COOMET. T-S4

COOMET PROJECT 744/RU-a/18

Supplementary Comparison in Thermometry, Thermophysical quantities

Comparison of combustion energy of coal samples with different sulfur content

FINAL REPORT

Pilot

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Final Report
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Abstract

The COOMET project 744/RU-a/18 was organized for the purpose of determination of the degree of equivalence of the national standards for combustion energy measurement. Three coal samples with different values of sulfur content (AH – 1,192 %, AL – 0,193 %, LC – 0,412 %) were used in the comparison. Six laboratories participated between July 2019 and November 2020: VNIIM, Russia; NIM, China; BelGIM, Belarus; BRML-NIM, Romania; UME, Turkey; PTB, Germany. All the participants sent their measurement reports to the coordinator. The measurement results were provided with the detailed uncertainty budgets of the participants. The reference value was determined in accordance with CIPM MRA *"Guidelines for organizing, participating and reporting"* and COOMET-R/GM/19:2016 *"COOMET Recommendation Guideline on COOMET supplementary comparison evaluation*". The degree of equivalence with the reference value was calculated for each sample and laboratory. The reported results were inconsistent, thus it was found necessary to process the data using DerSimonian-Laird method.

CONTENTS

Introduction

The scope of this work was the comparison of combustion energy of coal samples with different sulfur content. Measurements of combustion energy were taken with bomb calorimeters of Russia, Germany, Belarus, Romania, Turkey and China. The pilot laboratory (coordinator) was the VNIIM Laboratory of Calorimetry (Russia).

The samples were prepared by the coordinator VNIIM Laboratory of Calorimetry (Russia). These samples were presented in the powder form with grain size of no more than 212 μm. The samples were divided into equal parts of 30 g each and then were placed into dark hermetically sealed plastic containers. The coal samples heterogeneity was evaluated and stability was confirmed. Each participant received a marked copy of each sample prepared by the pilot laboratory.

Each sample was accompanied with an Information Sheet indicating period of time for the measurements to be made, value of the sulfur content and its uncertainty, uncertainty due to heterogeneity determined during sample preparation, and other additional information.

VNIIM shipped one copy of each sample to the participants through a shipping company. Where possible, VNIIM transferred the sample to a participant personally during any visits by one of the parties to another.

After receiving the samples and providing measurements, the participants sent a protocol to the coordinator.

Notation used

Notation	Description
Q^d_s	gross calorific value on a dry basis, kJ/kg
Q^a_s	gross calorific value on an as-determined basis, kJ/kg
$u(Q^a_s)$	uncertainty of gross calorific values on an as-determined value, kJ/kg
W^a	moisture content, %
$u(W^a)$	uncertainty of moisture content determination, %
n=6	number of participants of comparisons
q_j	measured value of specific combustion energy of the sample in the j-th experiment, kJ/kg
r	number of measurements
x_i	comparisons result obtained by the i-th participant ($x_i \equiv \overline{q}_j$), kJ/kg
u_A	standard uncertainty estimated by Type A, which was obtained during measurement of specific combustion energy, kJ/kg
u(m)	uncertainty of coal sample mass, kJ/kg
$u(Q_{HNO3})$	uncertainty of formation heat of nitric acid, kJ/kg
S^a	sulfur content, %
$u(S^a)$	uncertainty of sulfur content, kJ/kg
u_B	standard uncertainty estimated by Type B, kJ/kg
u_C	total standard uncertainty (quadratic sum of the uncertainties due to different sources) , kJ/kg
U	expanded uncertainty with the coverage factor k, kJ/kg. In this case k = 2
x_{ref}	reference value of the comparisons, kJ/kg

1 Participants of the Comparison

In the COOMET regional comparison took part six 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	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	Physikalisch-Technische Bundesanstalt (PTB)	Germany	Address: Bundesallee 100, 38116 Braunschweig, Germany E-mail: kai.moshammer@ptb.de Phone: + 49 531 592 3300 Contact person: Kai Moshammer
3	Romanian Bureau of Legal Metrology (BRML-NIM)	Romania	Address: 11 Sos. Vitan Bârzesti 75669 Bucharest Romania E-mail: camelia.stratulat@inm.ro Phone: +40 0758041556 Contact person: Camelia Stratulat
4	TÜBİTAK National Metrology Institute (UME)	Turkey	Address: Gebze Yerleşkesi Barış Mah. Dr. Zeki Acar Cad. No:1 41470 Gebze Kocaeli E-mail: kemal.ozcan@tubitak.gov.tr Phone: + 90 262 679 5000 ext. 6405 Contact person: Kemal Özcan
5	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
6	National Institute of Metrology (NIM)	China	Address: No.18, Bei San Huan Dong Lu, Chaoyang Dist Beijing 100029, P.R.China E-mail: wanghf@nim.ac.cn Phone: +86-10-64218565 Contact person: Wang Haifeng

A summary of the information about instruments and certified reference materials used by the participants is shown in Table 2.

Table 2 – Instruments and certified reference materials

NMI	Instrument	Certified reference material
VNIIM	Bomb Calorimeter "VIM"	Benzoic acid K-1
PTB	PARR 6200	Certified standard benzoic acid
BRML-NIM	PARR 6200	39j benzoic acid
UME	LECO AC600	39j benzoic acid
BelGIM	Liquid bomb comparative calorimeter with isothermal shell	Benzoic acid K-1
NIM	IKA C6000	Benzoic acid GBW 13021

2 The Comparison scheme

The comparison coordinator sent the Technical Protocol to the participants. The Technical Protocol established 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 was necessary to carry out calibration of the reference calorimeter, prepare the sample for combustion, and take measurements.

The Technical Protocol was 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 prepared samples and sent them to the participants. Participants performed measurements of the combustion energy of samples and processed the results of measurements. Participants sent the results to the coordinator for further analysis and preparation of the Final report.

3 Samples for the Comparison

All samples were prepared by the comparison coordinator VNIIM Laboratory of Calorimetry (Russia). VNIIM sent one copy of each sample to the participants of the comparison with the markings given in Table 3.

