Metrological Maintenance of Gas Calorimeters and Wobbe Index Analyzers

Karina A. Mishina, Elena N. Korchagina, and Iaroslav V. Kazartsev

Abstract This article studies the issues of metrological maintenance of measuring instruments: gas calorimeters and Wobbe index analyzers. The purpose of this research lies in developing reference materials (RMs) of gases with the certified value of inferior calorific value, which is traceable to a state primary standard. The initial set of pure candidate gases (hydrogen, methane, ethane, and propane) and the target uncertainty of inferior calorific value (0.3%) were selected based on the results of analyzing the metrological characteristics of calorimetric equipment. The certified value of inferior calorific value is traceable to the State Primary Standard of the Energy Units of Combustion, Specific Energy of Combustion and Volumetric Energy of Combustion GET 16. The certified value for the selected gases and its uncertainty were evaluated by applying standard calorimeters-comparators for combusting the high and low-calorie gases USVG and USNG from GET 16. The results obtained during experimental studies and characterization of reference materials confirmed the declared accuracy values. Further studies should focus on developing reference materials of gas mixture-imitators for natural, associated, and other gases, as well as including the Wobbe index in the list of certified characteristics.

Keywords Inferior calorific value · Wobbe index · Gas calorimetry · Thermophysical properties · Reference material

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Abbreviations

GET 16	State Primary Standard of Units of Combustion Energy, Specific Energy of Combustion, and Volumetric Energy of Combustion GET 16–2018
GET 154	State Primary Standard of Units of Molar Fraction, Mass Fraction, and Mass Concentration of Components in Gas and Gas Condensate Media GET 154–2019
RMs	Reference Materials
MI	Measuring Instrument

Introduction

The efficient use of energy sources is attracting wide research interest due to aggravating environmental problems. In various areas of industrial production, the focus is made on the sustainable use of both traditional gas fuels and production by-products, such as coke-oven and blast furnace gases, associated petroleum gas, methane from gas mines, etc. Large-scale research in the field of creating renewable energy sources has brought about new methods for extracting low- and high-calorific combustible gases, including biogas, from agricultural, paper, and other industrial waste. The use of such gas fuels is currently growing at an average rate of 1.8% per year, and is projected to continue mainly due to an increasing demand in countries with stringent environmental regulations [1].

The listed types of gas have significant differences from natural gas in combustion energy and composition. Their composition and quality are subject to fluctuations both in the long and short term [2]. Therefore, when used as a fuel, special attention should be paid to the interchangeability of gases in order to avoid an increase in harmful emissions and damage to equipment during combustion, as well as to maintain the energy efficiency of production.

The main characteristic of the interchangeability of gas fuels—the Wobbe index—reflects information about the heat load in the system, since gases with different component composition and combustion energy, but the same Wobbe index, have the same thermal power and can be used without replacing burners.

The Wobbe index (higher W_{high} or lower W_{low}) is defined as the ratio of the combustion energy (higher H_{high} or lower H_{low}) of a gas to the square root of its relative density d in the air (Formula 1):

$$W_{\text{high/low}} = \frac{H_{\text{high/low}}}{\sqrt{d}}, \tag{1}$$

The relative density of gas in the air d can be calculated as the ratio of the absolute gas density ρ_{g} to the air density ρ_{air}, which is 1.204449 kg $\cdot$ m^{-3} under normal conditions (293.15 K, 101.325 kPa) [3].

Table 1 Maximum permissible measurement errors in accordance with ISO 15971:2008 [4]

MI class	0	1	2	3
H_{high}	± 0.1%	± 0.1 MJ/m^3 (~0.25%)	± 0.2 MJ/m^3 (~0.25%)	± 0.5 MJ/m^3 (~0.25%)

Table 2 Maximum permissible measurement errors in accordance with OIML R 140:2007 [6]

Precision class	A	B	C
Energy content	± 1.0%	± 2.0%	± 3.0%
H_{high}	± 0.5%	± 1.0%	± 1.0%

The net calorific value H_{low} can be calculated in accordance with GOST 31,369–2008, using a calculation method for determining the combustion energy and other gas properties on the basis of its component composition (determined with a gas chromatograph) [3], or determined experimentally by the calorimetric measurement methods described in ISO 15971:2008 [4]. Compared to the calculation according to GOST 31,369–2008, calorimetric measurement methods have a number of advantages when analyzing unconventional types of gas fuels: absence of limitations in the content of components (for example, ethane and hydrogen), lower uncertainty and calorimeter response time, as well as the efficiency and simplicity (in terms of maintenance) of calorimetric systems, including procedures of their calibration [5].

