



Heriot-Watt University
Research Gateway

Development of a new method for measurement of the water dew/frost point of gas

Citation for published version:

Burgass, R, Chapoy, A & Filho, VDOC 2021, 'Development of a new method for measurement of the water dew/frost point of gas', *Fluid Phase Equilibria*, vol. 530, 112873. <https://doi.org/10.1016/j.fluid.2020.112873>

Digital Object Identifier (DOI):

[10.1016/j.fluid.2020.112873](https://doi.org/10.1016/j.fluid.2020.112873)

Link:

[Link to publication record in Heriot-Watt Research Portal](#)

Document Version:

Peer reviewed version

Published In:

Fluid Phase Equilibria

Publisher Rights Statement:

© 2020 Elsevier B.V.

General rights

Copyright for the publications made accessible via Heriot-Watt Research Portal is retained by the author(s) and / or other copyright owners and it is a condition of accessing these publications that users recognise and abide by the legal requirements associated with these rights.

Take down policy

Heriot-Watt University has made every reasonable effort to ensure that the content in Heriot-Watt Research Portal complies with UK legislation. If you believe that the public display of this file breaches copyright please contact open.access@hw.ac.uk providing details, and we will remove access to the work immediately and investigate your claim.

DEVELOPMENT OF A NEW METHOD FOR MEASUREMENT OF THE WATER DEW/FROST POINT OF GAS

Rod Burgass^{1*}, AntoninChapoy^{1,2}, Valdério de Oliveira Cavalcanti Filho¹

¹*Institute of GeoEnergy Engineering, Heriot-Watt University, Edinburgh, EH14 4AS, Scotland, U.K.*

²*Mines ParisTech, CTP – Centre of Thermodynamics of Processes, 77305 Fontainebleau, France*

Abstract

The water content of gas is of importance in a wide variety of areas such as oil and gas, carbon capture and storage, medical, nuclear, food and hydrogen cells. In cases where pressurised gas is being used or transported in pipelines (i.e. natural gas, carbon dioxide, compressed air....) changes in temperature or pressure may result in water condensing. The condensed water may cause a number of issues such as corrosion, ice and hydrate formation. In order to avoid water condensing the gas needs to be dried to a level where condensation will not occur at any temperature/pressure conditions encountered. There are a wide variety of methods and equipment available for making water content measurements in laboratory or industrial processes. The available devices vary in terms of different parameters such as accuracy, long-term stability, sensitivity to contaminants, response time, pressure rating, initial and running costs. This paper introduces a new method that can potentially be incorporated into equipment for use in both laboratory and field applications for accurate dew/frost point measurements at a wide range of pressures. Initial measurements have been made for nitrogen, methane and natural gas and the results have been compared with literature data and model predictions.

Keywords: Gas, water, dew point, frost point, modelling

*Corresponding author: rwb4@hw.ac.uk

29 1. Introduction

30

31 Accurate measurements of water content are required for two main reasons. Firstly, in
32 order to provide data that can be used to develop and validate thermodynamic models used
33 for optimisation of drying units required for safe and economical design of pipelines and
34 facilities. Secondly, in order to continuously monitor water content allowing early warning
35 of the presence of “off-spec” gas that may lead to significant problems. There are a number
36 of instrument technologies currently available for measurement of water content of gases
37 including capacitance sensors, quartz crystal microbalance (QCM), electrolytic cell, CaC₂-
38 GC, fibre optic sensor, Karl Fischer titration, chilled mirror, chilled surface acoustic wave
39 sensor and Tuneable Diode Laser Absorption Spectrometer (TDLAS). Detailed descriptions
40 of the different technologies have been presented [1] and comparisons of different equipment
41 have also been made [2-7].

42

43 As there have been a number of reviews comparing the attributes of the different technologies
44 it is not necessary to repeat the findings in detail. However, it is worth mentioning a few of
45 the main points relating to the most used equipment, in order to set out how the new method
46 may compare, should it prove a robust and reliable approach. The chilled mirror is
47 considered as the most reliable method as it directly measures the dew/frost point, a
48 thermodynamic property [8,9]. As such it is used as a NIST-referenced humidity transfer
49 standard [10]. In cases where components other than water may condense on the mirror such
50 as alcohols or hydrocarbons the measurements may not be accurate. In addition, if water
51 soluble salts are present and accumulate on the mirror surface erroneous readings will occur.
52 As with chilled mirror, Karl Fischer is also regarded as an absolute or fundamental method.
53 The test gas is passed through a small volume of absorbent solution, which is subsequently
54 titrated with Karl Fischer reagent [11,12]. Capacitance sensors use changes in the
55 impedance, measured as a function of water molecules adsorbed to the porous dielectric of a
56 capacitor [8,13,14,16]. Capacitance sensors are, in general, less accurate than chilled mirror
57 devices. They tend to drift and can be slow to react. In addition, the presence of alcohols
58 may have an influence on the measured values. On the plus side, they are very sensitive to
59 changes in water content, can be used at pressure and are less expensive than most other
60 devices. QCM devices use changes in the resonant frequency of a hygroscopic polymer

61 coated QCM to measure water content [8,10,13,14-16]. They are fast to react although they
62 are expensive and may require regular maintenance. TDLAS sensors work by applying the
63 Beer-Lambert Law to a beam of light at the water absorption frequency, passed through the
64 gas [17]. TDLAS hygrometers are quick to react and accurate, however they cannot be used
65 at pressure, need to be recalibrated if the background gas changes and are expensive. Fibre
66 optic or Fabry-Perot hygrometers work by measuring a shift in the spectrum of reflected light
67 dependent on the amount of adsorbed water in a hygroscopic Fabry-Perot filter [18]. They
68 can be used at line pressure, however can be slow to respond, are expensive and may drift
69 over time. It is difficult to compare the accuracy of all devices because different values are
70 quoted by different manufacturers. Accuracies are also indicated in terms of dew/frost point
71 or ppmV or as a percentage value. As there is not a linear relationship between dew/frost
72 temperature and ppmV, care should be taken when make comparisons. In the case of most
73 chilled mirror instruments on the market the dew/frost point is displayed along with the
74 calculated ppmV value adjusted for the pressure of the measurement cell. Overall, reviews
75 consider the chilled mirror to be the most accurate with a stated value of between ± 0.1 and
76 0.5K **Table 1** summarises uncertainty figures, for the methods described above, from two
77 different reviews. It should be mentioned that this is not a complete list of all available types
78 of hygrometer.

