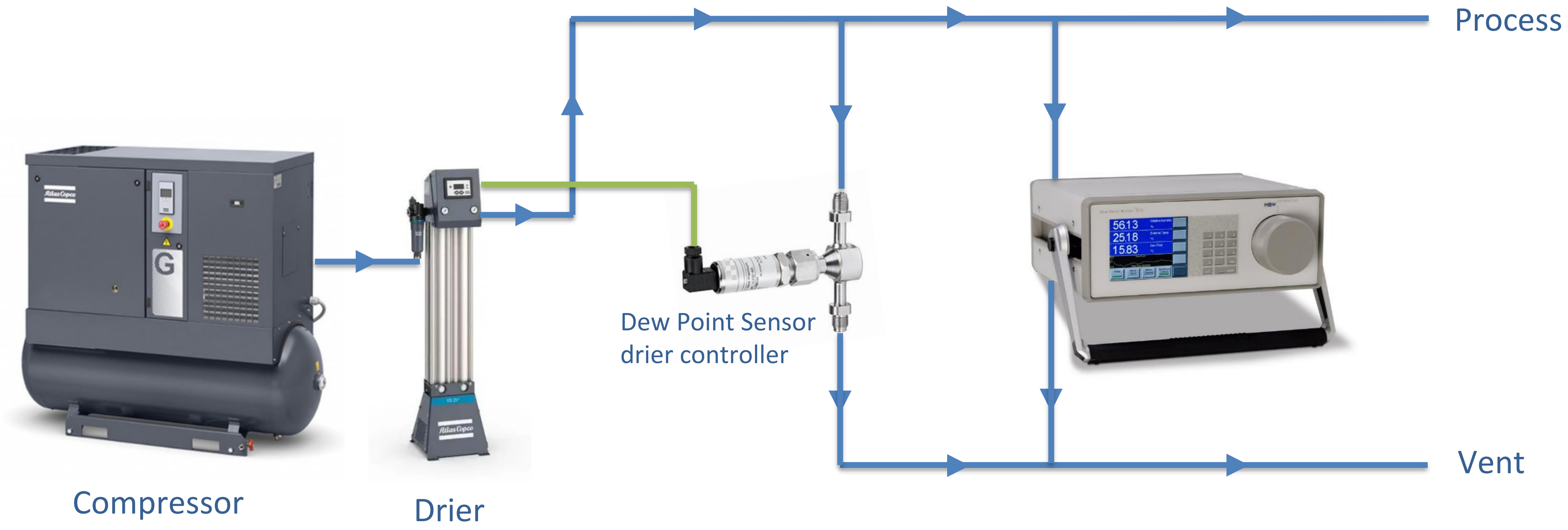
Example 2 – dew point sensors as control



Traceability vs Accreditation?

- No as found results
- Non-compliance to FDA requirement

Example 2 – Dew point sensors as control



Traceability vs Accreditation?

https://www.qrometric.com/case_studies/monitoring-humidity-in-compressed-air-systems/

