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Corresponding Author: Mr. Jaime Garcia Gallegos,

Corresponding Author's Institution: INTA

First Author: Jaime Garcia Gallegos

Order of Authors: Jaime Garcia Gallegos; Robert Benyon Puig, Dr.; Susana Avila Calzada, Dr.; Angel M Benito, Dr.; Roberto Gavioso, Dr.; Helmut Mitter, Dr.; Stephanie Bell, Dr.; Norbert Boese, Dr.; Volker Ebert, Dr.; Hannu Sairanen; Martti Heinonen, Dr.; Andrea Peruzzi, Dr.; Mark Stevens; Rien Bosma; Miroslava Vaľková

Abstract: Moisture content is a key factor regardless of the activity carried out inside the natural gas industry (production, processing, transmission, etc.). Not only does the efficiency of the final product, known as heating value, decrease when the water content is high, but it can also trigger potentially dangerous conditions due to the formation of hydrates, that can block pipelines and damage pumping devices and produce other negative effects. For these reasons, accurate measurement and control of humidity is absolutely essential. However, current practice for such moisture measurements is for the devices to be calibrated at atmospheric pressure and in nitrogen or air as the matrix gas, conditions that vary significantly from those present in the actual industrial process. For that, eleven hygrometers based on different measurement principles (chilled-mirror, electrolytic sensor, a spectroscopic analyzer, polymeric and metal oxide humidity sensors) have been compared at facilities of the main carrier of natural gas in Spain, using natural gas at absolute pressures between 0.1 MPa and 6 MPa, and for a range of water content from 13 ppmv to 250 ppmv. Their relative performance is described in terms of the response times, long term stability, hysteresis and behaviour under large pressure changes. Most instruments, exceptions are detailed in the article, show good behaviour regarding response time, hysteresis and under sudden pressure changes. In contrast, drift can be identified in most of the aluminium oxide probes tested.

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An investigation of the comparative performance of diverse humidity sensing techniques in natural gas

J. G. Gallegos[a, *], R. Benyon[a], S. Avila[b], A. Benito[b], R. M. Gavioso[c], H. Mitter[d], S. Bell[e], M. Stevens[f], N. Böse[g], V. Ebert[g], M. Heinonen[h], H. Sairanen[h], A. Peruzzi[i], R. Bosma[i], M. Val'ková[j]

[a] *INTA - Instituto Nacional de Técnica Aeroespacial, Madrid. Spain*

[b] *ENAGÁS, S.A., Zaragoza. Spain*

[c] *INRiM-Istituto Nazionale di Ricerca Metrologica, Torino. Italy*

[d] *E+E - E+E Elektronik,* Engerwitzdorf. *Austria*

[e] *NPL - National Physical Laboratory, Teddington. United Kingdom.*

[f] *UKAS – United Kingdom Accreditation Service. Feltham. United Kingdom.*

[g] *PTB - Physikalisch-Technische Bundesanstalt,* Braunschweig. *Germany*

[h] *MIKES - Mittatekniikan Keskus, Espoo. Finland*

[i] *VSL - Van Swinden Laboratory, Delft. Netherlands*

[j] *SMU - Slovenský Metrologický Ustav,* Bratislava *Slovakia*

Correspoding author. *Tel.:* +34 915 201 714. *Fax:* +34 915 201 645.

Email adresses: garciagaj@inta.es

Abstract

Moisture content is a key factor regardless of the activity carried out inside the natural gas industry (production, processing, transmission, etc.). Not only does the efficiency of the final product, known as heating value, decrease when the water content is high, but it can also trigger potentially dangerous conditions due to the formation of hydrates, that can block pipelines and damage pumping devices and produce other negative effects. For these reasons, accurate measurement and control of humidity is absolutely essential. However, current practice for such moisture measurements is for the devices to be calibrated at atmospheric pressure and in nitrogen or air as the matrix gas, conditions that vary significantly from those present in the actual industrial process. For that, eleven hygrometers based on different measurement principles (chilled-mirror, electrolytic sensor, a spectroscopic analyzer, polymeric and metal oxide humidity sensors) have been compared at facilities of the main carrier of natural gas in Spain, using natural gas at absolute pressures between 0.1 MPa and 6 MPa, and for a range of water content from 13 ppm_v to 250 ppm_v. Their relative performance is described in terms of the response times, long term stability, hysteresis and behaviour under large pressure changes. Most instruments, exceptions are detailed in the article, show good behaviour regarding response time, hysteresis and under sudden pressure changes. In contrast, drift can be identified in most of the aluminium oxide probes tested.

Keywords: comparison, hygrometer, natural gas, dew point, humidity, pressure.

1 Introduction

Several physical chemical properties, such as condensation behaviour, are critical to the efficient and safe use of energy gases, such as natural gas (NG). Humidity is a key parameter that must be monitored with high accuracy during several important operations in any gas processing activity: regasification of liquefied natural gas (LNG), dehydratation, contractual obligations in international exchanges, pumping stations, etc. (Mokhatab et al, 2006; Carroll, J., 2009).Water vapor can combine with other trace contaminants in the gas stream, namely H_2S and CO_2, and form potentially corrosive acids in the pipeline. This phenomenon must be avoided not just for safety reasons, but also to minimise pumping costs due to load losses in the national supply grids and to avoid drastic decreases in the life expectancy of the pipeline and its components (Sloan, 1998; Ávila, 1999; Mychajliw, 2002; Sloan et al., 2011).

The measurement of the moisture in natural gas can be achieved in many ways and expressed in different units that are linked by not always well defined complex factors that vary with pressure, temperature and gas composition. Depending on the sensing technologies employed it is often necessary to use pressure-reducing sampling lines, that together with the currently available conversion factors can lead to significant variations in the measured water dew-point.

As the water dew point is dependent of the gas composition, temperature and pressure, substantial extrapolations need be made. These extrapolations may well lead to deviations in the water dew point temperature of up to 10 °C (Panneman, 2009), where an accuracy of 1 °C to 3 °C is actually desired. Alternatively pressure-reducing sampling lines are applied when using humidity analysers based on detecting water vapour condensation or optical spectroscopy because they can only operate at low pressure. As a result of the effects of heat transfer, condensation and the optical properties of gases, on-site conditions may significantly affect the measurement results obtained with these types of instruments.

Metrology can play an important role in providing support in order to overcome some of the current challenges of this energy sector by avoiding inaccurate water vapour monitoring in order to maximise the performance of its processes, and in particular of non-renewable resources (Bell et al., 2008).

Lastly, another reason is the need to establish standards accepted by the producers, distributors and consumers that allow the easy, precise and reliable determination of humidity in natural gas, and thus really know the quality of the product. The current specifications that are to be met in the transmission of natural gas within Europe have been defined by the European Association for the Streamlining of Energy Exchange - gas (EASEE-gas) (EASEE-gas, 2005). In the case of hydrocarbon dew point (HCDP) it must be lower than -2 ºC at any pressure between 0.1 MPa to 7 MPa. For water dew point (WDP) it must be lower than -8 ºC at 7 MPa.

The work reported in this paper was performed in Zaragoza, at the central laboratory of ENAGAS, S.A., the technical manager of the Spanish gas system and main transmission system operator of natural gas in Spain. The temperature and pressure conditions of the sampled gas that was measured were approximately 22 ºC and maximum pressure of 6 MPa. During the measurements, the water vapour content expressed as a volumetric fraction, x_w, was in the range from 4 ppm_v to 8 ppm_v. These values are very close to the lower detection limits of the majority of the instruments compared, indicating that the gas transported is much drier than required by the EASEE-gas specification. Therefore, in order that this work covered a range of interest not just of the distributors of gas but also of the manufacturers of humidity analyzers and sensors for use in natural gas, a humidification system was constructed to provide different nominal moisture concentrations. This consisted of a simple flow-mixing generator that covered the range from 13 ppm_v to 250 ppm_v, integrated into a test rig sampling from the transmission pipeline.

