COOMET. T-S6

COOMET PROJECT 873/RU-a/23

Supplementary Comparison in Thermometry, Thermophysical quantities

Comparisons in the field of combustion energy of pure organic substances

FINAL REPORT

Pilot

Elena N. Korchagina, Natalia A. Gorshunova – VNIIM, Russia

Participants

Haifeng Wang, Ms. Li Jia – NIM, China

Alina G. Davidovskaya – BelGIM, Belarus

CONTENTS

Final Report
COOMET PROJECT 873/RU-a/23
COOMET. T-S6
Comparisons in the field of combustion energy of pure organic substances

Introduction

The scope of this work is the comparison of combustion energy of pure organic substances: dodecane and anthracene. Measurements of combustion energy are taken with bomb calorimeters of Russia, Belarus and China. The pilot laboratory (Coordinator) is the VNIIM Laboratory of Calorimetry (Russia).

The comparison uses two samples of pure organic substances: dodecane and anthracene prepared by VNIIM (Russia). The samples are prepared in accordance with the relevant regulations for each fuel with proven homogeneity and stability. Each Participant receives a marked copy of each sample prepared by the pilot laboratory.

Each sample is accompanied with an Information Sheet indicating period of time for the measurements to be made and other additional information.

VNIIM ships one copy of each sample to the Participants through a shipping company. Where possible, VNIIM transfers the sample to a Participant personally during any visits by one of the parties to another.

After receiving the sample and providing measurements, the Participants send a protocol to the Coordinator.

1 Participants of the Comparison

In the COOMET regional comparison take part three metrology institutes. The Coordinator is the VNIIM Laboratory of Calorimetry (Russia). Information about Participants is given in Table 1.

Table 1 – List of the participating metrology institutes

NMI	Instrument	Country	Contact information
D.I. Mendeleyev Institute for Metrology (VNIIM)	Calorimeter with static bomb "VIM", a part of the primary standard unit of the combustion energy (GET 16)	Russia	Address: 19, Moskovskiy pr., St. Petersburg 190005, Russia E-mail: E.N.Korchagina@vniim.ru Phone: +7 812 323 96 39 Contact person: Elena N. Korchagina
Belarusian State Institute of Metrology (BelGIM)	Bomb isothermal-shell calorimeter	Belarus	Address: 93, ul. Starovilenskiy Trakt, Minsk 220053, Belarus E-mail: davidov@belgim.by Phone: + 375 117 233 04 21 Contact person: Alina G. Davidovskaya
National Institute of Metrology (NIM)	The commercial oxygen bomb calorimeter (C6000) IKA Inc	China	Address: No.18, Bei San Huan Dong Lu, Chaoyang Dist Beijing 100029, P.R.China E-mail: ws@nim.ac.cn Phone: +86-10-64218565 Contact person: Wang Haifeng

2 The Comparison scheme

The comparison Coordinator sends the Technical Protocol to the Participants. The Technical Protocol establishes the schedule, the scheme and the procedure for the comparison, rules for selecting and preparing samples, and the procedure for sending samples. According to the comparison procedure, it is necessary to carry out calibration of the reference calorimeter, prepare the sample for combustion, and take measurements.

The Technical Protocol is agreed and accepted by all Participants of the comparison.

The comparison scheme is presented in the Final Report in Appendix A. In accordance with the accepted scheme, the Coordinator prepares samples and sends them to the Participants. Participants perform measurements of the combustion energy of samples and process the results of measurements. Participants send the results to the coordinator for further analysis and preparation of the Final Report.

3 Samples for the Comparison

All samples are prepared by the Comparison Coordinator VNIIM Laboratory of Calorimetry (Russia). Each sample is divided into three equal parts; one part is left in VNIIM (Russia), while the others are sent to BelGIM (Republic of Belarus) and NIM (China). VNIIM sends one copy of each sample to the Participants of the comparison with the markings given in Table 2.

Table 2 – Marking of the samples used for the comparison

№	Sample	Marking	NMI	Identical to
1	Dodecane	DO-RU	VNIIM (Russia)	DO-BY, DO-CH
2		DO-BY	BelGIM (Belarus)	DO-RU, DO-CH
3		DO-CH	NIM (China)	DO-BY, DO-RU
4	Anthracene	AN-RU	VNIIM (Russia)	AN-BY, AN-CH
5		AN-BY	BelGIM (Belarus)	AN-RU, AN-CH
6		AN-CH	NIM (China)	AN-BY, AN-RU

The first two symbols correspond to the type of the sample and the last letters describe the name of the country.

Each sample is accompanied by a corresponding label:

COOMET PROJECT 873/RU/23
COMPARISON SAMPLE

DODECANE

DO-BY/1

Федеральное государственное унитарное предприяти
«Всероссийский научно-исследовательский институт
метрологии им. Д.И. Менделеева»
190005, Санкт-Петербург, Московский пр., д. 19,
Тел.: (812) 323-96-53, факс: (812) 713-01-14
email: info@vniim.ru | www.vniim.ru

COOMET PROJECT 873/RU/23

COMPARISON SAMPLE
ANTHRACENE
AN-BY/01

Fig. 1. Labels for the comparison samples

4 Presentation of the measurement results

The protocol form for measurement results presentation is given in Annex B of the Final Report.

Measurement results are given below.

5 The first stage of the measurement results analysis

Measurement results of the Participants of the comparison are given in Table 3.

Table 3 – Measurement results of the gross calorific value

Participant	Measurement period	Gross calorific value, x_i, kJ/kg	$u_A(x_i)$, %	Number of experiments, n
DO				
VNIIM	May2024	47317	0,009	10
BelGIM	September 2024	47321	0,008	10
NIM	June 2024	47316	0,022	8
AN				
VNIIM	May 2024	39628	0,008	10
BelGIM	August 2024	39622	0,018	10
NIM	June 2024	39613	0,022	7

Each laboratory used its accepted measurement practice of gross calorific value of solid and liquid fuels taking into account the information given in the Information Sheet.

The results received by the Coordinator from the Participants were processed in two stages:

1st stage. The series of measurements taken by each Participant were processed for each sample. The first stage of the analysis consists of calculation of the arithmetic mean and estimation of the standard uncertainties u_A, u_B and u_C.

2d stage. The reference value and its standard uncertainty were calculated, the consistency of the results obtained by different Participants was checked, and the criterion confirming the uncertainties claimed by the Participants was calculated.

Tables 4 and 5 give the measurement results presented by the participants, as well as their claimed values of u_A, u_B and u_C.

5.1 Measurement results of combustion energy of anthracene sample – Sample AN

The measurement results of combustion energy of anthracene received from the Participants of the comparison (Sample AN) are given in Table 4.

Table 4 – Measurement results of combustion energy of anthracene (Sample AN)

Sample AN Gross calorific value, kJ/kg			
Participant	VNIIM	BelGIM	NIM
№ of measurement	q_j, kJ/kg	q_j, kJ/kg	q_j, kJ/kg
1	39614	39604	39633
2	39631	39604	39592
3	39638	39610	39619
4	39635	39616	39615
5	39627	39612	39649
6	39631	39624	39599
7	39642	39595	39585
8	39622	39651	
9	39628	39652	
10	39612	39655	
n	10	10	7
$x_i = \frac{\sum_{j=1}^{n} x_j}{n}$, kJ/kg	39628	39622	39613
$u_A = \sqrt{\frac{\sum_{j=1}^{n}(x_j - x_i)^2}{n(n-1)}}$, kJ/kg	3	7	9
u_B, kJ/kg	0,9	1,4	7
$u_C = \sqrt{u_A^2 + u_B^2}$, kJ/kg	3	7	11
$U = ku_c$, kJ/kg, k=2, P=0,95	6	14	22

5.2 Measurement results of combustion energy of dodecane sample – Sample DO

The measurement results of combustion energy of dodecane received from the Participants of the comparison (Sample DO) are given in Table 5.

Table 5 – Measurement results of combustion energy of dodecane (Sample DO)

Sample DO Gross calorific value, kJ/kg			
Participant №	VNIIM	BelGIM	NIM
№ of measurement	q_j, kJ/kg	q_j, kJ/kg	q_j, kJ/kg
1	47320	47321	47333
2	47294	47332	47288
3	47325	47304	47278
4	47315	47313	47334
5	47319	47338	47278
6	47324	47333	47347
7	47294	47309	47332
8	47315	47312	47339
9	47333	47335	
10	47328	47315	
n	10	10	8
$x_i = \frac{\sum_{j=1}^{n} x_j}{n}$, kJ/kg	47317	47321	47316
$u_A = \sqrt{\frac{\sum_{j=1}^{n}(x_j - x_i)^2}{n(n-1)}}$, kJ/kg	4	4	10
u_B, kJ/kg	1,1	1,6	13
$u_C = \sqrt{u_A^2 + u_B^2}$, kJ/kg	4	4	17
$U = ku_c$, kJ/kg, k=2, P=0,95	9	8	34

6 The second stage of the measurement results analysis

The processing of the comparison results performed in accordance with COOMET-R/GM/19:2016 *"COOMET Recommendation Guideline on COOMET supplementary comparison evaluation"* showed, that received results are consistent.

Notation used:

x_i – results of the comparison;

$u(x_i)$ – quoted standard uncertainties of the participants of comparison;

m – the number of the participants of comparison;

x_{ref} – the reference value;

$u(x_{ref})$ – standard uncertainty of the reference value;

NMI – National Metrology Institute.

On the basis of the measurement results and corresponding uncertainties, claimed by comparison participants, the χ^2 criterion value is calculated (1):

$$\chi^2 = \sum_{1}^{m} \frac{(x_i - x_{ref})^2}{u^2(x_i)} \tag{1}$$

where

$$x_{ref} = \frac{\sum_1^m \frac{x_i}{u^2(x_i)}}{\sum_1^m \frac{1}{u^2(x_i)}}, u^2(x_{ref}) = \frac{1}{\sum_1^m \frac{1}{u^2(x_i)}} \tag{2}$$

If the criterion value calculated in accordance with the data provided by the participants does not exceed the critical value χ^2 with the coverage level 0,95 and the degrees of freedom (m - 1)

$$\chi^2 < \chi^2_{0.95}(m-1), \tag{3}$$

then the data provided by different participants can be acknowledged as consistent.

The E_n criterion is determined for measurement capabilities confirmation:

$$E_n = \frac{|x - x_{ref}|}{2\sqrt{u^2(x) - u^2(x_{ref})}} < 1 \qquad (4)$$

If the criterion E_n does not exceed one, then the participant confirms its measurement capabilities.

The results of combustion energy of anthracene sample (Sample AN) are shown in fig. 2 and Table 6.

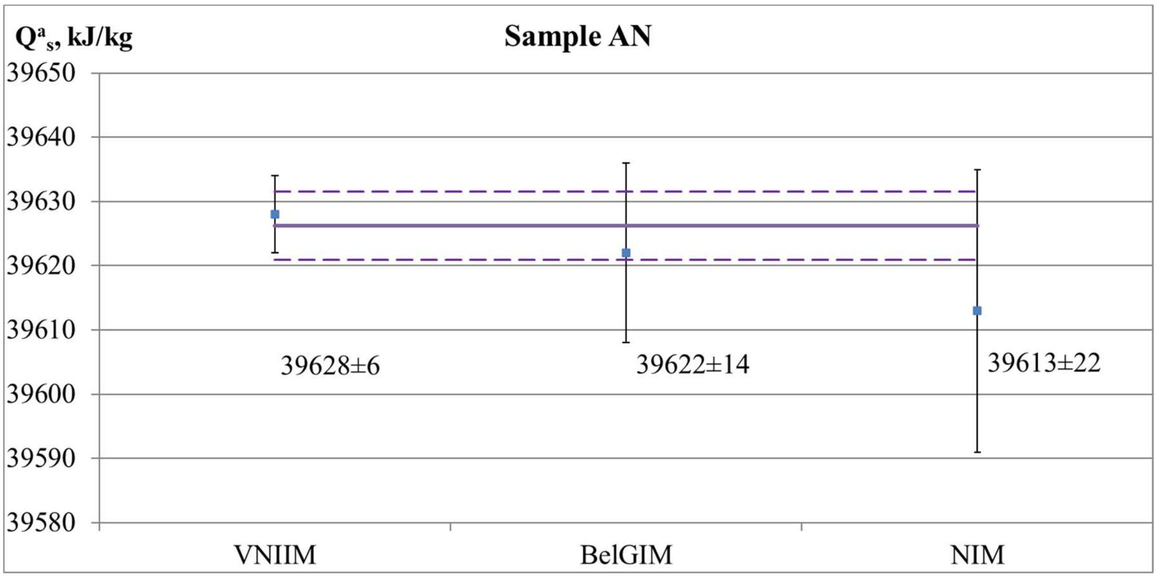


Fig. 2. Comparison results for the Sample AN

Table 6 – The evaluation of comparison data (Sample AN)

Participant	***x_i, kJ/kg***	***$u(x_i)$, kJ/kg***	***$U(x_i)$, kJ/kg***	***χ^2***	***E_n***
VNIIM	39628	3	6	0,35	0,65
BelGIM	39622	7	14	0,37	0,33
NIM	39613	11	22	1,45	0,62
x_{ref}=	39626				
$u(x_{ref})$=		3	5		
χ^2=				2,16	
χ_{max}^2=				5,99	

The criterion value χ^2 does not exceed the critical value χ^2_{max}: 2,16 < 5,99. Due to this fact the results of comparison (Sample AN) are consistent.