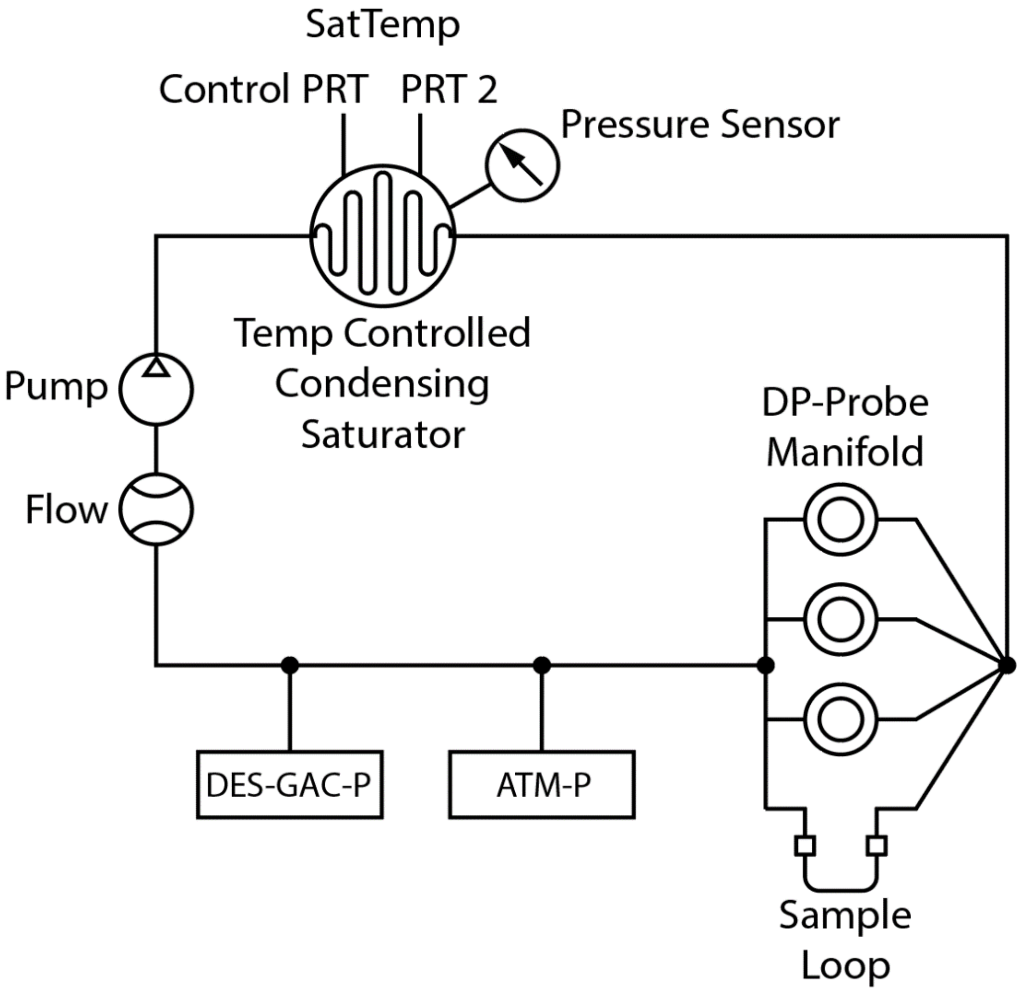
ppb-level Measurement Challenges

- Sensor performance and limitations
- Measurement drift, contamination by process
- Lack of timely calibration, ‘As Found’ results often omitted

Driven by audit-trail in pharmaceutical industry/FDA

FPG: the world's first transportable dew-frost point calibrator

Qrometric FPG – Principle of Operation



Qrometric FPG – Compatible with Most Hygrometers

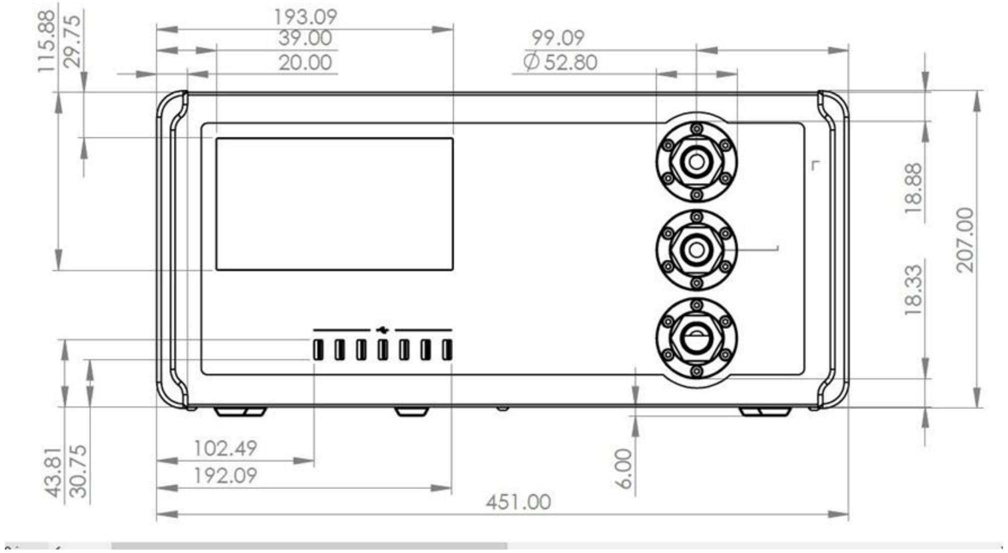
Three user configurable probe ports >>>

Probe adapters to suit all DPS on the market >>>

<<< External sample loop with VCR fittings

Qrometric FPG - Capabilities

- -100…+15°C frost/dew point (10ppbV to 17,000 ppmV)
- Uncertainty ±0.1…0.3°C



Qrometric FPG – Qualification and Traceability

- FPG validated with high performance MBW SLX Chilled Mirror Hygrometer as part of PROMETH2O
- Traceability of SLX to INRIM
- Validation demonstrates validity of traceability to temperature/pressure

