Physikalisch-Technische Bundesanstalt
Braunschweig und Berlin
Nationales Metrologieinstitut

EMRP 2013

ENG60 LNG II

Metrological support for LNG custody transfer and transport fuel applications

Guideline on the traceability of energy and enthalpy calculations

(Task D4.4.3)

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EMRP
European Metrology Research Programme
Programme of EURAMET

EURAMET
European Association of National Metrology Institutes

The research leading to the results discussed in this report has received funding from the European Metrology Research Program (EMRP). The EMRP is jointly funded by the EMRP participating countries within Euramet and the European Union

V3.0

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1. Introduction

This guideline is closely related to the preceding deliverable D4.4.2 ‘Report on the relevant physical quantities and current data used in enthalpy and calorific-value calculations’ and contains summary and conclusions of that preceding deliverable.

The task of this deliverable D4.4.3 ‘Guideline on the traceability of energy and enthalpy calculations’ is specified in the title itself. The JRP protocol demands that with the input from the previous activity (deliverable D4.4.2), a guideline shall highlight the physical quantities requiring scientific investigation in order to ensure traceability in enthalpy and calorific-value calculations. It will also include the status of the traceability of the relevant physical quantities for energy and enthalpy calculations and recommendations for improvement.

Therefore, this guideline is subdivided into three parts. The first one highlights the physical quantities requiring scientific investigation in order to ensure traceability in enthalpy and calorific-value calculations. The second part reports the current status of the traceability of the relevant physical quantities and the last part gives some recommendations for improvement.

The main topic of the preceding report (D4.4.2) and this guide is the traceability of measurement results. Traceability means ‘the property of a measurement result whereby the result can be related to a reference through a documented unbroken chain of calibrations, each contributing to the measurement uncertainty’ according to the BIPM (Bureau International des Poids et Mesures, http://www.bipm.org/en/bipm-services/calibrations/traceability.html). The traceability requires (among others; see BIPM homepage) a documented uncertainty statement. This involves uncertainty statements for the measurement result, uncertainty statements for all input quantities which are measured, uncertainty statements for the calibration standards used and a documented measurement procedure.

The preceding report tried to categorise the current data used for calorific value and enthalpy calculations in three defined categories A, B and C. Category A should ensure full traceability. The category B contains measurement results which traceability in the sense of an uncertainty statement is close to category A but with some limitations. In category C, all publications are collected which report no or only a claimed uncertainty without a deeper analysis. The quality of the uncertainty analysis serves as criterion for the traceability of the published measurement results. All uncertainties of the measurable input quantities should be reported. It is demanded that the combined uncertainty of the reported measurement result can be recalculated from the information given by the published work.

2. Physical quantities and substances

This paragraph reports the thermophysical quantities requiring scientific investigation to ensure the traceability in enthalpy and calorific value calculations. Its content is basically identical to explanations given in the report of deliverable D4.4.2. (chapter 2) and is not repeated here.

In principle, the identified thermophysical quantities are displayed in a matrix form (Table 1). The columns (substances) contain the hydrocarbons from methane up to pentane, nitrogen, water, carbon dioxide and oxygen. The rows (thermophysical properties) comprise standard enthalpies of formation, heats of combustion (superior calorific value), enthalpies of fusion, sublimation and vaporisation and temperature-dependent heat capacities of the gas, liquid and solid state. The matrix indicates thermophysical properties which are necessary for calculating the temperature-dependent enthalpies of an LNG sample.

3. Current status

Table 1 displays the relevant substances and thermophysical properties to calculate enthalpies of formation and calorific values over a wide range of temperatures from liquid to the gaseous state at a given pressure. The colour code reflects the traceability status of each thermophysical property and summarizes the results of the literature analysis in the report of deliverable D4.4.2.

Table 1: Physical quantities and substances (colour code see text).

		Methane	Ethane	Propane	Butane	i-Butane	Pentane	i-Pentane	Nitrogen	Water	Carbon Dioxide	Oxygen
Standard enthalpy of formation										x	x	
Heat of combustion/calorific value		x	x	x	x	x	x	x				
Enthalpies of	fusion									x		
	sublimation										x	
	vaporisation	x	x	x	x	x	x	x	x			
Heat capacity / Enthalpy	gas	x	x	x	x	x	x	x	x		x	x
	liquid	x	x	x	x	x	x	x	x	x		
	solid									x	x	

The colour 'green' indicates a fully traceable measurement result. Yellow marked physical quantities have only limited traceability but are close to 'green' results. Physical quantities labelled with the colour coded 'red' are not supported by traceable measurement results. The used colour code corresponds to the categories A (= green), B (= yellow) and C (= red) used for the classification of the traceability in the report of deliverable D4.4.2 (see chapter 3).

4. Recommendations for improvement

There are several ways to improve the traceability of the relevant data used for enthalpy and calorific-value calculations of a typical LNG sample. Such a typical LNG sample mainly consists of the hydrocarbon components listed in Table 1 and also of nitrogen. For the calculation of calorific values at various thermodynamic conditions the temperature dependence of the enthalpy of oxygen, water and carbon dioxide is necessary at a given pressure.

The recommendations comprise ideas how to deal with still published work and give some hints how to increase the amount of available dataset from future scientific investigations.

4.1. Substances and quantities

In Table 1 there are only a few thermophysical properties marked with 'green' as fully traceable results. The heat of combustion of methane, the heat capacities of methane, nitrogen and carbon dioxide in the gaseous phase are based on traceable measurements. This is also valid for the heat capacity of water in the liquid state.