A total of eleven instruments from five manufacturers based on five different measurement principles have been compared. Some are widely known and implemented in industry and others are of innovative design. The measurement technologies covered are: a condensation hygrometer, a spectroscopic analyzer, an electrolytic phosphorus pentoxide (P_2O_5) analyzer, a polymer sensor and several aluminium oxide (Al_2O_3) sensors. In addition to this, the HCDP was also monitored using three industrial condensation hygrometers. Finally, a limited number of experimental tests were conducted at 0.75 MPa, for natural gas samples humidified at volume water fractions between 140 ppm_v and 250 ppm_v, using a microwave quasi-spherical resonator realized at INRiM (Gavioso et al., 2014).

The hysteresis, response time, short-term drift and the influence of line pressure have been evaluated. (Løkken T.V, 2012) The tests performed address the relative performance of the instruments at the variable, pressure, temperature and gas composition of the inlet gas, consistent with a real industrial process. During the measurements, the hydrocarbon dew point was also monitored using an industrial analyzer, because of its potential influence about the hygrometers based on codensation techonolgy, like the chilled mirror, which has been proved several times in published literature. (Ávila, 1999; George D. L et el., 2005; Herring J., 2011; Galatro D. and Marín-Cordero F, 2014).

The experimental set-up, the instruments compared and the main parameters of the sampled gas are detailed in section 2. The results obtained are presented and discussed in section 3. Finally, the conclusions reached are presented in section 4 with suggestions for future work.

2 Experimental set-up

The test rig was designed in order to be able to perform all the measurements in one system, needing only to modify the valve configuration in order to control the pressure, flow-rate and direction of flow of the natural gas sample. All the components of the sampling system in contact with the gas are high-quality electro-polished stainless steel and polytetrafluoroethylene (PTFE) in the sampling system and the low-pressure vents, respectively.

Table 1 Details of instruments that have taken part in the tests

DEVICES	MANUFACTURER
Condumax II HCDP Condumax II WDP Easidew PRO Easidew transmitter	Michell Instruments Ltd.
Aurora Hygro PRO	General Electric Company
Accupoint LP 2	Meeco
DP Transmitter SDT Hygrometer sensor type ISI	Shaw
Apha Moisture	Alpha
EE371	E+E Elektronik

Table 1 lists all the instruments that have taken part in the comparison. The purpose of this work is to evaluate the relative performance of the instruments with a focus on the measurement principle involved. Therefore, in the presentation of the results obtained, a code (see table 2) is used to identify the devices.

Table 2 Summary of designations used in this work to compare the measured instruments in relation to the sensor technology.

TECHNOLOGY	INSTRUMENT CODE	
	WDP	HCDP
Al_2O_3	C, D, E, F, G, H, J, K1	
Chilled mirror		K2
Spectroscopic	A	
Electrolytic P_2O_5	B	
Polymer	I	

Due to the maximum allowable working pressure for certain instruments, these were divided into three groups: high, medium and low pressure. Figure 1 depicts the three levels: (a) maximum line pressure (≈ 5.8 MPa), intermediate pressure (2.8 MPa) and low pressure (0.55 MPa). The low-pressure line supplied the

spectroscopic and electrolytic (P_2O_5) analyzers. Two instruments were limited to intermediate pressures, whilst the rest were taken up to the full line pressure.

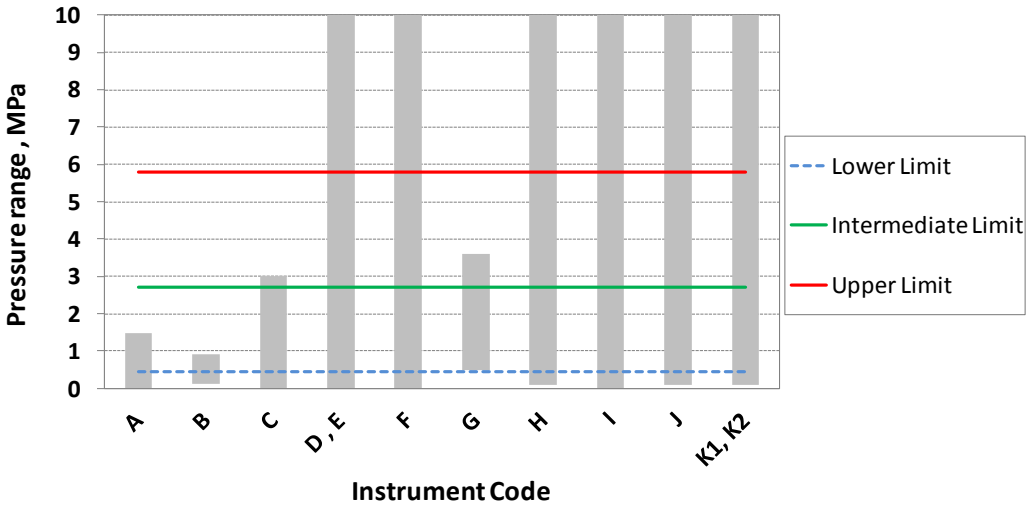


Fig. 1 Summary of pressure ranges of analyzed sensors showing the chosen pressure level.

Depending on the type of instrument, the measured humidity was expressed either as x_w or WDP (Oellrich, and Althaus, 2001). Therefore, in order to facilitate the comparison, all the values have been expressed as WDP, applying the conversions given in the ISO standard developed from the work done by the European Gas Research Group (GERG) (ISO, 2005).

2.1 Description of the test setup

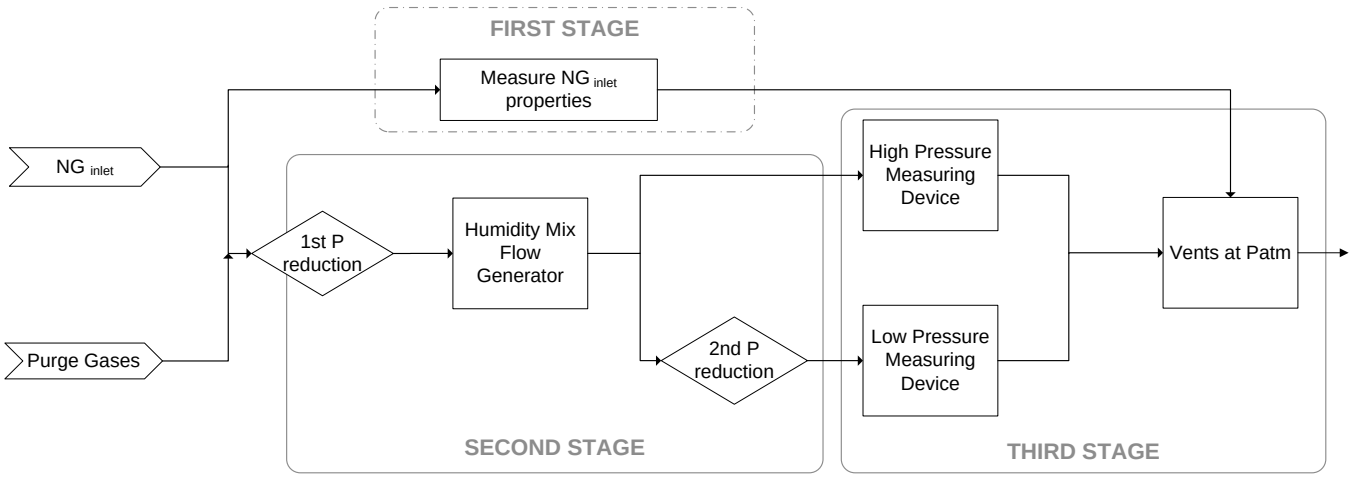


Fig. 2 Schematic block diagram of the test setup (NG denotes natural gas).

