MefHySto

Metrology for Advanced Hydrogen Storage Solutions

Deliverable D7

D7 Report on (i) the definition of underground gas storages (UGS)-relevant impurities, (ii) recommendations for measurements of hydrocarbon traces and (iii) an extension of the enhancement factor for hydrogen mixtures

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1 Introduction

1.1 WP 5 in the MefHySto-Project – Large-Scale Storage of Gases in Geological Storage Facilities

Hydrogen is seen as an important energy source of the future in politics and business worldwide. In various countries beyond Europe clear targets have been defined for the energy transition towards hydrogen. In order to secure supply underground storage of hydrogen is increasingly becoming the focus of politics and business. There is nowadays a great deal of experience worldwide in the storage of natural gas to meet medium-term demand and it is expected that some of this experience can be transferred to the storage of hydrogen.

There are basically two storage options for storing hydrogen in the geological subsurface:

- Pore storage (aquifers or depleted natural gas reservoirs) and
- Underground cavern storage (salt caverns or rock caverns).

Currently some 662 UGS facilities are in operation worldwide. Out of them 72 % are deployed in depleted hydrocarbon reservoirs, 15 % in salt caverns and 15 % in deep aquifers [1]. In Europe more than 100 underground gas storages (UGS) exist. For example, there are 49 ones operating currently in Germany, being porous structures used predominantly. However, so far no hydrogen or hydrogen mixtures are stored there. In contrast, storage in caverns is practiced only at a few selected locations (e.g., Teesside; 95 % H_2 + 3–4 % CO_2) and mainly for use by the chemical industry.

There is already a long experience accumulated through many years in handling hydrogen mixtures in underground storage facilities. This concerns mainly town gas (about 50 % H_2, 50 % CO), which has been stored underground in various types of storage facilities. This yields confidence on the feasibility of underground hydrogen storage, at least, in principle.

Projections of UGS demands for hydrogen are still uncertain. In general, the required total UGS-hydrogen working volume would be in a range of 580 – 600 bcm and this is similar or slightly greater than the total working volume of UGS available today.

When discussing about USG, a distinction must be made between storing pure hydrogen in new caverns or hydrogen + natural gas mixtures. Furthermore, because of the large investment necessary for new storages, the use of existing gas storage facilities and thus the successive transition to hydrogen is currently seen as the most realistic option.

The aim of this MefHySto work package, WP5, is to address metrological and thermodynamic issues in the large-scale storage of hydrogen in underground gas storages and the conversion of existing UGS from natural gas to hydrogen. WP5 will provide missing information on the thermodynamics in UGS studies. Additionally, it will develop and evaluate measurement methods for the conversion and subsequent use of the UGS for hydrogen.

1.2 WP 5 tasks

The measurement techniques on underground gas storage tanks are well established. There is extensive knowledge about their scope and measurement technology. Hydrogen changes characteristics and behaviour considerably regarding natural gas. Accordingly, tasks were defined in the project so that, on the one hand, they served to describe the problem and, on the other hand, to identify potential solutions. The specific aims of each Task are:

Task 5.1. To define the necessary metrological requirements for the introduction of hydrogen in storage

Task 5.2. To measure storage-relevant impurities and traces of hydrocarbons in hydrogen with existing and new GC methods

Task 5.3. To address current flow measurement issues for measuring hydrogen and natural gas mixtures in existing gas grids based on the simulation of the behaviour of hydrogen and hydrogen mixtures (ratios 20/80; 50/50; 80/20) in existing measuring sections.

The work carried out within the MefHySto project is described in the following chapters.

2 Definition of relevant impurities for underground gas storages (UGS)

2.1 Background

The aim of this task is to define the necessary metrological requirements for the introduction of hydrogen in underground storage. This will include analytical issues for storage, and geochemical, thermodynamic and microbiological influences. In addition, at operating UGS, chemicals (e.g., blanket chemicals, glycols, high water contents, corrosion inhibitors) are used, which are otherwise not used in the gas network, and their effect on storage needs to be determined.

According to existing experience with natural gas and town gas storage facilities, it is known which effects can in principle be expected in H_2 storage facilities. Besides, there are requirements independent of the type of UGS. Individual site-specific conditions must also be taken into account.

In addition, there are new requirements resulting from the utilisation of hydrogen in specific processes, as sensitive processes are ultimately catalytic processes, such as those in the chemical industry or in fuel cells.

2.2 Requirements to measure/control at UGS

Requirements for measurements result from the following aspects:

- Technical requirements of the storage operator - securing the storage integrity and technical process
- Requirements of the accepting gas providers
- Fiscal / financial settlement

Hydrogen differs significantly from methane in terms of viscosity, density and calorific value, for example. It is explosive, meaning that safety measures must be observed in the same way as for natural gas. This also means that emissions should be kept as low as possible during the measurement.

Nevertheless, the measurements can be carried out both in-line (e.g., H_2O) and out-of-line following a batch-mode separately after depressurization in a measuring building (e.g., GC-measurements in a laboratory).

2.2.1 Technical requirements / storage integrity:

Currently, a predefined technical basis (standardization) is not existing yet, and measurement of the components as well as definition of components to be measured are often not required. In the case of natural gas UGS, site-specific measurements of various parameters are carried out, but these procedures cannot be standardized for all products. The standard measurement according to these protocols is the water content or water vapor dew point after gas drying. Gas chromatographs are also installed to monitor the gas quality. These analyzers measure 11 or 16 components and calculate the combustion parameters. Hydrogen, however, is not measured.

Occasionally, other measurements are done:

- Oxygen – this also at the entrance to the storage facility
- Sulphur compounds (highly problematic for various operations)
- Hydrocarbon condensation point

At UGS the gas treatment includes gas drying and occasionally the HC (hydrocarbons) dew point setting (cooling or silica gel adsorption). Desulphurization is often not necessary in Natural Gas–UGS, except when microbiological processes are expected to occur during the underground storage.

In rare cases there is amine scrubbing – being relevant for gas extraction, not for gas storage.

In Europe, there are some special features in individual countries. In France, for example, odorised gas is stored. Odorisation is carried out using tetrahydrothiophene (THT) as an odorant. The concentration of THT is therefore measured. Other odorants are used for Hydrogen. Two conclusions can be drawn from this:

- The concentration of THT must continue to be monitored and
- if France continues to odorise centrally, any new odorant would also have to be monitored analytically.

Table 1: Measurement parameters based on technical requirements

Components	reason	Relevant for	Storage type*	Measurement actually	Necessary to measure
O_2	Microbiology	Natural Gas / H_2	A, B	x	x
Glycol	Gas drying	Natural Gas / H_2	A, B	–	depends on treatment system
Methanol / Glycol	Hydrate formation	Natural Gas / Mixture?	A, B	–	Glycol traces
Corrosion inhibitors, bactericides	Occasionally to protect the systems	Natural Gas / H_2	A, B	–	Hydrocarbon content?
Blanket (caverns)	Water reduction	Natural Gas / H_2	A	-	Hydrocarbon content
Sulfur compounds	Sometimes (e.g., storage of odorized gases in France – THT)	Natural Gas	A, B	–	x
Oil, fats (during gas injection)	Microbiology	Natural Gas / H_2	B	–	–

*A: caverns, B: pore reservoirs/aquifers

In addition to oxygen, the measurement of sulphur compounds will be technically necessary. The measurement of hydrocarbons (glycols, blanket, etc.) is being discussed; there are uncertainties regarding the possibilities of gas treatment. The measurement of these long-chain hydrocarbons could be carried out in the laboratory after enrichment sampling.

