	COOMET Recommendation **The Content and Procedure of Work on Reference Material Comparison within COOMET**	**COOMET R/RM/29:2016**
Considered at the 20th meeting of COOMET TC 1.12 "RMs" (September, 2015) *Agreed with Contact Persons of COOMET TC 1.12 "RMs" by correspondence (October, 2015)* *Agreed with the Chairmen of COOMET relevant TCs by correspondence (January 2016)* *Endorsed at the 14th meeting of COOMET JCMS (April 2016)* *Approved at the 26th meeting of COOMET Committee (April 2016)*		

This Recommendation specifies the content and procedure of work on comparison of reference materials[1], produced by organizations of COOMET member-countries, including National Metrology Institutes (NMIs).

Notes:

1. Recommendation covers reference materials, intended for measurement assurance of composition and properties of substances and materials

2. Recommendation ensures the implementation of the provisions, concerning reference material comparison, including those, provided under sub-clause 5.12 of ISO Guide 34.

Participation in reference material comparisons within COOMET is open to organizations, conforming to the rules of COOMET and having technical competence for each particular case.

This recommendation is based on the principles laid down in:

- COOMET D2/2010 COOMET Rules of Procedure;
- COOMET R/GM/11:2010 Regulations for comparison of measurement standards from the national metrological institutes of COOMET
- COOMET R/GM/23:2014 Procedure of organization and publishing the data about calibration and measuring services of COOMET national metrological institute on COOMET web resources"
- ISO Guide 34:2009 General requirements for the competence of reference material producers.

1. Basic terms and definitions

1.1 Comparison of reference materials within COOMET, comparison of reference materials: Comparison of metrological characteristics, reproduced and maintained by reference materials, leading to the determination of their degrees of equivalence.

1.2 Degree of equivalence of a reference material: the degree, to which the certified value of a reference material is consistent to the reference value of the reference material. It is expressed quantitatively as the deviation from the reference value of the reference material comparison and as the uncertainty of this deviation.

1.3 Pilot NMI: An NMI, responsible for planning and performance of a comparison and for processing of its results.

Notes – Planning and performance of a comparison, processing of comparison results are conducted by the pilot NMI with the involvement (by the decision of the pilot NMI) of organizations of COOMET member-countries, conforming to the rules of COOMET and having technical competence for each particular case.

1.4 Coordinator: a member of the pilot NMI, directly coordinating a comparison.

2. Underlying principles

2.1 Comparison of reference materials is recommended, when in COOMET member-countries:

a) to ensure uniformity and comparability of measurements, reference materials of substances (materials) with established characteristic value (s) of composition or property are used, for which, in

[1] RM in this recommendation is given as a generic term

the absence of national measurement standards of units, having recognized measurement capabilities in a particular measurement[1], it is impossible to establish metrological traceability;

b) reference materials of substances (materials) are used, metrological traceability of which is established to the measurement units, reproduced by national measurement standards of units, which have (in some COOMET member-countries) and do not have (in other COOMET member-countries) recognized measurement capabilities in a particular measurement[1];

c) reference materials of substances (materials) are used, metrological traceability of which is established against different reference values: national measurement standards of units of COOMET member-countries, national measurement standards of units of foreign countries, measurement standards of units of the 1st, 2nd and other orders, certified reference materials with established metrological traceability, including those of foreign issue, measurement results of reference laboratories, etc;

d) reference materials of substances (materials) are used, metrological traceability of which is established to measurement units, reproduced by national measurement standards of units, which have recognized measurement capabilities in a certain measurement[1] for the purpose to compare the degree of equivalence of reference materials being compared;

e) in the absence of national standard of unit, which has recognized measurement capabilities in a certain measurement, reference material producers should demonstrate the conformity of their quality management system to sub-clause 5.12 of ISO Guide 34:2009.

Notes:

1. Comparisons of reference materials of NMIs from COOMET member-countries may be performed in the framework of pilot, supplementary and key comparisons, based on comparisons of reference materials.

2. Comparisons of reference materials of producers from COOMET member-countries, other than NMIs, are performed in the framework of pilot comparisons.

2.2 The units of reference materials, which have one and the same purpose and certified characteristics, similar or different certified values are subject to comparison.

Note – Reference material comparison is usually performed for reference materials of COOMET NMIs, which, for various reasons are not included in Annex C MRA; for reference materials of organizations of COOMET member – countries.

2.3 Comparison of reference materials is performed with a view:

a) to compare the degree of equivalence of reference materials, listed under a) – d) of sub-clause 2.1 for the demonstration of capability to obtain comparable measurement results in testing laboratories of COOMET member-countries and other countries, which use these reference materials;

b) to evaluate the correlation of measurement results, obtained with the use of reference materials, submitted for comparison, with those, obtained with the use of reference materials, certified values of which are established with higher accuracy and which are higher in the hierarchy of metrological traceability, or reference materials of other countries, having established metrological traceability;

c) to define the possibility of mutual replacement of reference materials to be compared, when used as intented;

d) to evaluate measurement capabilities of reference material producers, whose reference materials are submitted for comparison;

e) to implement the provision of sub-clause 5.12 of ISO Guide 34:2009 by reference material producer if it is not possible to establish metrological traceability of its reference materials for future demonstration of conformity of its quality management system to the requirements of ISO Guide 34:2009.

Notes:

1 According to sub-clause 5.12 of ISO Guide 34:2009, comparison of reference materials is recommended with a view to evaluate the correlation of measurement results, obtained with the use of reference materials to be compared, if it is impossible to establish metrological traceability for one of the reference materials.

2 Reference materials of higher position in the hierarchy of metrological traceability, are reference materials of NMIs, metrological characteristics of which are established with the use of national measurement standards

3 Comparisons of reference materials, produced by reference material producers from COOMET member-countries other than NMIs, should be performed in the framework of COOMET pilot comparisons.

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[1]Measurements of certain characteristics of composition or properties of specific substances (materials).

2.4 Comparisons of reference materials are subdivided into paired and multiple.

Notes:

1. Paired comparison of reference materials is a comparison of two types of reference materials.

2. Multiple comparison of reference materials is a comparison of three or more types of reference materials.

2.5 It is the responsibility of a pilot NMI to plan, conduct comparisons within COOMET and to process measurement results, obtained in the framework of comparisons.

2.6 Comparison of reference materials is conducted within the project, registered according to COOMET D2/2010.

2.7 The work on comparisons of reference materials includes:

- preparation and registration of the project on COOMET comparisons;
- development of the technical protocol of reference material comparisons;
- distribution of reference materials to be compared for measuring;
- processing of measuring results;
- preparation of the report on the results of comparisons.

2.8 Comparisons of reference materials do not replace or substitute for:

- the determination of metrological characteristics of reference materials,
- the establishment of metrological traceability of reference materials.

3 The content of comparisons of reference materials

3.1 Comparison of reference materials stipulates the submission of reference materials to be compared to the preselected measurement laboratory by the pilot NMI.

3.2 Comparison of reference materials is conducted in one laboratory:

а) in a laboratory with calibration and measurement capabilities, recognized on the basis of results of key comparisons of International Bureau of Weights and measures;

б) in a laboratory, complying with the criteria, specified under sub-clause 3.3 (if the selection of a laboratory, complying with a) of sub-clause 3.2, is difficult).

3.3 A laboratory, capable of performing measurements in the framework of reference material comparisons, is selected, taking into consideration as follows:

- the competence of a laboratory in using a required measurement method (procedure) and equipment;
- the experience of a laboratory in participation in comparisons, including the international ones and in interlaboratory comparison tests;
- conformance of a laboratory to the requirements [1].

Notes:

1 Measurements in the framework of comparisons should be performed in an impartial competent laboratory.

2 When selecting a laboratory for performing measurements, preference should be given to a reference laboratory with measurement results, traceable to the unit, reproduced by the national measurement standard, having measurement capabilities, confirmed by key comparisons and/or COOMET comparisons.

3.4 The values of reference material characteristics to be certified in a laboratory in the framework of comparisons should be measured under repeatability conditions using the method (procedure), selected with the participation of the pilot NMI subject to the provisions of sub-clause 4.2/1

3.5 The algorithm of processing measurement results, obtained in the framework of reference material comparisons is given in Annex A.

4. Procedure of work on comparisons

4.1 Planning and registration of comparisons

4.1.1 The NMI's of COOMET member-countries propose to conduct comparisons according to the order, stipulated by the rules and procedures of COOMET.

4.1.2 The project on reference material comparisons is prepared and registered according to COOMET Rules of Procedure D2/2010.

4.1.3 COOMET TC 1.12 "Reference Materials" maintains the Programme of COOMET Reference Material Comparisons.

4.1.4 The work on reference material comparisons within the proposed COOMET project, agreed COOMET project as well as the preparation of intermediate and final reports on the project is carried out according to COOMET Rules of Procedure D2/2010.

4.1.5 Organizational and financial matters of reference material comparison are managed by COOMET structural and working bodies individually taking into account their collateral subordination.

4.2 Organization of comparisons

4.2.1. A Pilot NMI should take decisions on the following matters:

- to select reference materials to be compared within COOMET;
- to make a list of organizations, providing reference materials for a comparison within COOMET, including complete information about their mailing addresses and e-mails;
- to select the type of reference material comparison (paired or multiple);
- to select participating organization, which will perform measurements in the framework of reference material comparison;
- to select a measurement method (procedure) for performing measurements in the framework of reference material comparison;
- to define a period of time for performing comparisons; to establish a detailed schedule of work, equipment and traffic roads for transportation of reference materials;
- to determine the course of actions if the dates of carrying out the work in the framework of reference material comparison are not observed.

Notes:

1. Measurement procedure (method), used in the reference material comparison, should be selected, taking into consideration:

- intended use of reference materials, to be used for comparison;
- measurement methods (procedures), for metrological assurance of which reference materials to be used for comparison are intended;
- measurement range, which should cover measurement results, obtained when comparing reference materials.

2. Measurement procedure, used in a comparison, should be validated by a laboratory, performing measurements in the framework of the comparison.

4.2.2. A pilot NMI should provide with reference materials a laboratory, performing measurements in the framework of a comparison. If the dates of the comparison are not observed, the pilot NMI should revise the schedule of the reference material comparison and accordingly inform participants of the comparison.

4.2.3. A pilot NMI develops the technical protocol of a comparison. The technical protocol and the schedule of comparison are sent by the Pilot NMI directly to the participants of the reference material comparison as well as to COOMET TC and Secretariat.

4.2.4. The Coordinator should periodically (once every six months) inform the Chairman of TC about the course of the reference materials comparison.

5. Technical protocol of a comparison

5.1. The technical protocol of a comparison should contain a description of the sequence of operations during the comparison of reference materials, namely:

- description of reference materials: name, information on approval, technical and metrological characteristics (with the range of permissible certified values), details of homogeneity and stability;
- recommendations for handling reference materials during transportation, storage, unpacking, including the complete list of the packed content, weight and size of the package, etc.;
- conditions and method of the use of reference materials during measurements;
- details of the organization, which will make measurements in the framework of reference material comparison;
- details or description of the measurement method (procedure), information on the traceability of measurement results;
- list of the main components of the measurement uncertainty of a measurement result, that are to be evaluated by participant of the comparison, performing measurements (the participating NMIs may add here some other components, which they think to be significant) and recommendations for the uncertainty evaluation method;
- the form of reporting measurement results;
- measurement results should be submitted to the pilot NMI not later than one month after completing the measurements in the laboratory.

5.2 The Technical Protocol of a comparison is prepared by the pilot NMI;

5.3 Recommended template of the Technical Protocol is given in Annex 3 to this recommendation.

6 Preparation of the report of comparisons

6.1. A pilot NMI has the prime responsibility for the preparation of the report on comparisons.

6.2. Measurement results submitted to the pilot NMI are not disclosed until the organization, performing measurements in the framework of comparisons, sends its measurement results. The measurement result is not considered to be full without indicating the budget of uncertainty.