The test rig is divided into three stages as follows (see Fig. 2):

(a) The first stage: used to monitor the inlet HCDP, WDP, pressure and temperature.

(b) The second stage: solids and liquids present in the gas stream are filtered and the gas is regulated with a heated regulator from the full line pressure to 2.8 MPa. The gas is then fed to a simple flow-

mixing generator (details in Fig. 3). The output of the generator is divided into two streams, one of which is further regulated using a high-purity gas regulator set to 0.55 MPa and then supplied to the third stage.

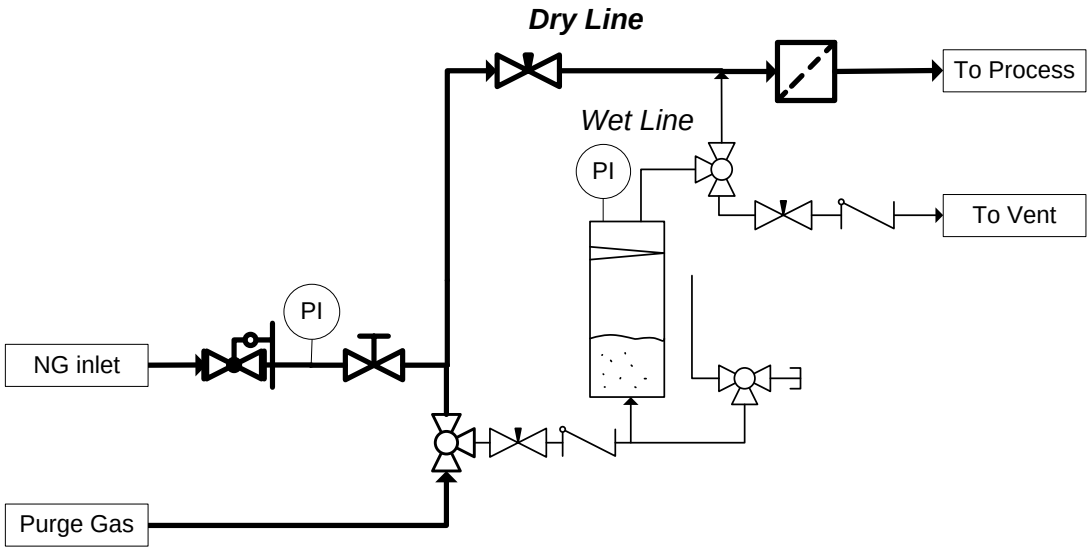


Fig. 3 Schematic of first step of pressure reduction and flow-mixing generator necessary to control gas conditions. This configuration allows the humidification of the gas, saturator filling and purging of this section of the test rig.

(c) The third stage: This has two groups of instruments at nominal line pressures of 2.8 MPa and 0.55 MPa. In compliance with the recognized good practice applicable to the installation of pressurized natural gas sampling systems (George and Burkey, 2008; ISO, 1997a,b) any line incorporating a sensor must have the following components: a pressure control system and isolation valve at the inlet, and a pressure reduction valve to pressure close to atmospheric, a flow controller and non-return valve. These were installed in this order and replicated for all the instrument outputs.

All the control and monitoring devices used to record the process variables (e.g. gauge pressure transmitters, barometric pressure sensors, flow meters, platinum resistance thermometers, data loggers, etc.) were calibrated at INTA prior to installation and the necessary corrections applied in the subsequent data analysis. Figure 4 shows the complete test rig as finally implemented.



(a)



(b)

Fig. 4 Photograph of the test rig: (a) On the left, the two low-pressure devices (spectroscopic and electrolytic P_2O_5), can be seen at the back and centre with the two chilled mirror instruments at the front. The rest of the sensors are connected behind these. (b) On the top left is the data acquisition system and the electronic displays and power supplies of the different analyzers and just below is the control panel with the three sampling lines. On the right is the instrument used to monitor the gas inlet conditions (HCDP and WDP).

2.2 Inlet gas conditions

In order to perform the necessary unit conversions to WDP (ISO, 2005), it is necessary to know the gas composition. The ENAGAS central laboratory provided the results of the gas composition analysis on a daily basis throughout the test period and chemical analysis was performed using gas chromatography (GC), providing the content of N_2, CO_2 and hydrocarbons from methane up to fraction C_{12}.

This was essential because the gas sampled from the main transmission pipeline is not a reference mixture of known and stable composition, but a system under continuous change depending on the demand and origin of the gas transported. In order to monitor the HCDP and WDP conditions of the sampled gas, a suitable instrument was employed to obtain a continuous record of the variations in order to assist in the subsequent interpretation of the results obtained during the tests. Figure 5 shows the WDP and HCDP at their respective pressures during the test period. As can be seen, the values are well below the upper limits specified by EASEE-gas, but continous variations of both signals complicate generate steady and perfectly known humidity levels.

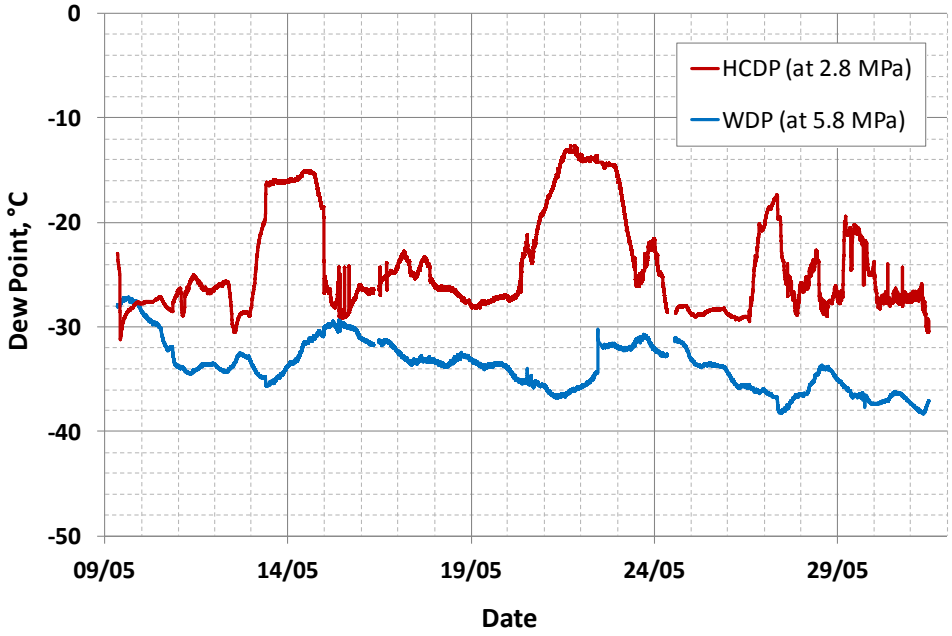


Fig. 5 Summary data of HCDP and WDP from feed of natural gas during the test period.

2.3 Tests performed

Throughout the experimental period, numerous measurements were performed modifying only two parameters: the moisture content of the gas and the sample pressure. Other parameters such as the dependence on the gas temperature or flow-rate through the sensors were not evaluated as such but were set in order not to affect the results. The gas flow through each sensor was maintained constant and within the individual instrument specifications. As regards temperature, the pressure regulators were heated as required to avoid condensation and the gas temperature was kept close to the laboratory ambient temperature.