2.2.2 Gas Quality Measurements at UGS sites

There are standards for natural gas and Hydrogen that define quality criteria for the gas customer (DIN EN 16726 natural gas group H [2]; DIN EN 16723, renewable gases [3], DIN EN 17124, hydrogen fuels [4]). Note: In Germany, a new hydrogen gas family with two qualities is currently being included in the German DVGW regulations.

Table 2: Measurement parameters based on quality requirements

Component / group	Natural Gas	Mixture	Hydrogen	Storage type*	note
O_2	x	x	x	A, B	1 - 10 ppm measurement range
H_2 (varying H_2-concentrations	–	x	?	A, B	10 – 99,995 Mol.-%
H_2O	x	x	x	A, B	
Sulfur compounds	x/–	x/–	x/–	(A), B	Depend on storage characteristics
Sulfur compounds (traces)	–	–	x	A, B	
Ammonia, halogens	–	–	–	A	Salt from caverns?
Hydrocarbon dewpoint	x	?	–	A, B	Occasional measurement
Gas composition	x	x	?	A, B	
CH_4 (trace)			?	A, B	
Hydrocarbon (trace) NMHC	–	–	x	A, B	
N_2	x	x	x ?	A, B	

*A: caverns, B: pore reservoirs/aquifers

To check the H_2 quality, several individual components, substance groups and the gas composition should be analysed. The scope will not only depend on the quality requirements of the current customer. It will be important for the operator of the UGS to maintain an overview of the incoming and outgoing gas quality.

2.2.3 Gas Quality Measurements for billing

Measurements for billing purposes are done in any case.

Table 3: Measurement parameters for billing requirements

Component / group	Natural Gas	Mixture	Hydrogen	note
Flow measurement	x	x	x	
Gas composition	x	x	?	Traces, rest hydrogen?
Physical properties	x	x	x	**calculation** (density, Wobbe number, heating value, compressibility factor, molar volume)

3 Recommendations for measurements of traces of hydrocarbons

DIN EN 17124:2019 [4] and ISO 14687: 2018 [5] define the concentrations of components that are permissible for various hydrogen applications. The applications for PEM fuel cells are particularly strict and demanding. The chemical industry has similar requirements for catalytic processes (catalyst poisoning). Combustion, on the other hand, is relatively insensitive regarding the absolute H_2 concentration and the proportion of traces.
These limits are defined from the user's point of view. From the point of view of network operators and storage operators, the trace contents of the above-mentioned components are particularly difficult to comply with. This also means that the measurement limitations of these components must be overcome metrologically.

Figure 1: Limits from ISO 14687 [5] for trace components in hydrogen Class D (high quality, 99,97 mol-% H_2)

Maximum concentration of individual contaminants	
Water (H_2O)	5 µmol/mol
Total hydrocarbons except methane [b] (C1 equivalent)	2 µmol/mol
Methane (CH_4)	100 µmol/mol
Oxygen (O_2)	5 µmol/mol
Helium (He)	300 µmol/mol
Nitrogen (N_2)	300 µmol/mol
Argon (Ar)	300 µmol/mol
Carbon dioxide (CO_2)	2 µmol/mol
Carbon monoxide (CO)[c]	0,2 µmol/mol
Total sulfur compounds[d]	0,004 µmol/mol

These limits have been adopted in various country-specific regulations but are currently the subject of intense debate and continuous review. Apart from these discussions, it is necessary to measure these components and achieve the required limits.

The discussion about hydrogen quality is still far from being solved. The main problem relies on the possible contamination of the H_2 by pipelines and storage facilities. A proposal from the Netherlands favours a "medium" quality of 99.5 mol% hydrogen. This allows higher concentrations of hydrocarbons but requires low CO and CO_2 concentrations of about 10 to 20 ppm with a low oxygen content of lower than 10 ppm. Irrespective of this, the measurement of the hydrocarbons must continue in the low ppm range to determine the input, even if the permissible concentrations are higher.

The MefHySto project focuses on some of the components and substance groups mentioned above. The results of the investigations are described below.

3.1 Determination of permanent gases in the trace range using gas chromatography/BID

Analysing gas mixtures using GC is an established standard method. What is new is that the required detection and measurement limits for hydrogen are much lower than for natural gas. This cannot be solved analytically in every case with current standardised (and validated) analytical methods. For this reason, a new, very sensitive GC detector was considered in the project.

The Barrier Ionization Discharge (BID detector) by Shimadzu generates a 17.7 eV helium plasma that ionizes almost all compounds but neon. A newly designed quartz dielectric chamber allows for a lower discharge current and higher operating temperature. The BID is a universal detector with sensitivity greater than 100 times compared to that of a TCD. It is therefore an ideal detector for trace levels of permanent gas, water, volatile fatty acids and light hydrocarbons [6] .

3.1.1 METHOD

The determination of the gases was divided between two GCs, both of which were equipped with a BID detector. Extensive validation was carried out for permanent gases, methane and CO. Validated test gases with higher hydrocarbons were not yet available. Therefore, the focus was placed on these gases.

Table 4: Measurement parameters for GC-BID

Analyte	Method	Device
CH_4, CO, H_2, Ar, O_2, N_2	Gas chromatographic determination of permanent gases in the trace range	Shimadzu Nexis GC-2030 with BID detection

The validation of the method in the individual points is shown below. For each of the analytes, additional methodological studies were carried out in the Excel® documents “DINTEST” and “QUAZRIC”. DINTEST evaluates the calibration data in accordance with DIN 32645 [7], but can only utilize 5 individual measurements per calibration point. QUAZRIC is a method validation document by one of the NORDTEST authors (M. Krysell).

Identity & selectivity

The identity of the individual analytes is confirmed by the retention times on the molecular sieve column. The chromatogram of a test gas containing the analytes hydrogen (H_2), argon (Ar), oxygen (O_2), methane (CH_4) and carbon monoxide (CO) can be seen in Figure 2.

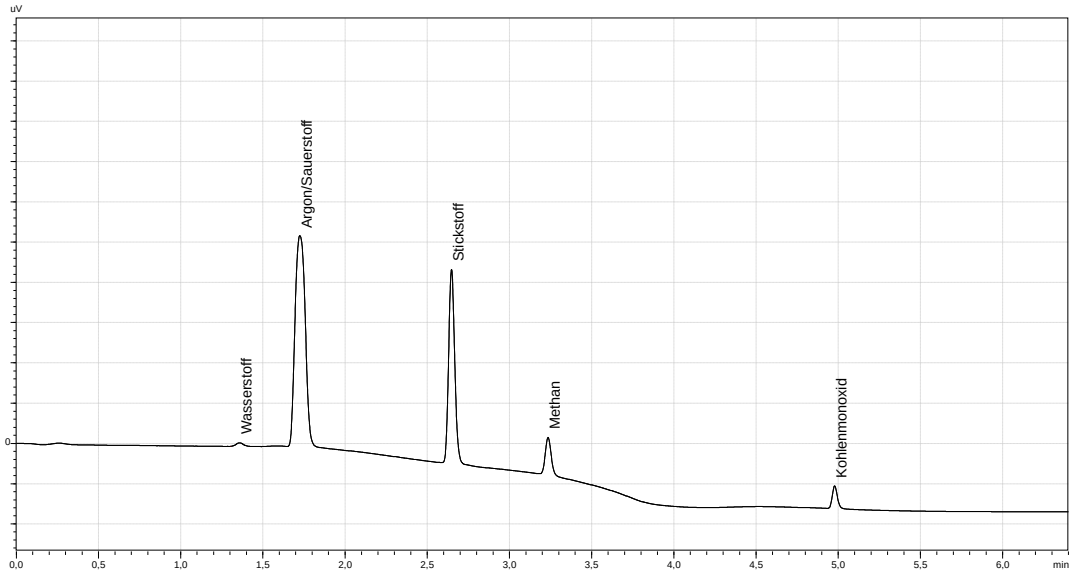

Figure 2: Chromatogram (signal intensity [µV] vs. retention time [min]) of a test gas containing hydrogen (H_2), argon (Ar), oxygen (O_2), methane (CH_4) and carbon monoxide (CO) in helium

If separation of argon and oxygen is required, the method with GC-(furnace) cooling with CO_2 is used.