At the moment, various types of measuring equipment are used for determining the combustion energy and the Wobbe index, the operation principles of which rely on calorimetric methods. International standards ISO 15971:2008 and OIML R 140:2007 describe the classification and regulatory requirements for the accuracy of such equipment (Tables 1 and 2).

The quality of the results obtained with such equipment depends significantly on the correctness of its calibration. In the absence of reference materials (RMs), the ability to perform these routine procedures is severely limited. ISO 15971:2008 proposes pure methane, gas mixtures with a calculated combustion energy value, and gases certified with reference calorimeters as calibration standards. For the equipment used in a range other than natural gas, the former two options are not optimal. The latter option is preferable, since it can achieve a lower uncertainty of combustion energy measurements and ensure direct traceability of the measurement results to the primary standard.

In Europe, various aspects of gas research are handled by GERG (European Gas Research Group, Belgium), founded in 1961 and currently comprising 24 organizations from 10 European countries.

Several years ago, in order to ensure traceability of measurements in this area, GERG conducted a project aimed at the development of reference gas calorimeters with a measurement uncertainty not exceeding ± 0.05% at PTB (Germany) and LNE (France) [7, 8]. The results obtained using these calorimeters and the KATET calorimeter from GET 16–2018[1] made it possible to clarify the value of methane combustion energy in ISO 6976:2016 [9] and to reduce the uncertainty of this value [10–12].

Currently, most of the research in the field of combustion energy measurements is focused on biogas and other gases from unconventional sources [13–15]. The tasks of obtaining reliable and consistent values during measurements using working measuring instruments (MI) are also relevant. Among other research problems are the use of computational methods in gas transmission networks [16] and mixed flows [17] and comparison of various methods and instruments for measuring combustion energy of gases [4, 17, 18]. It should be noted that, at the moment, other countries lack RMs of volumetric combustion energy traceable to national standards.

In Russia, until 2021, the metrological maintenance of measuring instruments in the field of gas calorimetry had been carried out with the use of working standards developed at the D. I. Mendeleyev Institute for Metrology (VNIIM)[2] in St. Petersburg and used for verification and testing of gas calorimeters for type approval purposes. However, these tools did not satisfy the need for available calibration standards with certified combustion energy values, which are required during periodic routine maintenance of calorimetric equipment.

Therefore, the aim of this study was to develop a set of certified reference materials (RMs) of the volumetric inferior (lower) calorific value (LCV) based on pure gases—hydrogen, methane, ethane, and propane. The estimated uncertainty of the certified inferior calorific value for this set shall not exceed 0.3%.

Materials and Methods

To develop RMs for establishing and monitoring the metrological characteristics of gas calorimeters and Wobbe index analyzers, 4 samples of pure gases were selected and studied—hydrogen, methane, ethane, and propane. The requirements for the metrological characteristics of the developed RMs, as well as the choice of the samples under study, were determined by the results of analyzing the metrological characteristics of working measuring instruments. The certified inferior calorific value for the studied samples and its uncertainty were calculated based on the experimental data obtained by direct calorimetric method using the calorimeters-comparators for combustion of high- and low-calorie gases (USVG and USNG) from the State Primary Standard of the Combustion Energy Units GET 16–2018.

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[1] GET 16-2018 State primary standard of units combustion energy, specific combustion energy and volumetric combustion energy. In: Federal Information Fund for Ensuring the Uniformity of Measurements. https://fgis.gost.ru/fundmetrology/registry/12/items/397905 (In Russ.).

