



## Comparison of traceable methods for determining the calorific value of non-conventional fuel gases



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### ABSTRACT

Energy-content measurements by direct methods (such as calorimetry) are used to validate the indirect method (from gas composition obtained by gas chromatography) which is generally adopted by grid operators for on-site gas control. A primary reference gas calorimeter and three field calorimeters were used for the first time to measure accurately the energy content of non-conventional gases (biogas and coal mine methane). The gas mixtures for this study were prepared by gravimetry and comprised three binary mixtures containing carbon dioxide and (up to 80 mol-%) methane, three ternary mixtures containing carbon dioxide, (up to 70 mol-%) methane and (up to 0.3 mol-%) hydrogen sulphide as well as a ten-component mixture with a methane content of approximately 64 mol-% which represents a typical coal mine methane. Associated uncertainty calculations were developed for each instrument and are presented here. Traceability of the measurements to the SI units is ensured in reference calorimetry, as calibration is accomplished by electrical simulation based on the Joule effect in order to obtain the heat capacity of the entire system. The results obtained with the four calorimeters are compared with each other and also with results calculated from the indirect method that is based on gas chromatography. Uncertainties ( $k = 2$ ) between 0.07 and 0.49% for the reference gases were obtained with the reference calorimeter, while uncertainties for the field calorimeters range between 0.18 and 2.48% for the same mixtures. Compared to the usual standard deviation observed by gas chromatography for a multi-component gas mixture of about 1%, it is demonstrated that the calorimetric method, although rarely used for non-conventional gases before, is appropriate for energy-content measurements of gases originating from renewable energy sources.

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## 1. Introduction

An increased amount of gaseous fuels from non-conventional sources is being injected into the European gas grids or used in vehicles in order to follow the objectives of the European Directive on Renewable Energies [1]. This has led to a wide diversification of gas composition.

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The heterogeneity observed in biogas or coal mine methane compositions associated with the numerous and diversified sources of these gases results in calorific values ranging from 15 MJ kg<sup>-1</sup> to 50 MJ kg<sup>-1</sup>. The term *calorific value* refers here to the superior calorific value (or gross calorific value)  $H_s$  as defined in the ISO standard 6976 [2]. The superior calorific value is defined as the amount of heat which would be released by the complete combustion of a specified quantity of gas in air, in such a way that the pressure  $p_1$  at which the reaction takes place remains constant, and all the products of combustion are returned to the same specified temperature  $t_1$  as that of the reactants. All these products are in the gaseous state except water formed by combustion, which is condensed to the liquid state at  $t_1$ .  $p_1$  and  $t_1$  are taken here as

1,01,325 Pa and 25 °C, respectively. Conversions between molar, volumetric and mass-related quantities were performed according to the algorithms and data given in the ISO standard 6976 [2]. The standard state for volumetric quantities is 101325 Pa and 0 °C.

As the commercial value of gas is directly related to its energy content, the calorific value of the gas is of prime importance. Furthermore, the resulting gas blends have to meet the requirements on the calorific value for injection into gas networks or for use as a vehicle fuel.

The calorific value measurements usually performed at gas companies cover those natural gases passing through the European gas grids and are executed by an indirect method using the gas composition determined by gas chromatography [3,4] coupled with reference calorific values taken from the ISO standard 6976 [2]. For multi-component gases like renewable gaseous fuels, this method has to be adapted and modified in order to determine every component even at low concentrations for accurate calorific value measurements.

Gas chromatography (GC), however, has certain disadvantages compared to other, more direct measurement methods like calorimetry. Apart from the acquisition costs of the instruments, the running costs of a gas chromatograph are much higher than for a calorimeter due to the fact that gas chromatographs require carrier gases (preferably helium) and calibration gases with defined composition and concentration. To achieve low uncertainty, the calibration is done with a number of calibration gases covering the working range of each component (multilevel calibration). Furthermore, unknown components in the measured gas might shift the targeted physical property, in particular the calorific value, in a systematic way. Hydrogen, which is under discussion as a possible means of storage of excess electrical energy from wind and photovoltaic generators and is also injected into the natural gas grid, would immediately render the standard process gas chromatographs currently employed in the natural gas sector useless, since they are not adapted for measuring hydrogen. A further disadvantage originates from the current international standard applied for the calculation of physical properties from composition, i.e., ISO 6976 [2]. This standard limits the application range for the calculation of the calorific value on a volumetric basis to such particular gas compositions, in which N<sub>2</sub> should not be present in amounts exceeding 30%, CO<sub>2</sub> and C<sub>2</sub>H<sub>6</sub> should each not exceed 15% and no other component should exceed 0.0005%. Only under these conditions the claimed trueness of the calculation is kept within 0.1%, but no information about the deviance from trueness depending on the concentrations is given. In contrast to these limitations, gas calorimetry is known to render calorific values for any gas composition within a reasonable working range. Because of the underlying measuring principle, calibration curves representing polynomials of higher order will not emerge, and the calibration gases just have to display different calorific values within this working range.