79
80 **Table 1. Uncertainty values for different methods as given in different reviews.**

Method	Uncertainty Løkken (2015) [1]	Uncertainty Mc Keogh (2019) [7]
Chilled mirror	$\pm 0.2 \text{ K}$	$\pm (0.1-0.5)\text{K}$
Karl Fischer	$\pm 10\%$	Not given
Capacitance sensor	$\pm (1-3)\text{K}$	$\pm 3\text{K}$
QCM	$\pm 10\%$	1 ppmV
TDLAS	Not given	$\pm 2\%$
Fibre-optic sensor	$\pm 2\text{K}$	Not given

81
82 Integrated experimental and thermodynamic investigations into the water content of gas
83 have been ongoing for the past 20 years at Heriot-Watt University. A number of
84 measurement options for water content have been evaluated, including GC, capacitance
85 aluminium oxide, silicon and polymer capacitance sensors, TDLAS and chilled mirror. Data
86 generated using the developed capabilities have been presented in several publications [19-
87 24]. In 2015 some of the published data was validated by new measurements made in other
88 international laboratories, the publication [25] stated that the good match between our data

89 and those from other laboratories directly influenced a decision on drying requirements for
90 the Alaska Stand Alone Pipeline translating to a cost saving of millions of US dollars.
91 Although successful in generating accurate data using existing technology, it has become
92 apparent that there is a requirement for an alternative method that can be used to make
93 accurate measurements over a wide range of water contents, pressure and temperature
94 conditions and compositions. This has been the driver to seek a new approach.

95

96 2. New method

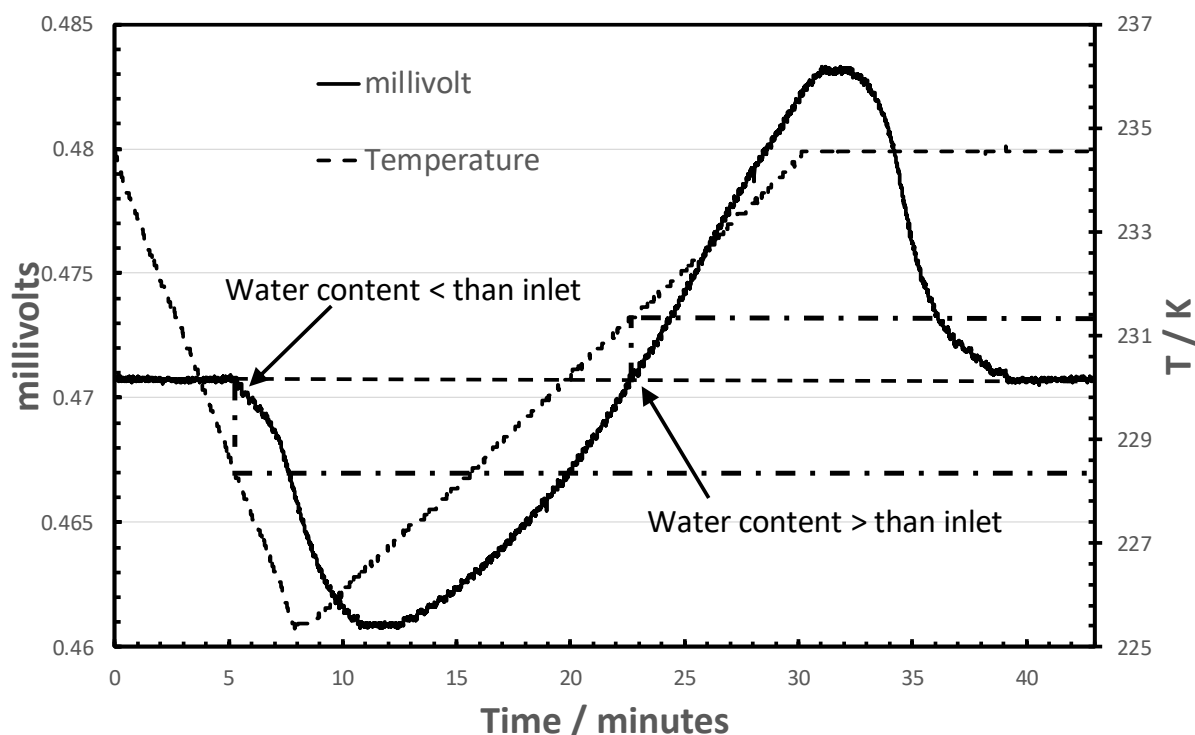
97

98 The method is based upon a relatively simple principle, similar to a chilled mirror, in that
99 it measures the dew or frost point which can then be used to calculate the water content [9].
100 This method is different to all other documented methods, as far as the authors are aware. In
101 the case of modern chilled mirror devices, the presence of water/ice on a chilled polished
102 surface is detected by monitoring reflected light. In the proposed method, the presence of
103 water/ice is detected by changes in the water content of gas passing through a temperature-
104 controlled tube. In the case of the chilled mirror devices, the mirror temperature is initially
105 cooled rapidly until water/ice is sensed and then the temperature is increased and decreased
106 until a temperature at which only a small amount of water/ice is present. In the new method,
107 in initial trials, the temperature of the tube is increased until water is no longer being removed
108 from the gas passing through it. This condition is determined by the water content of the gas
109 passing through the tube prior to cooling and checked by the water content after all the water
110 that was present on the tube walls in the form of water or ice has been removed. This method
111 is a direct measurement of the dew/frost point and can be carried out at any pressure required.