[2] D. I. Mendeleyev Institute for Metrology (VNIIM). https://www.vniim.ru/etalon.html (In Russ.).

Selection and Preparation of Initial RMs

We took into account that the RMs of gases under development are intended for evaluation of metrological characteristics of calorimetric equipment during verification, calibration, and type approval tests.

Table 3 shows the main metrological characteristics of gas calorimeters and complex analyzers, designed for measuring combustion energy and the Wobbe index that passed the type approval tests in the Russian Federation.

An analysis of the characteristics of working measuring instruments showed that the most common are gas calorimeters and Wobbe index analyzers with a wide measurement range, accuracy class 3 according to ISO 15971:2008 (accuracy class B according to OIML R 140: 2007) with a tolerance limit of ± 1.0% and more.

Table 3 Main metrological characteristics of gas calorimeters operated in the Russian federation

Measuring instrument	Measured value	Measuring range	Limits of the permissible measurement error, %
9610, Cosa Xentaur Corporation	$W_{\text{low/high}}$, $H_{\text{low/high}}$	1–95 MJ/m^3	± 1.0[a]
	d	0.1–3.0	± 0.6
NKS, Teplofizichiskie pribory	H_{low}	25–41 MJ/m^3	± 0.3
RBM 2000, Reineke Mes-und Regeltechnik GmbH	$W_{\text{low/high}}$, $H_{\text{low/high}}$	3–100 MJ/m^3	± 1.0[a]
		28–40 MJ/m^3	± 0.6[a]
	ρ	0–2 kg/m^3	± 1.0[a]
CWD 2000, UNION Instruments GmbH	H_{low}	2.5–50.0 MJ/m^3	± 1.0[a]
	W_{low}	2.5–55.5 MJ/m^3	± 1.0[a]
CWD 2005, UNION Instruments GmbH	$H_{\text{low/high}}$	3.0–5.0 MJ/m^3	± 1.0[a]
		12.5–21.0 MJ/m^3	
WI, Reineke Mes-und Regeltechnik GmbH	H_{low}	2.5–55.5 MJ/m^3	± 1.5[a]
	W_{low}	2.5–56.0 MJ/m^3	± 1.0[a]
KSNG-05, Teplofizichiskie pribory	H_{low}	25–50 MJ/m^3	± 0.5
		31.8–39.8 MJ/m^3	± 0.45
EMC 500, RMG Messtechnik GmbH	$H_{\text{low/high}}$	30.2–47.2 MJ/m^3	± 0.5
	ρ	0.65–1.3 kg/m^3	± 0.5
66, Reineke Mes-und Regeltechnik GmbH	H_{high}	32–42 MJ/m^3	± 0.5[a]
WIM 9900, Horbe Instruments B.V	W_{low}	40–60 MJ/m^3	± 2.0
	d	0–2	± 0.2
WIM Compas	$W_{\text{low/high}}$	0–90 MJ/m^3	± 1.0[a]
	$H_{\text{low/high}}$		± 0.7[a]
	d	0.5–1.7	± 1.0[a]

[a] Limits of permissible measurement error, reduced to the upper limit of the measurement range

Table 4 Certified characteristics, the range of permissible certified values, and permissible values of the expanded uncertainty of the RM of the inferior calorific value of gases (NOES VNIIM collection)[3]

GSO number in the collection	RM index in the collection	Interval of permissible certified values of the **inferior calorific value**, $H_{inf}^{25/20}$, MJ/m^{3a}	Permissible value relative to the extended uncertainty (U)^b with a coverage factor k = 2, %
GSO 11,662–2020	NOES-VNIIM-H_2	10.030–10.260	0.3
GSO 11,663–2020	NOES-VNIIM-CH_4	33.350–33.580	
GSO 11,664–2020	NOES-VNIIM-C_2H_6	59.740–59.980	
GSO 11,665–2020	NOES-VNIIM-C_3H_8	86.230–86.470	