6.3. The pilot NMI analyzes the comparison results. If the data of any participant diverge significantly, the pilot NMI accordingly informs this participant and suggests, that the results should be tested for the presence of statistical treatment errors. If this test does not detect the error, the measurement
results of this participant are left unchanged.

6.4 The pilot NMI (or the working group if it has been established) prepares a preliminary report (Report A) of comparisons and circulates it among the participants of the comparisons for discussion and comments. The Report A contains the results, obtained in the framework of comparisons.

6.5 The pilot NMI draws up and circulates among the participants a final report (Report B) taking into consideration the comments and suggestions of participating NMIs.

6.6 The report should contain an algorithm for treatment of the data submitted by the participants of comparisons.

6.7 After Report B is endorsed and approved, the comparison results are to be published.

6.8 The pilot NMI sends a brief form of the final report to the COOMET Secretariat.

6.9 Recommended template of the report is given in the Appendix B. Recommended algorithm for treatment of the results of reference material comparisons is given in Annex A.

7. Information on comparisons

7.1 Results of reference material comparisons may be presented for publication of calibration and measurement capabilities of COOMET member-countries on COOMET site.

Notes –The procedure of publishing the data on calibration and measurement capabilities, provided by metrological laboratories (centres) of member states, on COOMET site is described in COOMET R/GM/23:2014 "Procedure of organization and publishing the data about calibration and measuring services of COOMET national metrological institute on COOMET web resources"

7.2 Results of reference material comparisons are published in metrological journals. After the publication they may be used in other articles or oral presentations.

7.3 Results of comparisons, performed in the framework of key and supplementary comparisons undergo the review procedure in accordance with COOMET R/GM/11:2010.

8. Issuance of a certificate to participants of comparisons

The procedure of work on the reference material comparisons within COOMET stipulates the issuance of Certificate of participation in the reference material comparisons to participants of comparisons. The form of Certificate of participation in the reference material comparisons within COOMET is given in Annex D to this recommendation.

ANNEX A

RECOMMENDED ALGORITHM OF PROCESSING RESULTS OF COOMET REFERENCE MATERIAL COMPARISONS

A.1 General

Annex A of this recommendation specifies recommended algorithms of processing:
- paired comparison of reference materials (A.3);
- multiple comparison of reference materials (A.4);

A.2 Symbols

For the purposes of this recommendation in Annex A the following abbreviations and symbols are applied:

A_j certified value of j^{th} reference material;

x_{ij} measurement result of certified characteristic of j^{th} reference material;

n number of measurement results;

x_{refj} reference value of j^{th} reference material comparison;

$u(x_{refj})$ combined standard uncertainty of reference value of j^{th} reference material;

$U(A_j)$ expanded uncertainty of certified value of j^{th} reference material;

$U_{rel}(A_j)$ relative expanded uncertainty of certified value of j^{th} reference material;

$u_{rel}(A_j)$ relative standard uncertainty of certified value of j^{th} reference material;

k coverage factor;

$d_{j,rel}$ relative degree of equivalence of j^{th} reference material;

$u(d_{j,rel})$ standard uncertainty of relative degree of equivalence of j^{th} reference material comparison;

$u_{rel}(x_{refj})$ relative combined standard uncertainty of reference value x_{refj};

$u(x_{refj})$ combined standard uncertainty of reference value x_{refj};

$U(d_{j,rel})$ expanded uncertainty of relative degree of equivalence of j^{th} reference material comparison;

$d_{1,2,rel}$ paired difference of relative degree of equivalence of paired comparison of the 1st and the 2nd reference materials;

$u(d_{1,2,rel})$ standard uncertainty of paired difference of relative degree of equivalence of paired comparison of the 1st and the 2nd reference materials;

α term of reference dependence of multiple comparison of reference materials;

β term of reference dependence of multiple comparison of reference materials;

ε_j residual random error;

A_j' predicted value of certified characteristic of j^{th} reference material;

$\bar{x}_j$ mean value of measurement results of certified characteristic of j^{th} reference material, obtained under repeatability conditions;

$\bar{x}_j'$ mean predicted value of measurement results of certified characteristic of j^{th} reference material, calculated using reference dependence with regard for $\bar{x}_j$;

$u(\bar{x}_j)$ combined standard uncertainty of mean value of measurement results of certified characteristic of j^{th} reference material;

$u(\alpha)$ standard uncertainty of term α of reference dependence of multiple comparison of reference materials;

$u(\beta)$ standard uncertainty of term β of reference dependence of multiple comparison of reference materials;

K_p number of reference materials, submitted by

p^{th} participant of comparison;

$D_{kp,rel}$ relative degree of equivalence of p^{th} participant of comparison;

$U(D_{kp,rel})$ expanded uncertainty of relative degree of equivalence of p^{th} participant of comparison;

$u(D_{kз,rel})$ standard uncertainty of relative degree of equivalence.

A.3 Algorithm of processing measurement results in the framework of paired comparison of reference materials

A.3.1 General requirements

Reference materials, selected for comparison, should have certified values, falling within one measurement range of:

- measurement procedure, for which they are intended;
- measurement procedure, used in experimental work during comparison of reference materials.

The value of certified characteristic of reference materials is measured in a laboratory, complying with the requirements, stated under sub-clauses 3.2-3.3.

The measurements in the laboratory are performed according to a selected procedure (method) under repeatability conditions. The minimum number of measurement results *n* of the certified characteristic in each reference material being compared should not be less, than two. In performing comparison of reference materials *2n* results x_{i1} and x_{i2} are obtained (results with subscript 1 are referred to the first reference material and results with subscript 2 –to the second reference material), the number of results for each reference material is equal to *n*.

A 3.2 Processing measurement results, obtained in the framework of comparison, includes:

- calculation of the reference value of paired comparison of reference materials;
- calculation of the relative degree of equivalence of reference material comparison – the relative difference between the reference value and the corresponding certified value of reference materials and comparing of the obtained results;
- calculation of the paired difference of relative degrees of equivalence of reference material comparison and evaluation of obtained results.

A.3.3 Calculation of the reference value of paired comparison of reference materials

Reference values of paired comparison are calculated by the formula (A.3.1), (A.3.2) for each reference material being compared on the basis of the results of measuring certified characteristic, obtained for each reference material.

$$x_{ref\,1} = \frac{\sum_{i=1}^{n} x_{i1}}{n} \qquad (A.3.1)$$

$$x_{ref\,2} = \frac{\sum_{i=1}^{n} x_{i2}}{n} \qquad (A.3.2)$$

Combined standard uncertainty of reference values $x_{ref\,1}$ and $x_{ref\,2}$ - $u(x_{ref\,1})$ and $u(x_{ref\,2})$ is calculated taking into account recommendations [4].

A.3.4 Calculation of the relative degree of equivalence of reference material comparison, comparing of the obtained results

The relative degree of equivalence of reference materials $d_{j,rel}$ - the relative difference between the reference value $x_{ref\,1}$ and $x_{ref\,2}$ and the corresponding certified value of reference materials A_1 и A_2 is calculated by

$$d_{1,rel} = \left(\frac{A_1 - x_{ref1}}{x_{ref1}} \right) \cdot 100\% = \left(\frac{A_1}{x_{ref1}} - 1 \right) \cdot 100\%, \quad \text{(A.3.3)}$$

$$d_{2,rel} = \left(\frac{A_2 - x_{ref2}}{x_{ref2}} \right) \cdot 100\% = \left(\frac{A_2}{x_{ref2}} - 1 \right) \cdot 100\%. \quad \text{(A.3.4)}$$

The standard uncertainty of the relative degree of equivalence of the first reference material comparison $d_{1,rel}$ - $u(d_{1,rel})$ is calculated by

$$u(d_{1,rel}) = \frac{A_1}{x_{ref1}} \cdot \sqrt{u_{rel}^2(A_1) + u_{rel}^2(x_{ref1})}. \quad \text{(A.3.5)}$$

The standard uncertainty of the relative degree of equivalence of the second reference material comparison $d_{2,rel}$ - $u(d_{2,rel})$ is calculated by

$$u(d_{2,rel}) = \frac{A_2}{x_{ref2}} \cdot \sqrt{u_{rel}^2(A_2) + u_{rel}^2(x_{ref2})}, \quad \text{(A.3.6)}$$

where:

- $u_{rel}(A_j)$ is the relative standard uncertainty of the certified value of j^{th} reference material (in %), calculated taking into account the known value of the relative expanded uncertainty of the certified value of the reference material $U_{rel}(A_j)$ (in %) and the coverage factor k by

$$u_{rel}(A_j) = \frac{U_{rel}(A_j)}{k}; \quad \text{(A.3.7)}$$

where

- $u_{rel}(x_{refj})$ is the relative standard uncertainty of the reference value x_{refj} (in %), calculated by

$$u_{rel}(x_{refj}) = \frac{u(x_{refj})}{x_{refj}} \cdot 100\%, \quad \text{(A.3.8)}$$

where

- $u(x_{refj})$ is the combined standard uncertainty of the reference value x_{refj}.

Note - The derivation of the formulae (A.3.5) and (A.3.6) is presented in Annex F.

The expanded uncertainty of the relative degree of equivalence of j^{th} reference material comparison $U(d_{j,rel})$ is calculated by

$$U(d_{j,rel}) = 2 \cdot u(d_{j,rel}). \quad \text{(A.3.9)}$$

The claimed metrological characteristics of j^{th} reference material are confirmed with a probability 0,95, if the condition is met

$$\left| d_{j,rel} \right| \le U(d_{j,rel}). \quad \text{(A.3.10)}$$

A.3.5 Calculation of the paired difference of relative degrees of equivalence of paired comparison of reference materials and evaluation of obtained results.

The calculation of the paired difference of relative degrees of equivalence of paired comparison of reference materials $d_{1,2,rel}$ and uncertainty $u(d_{1,2,rel})$ is performed using

$$d_{1,2,rel} = d_{1,rel} - d_{2,rel}, \quad \text{(A.3.11)}$$

$$u(d_{1,2,rel}) = \sqrt{u^2(d_{1,rel}) + u^2(d_{2,rel}) - 2\,\mathrm{cov}(d_{1,rel}, d_{2,rel})}\ , \qquad \text{(A.3.12)}$$

where $\mathrm{cov}(d_{1,rel}, d_{2,rel})$ is covariation $d_{1,rel}, d_{2,rel}$.

The comparison is performed

$$\left|d_{1,2,rel}\right| < 2 \cdot u(d_{1,2,rel}). \qquad \text{(A.3.13)}$$

If the inequality is satisfied (A.3.13), then the difference between $d_{1,2,rel}$ is considered to be insignificant, which may indicate the interchangeability of reference materials.

Note – Positive results, obtained in the evaluation by the equations (A 3.10) and (A 3.13), indicate, that reference material producers, which submitted reference materials for comparison, demonstrate the capability of issuing reference materials, comparable in the degree of equivalence during their use.

A.4 Multiple comparison of reference materials

A.4.1 General requirements

Multiple comparison of reference materials is conducted for three or more reference materials, complying with the requirements of sub-clause 2.3 of this recommendation.

Measurements of the certified characteristic of reference materials are performed in a laboratory, complying with the requirements, stated under sub-clauses 3.2-3.3.