Table 3 – Marking of the samples used for the comparison

№	Sample name	Researcher	Identical to
1	AL-RU	VNIIM (Russia)	AL-DE, AL-RO, AL-TR, AL-BY, AL-CH
2	AL-DE	PTB (Germany)	AL-RU, AL-RO, AL-TR, AL-BY, AL-CH
3	AL-RO	BRML-NIM (Romania)	AL-RU, AL-DE, AL-TR, AL-BY, AL-CH
4	AL-TR	UME (Turkey)	AL-RU, AL-DE, AL-RO, AL-BY, AL-CH
5	AL-BY	BelGIM (Belarus)	AL-RU, AL-DE, AL-RO, AL-TR, AL-CH
6	AL-CH	NIM (China)	AL-RU, AL-DE, AL-RO, AL-TR, AL-BY
7	AH-RU	VNIIM (Russia)	AH-DE, AH-RO, AH-TR, AH-BY, AH-CH
8	AH-DE	PTB (Germany)	AH-RU, AH-RO, AH-TR, AH-BY, AH-CH
9	AH-RO	BRML-NIM (Romania)	AH-RU, AH-DE, AH-TR, AH-BY, AH-CH
10	AH-TR	UME (Turkey)	AH-RU, AH-DE, AH-RO, AH-BY, AH-CH
11	AH-BY	BelGIM (Belarus)	AH-RU, AH-DE, AH-RO, AH-TR, AH-CH
12	AH-CH	NIM (China)	AH-RU, AH-DE, AH-RO, AH-TR, AH-BY
13	LC-RU	VNIIM (Russia)	LC-DE, LC-RO, LC-TR, LC-BY, LC-CH
14	LC-DE	PTB (Germany)	LC-RU, LC-RO, LC-TR, LC-BY, LC-CH

15	LC-RO	BRML-NIM (Romania)	LC-RU, LC-DE, LC-TR, LC-BY, LC-CH
16	LC-TR	UME (Turkey)	LC-RU, LC-DE, LC-RO, LC-BY, LC-CH
17	LC-BY	BelGIM (Belarus)	LC-RU, LC-DE, LC-RO, LC-TR, LC-CH
18	LC-CH	NIM (China)	LC-RU, LC-DE, LC-RO, LC-TR, LC-BY

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

Each sample is accompanied by a corresponding label:

Comparison sample	
Material	Anthracite
Name	**AL-RU**
Weight	30 g
Manufacturer	VNIIM, Russia
For research in	**VNIIM, Russia**
Identical to	AL-DE, AL-RO, AL-TR, AL-BY, AL-CH
Packaged	DD/MM/YYYY

Comparison sample	
Material	Anthracite
Name	**AH-RU**
Weight	30 g
Manufacturer	VNIIM, Russia
For research in	**VNIIM, Russia**
Identical to	AH-DE, AH-RO, AH-TR, AH-BY, AH-CH
Packaged	DD/MM/YYYY

Comparison sample	
Material	Lean coal
Name	**LC-RU**
Weight	30 g
Manufacturer	VNIIM, Russia
For research in	**VNIIM, Russia**
Identical to	LC-DE, LC-RO, LC-TR, LC-BY, LC-CH
Packaged	DD/MM/YYYY

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 4.

Table 4 – Measurement results of the gross calorific value on a dry basis

Participant	**Measurement period**	**Gross calorific value on a dry basis, Q_s^d, kJ/kg**	**u_A, %**	**Moisture content, W^a, %**	**Number of experiments, r**
AL					
NIM	August 2019	31705	0,026	3,12	6
VNIIM	December 2019	31795	0,042	2,50	6
BelGIM	January 2020	31694	0,009	2,45	6
BRML-NIM	March 2020	31829	0,009	2,52-2,60	10
UME	November 2020	31787	0,013	3,86-4,12	6
PTB	October 2020	31270	0,067	2,63	5
AH					
NIM	August 2019	32099	0,038	2,64-2,73	6
VNIIM	December 2019	32298	0,047	2,00	6
BelGIM	January 2020	32084	0,009	1,97	6
BRML-NIM	April 2020	32182	0,008	2,32-2,38	10
UME	November 2020	32395	0,056	2,68-2,96	6
PTB	October 2020	32000	0,047	2,43	5
LC					
NIM	July 2019	30782	0,030	1,58	6
VNIIM	December 2019	30693	0,017	1,00	6
BelGIM	November 2019	30677	0,009	1,36	6
BRML-NIM	March 2020	30773	0,008	1,36-1,48	10
UME	November 2020	30738	0,031	1,51-1,75	6
PTB	October 2020	30600	0,088	1,31	5

Each laboratory used its accepted measurement practice of gross calorific value of solid fuels taking into account the information given in the Information Sheet. It was recommended to bring the sample to an air-dried basis before carrying out measurements. The determined value is the gross calorific value. It has to be recalculated to a dry basis of the fuel. Conversion of the gross calorific value to a dry basis (Q_s^d) should be made according to the following formula:

$$Q_s^d = Q_s^a \cdot \frac{100}{100 - W^a} \quad (1)$$

where:

Q_s^d – gross calorific value on a dry basis;

Q_s^a – gross calorific value on an as-determined basis;

W^a – moisture content.

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 in calculation of the arithmetic mean and estimation of the standard uncertainties u_A, u_B and u_C.

Each participant evaluates the components of the measurement uncertainty in accordance with the accepted reference documents.

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 5, 6 and 7 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 coal samples from the Participants – Sample AH (at 25 °C)

The measurement results of combustion energy of coals received from the participants of the comparison (Sample AH) are given in Table 5.

Table 5 – Measurement results of combustion energy of coals (Sample AH)

Sample AH Gross calorific value on a dry basis, Q^d_s, kJ/kg						
Participant	NIM	VNIIM	BelGIM	BRML-NIM	UME	PTB
№ of measurement	q_j, kJ/kg	q_j, kJ/kg	q_j, kJ/kg	q_j, kJ/kg	q_j, kJ/kg	q_j, kJ/kg
1	32127	32293	32079	32196	32413	31994
2	32092	32268	32089	32176	32344	31996
3	32078	32258	32078	32176	32422	32032
4	32071	32279	32096	32183	32335	31942
5	32080	32339	32087	32186	32442	32019
6	32144	32347	32080	32174	32416	
7				32175		
8				32185		
9				32193		
10				32172		
r	6	6	6	10	6	5
$\bar{q} = \frac{\sum_{j=1}^{m} q_j}{r}$, kJ/kg	32099	32298	32084	32182	32395	32000
$u_A = \sqrt{\frac{\sum_{j=1}^{m} (q_j - \bar{q})^2}{r(r-1)}}$, kJ/kg	12	15	2,8	2,6	18	15
u_B, kJ/kg	20	7,0	17	10	17	63
$u_c = \sqrt{u_A^2 + u_B^2}$, kJ/kg	23	17	17	10	25	65
$U = ku_c$, kJ/kg, k=2, P=0,95	46	34	34	21	50	130

5.2 Measurement results of combustion energy of coal samples from the Participants – Sample AL (at 25 °C)

The measurement results of combustion energy of coals received from the participants of the comparison (Sample AL) are given in Table 6.