2.3.1 Response time tests

Instrument response to step changes in the humidity of the sampled gas was evaluated in order to determine the stabilization times. Six step changes in increasing and decreasing order of humidity were performed: (13/30, 30/100, 13/250, 30/250, 100/250 and 200/250) ppm_v. The results were normalized to the initial and final steady state values for each instrument. The response time was determined by fitting to Eq. 1 (Benyon et al, 2012) that represents the humidity signal as a function of time, $\Delta H(t)$:

$$\Delta H(t) = \left(1 - e^{-t/\tau}\right)\Delta H_F \qquad (1)$$

Where ΔH_F is the final steady state humidity level and knowing that for $t = \tau$ a value of 63.2% of the step is reached and that for $t = 5\tau$ a value of 90% us obtained. The value of, $t = 0$ was taken as the instant that instrument A detected a change in signal, as in general it was the first to detect the change in humidity content of the gas.

2.3.2 Evaluation of drift

During the whole test period, the analyzers were measured on several occasions at nominal humidity levels of (13, 30, 70, 100 and 250) ppm_v. Their behaviour throughout the test period was evaluated comparing the results with respect to the three measurement technologies, each represented by one instrument: A, B and G for spectroscopic, electrolytic and Al_2O_3 technologies, respectively.

2.3.3 Hysteresis studies

A series of measurements was performed for increasing and decreasing levels of humidity at nominal values of (30, 55, 70, 85, 100 and 160) ppm_v. The line pressure was maintained constant at 2.8 MPa and 0.55 MPa in each of the sampling lines.

2.3.4 Response to pressure changes

The response to pressure changes was evaluated at a constant humidity level of 100 ppm_v after subjecting those instruments with the permissible operating pressure range, to the maximum line pressure (5.8 MPa) for four days. The effect is expressed as the difference between corrections of readings obtained at a pressure of 2.8 MPa, before and after subjecting the instruments to the high-pressure soak, taking instrument A as a reference.

3 Results and discussion

3.1 Environmental conditions

The temperature and relative humidity of the laboratory during the period of the measurements was continuously recorded using a calibrated temperature and relative humidity data logger. The results obtained are summarized in Table 3. WDP and HCDP were well below the upper limits specified by EASEE-gas.

Table 3 Summary of laboratory environmental conditions during the compete test period.

	Relative humidity, % rh	Temperature, °C
Maximum	57.6	26.2
Minimum	25.1	19.9
Average	37.4	22.9

3.2 Gas composition

In order to facilitate data analysis, especially the humidity conversions, it was decided to use the actual gas composition obtained on one day and apply this to all the data conversions. The values used are representative of the whole period as only small composition changes were detected and the variation is negligible in terms of the humidity conversions in the context of evaluation of the relative performance of the instruments at any given time. The gas composition used is shown in Table 4, where the molar fraction of each of the groups analyzed is represented in a simplified manner, whereas the gas chromatography analysis is much more complex as it detects the composition of a large number of chemical species that have been encompassed into the groups with more than four carbon atoms.

Table 4 Gas composition used as a reference for the conversion of humidity units in natural gas.

Gas composition analysis, % mol/mol			
N_2	0.846	n-C_4	0.313
CO_2	0.15	neo-C_5	0
C_1	90.576	i-C_5	0.047
C_2	6.468	n-C_5	0.043
C_3	1.293	C_{6+}	0.047
i-C_4	0.217		

3.3 Response time tests

The response time tests were compared using a common data acquisition system that ensured that the readings of the instrument analogue outputs were highly correlated and reduced the influence of any possible drift at the multimeter used. Figure 6 shows an example of all the result obtained for the changes in humidity specified in section 2.3.

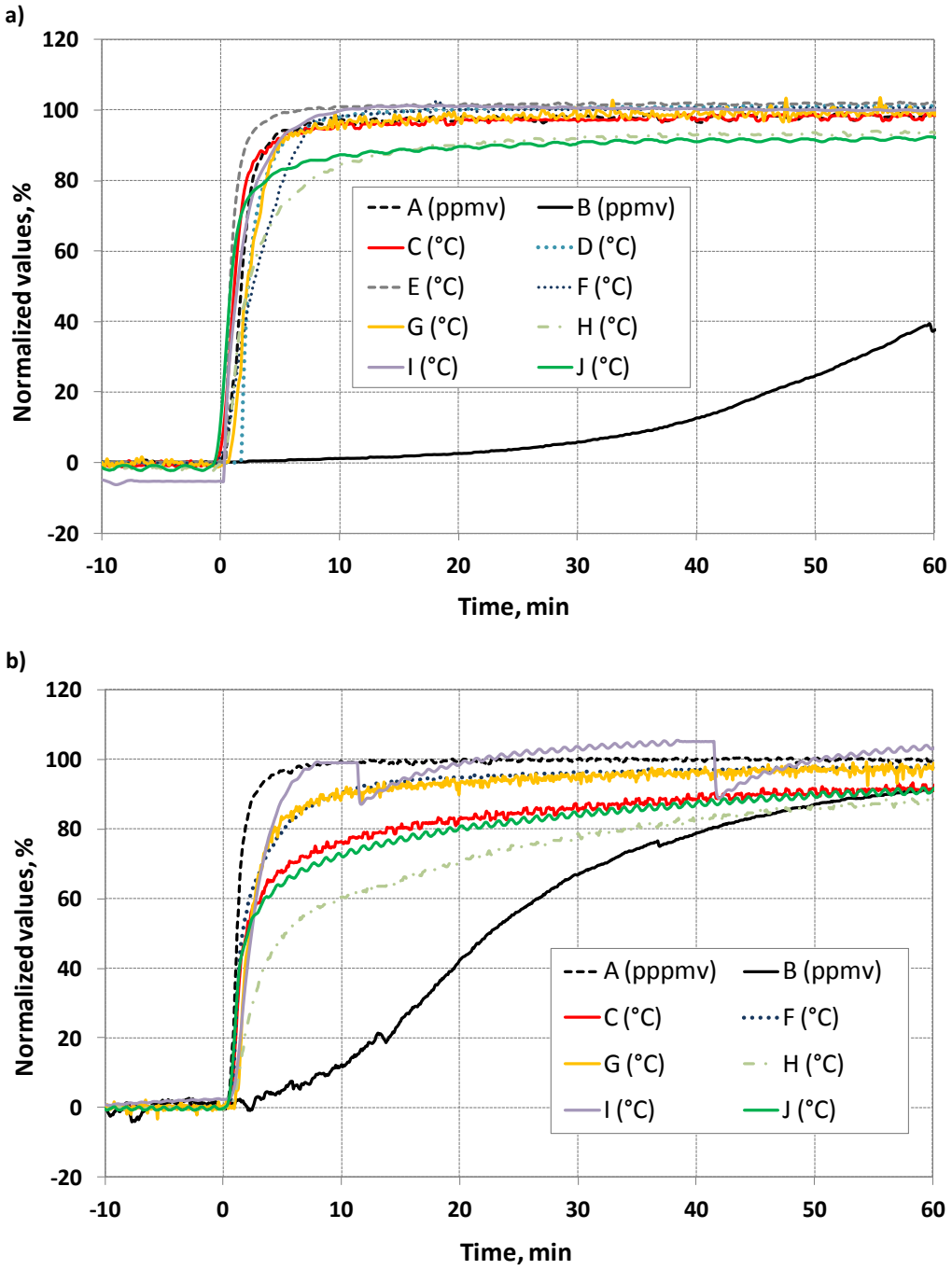


Fig. 6 Example of the comparative study of the response times of instruments for the same step change from (30 to 250) ppm_v. (a) Increasing humidity. (b) Decreasing humidity.

