Final Publishable JRP Summary Report for ENG01 Gas Characterisation of Energy Gases

Background

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. It has enabled 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).

The determination of the composition and calorific value of conventional natural gas is well established and supported by sound metrology. However for alternative fuel gases this metrological foundation is lacking. Where measurement methods exist, their scope is limited, or their accuracy is not at the level of state-of-the-art measurements of natural gas. Methods are 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. 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).

With energy gases, several physical chemical properties, such as condensation behaviour, are critical to the efficient and safe utilisation of 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 is 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 is evident that substantial extrapolations need 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 1-3 °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 were developed in this project to meet two needs: to allow industrial instruments to be calibrated with a gas matrix that resembles field conditions, and at a relevant pressure. Secondly, to allow the determination of the so-called "enhancement factors" with better accuracy than is currently the case, thus greatly enhancing the ability for the results of industrial instruments to be interpolated or extrapolated.

EMRP
European Metrology Research Programme
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Need for the project

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. This project addresses those EU level requirements for the inter-changeability of gaseous fuels between transporters and producers in different countries. **The project has put in place the metrology requirements for the safe and efficient trade and transportation of energy gases in the gas pipeline system within Europe.**

Scientific and technical objectives

In summary the scientific and technical objectives of this project, required to meet the interchangeability objective, were:

For the required **non-conventional gases composition determinations**:

- To develop and validate new highly accurate measurement methods to achieve the uncertainty required by the European industry 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.

For the **calorimetric measurements**:

- 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.

For **primary and reference humidity facilities**:

- 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.

For **evaluation of existing and novel humidity sensors**:

- 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.

Results and potential impact

The project has met all the scientific and technical objectives set at the outset.

- ***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').***

Achieved through:

- The delivery of traceable gas chromatography (GC) methods for the analysis of biogas composition, and fast optical spectroscopy methods for the analysis of trace-level impurities.
- The delivery of novel GC methods for natural-gas type mixtures, backed by a suite of traceable standards at the target uncertainties and validated though an international intercomparison (registered as Euramet 1255).
- Further impact was delivered through a Researcher Mobility Grant (RMG) which allowed a scientist attached to the project to develop new measurement techniques for the determination of ammonia in biogas and hydrogen chloride in syngas.

New GC techniques were developed and traceable gas standards produced. The project culminated in an international intercomparison exercise using real gas samples collected from sites across Europe. These included raw and processed biogases from Sweden, Germany and Hungary; coal mine gas from Germany and coal bed methane from Romania. The results showed a good level of comparability despite the extra complexity of the real-world nature of the samples collected. The outcome was presented at GAS 2013 in Rotterdam (June 2013) and won the "Best Poster" award at the conference.

Extra insight was gained into the collection of gas samples for trace contaminant analysis, with a study showing that gases held in treated cylinders were very stable but that low-level contaminant samples collected and held in commercial flexible plastic bags were at risk of quite rapid deterioration.

- ***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.***

  Met through:

  - Traceable standards and an analytical method for environmentally friendly and sulphur odorant species were developed by the project, together with a report on best-practice sampling methods for gases containing low-level odorant species.

  Non-sulphur acrylate based odorants are increasingly used in Europe. The project has ensured enhanced confidence in the analysis of energy gases for these non-sulphur odorants by providing the analytical methodology and traceable standards for their determination.

- ***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).***

  Achieved through:

  - The delivery of a new primary calorimeter especially adapted for non-conventional gases, accompanied by a detailed report on its development and validation.

  The primary reference calorimeter was modified to enable 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, it was used to validate the performance of the secondary field calorimeters.

- ***To develop and validate a range of field calorimeters for the measurement of the calorific value of non-conventional gases.***

  Achieved through:

- The delivery of a study of two types of commercial field calorimeters which operate on different principles. The modifications to each instrument to allow operation with non-conventional gases were identified. The relative strengths and weaknesses of each instrument were outlined including their operating parameters and the uncertainties of their measurement were verified. The field calorimeters results are now traceable to the primary calorimeter.

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 the use with non-conventional gases. Following the success of this aspect of the project, provided the recommendations are followed, the results from field calorimeters with non-conventional gases are now traceable to the laboratory primary calorimeter, greatly incresing the confidence in the measurements.

- ***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.***

  Achieved through:

  - Two new instruments delivered – a dew point generator to cover the high pressure range and a novel coulometric trace moisture generator for the low pressure range. All conditions typically occurring in the European gas distribution network are now covered.
  - Both instruments characterised and validated.

