ANALYSIS OF CALORIMETRIC METHOD OF MEASUREMENT OF NATURAL GAS CALORIFIC VALUE

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Abstract. The article considers the current methods of measuring the calorific value of natural gas which are valid in the up-to-date gasometry. The procedure for measuring the gross and net volume-basis specific calorific value of natural gas by the calorimetric method is analyzed. It is shown that to increase the accuracy and validity of measurement results, the experiment to determine the values of gross and net volume-basis specific calorific should be performed for at least 5 samples of the investigated gas. A methodology for estimating the accuracy of measuring the gross and net volume-basis specific calorific values of natural gas by the calorimetric method by finding estimates of the uncertainty of the obtained measurement results taking into account both random and systematic influencing factors are developed. The uncertainty budgets for measuring the gross and net volume-basis-specific calorific values of natural gas have been developed for the practical implementation of the methodology. The results of experimental studies of samples of one of the natural gas fields are given and the objective values of the gross and net volume-basis specific calorific with estimates of extended uncertainty are obtained.

Key words: Natural Gas, Calorific Value of Natural Gas, Calorific Method of Measurement, Uncertainty

1. Introduction

The largest sphere of natural gas (NG) applying today is industrial and communal services, in which gas is used as fuel. The main index of NG quality, which determines its energy value, is the specific volumetric heat of combustion or the calorific value of gas [1-3]. It is set as the amount of heat released during the complete combustion in the air of a certain volume of gas at constant pressure, p_{comb}, kPa and constant temperature, t_{comb}, $^{\circ}$C relative to the volume of dry gas determined under standard conditions, namely the pressure $p_{ref} = 101.325$ kPa and temperature $t_{ref} = 20$ $^{\circ}$C [4]. Complete combustion of gas, as well as any other fuel, is observed when there are no burning gas components or components of incomplete oxidation in gaseous combustion products. In gas analysis, there are net and gross specific volumetric heat of combustion of gas [5]. The volume-basis net specific calorific value $(H_V)_N$, MJ/m^3 is determined in the presence of water vapor in the combustion gas products at the temperature t_{comb}, $^{\circ}$C, and the volume-basis gross specific calorific value $(H_V)_G$, MJ/m^3 after complete condensation of water vapor contained in the combustion gas products at the temperature t_{comb}, $^{\circ}$C. The issue of natural gas quality has always attracted a lot of attention from specialists, as evidenced by a large number of publications [6-10]. At the same time, various aspects are analyzed, both in terms of natural gas energy value and environmental protection. The calorific value of gas as an index of its quality is especially important for the domestic sphere of NG consumption. In particular, in developed foreign countries, mutual settlements between consumers and gas suppliers are based on energy E, MJ of the consumed gas. According to [11], it is found as the product of the consumed volume of gas V, m^3 at its volume-basis gross specific calorific value $(H_V)_G$, MJ/m^3, i.e,

$E = V \cdot (H_V)_G$, MJ, and is used to determine the value of gas consumed. Therefore, the accuracy of measuring the NG calorific value directly affects the accuracy of estimating its energy value and, accordingly, the cost of gas.

2. Methods of Measuring the Natural Gas Calorific Value

Today, the values of gross $(H_V)_G$, MJ/m^3 and net $(H_V)_N$, MJ/m^3 volume-basis specific calorific value of gas according to [11] are measured by two main methods:

• by the method of *indirect measurement* by calculation based on the component composition and volume fractions of combustible components of the gas mixture;

• by *direct measurement* method or *calorimetric method* using a water calorimeter.

The method of *indirect measurement* is based on the preliminary determination of the component composition of the gas by the chromatographic method following the requirements of [12] and subsequent calculation of the gross and net volume-basis specific calorific values of gas according to the methodology described in [13]:

$$(H_V)_G = \sum_{i=1}^{k}(H_V)_{G,i} \cdot C_i \; ; \; (H_V)_N = \sum_{i=1}^{k}(H_V)_{N,i} \cdot C_i \, , (1)$$

where $(H_V)_{G,i}$ and $(H_V)_{N,i}$ are respectively gross and net (inferior volume-basis specific calorific value of the *i*-th component of the gas, determined by theoretical calculations and given in [13], MJ/m^3; C_i is the concentration of the *i*-th gas component in the gas mixture; *k* is the number of combustible components of the gas mixture.

The calculation method for determining the gas calorific value is easier to implement than the calorimetric one because it uses the results of chromatographic studies of the component composition of the gas, which are mandatory for gas production

companies. However, it should be noted that the obtained measurement results are inflated compared to the results of the calorimetric method and do not reflect the actual calorific value of the test gas. Because as it does not take into account gas humidity and the presence of non-combustible components, in particular carbon dioxide, nitrogen, helium, etc. Such results may be an objective assessment of the gas calorific value only for dried and purified gas.

The *calorimetric method* of measuring the gas calorific value is implemented using a gas water calorimeter of continuous action [14-16]. In this case, gas mixtures are studied, which in the process of measurement do not change their component composition and physicochemical properties, in particular, humidity and the presence of non-combustible components. The advantage of the calorimetric method, despite the complexity of the measurement process, is the objectivity of the results, as it takes into account gas humidity and the presence of non-combustible components in the extracted gas. So, it can be used for continuous monitoring of the energy value of extracted gas in real-time.

Thus, according to the analysis, the calorimetric method of measuring the specific volumetric heat of GHG combustion gives more objective measurement results than the theoretical one and is more promising in modern gasometry. Therefore, the research subject of this article is the analysis of the accuracy of measuring the gas calorific value by the calorimetric method.

The analysis of the accuracy of measuring the gas calorific value by the calorimetric method has several problems due primarily to the imperfection of existing regulations governing the requirements for accuracy of measurements and presentation of measurement results. In particular, according to [16], the arithmetic mean of the results of three independent experiments is taken as the measurement result of the gas calorific value, whose permissible deviation from the average value should not exceed $\pm 0,25$ MJ/m^3, if an obtained average value is not more than 25 MJ/m^3, and not exceed $\pm 1\%$ if the average value is more than 25 MJ/m^3. Therefore, in this case, it is talking only about the scattering of the results of individual experiments around the average value due to *random* influencing factors. It does not take into account the impact on the measurement result of *systematic* influencing factors, which are caused by the Type B uncertainty of the measurement results of the quantities by which the values of the gas calorific value gas are calculated. And their influence can significantly exceed the influence on the measurement result of random factors that is the obtained average value of the gas calorific value can differ significantly from its true value. It also makes it impossible to compare the results of NG studies carried out in different chemical analytical laboratories under the requirements of [15].