Qrometric FPG– ProMetH2O Qualification

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FPG DEW POINT CALIBRATOR

#	Result
1	-74.7918
2	-74.8132
3	-74.8196
4	-74.8446

#	Result A
1	-89.9556
2	-89.9533
3	-89.9238
4	-89.9765

#	Result A
1	-100.2066
2	-100.2188
3	-100.1889
4	-100.2403

	-75
MEAN	-74.84
STDEV	0.028
DOF	9
Repeatabil	0.0088

	-90
MEAN	-89.95
STDEV	0.022
DOF	3
Repeatabil	0.0109

	-100
MEAN	-100.21
STDEV	0.019
DOF	4
Repeatabil	0.0087

Qrometric FPG – Calibration Uncertainty Budgets

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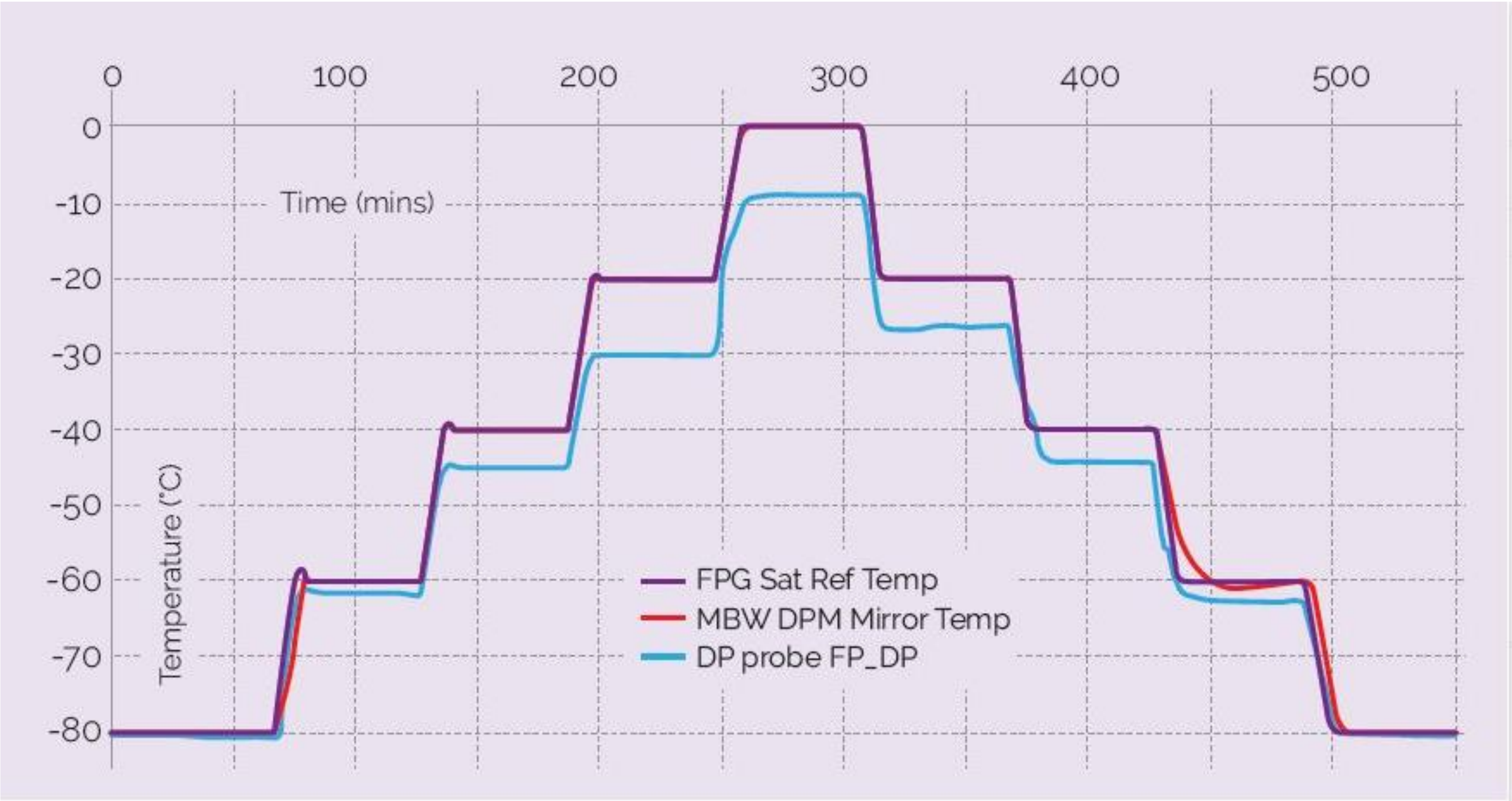
FPG
DEW POINT
CALIBRATOR