Comparing both graphs in Fig. 6 it is immediately apparent that most instruments rapidly detect the change in the humidity level of the gas, independently of how long they take to reach the final steady state value. It can also be seen that upon increasing the gas humidity, in the most critical situation depicted in Fig. 6a a larger percentage of the final stable value is reached, compared to the case of a drying process (Fig. 6.b) where the response is more gradual, possibly due to the desorption effects in the sampling line. The figures also show that the behaviour of instrument pairs C / J and D / E, are identical, as they expected for the same sensor models.

From both graphs shown in Fig. 6 it is apparent that the electrolytic sensor, B, is significantly slower than the rest. This cannot be attributed to the sampling system as even though the gas flow-rate through the cell is

low (0.1 L/min), the instrument has a bypass flow of 1 L/min, consistent with the flow rates in other sensors in the system. All instruments were tested in the "as received" condition. This instrument had been used extensively for up to two years for other evaluations in air/N_2 and methane by other partners in the project prior to the tests reported, without the performance of any specific maintenance. Figure 6.b) also shows that the instruments based on Al_2O_3 technology behave in a more heterogeneous manner for decreasing water content in the gas. The graphs also show the thermal regeneration cycles of the polymer sensor, instrument I, that occur approximately every 30 min.

Table 5 shows a summary of the complete response time tests performed in this study. The results show that the electrolytic analyzer, B, is the slowest in all the steps tested with a range of response times from 30 min to close to 120 min. In contrast, some of the aluminium oxide sensors such as instruments D, E and G are the fastest with response time of less than 5 min. The spectroscopic, polymer and rest of aluminium oxide sensors exhibit a very similar behaviour and are slightly slower to respond than the fastest. These summary conclusions are in agreement with the findings of Løkken, 2012.

Table 5 Summary of the response times of all instruments to increasing and decreasing humidity levels. The sampling interval used was 5 s. "—"indicates that instrument readings lie outside the programmed range of the indicator.

STEP, ppm_v		Time, s	A	B	C	D	E	F	G	H	I	J
Increase	13 - 30	τ (63.2%)	160	1715	100	—	—	280	75	195	60	110
		5τ (90.0%)	325	5290	495	—	—	755	270	1275	175	825
Decrease		τ (63.2%)	125	1720	265	—	—	475	165	400	255	445
		5τ (90.0%)	425	3535	2195	—	—	1215	770	2055	780	2610
Increase	30 - 100	τ (63.2%)	70	1910	40	30	15	105	40	50	85	50
		5τ (90.0%)	110	2955	195	90	50	285	105	405	95	710
Decrease		τ (63.2%)	85	1735	95	25	20	145	60	980	265	130
		5τ (90.0%)	135	3360	3255	30	20	540	95	3600	455	3160
Increase	13 - 250	τ (63.2%)	55	1900	45	30	10	85	50	55	50	45
		5τ (90.0%)	120	2690	205	120	55	175	105	250	140	535
Decrease		τ (63.2%)	95	1645	970	75	40	625	300	2105	260	1685
		5τ (90.0%)	235	4735	31870	85	45	35625	15890	38960	1090	35075
Increase	30 - 250	τ (63.2%)	50	1965	40	20	10	90	60	75	45	35
		5τ (90.0%)	95	2670	110	80	40	160	110	470	110	550
Decrease		τ (63.2%)	85	1530	185	100	50	110	105	665	165	230
		5τ (90.0%)	160	3255	2400	115	60	520	490	3895	275	2880
Increase	100 - 250	τ (63.2%)	60	840	65	40	20	60	40	95	105	55
		5τ (90.0%)	80	1515	3075	100	50	170	145	685	205	2635
Decrease		τ (63.2%)	75	1460	45	90	50	40	50	<5	145	55
		5τ (90.0%)	115	2120	375	260	145	140	155	695	245	1360
Increase	200 - 250	τ (63.2%)	395	20	40	25	<5	35	<5	70	355	35
		5τ (90.0%)	1180	80	125	85	105	50	200	270	730	550
Decrease		τ (63.2%)	720	15	40	45	45	<5	<5	10	95	230
		5τ (90.0%)	985	675	135	170	95	295	630	5420	365	2880

3.4 Evaluation of drift

In order to evaluate the stability of the instruments during the period of the measurements (21 days), the drift of the instruments at a number of nominal humidity levels was determined with respect to one of the instruments. As explained in section 2.3.2, the study was performed considering three instruments. Due to the similarity of results in all cases, this report was simplified to facilitate comprehension and limited to the spectroscopic case. For this instrument, the reference WDP was calculated from the readings of water content, converted to WDP units using the actual absolute pressure at each instant the standard gas composition given in Table 4.

The calculated correction, *c*, for each reading, *j*, is obtained as follows:

$$c(j) = r(j) - i(j) \tag{2}$$

Where *r* and *i* are the readings of the reference device and instrument, respectively. Thus, a positive correction indicates that the instrument reads drier than the reference device, A. Figure 7 shows all corrected values of WDP versus reference WDP generated for every humidity sensors.

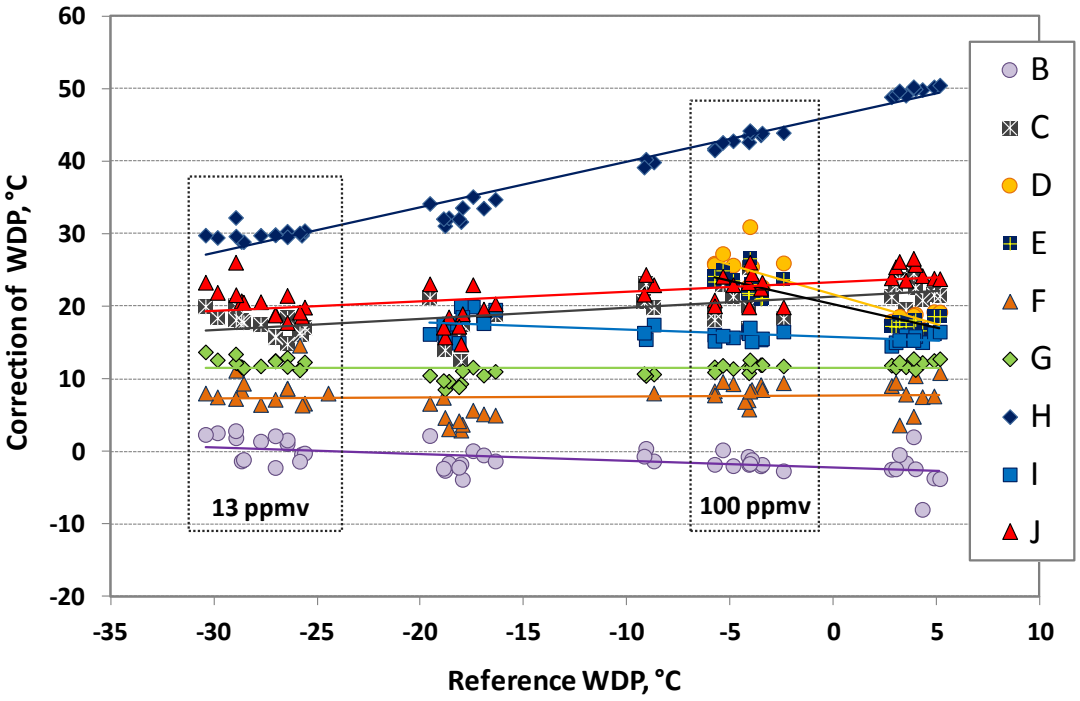


Fig. 7 Instrument corrections with respect spectroscopic device for five humidity levels generated.