The measurements in the laboratory are performed according to a selected procedure (method) under repeatability conditions. The minimum number of measurement results *n* of the certified characteristic in each reference material being compared under repeatability conditions should not be less, than two. The value of the certified characteristic for *J* reference materials to be compared is measured under repeatability conditions. In performing comparison of reference materials under repeatability conditions *n* measurement results x_j are obtained (where *i* is the subscript of i^{th} measurement result for j^{th} reference material, *j* is the subscript of j^{th} reference material)

A 4.2 Processing measurement results, obtained in the framework of comparison, includes:

- establishment of mutually consistent certified values of reference materials to be compared;
- calculation of the relative degree of equivalence of reference material comparison;
- calculation of standard and expanded uncertainty of the relative degree of equivalence of comparison of reference materials to be compared;
- intercomparison of the relative degree of equivalence and expanded uncertainty of the relative degree of equivalence of reference materials.

A.4.3 Establishment of mutually consistent certified values of reference materials to be compared

When high-accuracy measurement procedures are used for measuring the value of the certified characteristic of reference materials in the framework of comparison, then functional dependence between certified and determined values can be established, which by analogy with "reference value" of comparison can be considered as "reference dependence" of reference material comparison. The model of "reference dependence" of reference material comparison may be presented as:

$$x = \alpha + \beta \cdot A + \varepsilon, \qquad \text{(A.4.1)}$$

where: x is the value of measurement result of the certified characteristic of a reference material, obtained under repeatability conditions;

A is the certified value of a reference material;

α and β are the terms of linear dependence;

ε is a residual random error.

Notes:

1 Approach, based the use of "reference dependence", applied in comparison of several reference materials, is described in a number of publications, e.g. [6-8], some of which use parametric bootstrap Monte Carlo analysis.

2 As an example, the dependence $x_j = f(A_j)$ for five reference materials being compared is presented in fig. A.1 for visual reference.

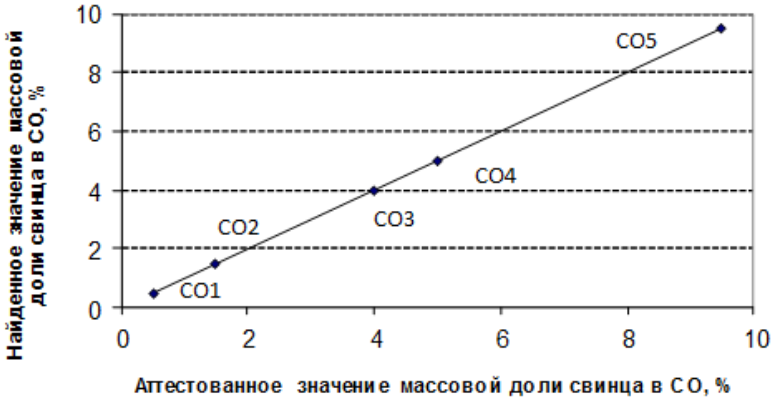


Fig. A.1 Reference dependence $x_j = f(A_j)$ for five reference materials being compared.

In order to establish mutually consistent values of certified characteristics of reference materials parameter ε should be calculated by

$$\varepsilon_j = (A_j - A_j^{'}) \cdot \sqrt{\sum_{j=1}^{J} \varepsilon_j^2 / J} \quad , \tag{A.4.2}$$

where ε_j^2 is a parameter, calculated by

$$\varepsilon_j^2 = \left[\frac{\left(A_j - A_j^{'}\right)}{U(A_j)/2} \right]^2 + \left[\frac{(\bar{x}_j - \bar{x}_j')}{u(\bar{x}_j)} \right]^2 , \tag{A.4.3}$$

where: A_j is the certified value of the certified characteristic of j^{th} reference material;

A_j' is the predicted value of the certified characteristic of j^{th} reference material, calculated using the equation of reference dependence, taking into account $\bar{x}_j$;

$\bar{x}_j$ - the mean value of measurement results of the certified characteristic of j^{th} reference material, obtained under repeatability conditions;

$\bar{x}_j'$ - the mean predicted value of the certified characteristic of j^{th} reference material, calculated using the equation of reference dependence, taking into account $\bar{x}_j$;

$U(A_j)$ is the expanded uncertainty of the certified value of j^{th} reference material;

$u(\bar{x}_j)$ is combined standard uncertainty of the mean value of measurement results of the certified characteristic of j^{th} reference material;

The predicted value of the certified characteristic of j^{th} reference material A_j' and the predicted value of the measurement result of the certified characteristic of j^{th} reference material $x_j^{'}$ are established respectively based on known data $\bar{x}_j$ and A_j by the predetermined reference dependence $\overline{x_j} = \alpha + \beta \cdot A_j$, treated by least-square method.

The mean value of measurement results of the certified characteristic of j^{th} reference material, obtained under repeatability conditions is calculated by

$$\overline{x_j} = \frac{\sum_{i=1}^{n} x_{ij}}{n} . \tag{A4.4}$$

The value ε_j for each reference material is calculated by corresponding ε_j^2 values. The values of ε_j^2 may be interpreted as the values of the standard deviation of results from the predetermined

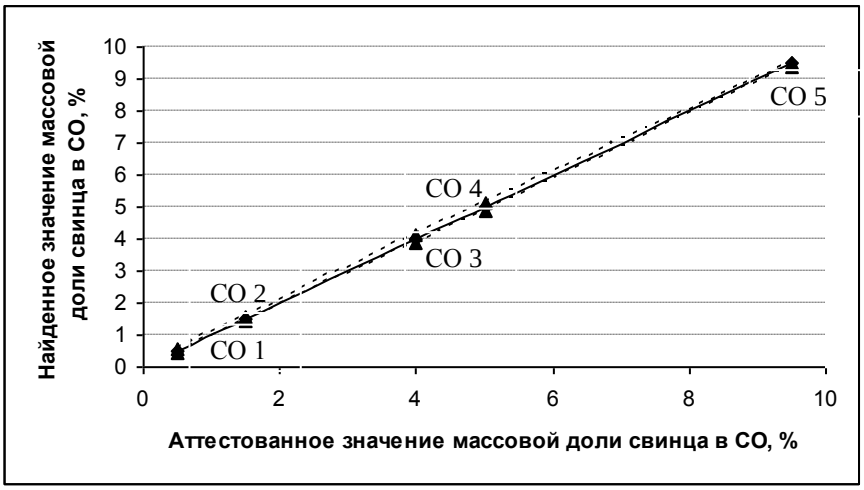
reference dependence. The sign "+" or "-" ε_j means whether the certified value of j^{th} reference material is more or less, than its predicted value.

To establish mutually consistent values of the certified characteristics of reference materials being compared, the reference dependence $\overline{x_j} = \alpha + \beta \cdot A_j$ should be plotted with indication of the expanded uncertainty of the reference dependence, calculated taking into account ε_j values and a coverage factor $k = 2$.

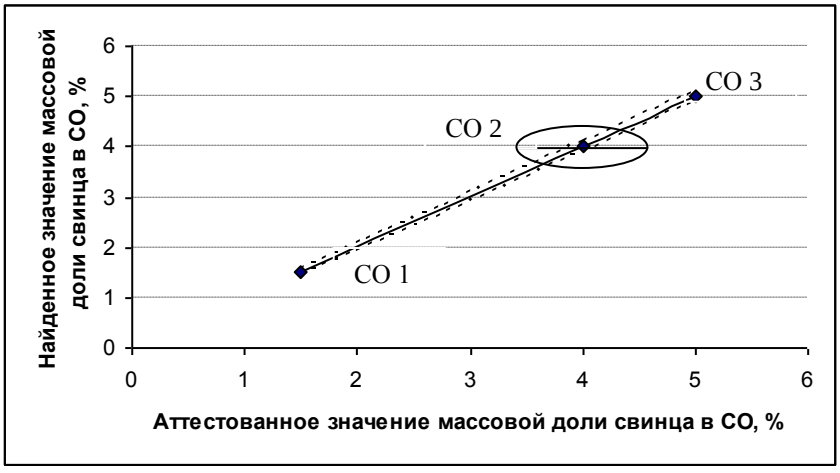
Table A.1 Presentation form for the data, required for processing in the framework of multiple comparison of reference materials.

No.	RM index	A_j, mg/dm^3	$u(A_j) = \frac{U(A_j)}{2}$	$\overline{x}_j$, mg/dm^3	$u(\overline{x}_j)$	α	β	$\overline{x}_j'$, mg/dm^3	A_j', mg/dm^3	ε_j^2	ε_j
1	**2**	**3**	**4**	**5**	**6**	**7**	**8**	**9**	**10**	**11**	**12**
1											
...											
J											

Example – As an example the reference dependence of multiple comparison of reference materials for composition of slag is presented in fig. A.2



a)



b)

Fig. A.2 An example of the reference dependence of multiple comparison of five reference materials for composition of slag

(a), an example of graphical presentation of the case, when the certified value of reference materials to be compared agrees with the reference dependence within their expanded uncertainty (b).

To establish mutually consistent certified values of reference materials to be compared, it is necessary to establish whether certified values of the reference materials agree with the reference dependence of multiple comparison within their expanded uncertainty. When this condition for

reference materials to be compared is met (fig. A.2 (b)), then mutual consistency of certified values of the reference materials is accepted.

Note – When the certified value for any of reference materials to be compared does not agree with the reference dependence within their expanded uncertainty, a thorough analysis of obtained results and initial data will be needed to take a decision on participation in a comparison of the reference material under consideration and/or on conducting additional experimental research.

A.4.4 Calculation of relative degree of equivalence of reference materials

For the case of multiple comparison of reference materials the relative degree of equivalence for each j^{th} reference material to be compared is calculated taking into account the plotted reference dependence $\overline{x_j} = \alpha + \beta \cdot A_j$ using

$$d_{j,rel} = \frac{A_j - A_j^{'}}{A_j^{'}} \cdot 100\% = \frac{A_j - (\overline{x_j} - \alpha)/\beta}{(\overline{x_j} - \alpha)/\beta} \cdot 100\% = (\frac{A_j \cdot \beta}{\overline{x_j} - \alpha} - 1) \cdot 100\%, \qquad (A.4.5)$$

where

- α and β are the terms of the reference dependence of multiple comparison of reference materials, calculated by the least-square method;
- A_j - the certified value of the certified characteristic of j^{th} reference material;
- A_j' - the predicted value of of the certified characteristic of j^{th} reference material, calculated using the equation of reference dependence, taking into account $\overline{x}_j$;

A.4.5 Calculation of standard and expanded uncertainty of the relative degree of equivalence of reference material comparison

Standard uncertainty of the relative degree of equivalence for j^{th} reference material (in %) is calculated by

$$u(d_{j,rel}) = 100 \cdot \sqrt{\left(\frac{\beta}{\overline{x_j} - \alpha}\right)^2 \cdot u^2(A_j) + \left(\frac{A_j}{\overline{x_j} - \alpha}\right)^2 \cdot u^2(\beta) + \left(\frac{A_j \cdot \beta}{(\overline{x_j} - \alpha)^2}\right)^2 \cdot u^2(\overline{x_j}) + \left(\frac{A_j \cdot \beta}{(\overline{x_j} - \alpha)^2}\right)^2 \cdot u^2(\alpha)}, \qquad (A.4.6)$$

where:

- $u(A_j)$ is the standard uncertainty of the certified value of j^{th} reference material;
- $u(\overline{x_j})$ is the combined standard uncertainty of the mean value of measurement results of the certified characteristic of j^{th} reference material;
- $u_{rel}(\alpha)$ is the standard uncertainty of the term α of the reference dependence;
- $u_{rel}(\beta)$ is the standard uncertainty of the term β of the reference dependence;

Notes:

1. The standard uncertainty of the term α of the reference dependence $u(\alpha)$ and the standard uncertainty of the term β of the reference dependence $u(\beta)$ may be calculated by the formulae, given in Annex G or with the use of the relevant statistical programmes.