The E_n criterion is less than one in all cases. Based on this fact all the participants confirm their measurement capabilities.

The results of combustion energy of dodecane sample (Sample DO) are shown in fig. 3 and Table 7.

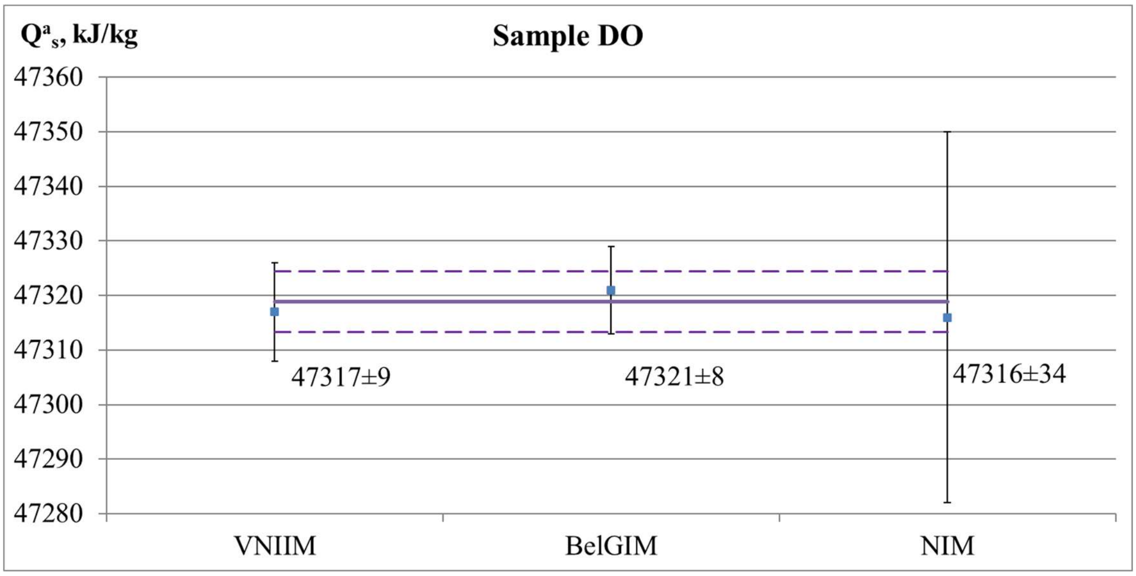


Fig. 3. Comparison results for the Sample DO

Table 7 – The evaluation of comparison data (Sample DO)

Participant	**x_i, kJ/kg**	**$u(x_i)$, kJ/kg**	**$U(x_i)$, kJ/kg**	**χ^2**	**E_n**
VNIIM	47317	4	9	0,23	0,33
BelGIM	47321	4	8	0,27	0,36
NIM	47316	17	34	0,03	0,09
x_{ref}=	47319				
$u(x_{ref})$=		3	6		
χ^2=				0,53	
χ_{max}^2=				5,99	

The criterion value χ^2 does not exceed the critical value χ^2_{max}:0,53 < 5,99. Due to this fact the results of comparison (Sample DO) are consistent.

The E_n criterion is less than one in all cases. Based on this fact all the participants confirm their measurement capabilities.

After data processing, the following reference values were obtained:

for anthracene sample (Sample AN): 39626±5 kJ/kg;

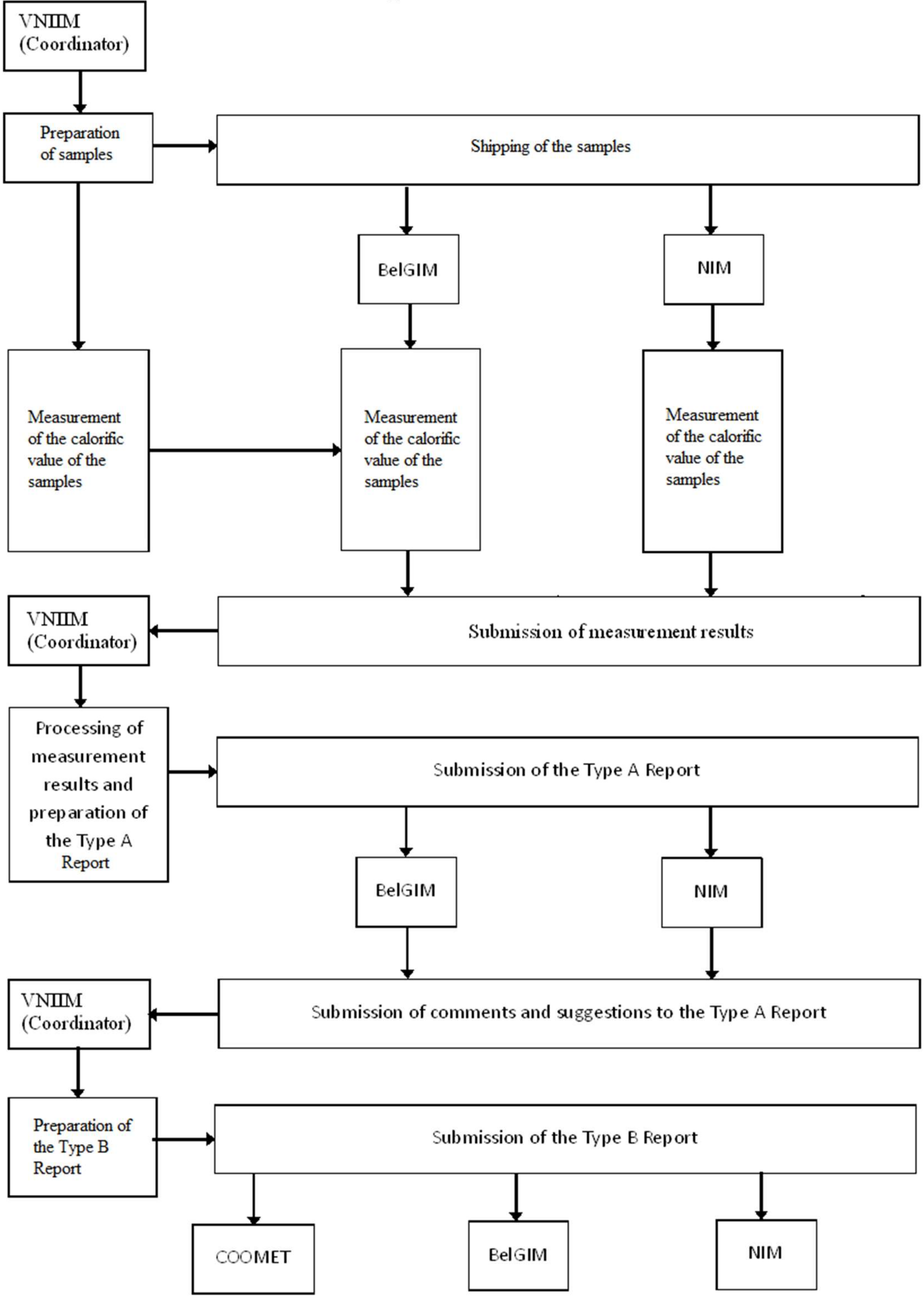
for dodecane sample (Sample DO): 47319±6 kJ/kg.

Conclusion

As a result, the values obtained by the Participants for the anthracene and dodecane samples (Sample AN and Sample DO) are consistent. Participants confirm their measurement capabilities.

ANNEX A

The comparison scheme



ANNEX B

Recommended form for the Gross Calorific Value Measurement Report

NMI VNIIM (Russia)
Sample AN-RU

Date: DD/MM/YYYY Signature: ____________________________

Calibration (if applicable):
Calibration conditions:

Ambient temperature, °C ________

Relative humidity, % ________

Atmospheric pressure, kPa ________

Calibration results

Number of experiments: n = ____

№	**Measurement date**	**Effective heat capacity, ε, J/K**	**Notes**
1			
…			
n			
Mean value of effective heat capacity, $\bar{\varepsilon}$, J/K			

Calibration technique

It is necessary to provide a description of the calibration procedure.

Measurement:
Measurement conditions:

Ambient temperature, °C ________

Relative humidity, % ________

Atmospheric pressure, kPa ________

Measurement results

Number of experiments: n = ____

№	Measurement date	Sample weight, g	Gross calorific value, Q, kJ/kg	Notes
1				
…				
n				
Mean value of the gross calorific value, $\bar{Q}$, kJ/kg				

Measurement technique

It is necessary to indicate either a reference to a standard method (e.g. ISO 1928) or a detailed description of the measurement technique used to calculate the measurement result and its uncertainty from experimental observations and input data including the measurement equation. If a standard method is used with any changes to it, these changes should be indicated.

Traceability statement

All the participants must be able to demonstrate traceability to an independent realization of each quantity, or make clear the route of traceability via another named laboratory.

Equipment used for measurement and calibration

Name of the National Measurement Standard: ____, comprised of:

№	Name	Manufacturer, model, serial number	Metrological characteristics
1	Name of the measurement instrument (e.g. electronic balance)	Manufacturer: Model: Serial No.: ____________	Measurement range: Error or measurement uncertainty: etc.
…			
1	Name of the calibration standard (e.g. benzoic acid)	Manufacturer: CRM No.: ____________	Certified value: Error or uncertainty of the certified value: etc.

Uncertainty budget

A detailed uncertainty budget should be provided in accordance with the ISO Guide for the Expression of Uncertainty in Measurement; all the components of the uncertainty should be indicated, and their evaluation must be fully documented. It is also necessary to indicate all the corrections and constants used, and their sources.

ANNEX C

COOMET PROJECT 873/RU/23

Comparisons in the field of combustion energy of pure organic substances

TECHNICAL PROTOCOL

Pilot Laboratory
D.I.Mendeleyev Institute for Metrology
(VNIIM, Russia)

Contact person:
Elena N. Korchagina
VNIIM, Russia
Research Laboratory of Measurement Standards in the field
of Combustion Calorimetry and High-Purity Substances for
Metrological Purposes
19, Moskovskiy pr.
St. Petersburg, 190005
Russia
Phone: (812) 323-96-39
Fax: (812) 713-01-14
Email: E.N.Korchagina@vniim.ru

TECHNICAL PROTOCOL
on the COOMET project 873/RU/23
Comparisons in the field of combustion energy of pure organic substances

Introduction

This work involves comparison in the field of combustion energy of pure organic substances: dodecane and anthracene using reference bomb calorimeters of Russia, China and Belarus.

1 Participants

Three metrology institutes that are taking part in the COOMET regional comparison are listed in Table 1. The Coordinator is the VNIIM Laboratory of Calorimetry (Russia).

Table 1 – List of the participating metrology institutes

№	NMI	Country	Contact information
1	D.I. Mendeleyev Institute for Metrology (VNIIM)	Russia	Address: 19, Moskovskiy pr., St. Petersburg 190005, Russia E-mail: E.N.Korchagina@vniim.ru Phone: +7 812 323 96 39 Contact person: Elena N. Korchagina
2	Belarusian State Institute of Metrology (BelGIM)	Belarus	Address: 93, ul. Starovilenskiy Trakt, Minsk 220053, Belarus E-mail: krivonos@belgim.by Phone: + 375 117 233 04 21 Contact person: Petr V. Krivonos
3	National Institute of Metrology (NIM)	China	Address: No.18, Bei San Huan Dong Lu, Chaoyang Dist Beijing 100029, P.R.China E-mail: ws@nim.ac.cn Phone: +86-10-64218565 Contact person: Wang Haifeng

2 Comparison scheme

The comparison is carried out according to the mixed scheme shown in Fig. 1.

