

## TOWARDS A EUROPEAN INFRASTRUCTURE FOR THE CHARACTERISATION OF ENERGY GASES

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**Abstract** – This paper describes the work being undertaken in the European Metrology Research Programme (EMRP) ‘Characterisation of Energy Gases’ project to develop traceable, high-accuracy measurement methods to underpin the characterisation of non-conventional energy gases.

The project will provide a metrology infrastructure to underpin the ‘interchangeability’ of greener, more environmentally friendly energy gases (*e.g.* biogas, coal bed methane and coal mine methane) so that gaseous fuels from non-conventional sources can access gas grids across Europe.

**Keywords:** Energy, non-conventional gas, interchangeability, biogas

### 1. INTRODUCTION

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, hydrogen enriched mixed natural gas and coal bed methane. The ‘Characterisation of Energy Gases’ project will put in place the necessary metrology infrastructure to enable the ‘interchangeability’ of energy gases so that gaseous fuels from non-conventional sources can access gas grids across the EU. 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.

Whereas a solid foundation for gas composition and calorific value measurements for natural gas already exists, such a foundation is lacking for alternative fuels. Where measurement methods do 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 [1]), 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 the project is highly desirable, but requires validation with gas calorimetry (a direct measurement method).

The project will also address the need for measurements of the carbon content of alternative fuel gases, such as refinery gases, 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). [2] The Directive establishing the ETS 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.

Several physical chemical properties, such as condensation behaviour, are relevant to the efficient and safe utilisation of non-conventional energy gases. Humidity is a parameter monitored during the glycol drying process used before supplying gas to a gas delivery grid. Although the development of traceable measurements for humidity are part of the project (see Section 2), they are not discussed in this paper.

The priority of the requirements addressed by the project, which are agreed at EU level and concern interchangeability of gaseous fuels between transporters and producers in different countries. The project will place the metrology requirements for the safe and efficient trade and transportation of energy gases in the gas pipeline system within Europe.

## 2. EMRP CHARACTERISATION OF ENERGY GASES PROJECT

The project is arranged into four technical workpackages:

- WP1: New methods for the measurement of the composition of non-conventional gases.
- WP2: Direct measurement of the calorific value of non-conventional gases.
- WP3: New primary and reference humidity facilities
- WP4: Evaluation and comparison of novel and existing techniques for humidity sensing in energy gases.

The National Measurement Institutes (NMIs) participating the project are shown in Figure 1:

|             |   |                 |
|-------------|---|-----------------|
| BAM         |    | Germany         |
| BRML INM    |    | Romania         |
| CEM         |    | Spain           |
| CMI         |    | Czech Republic  |
| INRIM       |    | Italy           |
| INTA        |    | Spain           |
| LNE         |    | France          |
| MIKES       |    | Finland         |
| MKEH        |    | Hungary         |
| NPL         |   | United Kingdom  |
| PTB         |  | Germany         |
| SMU         |  | Slovakia        |
| SP          |  | Sweden          |
| VSL         |  | The Netherlands |
| TUBITAK UME |  | Turkey          |

Fig. 1. Full List of NMIs participating in the EMRP Characterisation of Energy Gases project (listed in alphabetical order).

This paper now gives an overview of the work being carried out in WP1, and briefly discusses the interaction between WP1 & WP2. The humidity workpackages (WP3 & WP4) are not discussed here.

### 3. NEW METHODS FOR THE MEASUREMENT OF THE COMPOSITIONS OF NON-CONVENTIONAL ENERGY GASES

#### 3.1. Overview

Workpackage 1 of the EMRP project will develop an infrastructure for traceable and validated measurement techniques for a range of ‘non-conventional’ energy gases and hydrocarbon emissions gases of key strategic importance. This work will support Europe’s move towards more diverse and less carbon-intensive sources of energy.

‘Non-conventional’ energy gases include biogas, coal bed methane, coal mine methane and mixtures of hydrogen and natural gas. Accurate measurements and sampling techniques are urgently required for these new gases in order to ensure that they are ‘interchangeable’ with existing

energy supplies, *i.e.* that they can be used in existing European gas transmission networks and appliances. This work will be supported by the development of high-accuracy traceable measurement standards, which are an essential requirement of traceable measurements. Accurate measurement of the trace-level toxic impurities in biogases is also required in order to ensure the health of the public.