3.1.2 RESULTS

Detection limit

To determine the detection limit, a gas with a low analyte concentration was analysed 10 times and the standard deviation of the results was determined (STABWN). The detection limit of the analytes (see Table 5) is then calculated from three times the standard deviation.

Table 5: Detection limits of analytes using GC/BID.

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Analyte	Limit of detection (ppm)
Hydrogen	0,1
Argon	1,2
Oxygen	1,1
Nitrogen	1,9
Methane	0,03
Carbon monoxide	0,1

Limit of quantification

The limit of quantification was determined in the same way as the limit of detection, although the sixfold standard deviation of the measurements was used.

Table 6: Limits of quantification of analytes using GC/BID

Analyte	Limit of quantification (ppm)
Hydrogen	0,19
Argon	2,5
Oxygen	2,2
Nitrogen	3,9
Methane	0,07
Carbon monoxide	0,2

To integrate additional security, a so-called reporting limit can be introduced. This is the determination limit that is used for evaluation in routine laboratory operations (outside research projects).

The sensitivity of the detector is sufficiently high to fulfil the usual requirements for hydrogen purity even with a “reporting limit”.

Table 7: Reporting Limit of analytes using GC/BID

Analyte	Reporting Limit (ppm)
Hydrogen	0,3
Argon	5,0
Oxygen	3,5
Nitrogen	6,0
Methane	0,1
Carbon monoxide	0,3

Linearity and working range

The practical working range of the method extends over the range in which the calibration is a straight line. The currently confirmed ranges can be seen in Table 4. For the analytes H_2 and CO, extra calibrations were carried out with a gas mixing apparatus. The linearity at the top was not tested further. The aim was to reliably prove the required lower limits of the components. However, as the method is to be used for the trace range, the calibrations should primarily cover this range.

Table 8: Currently confirmed Upper Calibration Points

Analyte	Max. calibration point (ppm)
Hydrogen	1000 ppm
Argon	100 ppm
Oxygen	100 ppm
Nitrogen	100 ppm
Methane	100 ppm
Carbon monoxide	9900 ppm

When developing the method, attention is paid to linearity. A correlation index of at least 0.999 is a prerequisite for successful calibration, providing a true straight line is observed.

Accuracy

The accuracy of the value is made up of the precision and the correctness of the measurement results (trueness).

Precision describes the closeness of the measured values to each other and is described by the comparison (reproducibility) and repeatability standard deviation. The analysis is carried out several times in succession (repeatability conditions) or on different days and/or by different operators (comparison or reproducibility conditions) and the standard deviation of the analysis values is calculated (STABW in Excel).

Certified test gases from Linde GmbH, Germany, were used for the data listed in the following table.

Table 9: Precision of the method

Analyte	Repeat Standard Deviation (repeatability)	Comparative Standard Deviation (reproducibility)
	%	%
Hydrogen	1,0	4,6
Argon	1,6	1,1
Oxygen	2,5	6,6
Nitrogen	1,3	0,8
Methane	0,9	4,7
Carbon monoxide	0,6	3,0

In order to describe the trueness of a value, i.e., the closeness of the measured value to the true value, in addition to certified reference gases, comparative measurements with other analysis methods (e.g., OFCEAS for methane and carbon monoxide or TCD for hydrogen, oxygen and nitrogen) and participation in round robin tests are also possible.

A comparative analysis with the ProCeas® laser spectrometer from AP2E (OFCEAS technology) for the analytes methane and carbon monoxide was carried out in the reporting limit range and yielded the following results:

Table 10: Comparative analysis for the analytes CH_4 and CO in the low concentration range

Analyte	OFCEAS	GC/BID
	ppm	ppm
Methane	0,14	0,16
Carbon monoxide	0,25	0,32

Further comparisons between the two methods and among other laboratories will be carried out in the coming months.

Figure 3: Results of seven repeats at a target value of 9.6 ppm (methane)

Analyse	Ergebnis	
1	9,89	ppm
2	9,811	ppm
3	9,775	ppm
4	9,629	ppm
5	9,697	ppm
6	9,804	ppm
7	9,785	ppm
8		ppm

Standardabweichung	0,084	ppm
Relative Standabw.	0,86	%
Mittelwert	9,770	ppm
Wiederfindungsrate	101,04	%
Bias; syst. Abweichung	1,04	%

It is not yet possible to carry out a ring test for these components in this small concentration range because the methodology is not available yet throughout Europe.

Measurement uncertainty

The measurement uncertainty of the method (see Table 11) was calculated using the freeware document "mu11352_rel_en_v2.31.xltx" by Dr M. Koch. The method used there is based on the references listed in "71 SD 4 016":

- NORDTEST-Handbook for calculation of measurement uncertainty in environmental laboratories
- DIN ISO 11352 [8]

Table 11: Current measurement uncertainties for the GC/BID method

Analyt	Certain measurement uncertainty U (k = 2)
Hydrogen	13,6 %
Argon	16,9 %
Oxygen	14,3 %
Nitrogen	16,3 %
Methane	5,9 %
Carbon monoxide	9,5 %

The corresponding calculations are continuously updated over the course of the first 3 years. This means that as soon as a certified reference material is available, the uncertainties will be checked. The next available interlaboratory test will also be carried out and included in the calculations.
Currently, the measurement uncertainties for the 6 analytes using the GC/BID method are specified as 20 %.

4 Extension of the enhancement factor for hydrogen mixtures

4.1 Testing different hygrometers in background gases comprising hydrogen and methane mixtures

4.1.1 METHOD

NPL tested the background gas- and pressure-dependence of a variety of hygrometers loaned to the project by collaborators.

Tests were carried out by humidifying two hydrogen and methane mixtures using the NPL multi-gas, multi-pressure standard humidity generator. Test results were expressed in terms of error, defined as instrument reading minus reference value.

Two certified reference mixtures were purchased for use in this testing, with nominal compositions: 1) 80 % hydrogen + 20 % methane and 2) 50 % hydrogen + 50 % methane.

The NPL-based multi-gas, multi-pressure standard humidity generator has a dew-point temperature range of −60 °C to +15 °C and a pressure range of 0.1 MPa to 3 MPa. The following humidity test matrix was used: dew-point (frost point) temperatures of 60 °C, 40 °C, −20 °C and −5 °C, at pressures of 0.105 MPa and 3 MPa, respectively. Frost-point values were realised through direct saturation of background gases of the two hydrogen and methane mixtures, as well as in pure hydrogen, air and nitrogen.