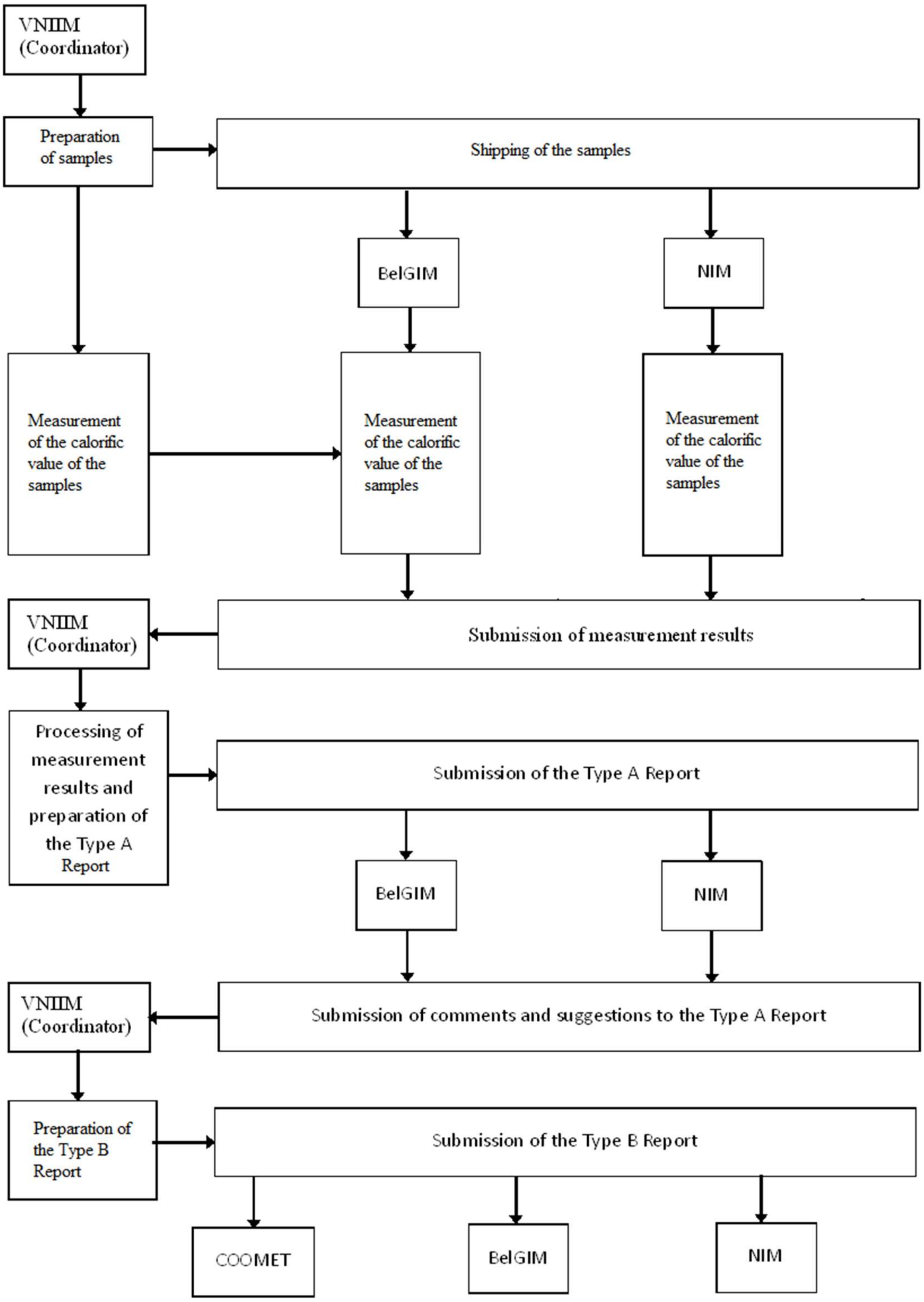


Fig. 1. Comparison scheme of the National Measuring Standards in the field of combustion energy of pure organic substances

3 Samples for the comparison

Coordinator of comparison is VNIIM Laboratory of Calorimetry (Russia). The comparison uses two samples of pure organic substances: dodecane and anthracene prepared by VNIIM (Russia). The samples are prepared in accordance with the relevant regulations for each fuel with proven homogeneity and stability. Each sample was divided into three equal parts; one part was left in VNIIM (Russia), while others were sent to BelGIM (Republic of Belarus) and NIM (China). VNIIM sends one copy of each sample to the Participants of the comparison with the markings given in Table 2.

Table 2 – Marking of the samples used for the comparison

№	Sample	Marking	NMI	Identical to
7	Dodecane	DO-RU	VNIIM (Russia)	DO-BY, DO-CH
8		DO-BY	BelGIM (Belarus)	DO-RU, DO-CH
9		DO-CH	NIM (China)	DO-BY, DO-RU
10	Anthracene	AN-RU	VNIIM (Russia)	AN-BY, AN-CH
11		AN-BY	BelGIM (Belarus)	AN-RU, AN-CH
12		AN-CH	NIM (China)	AN-BY, AN-RU

Each sample is accompanied by a corresponding label:

COOMET PROJECT 873/RU/23 COMPARISON SAMPLE

DODECANE

DO-BY/1

Федеральное государственное унитарное предприяти
«Всероссийский научно-исследовательский институт
метрологии им. Д.И. Менделеева»
190005, Санкт-Петербург, Московский пр., д. 19,
Тел.: (812) 323-96-53, факс: (812) 713-01-14
email: info@vniim.ru | www.vniim.ru

COOMET PROJECT 873/RU/23

COMPARISON SAMPLE
ANTHRACENE
AN-BY/01

Fig. 2. Labels for the comparison samples

3.1 Shipping samples

VNIIM will ship one copy of each sample to the Participants through a shipping company. Where possible, VNIIM can transfer the sample to a Participant personally during any visits by one of the parties to another.

The Participant must notify VNIIM in case of significant shipping delay or if it is impossible to carry out the measurements in the specified period for any other reason so that the comparison schedule could be adjusted by the Coordinator.

After receiving the sample, the Participants should make certain of the integrity of the sample and send an Inspection Report on receipt of the Sample to the Coordinator (recommended form is given in Appendix A).

4 Carrying out measurements

Each laboratory should use its accepted practice of measurement of gross calorific value of solid and liquid fuels taking into account the information given below.

4.1 Preparation of samples for comparisons

VNIIM prepares samples of anthracene and dodecane for the comparisons. The anthracene sample consists of 17 tablets with an approximate weight of 0.64 g in a tube pressed with a seal to avoid damage. The dodecane sample consists of 3 glass ampoules with a capacity of 3 cm^3.

4.2 Shipping samples

VNIIM sends 1 copy of anthracene sample and 3 ampoules of dodecane to BelGIM (Republic of Belarus) and NIM (China).

4.3 Calorimeter calibration - determination of the energy equivalent of the calorimeter

Each participant carries out the energy equivalent of the calorimeter and estimates its uncertainty in accordance with the regulatory documents used in the laboratory.

4.4 Preparing samples for combustion

4.4.1 Preparing an anthracene sample for combustion

- Make sure that the packaging with tablet samples is not damaged.
- Open the package with tableted samples.
- Dry anthracene samples in a desiccator over phosphorus pentoxide (P_2O_5) for 3 calendar days (or using another available dehumidifier).
- Prepare a platinum crucible (or another one used in the calorimetric experiments).
- Place 1 sample tablet in the crucible.

It is advisable to use no more than 10 tablets (10 measurement results), leaving the unburned tablets for control, which may be needed based on the results of comparisons.

4.4.2 Preparing a dodecane sample for combustion

- Make sure that the ampoules with liquid dodecane are not damaged.
- Open the ampoule with the sample.
- Prepare a platinum crucible (preferred).
- Select approximately 0.5-0.6 g of dodecane for one combustion experiment.

It is advisable to conduct 10 calorimetric experiments (10 measurement results).

4.5 Carrying out measurements

Measurements should be carried out in accordance with the “Operation Manual for the Standard” or other regulatory documents used in the laboratory for conducting calorimetric experiments.

The sample is burned ten times (n=10).

5 Comparison schedule

Tentative comparison schedule is given in Table 3. All Participants have to complete their measurements during the period specified in the Technical Protocol.

Table 3 – Tentative comparison schedule

Period		Duration	Task	NMI
Start	**End**			
February 2023	August 2023	7 months	Preparation of the samples	VNIIM
September 2023	January 2024	5 months	Shipping of the samples to the Participants	VNIIM
February 2024	June 2024	5 months	Measurement of the samples by the Participants	VNIIM, BelGIM, NIM
July 2024	August 2024	2 months	Preparation of the measurement reports	VNIIM, BelGIM, NIM
September 2024	September 2024	2 weeks	Sending of the calorific value measurement results to the Coordinator (VNIIM)	BelGIM, NIM
October 2024	January 2025	4 months	Preparation of the Type A Report by the Coordinator	VNIIM
February 2025	February 2025	2 weeks	Sending of the Type A Report to the Participants	VNIIM
March 2025	March 2025	1 month	Submission of comments and suggestions by the Participants	BelGIM, NIM
April 2025	May 2025	2 months	Preparation and sending of the Type B Report to the Participants	VNIIM
June 2025	June 2025	1 month	Submission of comments and suggestions by the Participants	BelGIM, NIM
July 2025	August 2025	2 months	Preparation of the Type B Report to COOMET	VNIIM

6 Presentation of measurement results

The Participants must submit their measurement results in the form of measurement report to the Coordinator within the time specified in the Technical Protocol. To calculate the gross calorific value we assume that in both samples (anthracene, dodecane) the mass fraction of sulfur is zero, the mass fraction of analytical moisture is zero.

The measurement report must include the following:

- name of the sample and the Participant,
- measurement conditions,
- measurement results,
- name of the National Measurement Standard and list of the measuring equipment used in the measurements with its metrological characteristics,
- detailed description of the measuring procedure or a reference to a standard method,
- traceability statement,
- uncertainty budget in accordance with the ISO Guide for the Expression of Uncertainty in Measurement.

If applicable, the report should also include information about performed calibration and its results.

ANNEX D

Information about the Samples for the Comparison

Dodecane Samples

Dodecane samples are ampoules with liquid dodecane. It was decided to take (0.5 – 0.6) g of dodecane for one combustion experiment. The dodecane has a low vapour pressure and can be weighed in the crucible.

NIM (China) used polyethylene capsules to determine the calorific value of the dodecane samples. The mass of the capsule is about 0.17 g, the average calorific value result is 46305 J/g with the standard deviation 17 J/g.

Laboratories of VNIIM (Russia) and BelGIM (Belarus) measured the calorific value of the dodecane samples in the platinum crucible. Fig. 3 and Table 7 show that all the results are consistent. Due to this, we have not found any difference when burning samples in a polyethylene capsule and without it.

Anthracene Samples

Anthracene samples are tablets weighing 0.64 g. This mass is specially selected. The combustion energy of 0.64 g of anthracene is equivalent to the combustion energy of 1 g of benzoic acid. This allows to measure the combustion energy of the sample as close as possible to the value obtained during the calibration procedure of the calorimeter.

All the participants adjusted the mass of the samples to vacuum weighing conditions. The mass in the air was modified into the mass in vacuum by using the air density.

Appendix A

Report on Receiving of the Sample

Was the package opened during shipping? (e.g. during customs clearing)	No
Is the package damaged?	No
Are there any visible signs of damage to the sample itself?	No
Are there any other troubles with the sample? (e.g. wrong marking, no Information Sheet, etc.)	No

If checked Yes for any of the questions above, please provide detailed information about the problem.