3. The Purpose of the Article and the Main Objectives of the Study

The *purpose* of the paper is to develop a method for estimating the accuracy of measuring the calorific value of natural gas by the calorimetric method and to ensure compliance with the measurement unity. To achieve the stated objective, the following *tasks* have been identified:

• analyzing the calorimetric method of measuring the calorific value of natural gas;

• developing the methodology for assessing the uncertainty of the measurements of the calorific value of natural gas by calorimetric method taking into account both random and systematic impact factors;

• carrying out studies of natural gas samples in the determination of calorific values and evaluation of the accuracy of the obtained results.

4. Analysis of the Calorimetric Method of Measuring the Calorific Value of Natural Gas

4.1. Elements of the calorimetric measuring process

To analyze the accuracy of measuring the calorific value of NG by the calorimetric method, first of all, it is necessary to obtain the transformation function of the calorimeter. To do this, we analyze the method of measuring the calorific value of NG using a calorimeter by [16]. The essence of the calorimetric method of determining the calorific value of NG is to measure with a gas water calorimeter the continuous action of the amount of heat released during the combustion of a certain volume of gas. At the same time, the mass of water vapor condensate formed during the complete combustion of the gas is measuring, based on which the gross, and net volume-basis specific calorific values of the test gas, are calculating.

The main *functional elements* of the calorimetric measuring system are:

• Gas water calorimeter;

• Gas meter;

• Aneroid or mercury barometer;

• Thermometer with a scale interval of 0.1 $^{\circ}$C;

• Timer with a scale interval of 0.1 s or 0.2 s;

• Rocker table scales with a measurement range of 5 or 10 kg with sets of calibrated weights.

To increase the accuracy and reliability of measurement results according to [17-19], the experiment to determine the values of the gross and net volume-basis specific calorific values of NG is carried out for *n* samples of the test gas, and, according to the authors, the number of samples n should be at least 5.

4.2. Measurement of the gross volume-basis specific calorific value of the test gas

The gross volume-basis specific calorific value $(H_V)_{G,i}$, MJ/m^3 of i-th test gas sample ($i = 1,...,n$) under standard conditions, that is pressure $p_{ref} = 101.325$ kPa and temperature $t_{ref} = 20$ ^{o}C [4], is determined by the formula:

$$(H_V)_{G,i} = \frac{c_w m_{w,i} \Delta\Theta_{w,i} f_{k,gr}}{V_{gw,i} f_{gm} K}, \qquad (2)$$

where $c_w = 4.187 \cdot 10^{-6}$ MJ/(g·°C) is the specific heat capacity of water; $m_{w,i}$ is the mass of water flow taken in the calorimeter for the i-th test gas sample, g; $\Delta\Theta_{w,i}$ is the average difference in water temperature at the outlet and inlet of the calorimeter for the i-th test gas sample, °C; $f_{k,gr}$ is the correction factor calorimeter readings for gross volume-basis specific calorific value, which meaning is determined in the process of the calorimeter calibration; $V_{gw,i}$ is the volume of the i-th test gas sample that burns in the calorimeter during water extraction, measured by the gas meter, m^3; f_{gm} is the correction factor for gas meter readings; K is the coefficient for bringing the volume of the test gas burned to standard conditions.

The value of the coefficient K is calculated by the formula:

$$K = \frac{293 \cdot (p_{air} + p_g - p_{wv})}{(273 + \Theta_g) \cdot 101.325}, \qquad (3)$$

where p_{air} is the barometric air pressure during the experiment, kPa; p_g is the gas pressure in the gas meter, kPa; p_{wv} is the partial pressure of water vapor in the saturated state at the gas temperature Θ_g in the gas meter, kPa; Θ_g is the gas temperature in the gas meter, °C. The measurement result of the gross volume-basis specific calorific value of the test gas $(H_V)_G$, MJ/m^3 is defined as the arithmetic mean of the results $(H_V)_{G,i}$ ($i = 1,...,n$) of the series of n experiments:

$$(H_V)_G = \frac{1}{n} \sum_{i=1}^{n} (H_V)_{G,i}. \qquad (4)$$

4.3. Measurement of the net volume-basis specific calorific value of the test gas

To determine the net volume-basis specific calorific value $(H_V)_{N,i}$, MJ/m^3 of i-th test gas sample ($i = 1,...,n$) the mass of condensate of water vapor formed during gas combustion is measured, and its value under standard conditions is calculated by the formula:

$$(H_V)_{N,i} = \left(\frac{(H_V)_{G,i}}{f_{k,gr}} - \frac{c_{con} m_{con,i} \Delta\Theta_{w,i}}{V_{gwv,i} f_{gm} K} \right) \cdot f_{k,nt}, \quad (5)$$

where $(H_V)_{G,i}$ is the value of the gross volume-basis specific calorific value of the i-th test gas sample ($i = 1,...,n$), calculated by the formula (2), MJ/m^3; $c_{con} = 2.454 \cdot 10^{-3}$ MJ/(g·°C) is the specific heat of water vapor condensation at pressure $p_{ref} = 101.325$ kPa and temperature $t_{ref} = 20$ ^{o}C; $m_{con,i}$ is the mass of collected condensate of water vapor for the i-th test gas sample, g; $V_{gwv,i}$ is the volume of the i-th test gas sample that burns in the calorimeter during the collection of water vapor condensate, measured by the gas meter, m^3; $f_{k,nt}$ is the correction factor calorimeter readings for net volume-basis specific calorific value, which meaning is determined in the process of the calorimeter calibration.