All other thermophysical quantities in Table 1 suffer a lack of traceable data and need further investigations. A very striking example for this need of further investigations are the standard enthalpies of formation of water and carbon dioxide. These two molecules are involved in each combustion process where carbon and oxygen participates. A solid foundation of the standard enthalpy of formation of water and carbon dioxide is desirable for traceable and, therefore, reliable results in thermochemistry whenever enthalpies of respective reactions partners are calculated.

For example, the temperature dependence of the calorific value of methane being the main component of natural gas, and LNG should be calculated. In order to determine the calorific value, the enthalpy of formation of water (also of carbon dioxide, oxygen and, for sure, of methane itself) is necessary. It is evident that the enthalpy of formation of water is a fundamental quantity for all combustion processes where hydrocarbons are involved.

The CODATA book for Key Values for Thermodynamics (Cox, Wagman and Medvedev, 1989) mentions the investigations of Rossini (JNBS 1931a and 1939) and King and Armstrong (JNBS 1968). The relative uncertainty (coverage interval k = 2) of Rossini's experimental value of the enthalpy of formation of water is approximately ten times smaller (±0.014%) than the uncertainty (± 0.12%) given by King and Armstrong.
Rossini determined the uncertainty by calculating the standard deviation of the measured mean values. This calculation procedure does not comply with current accepted procedures to estimate uncertainties of measurement like GUM (Guide to the expression of uncertainty in measurement), e. g. reporting an uncertainty budget. Therefore, a comparison with Rossini's experimental findings and usage as key thermodynamic value is doubtful.

Nevertheless, the experimental value and its uncertainty determined by Rossini still serve as reference value. Therefore, the guideline developed in this task recommends a fully traceable investigation with uncertainty budget of the enthalpy of formation of water according to GUM.

4.2. How to deal with traceability category B and C

Measurement data are a prerequisite for the development of generally accepted equations of state (EoS), for e. g. the GERG 2004 wide-range equation of state for natural gases and other mixtures (ISO 20765-2). The Helmholtz free energy is the central core of the GERG 2004 and, therefore, used to calculate all other types of thermal and pressure-dependent gas properties, e. g. density, speed of sound, heat capacities and enthalpies, by classical partial derivatives know from fundamental thermodynamics. In order to set up such an EoS like the GERG 2004 the input of caloric and thermal experimental data are necessary.

These days, the uncertainty statements of EoS like the GERG 2004 only reflect the deviation of the measurement data from the theoretical approximation and are not based on the uncertainties of the experimental data basis. To increase the reliability of the theoretically developed EoS, traceable data would be mandatory. The available data of category A (fully traceable) are rare. One recommendation would be to use also experimental data of category B (traceability quality close to category A but with limitations) if traceable category A data are available.

Some experimental data of category C were published without an uncertainty statement. Category C also contains data sources which make statements of the measurement uncertainty but without any further analysis or discussion. Uncertainties in measurement which only consist of the standard deviation of multiple measurement results are treated as category C. All these kinds of data classified by category C should be considered as ‘historical’ and no longer used as reference values or e.g. for the development of EoS. If there are no traceable data available, uncertainties have to be estimated and scientific work based on such data should point out the usage of non-traceable data.

4.3. Revision and supplement of publications

Published measurement data of category B have a limited traceability but are close to category A which means full traceability. In some cases, category B experimental data lack only one single information or a relative uncertainty statements should be supplemented by absolute values of the input quantities measured. The quality of this kind of measured data could be upgraded as far as the laboratories and respective researchers are still active. Scientific journals where such data are published should assume the responsibility to invite their authors to supplement already published work. For category C data, this also might be possible, but much more work could be necessary to revise published uncertainty statements.

4.4. Standard for uncertainty statements in scientific journals

The request for a standard for uncertainty statements in scientific journals is unnecessary. Most scientific journals have already committed themselves to the adherence and application of the GUM (Guide to the expression of uncertainty in measurement, International Organization for Standardization, 1995). The problem is the realisation in the review process for submitted papers. There should be a kind of checklist for the quality of an uncertainty statement used by the reviewer to support traceability of the published data.

Such a checklist might ask for

- definition of the quantity measured (model equation),
- input quantities (e. g. values measured, used constants or calibration standards),
- knowledge about the input quantities (e. g. source, probability distribution) and the estimated standard measurement uncertainty,
- sensitivity coefficients,
- combined measurement uncertainty and its components,
- effective degree of freedom and the level of confidence,
- methods used (including corrections) to evaluate the measurement results and its uncertainty and
- comprehensive uncertainty assessment starting from input quantities to combined uncertainty.

4.5. Verification of traceable data

The existence of traceable data including their uncertainty statements are no guarantee for systematic deviations from the so-called and unknown ‘true value’ of the quantity measured. An appropriate strategy to avoid systematic deviations of the measurement results is the arrangement of key comparisons and the application of different measuring techniques.

4.6. Literature guides for uncertainty assessment

There are several guides for the assessment of uncertainty. Also, instructions are available for the implementation of these guides.

List with recommendations:

- JCGM 100:2008. GUM 1995 with minor corrections 2008. Evaluation of measurement data - Guide to the Expression of Uncertainty in Measurement. 1st ed. 2008.
- EURACHEM/CITAC Guide. Quantifying uncertainty in analytical measurement. 3rd Ed. (2012).
- P. de Bièvre, H. Günzler. Measurement Uncertainty in Chemical Analysis. Springer (2003).
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- W. Schluz and K. D. Sommer, Uncertainty of measurement and error limits in legal metrology, OIML Bulletin Vol XL (4), 5-15 (1999).