Notes [a] superscript (25/20) designates combustion reference conditions—temperature 25 °C (298,15 K) and pressure 101.325 kPa, and metering reference conditions—temperature 20 °C (293,15 K) and pressure 101.325 kPa

[b] corresponds to the permissible relative error at a confidence level (P = 0.95)

Table 5 Technical characteristics of initial materials of the rms of the inferior calorific value of gases (NOES VNIIM collection)

RM Index in the collection	Initial substance	Regulatory documents for the initial materials to comply with
NOES-VNIIM-H2	Hydrogen (H_2)	TU 2114–016-78,538,315–2008[4] or GOST R 51,673–2000[5]
NOES-VNIIM-CH4	Methane (CH_4)	TU 51 841–87[6]
NOES-VNIIM-C2H6	Ethane (C_2H_6)	TU 6–09-2454–85[7]
NOES-VNIIM-C3H8	Propane (C_3H_8)	TU 51–882-90[8]

The established metrological and technical requirements for the developed RMs are presented in Tables 4 and 5. Since the control of the metrological characteristics of calorimetric equipment is required at several points throughout the entire measurement range, pure gases with different values of the lowest volumetric combustion

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[3] GSO 11,662–2020/GSO 11,665–2020 Standard Sample of the Lowest Volumetric Energy of Combustion of Gases (collection of NOES VNIIM—D.I. Mendeleyev All-Union Scientific Research Institute of Metrology). In: Federal Information Fund for Ensuring the Uniformity of Measurements. https://fgis.gost.ru/fundmetrology/registry/6/items/1384812 (In Russ.).

[4] TU 2114–016-78,538,315–2008 Highly Pure Hydrogen / NPK Nauka LLC. https://nauca.ru/content/hydrogen/HydrogenSpecification2114-016-78538315-2008.pdf (In Russ.).

[5] GOST R 51,673–2000 Gaseous Pure Hydrogen. Technical Specifications. Gosstandart Rossii, Moscow, 2000. (In Russ.).

[6] TU 51–841-87 Gaseous Methane / JSC Scientific Research and Design Institute of Urea and Organic Synthesis Products. http://www.1bm.ru/techdocs/kgs/tu/42/info/1351 (In Russ.).

[7] TU 6–09-2454–85 Isobutane for Chromatography and Spectroscopy of Chemically Pure Grade. https://www.standards.ru/document/3236550.aspx (In Russ.).

[8] TU 51–882-90 Liquefied Propane. https://www.standards.ru/document/3236550.aspx (In Russ.).

energy in the range of 10–90 MJ/m^3 were selected as the candidate substances in order to meet the need for metrological support. The target uncertainty of reference materials, taking into account the required ratio of the accuracy of the verification tool to the verified MI "1:3" was set at the level of 0.3%.

The choice of the technical characteristics of the initial materials was conditioned by the necessity to use commercially available substances.

Samples Under Study

When developing RMs, studies were carried out on the samples of pure gases, the technical characteristics of which are presented in Table 6.

When developing the RMs, the identification involved checking the accompanying documentation of the initial substances. The producer of initial materials (Monitoring Ltd., St. Petersburg) guarantees the compliance of pure gases with the requirements specified in Table 6, which is stated in the passports of initial materials. When developing the RMs, the gas analytical laboratory of VNIIM identified the main component and impurities for methane and propane. The results obtained showed that the molar fraction of the main component for the studied gases was not less than 99.99% mol., with the amount of each of the determined impurities (CO, CO_2, Ar + O_2, H_2, He, N_2) not exceeding 7 ppm.