The measurement result of the net volume-basis specific calorific value of the test gas $(H_V)_N$, MJ/m^3 is defined as the average value of the results $(H_V)_{N,i}$ ($i = 1,...,n$) of the series of n experiments:

$$(H_V)_N = \frac{1}{n} \sum_{i=1}^{n} (H_V)_{N,i}. \qquad (6)$$

5. Estimating the Uncertainty of NG Calorific Value Measurement Results

5.1. Establishment of uncertainty components of the NG calorific values

As can be seen from the above analysis of the calorimetric method of measuring the gross $(H_V)_G$, MJ/m^3, and net $(H_V)_N$, MJ/m^3 volume-basis specific calorific values of the test gas, the values of which are determined by formulas (4) and (6) taking into account the results (2) and (5), are *indirect measurements* with *multiple observations*. Therefore, the estimation of the uncertainty of the measurement results of both gross and net calorific values of NG should be carried out according to the method of processing the results of indirect measurements [18-19] calculating namely:

• Type B combined standard uncertainties $u_{cB}\{(H_V)_{G,i}\}$ and $u_{cB}\{(H_V)_{N,i}\}$ of the results of measuring the gross $(H_V)_G$, and net $(H_V)_N$ calorific values of i-th test gas sample, taking into account equations (3) and (5);

• Type A standard uncertainties $u_A\{(H_V)_G\}$ and $u_A\{(H_V)_N\}$ of the results of measuring the $(H_V)_G$, and $(H_V)_N$ calorific values of the test gas, taking into account equations (4) and (6);

• The combined standard uncertainties $u_c\left\{\left(H_V\right)_G\right\}$, and $u_c\left\{\left(H_V\right)_N\right\}$ of the results of measuring the $\left(H_V\right)_G$ $\left(H_V\right)_N$ calorific values of the test gas;

• The extended uncertainties $U_p\left\{\left(H_V\right)_G\right\}$ and $U_p\left\{\left(H_V\right)_N\right\}$ of the results of measuring the gross $\left(H_V\right)_G$, and $\left(H_V\right)_N$ calorific values of the test gas for a given confidence level p.

5.2. Determining of Type B combined standard uncertainty of the measurement result of the gross volume-basis specific calorific value of *i*-th test gas sample

Type B combined standard uncertainty $u_{cB}\left\{\left(H_V\right)_{G,i}\right\}$, MJ/m³ of the result of measuring the gross volume-basis specific calorific value $\left(H_V\right)_{G,i}$, MJ/m³ of *i*-th test gas sample $(i=1,...,n)$ has 7 components caused by 7 impact factors that are Type B standard uncertainties $u_B\left(x_j\right)$ of measurement results of measuring the quantities $x_j, j=1,...,7$ that are $c_w, m_w, \Delta\Theta_w, f_{k,gr}, V_g, f_{gm}, K$, included in the formula (3) for its calculating, namely:

• Type B standard uncertainty $u_B\left(c_w\right)$, MJ/(g·°C) of the value of specific heat capacity of water c_w;

• Type B standard uncertainty $u_B\left(m_{w,i}\right)$, g of the result of measuring the mass of water $m_{w,i}$ taken in the calorimeter for the *i*-th test gas sample;

• Type B combine standard uncertainty $u_{cB}\left(\Delta\Theta_{w,i}\right)$, °C of the result of measuring the average difference in water temperature $\Delta\Theta_{w,i}$ at the outlet and inlet of the calorimeter for the *i*-th test gas sample;

• Type B standard uncertainty $u_B\left(f_{k,gr}\right)$ of the calorimeter readings correction factor value $f_{k,gr}$ for the gross volume-basis specific calorific value of test gas;

• Type B standard uncertainty $u_B,\left(V_{g,i}\right)$, m³ of the result of measuring the volume $V_{gw,i}$ of the *i*-th test gas sample that burns in the calorimeter during water extraction, measured by the gas meter;

• Type B standard uncertainty $u_B\left(f_{gm}\right)$ of the correction factor value f_{gm} for gas meter readings;

• Type B combines standard uncertainty $u_{cB}\left(K\right)$ of the result of measuring the coefficient value K for bringing the volume of the test gas burned to standard conditions.

In the absence of correlation between the above quantities, the Type B combined standard uncertainty $u_{cB}\left\{\left(H_V\right)_{G,i}\right\}$, MJ/m³ of the result of measuring the gross volume-basis specific calorific value $\left(H_V\right)_{G,i}$, MJ/m³ of *i*-th test gas sample $(i=1,...,n)$ according to [18-19] is determined by the formula:

$$u_{cB}\left\{\left(H_V\right)_{G,i}\right\} = \sqrt{\begin{array}{l} C_{c_w}^2 \cdot u_B^2\left(c_w\right) + C_{m_{w,i}}^2 \cdot u_B^2\left(m_{w,i}\right) + C_{\Delta\Theta_{w,i}}^2 \cdot u_{cB}^2\left(\Delta\Theta_{w,i}\right) + \\ + C_{f_{k,gr}}^2 \cdot u_B^2\left(f_{k,gr}\right) + C_{V_{g,i}}^2 \cdot u_B^2\left(V_{g,i}\right) + C_{f_{gm}}^2 \cdot u_B^2\left(f_{gm}\right) + C_K^2 \cdot u_{cB}^2\left(K\right) \end{array}} , \quad (7)$$

where C_{c_w}, MJ/(g·°C) is the sensitivity coefficient of the uncertainty $u_B\left(c_w\right)$; $C_{m_{w,i}}$, MJ/(g·m³) is the sensitivity coefficient of uncertainty $u_B\left(m_{w,i}\right)$; $C_{\Delta\Theta_{w,i}}$, MJ/(°C·m³) is the sensitivity coefficient of the uncertainty $u_{cB}\left(\Delta\Theta_{w,i}\right)$; $C_{f_{k,gr}}$, MJ/m⁶ is the sensitivity coefficient of the uncertainty $u_B\left(f_{k,gr}\right)$; $C_{V_{g,i}}$, MJ/m³ is the sensitivity coefficient of the uncertainty $u_B,\left(V_{g,i}\right)$; $C_{f_{gm}}$, MJ/m³ is the sensitivity coefficient of the uncertainty $u_B\left(f_{gm}\right)$; C_K, MJ/m³ is the sensitivity coefficient of the uncertainty $u_{cB}\left(K\right)$.

