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JRP-Coordinator	
Name, title, organisation	Dr Dai Jones, Contract Manager, NPL
Tel:	+44 20 8943 8540
Email:	dai.jones@npl.co.uk
JRP website address	www.npl.co.uk/emrp-energygases
Other JRP-Partners	
Short name, country	<p>Funded partners:</p> <p>BAM, Germany BRML, Romania CEM, Spain CMI, Czech Republic INRIM, Italy INTA, Spain LNE, France MIKES, Finland MKEH, Hungary NPL, UK PTB, Germany SMU, Slovakia SP, Sweden TUBITAK, Turkey VSL, The Netherlands</p> <p>Unfunded partner:</p> <p>BEV / E+E, Austria</p>

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REG-Researcher

Researcher name, title
(Home organisation Short
name, country)

Simone Corbellini
POLITO DELEN, Italy

Start date:
01 Sept 2010
Duration: 33 months

RMG-Researcher

Researcher name, title
(Home organisation Short
name, country)

Katarina Hafner
IMBIH, Bosnia and Herzegovina

Start date:
01 October 2012
Duration: 4 months

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1 Executive Summary

This three-year project has brought Europe a step closer to the distribution of new non-conventional energy gases through the existing gas pipeline system. Our research will help facilitate the transition towards a stable energy supply for Europe.

The Problem

The EU faces an urgent need to reduce its dependency on fossil fuels as resources continue to decline. Alternative non-conventional gas fuels are under development, but if they are to succeed at a European level and have a substantial impact on the European alternative fuel scene, they must be allowed entry into the existing international pipeline system.

The problem is that the pipeline system was designed for relatively uniform natural gas with high methane content. Non-conventional gases have significantly different and varying chemical composition and subsequently different energy content and physical properties. These different properties have potentially serious economic, safety and infrastructure corrosion implications and therefore the gases cannot be allowed to enter the system without confirmation that they are safe to transmit.

The Solution

We set out to solve this problem by establishing the measurement basis to provide gas suppliers, traders and distributors with traceable methods to analyse these new non-conventional energy gases. This would allow informed decisions to be made on the suitability of each new gas to enter the existing distribution system.

The Impact

We successfully achieved all our major goals, and as such the impact of the project is as follows:

- The development of new chemical analysis techniques to determine the composition of non-conventional gases will ensure that toxic or corrosive components are below proscribed limits, indicating whether these gases can enter the existing pipeline system
- The establishment of a traceable link from commercial field calorimetry instruments back to the primary calorimeter standards enhances the confidence that can be placed in field measurements
- The development of the world's first fully traceable methods and equipment for generating precisely known humidity levels in energy gases supports product development at instrument manufacturing companies
- The field testing at commercial gas transmission plants in Spain of new humidity equipment and facilities that were developed within the project greatly increases confidence in the robustness and practicality of the laboratory developments

The project's success enables non-conventional gases to be accurately characterised so that informed decisions can be taken about allowing each source to enter the pipelines without compromising calorific value (how much energy the gas generates), infrastructure integrity (in terms of potential corrosion damage) or transmission safety. Ultimately the full impact of the project will depend on both the extent to which the EU delivers on its energy policies and the scope of uptake by the international community in the trade of non-conventional gases through existing pipelines.

2 Project context, rationale and objectives

Natural gas resources in the EU are declining. Consequently, various forms of diversification in the natural gas supply are taking place. Governments in the EU as well as gas producers and transporters support the “greening of gas” by the introduction of, for example, biogas, mixed natural gas and coal-bed methane. **This project put in place the necessary metrology infrastructure to enable the “inter-changeability” of energy gases so that gaseous fuels from non-conventional sources can access gas grids across the EU.** Interchangeable gases, in this context, are defined as when they may be substituted for each other without affecting the operation of gas burning appliances or equipment.

It will enable gas producers and transporters to make informed commercial, environmental and safety decisions based on comparable measurements of the energy content, carbon content and physical properties of alternative and renewable gaseous fuels. The project also addressed the need for measurements of the carbon content of alternative fuel gases, such as refinery gas and syngas that principally arise as by-products of coke and petroleum production. These are required for efficient trade within the scope of the EU Emissions Trading Scheme (ETS).

There is a long-standing solid foundation for gas composition and calorific value measurements for natural gas, but such a foundation was lacking for the alternative fuels addressed by this project. Where measurement methods existed, their scope is limited or their accuracy was not at the level of state-of-the-art measurements of natural gas. Methods were needed for analysing gas composition and determining calorific value (energy content) that are robust, and cover wide ranges of components in the gas. Furthermore, some gas streams contain impurities that are a threat to further processing or utilising the gas, so for operational purposes they need to be controlled closely. Examples of such impurities include siloxanes and ammonia in biogas.

For fiscal (custody transfer) purposes, the calorific value of the gas is of prime importance. In many cases, the calorific value is determined using an indirect method, *i.e.* calculation from the gas composition. For natural gas, there is a well-established written standard (ISO 6976:2005) which provides the basis for this calculation; however the scope of this standard is limited to natural gas. Wider application of this standard to the alternatives addressed in this project is highly desirable, but requires at least a validation of this indirect method with gas calorimetry (a direct method).

Several physical chemical properties, such as condensation behaviour, are critical to the efficient and safe utilisation of these alternative fuels. Humidity is a key parameter monitored during the glycol drying process used before supplying gas to a gas delivery grid. Current practice for such moisture measurements were that devices for measuring the water dew point are calibrated at atmospheric pressure and in nitrogen or air, conditions which vary significantly from real field conditions.

As the water dew point is dependent on the gas composition, temperature and pressure, it was evident that substantial extrapolations needed to be made. These extrapolations may well lead to deviations in the water dew point temperature of 10 °C or more, where an accuracy of 1 °C – 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 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.

Calibration facilities for water dew point at high-pressure as well as a new standard generator for low humidity working with the coulometric principle were developed in this project to allow industrial instruments to be calibrated with a gas matrix that resembles field conditions, and at a relevant pressure. The research and test facilities developed allow the determination of the water vapour enhancement factor and sensor characteristics in various gas matrices, thus greatly enhancing the use of industrial instruments in various conditions and measurement setups.

The deregulation of EU energy markets and the growth of a grid network for the transport and distribution of gas within the EU have led to the identification of the roles and interests of different parties including: producers, transporters, network operators and ultimately consumers. This project provided a metrological basis for the measurements of the properties of renewable and alternative energy gases as they are traded

between these parties. Consequently, this project proposal received support from stakeholders including: producers (e.g. EON, British Gas, Enagas, Transgaz, Gasum and SCEM) transporters (e.g. National Grid) and instrument manufacturers (e.g. Michell Instruments, BEV/E+E).

The transition towards a sustainable energy supply for Europe, has been stimulated by Directive 2009/73/EC, "Common rules for the internal market in natural gas and repealing Directive 2003/55/EC" which states (para 41):

"taking into account the necessary quality requirements, biogas and gas from biomass or other types of gas are granted non-discriminatory access to the gas system, provided such access is permanently compatible with the relevant rules and safety standards. These rules and standards should ensure, that these gases can technically and safely be delivered into, and transported, through the natural gas system and should also address the chemical characteristics of these gases."

The commitment to avoiding technical barriers to the use of energy from renewable sources is further emphasised by the "Promotion of the use of energy from renewable sources Directive" 2009/28/EC, which states (para 45):

"regulations and rules relating for example to levels of quality, testing methods or conditions of use, should not create barriers to trade in renewable energy equipment and systems"

Regulations used to implement this directive follow the guidance from the MARCOGAZ and EASEE-gas industry groupings, which are being formed into a new mandatory CEN standard by CEN BT/WG197. Examples of current regulations from several EU countries are given in ISO 13686:2005.

The Directive establishing the EU ETS (2003/87/EC) states in Annex IV that: "activity specific emission factors are acceptable for all fuels". Hence, there is a requirement for accurate and validated measurement methods for use in the estimation of such factors for high-value energy gases of variable composition, which are traded within the ETS.

The priority of the requirements addressed by this project, which are agreed at EU level and concern interchangeability of gaseous fuels between transporters and producers in different countries, provided a compelling case for the development of the necessary metrological infrastructure at European level.

The project therefore set these high level objectives:

- To develop and validate new highly accurate measurement methods to achieve the uncertainty required by the European Association for the Streamlining of Energy Exchange – Gas (EASEE-gas) for the physical properties of gases injected into the network and certified reference materials for the composition of non-conventional and renewable gaseous fuels (e.g. biogas, coal bed methane, coal mine methane and hydrogen enriched natural gas) and refinery gases (e.g. 'syngas').
- To develop highly accurate measurement methods for odorants in non-conventional and renewable gaseous fuels, matching where possible the current 1.0 % uncertainty of sulphur species in methane. Odorants are deliberately added to energy gases to ensure that potentially dangerous leaks can be detected.
- To validate the results of a new primary calorimeter able to produce very low uncertainty (0.2 %) on energy measurement of these gases in accordance with the principles of the "Guide to the Expression of Uncertainty in Measurement" (GUM).
- To develop and validate a range of field calorimeters for the measurement of the calorific value of non-conventional gases.
- To develop a new primary dew point standard for high pressure and a new water vapour amount fraction standard at low pressure to cover conditions typical of gas distribution across Europe.

- To improve the measurement validity in sampling and in conversions between humidity quantities by producing data on the effect of interactions between water and other gas molecules and developing new calculation methods.
- To develop measurement systems for 1) studying experimentally the effect of interactions between water and other gas molecules and 2) sensitivity of humidity sensors to variations in gas composition and measurement conditions.
- To develop and validate new methods for comparing humidity standards with humidity sensors used in industrial gas monitoring conditions.

3 Scientific and technological results and foreground

Scientific objectives

The project can be conveniently divided in to four areas of activity which are directly related to the desired outputs in terms of the interchangeability parameters.

Firstly, appropriate new methods for the **determination of the chemical composition** of non-conventional gases had to be developed. These methods had to be capable of dealing with the wide composition range of gases likely to be encountered and address not only the major desirable components (such as methane, ethane etc.) but also the low levels of deliberately added odorants and of the undesirable contaminants (such as ammonia and siloxanes). All the methods needed to have metrological traceability at low levels of uncertainty. Odorants are deliberately added to fuel gases (which are fundamentally odourless) to alert users of any accidental discharge or leaks.

Secondly, new procedures for determining the **calorific value** of non-conventional gases needed to be developed. This work had to cover both high accuracy primary calorimeters for laboratory use and field calorimeters for practical application at industrial sites. The results for the secondary calorimeters must be traceable back to the primary standard to be metrologically sound.

The third area covered **humidity** determination. Humidity is a major concern for gas distributors for a variety of reasons which include calorific value, corrosion and safety aspects. The project set out to develop a new primary dew-point standard for high pressures and a new water vapour fraction coulometric standard for low pressures to cover conditions typical of the distribution system in Europe. A further aspect of the humidity work was to improve the measurement validity in sampling gasses and in conversion between humidity quantities by producing data on the effect of interactions between water and other gas molecules and developing new calculation methods.

The fourth area concerned the evaluation of **existing and novel humidity sensors** both in closely controlled laboratory conditions and in industrial gas processing plants. This included the study of the co-condensation of hydro-carbons and water (i.e. on the mirror of a dew point mirror hygrometer) as well as intensive tests of traceable calibrated sensors at industrial sites.

Results

The project has successfully delivered on its objectives in all four science areas:

New methods for the measurement of the composition of non-conventional gases

The project has addressed the issues around the measurement of four families of non-conventional energy gases:

- Biogases (e.g. landfill gas and biosyngas).
- Natural-gas type mixtures (e.g. coal bed methane, coal mine methane and hydrogen-enriched natural gas).
- Refinery gases (e.g. coke oven gas, blast furnace gas, syngas and reformer gas).
- Energy gas odorants.

New accurate standards and methods were developed for each of these families of gases, and these were used in the concluding part of the project, which saw the JRP-Partners analyse a wide range of real non-conventional gas samples from around Europe.

The highlights of the work for each family of gases are described below:

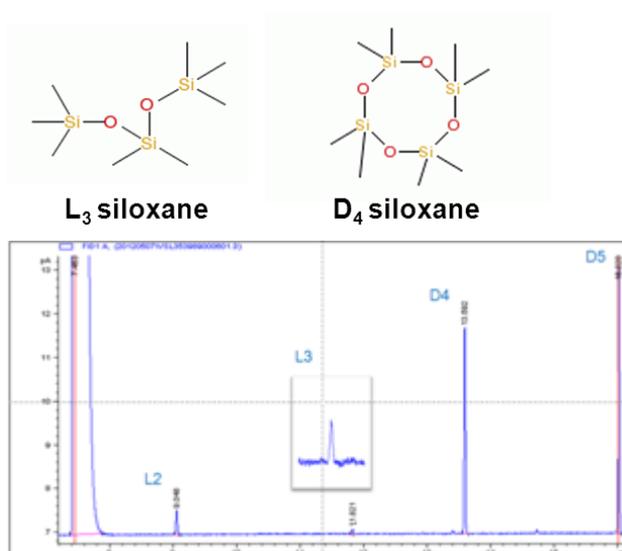
Biogases

The biogas work in the project focused on the development of new traceable methods for biogas composition and trace level impurities.

The accurate measurement of biogas composition is essential to enable physical properties such as calorific value and hydrocarbon dewpoint to be calculated. These properties ensure that the gas meets the specifications for injection into pipeline networks. In order to improve the accuracy of these measurements NPL prepared three high-accuracy primary reference gas mixtures for biogas composition analysis. These complex mixtures, which contained methane, carbon dioxide, nitrogen, oxygen, hydrogen, carbon monoxide, ethane, propane and hydrogen sulphide, were used to calibrate a gas chromatogram system used for biogas composition measurements at SP in Sweden. A significant improvement in the uncertainty of measurement was achieved by the use of these standards – the uncertainties achieved for some components have been improved by up to a factor of five.

The bulk of the work on biogases however focussed on developing novel reference gas mixtures and standards for the analysis of trace-level impurities. Impurities commonly found in biogas include siloxanes (which originate from soaps, cosmetics and consumer products, and can foul turbine engines), ammonia and sulphur compounds (both of which are highly toxic even at very low concentrations). It is therefore essential that the concentrations of these compounds are known accurately before biogases are injected into the natural gas network.

To meet these challenges, the project successfully developed a suite of novel siloxane gas standards at both NPL and VSL (a Researcher Mobility Grant researcher assisted VSL in this task, and also worked on syngas – see below) The mixtures contained four siloxanes (L2, L3, D4 & D5) at trace amount fractions ranging from 30 to 700 nmol/mol. The challenging validation of these mixtures was achieved by the development of a sensitive and repeatable GC-MS (gas chromatography – mass spectrometry) and GC-FID (gas chromatography – flame ionisation detection) methods. The chromatogram shown is a GC-FID chromatogram from a mixture of four siloxanes (2.19 ppm L2, 0.26 ppm L3, 7.04 ppm D4 & 0.44 ppm D5) in methane.