The homogeneity and stability of the RMs were evaluated in accordance with Clause 7 and Clause 8 of ISO Guide 35:2017, taking into account the provisions for pure substances. In general, the chemical and physical properties of the studied pure substances suggest their high homogeneity and stability. According to Clause 7.1 of ISO Guide 35:2017, there is no need to assess between-unit heterogeneity, since each RM unit is assigned its own certified value. Some variability from within-unit heterogeneity inevitably manifests itself in standard deviations determined in characterization and stability studies; therefore, the contribution from within-unit heterogeneity was not evaluated separately, but was taken into account in aggregate with other contributions. In addition, the instructions for the RM provided the user with recommendations for storage and use of the RM to ensure its homogeneity. The

Table 6 Technical characteristics of the studied samples of the RMs of the lowest volumetric combustion energy of gases (NOES VNIIM collection)

Sample	Initial substance	Gas tank (material, volume)	Molar fraction of the main component, no less than, %
NOES-VNIIM-H2	Hydrogen (H_2)	Carbon steel, 10 l	99.95
NOES-VNIIM-CH4	Methane (CH_4)	Aluminum alloy, 8 l	
NOES-VNIIM-C2H6	Ethane (C_2H_6)	Carbon steel, 10 l	
NOES-VNIIM-C3H8	Propane (C_3H_8)	Aluminum alloy, 10 l	

Table 7 Results of measurements of volumetric combustion energy of hydrogen, methane, ethane, and propane samples under study

Sample (tank no.)	Date of the first series of measurements	Average value of inferior calorific value in the first series of the measurements $H_{inf,1}$, MJ/m^3	Date of the second series of the measurements	Average value of inferior calorific value in the second series of the measurements $H_{inf,2}$, MJ/m^3	Deviation between the average values of inferior calorific value in the first and second series, $\Delta(H_{inf})$, MJ/m^3 (%)
Hydrogen (1032)	November 1, 2016	10.052	October 11, 2019	10.051	0.001 (0.01)
Methane (27,890)	May 22, 2017	33.440	October 11, 2019	33.425	0.015 (0.04)
Ethane (15,722)	November 1, 2015	59.883	August 17, 2017	59.874	0.009 (0.01)
Propane (24,960)	October 17, 2019	86.410	February 15, 2021	86.365	0.045 (0.05)

RM stability was assessed on the basis of the data obtained during preliminary studies of similar initial materials according to Clause 8.2.3. The results of the stability studies are shown in Table 7.

The deviations obtained in the stability studies do not exceed 0.05%, which is less than one-third of the target uncertainty of the RM inferior calorific value (0.3%). Therefore, the contribution from instability to the total uncertainty can be considered negligible.

Method for Determining the Certified Value

The standard gas calorimeters-comparators USVG and USNG, included in GET 16–2018 in the course of its improvement completed in 2018, were used to determine the certified value of the combustion energy of the studied samples. The expanded uncertainty of the measurement results in the range of 10–90 MJ/m^3, obtained with these calorimeters, is estimated at a level not exceeding 0.3%.

The standard gas calorimeters are designed to transfer a unit of volumetric energy of combustion to gases and to gas mixture in the range of 3–35 MJ/m^3 (USNG calorimeter) and 25–90 MJ/m^3 (USVG calorimeter). The calorimeters implement the direct method of measuring the volumetric heat of combustion, connected by the calibration dependence with the measured combustion time of a single gas portion.

Figure 1 shows the principle of operation of the calorimeters. Gas combustion is performed in the burner of the measuring cell (1) located inside the heating unit (2). The gas is fed from the closed tank (3) through the gas line (4) to the measuring cell

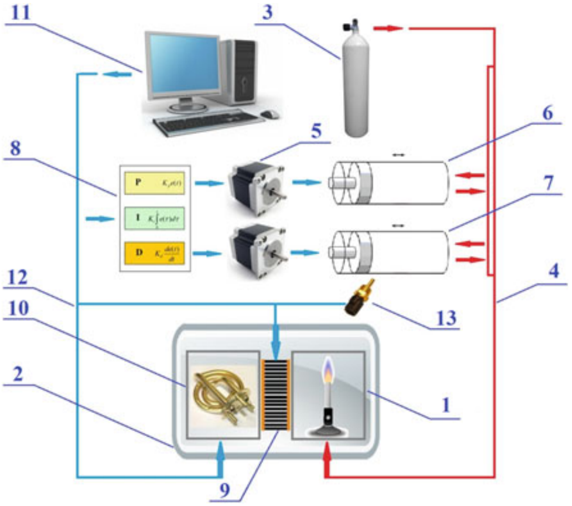

Fig. 1 The principle of operation of the reference gas calorimeters-comparators USVG and USNG included in the GET 16–2018. 1—burner of the measuring cell; 2—heating unit; 3—tank; 4—gas line; 5—stepper motors; 6 and 7—working cylinders; 8—PID controller; 9—differential module; 10—comparative cell; 11—personal computer; 12—system of auxiliary electronic units and electrical cables; 13—sensors