The technical requirements for interchangeability are defined in the Marcogaz report ‘Injection of Gases from Non-conventional Sources into Gas Networks’ [3]. This includes determination of the physical properties of the gases, such as calorific value, hydrocarbon dew point, relative density and Wobbe index (all of which are calculated from accurate composition measurements), and the measurement of the concentration of odorant species in the gases. These measurements ensure that gas can be transported safely, are compatible with use in domestic appliances and industrial applications, and that any hazardous leaks may be detected.

‘Refinery gas’ is a generic term for a family of gases (including coke oven gas, blast furnace gas, syngas and reformer gas) that are produced and emitted during the production and refining of petroleum products and solid fuels. Traceable determination of the composition of these gases is crucial in order to provide traceability and confidence to measurements of carbon emissions required by the European Emissions Trading Scheme.

The challenges facing the development of a metrological infrastructure for each of these ‘families’ of gases is now discussed in turn. Progress with the work to date is also discussed briefly.

#### 3.2. Biogas

Gases of biological origin (often termed biogases, *i.e.* gases produced by anaerobic fermentation or digestion of organic matter) have great potential to be used as ‘green’ alternative to natural gas. In the UK, National Grid have recently identified that biogas has the potential to provide 18% of the UK’s gas requirements.

Examples of biogases include biosyngases (gases manufactured from biomass using thermal gasification processes) and landfill gases (gases produced from natural decomposition processes in landfill sites).

The measurement methods and reference materials developed in the EMRP project will allow the composition of biogases to be determined accurately, thus ensuring the interchangeability of these gases. Measurements of trace-levels of toxic impurities (*e.g.* siloxanes), hydrogen sulphide and ammonia are crucial in ensuring the health and quality of life of the European public.

Work has commenced to prepared standards and develop measurement methods for a range of siloxanes at the trace

(parts-per-million and parts-per-billion) levels found in biogases. Some example data are shown in Figure 2.

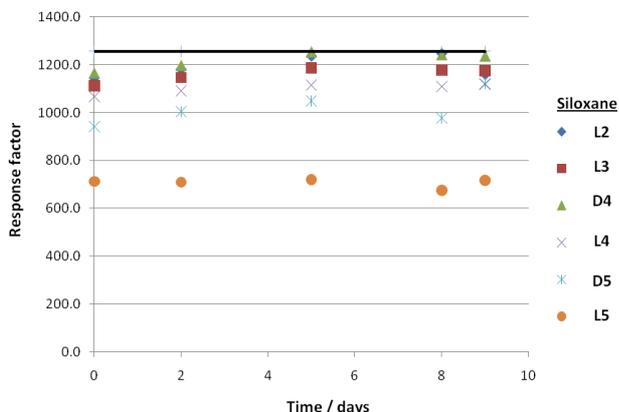


Fig.2. Results from short-term stability tests of trace-level siloxane standards prepared in sample bags

### 3.3. Natural gas-type mixtures (coal bed methane, coal mine methane and hydrogen enriched natural gas)

Traceable gaseous reference materials and measurement methods are also being developed for a family of gas mixtures whose compositions are similar to natural gas extracted from subterranean reservoirs that also be used as non-conventional fuels. These are:

(a) Coal mine methane, *i.e.* gas emitted from exposed coal in work coal seams. Coal mine methane comprises mainly of methane with higher levels of carbon dioxide and methane that would typically be found in natural gases (as the coal has been exposed to air), and other hydrocarbons. Low levels of oxygen may also be present.

(b) Coal bed methane, *i.e.* gas emitted from unworked coal seams. Coal bed methane comprises mainly of methane with small amounts of nitrogen, carbon dioxide and other hydrocarbons.

(c) Mixtures of hydrogen and natural gas. The European FP6 NaturalHy project has reported that large quantities (up to 20%) of hydrogen may be added to natural gas streams without compromising safety, or affecting the efficiency of domestic boiler systems [4]. The EASEE-gas report ‘Harmonisation of Natural Gas Quality’ [5] also identifies that: “future gas operations may lead to the use of gases containing significant levels of hydrogen or other synthetic / manufactured gases”. The natural gas currently transmitted in pipeline networks contains little or no hydrogen, so traceability is urgently required in this area.