A novel TD-GC-MS (thermal desorption-GC-MS) method was developed at SP and used to measure the concentration of siloxanes in gas sample bags, where significant decay of the higher vapour pressure siloxanes was observed immediately after sampling. SP also looked at ammonia and conducted a feasibility study on the possibility of analysing ammonia in biogas using cavity ringdown spectroscopy (CRDS). Gas standards were prepared from a suite of synthetic biogas mixtures and ammonia in nitrogen by means of calibrated mass flow controllers and measurements indicate that measurement of ammonia in biogas at the sub-ppb level is achievable.



Tests were also performed by SP to analyse ammonia by optical feedback cavity enhanced absorption spectroscopy (OFCEAS). This work revealed that concentrations of ammonia between 10 ppb and 50 ppb can be successfully analysed by OFCEAS when sampling from gas cylinders. For amount fractions of 50 $\mu\text{mol/mol}$, sampling can also be performed in Flexfoil bags with negligible losses, but at concentrations around 10 $\mu\text{mol/mol}$ substantial losses of ammonia were observed due to the adsorption of ammonia on the inner surface of the bags.

New analytical methods were also developed by NPL and VSL for the analysis of low concentrations of sulphur compounds, including the measurement of hydrogen sulphide using GC-AED (gas chromatography - atomic emission detection).

Coal bed methane and coal mine methane

In order to assess the need for traceable standards and methods for coal bed methane and coal mine methane, the project undertook a comprehensive literature review of the composition of coal gases throughout Europe.

Following this review, the composition of coal mine methane shown in the table was selected as being representative of such gases found in Europe, and BAM, NPL, VSL, SMÚ and ČMI took part in an inter-laboratory comparison to test their analytical capabilities for such a mixture. A number of mixtures of synthetic coal mine methane of this nominal composition were prepared by the comparison coordinator (BAM) and circulated to each of the participants, who measured the concentrations of each component.

Component	Amount fraction (mmol/mol)
Nitrogen	169
Oxygen	5.00
Carbon dioxide	173
Methane	643
Ethane	8.50
Propane	0.785
<i>i</i> -butane	0.109
<i>n</i> -butane	0.0575
<i>i</i> -pentane	0.0170
<i>n</i> -pentane	0.0075

The results from the comparison, which were processed by BAM, show that excellent comparability was achieved between the participating laboratories. All mean values calculated from the measurements by the participating institutes were compliant with the gravimetric value(s) within the standard deviation of the mean values.

Hydrogen-enriched natural gas

VSL developed a range of synthetic novel natural gas mixtures containing hydrogen at amount fractions between 10 mmol/mol and 150 mmol/mol, which were validated using a natural gas analyser with GC-TCD and GC-FID detectors. Traceable and accurate measurements of hydrogen-enriched natural gas are therefore now available. This moves Europe closer towards allowing hydrogen to be blended in natural gas transmission networks, thus making use of hydrogen which can be produced from renewable sources such as the electrolysis of water using energy created from wind turbines.

Refinery gases

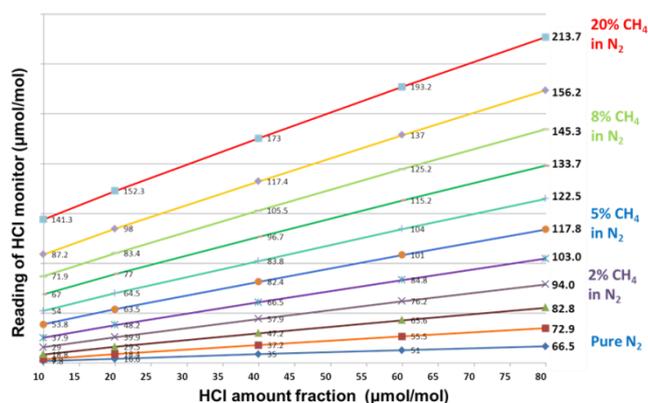
The work on refinery gases in the project aimed to improve the uncertainty and efficiency of current refinery gas analysis methods by devising a calibration method that could be used to measure a wide range of refinery gases with low uncertainties. Refinery gases are gases produced during the refining of petroleum products and accurate analysis of their composition is essential in order to provide industry and regulators

with confidence in measurements undertaken to comply with carbon trading legislations. The major challenges to be overcome in this project were to develop the method for the wide range of refinery gases and the matrix sensitivity of existing GC methods.

VSL (supported by NPL) produced mixtures of a wide range of refinery gases (including synthesis gas, biosyngas and coke oven gas). These standards contained carbon monoxide, hydrogen, methane, carbon dioxide, nitrogen and a range of unsaturated and saturated hydrocarbons. Stability tests performed using a multi column, multi-detector gas chromatograph refinery gas analyser system with GC-FID and GC-TCD detectors over the course of the project showed that the mixtures were highly stable in cylinders.

The work successfully led to a universally applicable calibration and reference method for the characterisation of a wide variety of refinery-gas and synthesis-gas-like mixtures.

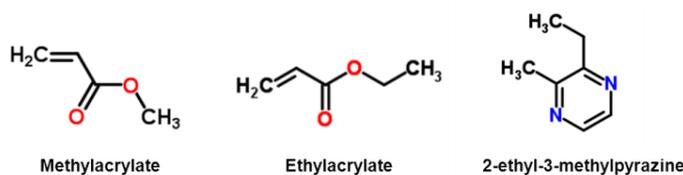
In addition to the work on composition measurements, VSL used the GC method to validate a suite of syngas mixtures prepared for a feasibility study into the analysis of hydrogen chloride in syngas (an RMG researcher assisted in this work). The hydrogen chloride content of these gas mixtures was measured using a novel gas filter IR spectroscopy method, which has a limit of detection of approximately 1 ppm for HCl in nitrogen. As shown in the figure, the study found that these measurements are matrix sensitive due to methane interference on the hydrogen chloride monitor, so further work is required before the method may be used for the analysis of real biogases, although IR spectroscopy is a highly promising candidate method to perform these measurements.



Odorants

The project also developed traceable and accurate standards and methods for the analysis of environmentally friendly, non-sulphur containing odorant species. The use of non-sulphur odorants in European gas transmission networks is increasing because of their lower levels of toxicity than conventional sulphur odorants such as sulphides, thiols (mercaptans) and tetrahydrothiophene. The most common non-sulphur odorant in use is 'Gasodor S-Free', which comprises methylacrylate, ethylacrylate and methylethylpyrazine at a total odorant concentration of approximately 11 mg.m⁻³. 'Gasodor S-Free' is used most widely in Germany, with a 25% market share. As with conventional sulphur-containing odorants, the accurate measurement of non-sulphur odorants is essential as concentration levels of these compounds have to be within defined limits – if the concentration is too low, the public are will not be able to detect potentially catastrophic gas leaks.

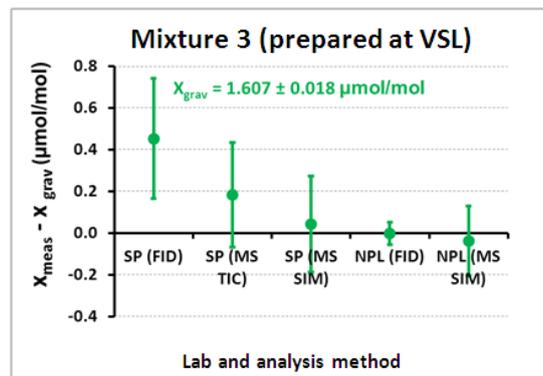
Three of the JRP-Partners (NPL, VSL & SP) developed a suite of novel gaseous reference materials containing the three components in the most widely-used commercial non-sulphur odorant mixture: methacrylate, ethylacrylate and 2-ethyl-3-methylpyrazine (the last of these components acts as a stabiliser) at challengingly low concentrations (approximately 1.2 µmol/mol (ppm), 1.6 µmol/mol and 55 nmol/mol (ppb) respectively, giving a total odorant concentration of approximately 11 mg.m⁻³). Two families of mixtures were produced at VSL, one from the three individual components, the other from a mixture of the odorants obtained from a commercial supplier.



Novel analysis methods were developed at all three JRP-Partner labs and these were used to validate the mixtures. NPL and VSL used GC-MS and GC-FID and SP used thermal desorption TD-GC-MS and TD-GC-FID using sorbent tubes (rather than injecting directly from gas cylinders). These methods were used to determine the stability of the gas mixtures - the acrylate species were found to be stable at these

concentrations for a period of at least one year. Stability tests on the mixtures in sample bags were also performed, and revealed a decrease in the measured concentration after only a few days, indicating that these compounds are far less stable in sample bags than they are in passivated cylinders.

The comparability of the standards and measurements at the three JRP-Partners was compared by exchanging mixtures between the laboratories. Three of VSL's gas mixtures were analysed at NPL and SP, and one of NPL's gas mixtures was analysed at SP. Excellent comparability between the labs was demonstrated, as illustrated in the graph.



Analysis of real non-conventional gases

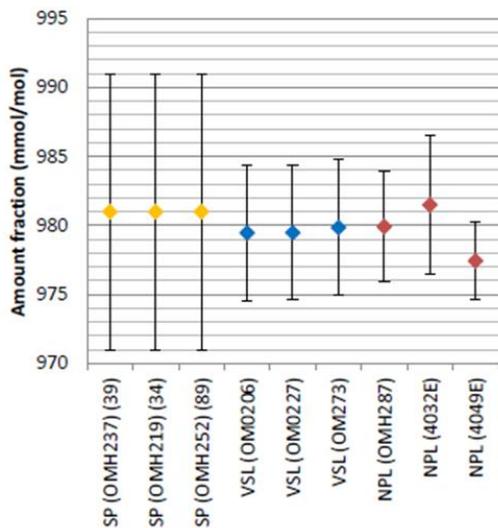
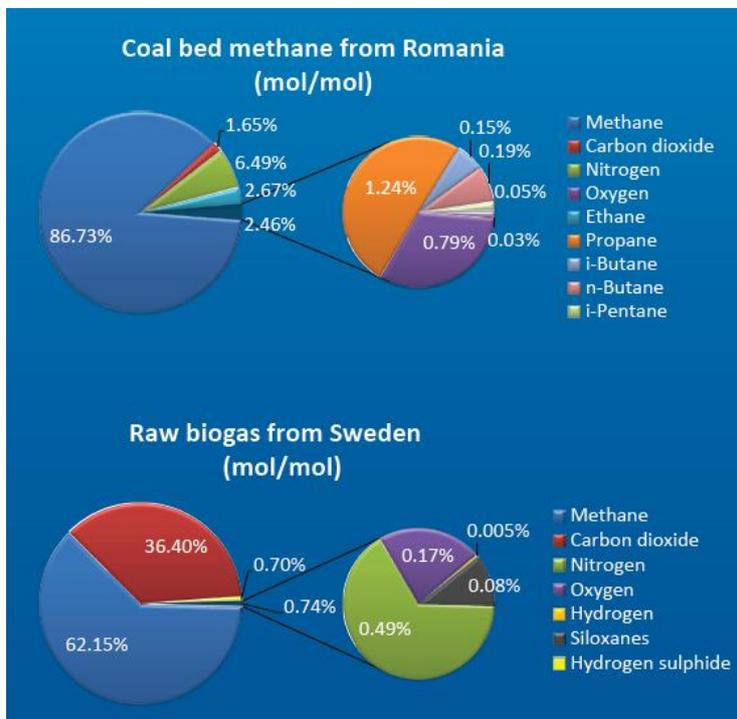
The project concluded by a number of the JRP-Partners participating in an exercise to measure the composition of, and impurities in, a wide range of real non-conventional gases obtained by the JRP-Partners (and their industrial contacts) from around Europe. The gases obtained and analysed in the study are shown below:

Sample	Obtained by	Labs performing analysis	Analytes
 Coal mine methane	BAM	NPL, VSL, SMÚ, ČMI, BAM	Composition
 Coal bed methane	BRML INM	NPL, VSL, SMÚ, ČMI, BAM	Composition
 Biogas (raw)	SP	NPL, VSL, SP	Composition, H ₂ S & siloxanes
 Biogas (part-processed)	SP	NPL, VSL, SP	Composition, H ₂ S & siloxanes
 Biogas (processed)	BAM	NPL, VSL, SP	Composition, H ₂ S & siloxanes
 Biogas (processed)	MKEH	NPL, VSL, SP	Composition, H ₂ S & siloxanes

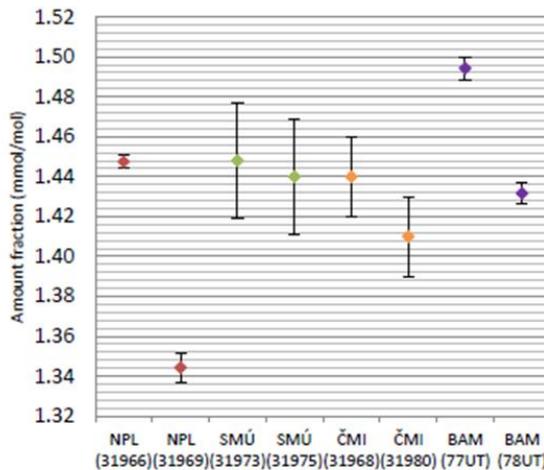
The analysis of these real samples was highly challenging due to a number of factors caused by the samples being real field samples (and not synthetic gas mixtures). These include the samples being at low pressure, containing a high amount of water and the presence of unexpected compounds.

Despite these challenges, the analyses, which used methods and gas standards developed under other deliverables in the project, were performed to schedule. Some results showing the composition of coal mine methane from Romania and raw biogas from Sweden are shown in the pie charts. The results showed good levels of comparability - some examples of the results from the comparison are shown in the charts below.

The results from the comparison were presented by Lucy Culleton (NPL) in a poster (*Results of an international comparison of the analysis of real 'non-conventional' gas samples*), which was awarded the 'Best Poster' prize from a strong selection of 36 posters at the Gas2013 international gas symposium, Rotterdam, June 2013.