Table 6 – Measurement results of combustion energy of coals (Sample AL)

Sample AL Gross calorific value on a dry basis, Q^d_s, kJ/kg						
Participant	NIM	VNIIM	BelGIM	BRML-NIM	UME	PTB
№ of measurement	q_j, kJ/kg	q_j, kJ/kg	q_j, kJ/kg	q_j, kJ/kg	q_j, kJ/kg	q_j, kJ/kg
1	31728	31834	31700	31837	31778	31187
2	31713	31841	31688	31836	31789	31318
3	31686	31786	31694	31838	31789	31275
4	31681	31768	31705	31834	31802	31258
5	31695	31769	31692	31838	31773	31285
6	31725	31776	31688	31822	31791	
7				31818		
8				31833		
9				31818		
10				31819		
r	6	6	6	10	6	5
$\bar{q} = \frac{\sum_{j=1}^{m} q_j}{r}$, kJ/kg	31705	31795	31694	31829	31787	31270
$u_A = \sqrt{\frac{\sum_{j=1}^{m} (q_j - \bar{q})^2}{r(r-1)}}$, kJ/kg	8,2	13	2,8	2,9	4,2	22
u_B, kJ/kg	19	6,1	12	11	13	72
$u_c = \sqrt{u_A^2 + u_B^2}$, kJ/kg	21	14	13	11	14	75
$U = ku_c$, kJ/kg, k=2, P=0,95	42	30	26	22	28	150

5.3 Measurement results of combustion energy of coal samples from the Participants – Sample LC (at 25 °C)

The measurement results of combustion energy of coals received from the participants of the comparison (Sample LC) are given in Table 7.

Table 7 – Measurement results of combustion energy of coals (Sample LC)

Sample LC Gross calorific value on a dry basis, Q^d_s, kJ/kg						
Participant	NIM	VNIIM	BelGIM	BRML-NIM	UME	PTB
№ of measurement	q_j, kJ/kg	q_j, kJ/kg	q_j, kJ/kg	q_j, kJ/kg	q_j, kJ/kg	q_j, kJ/kg
1	30760	30676	30676	30770	30759	30603
2	30777	30700	30690	30762	30714	30517
3	30762	30701	30669	30766	30725	30551
4	30819	30680	30679	30771	30714	30645
5	30779	30710	30673	30781	30751	30659
6	30798	30689	30673	30766	30766	
7				30782		
8				30779		
9				30782		
10				30771		
r	6	6	6	10	6	5
$\bar{q} = \frac{\sum_{j=1}^{m} q_j}{r}$, kJ/kg	30782	30693	30677	30773	30738	30600
$u_A = \sqrt{\frac{\sum_{j=1}^{m} (q_j - \bar{q})^2}{r(r-1)}}$, kJ/kg	9,2	5,3	2,9	2,4	9,5	27
u_B, kJ/kg	19	7,9	12	12	13	59
$u_c = \sqrt{u_A^2 + u_B^2}$, kJ/kg	21	9,5	12	12	16	65
$U = ku_c$, kJ/kg, k=2, P=0,95	42	19	24	24	32	130

6 The second stage of the measurement results analysis

The processing of the comparison results was performed in accordance with CIPM MRA-G-11 Measurement comparisons in the CIPM MRA *"Guidelines for organizing, participating and reporting"* and COOMET-R/GM/19:2016 *"COOMET Recommendation Guideline on COOMET supplementary comparison evaluation*". It has shown that received results are inconsistent. There was an assumption that it could be connected with the stability of the samples. Several laboratories took measurements later than it was specified in the comparison schedule due to the COVID-19 pandemic.

To clarify whether the samples are stable the additional measurements of the combustion energy of all coal samples (AL, AH, LC) were carried out to by the comparison coordinator VNIIM Laboratory of Calorimetry. These measurements are marked as VNIIM_2021. The results are shown in fig. 2, 3, 4.