A comprehensive study of the compositions of coal mine methane found across Europe has been undertaken, and the mixture shown in Table 1 has been agreed to be representative of such gases, and is the focus of this study.

| 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                     |

Table 1. Coal mine methane composition representative of that found in Europe.

### 3.4. Refinery gases

‘Refinery gases’ include coke oven gas, blast furnace gas, syngas and reformer gas. The project aims to develop and optimise a high-accuracy multi-column, multi-detector GC method (Figure 3) for the analysis of these mixtures. In order to improve the cost-effectiveness of the measurements, a novel data analysis technique will be developed to facilitate the measurement of a wide range of refinery gases using only a limited set of calibration gases, whilst still ensuring that a fit-for-purpose level of uncertainty is achieved. A range of traceable gas standards will also be produced to underpin these measurements.

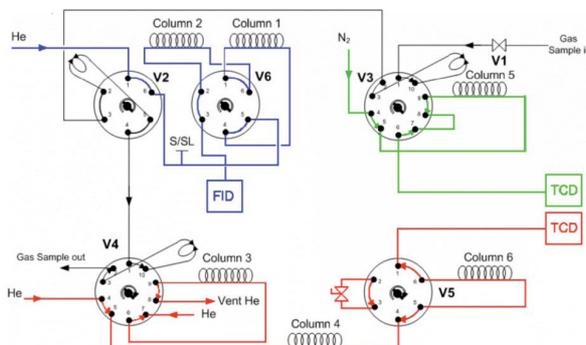


Fig.3. Multi-column, multi-detector GC system used for refinery gas analysis.

### 3.5. Environmentally-friendly odorants

Odorisation of gases is critical to ensure the safe supply of gas to consumers. Sulphur-containing odorants are currently used widely in natural gas to enable the detection of even minor leaks from gas pipelines.

The project will develop novel reference materials and a traceable measurement method for new environmentally friendly non-sulphurous odorants, whose use is already widespread in Germany, and is expanding elsewhere in Europe. These odorants consist of a mixture of three components: methyl acrylate, ethyl acrylate and 2-methyl-3-ethylpyrazine (Figure 4).

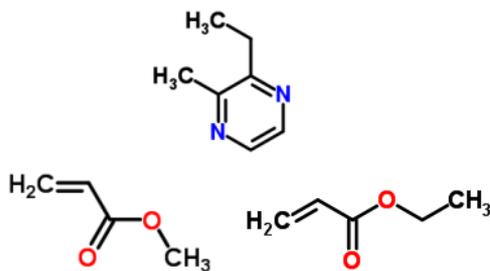


Fig.4. Non-sulphur containing components used to odourise natural gas

In parallel with this activity, a best-practice sampling method for gas mixtures containing low concentration odorant species will be developed and published. Representative sampling is crucial for accurate odorant analysis as these components have the propensity to adhere to the internal surfaces of cylinders, sampling equipment and transfer lines.

### 3.6. Measurements of real sample of non-conventional gases

The final stage in the project will be to use the methods and reference materials developed for the measurement of biogas and natural gas-type mixtures to analyse the composition of 'real' samples of biogas, coal bed methane, coal mine methane and hydrogen-enriched natural gas.

### 3.7. Interaction with WP2 (calorimetry)

A paper describing the work to provide direct measurement of the calorific values and density of non-conventional gases that is being undertaken in WP2 is being presented in this symposium [6]. High-accuracy reference gas mixtures developed by WP1 are currently being used to validate reference and field calorimeter by comparing their results with those calculated from the gravimetric composition of the mixtures.

## 4. CONCLUSIONS

The work being undertaken in the EMRP 'Characterisation of Energy Gases' project has been described in the paper. The project, which is a collaboration between a consortium of European National Metrology Institutes is developing a metrology infrastructure to underpin the 'interchangability' of greener, less carbon intensive gases such as biogas, coal mine methane and hydrogen enriched natural gas. The work will allow gaseous fuels from these non-conventional sources can access gas grids across Europe.

## ACKNOWLEDGMENTS

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