112

113 An example of data recorded during a test with a Spectra-Seal® 104 ppmV water in
114 CO₂certified standard is shown in *Figure 1*. In this test the standard is being passed through
115 the flow tube at atmospheric pressure, hence the water content can be accurately calculated
116 knowing the frost point temperature. As can be seen from *Figure 1* the temperature at which
117 water is removed from the gas, due to ice forming on the tube walls, is clearly seen as a
118 reduction in the millivolt signal. As the temperature is increased the rate at which water is
119 removed from the CO₂ reduces hence the millivolt signal increases. When the millivolt
120 signal is higher than the baseline millivolt signal, this means that ice is being removed from
121 the tube wall as it is no longer stable, in other words water is not being removed from the gas
122 passing through the tube. This temperature can be taken as the dew-point temperature. As

123 can be seen the initial temperature at which frost formed on the tube wall (228.2) is lower
 124 than the dissociation condition(231.2 K). This is seen in many measurements, such as
 125 hydrates and wax, where a new phase forms and some degree of sub-cooling is required to
 126 form the solid. The temperature at which the last solids dissociate is a point of
 127 thermodynamic equilibrium. In the test shown here the measured frost point temperature is
 128 231.2 K \pm 0.1 which, when calculated using the atmospheric pressure recorded when the test
 129 was conducted, gives a value of 105 ppmV water. This is within the uncertainty value (\pm
 130 5%) of the 104 ppmV certified standard.

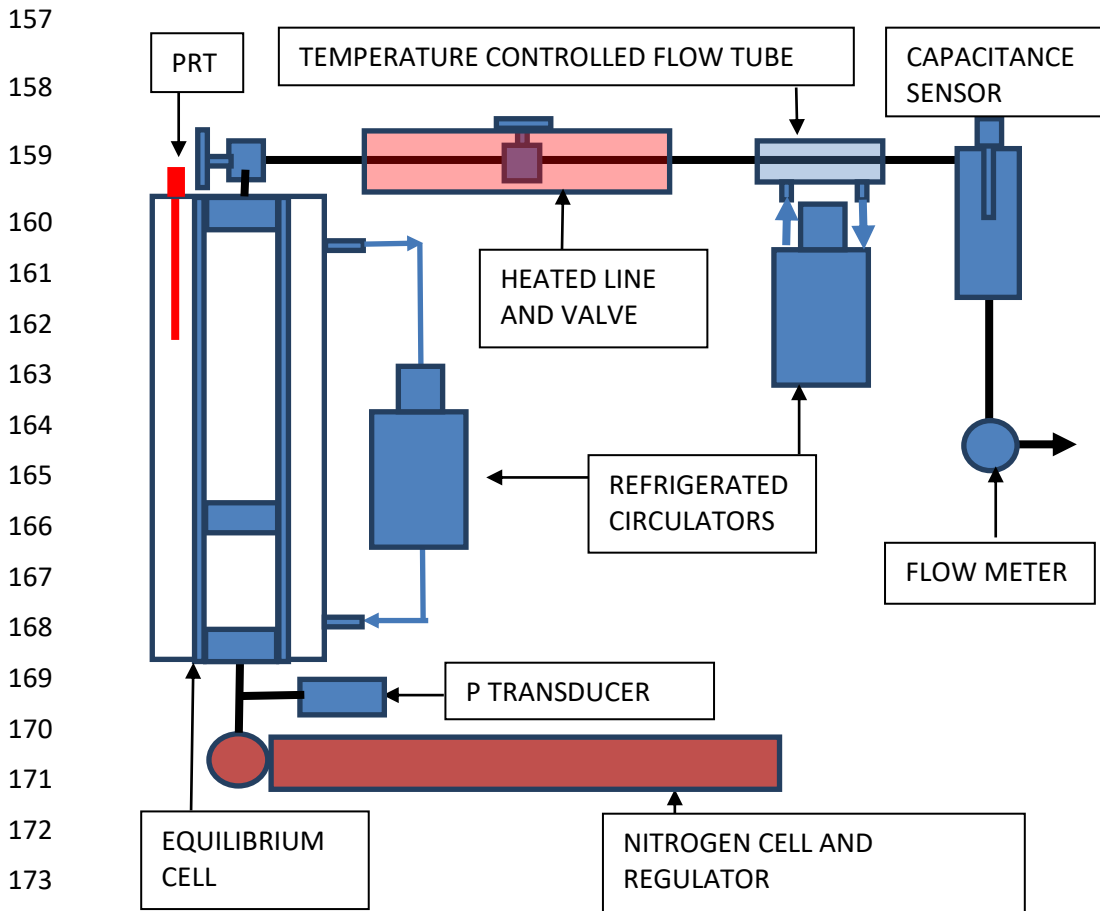


131
 132 **Figure 1.** Example of water content measurement for a 104 ppmV water in CO₂Spectra-
 133 Seal® certified standard. Measured dew point temperature 231.2 K at atmospheric pressure.

134 **3. Experimental equipment and methods**

135
 136 The experimental equipment (**Figure 2**) is comprised of a temperature controlled, variable
 137 volume equilibrium cell and a heated line and valve through which gas equilibrated with
 138 water, ice or hydrates is passed to the temperature controlled flow tube and then to the
 139 capacitance hygrometer. A flow meter is located after the hygrometer in order to monitor the
 140 flow rate of gas controlled by the heated valve. The equilibrium cell is a 300 mL, Titanium
 141 piston vessel rated to 69 MPa. The cell is surrounded by a jacket connected to a temperature-
 142 controlled circulator. The circulator can control the temperature of the fluid pumped through

143 the jacket within ± 0.1 K of the set-point and can be used at temperatures between -203 and
 144 373K. The cell temperature is measured using a Platinum Resistance Temperature probe
 145 (PRT) located in the jacket. Prior to using the set-up any variation between the jacket
 146 temperature and the temperature within the cell was measured using a reference probe
 147 mounted in the cell and any variation was accounted for. The cell pressure was measured
 148 using a Druck 960 strain gauge pressure transducer mounted on the lower end of the cell.
 149 The temperature probe was calibrated against a platinum resistance probe that has a
 150 certificate of calibration issued in accordance with NAMAS Accreditation Standard and
 151 NAMAS Regulations. The pressure transducer was checked for accuracy using a Budenberg
 152 dead weight tester. The stated accuracy of the Druck pressure transducer is ± 0.03 MPa in the
 153 range 0 to 41 MPa. The flow tube used in the initial tests is a 3.18 mm OD, 2.16 mm ID pipe
 154 with a Sulfinert electropolished internal wall. The temperature of the pipe is controlled by
 155 means of ethanol flowing through a jacket around the pipe from a temperature-controlled
 156 circulator.