  The new instruments developed can now collectively cover the low and high pressure ranges of gases typically encountered in the European distribution system.

- ***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.***

  Achieved through:

  - The use of the new gas mixture generator to produce experimental data on the “enhancement factors” (see below).
  - Development of calculation methods related to enhancement factors and the conversion of humidity quantities in energy gas measurements.
  - Recommendations made on appropriate comparison methods for the humidity standards for energy gases.

  The water vapour enhancement factor for methane was measured with the 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, a simple formula was derived for the enhancement factor.

- ***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.***

  Achieved through:

  - The construction and delivery of a new gas mixture generator for studying enhancement factors in the wide range of temperatures and pressures encountered in the European system (see above).
  - The development of a test facility for the characterisation of humidity sensors.

  The 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”. It has been long 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.

The facility for characterising humidity sensors was successfully developed. Its operation is based on blending saturated air with the test gas. Also, direct saturation is possible through a high pressure saturator. A 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.

- ***To develop and validate new methods for comparing humidity standards with humidity sensors used in industrial gas monitoring conditions.***

  Achieved through:

  - The use of the newly developed test facility for humidity sensors to characterise commercial sensors supplied by collaborators and other suppliers.
  - The characterisation and optimisation of the use of quasi-spherical resonator (QSR) microwave hygrometers.
  - The development and characterisation of novel laser optical hygrometers for up to 0.5 MPa in energy gases.
  - Characterising humidity sensors under field conditions at ENAGAS’s facility in Spain.
  - Further impact was delivered through a Researcher Excellence Grant (REG) which allowed a scientist attached to the project to develop a low-cost, electronic microwave cavity resonator, suitable for the determination of water content of nonconventional energy gases in mobile, field applications. The instrument was successfully delivered and was included in the field test at the ENAGAS facility (see below).

  A variety of sensors provided by industrial collaborators were evaluated using the test facility. A range of test conditions were applied in order to assess long-term stability or drift, response to condition changes, influence of long-term “soak” in measured gas, influence of pressure and species of background gas (otherwise known as “specificity” to water vapor), reproducibility, and trueness of reading (effectively calibration).The results were fed back to the suppliers.

  The microwave hygrometer developed is capable of estimating the water fraction in a gaseous mixture in two different situations. It can directly measure the dew point of a mixture saturated with water vapour at the temperature at which condensation occurs, or alternatively it can be used to estimate the water fraction of mixtures whose moisture content is much lower than the saturation value. This ability is believed to be unique among hygrometric instrumentation. 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.

  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 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.

  The results obtained have a direct impact on the instrument manufacturers as they provide information in conditions that cannot be easily reproduced in the laboratory as using bottled natural gas cannot readily match the operational flow rates encountered in practice. The collaboration of the stakeholder ENAGAS has provided a unique opportunity to obtain experimental data that allowed

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.

Impact

The impact of the above work was delivered through several routes, both immediate and beyond the end of the project.

Advances made in the **composition determination** have led to:

- Verification of the suitability of biogas to enter the distribution network through significant improvements in its characterisation:
    - Greatly improved uncertainties in the determination of siloxane impurities.
    - A new understanding of the stability of biogas samples in plastic bags.
    - Meeting stakeholders requirements for more rapid determination of impurities by demonstrating the feasibility of rapid instrumental analysis of ammonia in methane by spectroscopic methods.
    - Traceable GC methods and gas standards for biogas enabling, for example, field testing of calorimeters.
- Accurate monitoring of new environmentally friendly gas odorants through the provision of traceable standards allowing optimum effect at minimised material costs.
- The cost effective analysis of refinery gases and syngases with a wide composition range at industrially acceptable accuracy through the provision a multi-detector GC method, allowing more reliable measurement of compliance with the EU Emission Trading Scheme.
- SP are already exploiting the advances made in siloxane analysis in their support of the Swedish biogas industry.
- Similarly, three other companies with biogas interests, Gasum in Finalnd, Zalavíz Zrt in Hungary and VTZ in Spain were stakeholders in the project.

In the calorific value **measurement** area the work have resulted in:

- Increased confidence in field calorimeters determinations, which can now be provided by the link back to laboratory based primary calorimeters.
- Clear guidance on the suitability of commercial calorimeters for non-conventional gases in specific calorific value ranges.
- Feed-in to the TC408 technical committee to inform their decisions on biogas specifications.
- Information to allow manufacturers to improve their instruments to meet market requirements.
- Two instrument manufacturers have had direct links with the project, i.e. Union Instruments and Foster Cambridge.