NMI: National Institute of Metrology of China

Date: 04/25/2024 Signature: Haifeng Wang

Appendix B

Recommended form for the Gross Calorific Value Measurement Report

NMI	NIM (China)
Sample	Dodecane

Date: 025/06/2024 Signature: Haifeng Wang

Calibration (if applicable):

Calibration conditions:

Ambient temperature, °C	26.0
Relative humidity, %	52
Atmospheric pressure, kPa	100.41

Calibration results

Number of experiments: n = _6___

№	Measurement date	Effective heat capacity, ε, J/K	Notes
01	28/05/2024	8161	
02	28/05/2024	8158	
03	29/05/2024	8159	
04	29/05/2024	8142	
05	07/06/2024	8149	
06	07/06/2024	8148	
Mean value of effective heat capacity, $\bar{\varepsilon}$, J/K		8153	

As shown in Table above, the average of capacity was 8153 J/K and its relative standard deviation was 0.09%.

In the determination of calorific values, the capacity of calorimeter was checked by GBW 13021 benzoic acid.

Calibration technique

It is necessary to provide a description of the calibration procedure.

Instrument:

The commercial oxygen bomb calorimeter (C6000) was purchased from IKA Inc. The serial number of the calorimeter is 100075178.

Certified reference material (CRM)

The primary certified reference material for calorific value of benzoic acid (GBW 13021) was used to calibrate the heat capacity of calorimeter. The certified value is 26432 J/g and the relative uncertainty is 0.022% (*U*, *k*=2). The mass of benzoic acid is based on the value weighed in vacuum.

Experimentals

The calibration was performed according to ISO 1928-1995. The calibration was performed using GBW 13021. The mass of GBW 13021 is about 1.00 g. The energy of ignition (q_1) measured by instrument ranged from 64 to 66 J. The heat contribution from cotton wire (q_2) used to ignite the sample is 50 J per unit. The heat of nitric acid formation is calculated based on Eq. 1.

$$q_{\mathrm{N}} = Q_{\mathrm{HNO_3}} \cdot n_{\mathrm{HNO_3}} = Q_{\mathrm{HNO_3}} \cdot V_{\mathrm{NaOH}} \cdot c_{\mathrm{NaOH}} \tag{1}$$

where, q_{N} is the heat of nitric acid formation, J; Q_{HNO3} is the formation heat of nitric acid per mmol, 58, J/mmol; n_{HNO3} is the amount of substance of nitric acid, mmol; V_{NaOH} is the volume of NaOH solution at the equivalence point, mL; c_{NaOH} is the mole concentration of NaOH, mol/L.

The heat capacity of calorimeter is calculated according to Eq. (2).

$$\varepsilon = \frac{m_{\mathrm{BA}} \times Q_{\mathrm{BA}} + q_1 + q_2 + q_{\mathrm{N}}}{\Delta T} \tag{2}$$

where, ε is heat capacity, J/K; m_{BA} is the mass of benzoic acid, g; Q_{BA} is the calorific value of benzoic acid, 26432 J/K; q_1 is the heat of ignition, (64-64) J; q_2 is the heat of the cotton wire, 50 J; ΔT is the temperature increase of adiabatic calorimeter, K.

The capacity of the calorimeter varied. The repeatability of capacity within a day was better than that among days. So, the calibration was performed every day, and the average of the capacity results was used to calculate the calorific value of sample measured in the same day.

Measurement:

Measurement conditions:

Ambient temperature, °C 25.6
Relative humidity, % 58
Atmospheric pressure, kPa 100.33

Measurement results

Dodecane

The calorific value of dodecane was determined according to ASTM D4809-13. The dodecane has a low vapour pressure and can be weighed in the crucible. However, it was found that the calorific value determined without a capsule is lower than that determined with a polyethylene capsule. So, the dodecane sample was sealed in a polyethylene capsule and then was measured by the oxygen bomb calorimeter. Furthermore, it was found that the pressure-sensitive tape recommended by ASTM D4809 contained halogen and thus corroded the inner wall of oxygen bomb obviously. So, the polyethylene capsule was used as the container of the dodecane sample instead of the pressure-sensitive tape.

The caloric value of the polyethylene capsule was determined by the calorimeter. The sample mass was about 0.54 g. Six times of measurements of the calorific value of polyethylene were performed. The average of calorific value results was 46305 J/g, and the standard deviation was 17 J/g.

Number of experiments: n = 8

№	Measurement date	Sample weight, g	Polyethylene capsule weigh, g	Gross calorific value of sample, Q_s^a, kJ/kg
1	28/05/2024	0.39747	0.18616	47333
2	29/05/2024	0.38710	0.17479	47288
3	29/05/2024	0.38885	0.18123	47278
4	29/05/2024	0.36469	0.18479	47334
5	07/06/2024	0.36318	0.17703	47278
6	07/06/2024	0.37623	0.17423	47347
7	07/06/2024	0.37709	0.17026	47332
8	07/06/2024	0.39322	0.16987	47339
Mean value of the gross calorific value, $\overline{Q_s^d}$, kJ/kg				47316

As shown in the table above, the average of gross calorific values Q_s was 47316 J/g. The mass of sample is based on the value weighed in vacuum. The standard deviation was 29 J/g. The relative standard deviation was 0.062%.

Measurement technique

It is necessary to indicate either a reference to a standard method (e.g. ISO 1928) or a detailed description of the measurement technique used to calculate the measurement result and its uncertainty from experimental observations and input data including the measurement equation. If a standard method is used with any changes to it, these changes should be indicated.

Experimentals

Sample treatment

The sample is sealed in polyethylene capsule and then measured. The calorific value of the capsule was determined by the oxygen bomb calorimeter.

Fig. 1 The photograph of polyethylene capsule containing liquid sample.

Calorific value

The calibration was performed according to ASTM D4809-13. The room temperature ranged from 25.0 to 26.5 ºC, the atmospheric pressure ranged from 99.8 to 100.9 kPa, and the relative humidity ranged from 29 to 58%rh. When the mass of capsule or dodecane was weighed, the room temperature, atmospheric pressure and humidity were measured simultaneously. Then, the air density was calculated using the temperature, pressure and humidity. The mass in the air was modified into the mass in vacuum by using the air density.

After the measurement, the gross calorific value of dodecane sample (Q_s) was calculated according to Eq. (3).

$$Q_s = \frac{\varepsilon \cdot \Delta T - q_1 - q_2 - q_{HNO_3} - q_{PE}}{m} = \frac{\varepsilon \cdot \Delta T - q_1 - q_2 - q_{HNO_3} - Q_{PE} m_{PE}}{m} \tag{3}$$

where Q_s is the gross calorific value of dodecane sample, J/g; q_{PE} is the heat of polyethylene capsule, J; Q_{PE} is the calorific value of polyethylene capsule, J/g; m_{PE} is the mass of polyethylene capsule in vacuum, g; m is the mass of dodecane in vacuum, g.

The heat of nitric acid formation is calculated based on Eq. 1.

$$q_N = Q_{HNO_3} \cdot n_{HNO_3} = Q_{HNO_3} \cdot V_{NaOH} \cdot c_{NaOH}$$

The residue solution in oxygen bomb was transferred in a beaker and then was heated to boiling. When the solution was cooled, it was titrated by NaOH solution with a mole concentration of 0.10 mol/L using a Metrohm 905 Titrando.

Traceability statement

All the participants must be able to demonstrate traceability to an independent realization of each quantity, or make clear the route of traceability via another named laboratory.

Before the determination of calorific value of sample, the oxygen bomb calorimeter (IKA C6000) was calibrated using the primary CRM for calorific value of benzoic acid (GBW 13021). GBW 13021 with an expanded uncertainty (U_r=0.022%, k=2) was certified using the primary standard for calorific value of solid fuels. This primary standard was calibrated using the electric energy, which makes the calorific value traceable to SI unit of voltage, resistance, time and mass. So, the measured calorific value using IKA C6000 could be traceable to the SI units through the GBW 13021.

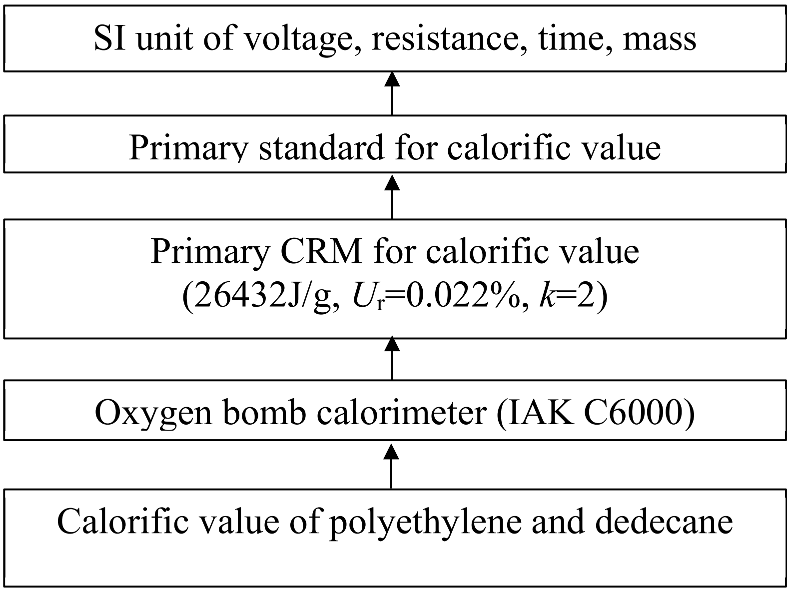


Fig. 1 traeablility chain of calorific value

Equipment used for measurement and calibration

Name of the National Measurement Standard: oxygen bomb calorimeter,
comprised of:

№	Name	Manufacturer, model, serial number	Metrological characteristics
1	Oxygen bomb calorimeter	Manufacturer: IKA Inc. from Germany Model: C6000 Serial No.: 100075178	Measurement range: <40,000J Error or measurement: RSD<0.15% uncertainty: / etc.
2	Electric balance	Manufacturer: Mettler-Toledo Inc. from Switzerland Model: XP205 Serial No.: B4421340837	Measurement range: <220g Error or measurement: 0.05mg Uncertainty (U, k=2): 0.06mg etc.

№	Name	Manufacturer, model, serial number	Metrological characteristics
3	Temperature, humidity and pressure meter	Manufacturer: Testo Inc. from Germany Model: 622 Serial No.: 3958140/0923	*U* of temperature: 0.1 °C *U* of humidity: 0.8 %RH *U* of pressure: 0.04 kPa
4	CRM for caloric value of benzoic acid	Manufacturer: NIM of China CRM No.: GBW 13021	Certified value: 26436J/g Uncertainty of the certified value (U_r, k=2): 0.022%
5	Polyethylene capsule	Manufacturer: BKMAM Inc. from China Model: 110205004	Volume: 1 mL Calorific value: 46305 J/g (U=14 J/g)

Uncertainty budget

A detailed uncertainty budget should be provided in accordance with the ISO Guide for the Expression of Uncertainty in Measurement (GUM); all the components of the uncertainty should be indicated, and their evaluation must be fully documented. It is also necessary to indicate all the corrections and constants used, and their sources.

$$Q_s = \frac{\varepsilon \cdot \Delta T - q_1 - q_2 - q_{HNO_3} - Q_{PE} m_{PE}}{m} \tag{3}$$

$$Q_s = \frac{\varepsilon \cdot \Delta T - Q_{PE} m_{PE}}{m} \tag{4}$$

The gross calorific value of sample (Q_s) was calculated according to Eq. 3. Eq. 3 can be simplified into Eq. 4. So, the uncertainty of calorific value ($u(Q_s)$) was evaluated based on Eq. 4 according to ISO guide Expression of Uncertainty in Measurement.

$$u_c^2(Q_s) = u_A^2(Q_s) + (\frac{\partial Q_s}{\partial \varepsilon})^2 \cdot u^2(\varepsilon) + (\frac{\partial Q_s}{\partial \Delta T})^2 \cdot u^2(\Delta T) + (\frac{\partial Q_s}{\partial m_{PE}})^2 \cdot u^2(m_{PE}) + (\frac{\partial Q_s}{\partial Q_{PE}})^2 \cdot u^2(Q_{PE}) + (\frac{\partial Q_s}{\partial m})^2 \cdot u^2(m) \tag{5}$$

$$c_{(\varepsilon)} = \frac{\partial Q_s}{\partial \varepsilon} = \frac{\Delta T}{m}$$

$$c_{(\Delta T)} = \frac{\partial Q_s}{\partial \Delta T} = \frac{\varepsilon}{m}$$

$$c_{(m_{PE})} = \frac{\partial Q_s}{\partial m_{PE}} = -\frac{Q_{PE}}{m}$$

$$c_{(Q_{PE})} = \frac{\partial Q_s}{\partial Q_{PE}} = -\frac{m_{PE}}{m}$$

$$c_{(m)}=\frac{\partial Q_{\mathrm{s}}}{\partial m}=-\frac{\varepsilon\cdot\Delta T-Q_{\mathrm{PE}}m_{\mathrm{PE}}}{m^{2}}$$

Uncertainty of calorific value of sample by Type A method ($u_A(Q_s)$)

The standard deviation of Q_s was 29 J/g. The times of measurement is eight. The standard deviation of the mean was used as the type A uncertainty of Q_s ($u_A(Q_s)$, 10.3 J/g).