175 *Figure 1. Schematic of experimental set-up.*

176

177 For each measurement, the test fluid is injected into the evacuated equilibrium cell along
 178 with around 2 mL of distilled water. In the case of tests where hydrates are present the
 179 temperature is cycled over a 24 hour period in order ensure all of the water is converted to
 180 hydrates. Once equilibrated at the desired P/T conditions the gas is passed through the flow
 181 tube, hygrometer and flow meter at a rate, in the tests reported here, of ~30 mL/minute. The
 182 temperature of the flow tube is then decreased and increased, as described above, in order to
 183 determine the water dew or frost point.

184

185 4. Test fluids

186

187 For the example test (*Figure 1*) with CO₂ a Spectra-Seal® 104 ppmV (±5%) water in
 188 CO₂certified standard supplied by BOC Ltd, was used. Nitrogen and Methane, with purities
 189 as shown in *Table 2* below were used. Natural gas with a composition shown in *Table 3*,
 190 supplied by BOC Ltd, was used. Distilled water was used in all tests.

191 *Table 2.* Composition of the Nitrogen and Methane used in this work (used without further
 192 purification).

Chemical	Symbol	CASRN	Purity	Supplier
Methane	CH ₄	74-82-8	99.995 vol%	BOC
Nitrogen	N ₂	7727-37-9	99.9992 vol%	Air Product

193

194 *Table 3.* Composition of natural gas as measured using GC.

Component	Mole%
N ₂	7.00
CH ₄	84.13
C ₂ H ₆	4.67
C ₃ H ₈	2.34
C ₄ H ₁₀	0.93
C ₅ H ₁₂	0.93

195

196 5. Thermodynamic modelling

197

198 A thermodynamic model, Heriot-Watt PVT (HWPVT), was used to help validate the
 199 experimental measurements along with literature data. The model uses the CPA-EoS to
 200 determine component fugacities in fluid phases. The CPA-EoS combines the well-known
 201 Soave-Redlich-Kwong (SRK) EoS for describing the physical interactions with the
 202 Wertheim's first-order perturbation theory, which can be applied to different types of

203 hydrogen-bonding compounds. The hydrate phase is modelled by using the solid solution
 204 theory of van der Waals and Platteeuw[26], as implemented by Parrish and Prausnitz [27]. A
 205 detailed description of the thermodynamic model used in this work can be found elsewhere
 206 [19, 28].

207

208 6. Results

209 6.1. Nitrogen

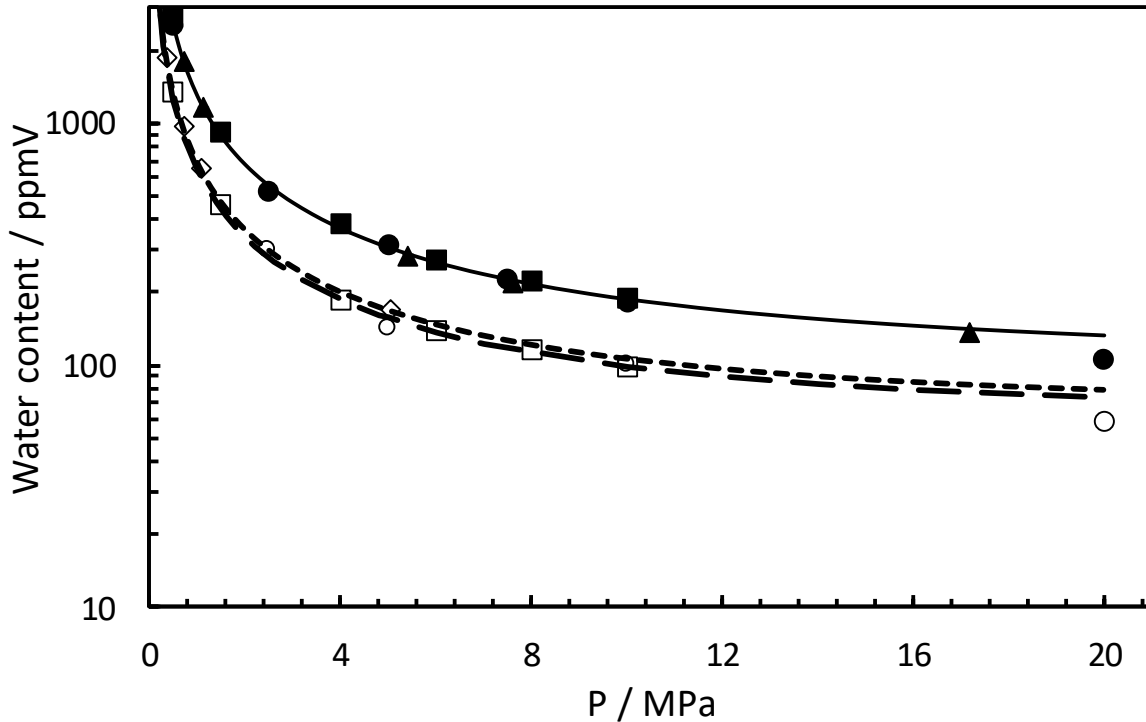
210 Measurements for the frost point of nitrogen equilibrated with water, at different
 211 pressures, were made at 274.1 and 283.1 K. The water contents calculated from the frost
 212 point temperature at atmospheric pressure are given in **Table 4** and plotted along with
 213 literature data and predicted values in **Figure 3**. As can be seen, for the data and predictions
 214 at 283.1K, there is a good agreement between experimental data and model predictions in all
 215 cases apart from the highest pressure value reported by Folas et. al. (2007) [29]. The data
 216 from this work at 274.1K are in good agreement with model predictions, as is the data from
 217 Oelrich et. al (1999) [30] at 273.1 K. This is also the case for the data from Folas et al.
 218 (2007) [29] apart from the highest pressure point. The measurements reported by Folas et al.
 219 were made using Karl Fisher and the differences might be attributed to the lower accuracy of
 220 the method as shown in **Table 1**, more obvious at the higher pressures/lower water contents
 221 when using a log scale on the y axis.