by a dosing device with an adjustable feed rate. The gas supply rate is controlled by changing the frequency of pulses supplied to the stepper motors (5), which with the help of worm-screw pairs drive the pistons in the working cylinders (6 and 7) into translational movements. The frequency control is performed by a PID controller (8), which maintains zero signal on the set of differential modules (9), such that the thermal power, released in the measuring cell due to the test gas combustion, is constant and equal to the power released in the comparative cell (10).

The power comparison method is based on the compensation method implemented on the basis of a differential thermal circuit with diathermic coupling through semiconductor converters, which are zero-organs between the cells—a measuring cell, in which the gas combustion process is carried out, and a comparative cell, in which an electric heater is located, which releases constant power.

The operation of the calorimeters is controlled by means of a personal computer (11) of industrial design with a system of auxiliary electronic units and electrical cables (12) forming control, regulation, power supply, and coordination units.

The calorimeter measurement mode is continuous-cyclic. Continuity is ensured by alternating operation of two piston pumps. Each measurement cycle is associated with extruding a portion of gas by one of the pumps. To bring the measurement results of the volumetric LCV to standard conditions, the metering device has a system of sensors (13), which provide the formation of signals that are sent to the control and regulation system for processing.

Statistical results were obtained by processing the array of measured data (single values of the volumetric LCV, issued by the calorimeter at the end of each measuring cycle), with the extraction of data for each of the studied gases from the general array with the measurement results.

Estimated Uncertainty of the Certified Value

Since the input values are independent, in accordance with ISO Guide 35:2017, the total standard uncertainty of the certified value was calculated with the following equation [19]:

$$u_{CRM} = \sqrt{u_{char}^2 + u_{hom}^2 + u_{lts}^2}, \tag{2}$$

where

u_{char}—uncertainty of the certified value obtained for the unit (characterization);

u_{hom}—uncertainty associated with the heterogeneity of the material in a single package (homogenity);

u_{lts}—uncertainty associated with material instability (stability).

Since the volumetric combustion energy is an additive value and directly depends on the component composition of the gas, the homogeneity and stability of RMs were confirmed by the positive results of experimental studies of the stability of RMs of the component composition (reference standards), which were manufactured using similar initial materials. The components of heterogeneity and instability were evaluated as negligible and were excluded from the estimation of total uncertainty.

The characterization of uncertainty u_{char} was estimated in accordance with the uncertainty budget of the USVG and USNG calorimeters:

$$u_{char} = u_c(H), \tag{3}$$

$$u_c(H) = \sqrt{u_b(H)^2 + u_a(H)^2}, \tag{4}$$

where

$u_b(H)$—the relative standard uncertainty of type B measurements of the volumetric energy of gas combustion;

$u_a(H)$—the relative standard uncertainty of type A measurements of the volumetric energy of gas combustion, calculated by the formula:

$$u_A(H) = \sqrt{\frac{\sum_{i-1}^{n} \left(H_i - \overline{H}\right)^2}{n-1}}, \tag{5}$$

where

H_i—value of the ith measurement result of the LCV, MJ/m^3;

$\overline{H}$—average value of measuring the LCV, MJ/m^3;

n—number of single measurement results.

The uncertainty $u_b(H)$ when transferring a unit of combustion energy using the USVG and USNG calorimeters was established earlier in the course of their studies as part of the improvement of GET 16–2018 and in the range of 10–90 MJ/m does not exceed $8 \cdot 10^{-4}$.