Methane in processed biogas from Hungary



i-butane in coal bed methane from Romania

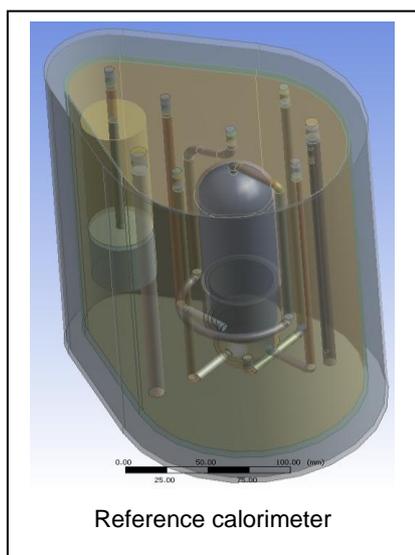
Direct measurement of the calorific value of non-conventional gases

Primary and commercial calorimeters for gaseous fuels able to measure calorific values with the lowest possible uncertainty have been adapted and validated for non-conventional gases. BAM and NPL collaborated to provide the reference gas mixtures used in the study; these mixtures are accompanied by certificates of composition which are traceable to the primary standards. Six synthetic biogas mixtures containing either CO₂ and CH₄ or CO₂, CH₄ and H₂S and one mixture that represents a synthetic coal mine methane have been then studied. The different H₂S concentrations in the biogas mixtures simulate gases from different purification steps in biogas upgrading. The presence of hydrogen sulphide in a wet environment can cause high corrosion damage in flanges and pipelines.

The calorific values and associated uncertainties obtained from the measurements of these gases have been compared, both between the calorimeters, and with the indirect method. These measurements are particularly challenging, as the presence of impurities, odorant species, moisture and process by-products at a low level all have effects on the energy content of the mixture.

Adaptation and improvement of the primary and field calorimeters

For the accurate determination of calorific values of non-conventional gases, four calorimeters were studied: three field calorimeters at PTB and BRML and one reference gas calorimeter at LNE.



The calorific value of a fuel gas obtained with the LNE reference calorimeter is directly proportional to the temperature rise of the calorimetric water bath $\Delta T_{ad,comb}$ resulting from the combustion of a given quantity of that gas. For superior (or gross) calorific value, the water released during the combustion has to be trapped in its liquid state at the bottom of the burner. The gross calorific value is calculated by the equation

$$H_s = \frac{C_{cal}\Delta T_{ad,comb} + K}{m_{gas}}$$

The term m_{gas} is the mass of the gas to be burned (kg) and K represents the different energetic corrections inherent in a combustion experiment, i.e., electrical energy released for ignition, energy due to water vapour leaving the calorimeter during the combustion and the energy due to the temperature gradient between gas inlet and gas outlet. The heat capacity of the calorimeter C_{cal} is calculated from a calibration in which an electrical dissipation is performed (an amount of electrical energy E_{cal} equivalent to the combustion is released by the

Joule effect).

The heat capacity determination by electrical dissipation in the calorimeter guarantees traceability of each calorific value assessment to the SI units. The measurements of the value of H_s of the non-conventional gases were performed after modifying the calorimeter to minimise the risk of damaging components, such as the gas burner or connecting pipework. Flame tests have been performed with different gas flows of oxygen and fuel gas to fix the conditions for a stable flame. The instability could be caused by the presence of carbon dioxide in the mixtures and also by the particular mode of the combustion that displays both a premixed and diffusion flame. Particular attention was given during the flame tests to the position of the flame at the outlet nozzle: for good combustion, the flame should be neither lifted nor be attached to it.

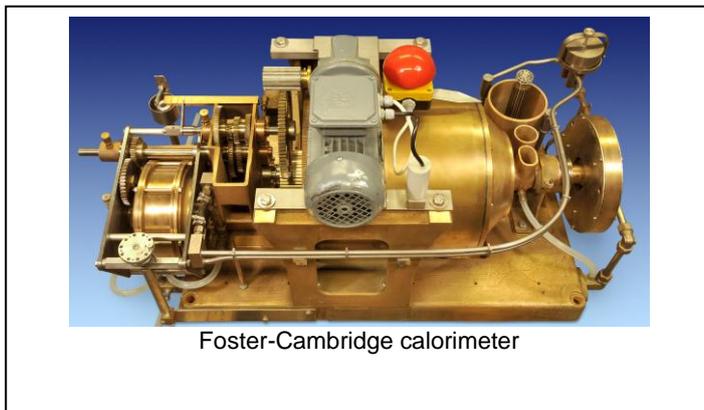
An infrared technique has been used to measure the CO and CO₂ content of the burned gas, and flame ionisation detection was used for measuring the total amount of unburned hydrocarbons in a measuring range from 1 up to 30000 $\mu\text{mol/mol}$. For sulphur containing compounds, analyses were performed by FTIR with a measuring range for SO₂ of up to 1000 $\mu\text{mol/mol}$.

Although traceable field calorimeters are currently commercially available for on-site measurements of natural gases to determine calorific values for billing purposes, these instruments have neither been tested nor validated for use with non-conventional gases.

A number of conditions are required for the development and qualification of field calorimeters for non-conventional fuel gases, such as appropriate air conditioning and environmental control in the respective laboratories, calibration gases, and tools for data acquisition and data evaluation. Three field calorimeters have been improved to perform accurate calorific value measurements of non-conventional gases: two from Union Instruments (at PTB and BRML) and one Foster-Cambridge calorimeter (PTB).



Union Instruments calorimeter



Foster-Cambridge calorimeter

The Union Instruments calorimeters have been adapted for biogas use by changing the nozzle. No prior conditioning of the gas is necessary.

Daily calibration with a standard gas defined by the manufacturer is recommended. The PTB calorimeter has a measurement range between 4 kWh/m³ to 8 kWh/m³; the BRML calorimeter is designed for measuring natural gas with a range between 7 kWh/m³ and 14 kWh/m³.

The Foster-Cambridge calorimeter is used as a so-called wet calorimeter with complete saturation of the fuel gas. The whole system is maintained at a temperature of 22.5 °C. After calibration of the system with a gas of a known calorific value, the calorific value of a test gas is calculated by the equation:

$$H_{s, \text{test}} = \frac{\Delta T_{\text{test}}}{\Delta T_{\text{cal}}} \cdot H_{s, \text{cal}}$$

The calorimeter can be operated in two measuring ranges of nominally 7 kWh/m³ to 14 kWh/m³ (natural-gas range) and 3.5 kWh/m³ to 7 kWh/m³ (town-gas range).

Application of the adapted calorimeters to reference gas mixtures

Reference gases and implementation of the field calorimeters

Seven different gas mixtures were used for the validation tests. These substances represent the main components of biogases. The composition of the multi-component coal mine methane mixture (CMM) was selected to be representative of coal mine methane found in Europe. All mixtures were prepared gravimetrically by NPL and BAM, in accordance with ISO 6142 and are traceable to primary standards. The compositions of the mixtures were validated in the respective laboratories using gas chromatography.

Composition (mmol/mol)	BIO 1	BIO 2	BIO 3	BIO 4	BIO 5	BIO 6	CMM
CH ₄	400.945 ± 0.047	599.322 ± 0.062	799.987 ± 0.081	500.01 ± 0.15	600.46 ± 0.16	698.18 ± 0.18	642.080 ± 0.051
CO ₂	599.054 ± 0.061	400.677 ± 0.040	200.01 ± 0.021	499.87 ± 0.15	398.83 ± 0.16	298.94 ± 0.15	173.123 ± 0.017
H ₂ S				0.03626 ± 0.00037	0.7125 ± 0.0072	2.864 ± 0.029	
N ₂							170.319 ± 0.019
O ₂							5.041 ± 0.001
C ₂ H ₆							8.466 ± 0.004
C ₃ H ₈							0.781 ± 4.064E ⁻⁴
<i>i</i> -C ₄ H ₁₀							0.107 ± 5.572E ⁻⁵
<i>n</i> -C ₄ H ₁₀							0.057 ± 3.026E ⁻⁵
<i>i</i> -C ₅ H ₁₂							0.0172 ± 3.446E ⁻⁵
<i>n</i> -C ₅ H ₁₂							0.0075 ± 1.504E ⁻⁵

Compositions of the seven different gas mixtures used for the validation tests

The field calorimeters were validated for use with non-conventional gases by experimental and computational investigations. The validation consisted of:

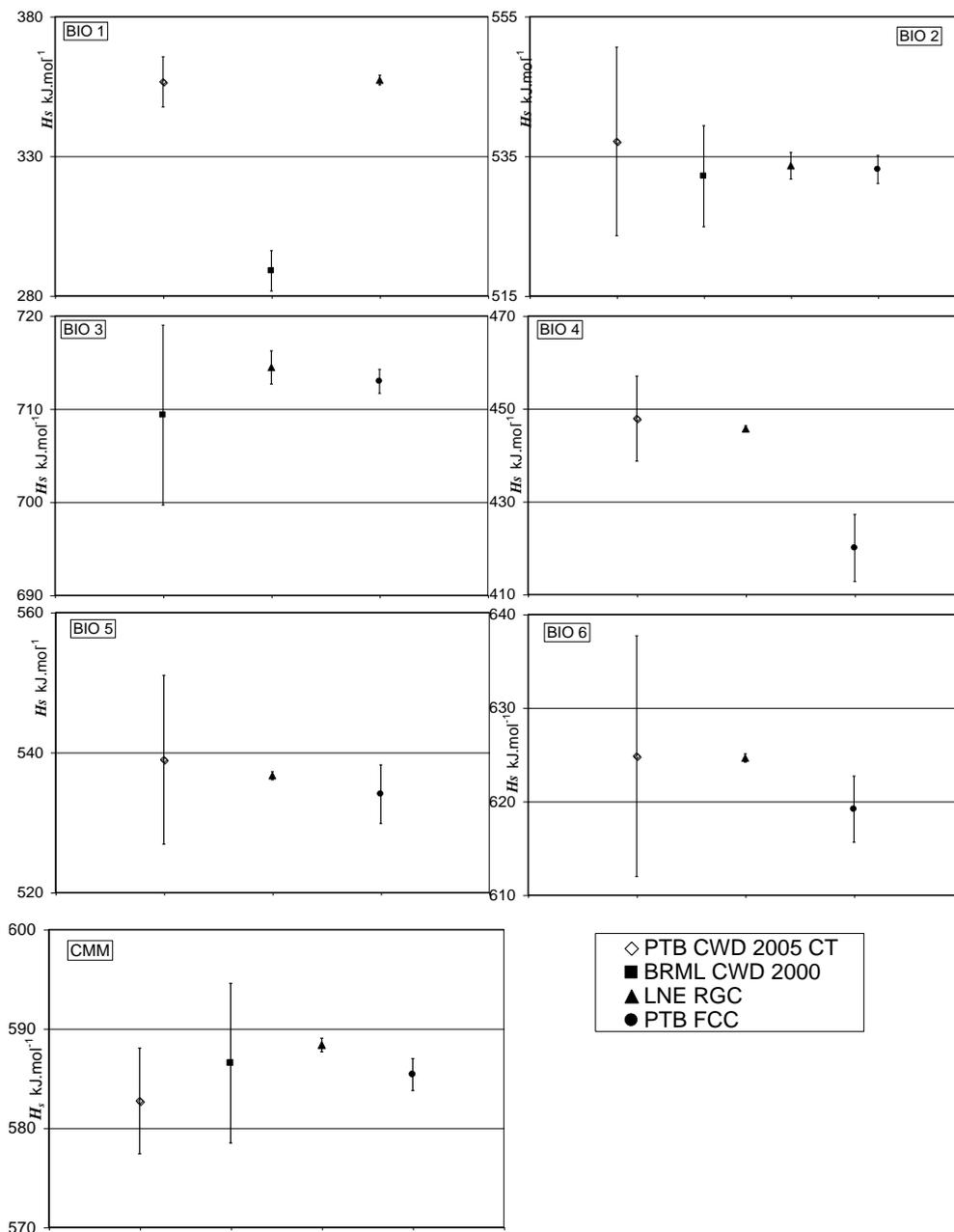
- The determination of influencing factors (atmospheric pressure, room temperature, atmospheric humidity and gas pressure).
- The development and application of a calibration strategy for each calorimeter.
- The determination of uncertainty of calorific values.

For the Foster-Cambridge calorimeter, three calibration gases were used for calibration in the natural gas measuring range and the uncertainty calculation was based on ISO 6143. This standard was originally written for gas analysis using gas chromatography but can in principle be applied to any analytical instrument, including calorimeters. It takes into account the uncertainty of the calibration gases and non-linear response curves.

For the Union Instruments calorimeter CWD 2005, the influence of environmental factors, such as room temperature or atmospheric pressure, on the overall uncertainty of the calorific value is negligible. Calibration according to the German standard DIN 51899 was applied to the two Union Instruments calorimeters with calibration gases supplied by the manufacturer, for the binary and ternary mixtures of the two institutes. The application of the standard DIN 51899 allowed the calculation of calorific values of the reference gases and the assigning of uncertainties. However, for the CWD 2005 calorimeter, the calorific value of coal mine methane was obtained from a quadratic calibration function with four calibration gases according to ISO 6143.

Calorific value measurements

LNE and PTB tested all seven gas mixtures with their calorimeters and BRML tested a subset of four gases with their calorimeter. For all the mixtures, the repeatability uncertainty is combined with the uncertainty calculation issued from the analytical method.



Calorific values in kJ.mol⁻¹ for all the gas mixtures and calculated uncertainties for the reference and field calorimeters. RGC and FCC are abbreviations for the reference gas calorimeter and Foster-Cambridge calorimeter respectively.

The primary reference calorimeter was modified to enable the measurement of reference gas mixtures of methane and carbon dioxide that correspond to non-conventional gas matrixes. Once its validation for non-conventional gases was realised after optimisation of the combustion, the calculated calorific values agreed with the values obtained by the field calorimeters (within their uncertainties). As an electrical calibration is undertaken before each experiment, the reference calorimeter is able to determine the calorific value of any fuel gas (with adapted flow rates of oxidisers) whatever its energetic behaviour. An uncertainty calculation was executed for each parameter of the mathematical model for the calorific value in which the law of uncertainty propagation according to the standard NF ENV 13005 was applied (with the consideration of correlations between uncertainties).

The Union Instruments CWD 2005 calorimeter was suitable for measuring calorific values in the range from $320 \text{ kJ}\cdot\text{mol}^{-1}$ to $640 \text{ kJ}\cdot\text{mol}^{-1}$. The BIO 3 mixture measurement (with a high calorific value) led to a high outlet temperature that was potentially dangerous for the device and triggered a safety switch. By using four calibration gases and a quadratic calibration function for CMM, the uncertainty was reduced to a value of 0.92 %.

The Foster-Cambridge calorimeter was suitable for measuring non-conventional and conventional fuel gases in the range of H_s from $480 \text{ kJ}\cdot\text{mol}^{-1}$ to $1000 \text{ kJ}\cdot\text{mol}^{-1}$. It was not possible to measure the mixture with the lowest calorific value, BIO 1, because the mixture could not be ignited.