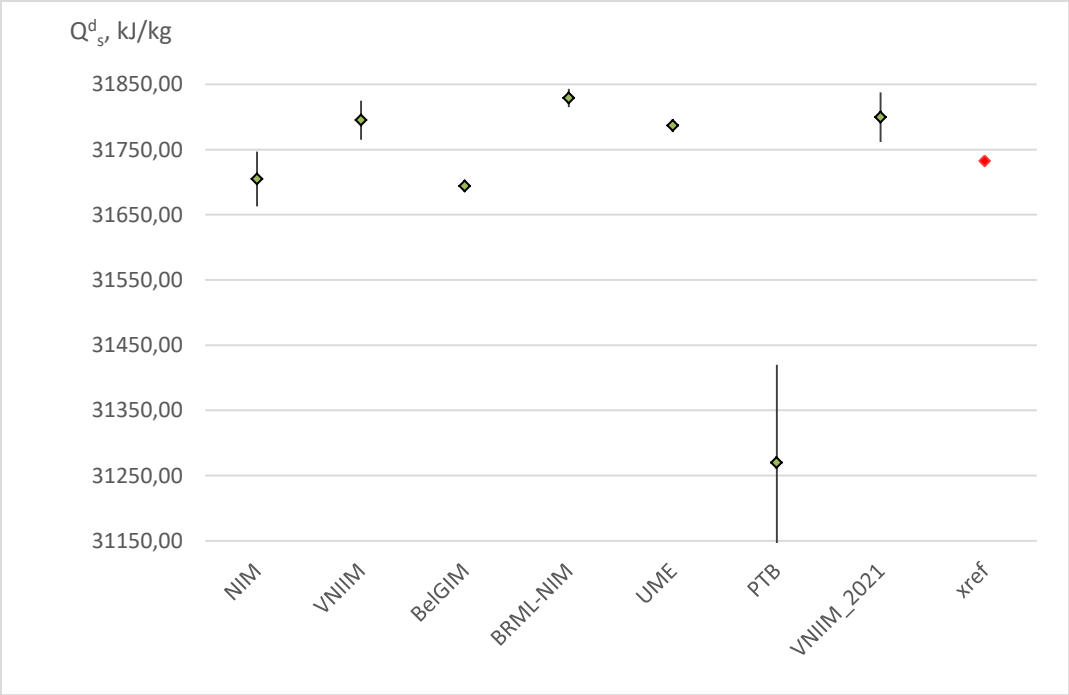


Fig. 2. Comparison results for the sample AL

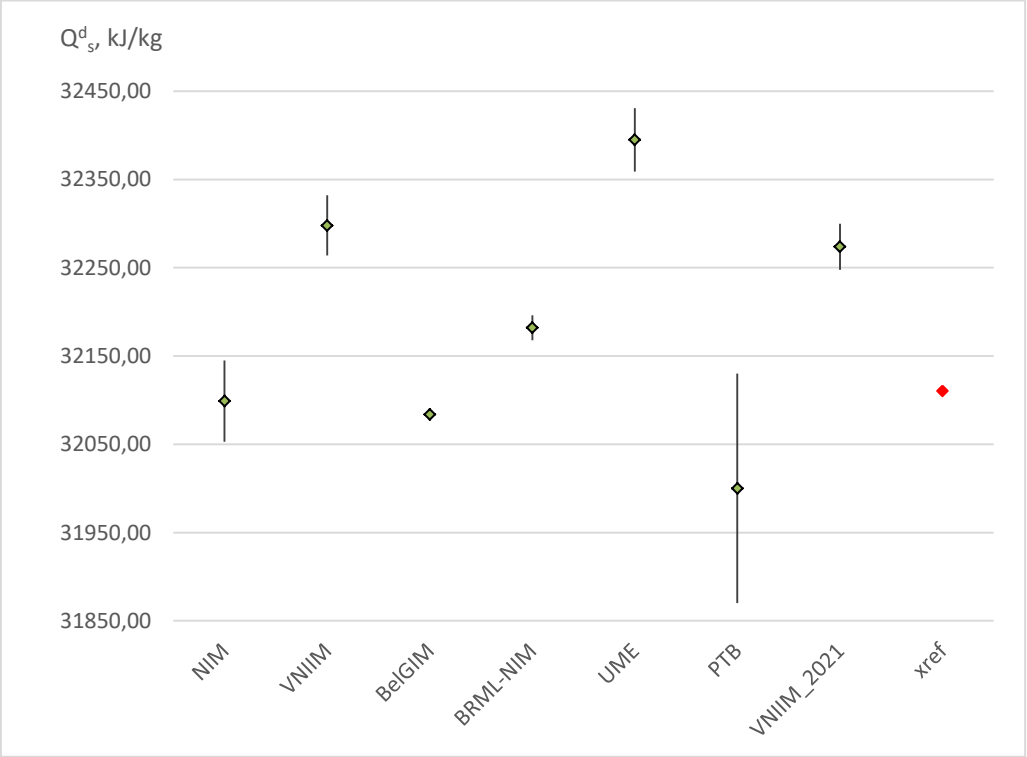


Fig. 3. Comparison results for the sample AH

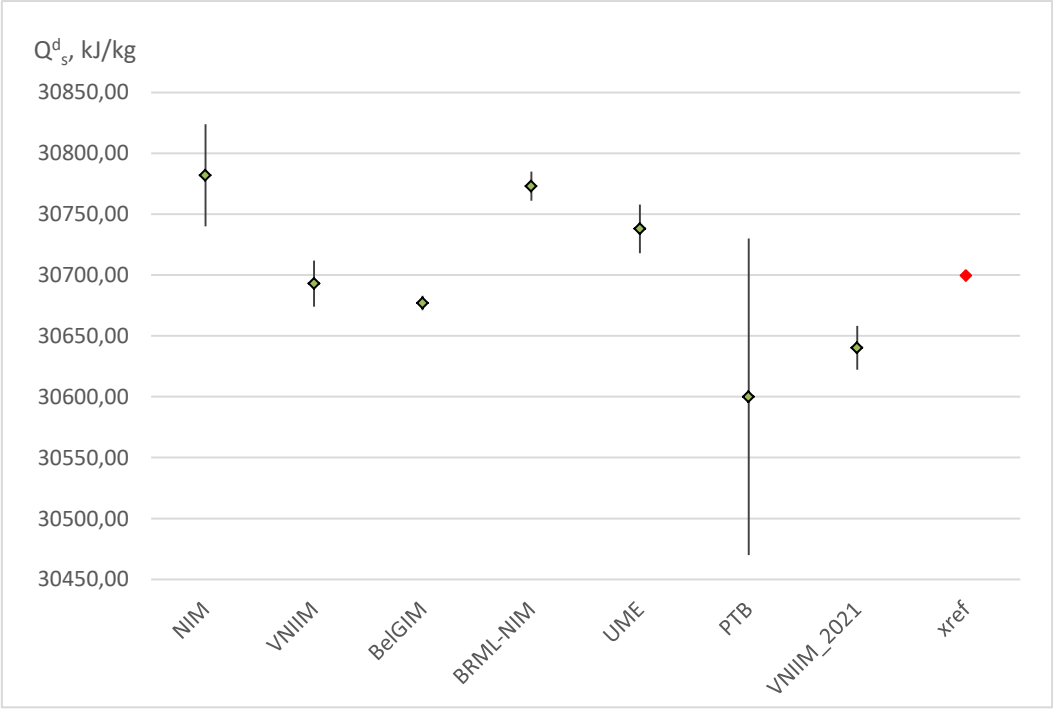


Fig. 4. Comparison results for the sample LC

The additional measurements reproducibility of the combustion energy showed that all the samples are stable. Thus, it was suggested to check the obtained results for the existence of unaccounted influencing factor.

Therefore, another method of data processing called DerSimonian-Laird procedure was applied. It is described in *"NIST Consensus Builder User's Manual"* Appendix 2.

The DerSimonian-Laird procedure implements a random effects model that expresses each measured value as an additive superposition of three elements for each of laboratories: the measurand, the denote laboratory (or, method) effects, the represent measurement error.

6.1 Comparison results for the sample AH

Table 8 – Comparison results for the sample AH

Participant	x_i, kJ/kg	u_C, kJ/kg	U, kJ/kg
NIM	32099	111	222
VNIIM	32298	110	220
BelGIM	32084	110	220
BRML-NIM	32182	109	218
UME	32395	111	223
PTB	32000	126	253

The comparison results for the sample AH are shown in the fig.5.

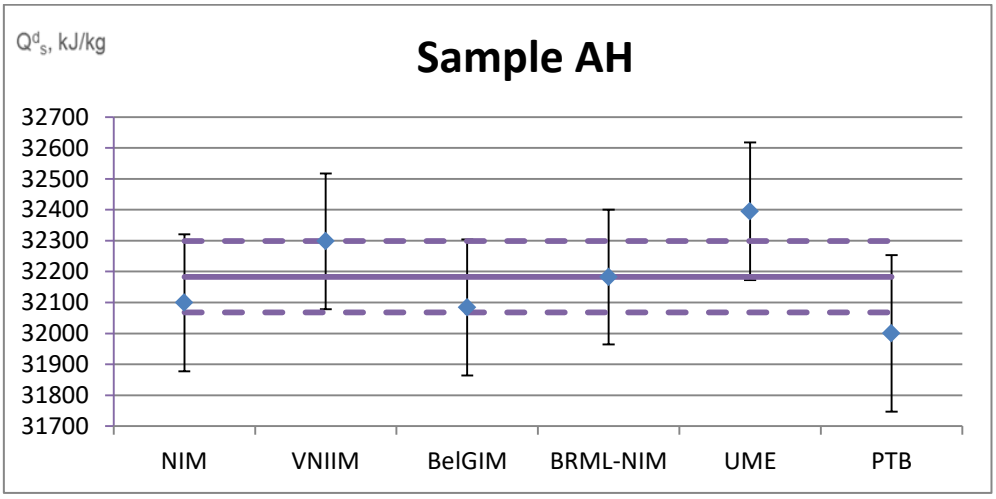


Fig. 5. Comparison results for the sample AH

6.2 Comparison results for the sample AL

Table 9 – Comparison results for the sample AL

Participant	x_i , kJ/kg	u_C , kJ/kg	U , kJ/kg
NIM	31705	79	157
VNIIM	31795	77	154
BelGIM	31694	77	154
BRML-NIM	31829	76	143
UME	31787	77	154
PTB	31270	107	213

The comparison results for the sample AL are shown in the fig.6.