2. The derivation of the formulae (A.4.6) is given in Annex F.

The expanded uncertainty of the of the relative degree of equivalence for j^{th} reference material is calculated by

$$U(d_{j,rel}) = 2 \cdot u(d_{j,rel}). \qquad (A.4.7)$$

A.4.6 The intercomparison of the relative degree of equivalence with expanded uncertainty of the relative degree of equivalence of reference materials.

The intercomparison of the relative degree of equivalence of reference materials to be compared with the expanded uncertainty of the relative degree of equivalence is conducted based on the following condition

$$\left|d_{j,rel}\right| \le U(d_{j,rel}) \qquad \text{(A.4.8)}$$

The claimed metrological characteristics of j^{th} reference material are confirmed with a probability 0,95, if the condition (A.4.8) is met.

Note – Calculation results of the relative degree of equivalence of reference materials to be compared may be presented graphically. As an example, graphical dependence of the relative degree of equivalence and the certified value of copper mass fraction (%) of slag reference materials is presented in fig. A.3

.

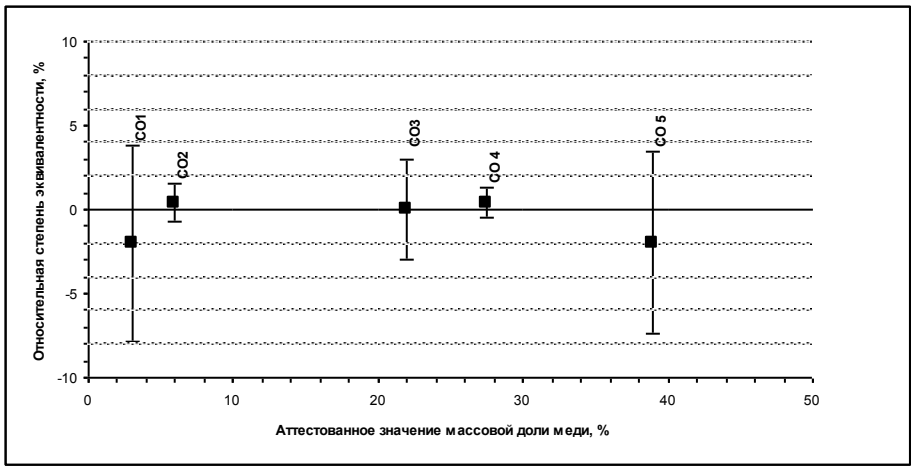


Fig. A.3 Dependence of the relative degree of equivalence and corresponding certified values of copper mass fraction (%) of slag reference materials.

Note – The results in fig. A.3 indicate, that in the course of comparison of reference materials, having different certified values of copper mass fraction, the relative degree of equivalence nor exceeding 2 %, was demonstrated for all reference materials. It was demonstrated for all reference materials, that the condition (A.4.8) was satisfied.

A.5 Evaluation of the degree of equivalence of comparison participants, which submitted several reference materials for comparison

If each p^{th} participant of comparison submitted K_p reference materials for comparison, then the relative degree of equivalence of p^{th} participant of comparison $D_{kp,rel}$ can be calculated by

$$D_{kp,rel} = \frac{\sum_{kp=1}^{Kp} d_{j,rel}}{Kp}, \qquad \text{(A.5.1)}$$

where: K_p is a number of reference materials, submitted by a participant of comparison;

$d_{kp,rel}$ is the relative degree of equivalence of reference materials, submitted by p^{th} participant of comparison.

The expanded uncertainty of the relative degree of equivalence of p^{th} participant of comparison is calculated by the

$$U(D_{kp,rel}) = 2 \cdot u(D_{kp,rel}), \qquad \text{(A.5.2)}$$

where $u(D_{k,rel})$ is the standard uncertainty of the relative degree of equivalence, calculated by

$$u(D_{I,rel}) = \begin{cases} u\left(d_{1,rel}\right), \text{если } Kp = 1; \\ \dfrac{\sum_{k=1}^{Kp} u(d_{j,rel})^2}{K_p} + \left(\dfrac{\sum_{k=1}^{Kp} \left(d_{j,rel} - D_{kp,rel}\right)^2}{Kp - 1} \right)^2, \text{если } Kp > 1 \end{cases} . \qquad \text{(A.5.3)}$$

Note – Calculation results of the relative degree of equivalence of reference materials to be compared may be presented graphically. As an example, graphical dependence

of the relative degrees of equivalence of comparison participants - producers of slag reference materials is presented in fig. A.4.

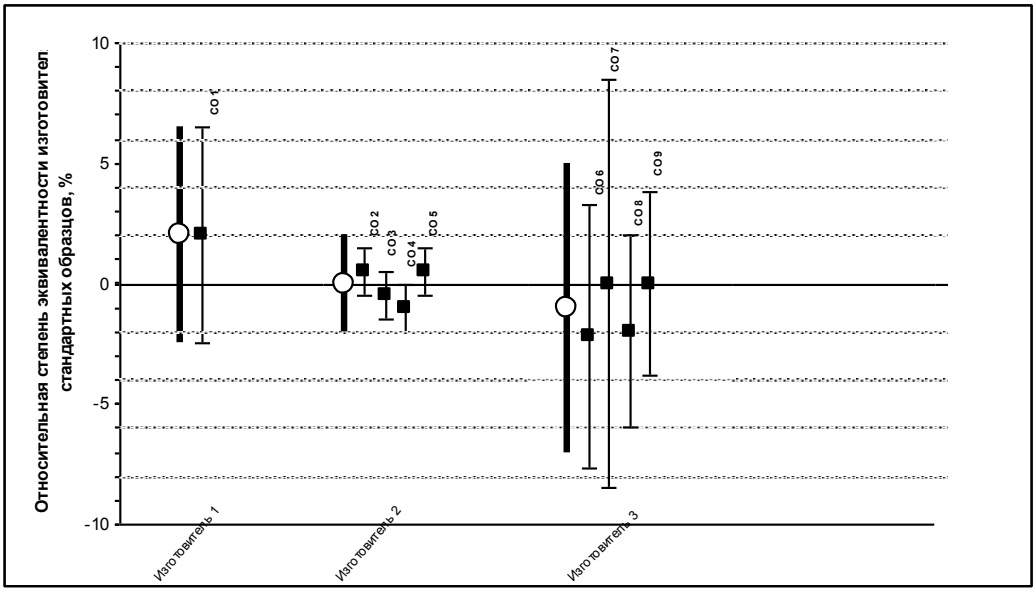


Fig. A.4 Relative degrees of equivalence of comparison participants – producers of slag reference materials (in bold).

If the mutual consistency of reference materials is approved, the condition (A.4.8) is satisfied, the relative degrees of equivalence of comparison participants agree within the expanded uncertainty fully or partially, overlapping «0», then it is possible to conclude, that comparison participants confirmed their capability to issue mutually consistent reference materials, ensuring the comparability of measurements in the user laboratories when using these reference materials.

If one of the above listed conditions is not satisfied, then a detailed analysis should be carried out, including that of results, obtained within the framework of comparisons in other involved competent laboratory (ies).

ANNEX B

RECOMMENDED TEMPLATE OF TECHNICAL PROTOCOL OF COOMET REFERENCE MATERIAL PILOT COMPARISON

TP Status and date
("Draft" or "Approved")

COOMET PROJECT No.

PROJECT NAME

TECHNICAL PROTOCOL

Pilot NMI name and acronym:
Contact person:
Mail address:
Telephone:
Fax:
E-mail:

Project description

Specify the goal and main details of comparisons, including the type of comparisons (paired, multiple).

1. Comparison participants

Provide details of producers of reference materials to be compared, organization (s), which will perform measurements in the framework of reference material comparisons

No.	Organizations, participating in comparisons	Acronym of organization, participating in comparisons	Address	Contact person	E-mail. telephone, fax

2. Comparison organization

Specify:

• type of comparisons (paired or multiple);

• description of comparison principle;

• schedule of comparisons

3. Information on reference materials

Specify:

• name of reference materials, submitted for comparisons;

• information on the approval of reference material type;

• metrological characteristics of reference materials (the range of permitted certified values, the uncertainty of certified values);

• batch number, date of issue;

• description (technical characteristics)of reference materials;.

• information on metrological traceability of reference materials (if known).

4. Recommendations on handling reference materials

Specify:

• means and routes of transportation of each reference material;

• conditions of transportation of reference materials;

• the sequence of actions in NMI or laboratory, involved in the experiment, in packing reference materials for shipment to the next participant (if applicable);

• the sequence of actions in NMI or laboratory, involved in the experiment, in unpacking reference materials;

• conditions of storage of reference materials;

• conditions and method of application of a reference material during measuremens.

5. Measurement procedure

In this section indicate requirements for:

• measurement method(s), (procedure(s)), used in a comparison;

• used measurement instruments;

• description of the procedure of measurements to be taken into account in reports of participating laboratories;

• accuracy control of measurement results (for interlaboratory comparison);

• scope, sequence and condition of measurements.

6. Form of reporting measurement results

This section should include requirements for:

• *information on measurement conditions, measurement method (s), procedure (s), metrological assurance of measurement instruments in use, accuracy control of measurement results (for interlaboratory comparison), confirmation of measurement capability of a laboratory (when conduction comparisons in a single laboratory);*

• *the form of reporting the results of measuring certified characteristic (s) of reference materials, obtained when conducting comparisons;*

• *the form of reported uncertainty budget:*

Standard uncertainty Components	**A**	**B**
1		
2		
…		
Combined standard uncertainty		
Expanded uncertainty (k=2)		
Confidence level		

7. Evaluation of comparison results

This section should give reference to procedure of evaluation of comparison results, recommended by COOMET or original procedure. In the latter case it is desirable to clarify why recommended procedures are less preferable in this particular case.

8. Report on comparison results

This section includes requirements for the report (type A, B), which should be prepared based on the comparison results and information on organizations, which will be submitted the report for consideration.

ANNEX C

RECOMMENDED TEMPLATE OF REPORT
OF COOMET REFERENCE MATERIAL COMPARISONS

REPORT TYPE (A, B)

COOMET PROJECT No.

PROJECT NAME

REPORT
(report type *A or B*)

Pilot NMI name and acronym:
Contact person:
Mail address:
Telephone:
Fax:
E-mail:

Abstract

Text

1. Introduction

Specify the goal and main details of comparisons, including the type of comparisons (paired, multiple).

2. Information on reference materials

Specify:

- *name of reference materials, submitted for comparisons;*
- *information on the approval of reference material type;*
- *metrological characteristics of reference materials (the range of permitted certified values, the uncertainty of certified values);*
- *batch number, date of issue;*
- *description (technical characteristics)of reference materials;*
- *information on metrological traceability of reference materials (if known).*

3. Comparison participants

Provide details of producers of reference materials to be compared, organization (s), which will perform measurements in the framework of reference material comparisons

No.	Organizations, participating in comparisons	Acronym of organization, participating in comparisons	Address	Contact person	E-mail. telephone, fax

4. Comparison organization

- *Scheme of comparisons (round robin, radial or mixed);*
- *Description of comparison principle;*
- *Schedule of comparisons;*
- *Routes of transportation of reference materials to be compared.*

5. Description of measurement procedure

This section should contain:

- *description of the measurand, measurement conditions, measurement instruments in use;*
- *agreed equation of measurements with account of introduced corrections;*
- *in case of using own measurement procedures by participants, the description of these procedures should be provided;*
- *details of a measurement instrument (measurement standard, reference material),used for accuracy control of measurement results;*
- *scope, sequence and condition of measurements.*

6. Comparison results

This section should contain:

- *measurement results, obtained in the framework of comparisons and combined standard uncertainties of these results;*
- *uncertainty budgets of measurement results;*

Standard uncertainty Components	**A**	**B**
1		
2		
…		
Combined standard uncertainty		
Expanded uncertainty (k=2)		
Confidence level		

7. Processing measurement results

This section should contain the algorithm of data processing, depending on the chosen type of comparisons, described in Annex A.