The same instruments were tested earlier in this project in background gases of pure hydrogen, nitrogen and air. Results of the earlier testing can be found in the D1 report "*Report on the development of new metrology for the measurement of key impurities in Hydrogen (water vapour and oxygen) produced from PEM water electrolysers, with fast response times of a few or tens of seconds*".

The hygrometers incorporated different measurement principles. The instruments were coded with letters A to H for anonymous presentation of results, However, feedback about the performance of their own instruments has been provided to the suppliers individually.

4.1.2 RESULTS

Background gas species effect on hygrometer measurement

Instruments B and E were only specified to operate at atmospheric pressure and therefore could only be evaluated for sensitivity to background gas species, not pressure. The graphs in Figure 4 illustrate their performance.

For instrument B, by the end of the project, the measurement error of the instrument had drifted substantially towards under-reading to an extent that a minimum measurement value of −100 °C became output when it was exposed to the −60 °C frost-point temperature reference gas in air, nitrogen and pure hydrogen background gases. For this instrument type, the user needs to input the background gas species into the control interface. However, in the instrument version tested there were only options available for pure background gas species to be selected, so it was not possible to make a correct setting for gas mixtures. Measurements in the hydrogen + methane mixtures were made with Instrument B set up as if it was measuring the humidity in pure hydrogen. In this mode, the instrument read higher with addition of 20 % methane, and higher still when the methane content was 50 %.

Instrument E was found to further under-read at the higher frost-point temperatures, when the background gas was pure hydrogen. The introduction of methane to the background gas mixture reduced the level of under-reading, getting closer towards the measurement errors found in pure air and nitrogen background gases – more so with increasing methane content.

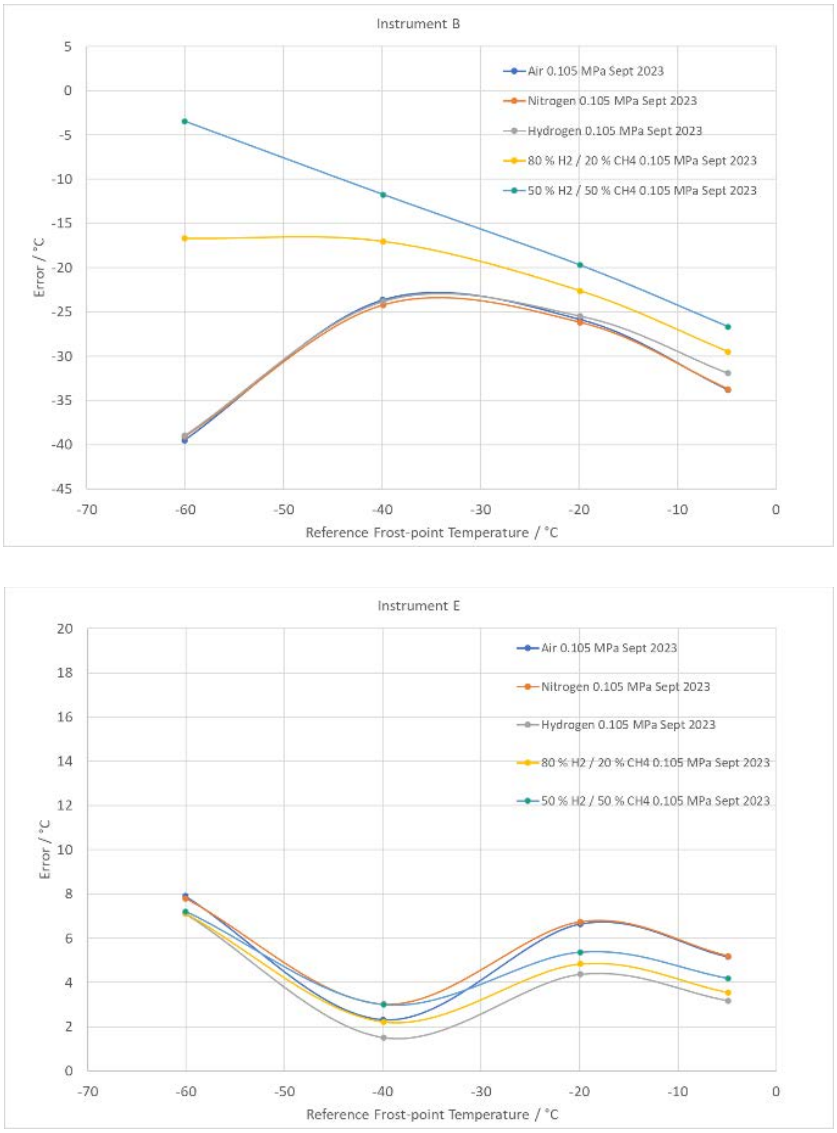


Figure 4 : Instrument B and Instrument E: Results demonstrating background gas species measurement error dependence at near atmospheric pressure.

Test pressure and background gas effect on measurement

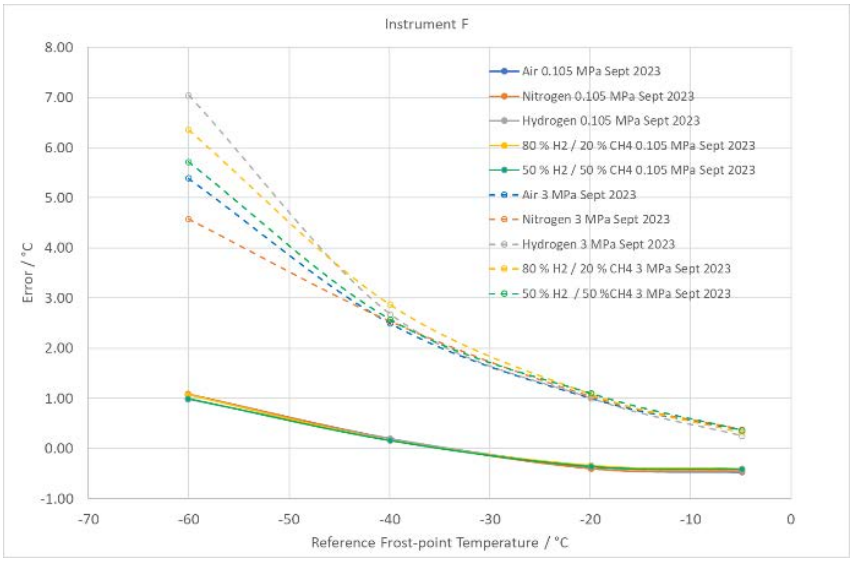
The graphs in Figure 4 show results of tests of the effects of both pressure and gas species for several hygrometers.