The expanded uncertainty was calculated by the formula

$$U_{CRM} = k \cdot u_{CRM}, \tag{6}$$

where the coverage factor is $k = 2$ with a confidence level of $P = 0.95$.

Results and Discussion

In the course of experimental studies, a certified value of inferior calorific value, traceable to the State Primary Standard, was obtained for the 4 samples under study, and its uncertainty was evaluated. The results of experimental studies are shown in Table 8.

Figures 2, 3, 4 and 5 show the results of measurements of the inferior calorific value of the studied samples. In order to obtain a sufficient amount of initial data to determine the desired value and estimate the budget of measurement uncertainty, each sample was burned for 24 h.

The stability and absence of a drift of the combustion energy of the studied samples additionally testify to the correctness of the choice of initial materials with the aim to develop on their basis the metrological means for verification, calibration, and testing of gas calorimetric equipment used in industry.

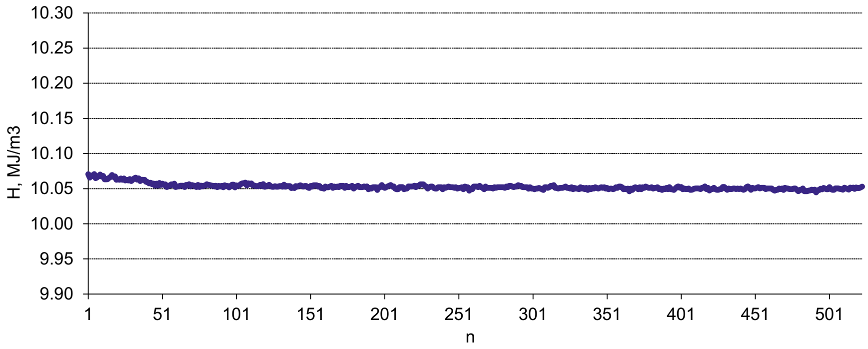

Fig. 2 Measurement of inferior calorific value when characterizing a hydrogen sample (USNG calorimeter-comparator)

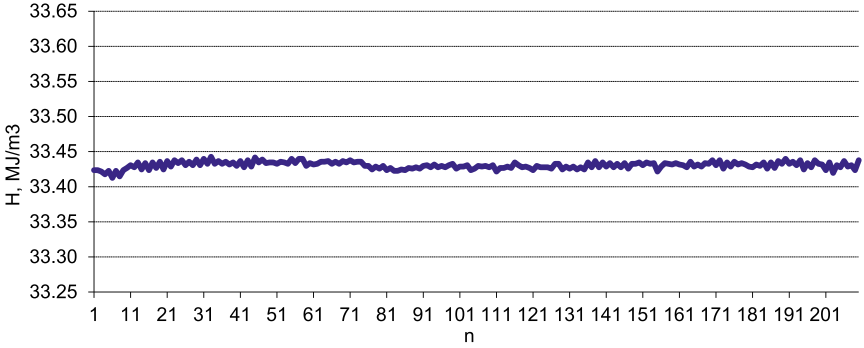

Fig. 3 Measurement of inferior calorific value when characterizing a methane sample (USVG calorimeter-comparator)

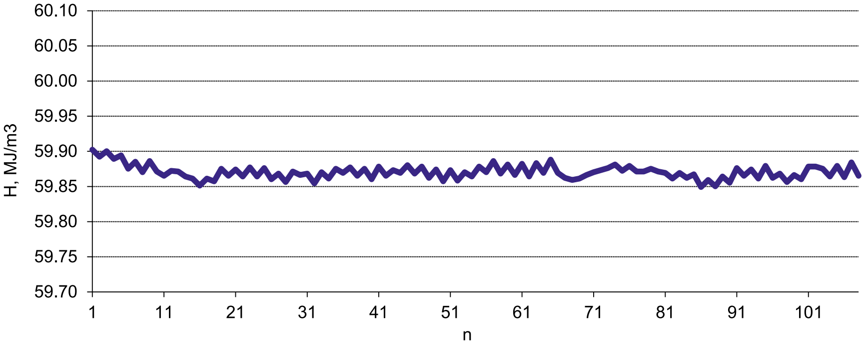

Fig. 4 Measurement of inferior calorific value when characterizing an ethane sample (USVG calorimeter-comparator)