The first thing that becomes apparent when looking at Fig. 7 and Fig. 8 is the large dispersion of the reported corrections. For example between the extreme values it is up to 50 ºC at a concentration of 100 ppm_v and nearly 30 ºC at 13 ppm_v. This effect has been observed throughout the study.

Secondly, the horizontal axis shows the ability to reproduce different humidity levels. For each humidity level there is a scatter in generated WDP attributable to the variations in the composition, water content and pressure of the natural gas at the inlet and thus in the final water content in the generated stream. Its effect

on the analysis of the relative performance of the instrument can be minimized by comparing the instrument corrections at each nominal point.

As in the previous study, the behaviour of those instruments which have the same model of measuring sensor is identical throughout the work. This is substantiated in in Fig. 7 for the pairs of series D/E and C/J. Another phenomenon perceived is that most of the instrument corrections have a shift close to their claimed uncertainty in whole range investigated, implying that they are not affected by the humidity level, with the exception of the aluminium oxide probes D, E and H, in which corrections clearly vary with the humidity level.

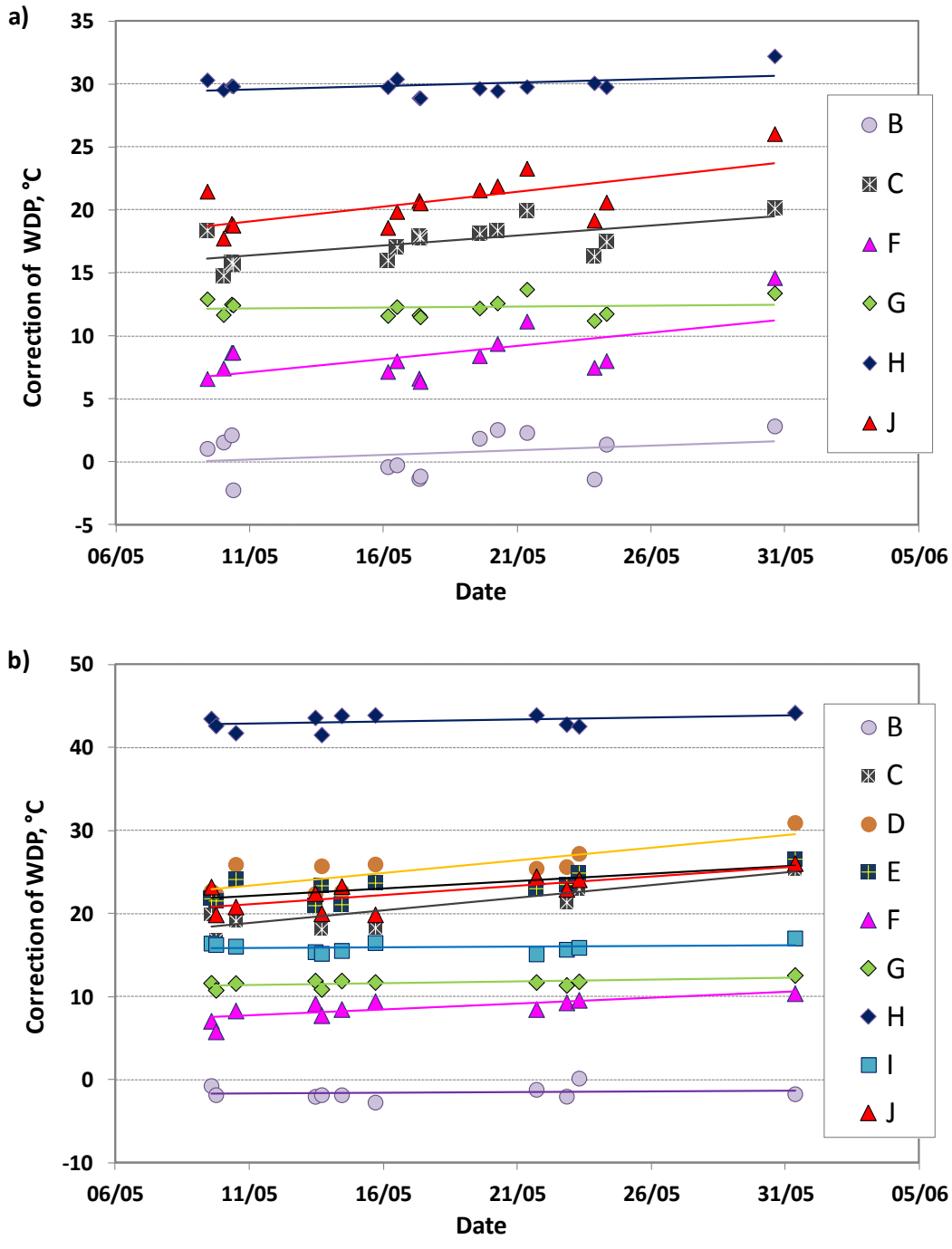


Fig. 8 Drift of corrections of all devices taking spectroscopic instrument as a reference. (a) For a nominal water content of 13ppm$_v$. (b) For a nominal water content of 100 ppm$_v$.

The relative drift of the WDP reading as a function of time for the different nominal humidity values generated can be estimated from the slope of a linear fit to each of the series. Figs. 8.a and b show the drift correction obtained at nominal values of 13 ppm_v and 100 ppm_v, respectively. The results obtained for all the instruments at different humidity levels are summarized in Table 6.

Table 6 Summary of the drift of the instruments corrected respect to the reference device for all the humidity levels measured. "—" indicates that readings were not available for a given point.

Reference Device	Nominal Water Content	Instrument									
		A	B	C	D	E	F	G	H	I	J
	ppm_v	°C/day									
A	13		-0.08	-0.16	—	—	-0.21	-0.02	-0.06	—	-0.24
	30		0.10	-0.15	—	—	-0.02	0.03	0.01	0.17	-0.08
	70		-0.08	-0.13	—	—	-0.10	0.00	0.02	0.11	0.02
	100		-0.02	-0.30	-0.30	-0.18	-0.14	-0.04	-0.05	-0.02	-0.22
	250		-0.10	-0.31	-0.12	-0.07	-0.24	-0.05	-0.05	0.00	-0.21
B	13	0.08		-0.08	—	—	-0.13	0.06	0.02	—	-0.16
	30	0.10		-0.12	—	—	-0.17	-0.07	-0.04	0.04	-0.01
	70	0.08		-0.05	—	—	-0.02	0.08	0.10	0.19	0.10
	100	0.02		-0.29	-0.33	-0.20	-0.14	-0.03	-0.02	0.00	-0.20
	250	0.10		-0.30	-0.11	-0.06	-0.23	0.06	-0.04	0.01	-0.20
G	13	0.02	-0.06	-0.15	—	—	-0.19		-0.03	—	-0.23
	30	-0.03	0.07	-0.18	—	—	-0.05		-0.02	0.14	-0.11
	70	0.00	-0.08	-0.13	—	—	-0.10		0.02	0.11	0.02
	100	0.04	0.03	-0.26	-0.26	-0.14	-0.10		-0.01	0.03	-0.18
	250	0.05	-0.06	-0.27	-0.07	-0.03	-0.20		-0.01	0.04	-0.02

Before drawing any conclusions on the instruments and/or technologies, the following two aspects must be taken into account: (a) the condition of instruments when received and (b) the internal instrument configuration. In the first case it must be pointed out that many of the instruments evaluated had been used previously by other project partners for up to two years where measurements were made in methane, nitrogen or air without performing any adjustments or specific maintenance, whilst others were supplied directly by the manufacturer shortly before the commencement of the tests. In the second case, some instruments had default parameters that assume a certain gas composition and these could only be adjusted to a certain extent to the actual composition of natural gas flowing in the ENAGAS line.