222

223 **Table 4.** Experimental and predicted water contents, in ppmV, for nitrogen in equilibrium
 224 with free water at different P/T conditions.

T / K ±0.1K	P / MPa ±0.03MPa	Water content ppmV Experimental±1%	Water content ppmV predicted
283.1	0.70	1,810	1,807
	1.13	1,165	1,140
	5.43	280	285
	7.62	218	222
	17.20	136	140
274.1	0.36	1,860	1,855
	0.70	965	970
	1.09	650	635
	5.05	170	166

225 Uncertainty of temperature is ±0.1 K, pressure is ±0.03 MPa and water content is ±1% of the
 226 water content in ppmV.



227

228 **Figure 3.** Water content measurements, in ppmV, for nitrogen in equilibrium with free water
 229 at different P/T conditions from this work and literature along with predictions made using
 230 HWPVT. (□): Oellrich and Althaus at 273.1 K[30]; (■): Oellrich and Althaus at 283.1
 231 K[30]; (○): Folas et al. at 273.1 K[29]; (●): Folas et al. at 283.1 K[29]; (◇): This work at
 232 274.1 K; (▲): this work at 283.1 K; (—): Model predictions at 283.1 K; (----): Model
 233 predictions at 274.1 K; (-·-·-): Model predictions at 273.1 K.

234

235

236 6.2. Methane

237

238 Measurements for the frost point of methane equilibrated with hydrates, at different
 239 pressures, were made at 283.1 K. The water contents calculated from the frost point
 240 temperature at atmospheric pressure are given in **Table 5** and plotted in **Figure 4**, along with
 241 literature data, predicted values and measurements made in previous work using a TDLAS
 242 hygrometer. As can be seen there is a good agreement between all the experimental data and
 243 the model predictions. The experimental data has been measured using three different
 244 methods, Karl Fischer [29], TDLAS and the new method hence it gives good confidence in
 245 the results obtained using the new method.

246

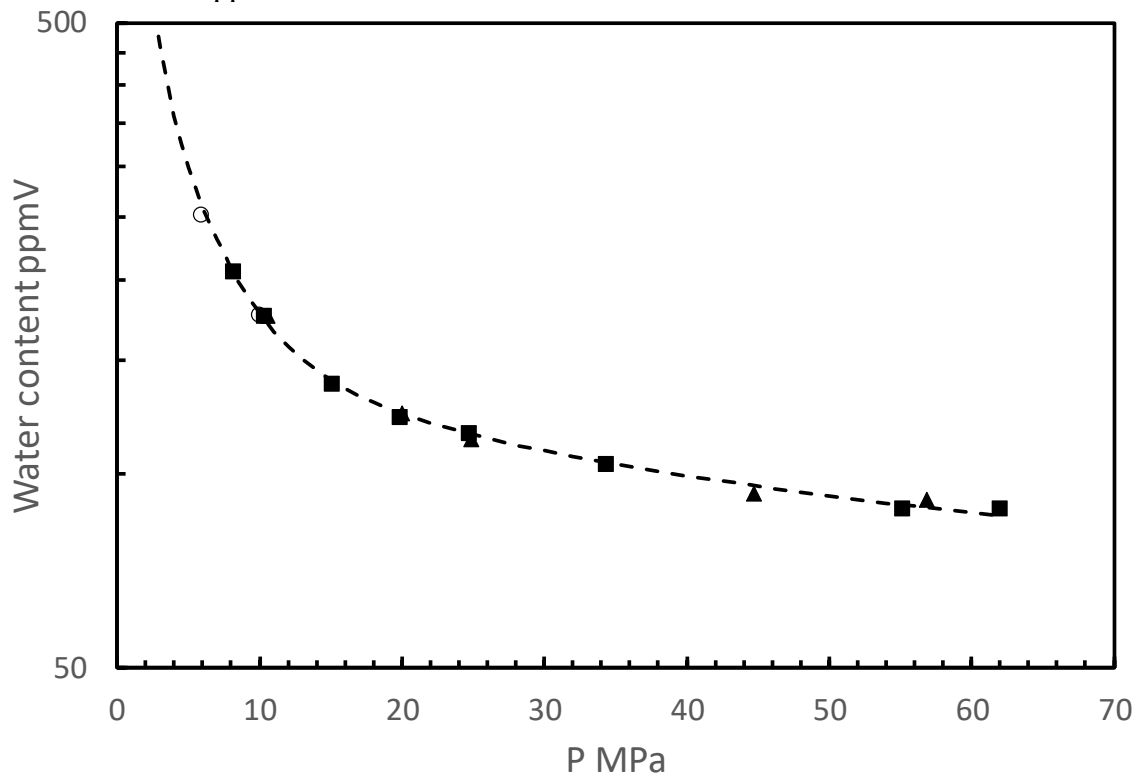
247

248

249 **Table 5.** Experimental and predicted water contents, in ppmV, for methane in equilibrium
 250 with hydrates at 283.1 K(± 0.1 K) at different P conditions.

P / MPa ± 0.03 MPa	Water content ppmV Experimental $\pm 1\%$	Water content ppmV predicted
10.57	176	176
20.04	124	123
24.88	113	115
44.74	93	95
56.84	91	87

251 Uncertainty of temperature is ± 0.1 K, pressure is ± 0.03 MPa and water content is $\pm 1\%$ of the
 252 water content in ppmV.