ANNEX D

D.1 Form of Certificate of Participation in Reference Material Comparisons within COOMET

EURO-ASIAN COOPERATION OF NATIONAL METROLOGICAL INSTITUTIONS

COOMET

ЕВРО-АЗИАТСКОЕ СОТРУДНИЧЕСТВО ГОСУДАРСТВЕННЫХ МЕТРОЛОГИЧЕСКИХ УЧРЕЖДЕНИЙ

КООМЕТ

CERTIFICATE OF PARTICIPANT OF EXPERIMENTAL WORK ON REFERENCE MATERIAL COMPARISON

The present Document certifies, that

_____

specify the name of the participant of reference material comparison - reference material producer, laboratory, which conducted experimental research

_____

specify the name of reference material producer or laboratory with the name of organization, which owns this laboratory
(font Times New Roman,20)

_____

specify the country (font Arial,16)

was the participant _____

specify the type of experimental work (font Arial,14)

in COOOMET project _____

specify the number of the project (font Arial,14)

_____

specify the name of the project (font Arial,16)

_____

specify the timeframe of the project (month, year of beginning and end), font Comic Sans MS, 16

The project is organized by _____

specify the name of coordinating organization of the project (font Monotype Corsiva, 16)

in accordance with COOMET Programme

Coordinator _____

the Project Coordinator's initials, surname, place of work, country

Chairman of TC 1.12 "Reference Materials" _____

the Chairman's signature, initials, surname

Secretariat of COOMET TC 1.12 "Reference Materials"

_____

name of organization, mail address of Secretariat of COOMET TC 1.12

Telephone: Fax: E-mail:

D.2 Form of Annex to Certificate of Participant of Experimental Work on Reference Material Comparison, submitted to the producer of reference material to be compared

EURO-ASIAN COOPERATION OF NATIONAL METROLOGICAL INSTITUTIONS

COOMET

ЕВРО-АЗИАТСКОЕ СОТРУДНИЧЕСТВО ГОСУДАРСТВЕННЫХ МЕТРОЛОГИЧЕСКИХ УЧРЕЖДЕНИЙ

КООМЕТ

ANNEX

TO CERTIFICATE OF PARTICIPANT OF EXPERIMENTAL WORK ON REFERENCE MATERIAL COMPARISON

Reference materials, submitted for comparison

Reference material parameters	Details of reference materials		
	1	....	p
➢ name			
➢ metrological characteristics			
➢ intended use			
➢ metrological traceability			
➢ producer			

The list of reference material parameters may be extended (if necessary)

Comparisons are completed

Specify the timeframe of comparisons, the name(s) of laboratory (ies), with participation of which comparisons are completed (font Times New Roman,20)

Comparison results

specify the results of reference material comparisons (font Times New Roman,20)

Chairman of TC 1.12 "Reference materials" _____

the Chairman's signature, initials, surname

ANNEX E

EXAMPLES OF PROCESSING RESULTS OF REFERENCE MATERIAL COMPARISONS

E.1 Example of processing measurement results, obtained in the framework of paired comparison of reference materials

Paired comparison of reference materials of lead mass concentration in solution - RM_1 and RM_2 is completed. Metrological characteristics of compared reference materials and measurement results, obtained in the framework of comparisons, are given in table E.1.

Table E.1. Metrological characteristics of reference materials, submitted for paired comparison and measurement results, obtained in the framework of paired comparison.

RM index	RM metrological characteristics		Measurement results of lead mass concentration, obtained in the framework of comparisons, x_{ij}, mg/dm^3
	Certified value of lead mass concentration, A_j, mg/dm^3	Relative expanded uncertainty of the certified value $U_{rel}(A_j)$, %, at k=2	
RM_1	1,00	1,0	0,97 0,99 1,00 1,01 0,98 1,02 0,98 1,00 0,99 1,00
RM_2	0,98	1,0	0,98 0,98 1,00 1,01 0,99 0,97 0,99 1,00 0,98 1,01

The reference value of paired comparison for each of reference materials being compared is calculated:

for RM_1:

$$x_{ref1} = \frac{\sum_{i=1}^{n} x_{i1}}{n} = \frac{(0,97 + 0,99 + 1,00 + 1,01 + 0,98 + 1,02 + 0,98 + 1,00 + 0,99 + 1,00)}{10} = 0,99;$$

For RM_2:

$$x_{ref2} = \frac{\sum_{i=1}^{n} x_{i2}}{n} = \frac{(0,98 + 0,98 + 1,00 + 1,01 + 0,99 + 0,97 + 0,99 + 1,00 + 0,98 + 1,01)}{10} = 0,99.$$

The reference degree of equivalence of reference material comparison is calculated:

for RM_1:

$$d_{1,rel} = (\frac{A_1}{x_{ref1}} - 1) \cdot 100\% = (\frac{1,00}{0,99} - 1) \cdot 100\% = 1,01\%;$$

for RM_2:

$$d_{2,rel} = (\frac{A_2}{x_{ref\,2}} - 1) \cdot 100\% = (\frac{0{,}98}{0{,}99} - 1) \cdot 100\% = -1{,}01\%\,.$$

The standard uncertainty of the relative degree of equivalence of reference materials is calculated:

for RM_1:

$$u(d_{1,rel}) = \frac{A_1}{x_{ref1}} \cdot \sqrt{u_{rel}^2(A_1) + u_{rel}^2(x_{ref1})} = \frac{1{,}00}{0{,}99} \cdot \sqrt{0{,}5^2 + 2{,}02^2} = 2{,}10\%\,,$$

for RM_2:

$$u(d_{2,rel}) = \frac{A_2}{x_{ref\,2}} \cdot \sqrt{u_{rel}^2(A_2) + u_{rel}^2(x_{ref\,2})} = \frac{0{,}98}{0{,}99} \cdot \sqrt{0{,}5^2 + 2{,}02^2} = 2{,}08\%$$

where:

$u_{rel}(A_1)$ is the relative standard uncertainty of RM_1 certified value (in %), calculated by:

$$u_{rel}(A_1) = \frac{U_{rel}(A_1)}{k} = \frac{1{,}0}{2} = 0{,}5\%\,;$$

$u_{rel}(A_2)$ is the relative standard uncertainty of RM_2 certified value (in %), calculated by

$$u_{rel}(A_2) = \frac{U_{rel}(A_2)}{k} = \frac{1{,}0}{2} = 0{,}5\%\,;$$

$u_{rel}(x_{ref1})$ is the relative standard uncertainty of the reference value x_{ref1} (in %), calculated by

$$u_{rel}(x_{ref1}) = \frac{u(x_{ref1})}{x_{ref1}} = \frac{0{,}02}{0{,}99} \cdot 100\% = 2{,}02\%\,;$$

$u_{rel}(x_{ref\,2})$ is the relative combined standard uncertainty of the reference value $x_{ref\,2}$ (in %), calculated by

$$u_{rel}(x_{ref\,2}) = \frac{u(x_{ref\,2})}{x_{ref\,2}} = \frac{0{,}02}{0{,}99} \cdot 100\% = 2{,}02\%\,,$$

where:

$u(x_{ref1})$ is the combined standard uncertainty of the reference value x_{ref1};

- $u(x_{ref\,2})$ is the combined standard uncertainty of the reference value $x_{ref\,2}$

The expanded uncertainty of the relative degree of equivalence of RM_1 comparison

$$U(d_{1,rel}) = 2 \cdot u(d_{1,rel}) = 2 \cdot 2{,}10 = 4{,}20\%$$

and the expanded uncertainty of the relative degree of equivalence of RM_2 comparison

$$U(d_{2,rel}) = 2 \cdot u(d_{2,rel}) = 2 \cdot 2{,}08 = 4{,}16\%.$$

is calculated.

Comparison of the relative degree of equivalence of RM_1 and RM_2 comparison respectively with the expanded uncertainty of the relative degree of equivalence of RM_1 and RM_2 comparison indicates, that condition (A.3.13) is met, i.e.:

.

for RM_1:

$$\left|d_{1,rel}\right| \le U(d_{1,rel}), \text{ т.е. } \left|1{,}01\right| < 4{,}20,$$

for RM_2:

$$\left|d_{2,rel}\right| \le U(d_{2,rel}), \text{ т.е. } \left|1{,}01\right| < 4{,}16,$$

which is a confirmation of the claimed metrological characteristics of compared reference materials with a probability 0,95. Dependence of the relative degree of equivalence and the corresponding certified values of lead mass concentration in compared reference materials is shown in fig. E.1.

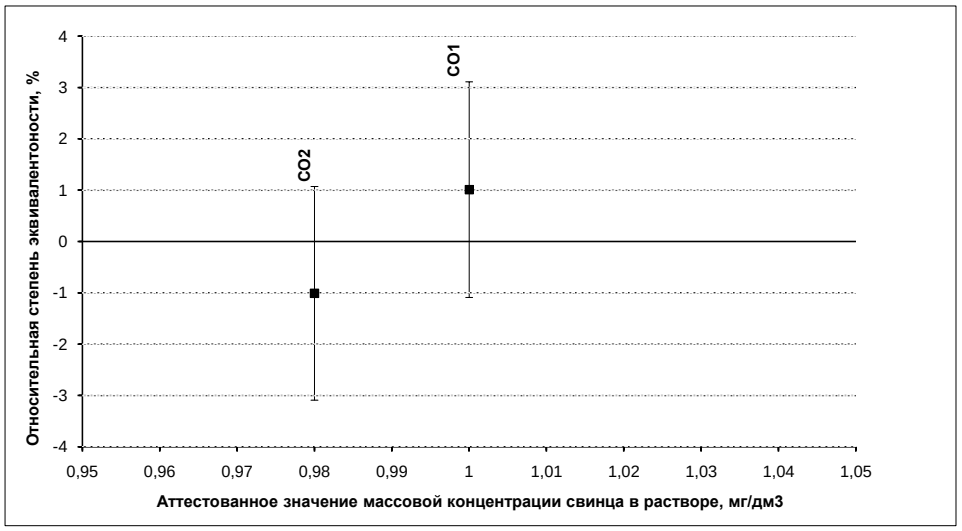


Fig. E. 1 Dependence of the relative degree of equivalence and the corresponding certified values of lead mass concentration in compared reference materials.

Paired difference of the relative degrees of equivalence of the paired comparison of reference materials is calculated by

$$d_{1,2,rel} = d_{1,rel} - d_{2,rel} = 1{,}01 - (-1{,}01) = 2{,}02,$$

the standard uncertainty of the paired difference of the relative degrees of equivalence of the paired comparison of reference materials is calculated by

$$u(d_{1,2,rel}) = \sqrt{u^2(d_{1,rel}) + u^2(_{d\,2,rel}) - 2\,\mathrm{cov}(d_{1,rel}, d_{2,rel})} = \sqrt{2{,}10^2 + 2{,}08^2 - 2\,\mathrm{cov}(d_{1,rel}, d_{2,rel})} = 2{,}96.$$

Comparison of the value $d_{1,2,rel}$ with the value $(2 \cdot u(d_{1,2,rel}))$

$$\left|d_{1,2,rel}\right| < 2 \cdot u(d_{1,2,rel}), \text{ т.е. } 2{,}02 < 5{,}92.$$

indicates the insignificance of the paired difference of the relative degree of equivalence of the paired comparison of reference materials $d_{1,2,rel}$ and characterizes the possibility of mutual replacement of reference materials, having one and the same intended use.