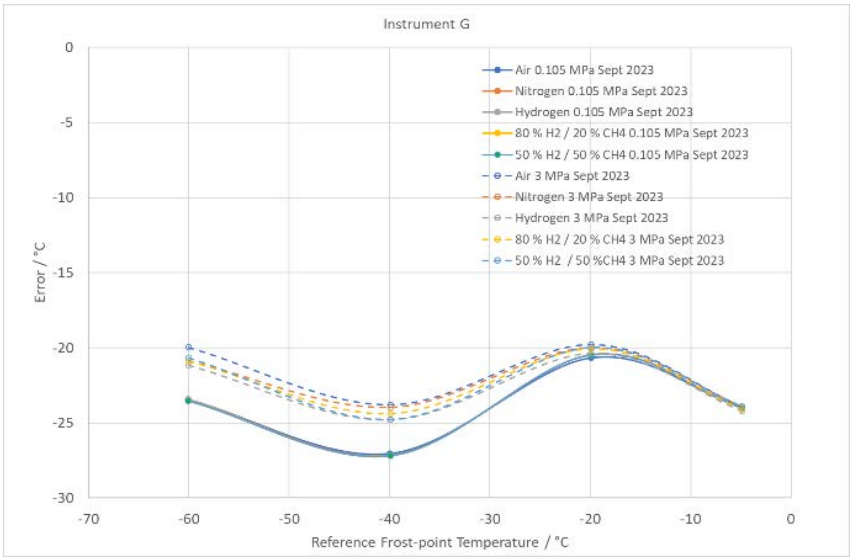
Instrument F demonstrated no dependency on gas species at pressure close to atmospheric. However, when the test pressure was increased to 3 MPa, the results show a clear pressure dependency of the measurement error of Instrument F, over-reading being pronounced at higher pressure. At the elevated pressure at dew-point temperatures below −40 ºC, all results showed dependence on gas species with errors of several degrees Celsius. Over-reading was maximum in pure hydrogen, followed by that in the

20-% methane mixture, then the 50-% methane mixture, then air, and minimum over-reading seen with nitrogen.

When initially tested in the project, Instrument G showed minimal sensitivity to background gas species and test pressure (see results in Document D1). However, in tests made two years after the initial calibration, a pressure-dependent shift towards over-reading with increasing background pressure was evident at dew-point temperatures of −40 ºC and below.

The measurement error of instrument H demonstrated a pressure-dependence, over-reading more with increasing background pressure at dew-point temperatures of −40 ºC and below. Increasing the concentration of methane in the background gas mixture resulted in the measurement error lowering compared to the error determined when air and nitrogen were the background gas.





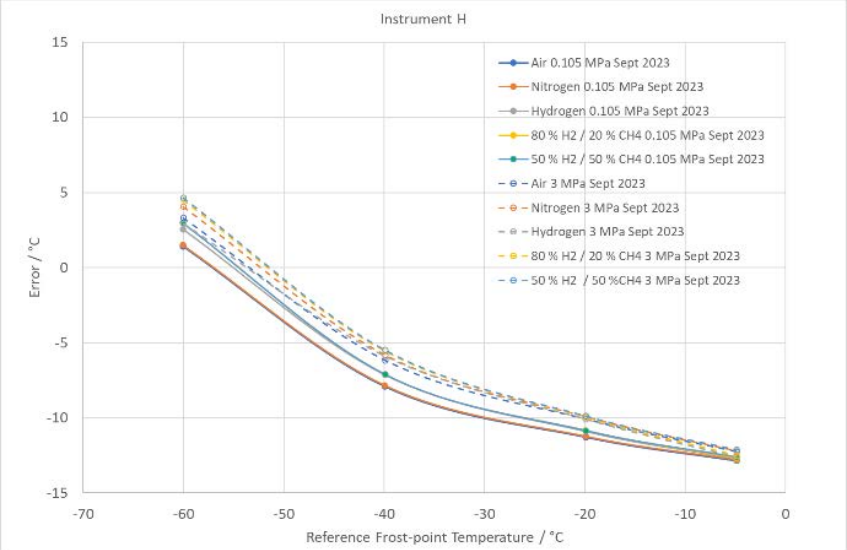


Figure 5: Instrument F, Instrument G and Instrument H: Results showing pressure and background gas species measurement error dependence.

Uncertainties

The instruments scaled in dew-point temperature units were calibrated directly against the NPL multi-gas, multi-pressure primary standard humidity generator in single-pressure mode.

The standard uncertainty of the generated dew-point temperature is calculated by combining the estimated uncertainties arising from the calibration, drift, self-heating and measurement of the reference PRT, the saturation efficiency, temperature conditioning, pressure measurement and pressure differences in the calibration system, the temperature variations in the generator bath, and the effects of leaks, desorption and contamination.

The expanded uncertainty of this generator in the range between −60 °C and +15 °C is 0.11 °C (at a coverage factor k = 2, providing a coverage probability of approximately 95 %). Using this traceability, high-performance instrument types, such as chilled-mirror hygrometers, would typically be calibrated with expanded measurement uncertainties of at least 0.12 °C once uncertainty contributions due to instrument performance during calibration are included.

For other instrument types, uncertainty contributions to the measurement uncertainty from irreproducibility of the instrument under test can increase the uncertainty considerably. Calibration uncertainties to an extent of degrees Celsius can be expected when the instrument under test is found to be irreproducible by amounts of this magnitude during calibration. Beyond calibration, the uncertainty in using these instruments should consider an allowance for potential drift since the date of calibration.

To convert reference dew-point temperature values at a given test pressure to water vapour amount fraction requires knowledge of a water vapour enhancement factor (in this case for hydrogen and the hydrogen + methane mixtures). Research in this project, reported in the following section, has helped to reduce the uncertainty in the estimation of this factor. For hydrogen and the hydrogen mixtures with

methane, there are few or not yet consolidated data or equations to describe the water vapour enhancement factor. Values can be approximated based on the NPL experimental measurements in the same temperature and pressure range with a suitable uncertainty allowance as discussed below.

4.2 Water vapour enhancement factor evaluation in hydrogen and hydrogen + methane mixtures

4.2.1 METHOD

The configuration in Figure 6 below was used to evaluate the water vapour enhancement factor for air, nitrogen and hydrogen as well as for the two hydrogen and methane mixture compositions, namely 1) 80 % hydrogen + 20 % methane and 2) 50 % hydrogen + 50 % methane.

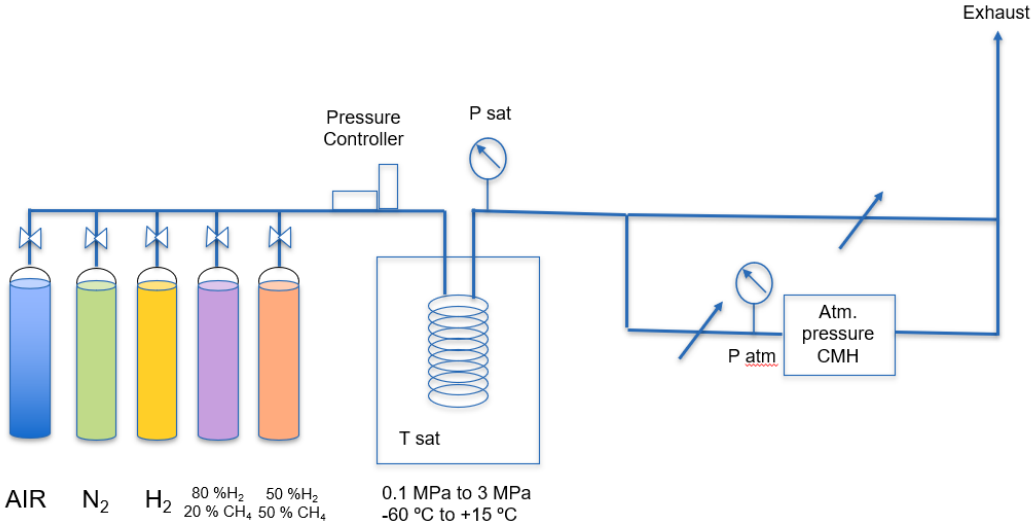


Figure 6: Test set-up for experimental evaluation of water vapour enhancement factor ratio, *f**