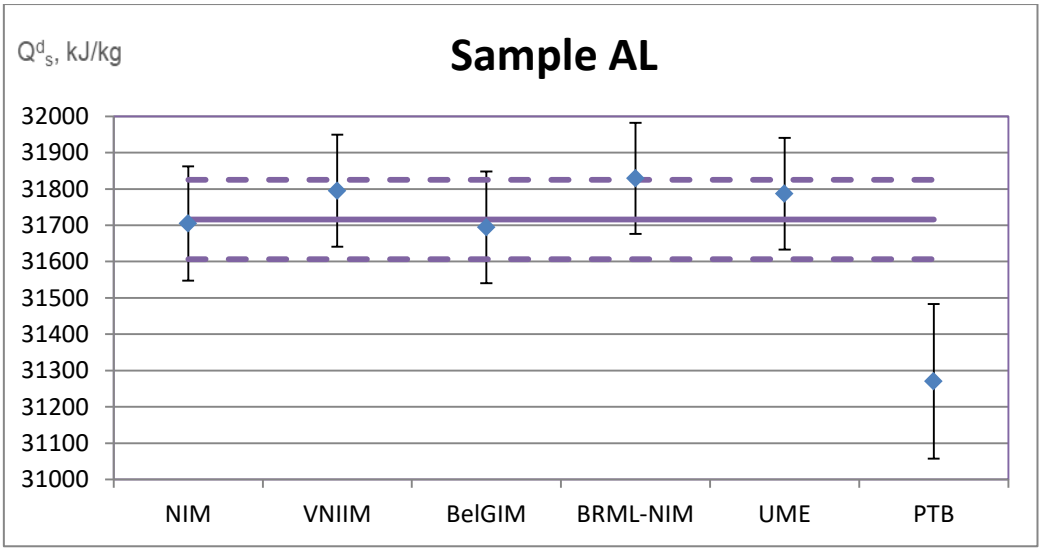


Fig. 6. Comparison results for the sample AL

6.3 Comparison results for the sample LC

Table 10 – Comparison results for the sample LC

Participant	x_i, kJ/kg	u_C, kJ/kg	U, kJ/kg
NIM	30782	50	99
VNIIM	30693	46	92
BelGIM	30677	47	93
BRML-NIM	30773	47	93
UME	30738	48	96
PTB	30600	79	158

The comparison results for the sample LC are shown in the fig.7.

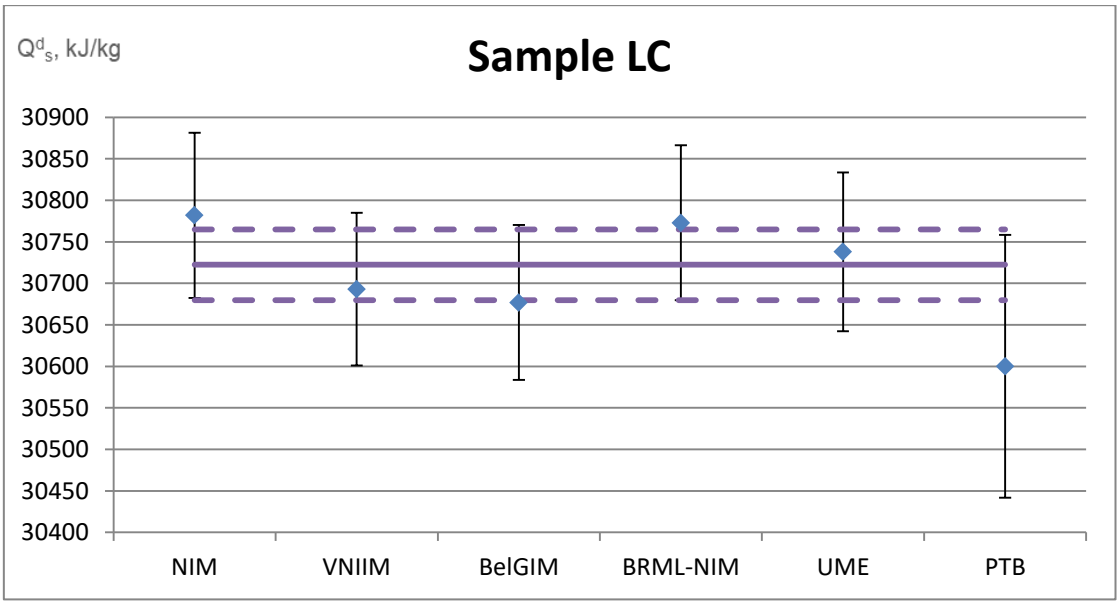


Fig. 7. Comparison results for the sample LC

After data processing using the DerSimonian-Liard method the following reference values were obtained:

for AH sample – 32183±116 kJ/kg;

for AL sample – 31716±109 kJ/kg;

for LC sample – 30722±43 kJ/kg.

7 Checking the comparison data consistency

In accordance with COOMET R/GM/19:2016 Guideline on COOMET supplementary comparison evaluation the data consistency was assessed. Based on the measurement results processing using DerSimonian-Laird procedure the χ^2 criterion value was calculated

$$\chi^2 = \sum_{i=1}^{n} \frac{(x_i - x_{ref})^2}{u^2(x_i)} \quad (2)$$

where

$$x_{ref} = \frac{\sum_{i=1}^{n} \frac{x_i}{u^2(x_i)}}{\frac{1}{u^2(x_i)}} \quad (3)$$

$$u^2(x_{ref}) = \frac{1}{\sum_{i=1}^{n} \frac{1}{u^2(x_i)}} \quad (4)$$

If the criterion value calculated in accordance with the data does not exceed the critical value χ^2 with the coverage level 0,95 and the degrees of freedom *n-1*

$$\chi^2 = \sum_{i=1}^{n} \frac{(x_i - x_{ref})^2}{u^2(x_i)} < \chi^2_{0.95}(n-1), \quad (5)$$

then the data can be acknowledged as consistent. That is the objective confirmation of the announced uncertainties.

Consequently, the critical value χ^2 with the coverage level 0,95 and the degrees of freedom 5 is 11,1.

After data analysis using formulas 2-5 for the consistency checking the following results were obtained.

Table 10 – Checking the comparison data consistency

Participant	Sample AH	Sample AL	Sample LC
NIM	0,58	0,02	1,61
VNIIM	1,09	1,05	0,32
BelGIM	0,82	0,08	0,80

BRML-NIM	0,00	2,19	1,35
UME	3,62	0,86	0,16
PTB	2,10	17,50	2,26
χ^2	8,2	21,7	6,5

As we can see from the Table 10, the inequation 5 holds for the samples AH and LC. Unfortunately, for the sample AL the χ^2 criterion value is bigger than the critical value for this degrees of freedom with the coverage level 0,95.

Conclusion

COOMET PROJECT 744/RU-a/18 was piloted by VNIIM (Russia). It was conducted during 2019 – 2021. Six NMIs tested the three coal samples with different values of sulfur content (AH – 1,192 %, AL – 0,193 %, LC – 0,412 %).