Compositions of non-conventional gases from different sources are presented in Table 1.

Jointly supported by the European Commission and the participating countries within the European Association of National Metrology Institutes (EURAMET), the European Metrology Research Programme (EMRP) has launched a call for project proposals in the energy domain. One of the selected projects, the Joint Research Project JRP ENG01 “Characterisation of Energy Gases”, proposes to put in place the necessary metrology infrastructure to promote the “inter-changeability” of energy gases so that gaseous fuels from non-conventional sources can access gas grids across the EU [8,9]. The three-year project started in June 2010 and consists of four work packages.

One of these work packages, namely “Direct measurements of the calorific value of non-conventional gases” involves four National Metrological Institutes and the University of Valladolid in Spain. It aims at energetic characteristics and thermophysical property measurements, such as the density and heat capacity of non-conventional gases with the smallest uncertainties.

The main objective of the work on energy-content measurement is to develop and validate a primary reference calorimeter as well as to adapt and validate several field calorimeters for non-conventional gases to be able to measure the calorific value with a minimum uncertainty. The gas mixtures studied in this work are six synthetic biogas mixtures containing either CO<sub>2</sub> and CH<sub>4</sub> or CO<sub>2</sub>, CH<sub>4</sub> and H<sub>2</sub>S and another synthetic mixture that represents coal mine methane. The different hydrogen sulphide concentrations in the biogas mixtures simulate gases from different purification steps in biogas upgrading. The presence of H<sub>2</sub>S in a wet environment may cause high corrosion damage in flanges and pipelines.

The calorific values and associated uncertainties obtained from the measurements of these gases were compared both between the various calorimeters and with the results from the indirect method. These measurements are particularly challenging, as even low levels of impurities, odorant species, moisture and process by-products all have effects on the energy content of the mixture. Density is another key parameter for the interchangeability of renewable gases to be injected into gas grids and enables Wobbe index calculations. Accurate density measurements on these gases are the subject of another study [10].

## 2. Development of the primary and field calorimeters

### 2.1. The primary reference calorimeter

For the accurate determination of calorific values of non-conventional gases, four calorimeters were employed: three field calorimeters and a reference gas calorimeter.

To allow traceability of the energy content measurements with the field calorimeters used in this work, a primary reference

**Table 1**

Average compositions of non-conventional gases from different sources [5–7] (OHCs stands for organo-halogenated compounds and % for % mol · mol<sup>-1</sup>).

	Biogas from household waste	Biogas from sewage sludge	Biogas from agricultural waste	Shale gas	Coal bed methane	Coal mine methane	Landfill gas
CH <sub>4</sub> (%)	50–60	60–75	60–75	79–95	90	65	30–60
CO <sub>2</sub> (%)	34–38	19–33	19–33	0.1–5	3.3	16.0	15–40
N <sub>2</sub> (%)	0–5	0–1	0–1	0.1–8	4.5	18.0	0–50
O <sub>2</sub> (%)	0–1	<0.5	<0.5			0.5	0–10
H <sub>2</sub> O (%)	6 (at 40 °C)	6 (at 40 °C)	6 (at 40 °C)				
H <sub>2</sub> S (mg · m <sup>-3</sup> )	100–900	1000–4000	3000–10,000		0–5	0–5	0–1000
Aromatic compounds (mg · m <sup>-3</sup> )	0–200						
OHCs (mg · m <sup>-3</sup> )	100–800						0–800
NH <sub>3</sub> (mg · m <sup>-3</sup> )			50–100				0–5
C <sub>2</sub> + (%)				0.1–20	2.2	1.5	

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