The budget of Type B combined standard uncertainty $u_{cB}\left\{\left(H_V\right)_{G,i}\right\}$, MJ/m³ of the result of measuring the gross volume-basis specific calorific value $\left(H_V\right)_{G,i}$, MJ/m³ of the *i*-th test gas sample $(i=1,...,n)$ is given in Table. 1.

Expressions for finding the sensitivity coefficients $C_j, j = 1,...,7$, which are given in Table 1, are obtained from equation (2) as partial derivatives of the measurement result of the gross volume-basis specific calorific value $\left(H_V\right)_{G,i}$, MJ/m³ for each argument $x_j, j=1,...,7$ that is for $c_w, m_w, \Delta\Theta_w, f_{k,gr}, V_g, f_{gm}, K$:

$$C_j = \frac{\partial\left(H_V\right)_{G,i}}{\partial x_j}, j=1,2,...,7. \quad (8)$$

5.3. Determining of Type B combined standard uncertainty of the measurement result of net volume-basis-specific calorific value of *i*-th test gas sample

Type B combined standard uncertainty $u_{cB}\left\{\left(H_V\right)_{N,i}\right\}$, MJ/m³ of the result of measuring the net volume-basis specific calorific value $\left(H_V\right)_{N,i}$, MJ/m³ of *i*-th test gas sample $(i=1,...,n)$ has 9 components caused by 7 influential factors that are Type B standard uncertainties $u_B\left(x_j\right)$ of measurement results of measuring the quantities $x_j, j=1,...,9$ that are $\left(H_V\right)_{G,i}, f_{k,gr}, c_{con}, m_{con,i}, \Delta\Theta_{w,i}, V_{gwv,i}, f_{gm}, K, f_{k,nt}$, included in the formula (5) for its calculating, namely:

Table 1

The budget of Type B combined standard uncertainty of measurement the gross volume-basis specific calorific value of *i*-th test gas sample

Input quantity x_j	Standard uncertainty $u(x_j)$	Type of evaluation, probability distribution	Sensitivity coefficient C_j	Contribution to the combined standard uncertainty $|C_j| \cdot u(x_j)$
c_w, MJ/(g·°C)	$u_B(c_w) = \dfrac{q_{c_w}}{2\sqrt{3}}$, MJ/(g·°C)	Type **B**, rectangular	$C_{c_w} = \dfrac{m_{w,i}\Delta\Theta_{w,i}f_{k,gr}}{V_{gw,i}f_{gm}K}$, (g·°C)/m³	$C_{c_w} \cdot u_B(c_w)$, MJ/m³
$m_{w,i}$, g	$u_B(m_{w,i}) = \dfrac{\Delta m_{w,mpe}}{\sqrt{3}}$, g	Type **B**, rectangular	$C_{m_{w,i}} = \dfrac{c_w\Delta\Theta_{w,i}f_{k,gr}}{V_{gw,i}f_{gm}K}$, MJ/(g·m³)	$C_{m_{w,i}} \cdot u_B(m_{w,i})$, MJ/m³
$\Delta\Theta_{w,i}$, °C	$u_{cB}(\Delta\Theta_{w,i})$, °C	Combined, by the methodology of indirect measurements, normal	$C_{\Delta\Theta_{w,i}} = \dfrac{c_w m_{w,i}f_{k,gr}}{V_{gw,i}f_{gm}K}$, MJ/(°C·m³)	$C_{\Delta\Theta_{w,i}} \cdot u_{cB}(\Delta\Theta_{w,i})$ MJ/m³
$f_{k,gr}$	$u_B(f_{k,gr}) = \dfrac{q_{f_{k,gr}}}{2\sqrt{3}}$	Type **B**, rectangular	$C_{f_{k,gr}} = \dfrac{c_w m_{w,i}\Delta\Theta_{w,i}}{V_{gw,i}f_{gm}K}$, MJ/m³	$C_{f_{k,gr}} \cdot u_B(f_{k,gr})$, MJ/m³
$V_{g,i}$, m³	$u_B(V_{g,i}) = \dfrac{\Delta V_{gm,mpe}}{\sqrt{3}}$, m³	Type **B**, rectangular	$C_{V_{gw,i}} = -\dfrac{c_w m_{w,i}\Delta\Theta_{w,i}f_{k,gr}}{V_{gw,i}^2 f_{gm}K}$, MJ/m⁶	$|C_{V_{g,i}}| \cdot u_B(V_{g,i})$, MJ/m³
f_{gm}	$u_B(f_{gm}) = \dfrac{q_{f_{gm}}}{2\sqrt{3}}$	Type **B**, rectangular	$C_{f_{gm}} = -\dfrac{c_w m_{w,i}\Delta\Theta_{w,i}f_{k,gr}}{V_{gw,i}f_{gm}^2 K}$, MJ/m³	$|C_{f_{gm}}| \cdot u_B(f_{gm})$ MJ/m³
K	$u_{cB}(K)$	Combined, by the methodology of indirect measurements, normal	$C_K = -\dfrac{c_w m_{w,i}\Delta\Theta_{w,i}f_{k,gr}}{V_{gw,i}f_{gm}K^2}$, MJ/m³	$|C_K| \cdot u_{cB}(K)$, MJ/m³
Output quantity	Type of evaluation, probability distribution	Type B combined standard uncertainty		
$(H_V)_{G,i}$, MJ/m³	Combined, by the methodology of indirect measurements, normal	$u_{cB}\{(H_V)_{G,i}\} = \sqrt{\begin{array}{l} C_{c_w}^2 u_B^2(c_w) + C_{m_{w,i}}^2 u_B^2(m_{w,i}) + C_{\Delta\Theta_{w,i}}^2 u_B^2(\Delta\Theta_{w,i}) + \\ + C_{f_{k,gr}}^2 u_B^2(f_{k,gr}) + C_{V_{g,i}}^2 u_B^2(V_{g,i}) + C_{f_{gm}}^2 u_B^2(f_{gm}) + C_K^2 u_B^2(K) \end{array}}$, MJ/m³		

q_{c_w} is the quantization interval or the unit of the least significant digit of the value of specific heat capacity of water c_w; $\Delta m_{w,mpe}$ is the maximum permissible error of scales for measuring the mass of water; $\Delta V_{gm,mpe}$ is the maximum permissible error of the gas meter; $q_{f_{k,gr}}$ is the quantization interval or the unit of the least significant digit of the coefficient $f_{k,gr}$ value; $q_{f_{gm}}$ is the quantization interval or the unit of the least significant digit of the coefficient f_{gm} value