Since amount fraction is conserved when the pressure and temperature of gas is changed [9, 10]:

$$x_{P_{sat}} = \frac{e_i(T_{sat})f_i(P_{sat},T_{sat})}{P_{sat}} = x_{P_{atm}} = \frac{e_i(T_{atm})f_i(P_{atm},T_{atm})}{P_{atm}},$$

Where: $x_{P_{sat}}$ = water vapour amount fraction at saturator pressure
P_{sat} = pressure of saturator
T_{sat} = frost-point temperature at saturator pressure measured by PRT
$x_{P_{atm}}$ = water vapour amount fraction at atmospheric pressure
P_{atm} = atmospheric pressure
T_{atm} = frost-point temperature measured by CMH at atmospheric pressure
e_i = water vapour pressure over ice, a function of temperature
f_i = water vapour enhancement factor, a function of temperature and pressure

Rearranging this gives: $$\frac{x_{P_{atm}}}{x_{P_{sat}}} = \frac{e_i(T_{atm})f_i(P_{atm},T_{atm})P_{sat}}{e_i(T_{sat})f_i(P_{sat},T_{sat})P_{atm}} = 1$$

The NPL study results do not yield the enhancement factor directly but an enhancement factor ratio instead that is derived from pressure ratio and related reduction of pure vapour pressure.
We can define *f** as a ratio of the enhancement factors at the two test pressures:

$$\frac{f_i(P_{sat},T_{sat})}{f_i(P_{atm},T_{atm})} = \frac{e_i(T_{atm})P_{sat}}{e_i(T_{sat})P_{atm}} = f^*$$

and this can be calculated from measurements of frost-point temperatures and pressures at the saturator pressure and at atmospheric pressure.

To derive an approximate enhancement factor at above-atmospheric pressures, the atmospheric pressure value of enhancement factor can approximate to unity (i.e., $f \approx 1$ at atmospheric pressure). This allows an approximation of enhancement factor by taking $f \approx f^*$ at pressures well above atmospheric.

Evaluation of *f** was completed at 0.5 MPa, 1 MPa, 2 MPa and 3 MPa at 10 °C frost-point temperature intervals from −50 °C to −10 °C.

4.2.2 RESULTS

Accepted formulae exist for the calculation of water vapour enhancement factor, *f*, in air [9] and these calculated values were compared to values of water vapour enhancement factor ratio, *f**, found experimentally using NPL's test approach, in order to validate the approach. This is shown graphically in Figure 7 below.

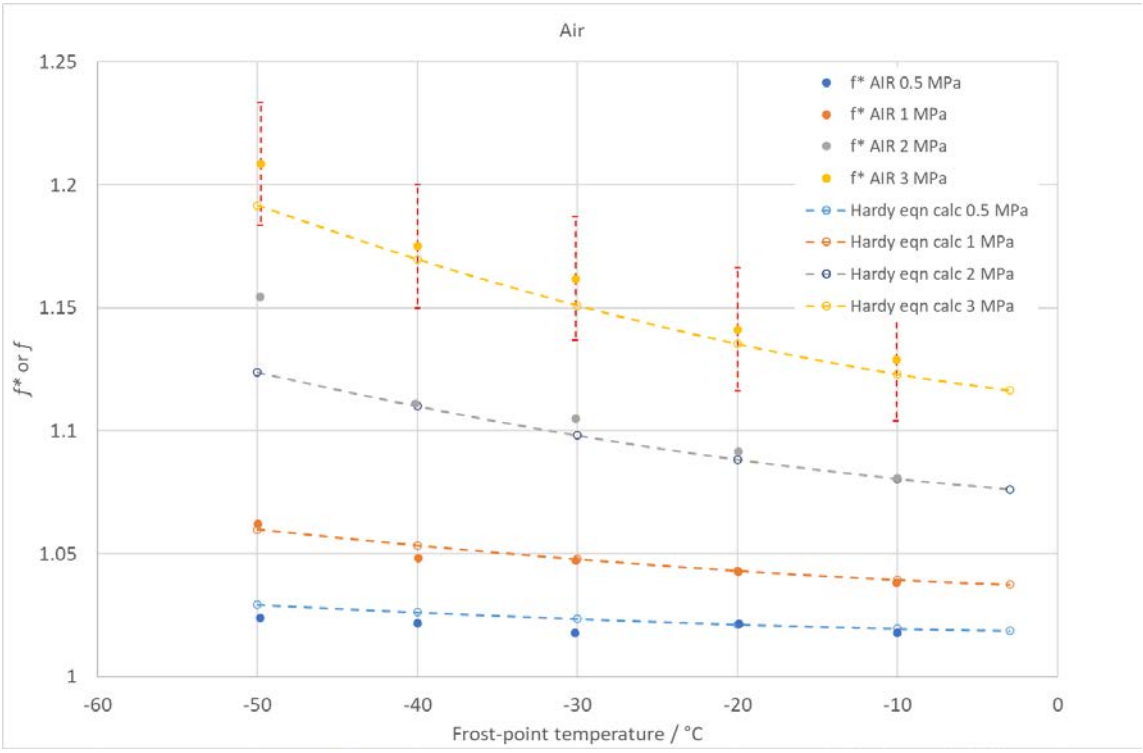


Figure 7: Experimental water vapour enhancement factor ratio, *f, results for air, and calculated values of water vapour enhancement factor, *f*, using Hardy's equations for air (Example error bars representing ±2.5 % of value shown on 3 MPa *f** series).**

Values of water vapour enhancement factor ratio, *f**, found experimentally using NPL's test approach in pure hydrogen are shown graphically below in Figure 8.