253 **Figure 4.** Water content measurements, in ppmV, for methane in equilibrium with hydrates at
 254 283.1 K at different pressures from this work, previous work using TDLAS and literature
 255 along with predictions made using HWPVT. (○): Folas et al. [29]; (▲) this work; (■):
 256 previous work using TDLAS; (----): Model predictions.
 257
 258

259 6.2. Natural gas

260

261 Measurements were made for the frost point of natural gas equilibrated with water or
 262 hydrates at different pressures at a temperature of 283.1 K. The water contents calculated
 263 from the frost point temperature at atmospheric pressure are given in **Table 6** and plotted
 264 along with model predictions in **Figure 5** and as can be seen the experimental data is in good
 265 agreement with the model predictions. This again gives good confidence in the data

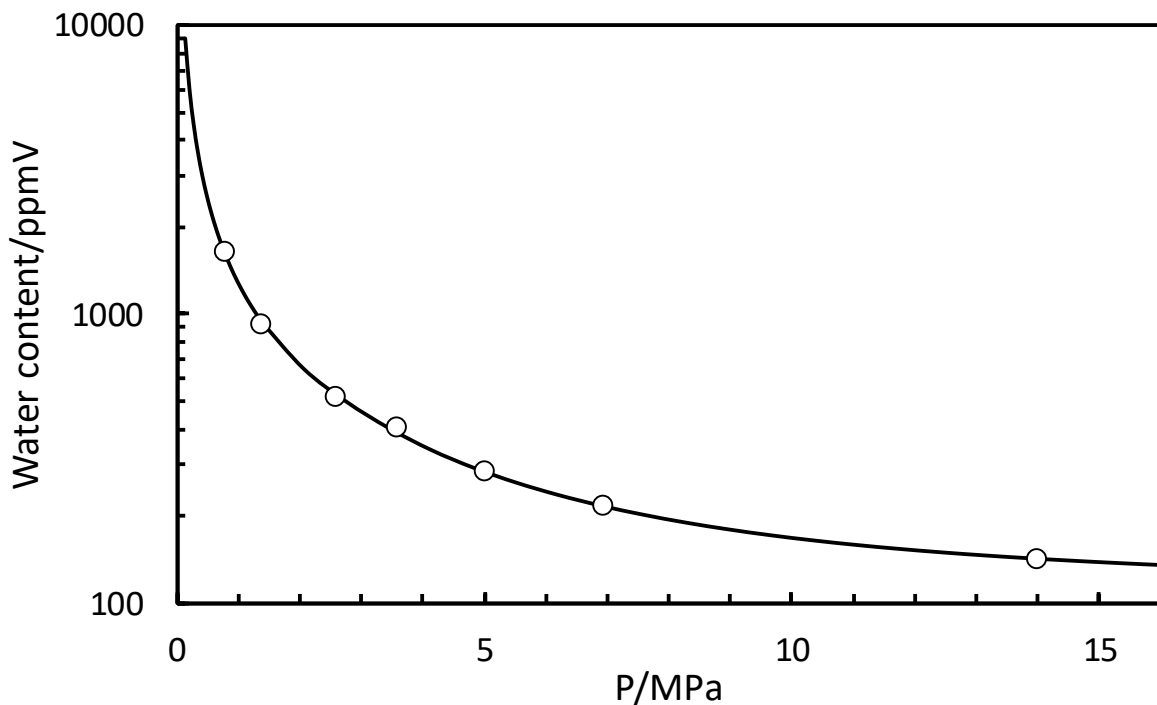
266 generated using the new approach. Although it is not possible at this stage to be totally
 267 confident, the initial results with pure methane, pure nitrogen, a natural gas and a certified
 268 CO₂ standard, appear to indicate that the background gas will have no effect upon the results.
 269 This is as might be expected as the same is the case for the chilled mirror which also makes a
 270 direct measurement of the dew or frost point. As to whether the problems associated with
 271 components other than water causing interference with chilled mirror equipment, also cause
 272 problems with this method will require to be investigated.

273

274 **Table 6.** Experimental and predicted water contents, in ppmV, for natural gas in equilibrium
 275 with free water or hydrates at 283.1 K(±0.1 K).

Phases present	P / MPa ±0.03MPa	Water content ppmV Experimental±1%	Water content ppmV predicted
Vapour / liquid	0.76	1,645	1,662
	1.35	925	957
	2.56	515	530
Vapour / hydrate	3.56	404	389
	5.00	287	284
	6.93	217	216
	13.97	143	142

276 Uncertainty of temperature is ±0.1 K, pressure is ±0.03 MPa and water content is ±1% of the
 277 water content in ppmV.



278

279 **Figure 5.** Water content measurements(○), in ppmV, for natural gas (Table 1) in equilibrium
 280 with free water or hydrate at different pressures at 283.1 K, along with predictions (solid
 281 line) made using HWPVT.

282

283 7. Discussion

284

285 As discussed in the introduction, accurate measurements of the water content of gases are
286 important to give data for validation of thermodynamic models and to monitor levels in
287 different facilities. This enables safe design and operation, avoiding problems such as
288 corrosion and the formation of ice or hydrates. The existing technologies, available for
289 making these measurements, have a number of pros and cons. This paper presents a new
290 approach based upon a simple principle, which may have significant benefits compared to
291 other methods, subject to further investigations, as discussed below.

292

293 The initial results clearly show that data measured using the proposed method are in good
294 agreement with both literature data and model predictions. Further work is required to
295 validate and optimise the method and if successful to develop new equipment. Validation
296 will be required in order to find the range of gases and water contents that can be measured
297 and in addition the effect of contaminants such as alcohols and heavy hydrocarbons. TDLAS
298 hygrometers can have difficulties with variations in background gas composition, because the
299 peak used to detect water content is interfered with by peaks caused by other components.
300 The presence of alcohols and heavy hydrocarbons can cause problems with chilled mirror and
301 capacitance hygrometers.