As a result of processing the comparison results the inconsistency of the values obtained by the Participants was revealed. After results processing using the DerSimonian-Liard procedure we have found the interlaboratory variance λ for all the samples (AH, AL, LC).

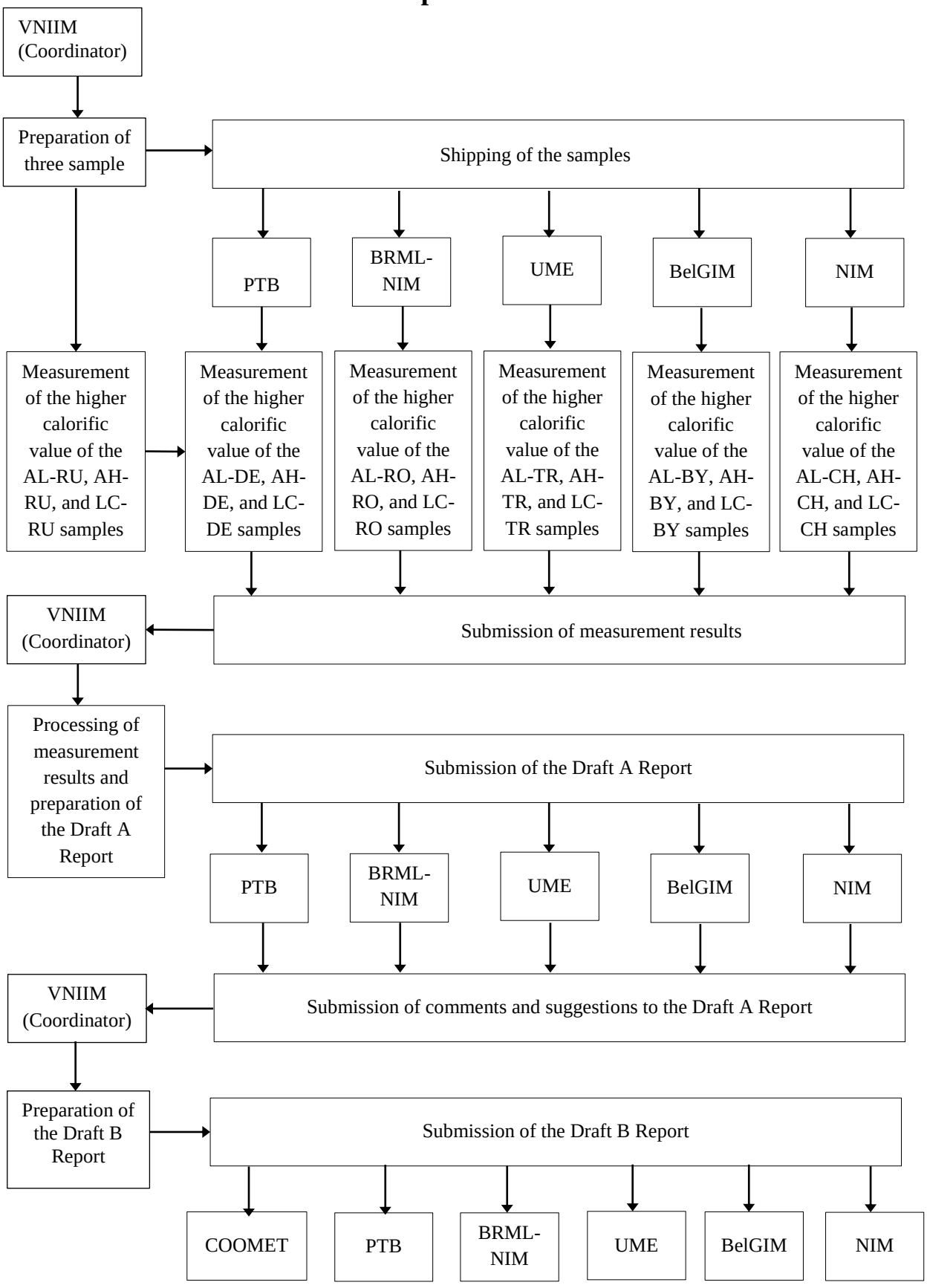
This inconsistency might be connected with the differences in moisture content determination carried out by the participants.

The DerSimonian-Laird method let us find the measurement uncertainties of the participants that could be connected with the random effect. After this procedure the results for the samples AH and LC became consistent (fig. 5, fig. 7). However, the result for the sample AL received from the PTB was inconsistent with the others (fig. 6).

The participants of the comparison carried out uncertainty budget estimation in different ways. Due to the fact that the determined value was gross calorific value on a dry basis Q^d_s, it was necessary to take into account the uncertainties of moisture content. This parameter has the greatest impact on the value of the measurand and its uncertainty contributes most to the total uncertainty.

The data consistency checking after the DerSimonian-Laird method using showed, that for the samples AH and LC the results are consistent (for the sample AH χ^2=8,2; for the sample LC χ^2=6,5; the critical value $\chi^2_{0.95}(n-1)$=11,1). The result for the sample AL is inconsistent (for the sample AL χ^2=21,7; the critical value $\chi^2_{0.95}(n-1)$=11,1).

ANNEX A
The comparison scheme



ANNEX B
Recommended form for the Gross Calorific Value Measurement Report

NMI VNIIM (Russia)
Sample AL-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
01			
…			
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 on an as-determined basis, Q_s^a, kJ/kg	Moisture content, %	Gross calorific value on a dry basis, Q_s^d, kJ/kg	Notes
01						
…						
n						
Mean value of the gross calorific value on a dry basis, $\overline{Q_s^d}$, 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 744/RU-a/18

Comparison of combustion energy of coal samples with different sulfur content

TECHNICAL PROTOCOL

Pilot Laboratory: Research Laboratory of Measurement Standards in the field of Combustion Calorimetry and High-Purity Substances for Metrological Purposes
Name and abbreviation of the NMI: D.I. Mendeleyev Institute for Metrology (VNIIM)

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
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TECHNICAL PROTOCOL
on the COOMET project 744/RU-a/18
Comparison of combustion energy of coal samples with different sulfur content

Introduction

This work involves comparison of reference bomb calorimeters of Russia, Germany, Belarus, Romania, Turkey and China using samples of coals with different values of total sulfur content.

1 Participants

Six metrology institutes that are took part in the COOMET regional comparison. 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	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	Physikalisch-Technische Bundesanstalt (PTB)	Germany	Address: Bundesallee 100, 38116 Braunschweig, Germany E-mail: ravi.fernandes@ptb.de Phone: + 49 531 592 3300 Contact person: Ravi Fernandes
3	Romanian Bureau of Legal Metrology (BRML-NIM)	Romania	Address: 11 Sos. Vitan Bârzesti 75669 Bucharest Romania E-mail: camelia.stratulat@yahoo.com Phone: +40 0758041556 Contact person: Camelia Stratulat
4	TÜBİTAK National Metrology Institute (UME)	Turkey	Address: Gebze Yerleşkesi Barış Mah. Dr. Zeki Acar Cad. No:1 41470 Gebze Kocaeli E-mail: kemal.ozcan@tubitak.gov.tr Phone: + 90 262 679 5000 ext. 6405 Contact person: Kemal Özcan
5	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
6	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.