Despite this, it is observed that the difference between the readings of the instruments has been very stable throughout the test period, allowing the relative performance of the instruments to be evaluated, even if the actual initial corrections in natural gas upon first exposure after leaving the factory is not known.

Comparison of the drift analysis of spectroscopic instrument (A) and aluminium oxide sensor (G) with respect to electrolytic instrument B (Table 6), shows that both exhibit the same drift characteristic at each point, leading to the conclusion that the study can be simplified by depicting a single technology.

From the results shown in Table 6, it can be concluded that instruments A, B, G, H and I, representative of all the measurement technologies studied, except condensation, have a very similar drift for water concentrations up to 100 ppm_v, that is the range of interest to the stakeholders in the natural gas industrial sector. The observed values of daily drift range from a maximum value of the order of -0.3 °C to the negligible value of ± 0.05 °C at the threshold of the system reproducibility. Both the maximum and the minimum values are very similar to those reported by other authors using N_2 as matrix gas (Løkken, 2012). However, the maximum and minimum values do not necessarily occur at the same applied humidity levels for all instruments. It can also be concluded that all the aluminium oxide sensors except G (that did not show any detectable drift), the drift is positive for the major part of the range studied, tending to successively indicate a dryer gas. This effect is well known to the users and metrology laboratories (Bell et al., 2004) from measurements performed in nitrogen and other gases, and are confirmed in natural gas, also.

3.5 Hysteresis studies

In this study the instruments have been compared by evaluating the difference in the instrument corrections with respect to the reference instrument. Figure 9 shows the results of the hysteresis study of the spectroscopic analyzer, instrument A, that has been taken as a reference due to its consistent performance over the range studied.

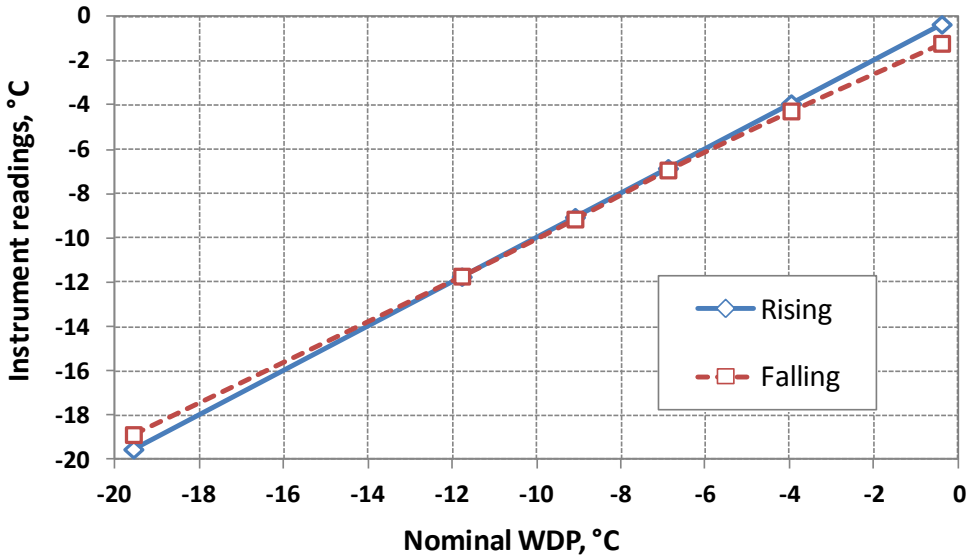


Fig. 9 Response of the spectroscopic analyzer (instrument A) to rising and falling levels of humidity as a function of the nominal value generated using the flow mixing generator.

The relative hysteresis study can be seen in Fig. 10, where the results for rising and falling humidity levels are represented.

If the results of the stability tests shown in Fig. 9 and Fig. 10 are compared with those of the hysteresis tests shown in Fig. 10, it can be seen that the readings of instruments A (spectroscopic) and B (electrolytic) are still very similar, resulting in relative values and corrections close to zero. Therefore it can be concluded that the differences observed in the study of drift with respect to the series of each of the instruments apply to the hysteresis results.

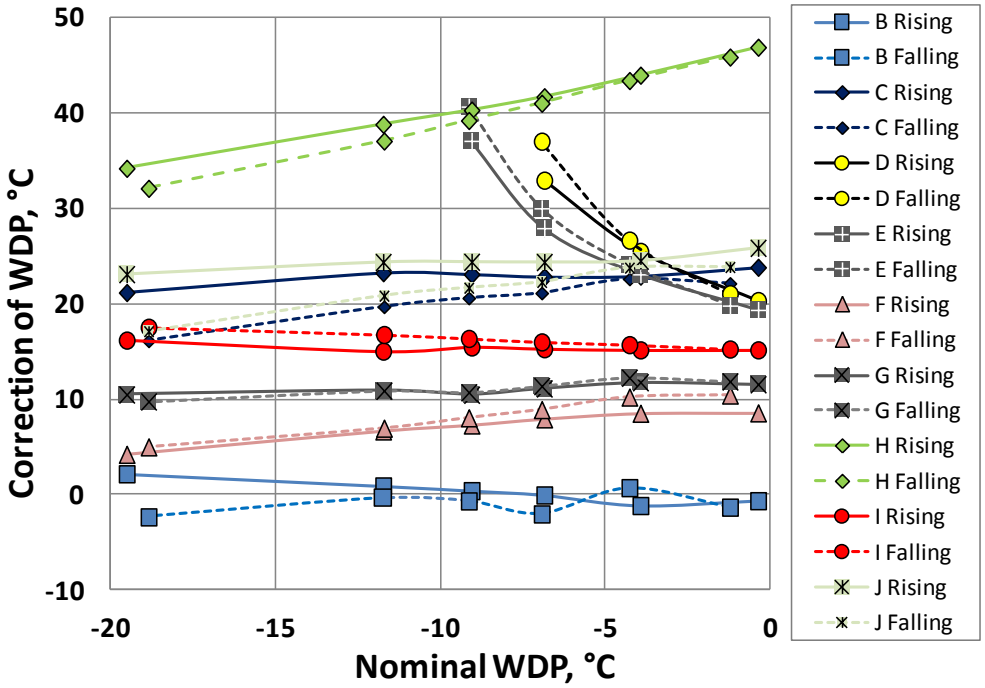


Fig. 10 Hysteresis of the instruments corrected with respect to the spectroscopic analyzer (A). The solid and dashed lines represent rising and falling values, respectively

From Fig. 10 it can be seen that instruments D and E exhibit a very different behaviour to the rest of devices but are very similar to each other, as expected for devices of the same model. Similarly, instruments C and J show the same behaviour because although the systems have different electronics, the sensor element is in fact from the same manufacturer.

Table 7 is a summary of all the values of hysteresis corrected for each of the nominal values generated. It can be seen from the results of instrument A, taken as the reference, that the nominal intermediate values generated are practically identical. However, the difference in the extreme nominal values is slightly larger. Despite this, considering the uncertainties that the European gas industry are currently working with, values below 1 ºC can be considered as practically the same generated humidity values.

Table 7 Summary of the results of the hysteresis studies. The hysteresis is expressed as the WDP difference (rising - falling) and is negative when the instrument reads dryer in descending humidity.