The results of paired comparison of reference materials RM_1 and RM_2 demonstrated:

а) the possibility of issuing reference materials, compatible in the degree of equivalence of reference materials RM_1 and RM_2;

б) the possibility of mutual replacement of compared reference materials RM_1 and RM_2, when they are used in accordance with their intended use in order to obtain compatible measurement results.

E.2 Example of processing measurement results, obtained in the framework of multiple comparison of reference materials

Multiple comparison of reference materials of copper mass concentration in solutions of the producer I (RM_1, RM_2, RM_3) and the producer II (RM_4, RM_5) is completed. Metrological characteristics of compared reference materials and measurement results, obtained in the framework of comparisons, are given in table E.2.

Table E.2. Metrological characteristics of reference materials, submitted for multiple comparison and measurement results, obtained in the framework of multiple comparison.

RM index	RM metrological characteristics		Measurement results of copper mass concentration, obtained in the framework of comparisons, x_{ij}, мг/дм^3	
	Certified value of copper mass concentration, A_j, mg/dm^3	Relative expanded uncertainty of the certified value $U_{rel}(A_j)$, %, at k=2		
Producer I				
RM_1	0,10	1,0	0,099 0,099 0,100 0,100 0,100	0,099 0,100 0,100 0,100 0,100
			$\bar{x}_1$ = 0,0997	
RM_2	1,00	1,0	1,00 1,00 0,99 1,00 0,99	1,00 0,99 1,00 1,00 1,00
			$\bar{x}_2$ = 0,997	
RM_3	5,0	1,0	5,0 4,9 5,0 5,0 4,9	5,0 5,0 5,1 5,0 5,0
			$\bar{x}_3$ = 5,01	
Producer II				
RM_4	0,50	1,0	0,500 0,500 0,499 0,500 0,499	0,500 0,500 0,500 0,499 0,500
			$\bar{x}_4$ = 0,4997	
RM_5	9,98	1,0	9,99 10,00 10,00 10,00 10,00	9,99 10,00 10,00 10,00 10,01
			$\bar{x}_5$ = 9,999	

E.2.1 Establishment of mutually consistent certified values of compared reference materials

Based on the results of measuring the values of the certified characteristic of each reference materials, obtained under repeatability conditions, the calculation was conducted of:

- $\bar{x}_j$ - mean values of the results of measuring copper mass concentration in reference materials by the formula A.4.4;

- $u(A_j)$ - the standard uncertainty of the certified value of j^{th} reference material, calculated by the $u(A_j) = \frac{U(A_j)}{2}$, where $U(A_j)$ is the expanded (absolute) uncertainty of the certified value of j^{th} reference material;

- $u(\overline{x_j})$ - the combined standard uncertainty of the mean value of the results of measuring the certified characteristic of j^{th} reference material;

- α - the term of reference dependence of the multiple comparison of reference materials by least square method;

β - the term of reference dependence of the multiple comparison of reference materials by least square method;

- $\bar{x}_j'$ - the mean predicted value of the results of measuring the certified characteristic of j^{th} reference material by the formula $\overline{x_j'} = \alpha + \beta \cdot A_j$;

- A_j' - predicted value of the certified characteristic of j^{th} reference material by the formula $A_j' = \dfrac{\bar{x}_j - \alpha}{\beta}$.

The calculation results are given in table E.3

Table E.3 The data for plotting reference dependence and evaluating mutual agreement of the certified values of reference materials

No.	RM index	A_j, mg/dm^3	$u(A_j) = \frac{U(A_j)}{2}$	$\bar{x}_j$, mg/dm^3	$u(\bar{x}_j)$	α	β	$\bar{x}_j'$, mg/dm^3	A_j', mg/dm^3	ε_j^2	ε_j
1	**2**	**3**	**4**	**5**	**6**	**7**	**8**	**9**	**10**	**11**	**12**
1	RM_1	0,10	0,0005	0,0997	0,0005	0	1,002	0,1002	0,0995	2	0,00074
2	RM_4	0,50	0,0025	0,4997	0,0005			0,501	0,4987	7,0304	0,00193
3	RM_2	1,00	0,005	0,997	0,005			1,002	0,995	2	0,00744
4	RM_3	5,0	0,025	5,01	0,035			5,01	5,0	0	0
5	RM_5	9,98	0,0499	9,999	0,006			10,00	9,979	0,0282	0,00149

In order to establish mutually consistent values of the certified characteristics of reference materials, parameters ε_j^2 and ε are calculated for each reference material by the formulae (A.4.2) and (A.4.3). As an example the calculation of parameters ε_j^2 and ε for RM_j is given below. The calculated values of ε_j^2 are given in table E.3.

$$\varepsilon_1^2 = \left[\frac{\left(A_1 - A_1'\right)}{U(A_1)/2}\right]^2 + \left[\frac{(\bar{x}_1 - \bar{x}_1')}{u(\bar{x}_1)}\right]^2 = \left[\frac{(0{,}10 - 0{,}0995)}{0{,}0005}\right]^2 + \left[\frac{(0{,}0997 - 0{,}1002)}{0{,}0005}\right]^2 = 2;$$

$$\varepsilon_4^2 = \left[\frac{\left(A_4 - A_4'\right)}{U(A_4)/2}\right]^2 + \left[\frac{(\bar{x}_4 - \bar{x}_4')}{u(\bar{x}_4)}\right]^2 = \left[\frac{(0{,}50 - 0{,}4987)}{0{,}0025}\right]^2 + \left[\frac{(0{,}4997 - 0{,}501)}{0{,}0005}\right]^2 = 7{,}0304;$$

$$\varepsilon_2^2 = \left[\frac{\left(A_2 - A_2'\right)}{U(A_2)/2}\right]^2 + \left[\frac{(\bar{x}_2 - \bar{x}_2')}{u(\bar{x}_2)}\right]^2 = \left[\frac{(1{,}00 - 0{,}995)}{0{,}005}\right]^2 + \left[\frac{(0{,}997 - 1{,}002)}{0{,}005}\right]^2 = 2;$$

$$\varepsilon_3^2 = \left[\frac{\left(A_3 - A_3'\right)}{U(A_3)/2}\right]^2 + \left[\frac{(\bar{x}_3 - \bar{x}_3')}{u(\bar{x}_3)}\right]^2 = \left[\frac{(5{,}0 - 5{,}0)}{0{,}025}\right]^2 + \left[\frac{(5{,}01 - 5{,}01)}{0{,}035}\right]^2 = 0;$$

$$\varepsilon_5^2 = \left[\frac{\left(A_5 - A_5'\right)}{U(A_5)/2}\right]^2 + \left[\frac{(\bar{x}_5 - \bar{x}_5')}{u(\bar{x}_5)}\right]^2 = \left[\frac{(9{,}98 - 9{,}979)}{0{,}0499}\right]^2 + \left[\frac{(9{,}999 - 10{,}000)}{0{,}006}\right]^2 = 0{,}0282.$$

$$\varepsilon_1 = (A_1 - A_1') \cdot \sqrt{\sum_{j=1}^{J} \varepsilon_j^2 / J} = (0{,}1 - 0{,}0995) \cdot \sqrt{\sum_{j=1}^{5} \frac{2 + 7{,}0304 + 2 + 0 + 0{,}02818}{5}} = 0{,}00074;$$

$$\varepsilon_4 = (A_4 - A_4') \cdot \sqrt{\sum_{j=1}^{J} \varepsilon_j^2 / J} = (0{,}5 - 0{,}49870) \cdot 1{,}4872 = 0{,}00193;$$

$$\varepsilon_2 = (A_2 - A_2') \cdot \sqrt{\sum_{j=1}^{J} \varepsilon_j^2 / J} = (1{,}00 - 0{,}9950) \cdot 1{,}4872 = 0{,}00744;$$

$$\varepsilon_3 = (A_3 - A_3') \cdot \sqrt{\sum_{j=1}^{J} \varepsilon_j^2 / J} = (5{,}0 - 5{,}0) \cdot 1{,}4872 = 0;$$

$$\varepsilon_5 = (A_5 - A_5^{'}) \cdot \sqrt{\sum_{j=1}^{J} \varepsilon_j^2 / J} = (9{,}98 - 9{,}97904) \cdot 1{,}48728 = 0{,}00149 .$$

Calculation results $\bar{x}_j$ are given in tables E.2 and E.3.

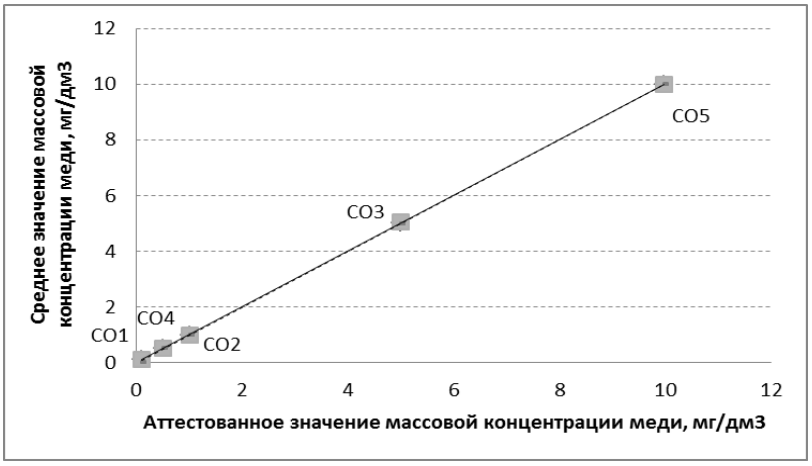


Fig. E.2 Reference dependence $\bar{x}_j = f(A_j)$ for five reference materials to be compared.

The sign "+" ε_j means, that the certified value of j^{th} reference material is more, than its predicted value. To establish mutually consistent values of the certified characteristics of reference materials to be compared, the reference dependence $\overline{x_j} = \alpha + \beta \cdot A_j$ should be plotted with indication of the expanded uncertainty, calculated with account for the values of ε_j and the coverage factor $k = 2$ (fig. E.2). Mutual agreement of certified values of compared reference materials is established, i.e. the certified values of the reference materials agree within their expanded uncertainty with the reference dependence of multiple comparison of reference materials

E.2.2 Calculation of the relative degree of equivalence of reference materials

The calculation of the relative degree of equivalence for each j^{th} reference material to be compared is performed taking into account the reference dependence $\overline{x_j} = \alpha + \beta \cdot A_j$ by the formula (A.4.5). The calculation of the relative degree of equivalence for each $1^{st} - 5^{th}$ reference material being compared:

$$d_{1,rel} = (\frac{A_1 \cdot \beta}{\overline{x_1} - \alpha} - 1) \cdot 100\% = \left(\frac{0{,}1 \cdot 1{,}002}{0{,}0997} - 1 \right) \cdot 100\% = 0{,}5\%;$$

$$d_{4,rel} = (\frac{A_4 \cdot \beta}{\overline{x_4} - \alpha} - 1) \cdot 100\% = \left(\frac{0{,}5 \cdot 1{,}002}{0{,}4997} - 1 \right) \cdot 100\% = 0{,}26\%;$$

$$d_{2,rel} = (\frac{A_2 \cdot \beta}{\overline{x_2} - \alpha} - 1) \cdot 100\% = \left(\frac{1{,}0 \cdot 1{,}002}{0{,}997} - 1 \right) \cdot 100\% = 0{,}5\%;$$

$$d_{3,rel} = (\frac{A_3 \cdot \beta}{\overline{x_3} - \alpha} - 1) \cdot 100\% = \left(\frac{5{,}0 \cdot 1{,}002}{5{,}01} - 1 \right) \cdot 100\% = 0;$$

$$d_{5,rel} = (\frac{A_5 \cdot \beta}{\overline{x_5} - \alpha} - 1) \cdot 100\% = \left(\frac{9{,}98 \cdot 1{,}002}{9{,}999} - 1 \right) \cdot 100\% = 0{,}01\% .$$

E.2.3 Calculation of the

standard and expanded uncertainty of the relative degree of equivalence of reference materials to be compared.