Type B combined standard uncertainty $u_{cB}\{(H_V)_{G,i}\}$, MJ/m³ of measurement of the gross volume-basis specific calorific value $(H_V)_{G,i}$, MJ/m³ of *i*-th test gas sample;

• Type B standard uncertainty $u_B(f_{k,gr})$ of the calorimeter readings correction factor value $f_{k,gr}$ for the gross volume-basis specific calorific value of test gas;

• Type B standard uncertainty $u_B(c_{con})$ of the value of specific heat of water vapor condensation c_{con};

• Type B standard uncertainty $u_B(m_{con,i})$, g of the result of measuring the mass $m_{con,i}$ of collected condensate of water vapor for the *i*-th test gas sample;

• Type B combined standard uncertainty $u_B(\Delta\Theta_{w,i})$, °C of the result of measuring the average difference in water temperature $\Delta\Theta_{w,i}$ at the outlet and inlet of the calorimeter for the *i*-th test gas sample;

• Type B standard uncertainty $u_B,(V_{gwv,i})$, m³ of the result of measuring the volume $V_{gwv,i}$ of the *i*-th test gas

sample that burns in the calorimeter during the collection of water vapor condensate, measured by the gas meter;

• Type B standard uncertainty $u_B\left(f_{gm}\right)$ of the correction factor value f_{gm} for gas meter readings;

• Type B combined standard uncertainty $u_{cB}\left(K\right)$ of the result of measuring of the coefficient value K for bringing the volume of the test gas burned to standard conditions;

• Type B standard uncertainty $u_B\left(f_{k,nt}\right)$ of the calorimeter readings correction factor value $f_{k,nt}$ for the net volume-basis specific calorific value of test gas.

In the absence of correlation between the above quantities, the Type B combined standard uncertainty $u_{cB}\left\{\left(H_V\right)_{N,i}\right\}$, MJ/m^3 of the result of measuring the net (inferior)volume-basis specific calorific value $\left(H_V\right)_{N,i}$, MJ/m^3 of *i*-th test gas sample ($i = 1,...,n$) according to [13,14] is determined by the formula:

$$u_{cB}\left\{\left(H_V\right)_{N,i}\right\} = \sqrt{\begin{array}{l} C^2_{\left(H_V\right)_{G,i}} \cdot u^2_{cB}\left\{\left(H_V\right)_{G,i}\right\} + C^2_{f_{k,gr}} \cdot u^2_B\left(f_{k,gr}\right) + \\ + C^2_{c_{con}} \cdot u^2_B\left(c_{con}\right) + C^2_{m_{con,i}} \cdot u^2_B\left(m_{con,i}\right) + C^2_{\Delta\Theta_{w,i}} \cdot u^2_{cB}\left(\Delta\Theta_{w,i}\right) + C^2_{V_{gwv,i}} \cdot u^2_B\left(V_{gwv,i}\right) + \\ + C^2_{f_{gm}} \cdot u^2_B\left(f_{gm}\right) + C^2_K \cdot u^2_{cB}\left(K\right) + C^2_{f_{k,nt}} \cdot u^2_B\left(f_{k,nt}\right), \end{array}}$$

(9)

where $C_{\left(H_V\right)_{G,i}}$ is the sensitivity coefficient of the uncertainty $u_{cB}\left\{\left(H_V\right)_{G,i}\right\}$; $C_{f_{k,gr}}$, MJ/m^3 is the sensitivity coefficient of $u_B\left(f_{k,gr}\right)$; $C_{c_{con}}$, g/m^3 is the sensiti-

vity coefficient of $u_B\left(c_{con}\right)$; $C_{m_{con,i}}$, MJ/(g· °C·m^3) is the sensitivity coefficient of $u_B\left(m_{con,i}\right)$; $C_{\Delta\Theta_{w,i}}$, MJ/(°C • m^3) is the sensitivity coefficient of $u_{cB}\left(\Delta\Theta_{w,i}\right)$; $C_{V_{gwv,i}}$, MJ/(°C·m^6 is the sensitivity coefficient of $u_B\left(V_{gwv,i}\right)$; $C_{f_{gm}}$, MJ/(°C·m^3) is the sensitivity coefficient of $u_B\left(f_{gm}\right)$; C_K, MJ/(°C·m^3) is the sensitivity coefficient of $u_{cB}\left(K\right)$; $C_{f_{k,nt}}$, MJ/m^3 is the sensitivity coefficient of $u_B\left(f_{k,nt}\right)$.

The budget of Type B combined standard uncertainty $u_{cB}\left\{\left(H_V\right)_{N,i}\right\}$, MJ/m^3 of the result of measuring the net (inferior) volume-basis-specific calorific value $\left(H_V\right)_{N,i}$, MJ/m^3 of *i*-th test gas sample ($i = 1,...,n$) is given in Table 2.

Expressions for finding the sensitivity coefficients $C_j, j = 1,...,9$, which are given in Table 2, are obtained from equation (5) as partial derivatives of the measurement result of the net volume-basis specific calorific value $\left(H_V\right)_{N,i}$, MJ/m^3 for each argument $x_j, j = 1,...,9$, that is for $\left(H_V\right)_{G,i}, f_{k,gr}, c_{con}, m_{con,i}, \Delta\Theta_{w,i}, V_{gwv,i}, f_{gm}, K, f_{k,nt}$:

$$C_j = \frac{\partial\left(H_V\right)_{N,i}}{\partial x_j}, j = 1,...,9.$$

(10)

Table 2

The budget of Type B combined standard uncertainty of measurement
the net volume-basis specific calorific value of *i*-th test gas sample