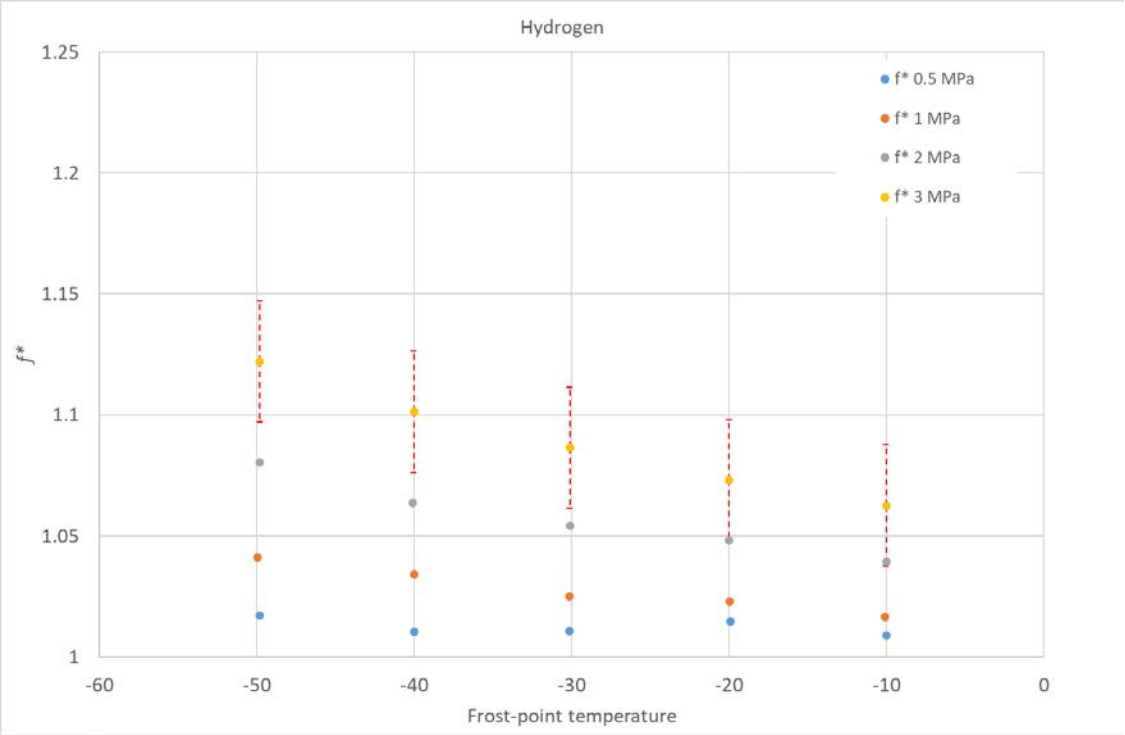


Figure 8: Experimental water vapour enhancement factor ratio, *f, results for hydrogen (Example error bars representing ±2.5 % of value shown on 3 MPa *f** series).**

Values of water vapour enhancement factor ratio, *f**, found experimentally using NPL's test approach in an 80 % hydrogen + 20 % methane mixture are shown graphically below in Figure 9.

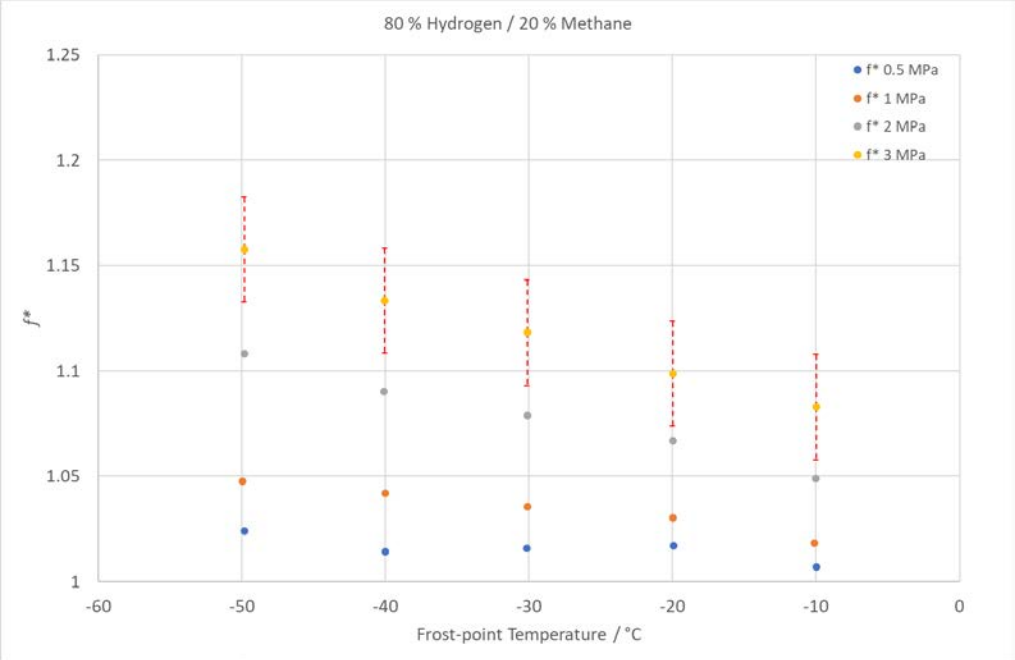


Figure 9: Experimental water vapour enhancement factor ratio, *f, results for an 80 % hydrogen + 20 % methane mixture (Example error bars representing ±2.5 % of value shown on 3 MPa *f** series).**

Values of water vapour enhancement factor ratio, *f**, found experimentally using NPL's test approach in a 50 % hydrogen + 50 % methane mixture are shown graphically below in Figure 10.

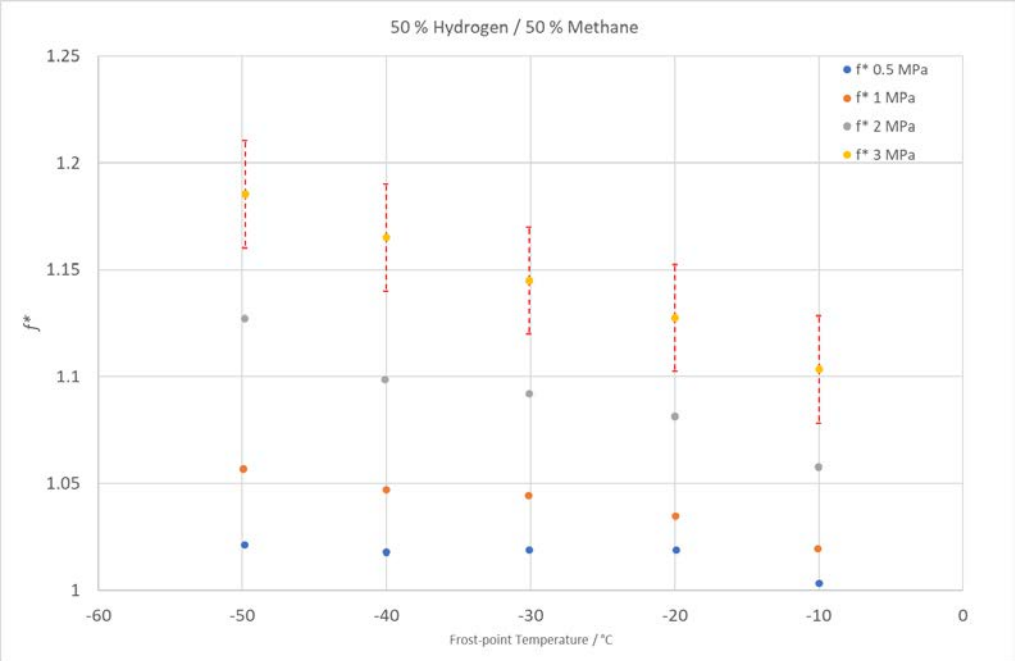


Figure 10: Experimental water vapour enhancement factor ratio, *f, results for a 50 % hydrogen + 50 % methane mixture (Example error bars representing ±2.5 % of value shown on 3 MPa *f** series).**

Values of water vapour enhancement factor ratio, *f**, are shown in the following tables. Uncertainty evaluation is discussed further below.