FPG Uncertainty at -60 ˚C Uncertainty Contributions	Type	Value	Units	Sensitivity	Distribution	Divisor	Std. Un.
Temperature Effects							
FPG SatT control PRT calibration uncertainty	B	0.040	˚C	1.00	Normal 2s	2.00	0.020
FPG SatT control PRT drift	B	0.005	˚C	1.00	Rectangular √3	1.73	0.003
FPG SatT control PRT stem conduction	B	0.005	˚C	1.00	Rectangular √3	1.73	0.003
FPG SatT control PRT self-heating and residual heat fluxes	B	0.005	˚C	1.00	Rectangular √3	1.73	0.003
FPG SatT control uncorrected deviations	B	0.005	˚C	1.00	Rectangular √3	1.73	0.003
FPG Display Resolution	B	0.0005	˚C	1.00	Rectangular √3	1.73	0.000
FPG SatT Repeatability	A	0.004	˚C	1.00	Normal 1s	1.00	0.004
Temperature Effects combined uncertainty							**0.0212**
Saturator Contributions:							
Saturation efficiency	B	0.0001	˚C	1.00	Rectangular √3	1.73	0.000
Saturator contamination	A	0.001	˚C	1.00	Normal 1s	1.00	0.001
Temperature gradient between saturator surface and PRT	A	0.01	˚C	1.00	Normal 1s	1.00	0.010
Saturator Temperature homogeneity	A	0.01	˚C	1.00	Normal 1s	1.00	0.010
Saturator Temperature stability	A	0.001	˚C	1.00	Normal 1s	1.00	0.001
Saturator Contributions combined uncertainty							**0.0142**
Pressure Effects							
FPG internal pressure sensor calibration uncertainty	B	70	Pa	0.00006	Normal 1s	1.00	0.004
FPG internal pressure sensor drift	B	300	Pa	0.00006	Rectangular √3	1.73	0.010
FPG pressure resolution	B	0.5	Pa	0.0001	Rectangular √3	1.73	0.000
FPG internal pressure sensor repeatability	A	300	Pa	0.00006	Rectangular √3	1.73	0.010
Stability	B	150	Pa	0.00006	Normal 1s	1.00	0.009
Pressure differences between Saturator and Manifold	A	460	Pa	0.00008	Normal 1s	1.00	0.035
Pressure Effects combined uncertainty							**0.0394**
Flow Effects							
Flow dependency related to Pressure differentials	A	390	Pa	0.00008	Normal 1s	1.00	0.030
Flow Effects combined uncertainty							**0.0299**
Other Uncertainties							
Internal sorption/desorption/leaks effects	B	0.5	Pa	0.0001	Rectangular √3	1.73	0.00003
Flow Effects combined uncertainty							**0.0000**
FPG combined uncertainty							**0.06**
FPG expanded uncertainty						95% confidence	**0.11**

Qrometric FPG – Typical Calibration Profile



Qrometric FPG – Temperature Measurement & Control

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FPG
DEW POINT
CALIBRATOR

- PRT for saturator temperature measurement and control
- Second PRT can be used for independent validation of saturator temperature…
- Measurement traceability to temperature and pressure