Input quantity x_j	Standard uncertainty $u\left(x_j\right)$	Type of evaluation, probability distribution	Sensitivity coefficient C_j	Contribution to the combined standard uncertainty $\left\|C_j\right\|\cdot u\left(x_j\right)$
1	2	3	4	5
$\left(H_V\right)_{G,i}$, MJ/m^3	$u_{cB}\left\{\left(H_V\right)_{G,i}\right\}$, MJ/m^3	Combined, by the methodology of indirect measurements, normal	$C_{\left(H_V\right)_{G,i}} = \dfrac{f_{k,nt}}{f_{k,gr}}$	$C_{\left(H_V\right)_{G,i}} \cdot u_{cB}\left\{\left(H_V\right)_{G,i}\right\}$ MJ/m^3
$f_{k,gr}$	$u_B\left(f_{k,gr}\right) = \dfrac{q_{f_{k,gr}}}{2\sqrt{3}}$	Type **B**, rectangular	$C_{f_{k,gr}} = -\dfrac{\left(H_V\right)_{G,i} \cdot f_{k,nt}}{f^2_{k,gr}}$, MJ/m^3	$\left\|C_{f_{k,gr}}\right\| \cdot u_B\left(f_{k,gr}\right)$, MJ/m^3
c_{con}, MJ /(g·°C)	$u_B\left(c_{con}\right) = \dfrac{q_{c_{con}}}{2\sqrt{3}}$, MJ /(g·°C)	Type **B**, rectangular	$C_{c_{con}} = -\dfrac{m_{con,i}\Delta\Theta_{w,i}f_{k,nt}}{V_{gwv,i}f_{gm}K}$, (g·°C)/m^3	$\left\|C_{c_{con}}\right\| \cdot u_B\left(c_{con}\right)$, MJ/m^3
$m_{con,i}$, g	$u_B\left(m_{con,i}\right) = \dfrac{\Delta m_{wv,mpe}}{\sqrt{3}}$ г	Type **B**, rectangular	$C_{m_{con,i}} = -\dfrac{c_{con}\Delta\Theta_{w,i}f_{k,nt}}{V_{gwv,i}f_{gm}K}$, MJ/(g·m^3)	$\left\|C_{m_{con,i}}\right\| \cdot u_B\left(m_{con,i}\right)$, MJ/m^3

Continuation of Table 2

1	2	3	4	5
$\Delta\Theta_{w,i}$, °C	$u_{cB}(\Delta\Theta_{w,i})$, °C;	Combined, by the methodology of indirect measurements, normal	$C_{\Delta\Theta_{w,i}} = -\dfrac{c_{con}m_{con,i}f_{k,nt}}{V_{gwv,i}f_{gm}K}$, MJ /(°C·m³)	$\left\lvert C_{\Delta\Theta_{w,i}}\right\rvert \cdot u_{cB}(\Delta\Theta_{w,i})$ MJ/m³
$V_{gwv,i}$, M³	$u_B(V_{gwv,i}) = \dfrac{\Delta V_{gm,mpe}}{\sqrt{3}}$, m³	Type **B**, rectangular	$C_{V_{gwv,i}} = \dfrac{c_{con}m_{con,i}\Delta\Theta_{w,i}f_{k,nt}}{V_{gwv,i}^2 f_{gm}K}$, MJ/m⁶	$C_{V_{gwv,i}} \cdot u_B(V_{gwv,i})$, MJ/m³
f_{gm}	$u_B(f_{gm}) = \dfrac{q_{f_{gm}}}{2\sqrt{3}}$	Type **B**, rectangular	$C_{f_{gm}} = \dfrac{c_{con}m_{con,i}\Delta\Theta_{w,i}f_{k,nt}}{V_{gwv,i}f_{gm}^2 K}$, MJ/m³	$C_{f_{gm}} \cdot u_B(f_{gm})$ MJ/m³
K	$u_{cB}(K)$	Combined, by the methodology of indirect measurements, normal	$C_K = \dfrac{c_{con}m_{con,i}\Delta\Theta_{w,i}f_{k,nt}}{V_{gwv,i}f_{gm}K^2}$, MJ/m³	$C_K \cdot u_{cB}(K)$, MJ/m³
$f_{k,nt}$	$u_B(f_{k,nt}) = \dfrac{q_{f_{k,nt}}}{2\sqrt{3}}$	Type **B**, rectangular	$C_{f_{k,nt}} = \dfrac{(H_V)_{G,i}}{f_{k,gr}} - \dfrac{c_{con}m_{con,i}\Delta\Theta_{w,i}}{V_{gwv,i}f_{gm}K}$ MJ/m³	$C_{f_{k,nt}} \cdot u_B(f_{k,nt})$, MJ/m³
Output quantity	Type of evaluation, probability distribution	Type B combined standard uncertainty		
$(H_V)_{N,i}$, MJ/m³	Combined, by the methodology of indirect measurements, normal	$u_{cB}\{(H_V)_{N,i}\} = \sqrt{C_{(H_V)_{G,i}}^2 \cdot u_{cB}^2\{(H_V)_{G,i}\} + C_{f_{k,gr}}^2 \cdot u_B^2(f_{k,gr}) + C_{c_{con}}^2 \cdot u_B^2(c_{con}) + C_{m_{con,i}}^2 \cdot u_B^2(m_{con}}$ $\overline{+\, C_{\Delta\Theta_{w,i}}^2 \cdot u_{cB}^2(\Delta\Theta_{w,i}) + C_{V_{gwv,i}}^2 \cdot u_B^2(V_{gwv,i}) + C_{f_{gm}}^2 \cdot u_B^2(f_{gm}) + C_K^2 \cdot u_B^2(K) + C_{f_{k,nt}}^2 \cdot u_B^2(f_{k,nt})}$, MJ/m³		

$q_{f_{k,gr}}$ is the quantization interval or the unit of the least significant digit of the coefficient $f_{k,gr}$ value; $q_{c_{con}}$ is the quantization interval or the unit of the least significant digit of water vapor condensation c_{con}; $\Delta m_{wv,mpe}$ is the maximum permissible error of scales for measuring the mass of water vapor; $\Delta V_{gm,mpe}$ is the maximum permissible error of the gas meter; $q_{f_{gm}}$ is the quantization interval or the unit of the least significant digit of the coefficient f_{gm} value; $q_{f_{k,nt}}$ is the quantization interval or the unit of the least significant digit of the coefficient $f_{k,nt}$ value.