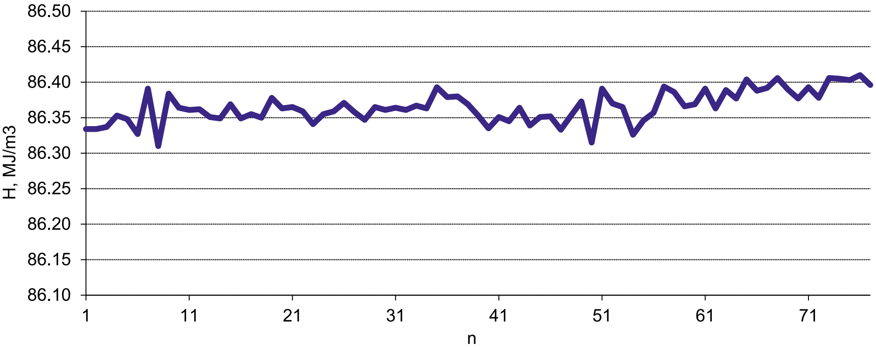

Fig. 5 Measurement of inferior calorific value when characterizing a propane sample (USVG calorimeter-comparator)

Table 8 Measurements of volumetric combustion energy of hydrogen, methane, ethane, and propane samples under study

Sample (calorimeter)	Measured value of inferior calorific value H_{inf}, MJ/m^3	SD of the measurement result, s_r, MJ/m^3 (in 24 h, n—number of single measurement results)	Standard characterization uncertainty, u_{char}, MJ/m^3	Relative expanded uncertainty U_{crm} at coverage factor $k = 2$, MJ/m^3 (%)
Hydrogen (USNG)	10.053	0.004 ($n = 523$)	0.009	0.018 (0.18)
Methane (USVG)	33.431	0.005 ($n = 210$)	0.027	0.054 (0.16)
Ethane (USVG)	59.870	0.010 ($n = 108$)	0.079	0.158 (0.26)
Propane (USVG)	86.365	0.022 ($n = 77$)	0.115	0.230 (0.27)

The additional characteristics of the reference materials—relative density and the Wobbe index—can be further calculated using the equations of state given in the GSSSD standards[9] [20–22] (Table 8).

Conclusion

In this article, we considered the possibility of developing a certified RM for inferior calorific value based on pure gases—hydrogen, methane, ethane, and propane. On the basis of our studies, we developed and certified a reference material of the approved type of the inferior calorific value of gases (collected at NOES VNIIM) GSO 11,662–2020/GSO 11,665–2020. The RM set is designed to establish and control the metrological characteristics of gas calorimeters and Wobbe index analyzers. The following certified inferior calorific values were established for the studied samples of pure gases: hydrogen (10.053 ± 0.018) MJ/m^3, methane (33.431 ± 0.054) MJ/m^3, ethane (59.870 ± 0.158) MJ/m^3, and propane (86.365 ± 0.230) MJ/m^3. The certified values were obtained using a direct calorimetric method, traceable to the State Primary Standard GET 16, and meet the requirements for metrological characteristics given in the description of the RM type and in Table 4. In the future, the applied method will expand the metrological support of this measurement area by expanding the range of RMs of gas mixtures—imitators of combustible gases. The analysis also showed the need for RMs of the Wobbe index, the development of which requires

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[9] GSSSD—Gosudarstvennaya sluzhba standartnykh spravochnykh dannykh o fizicheskikh konstantakh i svoystvakh veshchestv i materialov [State Service for Standard Reference Data on the Physical Constants and Properties of Substances and Materials].

further research, in particular, the choice of a method for determining the value of the relative density of gases.

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Author Contributions K. A. Mishina: literature review; data analysis and discussion; initial draft preparation.

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I. V. Kazartsev: data collection and analysis; text revision and editing.

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