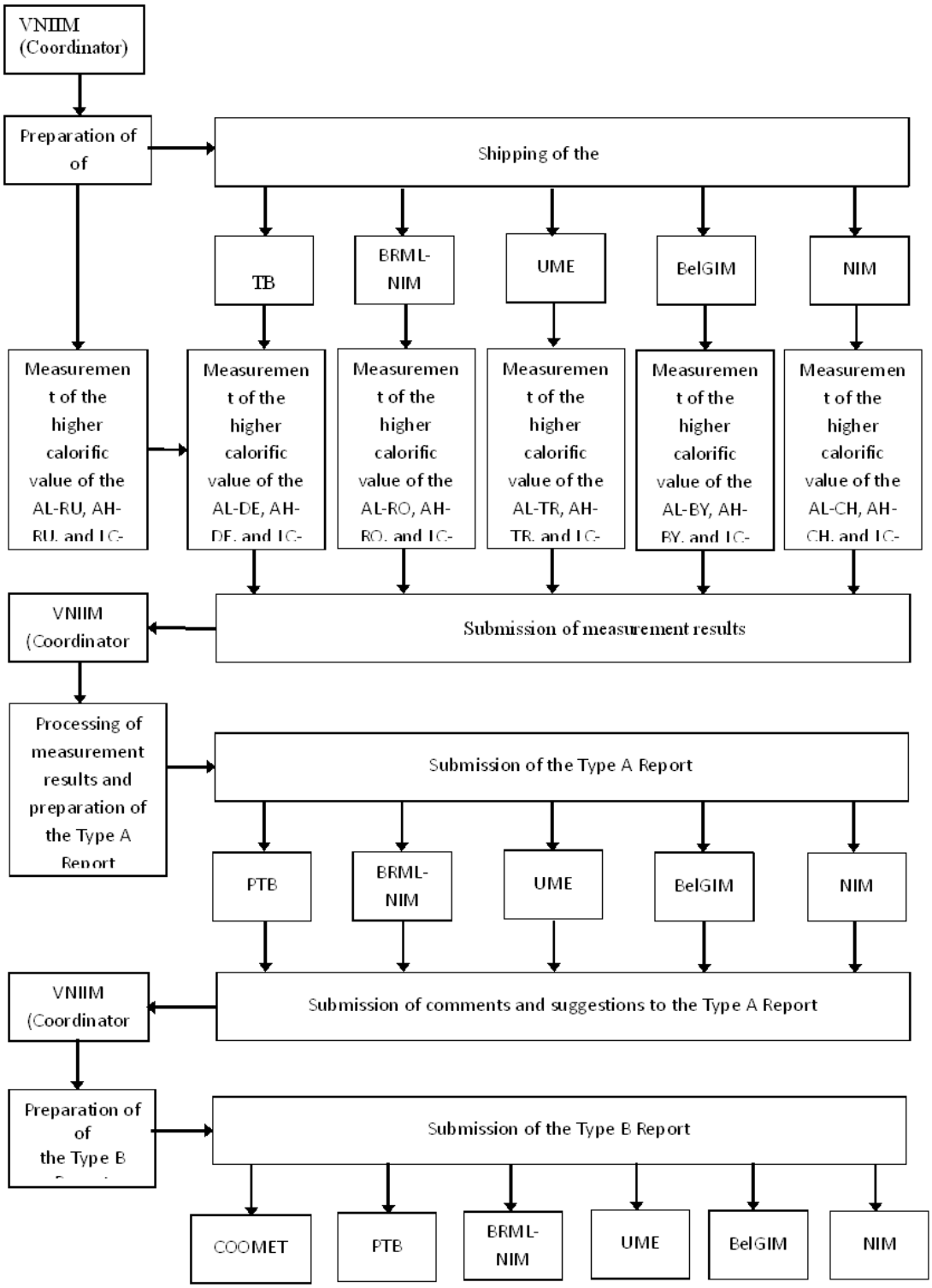

Fig. 1. Comparison scheme of the National Measuring Standards of unit of gross calorific value using coal samples with different values of total sulfur content

3 Samples for the comparison

The comparison uses three coal samples with different values of total sulfur content prepared by the Coordinator – VNIIM Laboratory of Calorimetry (Russia). The samples are presented in the powder form with grain size of no more than 212 μm. After the preparation, evaluation of heterogeneity and confirmation of stability, the samples are divided into equal parts of 30 g each – sample copies – and then placed into dark hermetically sealed plastic containers. VNIIM sends one copy of each sample to the Participants of the comparison with the markings given in Table 2.

NOTE: it is recommended to use no more than 20 g of the sample for the research; the remaining amount should be saved for control purposes, which may be necessary after the comparison results are known.

Table 2 – Marking of the samples used for the comparison

№	Sample material	Sample name	Researcher	Identical to
1	Anthracite	AL-RU	VNIIM (Russia)	AL-DE, AL-RO, AL-TR, AL-BY, AL-CH
2		AL-DE	PTB (Germany)	AL-RU, AL-RO, AL-TR, AL-BY, AL-CH
3		AL-RO	BRML-NIM (Romania)	AL-RU, AL-DE, AL-TR, AL-BY, AL-CH
4		AL-TR	UME (Turkey)	AL-RU, AL-DE, AL-RO, AL-BY, AL-CH
5		AL-BY	BelGIM (Belarus)	AL-RU, AL-DE, AL-RO, AL-TR, AL-CH
6		AL-CH	NIM (China)	AL-RU, AL-DE, AL-RO, AL-TR, AL-BY
7	Anthracite	AH-RU	VNIIM (Russia)	AH-DE, AH-RO, AH-TR, AH-BY, AH-CH
8		AH-DE	PTB (Germany)	AH-RU, AH-RO, AH-TR, AH-BY, AH-CH
9		AH-RO	BRML-NIM (Romania)	AH-RU, AH-DE, AH-TR, AH-BY, AH-CH
10		AH-TR	UME (Turkey)	AH-RU, AH-DE, AH-RO, AH-BY, AH-CH
11		AH-BY	BelGIM (Belarus)	AH-RU, AH-DE, AH-RO, AH-TR, AH-CH
12		AH-CH	NIM (China)	AH-RU, AH-DE, AH-RO, AH-TR, AH-BY
13	Lean coal	LC-RU	VNIIM (Russia)	LC-DE, LC-RO, LC-TR, LC-BY, LC-CH
14		LC-DE	PTB (Germany)	LC-RU, LC-RO, LC-TR, LC-BY, LC-CH
15		LC-RO	BRML-NIM (Romania)	LC-RU, LC-DE, LC-TR, LC-BY, LC-CH
16		LC-TR	UME (Turkey)	LC-RU, LC-DE, LC-RO, LC-BY, LC-CH
17		LC-BY	BelGIM (Belarus)	LC-RU, LC-DE, LC-RO, LC-TR, LC-CH
18		LC-CH	NIM (China)	LC-RU, LC-DE, LC-RO, LC-TR, LC-BY