Irrespective of the gas composition, the uncertainty with this calorimeter was lower than the CWD calorimeters, and the calorific values are in agreement with the values from the primary calorimeter within the combined uncertainties.

For the CWD 2000 calorimeter used at BRML, the gas with the highest calorific value (BIO 3) was measured with nozzles suitable for natural gas and the calorimeter was calibrated with pure methane. The other gases were measured with nozzles adjusted to the low-calorific value range. The calibration process followed the German standard DIN 51899 with a single-point calibration. The calorific value for BIO 1 deviated considerably from the others which indicated that the lower end of the linear measuring range of the calorimeter had been exceeded.

It can be concluded from the experiments that the measurement ranges of field calorimeters could be extended for specific use with non-conventional gases or biogases (after some modifications of the burning system). By doing that, it was possible to successfully carry out accurate measurements even at extreme ends of the measuring ranges. Moreover and in order to reach consistent and true energy content values, a combination of an advanced calibration processes and certified calibration gases covering the entire measuring ranges of those commercial instruments are mandatory.

Comparison of the indirect method with ISO 6976 values

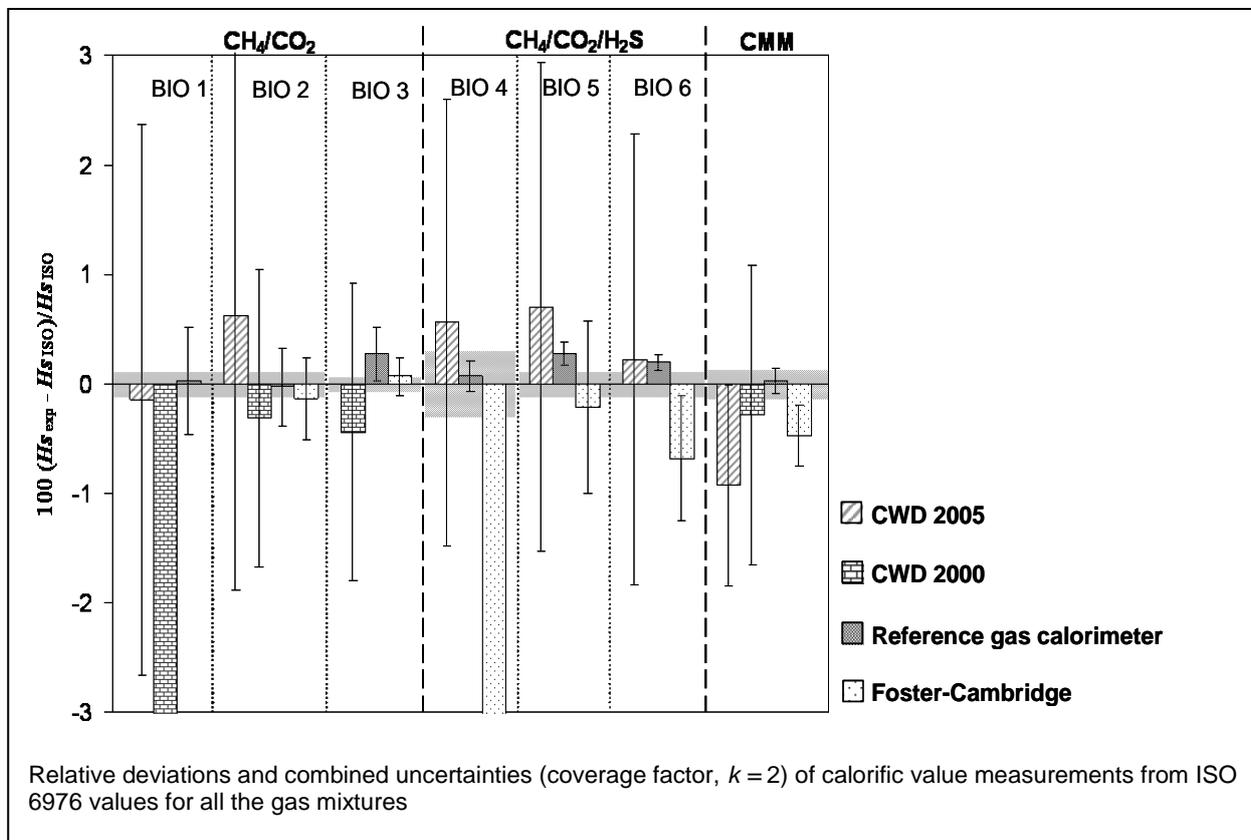
The figure below plots the differences between the calorific values obtained by calorimetry and those calculated according to the method proposed in ISO 6976. The grey shaded areas represent the uncertainties in the calorific values calculated by ISO 6976. The calorific values agree well with the values obtained from the indirect method and ISO 6976.

Large deviations have, however, been observed for the lowest energetic mixtures (i.e., BIO 1 and BIO 4) with the field calorimeter CWD 2000 at BRML and the Foster-Cambridge calorimeter at PTB, respectively.

Thus, the linear measuring range of these calorimeters was less than that specified by the manufacturer. However, adjusted calibration gases could in that particular case decrease this deviation and overcome these shortcomings. The deviation observed for the mixture BIO 4 with the commercial Foster-Cambridge calorimeter could be explained by the irregular behaviour of the flame in the calorimeter. The selection of the gases for calibration and the procedure to calculate uncertainties are of key importance in obtaining repeatable and reliable calorific values from field calorimeters.

Taking into account this last fact, the results from the CWD 2005 calorimeter agree within the uncertainty range with the ISO values for mixtures where combustion was possible. Considering the expected biogases and non-conventional gases to be studied in future, a field calorimetry that has been improved by accurate calibration processes could be employed for investigations over a broad range. The calorific values measured by the reference calorimeter displayed the lowest deviations from ISO 6976 values and also the

lowest uncertainties compared to the field calorimeters. However, cross-checked uncertainties agree only for the gases BIO 5 and BIO 6. The presence of hydrogen sulphide could cause combustion instabilities.



Thermophysical properties: Density and speed of sound measurements

Experimental characterisation of the thermodynamic behaviour of fuel gas binary mixtures is of great importance due to the proven lack of reliable data on the thermodynamic properties of such mixtures. These data are essential not only for the improvement and test of the current reference equation of state for natural gases and related mixtures, GERG-2008, but also for the indirect determination of other properties.

CEM led this work and accessed equipment at the University of Valladolid. Accurate density and speed of sound measurements of several binary and multicomponent synthetic gas mixtures, similar to real non-conventional gases have been performed, at temperatures between 250 K and 400 K and pressures up to 20 MPa. A single sinker densimeter with magnetic suspension coupling was used for density determination and a spherical resonator for indirect calorific value determination of non-conventional energy gases and isobaric heat capacity determinations. No previous density or speed of sound data of synthetic mixtures with similar compositions to that of non-conventional gas fuels, such as biogas or CMM, can be found in the literature.

Mixture preparation

CEM has prepared several binary mixtures (reference gas mixtures by the gravimetric method according to ISO 6142) whose density and associated speed of sound were determined at the facilities at the University of Valladolid.

The nominal compositions of the mixtures are:

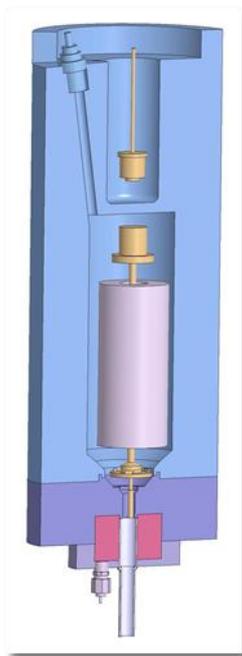
x (mol/mol)	CH ₄	CO ₂	N ₂	CO
Binary mixture 1			0.95	0.05
Binary mixture 2			0.90	0.10
Binary mixture 3		0.10	0.90	
Binary mixture 4		0.15	0.85	
Binary mixture 5		0.20	0.80	
Binary mixture 6		0.50	0.50	
Binary mixture 7	0.80	0.20		
Binary mixture 8	0.60	0.40		
Binary mixture 9	0.40	0.60		



Mixture preparation facility at CEM

Density determination

CEM again accessed University of Valladolid equipment to obtain accurate experimental (p , ρ , T) data in the supercritical and gaseous state at temperatures ranging from 250 K to 400 K and pressures up to 20 MPa were obtained by using a single-sinker densimeter with magnetic suspension coupling. The densimeter is based on the Archimedes' Principle measuring the buoyancy force on a sinker immersed in a fluid, proportional to the density of the fluid and the volume of the sinker. With the magnetic coupling, it is possible to measure the sinker mass with an accurate balance for wide temperature ranges from (250 to 400) K ($U = 4$ mK) and pressure ranges up to 20 MPa, ($U = 0,015$ %) with an uncertainty for density between 0.02 % and 0.34 % ($k = 2$).



Single Sinker densimeter

Speed of sound determination

Accurate experimental speed of sound data in the supercritical and gaseous state at temperatures ranging from (250 to 400) K and pressures up to 20 MPa were obtained by using a spherical resonator provided by the University of Valladolid. The spherical resonator consists of a spherical cavity, an acoustic transducer and an acoustic receptor for the measurement of speed of sound: an acoustic synthesizer sweeps a frequency in the range of the theoretical resonance frequency to locate and measure the real resonance frequencies. Isobaric heat capacities can be calculated from the speed of sound data taken at temperatures from 200 K to 475 K ($U = 4$ mK) and pressure ranges up to 20 MPa ($U = 0.015$ %) with an uncertainty of $1 \cdot 10^{-3} c_p \text{ J} \cdot \text{kg}^{-1} \cdot \text{K}^{-1}$ ($k = 2$).



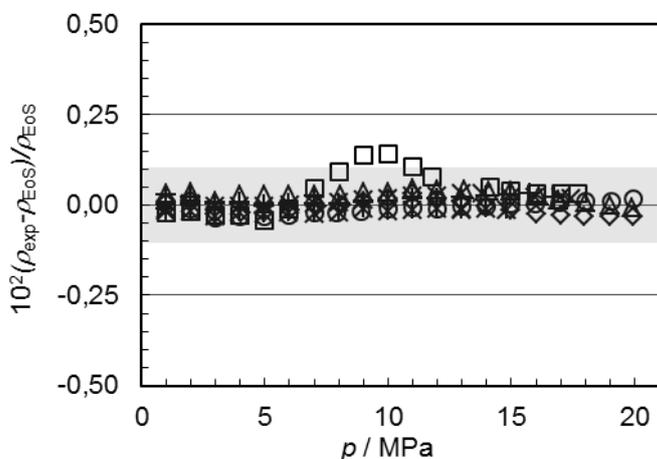
Spherical resonator for speed of sound measurement

Experimental results

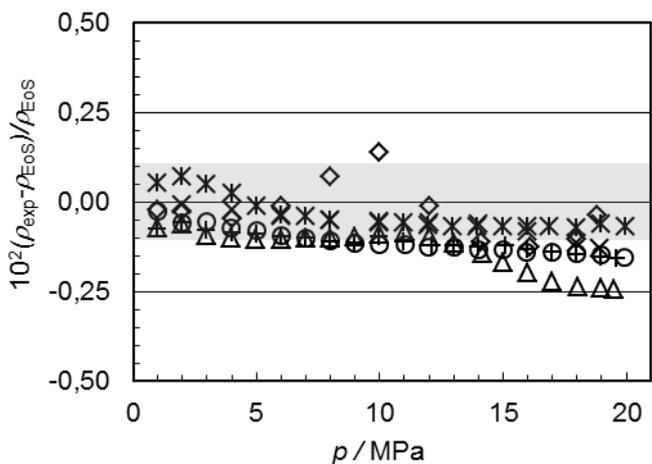
Accurate density measurements for three binary mixtures of carbon dioxide with methane ($x_{CO_2} = 0.20, 0.40, 0.60$) mol/mol were performed at temperatures between 250 K and 400 K, and pressures up to 20 MPa, using a single sinker densimeter with magnetic suspension coupling, which is one of the state of the art methods for density determination over wide ranges of temperature and pressure. Experimental densities were compared with the GERG-2008 equation of state and with the experimental data reported by other authors for similar mixtures. Relatively large deviations from the equation of state observed at low temperatures suggests the possibility of higher uncertainties of the GERG model in the low temperature range.

The next figures show the percentage density deviations of experimental (p, ρ, T) data of $CO_2 + CH_4$ binary mixtures from density values ρ_{EoS} calculated from the GERG-2008 equation of state versus pressure:

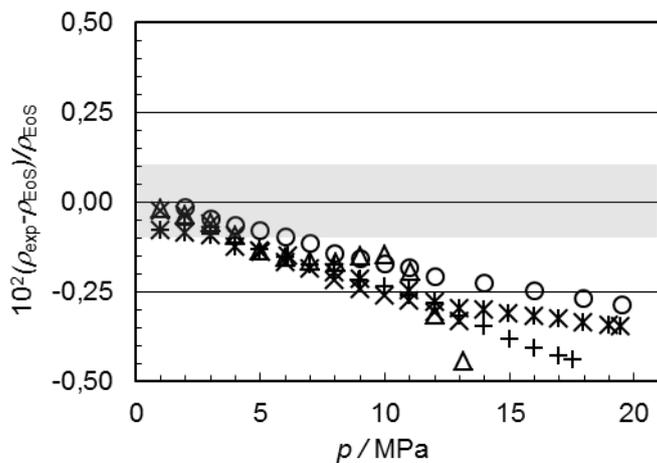
□ 250 K; ◇ 275 K; △ 300 K; x 325; + 350 K; ○ 375 K; * 400 K.