Developments in **new primary and reference humidity facilities** have led to**:**

- Meeting industries need for traceability of humidity measurements relevant to the transport and trade of energy gases – no such traceability was available prior to the project.
- Enhancing safety by improving the management of the risk of condensation in pipelines by the experimental determination and theoretical fitting of enhancement factors for energy gases.

- The provision of a new facility for the evaluation of electronic humidity sensors and hygrometers under typical field conditions, which have already been taken up by industrial companies.

The project's provision of the humidity facilities has enabled independent **evaluation of existing and novel humidity sensors:**

- Greatly assisting European manufacturers with independent test and verification capability.
- Increasing end-user confidence in new sensors through the provision of traceability to national humidity standards.
- Enhance industrial confidence in new and existing sensor types by their live deployment on European gas distribution facilities via the access provided by the project collaborators.
- Developing and critically evaluating new instrumental humidity determination techniques through the development of a tuneable diode laser absorption spectroscopy (TDLAS) hygrometer and a quasi-sherical microwave resonator (QSR) based hygrometer.
- Two hygrometry instrument manufacturers were formal collaborators in the project - MBW Calibrations and Michell Instruments and numerous sensor manufacturers supplied sensors for evaluation and received feedback on the performance.

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

List of all publically available publications

- *"Investigation of the equivalence of national dew-point temperature realizations in the −50 °C to + 20 °C range".*
  M. Heinonen et al
  Int J, Thermophysics, DOI 10.1007/s10765-011-0950-x, 2011
- *"Microwave Determination of Water Mole Fraction in Humid Gas Mixtures".*
  R. Cuccaro, R. M. Gavioso, G. Benedetto, D. Madonna Ripa, V. Fernicola, C. Guianvarc'h
  Int J, Thermophysics, 33 (2012) 1352-1362 DOI: 10.1007/s10765
- *"Outgassing of water vapour, and its significance in experiments to determine the Boltzmann constant".*
  Michael de Podesta, Gavin Sutton, Robin Underwood, Stephanie Bell, Mark Stevens, Thomas Byrne, Patrick Josephs-Franks
  Metrologia, 48 L1 (2011) doi: 10.1088/0026-1394/48/1/L01
- *"A Microwave System for Humidity Measurement".*
  Y. Gülmez, T. Özkan, G. Gülmez, E. Turhan
  Conference on Precision Electromagnetic Measurement (CPEM 2012) Digest, 01 July 2012
- *"A microwave resonance dew-point hygrometer".*
  R. J. Underwood, R. Cuccaro, S. Bell, R.M. Gavioso, D. Madonna Ripa, M. Stevens and M.de Podesta,
  Meas. Sci. Technol. 23 (2012) 085905

- *"Development of a Dew-Point Generator for Gases Other than Air and Nitrogen and Pressures up to 6 MPa".*
  R. Bosma, A. Peruzzi
  Int. J. Thermophys 2012, DOI: 10.1007/s10765-012-1214-0

- *"Validation of a Dew point Generator for Pressures up to 6 MPa using nitrogen and air"*
  R.Bosma, D.Mutter, A.Peruzzi
  Metrologia, 49:597 (2012), DOI: 10.1088

- *"Experimental determination of (p, ρ, T) properties for mixtures of carbon dioxide with methane for the thermodynamic characterization of non-conventional energy gases".*
  M.E. Mondéjar,T.E. Fernández-Vicente, F. Haloua, C.R. Chamorro J. Chemical & Engineering Data, 2012, 57 (9)

- *"A Low-Cost Instrument for the Accurate Measurement of Resonances in Microwave Cavities".*
  S. Corbellini, R. M. Gavioso
  IEEE Trans. Instr. Meas. (accepted)

- *"Enhancement factor for water vapour pressure correction in humid methane".*
  H. Sairanen, M. Heinonen, Int. J. Thermophys (submitted)

- *"Measuring humidity in methane and natural gas with a microwave technique".*
  R. M. Gavioso, D. Madonna Ripa, R. Benyon, J. G. Gallegos, F. Perez-Sanz, S. Corbellini, S. Avila and A.M. Benito Int. J. Thermophys, (submitted).

- *"An investigation of the comparative performance of diverse humidity sensing techniques in natural gas".*
  R. Benyon, J. G. Gallegos, S. Avila, A. Benito , H. Mitter, R. M. Gavioso, V. Ebert
  Int. J. Thermophys, (submitted).

- *"A new calibration method for liquid microflow".*
  H. Sairanen, M. Heinonen Micro- and Nanofluidics, (submitted).

JRP start date and duration :	01 June 2010 for 3 years
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