The standard and expanded uncertainty of the relative degree of equivalence for j^{th} reference materials is calculated by the formula (A.4.6). The calculation of the relative degree of equivalence for reference materials being compared:

$$u(d_{1,rel}) = 100 \cdot \sqrt{\left(\frac{1{,}002}{0{,}0997}\right)^2 \cdot 0{,}0005^2 + \left(\frac{0{,}10}{0{,}0997}\right)^2 \cdot 0{,}0003^2 + \left(\frac{0{,}10 \cdot 1{,}002}{0{,}0997^2}\right)^2 \cdot 0{,}0005^2 + \left(\frac{0{,}10 \cdot 1{,}002}{0{,}0997^2}\right)^2 \cdot 0{,}0013^2} = 1{,}5\%;$$

$$u(d_{4,rel}) = 100 \cdot \sqrt{\left(\frac{1{,}002}{0{,}4997}\right)^2 \cdot 0{,}0025^2 + \left(\frac{0{,}50}{0{,}4997}\right)^2 \cdot 0{,}0003^2 + \left(\frac{0{,}50 \cdot 1{,}002}{0{,}4997^2}\right)^2 \cdot 0{,}0005^2 + \left(\frac{0{,}50 \cdot 1{,}002}{0{,}4997^2}\right)^2 \cdot 0{,}0013^2} = 0{,}57\%;$$

$$u(d_{2,rel}) = 100 \cdot \sqrt{\left(\frac{1{,}002}{0{,}997}\right)^2 \cdot 0{,}005^2 + \left(\frac{1{,}0}{0{,}997}\right)^2 \cdot 0{,}0003^2 + \left(\frac{1{,}0 \cdot 1{,}002}{0{,}997^2}\right)^2 \cdot 0{,}005^2 + \left(\frac{1{,}0 \cdot 1{,}002}{0{,}997^2}\right)^2 \cdot 0{,}0013^2} = 0{,}73\%;$$

$$u(d_{3,rel}) = 100 \cdot \sqrt{\left(\frac{1{,}002}{5{,}01}\right)^2 \cdot 0{,}025^2 + \left(\frac{5{,}0}{5{,}01}\right)^2 \cdot 0{,}0003^2 + \left(\frac{5{,}0 \cdot 1{,}002}{5{,}01^2}\right)^2 \cdot 0{,}035^2 + \left(\frac{5 \cdot 1{,}002}{5{,}01^2}\right)^2 \cdot 0{,}0013^2} = 0{,}86\%;$$

$$u(d_{5,rel}) = 100 \cdot \sqrt{\left(\frac{1{,}002}{9{,}999}\right)^2 \cdot 0{,}0499^2 + \left(\frac{9{,}98}{9{,}999}\right)^2 \cdot 0{,}0003^2 + \left(\frac{9{,}98 \cdot 1{,}002}{9{,}999^2}\right)^2 \cdot 0{,}006^2 + \left(\frac{9{,}98 \cdot 1{,}002}{9{,}999^2}\right)^2 \cdot 0{,}0013^2} = 0{,}50\%.$$

Note – The standard uncertainties of the term α of the reference dependence $u(\alpha)$ and the standard uncertainty of the term β of the reference dependence $u(\beta)$ may be calculated by the formulae, presented in Annex G or with the use of the relevant statistical programmes.

The expanded uncertainty of the relative degree of equivalence for j^{th} reference material calculated by the formula (A.4.7):

- the expanded uncertainty of the relative degree of equivalence for the 1st reference material $U(d_{1,rel}) = 2 \cdot 1{,}5 = 3\%$;
- the expanded uncertainty of the relative degree of equivalence for the 4th reference material $U(d_{4,rel}) = 2 \cdot 0{,}57 = 1{,}14\%$;
- the expanded uncertainty of the relative degree of equivalence for the 2nd reference material $U(d_{2,rel}) = 2 \cdot 0{,}73 = 1{,}46\%$;
- the expanded uncertainty of the relative degree of equivalence for the 3rd reference material $U(d_{3,rel}) = 2 \cdot 0{,}86 = 1{,}72\%$;
- the expanded uncertainty of the relative degree of equivalence for the 5th reference material $U(d_{5,rel}) = 2 \cdot 0{,}50 = 1{,}0\%$.

D.2.4 Intercomparison of the relative degree of equivalence the expanded uncertainty of the relative degree of equivalence of reference materials

The intercomparison of the relative degree of equivalence of reference materials being compared with the expanded uncertainty of the relative degree of equivalence is conducted on the basis of the following condition (A.4.8). The results of the intercomparison are as follows:

- for RM_1:

$|d_{1,rel}| < U(d_{1,rel})$, as. $0{,}5 < 3$;

- for RM_4:

$|d_{4,rel}| < U(d_{4,rel})$, as $0{,}26 < 1{,}14$;

- for RM_2:

$|d_{2,rel}| < U(d_{2,rel})$, as $0{,}5 < 1{,}46$;

- for RM_3:

$|d_{3,rel}| < U(d_{3,rel})$, as $0 < 1{,}72$;

- for RM_5:

$|d_{5,rel}| < U(d_{5,rel})$, as $0{,}01 < 1{,}0$.

The claimed metrological characteristics of all five compared reference materials are confirmed with a probability 0,95, because the condition (A.4.8) is met.

Graphical dependence of the relative degree of equivalence and the certified value of copper mass concentration (mg/dm^3) of compared reference materials for composition of copper solution is shown in Fig. E.3

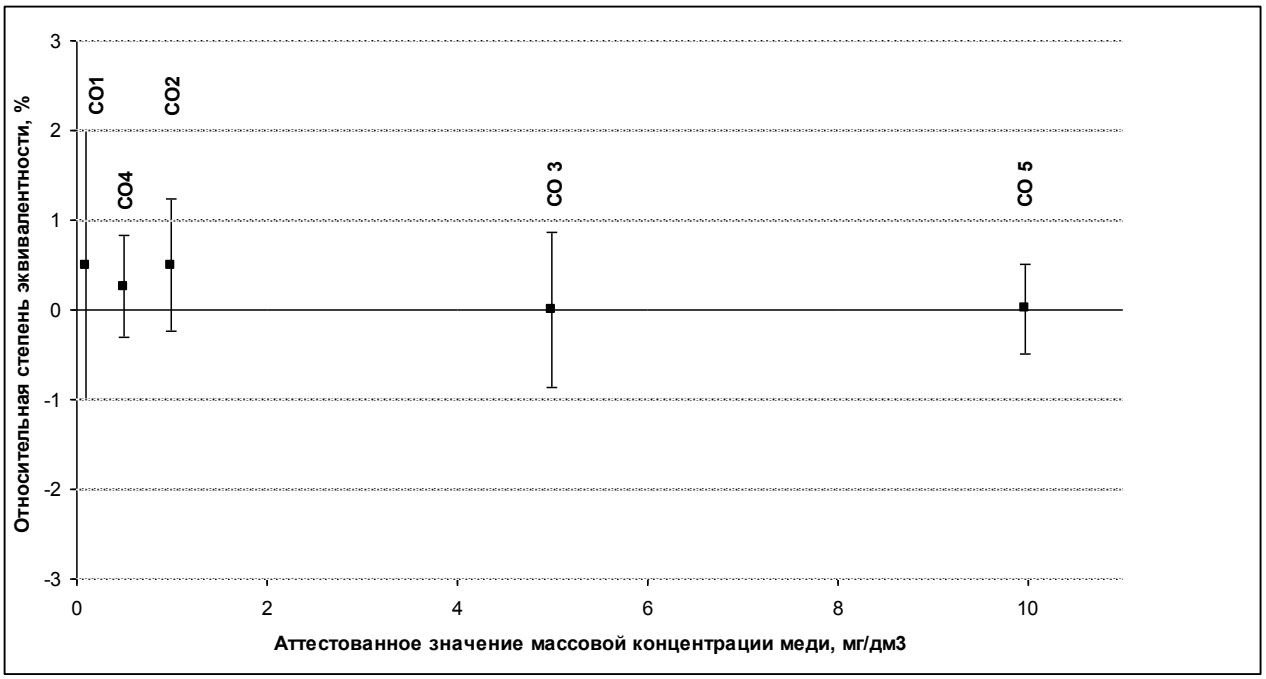


Fig. E.3 dependence of the relative degree of equivalence and the corresponding certified values of copper mass concentration in compared reference materials.

The results in fig.E.3 indicate, that when comparing reference materials, having different certified values of copper mass concentration, the relative degree of equivalence not exceeding 0,5 % was demonstrated for all reference materials. Fulfillment of condition (A.4.8) is demonstrated for all reference materials.

E.2.5 Evaluation of the degree of equivalence of comparison participants, which submitted several reference materials for comparison

Two participants took part in a comparison (producer I and producer II); producer I submitted 3 reference materials for comparison, producer II – 2 reference materials (table E.2).

E.2.5.1 Evaluation of the degree of equivalence of the 1st comparison participant, which submitted 3 reference materials for comparison

The relative degree of equivalence of the 1st comparison participant (producer I), which submitted 3 reference materials for comparison, $D_{I,rel}$, is calculated by:

$$D_{I,rel} = \frac{\sum_{k_p=1}^{3} d_{j,rel}}{3},$$

where:

Kp is the number of reference materials, submitted by the 1st comparison participant, *Kp*=3;

$d_{j,rel}$ is the relative degree of equivalence of RM_1, RM_2, RM_3, submitted by the 1st participant for comparison.

$$D_{I,rel} = \frac{0{,}5 + 0{,}5 + 0}{3} = 0{,}33\%.$$

The expanded uncertainty of the relative degree of equivalence of the 1st comparison participant is calculated by

$$U(D_{I,rel}) = 2 \cdot u(D_{I,rel}) = 2{,}5,$$

where $u(D_{I,rel})$ is the standard uncertainty of the relative degree of equivalence, calculated by

$$u(D_{I,rel}) = \frac{\sum_{k=1}^{Kp} u(d_{j,rel})^2}{K_p} + \left(\frac{\sum_{k=1}^{Kp} \left(d_{j,rel} - D_{kp,rel} \right)^2}{Kp - 1} \right)^2 =$$

$$= \frac{1{,}5^2 + 0{,}73^2 + 0{,}86^2}{3} + \left(\frac{(0{,}5 - 0{,}33)^2 + (0{,}5 - 0{,}33)^2 + (0 - 0{,}33)^2}{3 - 1} \right)^2 = 1{,}25.$$

E.2.5.2 Evaluation of the degree of equivalence of the 2nd comparison participant, which submitted 2 reference materials for comparison

The relative degree of equivalence of the 2nd comparison participant (producer II), which submitted 2 reference materials for comparison, $D_{II,rel}$, is calculated by:

$$D_{II,rel} = \frac{\sum_{k_p=1}^{2} d_{j,rel}}{2},$$

where:

K_p is the number of reference materials, submitted by the 2nd comparison participant, *Kp*=2;

$d_{j,rel}$ is the relative degree of equivalence of RM_4, RM_5, submitted by the 2nd participant for comparison.

$$D_{II,rel} = \frac{0{,}26 + 0{,}01}{2} = 0{,}14\%.$$

The expanded uncertainty of the relative degree of equivalence of the 2nd comparison participant is calculated by:

$$U(D_{II,rel}) = 2 \cdot u(D_{II,rel}) = 2 \cdot 0{,}58 = 1{,}16,$$

where $u(D_{II,rel})$ is the standard uncertainty of the relative degree of equivalence, calculated by:

$$u(D_{kp,rel}) = \frac{0{,}57^2 + 0{,}50^2}{2} + \left(\frac{(0{,}26 - 0{,}14)^2 + (0{,}01 - 0{,}14)^2}{2 - 1} \right)^2 = 0{,}58$$

The results of the calculation of the relative degree of equivalence of comparison participants can be presented graphically. In fig. E.4 the relative degrees of equivalence of comparison participants – reference material producer I and producer II are shown.