Nominal Water Dew Point	Instrument										
	A	B	C	D	E	F	G	G_{Dig}	H	I	J
°C	°C										
-19.5	-0.7	4.5	5.1	—	—	-0.8	0.7	0.7	2.1	-1.7	6.0
-12.0	0.0	1.2	3.6	—	—	-0.3	0.0	-0.5	1.7	-0.9	3.5
-9.0	0.1	1.1	2.5	—	-3.6	-0.8	-0.3	-0.2	1.1	-0.6	2.7
-7.0	0.1	2.0	1.7	-4.1	-2.1	-1.0	-0.2	-0.3	0.7	-0.5	2.1
-4.0	0.3	-1.9	0.3	-1.2	-1.0	-1.7	-0.5	-0.6	0.6	-0.5	0.7
-0.5	0.9	0.7	1.7	-0.7	-0.5	-1.9	-0.3	-0.3	1.0	-0.2	2.0

From Fig. 10 and results in Table 7 it can be seen that in the range studied, the majority of instruments do not exhibit appreciable hysteresis irrespective of their technology, with the exception of instruments B (electrolytic P_2O_5), C y J (Al_2O_3) that exhibit a large positive hysteresis for WDP lower than -12 ºC.

3.6 Response to pressure changes

The variable conditions of temperature, pressure and composition of the inlet gas make it difficult to ensure the exact generation of an identical WDP after a significant pressure change. In order to minimize the error derived from the indefinition of the nominal WDP, the equipment readings were corrected with respect to instrument A, that inherently operates on a non pressure-dependent unit, and the pressure at the inlet of each of the instruments displaying WDP was monitored. Due to the maximum allowable working pressure limits of some instruments, in this tests only the Al_2O_3 and polymer sensors were compared. Fig. 11 shows that all the sensors read much dryer after having been subjected to the maximum line pressure. Despite this, the relative difference of the instruments is close to their expected reproducibility (± 2 °C), implying that the changes to line pressure do not significantly affect their performance. Sensors D and E are identical and from the results can be inferred that they suffer some larger variations due to pressure changes.

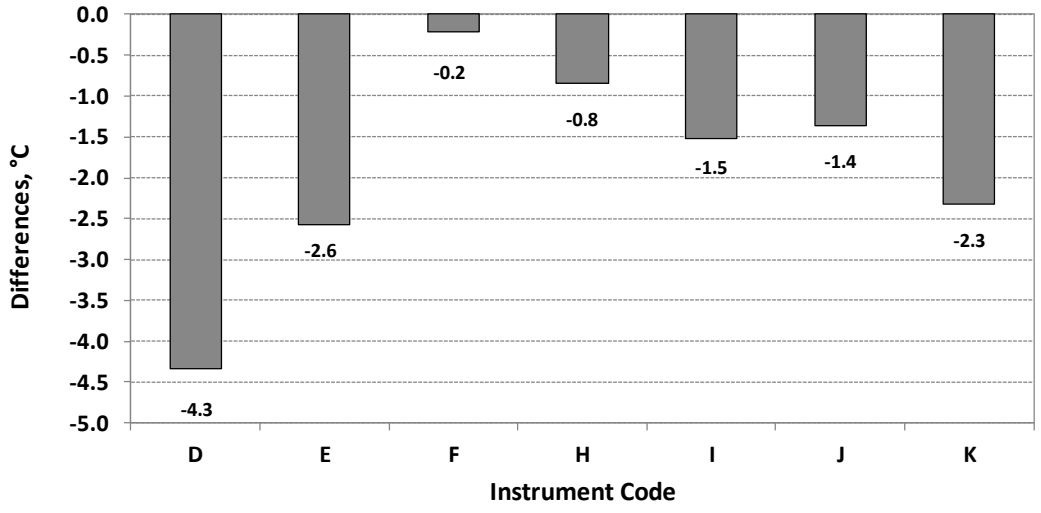


Fig. 11 Relative difference of measured WDP after having been subjected to the maximum line pressure.

3.7 Stability test performed in methane (NPL)

The instruments, which were received from NPL, had been calibrated with binary mixtures of methane and air at different moisture concentrations. After the industrial tests reported had been completed, the instruments were returned to NPL for control measurements to quantify the level of any significant drift. The results show that the spectroscopic and electrolytic instruments have very similar corrections but of opposite sign. The first shows a small downward drift and the second in the opposite direction. This is consistent with the results obtained in natural gas during the work reported, as the drift of instruments A and B are of the same order and of opposite sign, as can be seen in table 6.

The post calibration of the electrolytic sensor shows that it is within its specifications for water vapour concentrations below 100 ppm_v, and can be considered a good long-term stability. However, the spectroscopic instrument exhibits a drift close to 6 % of the reading for concentrations above 100 ppm_v.

In the case of aluminium oxide sensors the results are varied and in most cases inconclusive. Very large corrections ranging from 4 ºC to 20 ºC, always in a downward direction. These discrepancies in the measurements have been observed throughout the work reported, being even larger when the sensors were tested in natural gas. This suggests that the dispersion cannot be attributed to the dependence on the gas composition but is more likely to be associated to the different condition in which the instruments were received at the beginning of the industrial tests.

4 Conclusions and future work

The results obtained and the comparisons performed have to be considered carefully before drawing certain conclusions due to multiple factors including the industrial conditions of the gas and the initial conditions of the supplied instruments.

It is important to emphasize that whilst some of the instruments received directly from the manufacturers were in an as left condition for new instruments leaving the factory, others had been used extensively for up to two years for other evaluations in air/N_2 and methane by other partners in the project. During this period no adjustments or recommended maintenance operations were specifically carried out, with the instruments outside the recommended recalibration interval. Hence, the absolute instrument corrections at the commencement of the work reported and their value with respect to the manufacturer's specification should not be taken into account in the context of this work. On the other hand, the comparative results of the instrument behaviour with respect to the initial measurements performed at the ENAGAS facilities in natural gas can be considered valid in the context of the discussions and interpretation of results.

Despite these factors and the great dispersion of all the measured values, also observed during the control measurements performed by NPL in methane, it has been shown that all instruments exhibited a constant individual performance throughout all the tests performed.

Taking this into consideration and through an adequate treatment of the data recorded and the selection of one or more instruments as a reference, it is possible to compare certain characteristics associated to the instrument measurement technologies. The fact that pairs of instruments fitted with the same sensor have exhibited the same behaviour in all properties evaluated, denotes a high confidence level in the result obtained in this work.

All the aluminium oxide sensors, except instrument G (which did not exhibit any appreciable drift), exhibited a tendency to drift downwards, readING drier as a function of time, consistent with the findings of Løkken T.V, 2012. On the other hand, the polymer sensor showed a slightly positive drift. The spectroscopic and electrolytic based analyzers did not show an appreciable drift for a water vapour concentration below 250 ppm_v.

The instruments detected almost instantly any variations in the line humidity, with certain types of aluminium oxide sensors being the fastest in achieving a reading of 90% of the step change. The rest of the Al_2O_3 and other technologies have very acceptable values, with the exception of the electrolytic P_2O_5 analyzer that needed up to two hours to reach the final values. Independently of the technology, all instruments need longer times when drying down.

It was observed that the majority of instruments did not exhibit significant hysterisis in the range from (30 to 160) ppm_v. However, for a moisture concentration below 30 ppm_v the electrolytic sensor and some of the alumnium oxide sensors, e.g. C and J, had a positive hysterisis between 4 ºC and 6 ºC at the driest point. It was also shown that both the aluminium oxide and polymer sensors showed a good behaviour when subjected to large pressure changes, with the exception of D whose difference is much higher than the assigned expanded uncertainty.

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Nomenclatures

Abbreviation

EASEE-gas	European Association for the Streamlining of Energy Exchange - gas
EMRP	European Metrology Research Program
EURAMET	European Association of National Metrology Institutes
GERG	European Gas Research Group
HCDP	Hydrocarbon dew point
LNG	Liquified natural gas
NG	Natural gas
NMI	National Metrology Institute
PTFE	Polytetrafluoroethylene
WDP	Water dew point

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