Qrometric Accredited Calibration Laboratory

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UKAS CALIBRATION
27982

FPG
DEW POINT CALIBRATOR

- ISO17025 Accreditation granted 21.09.2023
- https://www.ukas.com/download-schedule/27982/Calibration/
- QroLab - powered by **FPG**

FPG: the world's first transportable dew-frost point calibrator

https://www.qrometric.com/dew-frost-point-calibration-made-easy/

Further reading

PROMETH2O

Qrometric
industrial and scientific metrology

FPG DEW POINT CALIBRATOR

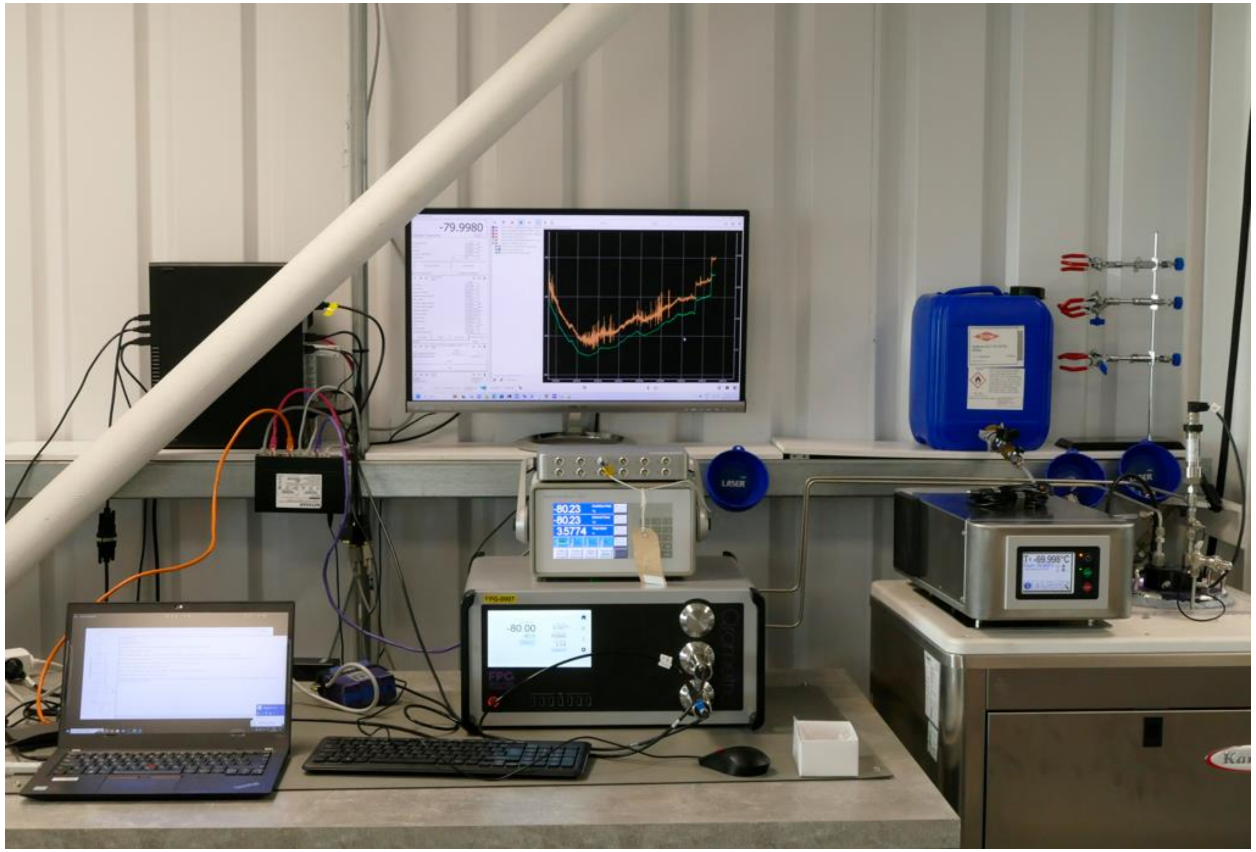
Thank you for your interest, may I take your questions?