Uncertainty of capacity ($u(\varepsilon)$)

Eq. 2 was simplified as Eq. 6 which was used as the mathematical model for the of $u(\varepsilon)$.

$$\varepsilon\approx\frac{Q_{\mathrm{BA}}m_{\mathrm{BA}}}{\Delta T} \tag{6}$$

According to ISO Guide for GUM, the relative uncertainty of bomb calorific value ($u_r(\varepsilon)$) was calculated based on the uncertainty of Q_{BA}, ΔT and m_{BA} as below.

$$u_{\mathrm{r}}(\varepsilon)=\sqrt{u_{\mathrm{r,A}}(\varepsilon)^{2}+u_{\mathrm{r}}(Q_{\mathrm{BA}})^{2}+u_{\mathrm{r}}(m_{\mathrm{BA}})^{2}+u_{\mathrm{r}}(\Delta T)^{2}}$$

The uncertainty from the repeatability of measurement results of ε is contained in the uncertainty from the repeatability of measurement results of Q_s, so $u_{A,r}(\varepsilon)$ is omitted. The type B uncertainty of ε mainly come from the uncertainty of calorific value of benzoic acid CRM, mass of benzoic acid and the temperature increase. The relative uncertainty of calorific value of benzoic acid is 0.011%. The relative uncertainty of mass of benzoic acid is 0.003%. The uncertainty of temperature is little. Furthermore, most of the systematic error of temperature was reduced during the calculation of temperature increase. The calibration and measurement procedure employed the same method to determine the temperature increase. Therefore, the systematic error from the temperature increase was reduced further. So, the uncertainty from the temperature increase was omitted. So, $u_r(\varepsilon)$ was 0.012% and $u(\varepsilon)$ was 0.98 J/K.

$$u_{\mathrm{r}}(\varepsilon)=\sqrt{u_{\mathrm{r,A}}(\varepsilon)^{2}+u_{\mathrm{r}}(Q_{\mathrm{BA}})^{2}+u_{\mathrm{r}}(m_{\mathrm{BA}})^{2}+u_{\mathrm{r}}(\Delta T)^{2}}=\sqrt{0^{2}+0.011\%^{2}+0.003\%^{2}+0^{2}}=0.012\%$$

where, $u_r(\varepsilon)$ is the relative uncertainty of ε; $u_r(Q_{BA})$ is the relative uncertainty of calorific value of benzoic acid CRM; $u_r(m_{BA})$ is the relative uncertainty of mass of benzoic acid CRM; $u_r(\Delta T)$ is the uncertainty come from the temperature increase.

Uncertainty of temperature increase ($u(\Delta T)$)

As described above, $u(\Delta T)$ is omitted.

Uncertainty of mass of polyethylene capsule ($u(m_{PE})$)

$u(m_{PE})$ is 0.03 mg.

Uncertainty of calorific value of polyethylene capsule ($u(Q_{PE})$)

The relative uncertainty of calorific value of polyethylene capsule is 0.039%, so $u(Q_{PE})$ is 18.1 J/g.

Uncertainty of mass of sample ($u(m)$)

$u(m)$ is 0.03 mg.

According to Eq. 5, the $u(Q_s)$ was calculated as below.

$$u(Q_s)=\sqrt{\begin{aligned}&u_A^2(Q_s)+(\frac{\Delta T}{m})^2\cdot u^2(\varepsilon)+(\frac{\varepsilon}{m})^2\cdot u^2(\Delta T)+(-\frac{Q_{PE}}{m})^2\cdot u^2(m_{PE})+(-\frac{m_{PE}}{m})^2\cdot u^2(Q_{PE})\\&+(-\frac{\varepsilon\cdot\Delta T-Q_{PE}m_{PE}}{m^2})^2\cdot u^2(m)\end{aligned}}$$

According to the information listed in the table below, $u(Q_s)$ of dodecane was 17 J/g.

$$u(Q_s)=\sqrt{\begin{aligned}&10.3^2+(8.45\times0.98)^2+(20383\times0)^2+(-115763\times0.00003)^2\\&+(-0.45\times18.1)^2+(-120139\times0.00003)^2\end{aligned}}=17\text{J/g}$$

Finally, the expanded uncertainty of gross calorific value of dodecane (U, k=2) was 34 J/g.

The details of uncertainty budget of calorific value of dodecane samples.

Uncertainty of variance	Uncertainty source	Sensitivity coefficient	Value of sensitivity coefficient	Standard uncertainty of variance	$u_i=\|c_i\|u(x_i)$ （J/g）
$u_A(Q_s)$	Repeatability	1	1	10.3 (J/g)	10.3
$u(\varepsilon_i)$	Capacity	$\frac{\Delta T}{m}$	8.45	0.98 (J/K)	8.3
$u(\Delta T)$	Temperature increase	$\frac{\varepsilon}{m}$	20383	0 (°C)	0
$u(m_{PE})$	Mass of PE	$-\frac{Q_{PE}}{m}$	-115763	0.00003 (g)	3.5
$u(Q_{PE})$	Calorific value of PE	$-\frac{m_{PE}}{m}$	-0.45	18.1 (J/g)	8.2
$u(m)$	Mass of sample	$-\frac{\varepsilon\cdot\Delta T-Q_{PE}\cdot m_{PE}}{m^2}$	-120139	0.00003 (g)	3.7
$u(Q_s)$	Calorific value of sample	/	/	/	16.4

Recommended form for the Gross Calorific Value Measurement Report

NMI	NIM (China)
Sample	Anthracene

Date: 025/06/2024

Signature: Haifeng Wang

Calibration (if applicable):

Calibration conditions:

Ambient temperature, °C	24.0
Relative humidity, %	55
Atmospheric pressure, kPa	99.8

Calibration results

Number of experiments: n = 5

№	Measurement date	Effective heat capacity, ε, J/K	Notes
01	30/05/2024	8155	
02	30/05/2024	8151	
03	30/05/2024	8155	
04	31/05/2024	8154	
05	31/05/2024	8159	
Mean value of effective heat capacity, $\bar{\varepsilon}$, J/K		8155	

As shown in Table above, the average of capacity was 8155 J/K and its relative standard deviation was 0.04%.
In the determination of calorific values, the capacity of calorimeter was checked by GBW 13021 benzoic acid.

Calibration technique

It is necessary to provide a description of the calibration procedure.

The calibration technique is same to that for dodecane.

Measurement:

Measurement conditions:

Ambient temperature, °C 24.4

Relative humidity, % 55

Atmospheric pressure, kPa 99.8

Measurement results

Anthracene

The calorific value of anthracene was determined according to ISO 1928.

Number of experiments: n = _7___

№	**Measurement date**	**Sample weight, g**	**Temperature increase, K**	**Gross calorific value of sample, Q_s^a, kJ/kg**
1	30/05/2024	0.62991	3.0832	39633
2	30/05/2024	0.63243	3.0916	39592
3	30/05/2024	0.63156	3.0896	39619
4	31/05/2024	0.63021	3.0816	39615
5	31/05/2024	0.63189	3.0927	39649
6	31/05/2024	0.63151	3.0870	39599
7	31/05/2024	0.63047	3.0804	39585
Mean value of the gross calorific value, $\overline{Q_s^d}$, kJ/kg				39613

As shown in the table above, the average of gross calorific values (Q_s) was 39613 J/g. The standard deviation was 23 J/g. The relative standard deviation was 0.058%.

Measurement technique

It is necessary to indicate either a reference to a standard method (e.g. ISO 1928) or a detailed description of the measurement technique used to calculate the measurement result and its uncertainty from experimental observations and input data including the measurement equation. If a standard method is used with any changes to it, these changes should be indicated.

Experimentals

The calibration was performed according to ISO 1928. The room temperature ranged from 25.0 to 26.5 °C, the atmospheric pressure ranged from 99.8 to 100.9 kPa, and the relative humidity ranged from 29 to 58%rh. When the mass of anthracene was weighed, the room temperature, atmospheric pressure and humidity were measured simultaneously. Then, the air density was calculated using the temperature, pressure and humidity. The mass in the air was modified into the mass in vacuum by using the air density.

After the measurement, the gross calorific value of anthracene sample (Q_s) was calculated according to Eq. (7).

$$Q_s = \frac{\varepsilon \cdot \Delta T - q_1 - q_2 - q_{\mathrm{HNO_3}}}{m} = \frac{\varepsilon \cdot \Delta T - q_1 - q_2 - q_{\mathrm{HNO_3}}}{m} \tag{7}$$

where Q_s is the gross calorific value of anthracene sample, J/g; m is the mass of anthracene in vacuum, g.

The heat of nitric acid formation is calculated based on Eq. 1.

$$q_{\mathrm{N}} = Q_{\mathrm{HNO_3}} \cdot n_{\mathrm{HNO_3}} = Q_{\mathrm{HNO_3}} \cdot V_{\mathrm{NaOH}} \cdot c_{\mathrm{NaOH}} \tag{1}$$

The residue solution in oxygen bomb was transferred in a beaker and then was heated to boiling. When the solution was cooled, it was titrated by NaOH solution with a mole concentration of 0.10 mol/L using a Metrohm 905 Titrando.

Traceability statement

All the participants must be able to demonstrate traceability to an independent realization of each quantity, or make clear the route of traceability via another named laboratory.

Before the determination of calorific value of sample, the oxygen bomb calorimeter (IKA C6000) was calibrated using the primary CRM for calorific value of benzoic acid (GBW 13021). GBW 13021 with an expanded uncertainty (U_r=0.022%, k=2) was certified using the primary standard for calorific value of solid fuels. This primary standard was calibrated using the electric energy, which makes the calorific value traceable to SI unit of voltage, resistance, time and mass. So, the measured calorific value using IKA C6000 could be traceable to the SI units through the GBW 13021.

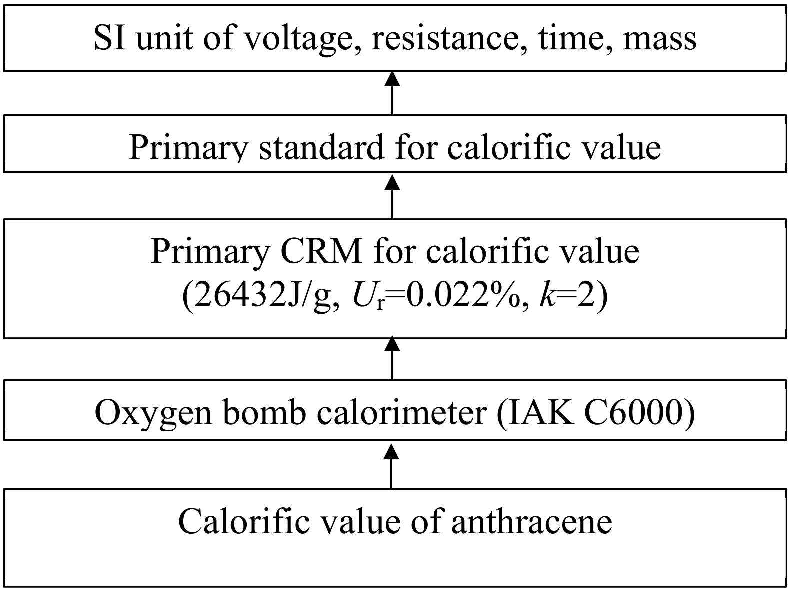


Fig. 2 traeablility chain of calorific value

Equipment used for measurement and calibration

Name of the National Measurement Standard: <u>oxygen bomb calorimeter</u>, comprised of:

№	Name	Manufacturer, model, serial number	Metrological characteristics
1	Oxygen bomb calorimeter	Manufacturer: IKA Inc. from Germany Model: C6000 Serial No.: 100075178	Measurement range: <40,000J Error or measurement: RSD<0.15% uncertainty: / etc.
2	Electric balance	Manufacturer: Mettler-Toledo Inc. from Switzerland Model: XP205 Serial No.: B4421340837	Measurement range: <220g Error or measurement: 0.05mg Uncertainty (*U*, *k*=2): 0.06mg etc.
3	Temperature, humidity and pressure meter	Manufacturer: Testo Inc. from Germany Model: 622 Serial No.: 3958140/0923	*U* of temperature: 0.1 °C *U* of humidity: 0.8 %RH *U* of pressure: 0.04 kPa
4	CRM for caloric value of benzoic acid	Manufacturer: NIM of China CRM No.: GBW 13021	Certified value: 26436J/g Uncertainty of the certified value (U_r, *k*=2): 0.022%

Uncertainty budget

A detailed uncertainty budget should be provided in accordance with the ISO Guide for the Expression of Uncertainty in Measurement (GUM); all the components of the uncertainty should be indicated, and their evaluation must be fully documented. It is also necessary to indicate all the corrections and constants used, and their sources.

$$Q_\mathrm{s} = \frac{\varepsilon \cdot \Delta T - q_1 - q_2 - q_{\mathrm{HNO_3}}}{m} \tag{7}$$

$$Q_\mathrm{s} = \frac{\varepsilon \cdot \Delta T}{m} \tag{8}$$

The gross calorific value of sample (Q_s) was calculated according to Eq. 7. Eq. 7 can be simplified into Eq. 8. So, the uncertainty of calorific value ($u(Q_\mathrm{s})$) was evaluated based on Eq. 8 according to ISO guide Expression of Uncertainty in Measurement.

$$u_\mathrm{c}^2(Q_\mathrm{s}) = u_\mathrm{A}^2(Q_\mathrm{s}) + (\frac{\partial Q_\mathrm{s}}{\partial \varepsilon})^2 \cdot u^2(\varepsilon) + (\frac{\partial Q_\mathrm{s}}{\partial \Delta T})^2 \cdot u^2(\Delta T) + (\frac{\partial Q_\mathrm{s}}{\partial m})^2 \cdot u^2(m) \tag{9}$$

$$c_{(\varepsilon)} = \frac{\partial Q_\mathrm{s}}{\partial \varepsilon} = \frac{\Delta T}{m}$$

$$c_{(\Delta T)} = \frac{\partial Q_\mathrm{s}}{\partial \Delta T} = \frac{\varepsilon}{m}$$

$$c_{(m)} = \frac{\partial Q_\mathrm{s}}{\partial m} = -\frac{\varepsilon \cdot \Delta T}{m^2}$$

Uncertainty of calorific value of sample by Type A method ($u_\mathrm{A}(Q_\mathrm{s})$)

The standard deviation of Q_{s} was 23 J/g. The times of measurement is seven. The standard deviation of the mean was used as the type A uncertainty of Q_{s} ($u_{\mathrm{A}}(Q_{\mathrm{s}})$, 8.7 J/g).

Eq. 2 was simplified as Eq. 6 which was used as the mathematical model for the of $u(\varepsilon)$.

$$\varepsilon \approx \frac{Q_{\mathrm{BA}} m_{\mathrm{BA}}}{\Delta T} \tag{6}$$

According to ISO Guide for GUM, the relative uncertainty of bomb calorific value ($u_{\mathrm{r}}(\varepsilon)$) was calculated based on the uncertainty of Q_{BA}, ΔT and m_{BA} as below.

$$u_{\mathrm{r}}(\varepsilon) = \sqrt{u_{\mathrm{r,A}}(\varepsilon)^2 + u_{\mathrm{r}}(Q_{\mathrm{BA}})^2 + u_{\mathrm{r}}(m_{\mathrm{BA}})^2 + u_{\mathrm{r}}(\Delta T)^2}$$

The uncertainty from the repeatability of measurement results of ε is contained in the uncertainty from the repeatability of measurement results of Q_{s}, so $u_{\mathrm{A,r}}(\varepsilon)$ is omitted. The type B uncertainty of ε mainly come from the uncertainty of calorific value of benzoic acid CRM, mass of benzoic acid and the temperature increase. The relative uncertainty of calorific value of benzoic acid is 0.011%. The relative uncertainty of mass of benzoic acid is 0.003%. The uncertainty of temperature is little. Furthermore, most of the systematic error of temperature was reduced during the calculation of temperature increase. The calibration and measurement procedure employed the same method to determine the temperature increase. Therefore, the systematic error from the temperature increase was reduced further. So, the uncertainty from the temperature increase was omitted. So, $u_{\mathrm{r}}(\varepsilon)$ was 0.012% and $u(\varepsilon)$ was 0.98 J/K.

$$u_{\mathrm{r}}(\varepsilon) = \sqrt{u_{\mathrm{r,A}}(\varepsilon)^2 + u_{\mathrm{r}}(Q_{\mathrm{BA}})^2 + u_{\mathrm{r}}(m_{\mathrm{BA}})^2 + u_{\mathrm{r}}(\Delta T)^2} = \sqrt{0^2 + 0.011\%^2 + 0.003\%^2 + 0^2} = 0.012\%$$

where, $u_{\mathrm{r}}(\varepsilon)$ is the relative uncertainty of ε; $u_{\mathrm{r}}(Q_{\mathrm{BA}})$ is the relative uncertainty of calorific value of benzoic acid CRM; $u_{\mathrm{r}}(m_{\mathrm{BA}})$ is the relative uncertainty of mass of benzoic acid CRM; $u_{\mathrm{r}}(\Delta T)$ is the uncertainty come from the temperature increase.

Uncertainty of temperature increase ($u(\Delta T)$)

As described above, $u(\Delta T)$ is omitted.

Uncertainty of mass of sample ($u(m)$)

$u(m)$ is 0.03 mg.

According to Eq. 9, the $u(Q_{\mathrm{s}})$ was calculated as below.

$$u(Q_{\mathrm{s}}) = \sqrt{u_{\mathrm{A}}^2(Q_{\mathrm{s}}) + (\frac{\Delta T}{m})^2 \cdot u^2(\varepsilon) + (\frac{\varepsilon}{m})^2 \cdot u^2(\Delta T) + (-\frac{\varepsilon \cdot \Delta T}{m^2})^2 \cdot u^2(m)}$$

According to the information listed in the table below, $u(Q_{\mathrm{s}})$ of anthracene was 11 J/g.

$$u(Q_{\mathrm{s}}) = \sqrt{8.7^2 + (4.89 \times 0.98)^2 + (12912 \times 0)^2 + (-63086 \times 0.00003)^2} = 11\,\mathrm{J/g}$$

Finally, the expanded uncertainty of gross calorific value of anthracene (U, k=2) was 22 J/g.

The details of uncertainty budget of calorific value of anthracene samples.

Uncertainty of	Uncertainty source	Sensitivity coefficient	Value of sensitivity	Standard uncertainty of	$u_i = \lvert c_i \rvert u(x_i)$ （J/g）

variance			coefficient	variance	
$u_A(Q_s)$	Repeatability	1	1	8.70(J/g)	10.3
$u(\varepsilon_i)$	Capacity	$\frac{\Delta T}{m}$	4.89	0.98 (J/K)	4.8
$u(\Delta T)$	Temperature increase	$\frac{\varepsilon}{m}$	12912	0 (℃)	0
$u(m)$	Mass of sample	$-\frac{\varepsilon \cdot \Delta T}{m^2}$	-63086	0.00003 (g)	1.9
$u(Q_s)$	Calorific value of sample	/	/	/	11

D.I. Mendeleyev Institute for Metrology (VNIIM)

Measurement Report

Calibration technique

Instrument:

Isoperibolic calorimeter with static bomb "VIM" is a part of the primary standard unit of the combustion energy (GET 16).

Fig. 1 The photograph of Bomb Calorimeter «VIM»

It is located in the Laboratory of Combustion Calorimetry and High-Pure Organic Substances for Metrological Purposes of VNIIM (here and after referred to as the Calorimetric Laboratory of VNIIM). Its scientific activities are connected with the metrological assurance of measuring the combustion energy of all types of fuels.

Resolution of temperature measurements of the calorimetric vessel and the shell is 10^{-5} K.

Certified reference material CRM:

The high-pure benzoic acid K-1 is used as a CRM 262-72 for reproduction of the unit size of combustion energy in bomb calorimetry (Metrology: national standard reference data service 50–83. Benzoic acid. Combustion energy). Its energy of combustion is assumed to be equal to its physical constant (26434,4 ± 0,6) kJ/kg, when it is calculated for vacuum, provided that the molar fraction of the main component of K-1 benzoic acid is not less than $(99{,}995 \pm 0{,}001)$ %. The Calorimetric Laboratory of VNIIM carries out generation of high-pure benzoic acid K-1 and its certification by the molar fraction of the main component by the criometric method, using original equipment, that was designed and built by the Laboratory.

Experimental:

The data processing is performed in accordance with GOST 147-2013 (ISO 1928-2009) Solid mineral fuels — Determination of gross calorific value by the bomb calorimetric method and calculation of net calorific value, GOST 21261-2021 Petroleum products. Method for determination of gross calorific value and calculation of net calorific value and GOST 34100.3-2017/ISO/IEC Guide 98-3:2008 Uncertainty of measurement. Part 3. Guide to the expression of uncertainty in measurement.

The energy equivalent of the calorimeter (C) is determined when burning a briquette of benzoic acid K-1 mass ($m'_{(K1)}$), with a known gross calorific value ($Q_{(K1)}$), by measuring the temperature rise during combustion adjusted for heat transfer (ΔT_{corr1}), taking into account additional factors (ignition energy (Q_{ign}), the energy of formation and dissolution of nitric acid (Q_{HNO_3})):

$$C = \frac{m'_{(K1)} \cdot Q_{(K1)} + Q_{ign} + Q_{HNO_3}}{\Delta T_{corr1}} \qquad (1)$$

Note - the energy of formation and dissolution of nitric acid (Q_{HNO_3}) is equal to zero, because the bomb is purged with the oxygen.

Energy equivalent of the calorimeter

№	Energy equivalent, J/K
1	6983,42
2	6982,48
3	6982,48
4	6983,72
5	6983,71
6	6982,42
Mean value of energy equivalent	6983,04

The mean value of energy equivalent is 6983,04 J/K. The relative standard deviation (RSD) is 0,004%.

The bomb calorific value Q^a_b, J of sample is calculated according to Eq. (2).

$$Q_b^a = \frac{C * \Delta T - Q_1}{m} \qquad (2)$$

where m is the mass of the sample reduced to vacuum, g;

C is the mean value of energy equivalent, J/K;

ΔT is the temperature rise adjusted for heat transfer, K;

Q_1 is the heat released during the combustion of cotton thread, J.