Table 12: Experimental water vapour enhancement factor ratio, *f, results for air, hydrogen, an 80 % hydrogen + 20 % methane mixture and a 50 % hydrogen + 50 % methane mixture at 0.5 MPa.**

Saturator Temperature / °C	Air	Nitrogen	Hydrogen	80 % Hydrogen + 20 % Methane	50 % Hydrogen + 50 % Methane
−10	1.018	1.019	1.009	1.007	1.003
−20	1.022	1.023	1.015	1.017	1.019
−30	1.018	1.022	1.011	1.016	1.019
−40	1.022	1.020	1.011	1.014	1.018
−50	1.024	1.028	1.017	1.024	1.021

Table 13: Experimental water vapour enhancement factor ratio, *f, results for air, hydrogen, an 80 % hydrogen + 20 % methane mixture and a 50 % hydrogen + 50 % methane mixture at 1 MPa.**

Saturator Temperature / °C	Air	Nitrogen	Hydrogen	80 % Hydrogen + 20 % Methane	50 % Hydrogen + 50 % Methane
−10	1.038	1.042	1.017	1.018	1.019
−20	1.043	1.046	1.023	1.030	1.035
−30	1.047	1.051	1.025	1.036	1.044
−40	1.048	1.055	1.034	1.042	1.047
−50	1.062	1.061	1.041	1.048	1.057

Table 14: Experimental water vapour enhancement factor ratio, *f, results for air, hydrogen, an 80 % hydrogen + 20 % methane mixture and a 50 % hydrogen + 50 % methane mixture at 2 MPa.**

Saturator Temperature / °C	Air	Nitrogen	Hydrogen	80 % Hydrogen + 20 % Methane	50 % Hydrogen + 50 % Methane
−10	1.081	1.087	1.039	1.049	1.058
−20	1.092	1.099	1.048	1.067	1.081
−30	1.105	1.111	1.054	1.079	1.092
−40	1.111	1.118	1.064	1.090	1.098
−50	1.155	1.146	1.081	1.108	1.127

Table 15: Experimental water vapour enhancement factor ratio, *f, results for air, hydrogen, an 80 % hydrogen + 20 % methane mixture and a 50 % hydrogen + 50 % methane mixture at 3 MPa.**

Saturator Temperature / °C	Air	Nitrogen	Hydrogen	80 % Hydrogen + 20 % Methane	50 % Hydrogen + 50 % Methane
−10	1.129	1.138	1.063	1.083	1.103
−20	1.141	1.152	1.073	1.099	1.127
−30	1.162	1.173	1.087	1.118	1.145
−40	1.175	1.190	1.101	1.133	1.165
−50	1.208	1.224	1.122	1.158	1.185

Discussion

For air, experimental values agree well with calculations based on Hardy's formulae [9].

The values of *f** for pure hydrogen found from the measurements in this work were all lower than the equivalent air values.

Increasing the methane fraction in a mixture with hydrogen raises the *f** value compared to those for pure

hydrogen. The *f** values for the mixture of 50 % hydrogen + 50 % methane were higher than those of the mixture 80 % hydrogen + 20 % methane.

The DBI measured the water content in pure hydrogen using the Tiger Optics Spark diode laser spectrometer. This was done by saturating the hydrogen with water and then cooling the gas to the desired freezing point. In the process known as CW-CRDS* (Continuous Wave Cavity Ring Down Spectroscopy), the ring-down time is determined in which the light intensity drops to zero after the laser light source is deactivated. The concentration of the target gas in the measuring cuvette can be determined directly from this decay time.
Absolute measurement of the water content in mixtures is currently only possible using Karl Fischer titration. However, this can only be used to a limited extent below 10 mg/m³, so that it is not possible to validate the water content below this concentration for gas mixtures.

Table 16: Measurements of water content according to dew point specification in hydrogen

Gas	pressure bara	Frost point Default °C	Frost point Mirror °C	Tiger optics water content ppm	remark
H_2	46,3	−40	−39,6	3,46	
H_2	72,6	−40	−40,1	2,42	
H_2	97,3	−40	−40,1	1,9 – 2,0	wavelike over a longer period of time
H_2	96,3	−30	−29,8	5,2 – 5,5	wavelike over a longer period, Average value?
H_2	74,4	−30	−29,9	6,50 – 6,65	individual values are slightly higher, rather the low value
H_2	48	−30	−29,8	9,47	

The laser diode spectrometer fluctuated over the measurement periods. Bandwidths are therefore given here. The cause of this fluctuation could not be determined so far. The measurements were taken over a longer measuring period and all pressure regulators were heated to prevent adsorption phenomena. The frost point indicated by the mirror, however, proved to be stable.

Uncertainty in estimates of enhancement factor ratio *f

Uncertainty was evaluated approximately, considering main contributions:

- Uncertainty in primary frost-point generation, which is well established as part of a UKAS-accredited capability for humidity in multiple gases up to 3 MPa.
- Uncertainty in measurements using a frost-point hygrometer for measurement of frost point, traceable to the multi-gas facility (in non-air gases) and traceable to NPL's Low Frost-point Generator (for measurement in air). The traceability in air has a lower uncertainty.
- Uncertainty in pressure measurement which is of approximately 0.25 percent of reading (k = 2)

worst case at saturator pressure, 0.1 percent of reading (k = 2) worst case at atmospheric pressure

- Uncertainty in formulation of saturation pressure of pure water, in ice range (see Sonntag, 1990 [10]).

The NPL study results did not directly determine an enhancement factor but an enhancement factor ratio, derived from pressure ratio and related reduction of pure vapour pressure. To derive an approximate enhancement factor at above-atmospheric pressures, the atmospheric pressure value of the enhancement factor has been approximated to unity and therefore $f \approx f^*$, at pressures well above atmospheric. In air, at 0.1 MPa, between 0 °C and −60 °C, the enhancement factor [9] ranges between 1.004 and 1.006. Neglecting this (because of approximating it as equal to 1) would cause an error of up to 0.6 percent of value. In hydrogen, the general measured data suggest that the enhancement factor is less than in air, perhaps close to 0.4 percent of value. This approximation can be treated as an uncertainty (with worst-case limits selected to bracket the uncorrected error) or, alternatively, a generalised correction could be estimated, with slightly reduced uncertainty.
The calculated results are derived from quotients of vapour pressures and pressures. Because of this, some components of uncertainty that could potentially be correlated (such as for measured pressure, and measured frost point values, and vapour pressure formulae) can be expected to cancel at least partially. Because of this, although correlation is not assessed in detail, it is assumed that this correlation would not increase the estimate of uncertainty.
Overall, the uncertainty in values of enhancement factor from the NPL measurements is approximately 2 % to 2.5 % of value (at a coverage factor k = 2, corresponding to coverage probability of approximately 95 %). Future work could detail this further.
In addition, the enhancement factor in air up to 2 MPa [9] was calculated and plotted for comparison, but that value and uncertainty did not contribute to the measured values.

5 Summary

5.1 Summary WP 5

It has been confirmed that the measurement effort required for underground gas storage will increase with the switch to hydrogen. The discussion about the limit values and gas qualities is not yet settled. However, there are ambiguities in the necessary analytical setup measurement implementation.

The measurement of hydrocarbons and other gases in hydrogen in the trace range is possible with the GC equipped with BID. However, this configuration is currently a laboratory device, and as a process gas chromatograph qualified for field applications it would have to be structured differently.

The water content measurement in hydrogen and hydrogen-containing mixtures is possible with existing sensors. Importantly, the calibration of the sensors needs to be adjusted. Depending on the hydrogen concentration, the possible water contents in the gas mixture change.

5.2 Recommendations for further investigations

The project implemented initial steps to record and check requirements and options for measuring relevant parameters at underground gas storage facilities (UGS). Approaches to solutions were found that require expansion in further stages.

The following necessary points for further investigation are seen:

- Expansion of the measurement base
- Creation of the thermodynamic basis regarding the solubility of other components (e.g., glycols) in hydrogen in the relevant pressure range.
- Proof of the possibilities of measuring higher hydrocarbons

Reference should be made to the lack of thermodynamic data regarding the solubility of hydrocarbons. This data is important when converting underground gas storage based on exhausted gas or oil fields.

Particular reference should be made to the lack of thermodynamic data regarding the solubility of hydrocarbons. This data is important when converting underground gas storage based on exhausted gas or oil fields.

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