5.4. Determining estimates of the uncertainty of the measurement results of the gross and net volume-basis specific calorific values of the test gas

5.4.1. Determining type A standard uncertainties of the results of measuring the gross, and net calorific values of the test gas. As mentioned above, to increase the accuracy and validity of the measurement results of the gross $(H_V)_G$, MJ/m³, and net $(H_V)_N$, MJ/m³ volume-basis specific calorific values of NG, the experiment is performed for n samples of the test gas. Their meanings are found as the average values by formulas (4) and (6) of the $(H_V)_{G,i}$, MJ/m³ and $(H_V)_{N,i}$, MJ/m³ measurement results for i-th test gas sample ($i = 1,...,n$). Respectively, the Type A standard uncertainties $u_A\{(H_V)_G\}$, MJ/m³ and $u_A\{(H_V)_N\}$, MJ/m³ of the results of measuring the gross $(H_V)_G$, and net $(H_V)_N$ calorific values of the test gas, taking into account equations (4) and (6) are found by such formulas:

$$u_A\{(H_V)_G\} = \frac{s_{(H_V)_G}}{\sqrt{n}}, \text{ and } u_A\{(H_V)_N\} = \frac{s_{(H_V)_N}}{\sqrt{n}}, \quad (11)$$

here $s_{(H_V)_G}$ and $s_{(H_V)_N}$ are estimates of standard deviations of individual values $(H_V)_{G,i}$ and $(H_V)_{N,i}$, accordingly, from the average values $(H_V)_G$ and $(H_V)_N$, that are found by formulas (4) and (6), which are equal to:

$$s_{(H_V)_G} = \sqrt{\frac{1}{n-1}\sum_{i=1}^{n}\left\{(H_V)_{G,i} - (H_V)_G\right\}^2},$$

$$\text{and } s_{(H_V)_N} = \sqrt{\frac{1}{n-1}\sum_{i=1}^{n}\left\{(H_V)_{N,i} - (H_V)_N\right\}^2}. \quad (12)$$

According to [11], the number of experiments equals $n = 3$. However, to obtain reliable measurement results $(H_V)_G$, and $(H_V)_N$, it is advisable to perform the study at least for 5 gas samples.

5.4.2. Determining the combined standard uncertainties of the results of measuring the gross and net calorific values of the test gas. Since the measurements of both of the gross $(H_V)_G$, MJ/m³, and net $(H_V)_N$, MJ/m³ volume-basis specific calorific values of the *i*-th test gas sample ($i = 1,...,n$) are carried out by the same measuring instruments, and under the same conditions, the measurements are performed with the same accuracy. Therefore, it can be stated that Type B combined standard uncertainties $u_{cB}\{(H_V)_G\}$, MJ/m³ and $u_{cB}\{(H_V)_N\}$, MJ/m³ of the measurement results of the gross $(H_V)_G$, MJ/m³, and net $(H_V)_N$, MJ/m³ volume-basis specific calorific values of the test gas are equal, respectively, to the Type B combined standard uncertainties $u_{cB}\{(H_V)_{G,i}\}$, MJ/m³ and $u_{cB}\{(H_V)_{N,i}\}$, MJ/m³ of the measurement results of the gross $(H_V)_{G,i}$, MJ/m³, and net $(H_V)_{N,i}$, MJ/m³ volume-basis specific calorific values the *i*-th test gas sample, that is:

$$u_{cB}\{(H_V)_G\} = u_{cB}\{(H_V)_{G,i}\},$$
$$\text{and } u_{cB}\{(H_V)_N\} = u_{cB}\{(H_V)_{N,i}\}. \quad (13)$$

Then, the estimates of the combined standard uncertainties $u_c\{(H_V)_G\}$, MJ/m³ and $u_c\{(H_V)_N\}$, MJ/m³ of the measurement results of the gross $(H_V)_G$, MJ/m³, and net $(H_V)_N$, MJ/m³ volume-basis specific calorific values of the test gas according to [18-19] are defined as the square root of the sum of squares of the found values of Type A standard uncertainties $u_A\{(H_V)_G\}$ and $u_A\{(H_V)_N\}$, and Type B combined standard uncertainties $u_{cB}\{(H_V)_{G,i}\}$ and $u_{cB}\{(H_V)_{N,i}\}$ by the formulas:

$$u_c\{(H_V)_G\} = \sqrt{u_A^2\{(H_V)_G\} + u_{cB}^2\{(H_V)_{G,i}\}},$$
$$\text{and } u_c\{(H_V)_N\} = \sqrt{u_A^2\{(H_V)_N\} + u_{cB}^2\{(H_V)_{N,i}\}}. \quad (14)$$

5.4.3. Determination of the extended uncertainties of the results of measuring the gross and net calorific values of the test gas. The extended uncertainties, $U_p\{(H_V)_G\}$, MJ/m³ and $U_p\{(H_V)_N\}$, MJ/m³ of the results of measuring the gross $(H_V)_G$ and net $(H_V)_N$ calorific values of the test gas for a given confidence level *p* are calculated by the formulas:

$$U_p\{(H_V)_G\} = k_p \cdot u_c\{(H_V)_G\},$$
$$\text{and } U_p\{(H_V)_N\} = k_p \cdot u_c\{(H_V)_N\}, \quad (15)$$

where k_p is a coverage factor, the value of which depends on the level of confidence *p* and the density of probability distribution of the measured values the gross $(H_V)_G$ and net $(H_V)_N$ volume-basis-specific calorific values of the test gas; $u_c\{(H_V)_G\}$ and $u_c\{(H_V)_N\}$ are the combined standard uncertainties of the measured values the gross $(H_V)_G$ and net $(H_V)_N$ volume-basis specific calorific values of the test gas which is calculated by the formula (14).