(0.20 CO₂ + 0.80 CH₄) binary mixture

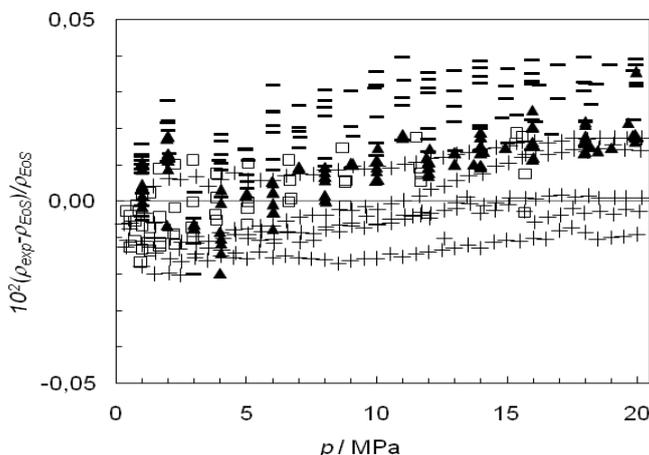


(0.40 CO₂ + 0.60 CH₄) binary mixture



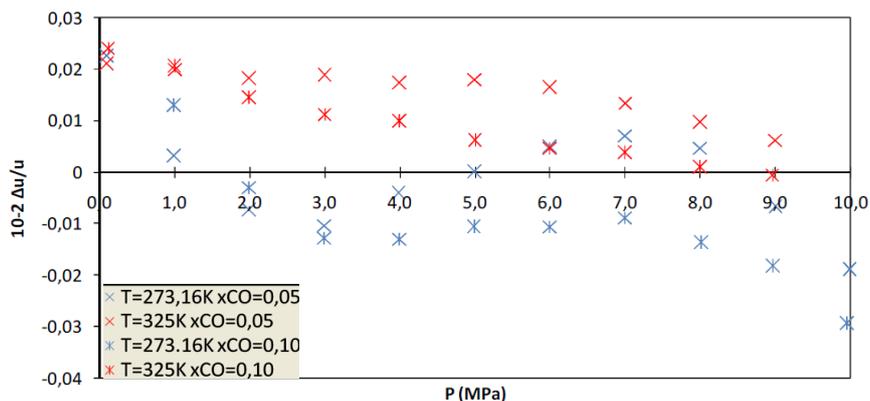
(0.60 CO₂ + 0.40 CH₄) binary mixture

As an example of the combined results obtained with this research, density and speed of sound data on two binary mixtures of CO in N₂, with some derived properties, have been obtained. The figures below show, for (0.10 CO + 0.90 N₂) and (0.05 CO + 0.95 N₂) mixtures, the deviations of experimental (p, ρ, T) data from density values ρ_{EoS} calculated from the GERG-2008 equation of state and the perceptual deviation of speed of sound measurements from the same equation, respectively, versus pressure. There is good agreement with the GERG model.



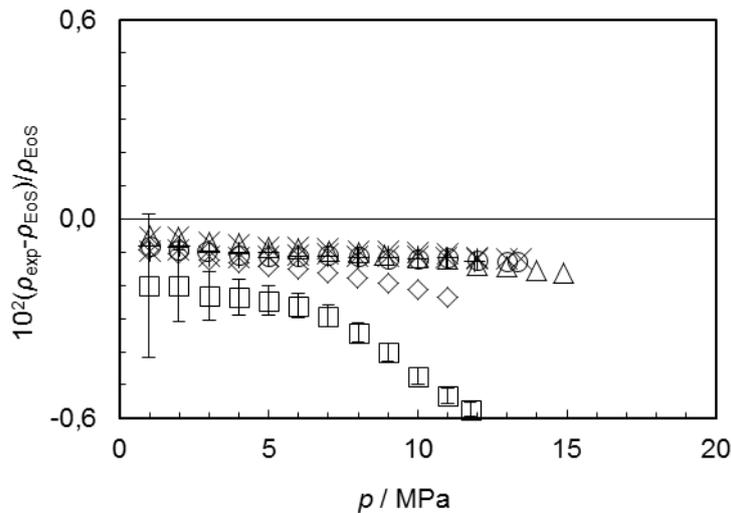
Density results in the temperature range (250 to 400) K and pressures up to 20 MPa:

▲ for $x_{CO} = 0.05$ mol/mol; – for $x_{CO} = 0.10$ mol/mol



Speed of sound data taken at temperatures between 273.16 K and 325 K and pressures up to 10 MPa

A synthetic coal mine methane mixture, prepared gravimetrically at BAM (described in the previous section) was also included in this thermodynamic study. Relative deviations in density of experimental (p, ρ, T) data of the synthetic coal mine methane mixture from density values calculated from the GERG-2008 equation of state, versus pressure, at 250 K; 275 K; 300 K; 325; 350 K; 375 K; 400 K are shown in the next figure. Error bars on the 250 K isotherm indicate the expanded uncertainty ($k = 2$) of the experimental data. Relative deviations between experimental data and estimates were within a 0.2 % band for temperatures above 275 K. However, data at 250 K and at 275 K and pressures above 10 MPa showed larger deviations which increased with pressure.



Experimental density data compared to GERG-2008 for a CMM mixture

New primary and reference humidity facilities

Humidity generators

Two separate routes were followed to develop novel humidity generators for non-conventional gases, one to cover “high” pressures (up to 6 MPa) and the other to cover “low” pressure (up to 0.5 MPa). The low pressure reference generator unit developed by PTB utilises an electrochemical technique which has not previously been applied to non-conventional gases. Completely dry gases are humidified by introducing dry hydrogen and oxygen in to the gas stream in precisely controlled amounts. The gas stream is then passed over a catalytic Pt/Pd-converter at about 140 °C which re-transforms the hydrogen and oxygen to water and thus the gas stream is humidified. The hydrogen and oxygen are introduced in very precise amounts by electrolysing water in a separate part of the apparatus and thoroughly drying in a cooling trap at -170 °C before passing on over the above mentioned catalytic converter to the mixing area. Electrical control of the current gives very accurate quantities of hydrogen and oxygen according to Faraday’s law and they are as a matter of course produced in exactly the correct stoichiometric quantities for recombination as water. The approach has proven very successful for methane and the apparatus has been validated using chilled mirror hygrometers and performing extensive analysis on the system. The “Coulometric Trace Humidity Generator” has been shown to be capable of generating humidity in the 10 ppm to 1000 ppm (by volume). The expanded relative uncertainty at 1.0×10^{-5} kg/kg is 4.7 % ($k=2$). With better determination of the blind level of water in methane further significant improvement of the uncertainty will be possible. A schematic diagram of the system is shown in Figure 1:

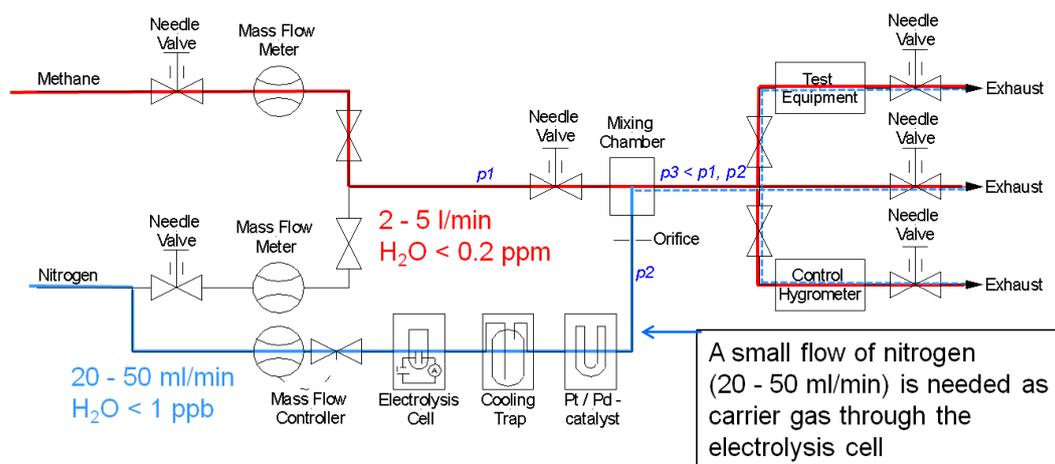


Figure 1. Scheme of the Coulometric Trace Humidity Generator developed at PTB

The high pressure generator developed by VSL followed a different approach. The dry gas mixture is passed through a saturator unit consisting of a convoluted labyrinth where the dry gas is exposed to liquid water or ice (at the bottom of the system shown in Figure 2). The efficiency of the generator was validated with chilled mirror hygrometers. The equipment demonstrated excellent performance with an uncertainty of 0.04 °C in the range -41 °C to +15 °C at up to 6 MPa with nitrogen. With methane the achieved range is limited by the formation of methane-hydrates. The generator is illustrated in Figure 3.



Figure 2. A photograph showing the saturator of the high pressure generator developed at VSL

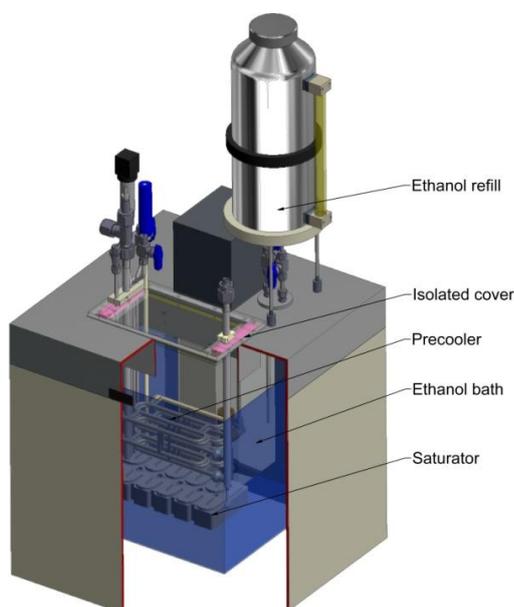


Figure 3. Construction of the high pressure generator developed at VSL

The project therefore delivered the objective through collaboration between PTB and VSL, with both low and high pressure humidity generators compatible with methane and non-conventional gases.

Gas mixture generator and enhancement factors

It has long been recognised that interaction of gas molecules with water molecules results in a small increase in the saturated vapour pressure of water in air compared to the saturated vapour pressure of pure water vapour. An enhancement factor is commonly used to correct for this and is defined as the ratio of saturated vapour pressure of water in moist air to the saturated vapour pressure of pure water. When estimating the risk of water vapour condensation in pipelines, humidity should be known in terms of dew-point temperature. In a large number of instruments, however, the output signal is primarily a function of water vapour pressure or water vapour amount fraction. These quantities are interrelated to each other through saturation water vapour pressure data. The data is also needed when calculating the effect of pressure drop in a sampling line. This effect can be taken into account by introducing the enhancement factor in calculations. However, the available enhancement factor formulae are too limited in variety of gas compositions and temperatures for the field of non-conventional energy gases. To improve the calculations, the water vapour enhancement factor in methane was studied empirically with the novel gas mixture generator system developed by MIKES for this purpose in this project.

The MIKES gas mixture generator comprises a precision water vapour mixing unit and a cooled coil dew-point indicator in series allowing direct comparison between the water amount fraction and dew-point temperature which is needed to determine the enhancement factor. As the system forms a closed loop with a dryer and compressor unit (see Figure 4), the consumption of gas is very small enabling long experiments with various types of gases. The operation range of the system covers the saturation temperatures and pressures $-50\text{ }^{\circ}\text{C}$ to $+15\text{ }^{\circ}\text{C}$ and 0.1 MPa to 7 MPa , respectively. To obtain traceable water injection in the generator system, a novel calibration method was developed for ultralow liquid flows.

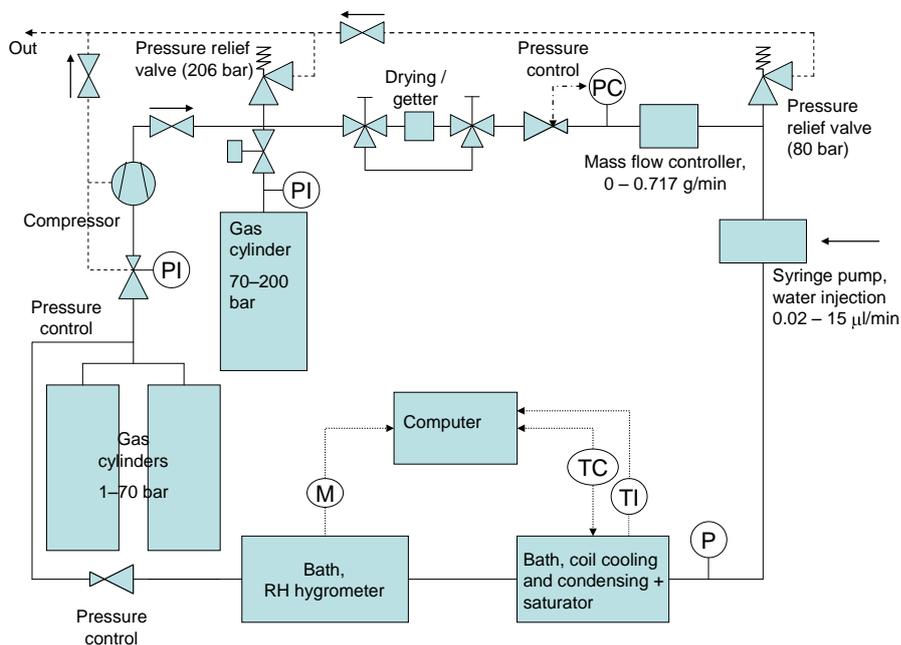


Figure 4. Schematic diagram of the gas mixture generator developed at MIKES for measuring the water vapour enhancement factor in energy gases

The water vapour enhancement factor for methane was measured with the MIKES gas mixture generator in the pressure range from atmospheric pressure up to 70 bar and the dew-point temperature range from +15 °C down to hydrate forming temperatures. Using the measurement results amended with data calculated from published results on water-methane phase equilibria, MIKES (assisted by SMU) derived a simple formula for the enhancement factor, as shown in Figure 5.

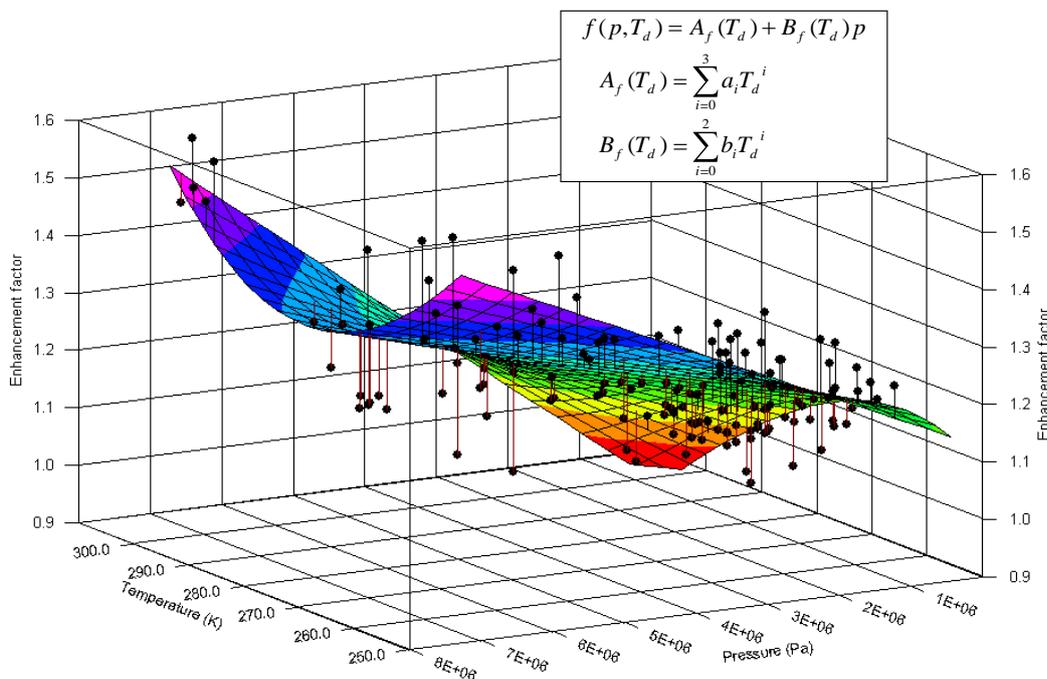


Figure 5. New formula for the water vapour enhancement factor in methane was derived by multiparameter nonlinear fitting

Development and validation of a test facility for the characterisation of humidity sensors

As hygrometers and humidity sensors respond differently in different gases and water vapour behaves differently in different gases, hygrometers should be calibrated under conditions as close as possible to their actual use. For practical reasons it is unreasonable to expect end users to be able to do this across the entire range of conditions expected. Therefore, the project aimed to develop a facility which would allow hygrometers and sensors to be calibrated/characterised across a wide range from 30 ppm to 2 % moisture at pressures of 0.1 MPa to 3 MPa.