Gross Calorific Value Measurement Report of samples DO-RU and AN-RU

NMI VNIIM
Sample DO-RU

Date: 15.03.2024

Signature: E.N.Korchagina

Measurement conditions:

Ambient temperature, °C	22,0 - 23,4
Relative humidity, %	35,5 - 38,4
Atmospheric pressure, kPa	101,7 – 102,9

Measurement technique:

1) Instrument: Bomb Calorimeter «VIM»
2) Certified reference material (CRM) for calibration: Benzoic acid K-1

Measurement results:

Number of experiments: n=10

№	Measurement date	Gross calorific value an as-determined basis, Q_b^a, kJ/kg	Notes
1	04.03.2024	47319,98	
2	04.03.2024	47294,23	
3	04.03.2024	47325,31	
4	05.03.2024	47315,30	
5	05.03.2024	47319,39	
6	11.03.2024	47324,38	
7	11.03.2024	47293,57	
8	11.03.2024	47314,56	
9	12.03.2024	47333,44	
10	12.03.2024	47327,89	
Mean value of the gross calorific value, kJ/kg			47317
Total results			
Standard uncertainty estimated by type A, u_A, kJ/kg, %			4 0,009
Standard uncertainty estimated by type B, u_B, kJ/kg, %			1,1 0,0023
Total standard uncertainty, u_c, kJ/kg, %			4 0,009
Expanded uncertainty, U, kJ/kg, %			9 0,018

NMI VNIIM
Sample AN-RU

Date: 20.03.2024 Signature: E.N.Korchagina

Measurement conditions:

Ambient temperature, °C	21,9 - 22,6
Relative humidity, %	33,8 - 38,3
Atmospheric pressure, kPa	101,9 – 102,3

Measurement technique:

1) Instrument: Bomb Calorimeter «VIM»
2) Certified reference material (CRM) for calibration: Benzoic acid K-1

Measurement results:

Number of experiments: n=10

№	Measurement date	Gross calorific value an as-determined basis, Q_b^a, kJ/kg	Notes
1	13.03.2024	39613,82	
2	13.03.2024	39631,39	
3	13.03.2024	39638,12	
4	14.03.2024	39635,21	
5	14.03.2024	39626,98	
6	18.03.2024	39630,84	
7	18.03.2024	39641,74	
8	18.03.2024	39621,87	
9	19.03.2024	39628,44	
10	19.03.2024	39611,97	
Mean value of the gross calorific value, kJ/kg			39628
Total results			
Standard uncertainty estimated by type A, u_A, kJ/kg, %			3 0,008
Standard uncertainty estimated by type B, u_B, kJ/kg, %			0,9 0,0023
Total standard uncertainty, u_c, kJ/kg, %			3 0,008
Expanded uncertainty, U, kJ/kg, %			6 0,016

Uncertainty budget

In accordance with GOST 34100.3-2017/ISO/IEC Guide 98-3:2008 Uncertainty of measurement. Part 3. Guide to the expression of uncertainty in measurement, point 5.1.2 total standard uncertainty can be estimated as followed:

$$u_c^2(\mathrm{y}) = \sum_{i=1}^{N} \left(\frac{\partial f}{\partial x_i}\right)^2 u^2\,(x_i) \qquad (5)$$

DO-RU

Variable	Estimation	Unit	Standard uncertainty *u(x_i)*	Type	Sensitivity coefficient (∂f/∂x_i)		Uncertainty *u_i(y)*= (∂f/∂x_i)* *u(x_i)*, kJ/kg
					Value	Unit	
$Q^a{}_b$	47 317	kJ/kg	1,1	B	1	kJ/kg	1,1
$Q^a{}_b$	47 317	kJ/kg	4	A	1	kJ/kg	4
$Q^a{}_b$	**47 317**	**kJ/kg**					4
Total standard uncertainty, u_c, kJ/kg, %							4 0,009
Expanded uncertainty (*P=0,95, k=2*), *U*, kJ/kg, %							**9** **0,018**

AN-RU

Variable	Estimation	Unit	Standard uncertainty *u(x_i)*	Type	Sensitivity coefficient (∂f/∂x_i)		Uncertainty *u_i(y)*= (∂f/∂x_i)* *u(x_i)*, kJ/kg
					Value	Unit	
$Q^a{}_b$	39 628	kJ/kg	0,9	B	1	kJ/kg	0,9
$Q^a{}_b$	39 628	kJ/kg	3	A	1	kJ/kg	3
$Q^a{}_b$	**39 628**	**kJ/kg**					3
Total standard uncertainty, u_c, kJ/kg, %							3 0,008
Expanded uncertainty (*P=0,95, k=2*), *U*, kJ/kg, %							**6** **0,016**

After data processing the following measurement results were obtained:

for DO-RU sample – (47 317±9) kJ/kg;

for AN-RU sample – (39 628±6) kJ/kg.

Republican Unitary Enterprise
"Belarusian State Institute of Metrology"
220053, Minsk, Starovilensky tract, 93. tel. 3350468

Protocol №10-45.1-9-33/55

measurements of specific combustion energy
sample AH-BY (anthracene)(to vacuum)

1. Conditions for carrying out measurements:

- ambient air temperature	21,87 °C - 23,35 °C
- scale display case temperature	21,78 °C - 22,61 °C
- relative humidity	33,1 % - 58,3 %
- atmospheric pressure	99,1 kPa -100,0 kPa

2. Sample Information:

- anthracene sample AH-BY

3. Bomb filling information:

- oxygen pressure, MPa 2,94

4. Measuring instruments used in research:

Table 1

Name and type of measuring instruments	Serial number	Date of last verification/calibration
Liquid bomb calorimeter-comparator	13.02.001	-
Calorimetric bomb	1810366	06.02.2024
Analytical scales XP 205	B132190196	14.12.2023
Laboratory scales XP 8002S	B132190337	14.12.2023
Laboratory electronic thermometer LT-300	301440	27.03.2024
Thermo-hygrometer UniTess THB1	170099	12.02.2024

5. Measurement results:

5.1 External inspection: meets the requirements MVI.MN 4249-2012, GOST 147-2013

5.2 Mass of a calorimetric vessel with water and a bomb : M=5800 g

5.3 Determination of metrological characteristics:

5.3.1 Determination of the specific combustion energy of a sample

Before measuring the specific combustion energy of the anthracene sample AH-BY, the energy equivalent value of the calorimeter is determined, $\bar{C}$=10410,37 J/°C.

The anthracene sample was obtained in the form of tablets. Before testing, the tablets are dried in a desiccator with $CaCl_2$ for at least 72 hours. Immediately before the experiment, the tablet is weighed on an analytical balance, the mass is reduced to vacuum. The tablet is burned in a platinum crucible, a platinum wire is used as an ignition wire. The crucible with the tablet is placed in the ring of the bomb holder. The ends of the ignition wire are fixed on the electrode. The wire is pulled out into a loop, it should fit tightly to the tablet. Using a pipette, (1,0 ± 0,1) cm^3 of distilled water is poured into the bomb body. The bomb is assembled. The bomb is placed in the stand and connected to the device for filling the bomb with oxygen. The bomb is slowly filled with oxygen to a pressure of 2,94 MPa. Then it is placed in a vessel, which is filled with distilled water. The vessel with water and the bomb is weighed and placed in the calorimeter socket. The experiment is conducted. After its completion, the bomb is disassembled, the remains of the ignition wire are collected and weighed on an analytical scale. The lid, body and crucible are washed with distilled water. Two drops of methyl red indicator are added to the wash water and titrated with 0,1 N sodium hydroxide solution to determine the correction for the formation of nitric acid.

The measurement results are processed (table 2-4).

Table 2

№	t,	φ,	p,	*Date*	*Protocol №*	m'	$\bar{C}$,	$\Delta T_{испр2}$,	$q_{вещ}$,
	°*C*	%	*кPa*			*g*	*J/°C*	°*C*	*кДж/кг*
1	22,18	51,1	99,4	25.06.2024	11	0,63683	10410,37	2,42583	39603,61
2	22,14	49,7	99,4	25.06.2024	12	0,63847		2,43211	39604,24
3	22,12	58,3	99,4	26.06.2024	13	0,63752		2,42905	39609,67
4	22,17	50,4	99,4	26.06.2024	14	0,63489		2,41936	39615,77
5	21,90	50,8	100,0	28.08.2024	24	0,63065		2,40288	39612,31
6	21,88	51,8	100,0	28.08.2024	25	0,63686		2,42733	39624,00
7	21,78	54,4	99,9	28.08.2024	26	0,63131		2,40428	39595,37
8	21,92	32,4	99,1	04.09.2024	31	0,63436		2,41926	39650,89
9	22,26	33,1	99,1	04.09.2024	32	0,63688		2,42895	39652,40
10	22,61	33,8	99,1	04.09.2024	33	0,63346		2,41617	39654,61
Average specific energy of combustionя, кJ/кg									39622,29
Standard deviation of the measurement result $S_0(q)$ *with 10 independent measurements, кJ/кg*									7,05
, %									17,79

5.3.2 Determination of the error in the transfer of a unit of combustion energy from a standard to a sample of anthracene

Table 3

Name of metrological characteristics	**The value of the standardized characteristic**	**Designation**
Average specific energy of combustion, кJ/кg	39622,29	$\bar{q} = \frac{C \cdot \Delta T_{испр2} - Q_э - Q_{HNO_3}}{m'_в}$
Standard deviation of the result of measurements of the specific energy of combustion	$17{,}79 \cdot 10^{-5}$	$S(q) = \sqrt{\frac{\sum_{i=1}^{n}(q_i - \overline{q})^2}{n(n-1)}}$ with n=10 $S_o(q) = \frac{S(q)}{\bar{q}}$
Limit of unexcluded systematic error (USE) in measurements of specific combustion energy	$4{,}62 \cdot 10^{-5}$	$\Theta_0(q) = \frac{\Theta(q)}{q} = 1{,}1\sqrt{(S_{\Sigma 0}(C))^2 + (\Theta_0(m'_в))^2 + \left(\Theta_0(\Delta T_{испр2})\right)^2 + (\Theta_0(Q_э))^2 + \left(\Theta_0(Q_{HNO_3})\right)^2 + (\Theta_0(f))^2}$
Standard deviation of the sum of the NSP and random errors in measuring the energy equivalent of benzoic acid K-1	$3{,}09 \cdot 10^{-5}$	$S_{\varepsilon\Sigma o}(C) = \sqrt{(S_o(C))^2 + (S_{\Theta o}(C))^2}$
Error in measuring the mass of a briquette of benzoic acid reduced to vacuum	$2{,}59 \cdot 10^{-5}$	$\Theta_0(m'_в)$

Error in measuring the temperature rise, taking into account the correction for heat exchange	$0{,}12 \cdot 10^{-5}$	$\Theta_0(\Delta T_{\text{испр2}})$
Ignition energy correction calculation error	$0{,}1 \cdot 10^{-5}$	$\Theta_0(Q_э)$
Error in the energy of formation and dissolution of nitric acid	$1 \cdot 10^{-5}$	$\Theta_0(Q_{HNO_3})$
Error in converting combustion energy to standard conditions	$0{,}6 \cdot 10^{-5}$	$\Theta_0(f)$
Standard deviation of the NSP amount	$3{,}50 \cdot 10^{-5}$	$S_{\Theta 0}(q) = \frac{S_\Theta(q)}{q} = \sqrt{(S_{\varepsilon\Sigma 0}(C))^2 + \frac{1}{3}\left((\Theta_0(m'_в))^2 + \left(\Theta_0(\Delta T_{\text{испр2}})\right)^2 + (\Theta_0(Q_э))^2 + \left(\Theta_0(Q_{HNO_3})\right)^2 + (\Theta_0(f))^2\right)}$
Standard deviation of the sum of NSP and random errors in measuring the specific energy of combustion	$18{,}13 \cdot 10^{-5}$	$S_{\varepsilon\Sigma o}(q) = \sqrt{(S_0(q))^2 + (S_{\Theta o}(q))^2}$
Confidence probability coefficient P=0,95	3,59	$t_{\varepsilon\Sigma} = \frac{\Theta_o(q) + t_x S_o(q)}{S_{\Theta o}(q) + S_o(q)}$
Confidence limits of the total error in measuring combustion energy	$65{,}0 \cdot 10^{-5}$ 25,77 кJ/кg	$t_{\varepsilon\Sigma} S_{\varepsilon\Sigma o}(q)$

5.3.3 Estimation of the uncertainty budget for the specific energy of combustion of anthracene

Table 4

Name of metrological characteristics	**The value of the standardized characteristic**	**Designation**
Average specific energy of combustion, кJ/кg	39622,29	$\bar{q} = \frac{\bar{C} \cdot \Delta T_{\text{испр2}} - Q_э - Q_{HNO_3}}{m'_в}$
Standard uncertainty of specific energy of combustion estimated by Type A	$17{,}79 \cdot 10^{-5}$	$u_A(q) = \sqrt{\frac{\sum_{i=1}^{n}(q_i - \overline{q})^2}{n(n-1)}}$ with n=10 $u_{0A}(q) = \frac{u_A(q)}{\bar{q}}$
Type B estimated standard uncertainty	$3{,}42 \cdot 10^{-5}$	$u_{0B}(q) = \sqrt{(u_C(C))^2 + (u_B(m'_в))^2 + \left(u_B(\Delta T_{\text{испр2}})\right)^2 + (u_B(Q_э))^2 + \left(u_B(Q_{HNO_3})\right)^2 + (u_B(f))^2}$
Total uncertainty of measurement of energy equivalent of benzoic acid K-1	$3{,}09 \cdot 10^{-5}$	$u_C(\mathrm{C})$
Uncertainty in the measurement of the mass of a briquette of benzoic acid reduced to vacuum	$1{,}30 \cdot 10^{-5}$	$u_B(m'_в)$
Uncertainty in measuring temperature rise, taking into account heat transfer correction	$0{,}07 \cdot 10^{-5}$	$u_B(\Delta T_{\text{испр2}})$

Uncertainty in calculating the ignition energy correction	$0{,}06 \cdot 10^{-5}$	$u_B(Q_э)$
Uncertainty of the energy of formation and dissolution of nitric acid	$0{,}58 \cdot 10^{-5}$	$u_B(Q_{HNO_3})$
Uncertainty in reducing combustion energy to standard conditions	$0{,}35 \cdot 10^{-5}$	$u_B(f)$
Total standard uncertainty of the result of measurement of the specific energy of combustion	$18{,}12 \cdot 10^{-5}$	$u_C(q) = \sqrt{(u_A(q))^2 + (u_B(q))^2}$
Coverage coefficien, P=0,95	2	k
Expanded uncertainty of the result of determination of combustion energy	$36{,}24 \cdot 10^{-5}$ 14,36 кJ/кgr	$U_P(q) = k \cdot u_C(q)$

Conclusion: The specific combustion energy of the anthracene sample AN-BY is (39622,29±14,36) kJ/kg, where the number following the “±” sign is the numerical value of the expanded uncertainty, which is obtained by multiplying the combined standard uncertainty by the coverage factor k=2, corresponding to a confidence level of approximately 95%, assuming a normal distribution.