Each sample is accompanied by a corresponding label:

Comparison sample	
Material	Anthracite
Name	**AL-RU**
Weight	30 g
Manufacturer	VNIIM, Russia

Comparison sample	
Material	Anthracite
Name	**AH-RU**
Weight	30 g
Manufacturer	VNIIM, Russia

For research in	**VNIIM, Russia**
Identical to	AL-DE, AL-RO, AL-TR, AL-BY, AL-CH
Packaged	DD/MM/YYYY

For research in	**VNIIM, Russia**
Identical to	AH-DE, AH-RO, AH-TR, AH-BY, AH-CH
Packaged	DD/MM/YYYY

Comparison sample	
Material	Lean coal
Name	**LC-RU**
Weight	30 g
Manufacturer	VNIIM, Russia
For research in	**VNIIM, Russia**
Identical to	LC-DE, LC-RO, LC-TR, LC-BY, LC-CH
Packaged	DD/MM/YYYY

Fig. 2. Labels for the comparison samples

Each sample is accompanied with an Information Sheet indicating period of time for the measurements to be made, value of the total sulfur content and its uncertainty, uncertainty due to heterogeneity determined during sample preparation, and other additional information.

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.

4 Carrying out measurements

Each laboratory should use its accepted practice of measurement of gross calorific value of solid fuels taking into account the information given in the Information Sheet. It is recommended to bring the sample to an air-dried basis before carrying out measurements. The determined value – gross calorific value – must be recalculated to a dry basis of the fuel. Conversion of the gross calorific value to a dry basis (Q_s^d) is made according to the following formula:

$$Q_s^d = Q_s^a \cdot \frac{100}{100 - W^a} \qquad (1)$$

where:

Q_s^d – gross calorific value on a dry basis;

Q_b^a – gross calorific value on an as-determined basis;

W^a – moisture content.

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 and Information Sheet attached to the sample.

Table 3 – Tentative comparison schedule

Period		Duration	Task	NMI
Start	End			
January 2019	June 2019	6 months	Preparation of the samples	VNIIM
June 2019	September 2019	3 months	Shipping of the samples to the Participants	VNIIM
September 2019	November 2019	2 months	Measurement of the samples by the Participants	VNIIM, PTB, BRML-NIM, UME, BelGIM, NIM
November 2019	January 2020	2 months	Preparation of the measurement reports	PTB, BRML-NIM, UME, BelGIM, NIM
January 2020	January 2020	2 weeks	Sending of the calorific value measurement results to the Coordinator (VNIIM)	PTB, BRML-NIM, UME, BelGIM, NIM
January 2020	April 2020	4 months	Preparation of the Type A Report by the Coordinator	VNIIM
April 2020	April 2020	2 weeks	Sending of the Type A Report to the Participants	VNIIM
May 2020	July 2020	2 months	Submission of comments and suggestions by the Participants	PTB, BRML-NIM, UME, BelGIM, NIM
July 2020	October 2020	3 months	Preparation and sending of the Type B Report to the Participants	VNIIM
October 2020	November 2020	1 months	Submission of comments and suggestions by the Participants	PTB, BRML-NIM, UME, BelGIM, NIM
November 2020	December 2020	1 months	Submission 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 and Information Sheet. The report must be sent both by email and in signed paper form.

The measurement report must include the following:

- name of the sample and the Participant,
- measurement conditions,
- results of the gross calorific value measurements on a dry basis,

- 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
Summary Table of the Comparison results

Country	Sample	Q^d_s, kJ/kg	W^a, %	$u(W^a)$, kJ/kg	u_A, kJ/kg	u_A, %	u(m), kJ/kg	$u(Q_{HNO3})$, kJ/kg	u(S), kJ/kg	u_B, kJ/kg	u_B, %	u_C, kJ/kg	u_C, %	U, kJ/kg	U, %
	AL	31705	3,1	15,85	8,2	0,03	0,3	1,8	2,4	19,3	0,06	21	0,07	42	0,13
NIM	AH	32099	2,6	16,05	12,2	0,04	0,3	1,8	4,0	19,9	0,06	23	0,07	46	0,14
	LC	30782	1,6	15,39	9,2	0,03	0,3	1,8	2,2	18,8	0,06	21	0,07	42	0,14
	AL	31795	2,5	5,39	13,5	0,04	0,3	0,005	2,4	6,1	0,02	15	0,05	30	0,09
VNIIM	AH	32298	2,0	5,45	15,3	0,05	0,3	0,005	4,1	7,0	0,02	17	0,05	34	0,10
	LC	30693	1,3	5,16	5,3	0,02	0,3	0,005	2,2	7,9	0,03	9	0,03	19	0,06
	AL	31694	2,5	12,14	2,8	0,01	0,3	0,2	2,4	12,5	0,04	13	0,04	26	0,08
BelGIM	AH	32084	2,0	16,20	2,8	0,01	0,3	0,2	4,1	16,8	0,05	17	0,05	34	0,11
	LC	30677	1,4	11,37	2,9	0,01	0,3	0,2	2,2	11,7	0,04	12	0,04	24	0,08
	AL	31829	2,6	8,56	2,9	0,01	0,5	0,2	2,4	10,7	0,03	11	0,03	22	0,07
BRML-	AH	32182	2,4	8,01	2,6	0,01	0,5	0,2	4,0	10,0	0,03	10	0,03	21	0,06
NIM	LC	30773	1,5	10,43	2,4	0,01	0,5	0,2	2,0	11,9	0,04	12	0,04	24	0,08
	AL	31787	4,0	12,71	4,2	0,01	0,3	0,4	3,0	13,0	0,04	14	0,04	28	0,09
UME	AH	32395	2,8	16,20	18,2	0,06	0,3	0,4	3,0	17,0	0,05	25	0,08	50	0,15
	LC	30738	1,6	12,30	9,5	0,03	0,3	0,4	2,0	13,0	0,04	16	0,05	32	0,10
	AL	31270	2,6		22	0,07				72	0,23	75	0,24	150	0,48
PTB	AH	32000	2,4		15	0,05				63	0,20	65	0,20	130	0,41
	LC	30600	1,3		27	0,09				59	0,19	65	0,21	130	0,42
VNIIM	AL	31800	1,4	7,47	12,1	0,038	0,3	0,005	2,4	8	0,025	14,5	0,046	29	0,09
2021	AH	32274	1,6	9,64	7,1	0,022	0,3	0,005	4,1	10,6	0,033	12,8	0,04	26	0,08
	LC	30640	1	5,11	5,1	0,017	0,3	0,005	2,2	5,76	0,019	7,69	0,025	15	0,05