302

303 Aspects of both the equipment and method require to be optimised. These include
304 parameters such as the length, ID and material of the flow tube. This will involve a series of
305 measurements with different pipes. In addition, the type of moisture indicator requires
306 investigation. So far a capacitance sensor has been used and other options such as a QCM
307 coated with a hygroscopic polymer could be studied. Such QCM sensors may have
308 advantages over capacitance sensors in terms of speed of reaction as discussed by Løkken[1].
309 One important factor, if the method is to be used in commercial equipment, will be how
310 quickly the measurements can be made. The initial set-up uses a refrigerated circulator to
311 control the tube temperature. More rapid cooling, up to 10 times faster, can be achieved
312 using Peltier elements as used in chilled mirror devices. Optimising control of the pipe
313 temperature combined with the use of a high accuracy thermistor for temperature
314 measurement, also used in chilled mirror devices, will enable faster and more precise

315 measurements. Other factors such as the accuracy/repeatability and costs of both equipment
316 and maintenance need to be evaluated.

317

318 As a capacitance sensor is used to detect changes in water content of the flowing gas it
319 could be argued that the water content reading from a calibrated sensor is sufficient to give an
320 accurate reading. As the stated accuracy of capacitance sensors is generally >1 K (Table 1)
321 and an initial estimate of the accuracy of the proposed procedure is ± 0.1 K, this is a
322 significant improvement. Moreover, it is clear that, as the new method relies on the detection
323 of water content variation, no calibration is required. In addition it could be used as a simple
324 method to calibrate capacitance sensors, a task that is normally required at least once every
325 year. Calibration is not only expensive, requiring units to be removed, but can also lead to
326 significant downtime.

327

328 One advantage of the method is that it can be conducted at high pressure by having the
329 temperature-controlled flow tube situated prior to the heated line and valve, and monitoring
330 water content either at atmospheric pressure after the heated valve or using a high pressure
331 sensor situated after the flow tube. The pressure limitation is dictated by the flow tube
332 specifications, currently 70 MPa is the maximum. In tests not reported here, a high-pressure
333 flow tube was used to measure the dew point of nitrogen equilibrated with water at 283.1 K.
334 As expected, the dew point of the nitrogen was found to be 283.1 K. This shows that, if it is
335 possible to place the temperature-controlled flow tube in line, then there is no requirement to
336 reduce gas pressure as is often necessary, thus avoiding potential problems with changing
337 composition on pressure reduction due to undesired condensation. As the dew/frost point at
338 linepressure is the most important parameter, the ability to conduct a measurement in line
339 will give a clear indication of the condensation temperature, thus providing an early warning
340 device of possible problems with water/ice/hydrates/corrosion etc.

341

342 It is well known that in natural gas pipelines, for systems where the gas has certain water
343 contents, gas hydrates are predicted to form at temperatures higher than the dew/frost point of
344 water hence the system changes from vapour to vapour/hydrate. If the amount of hydrate
345 increases significantly over time this will lead to pipeline restriction and in the worst-case
346 blockage. This transition can be measured using the proposed method because the formation
347 of hydrates will result in a reduction in the water content of the gas as it passes through the
348 flow tube at temperatures inside the hydrate stability zone. Heating the flow tube to melt the

349 hydrates will also give an accurate hydrate dissociation point that, being a point of
350 thermodynamic equilibrium, can be used to validate predictions from a thermodynamic
351 model.

352

353 8. Conclusions

354 This paper presents a new approach to measurement of water dew/frost point in gases.
355 Experimental measurements have been made, using a prototype set-up, for nitrogen, methane
356 and natural gas. The results are in good agreement with both literature data and model
357 predictions thus validating the new method. The estimated accuracy of this method (± 0.1 K)
358 is equivalent to chilled mirror hygrometers, which are currently considered to be the most
359 reliable devices for water dew/frost point measurements. Subject to further extensive
360 validation and optimisation of the method and equipment, the new approach may have
361 important benefits such as:

362

- 363 • High accuracy over a wide range of pressures and temperatures.
- 364 • No effect of gas composition.
- 365 • No requirement for calibration.
- 366 • Measurements of water dew/frost point at pipeline pressure/temperature, removing the
367 requirement to reduce sample pressure, risking potential problems such as
368 condensation and compositional changes.
- 369 • Ability to measure hydrate formation/dissociation where hydrates are predicted to
370 form without the presence of free water/ice.

371

372 9. Acknowledgements

373

374 This work is being conducted in support of projects being supported by Galp Energia,
375 Linde AG, Petrobras, Petronas, Equinor and Total which is gratefully acknowledged.

376 Valderio de Oliveira Cavalcanti Filho acknowledges financial support from Petrobras
377 through his PhD grant.

378

379 10. References

380

381 [1] Løkken, T.V., 2015. Comparison of hygrometers for monitoring of water vapour in
382 natural gas. Thesis for the degree of Philosophiae Doctor Trondheim, January 2015