Figure 6. The facility developed at NPL for characterising humidity sensors with various gas mixtures

The facility shown in Figure 6 was successfully developed at NPL. Its operation is based on blending saturated air with the test gas. Also, direct saturation is possible through a high pressure saturator. Wide operating range is obtained by several mass flow controllers in series. The system can be operated with a range of gases (e.g. nitrogen, argon, methane and methane-hydrocarbon mix with hydrocarbons up to C6). Its performance was verified with a calibrated hygrometer. Within this project, this facility was used in the evaluation of metal oxide sensors (described below).

Comparison methods for primary and secondary humidity standards in energy gases

Inter-laboratory comparisons are needed by industrial calibration laboratories to obtain impartial evidence on their competence. These are usually arranged by national metrology institutes to ensure the reliability of the results at the level needed by the participants. Prior to the project there was no agreed satisfactory method for humidity intercomparisons in the field of energy gases. However within the project, PTB (in collaboration with MIKES, VSL and NPL) has produced a recommendation amending existing general guidelines for intercomparisons and giving guidance on aspects specific to humidity measurements in energy gases. Applying this document the comparisons can proceed with greater confidence in future.

Evaluation and comparison of novel and existing techniques for humidity sensing in energy gases

Chilled mirror hygrometers

The chilled mirror hygrometer is a classical method for determining dew-point in a variety of gases. When humid energy gases are studied the main problem is that the instrument is sensitive to condensation in general, and does not differentiate between hydrocarbon condensation and water condensation. A further complication is that hydrocarbons can condense as continuous thin films which some instruments find difficult to detect or discern. In this project PTB worked closely with industrial collaborators on modifying an existing instrument to include, for the first time, a microscope head and a video camera so that energy gas condensation behaviour could be studied in detail.

PTB, supported by INTA, performed co-condensation experiments with propane/water mixtures in a pressure range of 1 bar to 6 bar. The results showed that the condensation behaviour was slow to achieve equilibrium and that results were very dependent on the rate of temperature change at the mirror surface. Even the simple binary propane/water mixture showed complex phases. Figures 7 and 8 give an impression of the different observed phases. At the lower pressures of the studied range, the sequence of phases on cooling the system is as follows:

- Firstly, the formation of a water-containing crystalline layer around existing seed crystals was observed (Figure 7).
- Secondly, the crystals grew with decreasing temperature.
- Later, the crystalline layer was covered by a liquid after further decreasing temperature, starting with smoothing the crystalline structure followed by the formation of large droplets after further cooling down of only a few degrees Celsius.

At the higher pressure of 0.6 MPa the condensation of liquid droplets was the first observed phase change at 8 °C (Figure 8). The droplets expanded to a closed liquid layer with decreasing temperature.

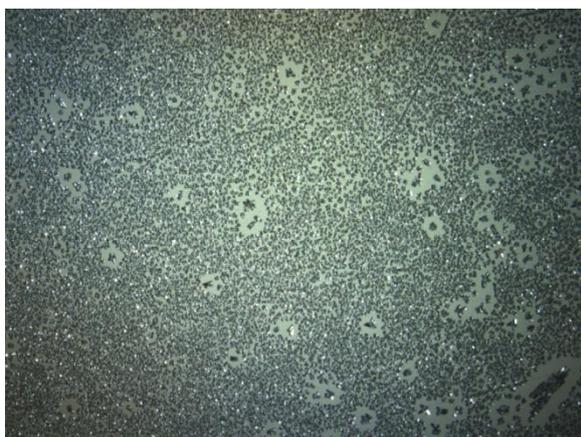


Figure 7. Formation of water containing crystals from propane with a purity of 99.95 vol. %; the dew point mirror was defrosted from -40 °C to -27 °C at a pressure of 0.1 MPa



Figure 8. Fluctuating droplets from propane with a purity of 99.95 vol. % at 7.8 °C and a pressure of 0.6 MPa

Development and characterisation of novel laser optical hygrometers

There has long been a desire to use accurate optical laser instruments to directly measure the water content of energy gases at high pressures. However, so far, most optical hygrometers used in the natural gas industry are used in the extractive gas sampling mode where gas is expanded from pipeline line pressure (≈ 8 MPa) to about 0.1 MPa in the gas cell. This pressure drop causes a temperature drop of the gas in the gas cell, leading to condensation of the water. In addition, the extraction process can easily lead to the contamination of the sample. Previous attempts for water measurements at high gas pressures have run in to the immediate problems of spectra overlap, e.g. of water and methane, and significant line-broadening. PTB's approach to overcome this problem was first to select a suitable water transition with very low inference from neighbouring water lines or from hydrocarbon molecules, at pressures greater than the typically used 0.1 MPa. Then, the project set out to develop and characterise a new laser hygrometer based on newly available short wave mid infrared tuneable diode lasers for application in energy gases at pressures of at-least 0.5 MPa and make recommendations for its calibration and extension to higher pressures. A tuneable diode laser absorption spectroscopy (TDLAS) hygrometer operating at pressures up to 0.5 MPa was developed, characterised and delivered the targeted performance for water measurements in energy gases.

The PTB optical hygrometer is equipped with a distributed feedback diode laser emitting at $2.7 \mu\text{m}$, a variable path length high pressure gas cell (0.0 – 0.5 MPa, extendable to 2 MPa), a high precision pressure sensor, two PT100 temperature sensors (T_1 , T_2) inserted into the cell at both ends (temperature gradient during gas flow < 90 mK) and an InAs photo detector for signal detection. A 16 bits data acquisition card (A/D card) is used to digitise the electrical signals from the photo diode at a sampling rate of 600 kS/s. Briefly, a triangular-shaped laser current is applied to sweep the diode laser wavelength across the water line. With the gas cell filled with a water-gas mixture, the transmitted laser radiation (absorption signal) through the gas cell is recorded by the photo diode. The recorded absorption signal is then transformed to absorbance. The Beer Lambert law that relates the incident radiation and the transmitted radiation through the gas cell is used to derive an expression for calculating the water amount fraction in the gas cell. The entire hygrometer is placed in a vessel to protect against any potential explosion of methane mixtures and also to shield the photo detector from background radiation. The laser-optical hygrometer is calibrated with the Coulometric Trace Humidity Generator (Figure 1, above).

Evaluation and calibration of metal oxide sensors

A variety of sensors were provided by industrial collaborators were evaluated at NPL using the test facility developed within the project (see above). In monitoring of fuel gases, the sensor type predominantly used is the metal-oxide sorptive "dew-point probe", so the study focused mainly on a selection of these. The performance of these hygrometers can vary significantly, and so a study using relevant test gases is very much needed. A variety of test conditions were applied in order to assess or demonstrate long-term stability or drift, response to condition changes, influence of long-term "soak" in measured gas, influence on pressure and species of background gas (otherwise known as "specificity" to water vapour), reproducibility, and trueness of reading (effectively calibration). Results presented publicly have been grouped by sensor type without identifying instrument make or model, but additional specific feedback has been given privately to each collaborator who loaned hygrometers for study.

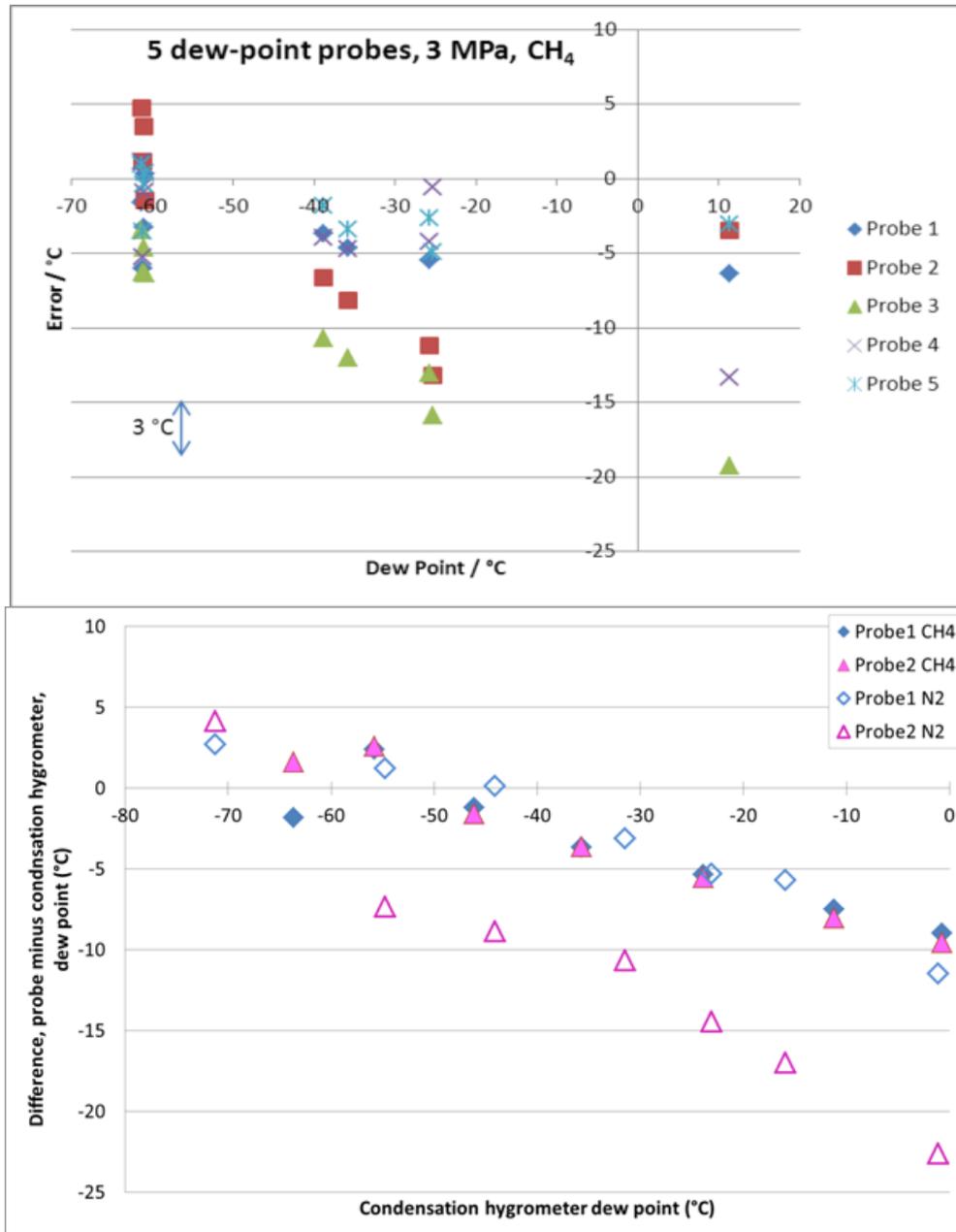


Figure 9. Graphs showing response of several dew-point probes at a range of humidities (a) in methane at 3 MPa and (b) in both methane and nitrogen at 0.5 MPa

Development of a novel microwave resonator based hygrometer

The application of microwave resonator technology for hygrometry was first demonstrated at NIST, using a radio-frequency re-entrant cavity. Later, the technique was used at the University of Western Australia (UWA) to determine the dew point of hydrocarbon mixtures. Triggered by these successful attainments and by the recent development of Quasi-Spherical Resonators (QSRs), it was proposed for this project that the enhanced precision and the ruggedness of this type of cavity (Figure 10) would suit the accurate determination of humidity in hydrocarbon mixtures. INRIM therefore led the development of a novel resonator based hygrometer.

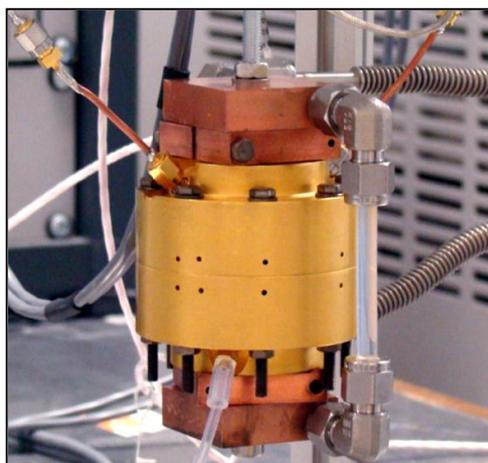


Figure 10. A QSR assembled and fitted for dew point measurement

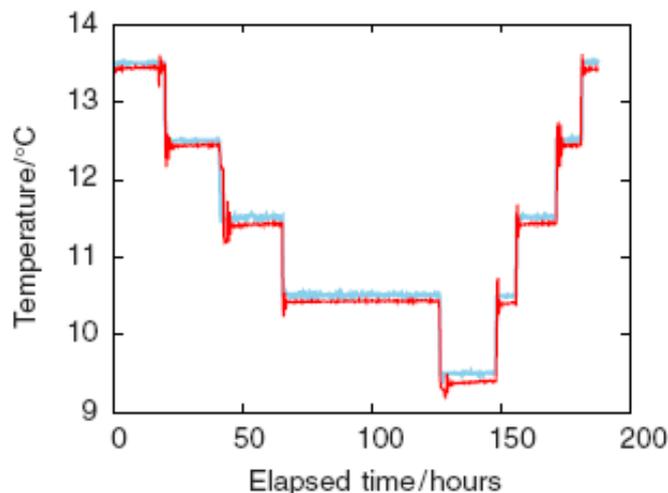


Figure 11. QSR used as a dew point tracking device (red) and compared to a chilled mirror (blue)

The demonstration of this proposal proceeded along successive steps. Firstly, accurate vapour-phase humidity measurements were obtained using a QSR at ambient pressure between 240 K and 290 K with humid air and nitrogen mixtures prepared using an INRIM standard humidity generator and a commercial two-pressure humidity generator. Secondly, thanks to the main contribution of NPL, it was demonstrated that QSR may also directly determine the dew- or frost-point temperature of a humid mixture working in saturation conditions, i.e. in condensation mode (Figure 11), suggesting that the direct determination of the enhancement factor of the mixture can be achieved by this technique. Finally, in view of the industrial application of the technique with a natural gas sample, additional measurements were conducted at INRIM, including vapour phase and condensation tests with humid methane mixtures between 273 K and 300 K for pressures up to 1 MPa. This preparatory work highlighted the criticality of achieving useful accuracy for vapour phase measurements with mixtures having a water molar fraction x_w below 1000 ppm. To mitigate this difficulty, an original measurement procedure was conceived which implies the consecutive flow through the microwave cavity of the humid mixture and of its dry fraction. Upon realisation of a suitable chemical drying manifold (Figure 12), this procedure was implemented for a few on-site tests with a natural gas sample and compared to the response of several commercial or prototype instruments, as described in the following section.