Ned Hawes: ned@qrometric.com

EMPIR EURAMET
The EMPIR initiative is co-funded by the European Union's Horizon 2020 research and innovation programme and the EMPIR Participating States

ProMetH2O Test Bed 1

- Vaisala Dew Point Sensors compared with FPG/MBW SLX



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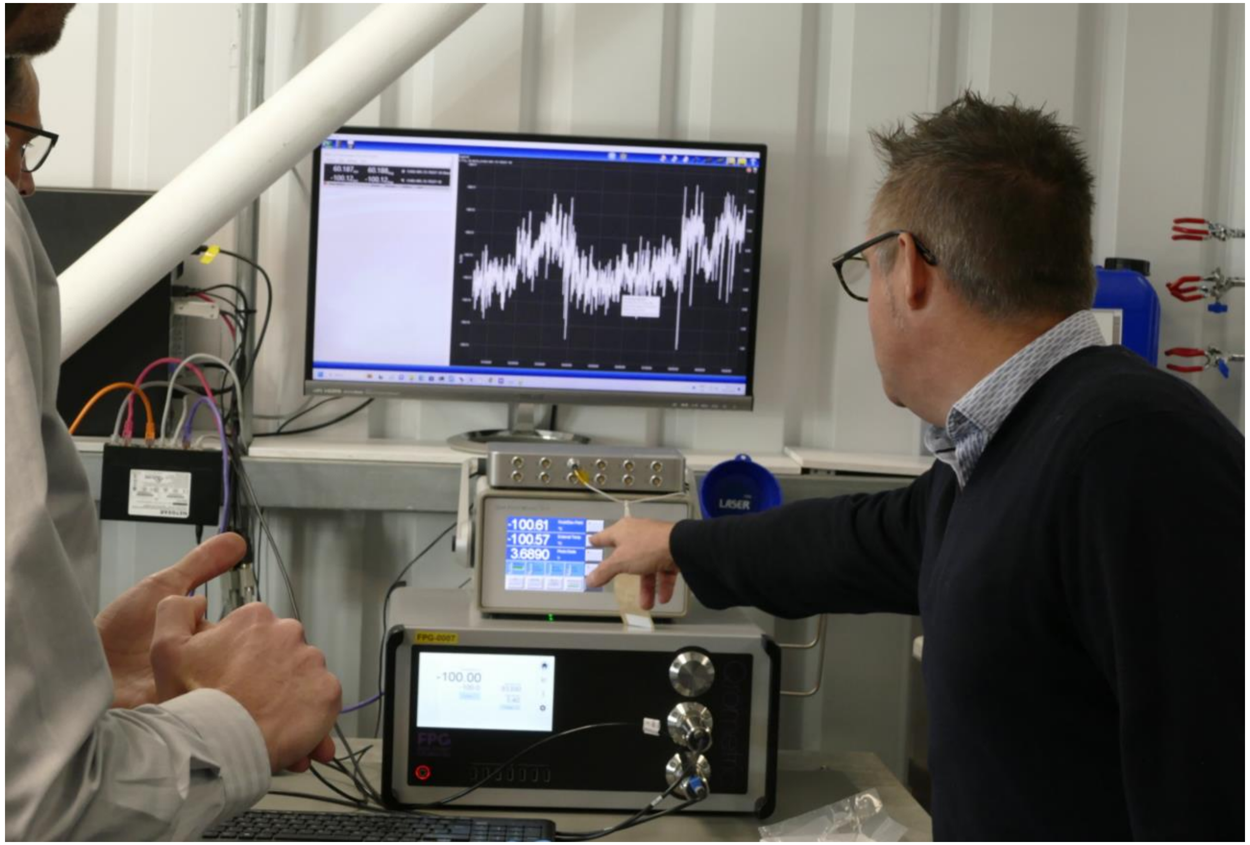
ProMetH2O Test Bed 1

- Vaisala Dew Point Sensors compared with FPG/MBW SLX



ProMetH2O Test Bed 1

- Dew point measurements in CO_2

ProMetH2O Test Bed 1

- Discussion on FPG uncertainty budget

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CALIBRATOR

ProMetH2O Test Bed 1

- Prototype High Pressure FPG with pressurized pump

ProMetH2O Test Bed 1

- Far UV Spectrometer testing with prototype high pressure FPG

Other ProMetH2O Achievements

- Prototype High Pressure FPG purged with Argon and compared with DTU Far UV Spectrometer. Condition: 13ppb