- 383 Norwegian University of Science and Technology Faculty of Natural Sciences and
384 Technology Department of Chemistry.
- 385 [2] Løkken, T.V., 2012a. Comparison of hygrometers for monitoring of water vapour in
386 natural gas. *Journal of Natural Gas Science and Engineering*, 6: 24-36.
- 387 [3] Løkken, T.V., 2012b. Water vapour monitoring in natural gas in the presence of
388 methanol. *Journal of Natural Gas Science and Engineering*, 7: 7-15.
- 389 [4] Løkken, T.V., 2013. Water vapour measurements in natural gas in the presence of
390 ethylene glycol. *Journal of Natural Gas Science and Engineering*, 12: 13-21.
- 391 [5] Løkken, T.V., Bersås, A., Christensen, K.O., Nygaard, C.F. and Solbraa, E., 2008. Water
392 content of high pressure natural gas: Data, prediction and experience from field,
393 International Gas Research Conference. Curran Associates Inc., Paris.
- 394 [6] J. G. Gallegosa, S. Avilab , R. Benyona, G. McKeogh, A. Stokes, Experimental
395 evaluation of the performance of humidity analyzers in natural gas under industrial
396 conditions, *Journal of Natural Gas Science and Engineering*, 2016, 31, C, 293-304.
- 397 [7] G. Mc Keogh, Moisture Measurement Technologies for Natural Gas.
398 [https://www.bakerhughesds.com/sites/g/files/cozyhq596/files/2019-](https://www.bakerhughesds.com/sites/g/files/cozyhq596/files/2019-05/moisture_measurement_technologies_for_natural_gas_white_paper.pdf)
399 [05/moisture_measurement_technologies_for_natural_gas_white_paper.pdf](https://www.bakerhughesds.com/sites/g/files/cozyhq596/files/2019-05/moisture_measurement_technologies_for_natural_gas_white_paper.pdf) .
- 400 [8] Funke, H.H., Grissom, B.L., McGrew, C.E. and Raynor, M.W., 2003. Techniques for the
401 measurement of trace moisture in high-purity electronic specialty gases. *Rev. Sci.*
402 *Instrum.*, 74(9): 3909-3933.
- 403 [9] Wiederhold, P.R., 2000. The principles of chilled mirror hygrometry. *Sensors*, 17 (7): 46-
404 51.
- 405 [10] McAndrew, J.J. and Boucheron, D., 1992. Moisture analysis in process gas streams.
406 *Solid State Technol.*, 35(2): 52-60.
- 407 [11] ISO, 1993a. ISO 10101-1:1993: Natural gas - Determination of water by the Karl Fischer
408 method - Part 1: Introduction. International Organization for Standardization, Genève.
- 409 [12] ISO, 1993b. ISO 10101-3:1993: Natural gas - Determination of water by the Karl Fischer
410 method - Part 3: Coulometric procedure. International Organization for Standardization,
411 Genève.
- 412 [13] Carr-Brion, K., 1986. Moisture sensors in process control. Elsevier Applied Science
413 publishers, London and New York, 122 pp.
- 414 [14] Wiederhold, P.R., 1997a. Water Vapor Measurement. Marcel Dekker Inc., New York,
415 357 pp.

- 416 [15] Blakemore, C.B., Steichen, J.C., Dallas, G. and Rossum, G.J.v., 1986. Continuous trace
417 moisture analysis. In: G.J.v. Rossum (Editor), *Gas Quality*. Elsevier Science Publishers
418 B.V., Groningen, pp. 327-335.
- 419 [16] McAndrew, J.J.F., 1997. Humidity measurement in gases for semiconductor processing.
420 In: J.D. Hogan (Editor), *Speciality gas analysis: A practical guidebook*. Wiley-VCH,
421 New York, pp. 21-42.
- 422 [17] Lackner, M., 2007. Tunable diode laser absorption spectroscopy (TDLAS) in the process
423 industries – a review. *Reviews in Chemical Engineering*, 23(2): 65-147.
- 424 [18] Rittersma, Z.M., 2002. Recent achievements in miniaturised humidity sensors—a review
425 of transduction techniques. *Sensors and Actuators A: Physical*, 96(2-3): 196.
- 426 [19] A. Chapoy, H. Haghghi, R. Burgass and B. Tohidi, “Gas hydrates in low water content
427 gases: Experimental measurements and modelling using the CPA equation of state” *Fluid
428 Phase Equilib.*, 296, 9-14, 2010.
- 429 [20] L. Zhang, R. Burgass, A. Chapoy and B. Tohidi, “Measurement and modelling of water
430 content in low temperature hydrate-methane and hydrate-natural gas systems”, *J. Chem.
431 Eng. Data* 56, 2932–2935, 2011.
- 432 [21] R. Burgass, A. Chapoy, B. Tohidi, *Experimental And Modelling Low Temperature
433 Water Content In Multicomponent Gas Mixtures*, 7th International Gas Hydrate
434 Conference (ICGH 2011), Edinburgh, Scotland, UK, July 17-21, 2011.
- 435 [22] H. Haghghi, A. Chapoy, R. Burgass, B. Tohidi, *On The Phase Behaviour Of The Carbon
436 Dioxide - Water Systems At Low Temperatures*, 7th International Gas Hydrate
437 Conference (ICGH 2011), Edinburgh, Scotland, UK, July 17-21, 2011.
- 438 [23] R. Burgass, A. Chapoy, P. Duchet-Suchaux, B. Tohidi, *Experimental Water Content
439 Measurements of Carbon Dioxide in Equilibrium with Hydrates at 223.15 to 263.15 K
440 and 1.0 to 10.0 MPa*, *The Journal of Chemical Thermodynamics*, Volume 69, February
441 2014.
- 442 [24] R. Burgass, A. Chapoy, B. Tohidi, *Solid-Liquid Equilibrium in Water-Glycol Systems:
443 Measurements and Modelling*, 8th International Conference on Gas Hydrates, 2014.
- 444 [25] L. V. Jaspersen, J. Won Kang, C. S. Lee, D. Macklin, P. M. Mathias, R. J. McDougal,
445 W. Gu Rho, and D. Von Niederhausen, *Experimental Determination of the Equilibrium
446 Water Content of CO₂ at High Pressure and Low Temperature*, Published as part of *The
447 Journal of Chemical and Engineering Data* special issue “Proceedings of the 19th
448 Symposium on Thermophysical Properties” 2015.

- 449 [26] J.H. van der Waals, J.C. Platteeuw. Clathrate Solutions, Adv. Chem. Phys. 2 (1959) 2-
450 57.
- 451 [27] W.R. Parrish, J.M. Prausnitz. Dissociation Pressures of Gas Hydrates Formed by Gas
452 Mixtures Ind. Eng. Chem. Process. Des. Develop. 11 (1972) 26-34.
- 453 [28] A. Chapoy, H. Haghghi, R. Burgass, B. Tohidi, Journal of Chemical Thermodynamics
454 47 (2012) 6-12.
- 455 [29] G.K. Folas, E.W. Froyna, J. Lovland, G.M. Kontogeorgis, and E. Solbraa, 2007. Data and
456 prediction of water content of high pressure nitrogen, methane and natural gas. Fluid Phase
457 Equilib., 252(1-2): 162-174.
- 458 [30] L. R., Oellrich, K. Althaus, 1999. Messung und Berechnung von Wassergehalten
459 kohlenwasserstoffhaltiger Gasgemische. Fortschritt-Berichte VDI, Row 3, no. 590. VDI Verlag
460 GmbH, Düsseldorf, 193 pp.
- 461
- 462
- 463