The value of the coverage factor k_p, in general, is defined as $k_p = t_p(v_{eff})$, where $t_p(v_{eff})$ is the Student's distribution or *t*-distribution quantile, determined by the corresponding effective degrees of freedom v_{eff} and the level of confidence *p* [18]. The effective degrees of freedom v_{eff} of the combined standard uncertainty $u_c\{(H_V)_G\}$, which contains Type A $u_A\{(H_V)_G\}$ and Type B $u_{cB}\{(H_V)_G\}$ components, provided that all components of Type B combined uncertainty $u_{cB}\{(H_V)_G\}$ is calculated by rectangular distributions, that is $v_{eff,B} = \infty$, can be calculated by the corresponding Welch-Satterthwaite formula:

$$v_{eff} = v_{eff,A} \cdot \left(1 + \frac{u_{cB}^2\{(H_V)_G\}}{u_A^2\{(H_V)_G\}}\right)^2, \quad (16)$$

where $v_{eff,A}$ are the effective degrees of freedom of the component uncertainty $u_A\{(H_V)_G\}$ found by Type A evaluation, which in this case is equal to $v_{eff,A} = n-1$, where *n* is the number of experiments.

6. Studies of Natural Gas Samples by the Calorimetric Method

The authors carried out the study of 5 samples of natural gas in the analytical laboratory of the Gas Production Division LvivGasVydobuvannya to determine its gross $(H_V)_G$, MJ/m³ and net $(H_V)_N$, MJ/m³ volume-basis-specific calorific values by the calorimetric method. The analysis of the accuracy of the obtained measurement results by estimating their uncertainty was also performed. The results of processing the studies are given in Tables 3-4.

After processing the experimental data, the following result of measuring the gross volume-basis specific calorific value of the studied natural gas was obtained:

$$(H_V)_G = (38.35 \pm 0.25) \text{ MJ/m}^3; \ U_p\{(H_V)_G\} =$$
$$= 0.25 \text{ MJ/m}^3; \ p = 0.95; \ k_p = 1.96.$$

Table 3

**The results of measuring the gross volume-basis specific calorific value
of the test gas by the calorimetric method**

№	Name, symbol, and dimension of the input quantity $x_j, j = 1,..,7$	The numeric value of the input quantity x_j	Maximum permissible error $\Delta x_{j,mpe}$	Standard uncertainty $u_B(x_j)$
1	Specific heat capacity of water c_w, MJ/(g·°C)	$4.187 \cdot 10^{-6}$	$\pm 0.43 \cdot 10^{-7}$	$0.234 \cdot 10^{-7}$
2	Mass of water flow m_w, g	3500	± 1.00	0.58
3	The average difference in water temperature at the outlet and inlet of the calorimeter $\Delta \Theta_w$, °C	10.35	± 0.12	0.07
4	Correction factor for calorimeter readings during the measurement $(H_V)_G$, $f_{k,gr}$	1.0061	$\pm 2.0 \cdot 10^{-3}$	$1.16 \cdot 10^{-3}$
5	The volume of the test gas burned V_{gw}, m³	4.000	± 0.020	0.0115
6	Correction factor for gas meter readings f_{gm}	1.004	$\pm 1.0 \cdot 10^{-3}$	$0.58 \cdot 10^{-3}$
7	The coefficient for bringing the volume of the test gas burned to standard conditions K	1.003	$\pm 1.0 \cdot 10^{-3}$	$0.58 \cdot 10^{-3}$

Note. The table shows the average values of m_w, g, $\Delta \Theta_w$, °C and, V_{gw}, m³, obtained from the results of the study of 5 test gas samples.

Table 4

**The results of measuring the net volume-basis specific calorific value
of the test gas by the calorimetric method**

№	Name, symbol, and dimension of the input quantity $x_j, j = 1,..,9$	The numeric value of the input quantity x_j	Maximum permissible error $\Delta x_{j,mpe}$	Standard uncertainty $u_B(x_j)$
1	Gross volume-basis specific calorific value of the test gas $(H_V)_G$, MJ/m³	38.,35	± 0.43	0.25
2	Correction factor for calorimeter readings during the measurement $(H_V)_G$, $f_{k,gr}$	1.0061	$\pm 2.0 \cdot 10^{-3}$	$1.16 \cdot 10^{-3}$
3	The specific heat of water vapor condensation c_{con}, MJ/(g·°C)	$2.454 \cdot 10^{-3}$	$\pm 0.25 \cdot 10^{-4}$	$0.145 \cdot 10^{-4}$
4	The mass of collected condensate of water vapor m_{con}, g	60.50	± 1.00	0.58
5	The average difference in water temperature at the outlet and inlet of the calorimeter $\Delta \Theta_w$, °C	10.35	± 0.12	0.07
6	The volume of the test gas that burns in the calorimeter during the collection of water vapor condensate V_{gwv}, m³	40.500	± 0.020	0.0115
7	Correction factor for gas meter readings f_{gm}	1.004	$\pm 1.0 \cdot 10^{-3}$	$0.58 \cdot 10^{-3}$
8	The coefficient for bringing the volume of the test gas burned to standard conditions K	1.003	$\pm 1.0 \cdot 10^{-3}$	$0.58 \cdot 10^{-3}$
9	Correction factor for calorimeter readings during the measurement $(H_V)_N$, $f_{k,nt}$	1.0068	$\pm 2.0 \cdot 10^{-3}$	$1.16 \cdot 10^{-3}$

Note. The table shows the average values of m_{con}, g, $\Delta \Theta_w$, °C, and V_{gwv}, m³, obtained from the results of the study of 5 test gas samples.

After processing the experimental data, the following result of measuring the net volume-basis specific calorific value of the studied natural gas was obtained:

$$(H_V)_N = (34.65 \pm 0.35) \text{ MJ/m}^3; \; U_p\left\{(H_V)_N\right\} =$$
$$= 0.35 \text{ MJ/m}^3; \; p = 0.95; \; k_p = 1.96.$$

7. Conclusions

1. The calorimetric method provides precise and valid results of measuring the gross and net volume-basis-specific calorific values of natural gas in modern gasometry.

2. The methodology of estimating the accuracy of measuring the gross and net volume-basis-specific calorific values of natural gas by the developed calorimetric method, based on computing uncertainty of the measurement results by assessing both random and systematic impact factors, fully meets the requirements in ensuring the measurements unity; it can be recommended to apply in gasometry.

8. Gratitude

9. Conflict of interest

The authors state that there are no financial or other potential conflicts regarding this work.

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