A REG researcher successfully worked in parallel with INRIM to develop a low-cost, portable electronic hygrometer based on these principles.

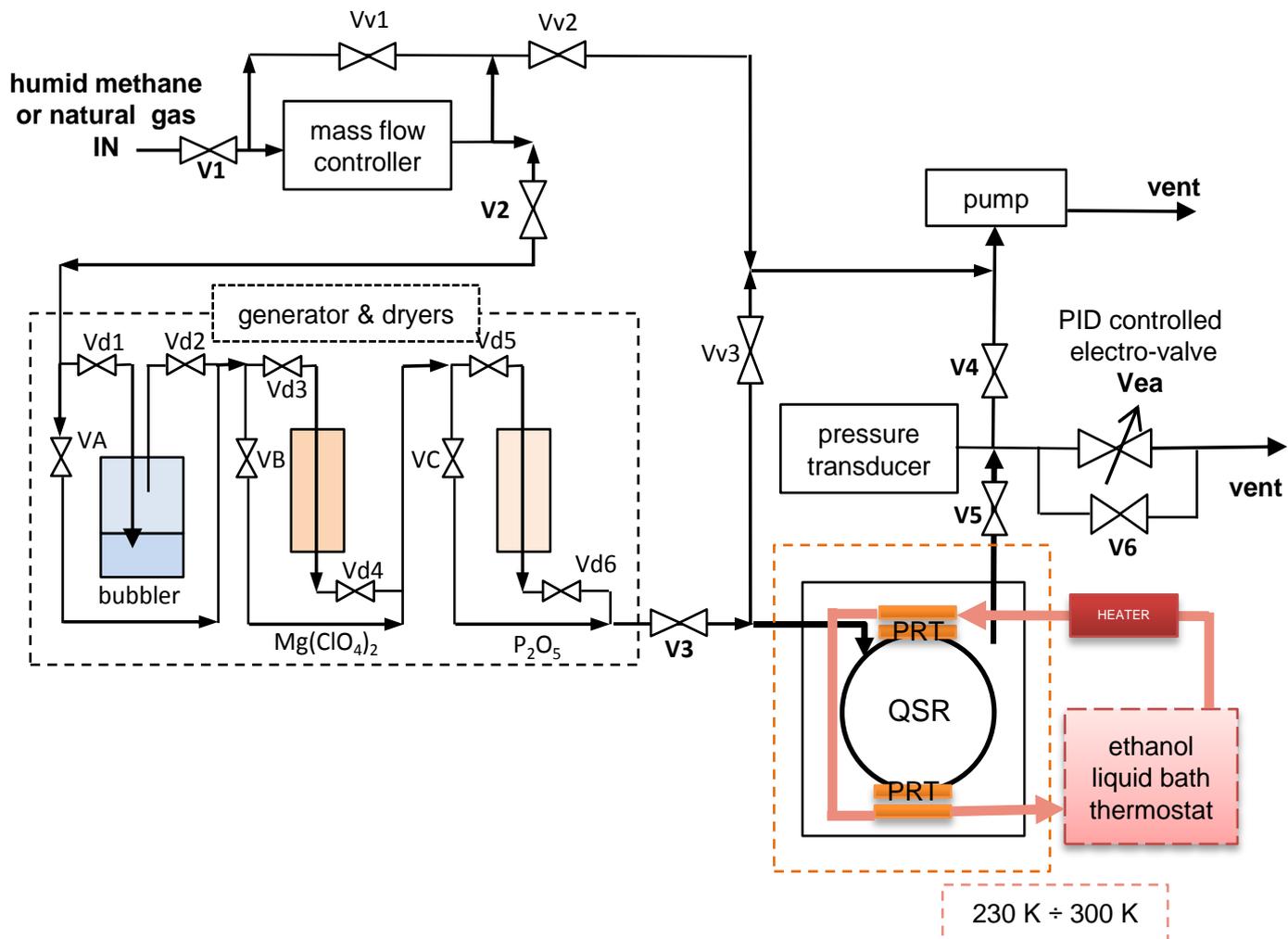


Figure 12. Schematic diagram of the gas manifold used for microwave measurements in humid methane and natural gas

Sensor intercomparison and validation under industrial conditions

The sensor intercomparison and validation was performed at two distinct ENAGAS sites in Spain: (a) the central research facility located in Zaragoza, and (b), the Serrablo underground storage facility in Huesca. In both cases, measurements were made in dry natural gas, sampled directly from the transmission pipeline.

(a) Measurements performed at the Zaragoza facility

Gas was sampled directly from the main pipeline and taken via a heated line to a purpose built laboratory set-up by ENAGAS with the necessary safety features. In order to achieve the necessary moisture concentrations, the dry gas was humidified using a flow-mixing generator integrated in a test rig with a sampling system constructed by INTA. The schematic is shown in Figure 13.

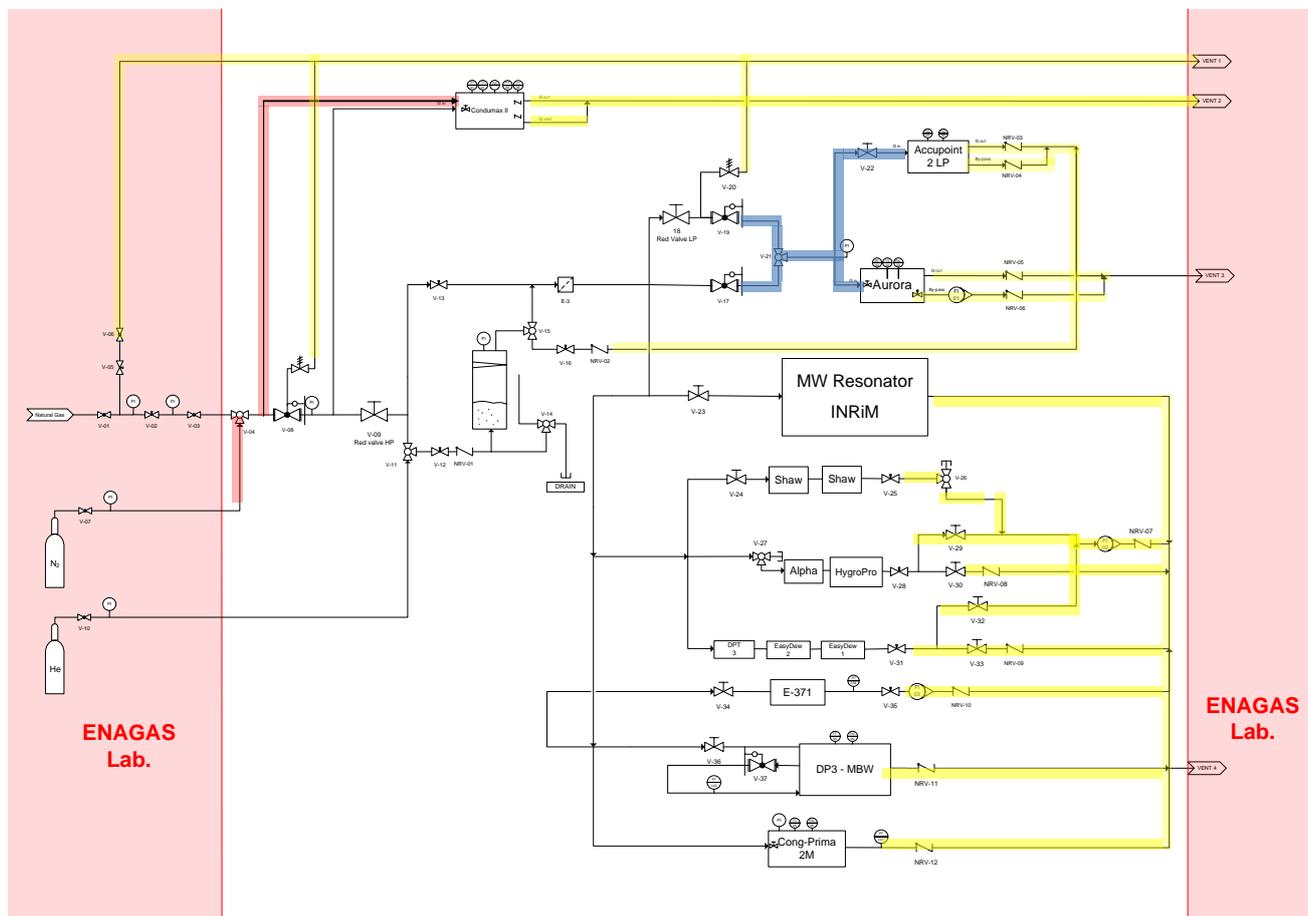


Figure 13. Schematic diagram of the test rig, showing the high pressure branch (red), medium pressure branch (black), low pressure branch (blue) and vents (yellow)

The test rig (see Figure 14) was designed to provide a varying humidity level and two sampling systems for low pressure (0.5 MPa) and medium pressure (3 MPa). A bypass was introduced after the measurements with varying humidity were completed, in order to perform measurements at full line pressure with those instruments designed for operation in this range.

This facility was suitable for the tests to be performed on prototype and other non-ATEX certified devices with the provision of the necessary safety features and extensive helium leak testing at the operating pressures prior to measurements in natural gas by INTA staff, and under the direct supervision of the ENAGAS specialists (“ATEX” = EU Certified electrical equipment for explosive atmospheres).

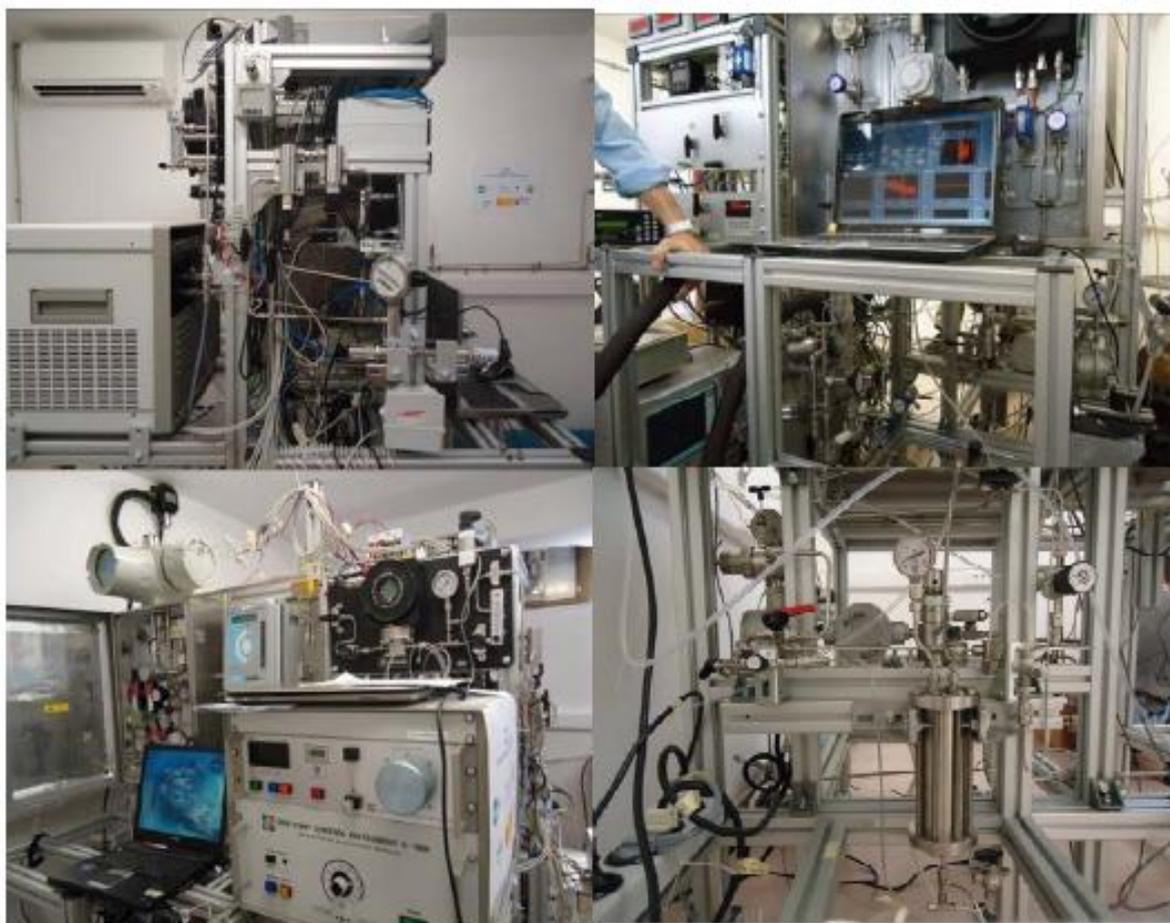


Figure 14. Overview of the test set-up at Zaragoza

The first tests were performed on the microwave hygrometer. The microwave apparatus underwent modifications in order to be adapted to the industrial measurement conditions, including the substitution of the bulky and costly network analyser ordinarily used for excitation and detection of resonances with a prototype electronic instrument developed by Politecnico di Torino (REG01). The limited frequency range of this prototype allowed measurements with just one TM mode preventing the resonator to be used in condensation mode. In spite of this limit, the microwave technique could be used at 750 kPa to measure the permittivity ratio between humid natural gas samples prepared using the humidity generator, with nominal water volume fraction between 140 ppm and 250 ppm, and a chemically dried natural gas sample. Calculated from these ratios, the microwave determinations of x_w for these samples were found to be consistent, and favourably comparable in terms of their estimated uncertainty, with the recorded response of a set of commercial humidity sensors.