Date of research: 25.06.2024-02.09.2024

Measurements were taken:

leading metrology engineer - researcher E.L. Serko

leading metrology engineer - researcher L.I. Minchuk

Republican Unitary Enterprise
"Belarusian State Institute of Metrology"
220053, Minsk, Starovilensky tract, 93. tel. 3350468

Protocol № 10-45.1- 15-30/55
measurements of specific combustion energy dodecane sample DO-BY (dodecane) to vacuum

Factory number of the calorimeter: 13.02.001
Factory number of the calorimetric bomb: 1810366 от 06.02.2024
Methodology for performing measurements: MVI.MN 4249-2012, GOST 21261-2021
Calorimeter operating mode: isoperibol

Conditions for carrying out measurements:

- ambient air temperature	22,27 °C - 23,29 °C
- scale display case temperature	22,29 °C - 22,98 °C
- relative humidity	47,8 5 % - 61,4 %
- atmospheric pressure	99,1 kPa - 99,2 kPa

Sample Information:
- dodecane sample DO-BY от 10.07.2023

Bomb filling information:
- oxygen pressure, MPa 2,94

Measuring instruments used in research:
Table 1

Name and type of measuring instruments	Serial number	Date of last verification/calibratio
Analytical scales XP 205	B132190196	14.12.2023
Laboratory scales XP 8002S	B132190337	14.12.2023
Laboratory electronic thermometer LT-300	301440	27.03.2024
Thermo-hygrometer UniTess THB1	170099	12.02.2024

Measurement results:
External inspection: meets the requirements MVI.MN 4249-2012, GOST 21261-2021
Determination of metrological characteristics:
Determination of the specific combustion energy of a sample
Mass of a calorimetric vessel with water and a bomb : M=5800 g

Before measuring the specific combustion energy of the dodecane sample DO-BY, the energy equivalent value of the calorimeter is determined, $\bar{C}$=10410,37 J/°C.

The dodecane sample was obtained in the form of ampoules with liquid dodecane. Immediately before the experiment, the sample is injected into a platinum crucible with a syringe and weighed on an analytical balance, the mass is reduced to vacuum. A platinum wire is used as an ignition wire. The crucible with the sample is placed in the ring of the bomb holder. The ends of the ignition wire are fixed on the electrode. The wire is pulled into a loop, the pulled middle part of the wire should be immersed in the sample. Using a pipette, (1,0 ± 0,1) cm^3 of distilled water is poured into the bomb body. The bomb is assembled. The bomb is placed in the stand and connected to the device for filling the bomb with oxygen. The bomb is slowly filled with oxygen to a pressure of 2.94 MPa. Then it is placed in a vessel, which is filled with distilled water. The vessel with water and the bomb is weighed and placed in the calorimeter socket. The experiment is conducted. After its completion, the bomb is disassembled, the remains of the ignition wire are collected and weighed on an analytical scale. The lid, body and crucible are washed with distilled water. Two drops of methyl red indicator are added to the wash water and titrated with 0,1 N sodium hydroxide solution to determine the correction for the formation of nitric acid.

The measurement results are processed (table 2-4).

Таблица 2

№	*t,*	*φ,*	*p,*	*Date*	*Protocol №*	*m′ ,*	*c̄ ,*	$\Delta T_{\text{испр2}}$,	*q ,*
	°C	%	*кПа*			*г*	*J/°C*	°C	*кДж/кг*
1	22,78	47,8	99,2	26.06.2024	16	0,59708	10410,37	2,72037	47321,08
2	22,53	58,4	99,2	27.06.2024	17	0,61316		2,79341	47332,01
3	22,77	50,0	99,2	27.06.2024	18	0,57323		2,61179	47303,99
4	22,98	48,2	99,1	27.06.2024	19	0,55659		2,53528	47313,21
5	22,29	54,3	99,2	28.06.2024	21	0,56077		2,55580	47338,35
6	22,29	54,4	99,2	27.06.2024	22	0,48649		2,21730	47332,81
7	22,67	65,8	99,8	30.08.2024	27	0,50201		2,28824	47308,91
8	23,51	57,8	99,5	02.09.2024	28	0,50049		2,28184	47311,75
9	21,97	49,7	99,4	02.09.2024	29	0,51972		2,36979	47334,80
10	21,97	52,7	100	04.09.2024	30	0,50773		2,31533	47315,38
Average specific energy of combustionя, кJ/кg									47321,23
Standard deviation of the measurement result $S_0(q)$ *with 10 independent measurements, кJ/кg*									3,89
, %									8,23

2.2 Determination of the error in the transfer of a unit of combustion energy from a standard to a sample of dodecane

Table 3

Name of metrological characteristics	**The value of the standardized characteristic**	**Designation**
Average specific energy of combustion, кJ/кg	47321,23	$\bar{q} = \frac{C \cdot \Delta T_{\text{испр2}} - Q_э - Q_{HNO_3}}{m'_{\text{в}}}$
Standard deviation of the result of measurements of the specific energy of combustion	$8{,}23 \cdot 10^{-5}$	$S(q) = \sqrt{\frac{\sum_{i=1}^{n}(q_i - \overline{q})^2}{n(n-1)}}$ with n=10 $S_o(q) = \frac{S(q)}{\bar{q}}$
Limit of unexcluded systematic error (USE) in measurements of specific combustion energy	$4{,}60 \cdot 10^{-5}$	$\Theta_0(q) = \frac{\Theta(q)}{q} = 1{,}1\sqrt{(S_{\Sigma 0}(C))^2 + (\Theta_0(m'_{\text{в}}))^2 + \left(\Theta_0(\Delta T_{\text{испр2}})\right)^2 + (\Theta_0(Q_э))^2 + \left(\Theta_0(Q_{HNO_3})\right)^2 + (\Theta_0(f))^2}$
Standard deviation of the sum of the NSP and random errors in measuring the energy equivalent of benzoic acid K-1	$3{,}09 \cdot 10^{-5}$	$S_{\varepsilon\Sigma o}(C) = \sqrt{(S_o(C))^2 + (S_{\Theta o}(C))^2}$
Error in measuring the mass of a briquette of benzoic acid reduced to vacuum	$2{,}56 \cdot 10^{-5}$	$\Theta_0(m'_{\text{в}})$
Error in measuring the temperature rise, taking into account the correction for heat exchange	$0{,}13 \cdot 10^{-5}$	$\Theta_0(\Delta T_{\text{испр2}})$
Ignition energy correction calculation error	$0{,}1 \cdot 10^{-5}$	$\Theta_0(Q_э)$
Error in the energy of formation and dissolution of nitric acid	$1 \cdot 10^{-5}$	$\Theta_0(Q_{HNO_3})$
Error in converting combustion energy to standard conditions	$0{,}6 \cdot 10^{-5}$	$\Theta_0(f)$
Standard deviation of the NSP amount	$3{,}49 \cdot 10^{-5}$	$S_{\Theta 0}(q) = \frac{S_\Theta(q)}{q} = \sqrt{(S_{\varepsilon\Sigma 0}(C))^2 + \frac{1}{3}\left((\Theta_0(m'_{\text{в}}))^2 + \left(\Theta_0(\Delta T_{\text{испр2}})\right)^2 + (\Theta_0(Q_э))^2 + \left(\Theta_0(Q_{HNO_3})\right)^2 + (\Theta_0(f))^2\right)}$
Standard deviation of the sum of NSP and random errors in measuring the specific energy of combustion	$8{,}94 \cdot 10^{-5}$	$S_{\varepsilon\Sigma o}(q) = \sqrt{(S_0(q))^2 + (S_{\Theta o}(q))^2}$
Confidence probability coefficient P=0,95	1,98	$t_{\varepsilon\Sigma} = \frac{\Theta_o(q) + t_x S_o(q)}{S_{\Theta o}(q) + S_o(q)}$
Confidence limits of the total error in measuring combustion energy	$17{,}7 \cdot 10^{-5}$ 8,38 кJ/кg	$t_{\varepsilon\Sigma} S_{\varepsilon\Sigma 0}(q)$

2.3 Estimation of the uncertainty budget for the specific energy of combustion of dodecane

Table 4

Name of metrological characteristics	The value of the standardized characteristic	Designation
Average specific energy of combustion, кJ/кg	47321,23	$\bar{q} = \frac{\bar{C} \cdot \Delta T_{\text{испр2}} - Q_{\text{э}} - Q_{HNO_3}}{m'_{\text{в}}}$
Standard uncertainty of specific energy of combustion estimated by Type A	$8{,}23 \cdot 10^{-5}$	$u_A(q) = \sqrt{\frac{\sum_{i=1}^{n}(q_i - \bar{q})^2}{n(n-1)}}$ $u_{0A}(q) = \frac{u_A(q)}{\bar{q}}$ with n=10
Type B estimated standard uncertainty	$3{,}41 \cdot 10^{-5}$	$u_{0B}(q) = \sqrt{(u_C(C))^2 + (u_B(m'_{\text{в}}))^2 + (u_B(\Delta T_{\text{испр2}}))^2 + (u_B(Q_{\text{э}}))^2 + (u_B(Q_{HNO_3}))^2 + (u_B(f))^2}$
Total uncertainty of measurement of energy equivalent of benzoic acid K-1	$3{,}09 \cdot 10^{-5}$	$u_C(\text{C})$
Uncertainty in the measurement of the mass of a briquette of benzoic acid reduced to vacuum	$1{,}28 \cdot 10^{-5}$	$u_B(m'_{\text{в}}) = \frac{U(m'_{\text{в}})}{k}$
Uncertainty in measuring temperature rise, taking into account heat transfer correction	$0{,}07 \cdot 10^{-5}$	$u_B(\Delta T_{\text{испр2}})$
Uncertainty in calculating the ignition energy correction	$0{,}06 \cdot 10^{-5}$	$u_B(Q_{\text{э}})$
Uncertainty of the energy of formation and dissolution of nitric acid	$0{,}58 \cdot 10^{-5}$	$u_B(Q_{HNO_3})$
Uncertainty in reducing combustion energy to standard conditions	$0{,}35 \cdot 10^{-5}$	$u_B(f)$
Total standard uncertainty of the result of measurement of the specific energy of combustion	$8{,}91 \cdot 10^{-5}$	$u_C(q) = \sqrt{(u_A(q))^2 + (u_B(q))^2}$
Coverage coefficien, P=0,95	2	k
Expanded uncertainty of the result of determination of combustion energy	$17{,}82 \cdot 10^{-5}$ 8,43 кJ/кg	$U_P(q) = k \cdot u_C(q)$

Conclusion: The specific combustion energy of the dodecane sample is (47321,23±8,43) kJ/kg, where the number following the "±" sign is the numerical value of the expanded uncertainty, which is obtained by multiplying the combined standard uncertainty by the coverage factor k=2, corresponding to a confidence level of approximately 95%, assuming a normal distribution.

Date of research: 26.06.2024-04.09.2024

Measurements were taken:

leading metrology engineer - researcher E.L. Serko

leading metrology engineer - researcher L.I. Minchuk