After the tests on the microwave prototype were completed, a total of nine water concentration measuring instruments from eight manufacturers were successfully intercompared in natural gas at nominal moisture levels from 13 ppmV to 250 ppmV at nominal absolute pressures of 3 MPa and 0.5 MPa using the test rig. Sensors included electrolytic (P_2O_5), metal oxide (Al_2O_3), spectroscopic (TDLAS), condensation and polymer sensors.

Throughout the measurements the hydrocarbon dew-point and water dew-point were monitored at the sampling point at absolute pressure of 2.7 MPa and 6.1 MPa, respectively. At the completion of these measurements, all the instruments that could take the full line pressure (5.5 MPa) were intercompared in the actual pipeline gas without any moisture addition. Limited measurements were also performed using a laboratory high pressure precision chilled mirror dew-point hygrometer and a cycling condensation hygrometer, where compatible with the hydrocarbon and/or water condensation temperatures.

The relative performance of the instruments was evaluated in terms of hysteresis, time response and long-term stability (soak tests) throughout the period of measurement.

Certificates of analysis of the gas composition were provided regularly by ENAGAS throughout the test period, from samples taken from the pipeline.

(b) Measurements performed at the Serrablo underground storage facility

A second spectroscopic TDLAS analyser, was installed in parallel with a metal oxide sensor used to monitor the gas in the pipeline at the ENAGAS underground storage facility in Huesca (close to the French border). A pressure regulator was installed in the heated enclosure to reduce the pressure to the inlet pressure required for the TDLAS system in its own heated enclosure (see Figure 15).



Figure 15. Overview of the test set-up at the ENAGAS facilities in Serrablo (Huesca)

Both these ATEX certified systems were compared in the real environmental conditions of the industrial facility in order to obtain further information on the effects of ambient temperature and evaluate the relative performance with respect to the same TDLAS system installed in the Zaragoza research facility. The effects of the extreme heat and effects of direct solar radiation on the enclosures was evaluated and compared to the results obtained in the temperature controlled facilities in Zaragoza. The results corroborated the need to control the enclosures at a fixed nominal temperature above the ambient temperature and not just the use of heating when the temperature falls below a certain set-point value.

4 Actual and potential impact

4.1 Scientific Impact

As noted above (in section 3) the scientific objectives of the project fell in to four areas and considerable progress and impact has been made in each of these

Determination of the chemical composition

The interaction with the standards bodies benefits European industry by moving far closer to the situation where the chemical composition of non-conventional energy gases can be accurately characterised to determine whether they can be admitted to the European gas distribution system.

Some immediate benefit has been seen in the interaction with the Swedish biogas industry, already enhancing the analytical support offering with improved uncertainties on siloxane analysis, enabling better decisions to be made about the treatment level required to protect combustion equipment from the erosive effects of siloxane contamination.

The analytical methods and standards developed within the project have been validated through an international intercomparison (officially recorded with BIPM). This will impact through increased confidence in the reliability of international composition analysis across the EU.

NPL, SP and VSL jointly authored a best practice guide for sampling gas mixtures containing low-concentration sulphur-containing compounds. This will be of particular benefit to the biogas industry which has an urgent need for traceable and accurate analysis of sulphur compounds. There are an estimated 12,400 biogas plants operating in Europe. At present each European nation has its own specified maximum concentration of sulphur compounds, hydrogen sulphide and thiols allowable in their gas distribution systems.

Direct measurement of calorific value of non-conventional of gases

Virtually all the information, calorimeters and analytical techniques for the direct measurement of the calorific value of energy gases were restricted to natural gas. Following the success of this aspect of the project there is now clear guidance on the selection, modification and use of commercial field calorimeters for use with the direct calorimetric measurement of non-conventional gases. Furthermore these results can be traced back to the primary calorimeter values.

This work has benefited European industry by providing a traceable link from commercial field instruments back to the primary calorimeter standards, greatly enhancing the confidence that can be placed in their field measurements and eliminating the need to calculate calorific values from composition measurements.

New primary and reference humidity facilities

Up until this project there was no traceable method for generating humidity in energy gases. The joint research in the project led to the development of two different generators for a traceable, defined amount of humidity in a synthetic energy gas (methane), and this represents clear progress beyond the state of the art.

On the basis of data generated by the project, a new and simple equation for water vapour enhancement in methane was derived covering the pressure range from atmospheric pressure up to 70 bar and the dew-point temperature range from +15 °C down to hydrate forming temperatures. Because of the simple form, the equation is easy to implement in various measurement instruments and systems.

For the first time, documented guidance was given to underpin intercomparisons of humidity calibrations in energy gases. This concise document covers issues specific to energy gases as the measurement fluid and thus helps metrology institutes and industrial calibration laboratories to arrange valid and efficient comparisons.

Validations of both primary humidity standards and the humidity test facility for energy gases were completed enabling dissemination of traceability to stakeholders. This will enhance product development at instrument manufacturing companies through improved characterisation of instruments.

Evaluation and comparison of novel and existing techniques for humidity sensing in energy gases

The results obtained in industrial conditions will provide useful information on the relative performance of the different measurements technologies employed in instrumentation used for the measurement of water vapour concentration in natural gas. The measurements were carried out with the instruments under real field conditions and calibrated in methane, using the standards developed at the participating partners. The results obtained have a direct impact on the manufacturers in that they provide information under conditions that cannot be easily reproduced in the laboratory using bottled gas i.e. using natural gas at the operational flow rates. The collaboration of the stakeholder ENAGAS has provided a unique opportunity to obtain experimental data that will allow manufacturers to further develop their instruments for improved humidity measurement in natural gas and permit the JRP-Partners to validate calculations based on the new values of enhancement factors.

4.2 Main Dissemination Activities

The dissemination activity of the project has tackled the aspects of industrial presentation, scientific output, formal training and technical standards.

- Presentations were made to the relevant industrial audiences through various conferences and exhibitions:
 - GAS2011

The biennial “GAS” conference is the premier European event for the gas analysis community and therefore highly relevant to the project’s aims. A presentation and a poster session were delivered.
 - IMEKO-MI2011

Presentations were made on the overall aim of the project “*Towards a European infrastructure for the characterisation of energy gases*” and specific technical results in the calorimetry aspect, “*Caloric quantities and density measurement of non-conventional gases*”.
 - GAS2013

This event was particularly well timed, falling right at the end of the project. There was strong representation from JRP-Partners with 9 presentations and 6 poster sessions covering all the aspects of the project.

Lucy Culleton (from NPL) won the “best poster” award at the exhibition for her poster entitled “*Results of an international comparison of the analysis of real “non-conventional” gas samples*”.
 - 5^o Congreso Español de Metrología, Madrid, Spain, June 2013

A joint presentation was made by CEM, a JRP-Partner and the University of Valladolid, a collaborator.

Several local presentations were made to individual organisations, e.g.

 - GASUM in Finland.
 - Energy Networks Association in the UK.
 - Kelvin Club, Finland.
 - Bacton Interconnector Gas Terminal, UK.

and at relevant trade events:

 - World Biofuels Markets Congress in the Netherlands.

This event occurred at an early stage of the project (March 2011) and enabled a presentation to be made outlining the aims and intentions of the project, particularly those relating to reference materials and analytical methods for biogas

- In terms of the scientific output the project has already published **15** peer reviewed papers with **6** further papers submitted for publication.

The scientific and academic community were also addressed through international congresses and conferences.

- 8th International Conference on Tunable Diode Laser Spectroscopy, July 2011, Zermatt, Switzerland.
- FLAIR 2011 - Field Laser Applications in industry and Research, September 2011, Murnau, Germany.
- 18th Symposium of Thermophysical Properties, June 2012, Boulder, USA.
- Deutsche Physikalische Gesellschaft (DPG), March 2012, Berlin, Germany.
- Formal training was delivered through:
 - Workshops, such as the Humidity in Energy Gases workshop, held in Istanbul.
 - The Istanbul workshop was very successful and attracted presenters from external organisations as well as the JRP-Partners. It proved an excellent medium for raising awareness of the progress and developments emanating from the project during its course.
 - A workshop focussing on the determination of chemical composition and the determination of the calorific value was held shortly after the formal end of the project at the GAS 2013 event in June 2013. This benefited from having a very receptive audience concentrated in Rotterdam for the premier international event for gas analysis.
 - Individual training, such as the training for an INTA metrologist at NPL and Michell Instruments in the UK, and training at INRIM for a Ph.D. student from the University of Valladolid.
- JRP-Partners have a strong presence on several relevant technical standards committees and have contacts with others, which will ensure that the results of the project are disseminated and inform the appropriate decision making bodies, e.g. :
 - CEN TC234/WG9 (injection of non-conventional gas into gas grids)
 - ISO TC 158 (Gas analysis)
 - ISOTC 193 (Natural Gas)
 - CEN TC408 Natural gas and biomethane for use in transport and biomethane for injection in the natural gas grid
 - CEN BT/WG 197 Gas Qualities
 - CEN TC19/WG9 Gaseous and liquid fuels, lubricants and related products of petroleum, synthetic and biological origin / chromatographic methods.

4.3 Exploitation of Results

Some of the results from the work on the determination of chemical composition have already been exploited. For example SP are regularly using the improved uncertainties in siloxane determination in their routine analysis of Swedish biogas samples.

The high pressure generator and the test facility for characterising humidity sensors have already been used for providing metrology services to industrial stakeholders. The full capacity of the two primary generators and the test facility will be used for disseminating traceability to the stakeholders in the near future. This will improve the reliability of humidity measurements and instruments in the field of energy gases. With the improving reliability, excessive safety margins in gas drying can be confidently reduced implying reduced costs and energy consumption.

It is intended to use the developed research and test facilities to obtain vital information on the effect of gas composition variations on the water vapour enhancement factor and the performance of humidity sensors in a new EMRP project currently in its planning phase.

Following a request from the Technical University of Denmark (DTU), it has been agreed that the new data on the water vapour enhancement factor will be delivered to DTU to be used in the thermodynamic modelling of the water content in natural gas mixtures.

The new enhancement factor formula will be delivered to manufacturers of humidity instruments using the extensive contacts in the JRP-Consortium. Implementing the formula the manufacturers can improve the software and thus the usability of their products.

The TDLAS hygrometer introduces two innovative properties. First of all it offers a new wavelength range which has higher sensitivity and minimised spectral interferences with hydrocarbons. The direct TDLAS approach has the highly important property which allows self-calibrating operation, which can bring metrological transfer standard performance to the end user. Further this approach can also significantly reduce the cost of ownership by a strict minimisation of calibration efforts.

The dual operating mode of microwave QSR hygrometers, being capable of estimating the water fraction in a gaseous mixture away from saturation, or alternatively, of a direct measurement of the dew point, is possibly unique among hygrometric instrumentation. Such versatility combined with the ruggedness of the technique make it the ideal complement to novel humidity generators which are being developed at primary laboratories for hygrometry of non-air gases over extended pressure, temperature and humidity intervals. This improvement and extension of the capability of humidity standards may provide crucial support for several energy and environmental applications. Microwave hygrometry has so far been developed at a prototype (laboratory) stage only and it suffers from limitations (slow response, need for costly accessory instrumentation) which have limited its industrial use. However, minor additional research and engineering effort might take this technology to the point where it can be put into production and commercialised. This potential has been advertised to European manufacturers of hygrometric instrumentation.

Conoco Phillips (an end-user) has already commissioned an instrument study to be carried out on the NPL facility, involving water vapour in methane and in a synthetic natural gas mixture. NPL plans further service provision using the facility that was developed in the project, and is preparing an application for UKAS (ISO 17025) calibration accreditation. It is further proposed to extend the application of the facility to the field of biogas.

The sensor intercomparison results obtained in industrial conditions at ENAGAS will provide useful information on the relative performance of the different measurement instrument technologies used for the measurement of water vapour concentration in natural gas in industrial conditions (using calibrations performed at limited pressure in methane, and using the standards developed at the participating NMIs). The results obtained have a direct impact on the instrument manufacturers as they provide information in real conditions that cannot be easily reproduced in the laboratory as using bottled natural gas cannot readily match the pipeline operational flow rates encountered in practice. The collaboration of the stakeholder ENAGAS has provided a unique opportunity to obtain experimental data that will allow manufacturers to further develop their instruments for improved humidity measurement in natural gas and permit the NMIs to validate calculations using new values of enhancement factors, based on the results obtained at different pressures.

The shear breadth of experience within the EMRP JRP-Consortium, representing 16 NMI JRP-Partners from 14 countries, backed by industrial collaborators from the gas distribution community and instrument manufacturers, strongly reinforce the credibility and authority of the project's recommendations and will lead to their speedy implementation.

4.4 Socio-Economic / Policy Impact

The driving force behind this project was the EU's requirement to reduce its dependency on fossil fuels ("Promotion of the use of energy from renewable sources Directive" 2009/28/EC). To do so the EU has encouraged the "greening" of the gas supply by switching from natural gas to renewables and non-conventional fuel gases (Directive 2009/73/EC, "Common rules for the internal market in natural gas and repealing Directive 2003/55/EC"). The purpose of the project was to put in place the metrology required to

allow non-conventional gases to enter the extensive European gas distribution system and its successful outcome will impact directly on these directives.

The technical success of the project will now enable non-conventional gases to be accurately characterised so that informed decisions can be taken about allowing each source to enter the distribution system without compromising calorific quality, infrastructure integrity (in terms of potential corrosion damage) or transmission safety.

The social and economic impact of the project is to move Europe closer to the point where it can economically and safely trade non-conventional energy gases across the European distribution system. Ultimately the full impact will depend on the extent to which the EU delivers on its energy policies and to what extent the envisaged international trade in non-conventional gases through the pipeline distribution system is taken up by the community.

5 Website address and contact details

- **JRP-Coordinator:**

Dr Dai Jones, NPL, UK

dai.jones@npl.co.uk

+44 20 8943 8540

For specific technical information the appropriate contacts are;

- **New methods for the measurement of the composition of non-conventional gases.**

Dr Andrew Brown, NPL, UK

andrerw.brown@npl.co.uk

+44 20 8943 6831

- **Direct measurement of calorific value of non-conventional of gases.**

Dr Frederique Haloua, LNE, France

frederique.haloua@lne.fr

+33 1 30 69 32 57

- **Primary and reference humidity facilities.**

Dr Martti Heinonen, MIKES, Finland

Martti.Heinonen@mikes.fi

+358 29 5054

- **Evaluation and comparison of novel and existing techniques for humidity sensing in energy gases.**

Prof Volker Ebert, PTB, Germany

Volker.Ebert@ptb.de

+49.531.592-3201

JRP Website address:

<http://www.npl.co.uk/emrp-energygases>