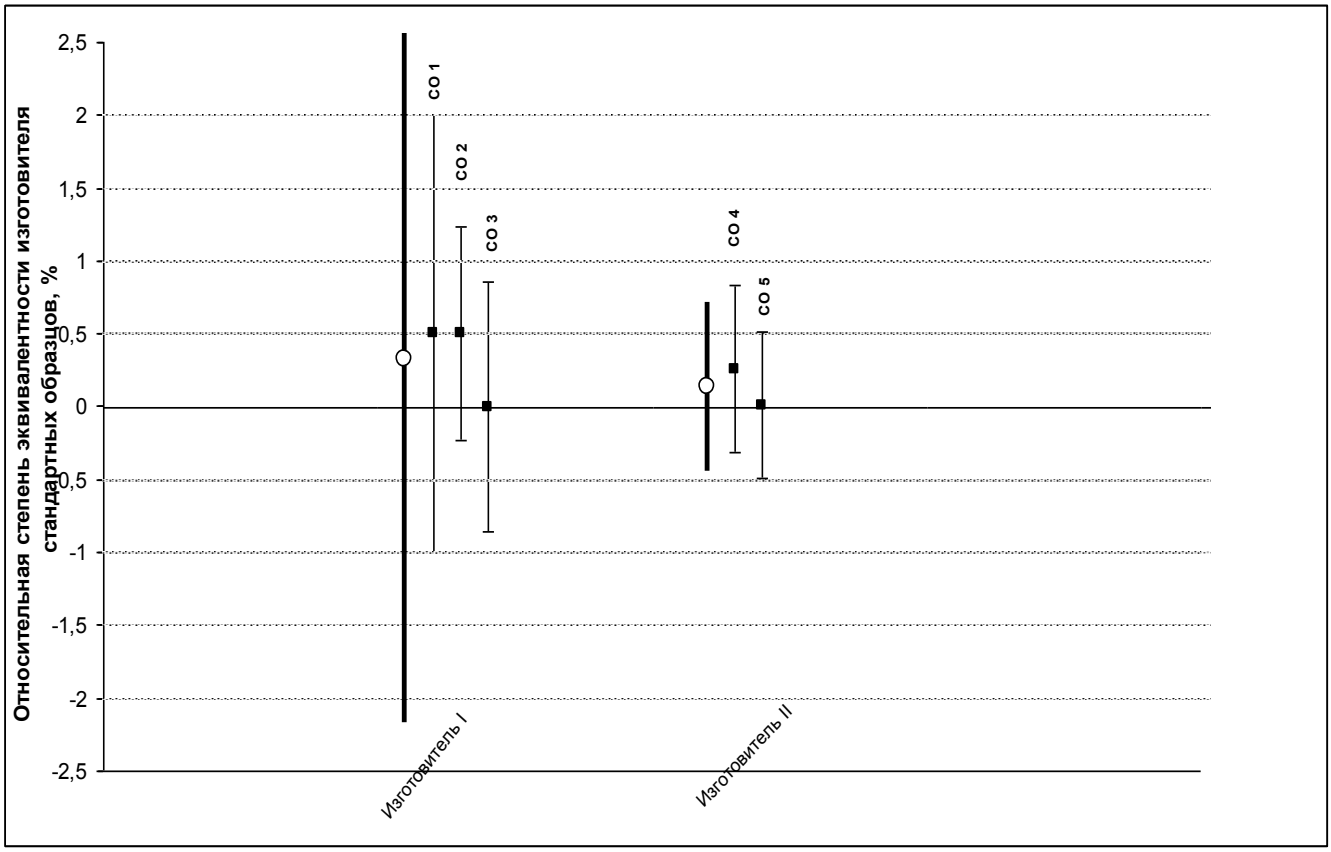


Fig. E.4 The relative degree of equivalence of comparison participants – reference material producer I and producer II (in bold).

The mutual consistence of reference materials RM_1, RM_2, RM_3, RM_4, RM_5 is confirmed, the condition (A.4.8) is met the relative degrees of equivalence of comparison participants agree within the expanded uncertainty in full, overlapping "0", it may be concluded, that the comparison participants ((producer I and producer II) confirmed their capability to issue mutually consistent reference materials, ensuring comparability of measurements in the user laboratories, based on these reference materials

ANNEX F

DERIVATION OF SOME FORMULAE, PRESENTED IN THE DOCUMENT

F.1 Derivation of the formula A.3.5 and A.3.6

The calculation of the relative degree of equivalence of the first reference material $d_{j,rel}$ - the relative difference between the reference value $x_{ref\,1}$ and $x_{ref\,2}$ and the certified value of the first reference material A_1 is performed using:

$$d_{1,rel} = \frac{A_1 - x_{ref1}}{x_{ref1}} = \frac{A_1}{x_{ref1}} - 1. \tag{F.1}$$

The derivation of the formula to calculate the squared standard uncertainty of the relative degree of equivalence of the first reference material comparison $d_{1,rel}$ - $u^2(d_{1,rel})$:

$$\begin{aligned} u^2(d_{1,rel}) &= \frac{u^2(A_1)}{x_{ref1}^2} + \frac{A_1^2 \cdot u^2(x_{ref1})}{x_{ref1}^4} - 2 \cdot \frac{A \cdot \mathrm{cov}(A_1, x_{ref1})}{x_{ref1}^3} + u^2(1) = \\ &\frac{A_1^2}{x_{ref1}^2} \cdot \left[\frac{u^2(A_1)}{A_1^2} + \frac{u^2(x_{ref1})}{x_{ref1}^2} - 2 \cdot \frac{\mathrm{cov}(A_1, x_{ref1})}{A \cdot x_{ref1}} + \frac{A_1^2}{x_{ref1}^2} \cdot 0 \right] = \\ &\frac{A_1^2}{x_{ref1}^2} \cdot \left[u_{rel}^2(A_1) + u_{rel}^2(x_{ref1}) \right]. \end{aligned} \tag{F.2}$$

Taking into consideration, that covariations A_1 and x_{ref1} may be neglected, since measurements for A_1 and x_{ref1} are (should be) independent, the formula for the calculation of the standard uncertainty of the relative degree of equivalence of the first reference material comparison $d_{1,rel}$ - $u^2(d_{1,rel})$ is as follows:

$$u(d_{1,rel}) = \frac{A_1}{x_{ref1}} \cdot \sqrt{u_{rel}^2(A_1) + u_{rel}^2(x_{ref1})}\,. \tag{F.3}$$

The derivation of the formula to calculate the standard uncertainty of the relative degree of equivalence of the second reference material comparison $d_{2,rel}$ - $u(d_{2,rel})$ is similar. The calculation of the standard uncertainty of the relative degree of equivalence $u(d_{2,rel})$ is performed using:

$$u(d_{2,rel}) = \frac{A_2}{x_{ref\,2}} \cdot \sqrt{u_{rel}^2(A_2) + u_{rel}^2(x_{ref\,2})}\,. \tag{F.4}$$

F.2 Derivation of the formula A.4.6

For the case of multiple comparison of reference materials the calculation of the relative degree of equivalence for each j^{th} reference material being compared is performed by using:

$$d_{j,rel} = \frac{A_j - A_j^{'}}{A_j^{'}} = \frac{A_j - (\overline{x_j} - \alpha)/\beta}{(\overline{x_j} - \alpha)/\beta} = \frac{A_j \cdot \beta}{\overline{x_j} - \alpha} - 1, \tag{F.5}$$

where α and β are the terms of the reference dependence of multiple comparison of reference materials, calculated by the least-square method.

The derivation of the formula to calculate the squared standard uncertainty of the relative degree of equivalence of j^{th} reference material comparison $d_{j,rel}$ - $u^2(d_{j,rel})$:

$$u^2(d_{j,rel}) = \left[\frac{\partial}{\partial A_j}\left(\frac{A_j \cdot \beta}{\overline{x_j} - \alpha} - 1\right)\right]^2 \cdot u^2(A_j) + \left[\frac{\partial}{\partial \beta}\left(\frac{A_j \cdot \beta}{\overline{x_j} - \alpha} - 1\right)\right]^2 \cdot u^2(\beta) + \left[\frac{\partial}{\partial \overline{x_j}}\left(\frac{A_j \cdot \beta}{\overline{x_j} - \alpha} - 1\right)\right]^2 \cdot u^2(\overline{x_j}) +$$

$$+ \left[\frac{\partial}{\partial \alpha}\left(\frac{A_j \cdot \beta}{\overline{x_j} - \alpha} - 1\right)\right]^2 \cdot u^2(\alpha) = \tag{E.6}$$

$$= \left(\frac{\beta}{\overline{x_j} - \alpha}\right)^2 \cdot u^2(A_j) + \left(\frac{A_j}{\overline{x_j} - \alpha}\right)^2 \cdot u^2(\beta) + \left(\frac{A_j \cdot \beta}{(\overline{x_j} - \alpha)^2}\right)^2 \cdot u^2(\overline{x_j}) + \left(\frac{A_j \cdot \beta}{(\overline{x_j} - \alpha)^2}\right)^2 \cdot u^2(\alpha)$$

The standard uncertainty of the relative degree of equivalence of j^{th} reference material is calculated by

$$u(d_{j,rel}) = \sqrt{\left(\frac{\beta}{\overline{x_j} - \alpha}\right)^2 \cdot u^2(A_j) + \left(\frac{A_j}{\overline{x_j} - \alpha}\right)^2 \cdot u^2(\beta) + \left(\frac{A_j \cdot \beta}{(\overline{x_j} - \alpha)^2}\right)^2 \cdot u^2(\overline{x_j}) + \left(\frac{A_j \cdot \beta}{(\overline{x_j} - \alpha)^2}\right)^2 \cdot u^2(\alpha)} \,. \tag{E.7}$$

ANNEX G

FORMULAE FOR CALCULATION OF THE TERMS OF THE REFERENCE DEPENDENCE AND THEIR STANDARD UNCERTAINTY

G.1 Formula for calculation of the term α of the reference linear dependence

$$\alpha = \frac{\sum_{j=1}^{J} A_j^2 \cdot \sum_{j=1}^{J} \overline{x_j} - \sum_{j=1}^{J} A_j \sum_{j=1}^{J} (A_j \cdot \overline{x_j})}{J \cdot \sum_{j=1}^{J} A_j^2 - \left(\sum_{j=1}^{J} A_j \right)^2}. \quad \text{(G.1)}$$

G.2 Formula for calculation of the term β of the reference linear dependence

$$\beta = \frac{J \cdot \sum_{j=1}^{J} (A_j \cdot \overline{x_j}) - \sum_{j=1}^{J} A_j \cdot \sum_{j=1}^{J} \overline{x_j}}{J \cdot \sum_{j=1}^{J} A_j^2 - \left(\sum_{j=1}^{J} A_j \right)^2}. \quad \text{(G.2)}$$

G.3 Formula for calculation of the standard uncertainty $u(\alpha)$ of the term α of the reference dependence

$$u(\alpha) = \sqrt{\frac{\sum_{j=1}^{J} A_j^2}{\left(J \cdot \sum_{j=1}^{J} A_j^2 - \left(\sum_{j=1}^{J} A_j \right)^2 \right)} \cdot \left(\frac{\sum_{j=1}^{J} \overline{x}_j^2}{J-2} - \frac{\left(\sum_{j=1}^{J} \overline{x_j} \right)^2}{J \cdot (J-2)} - \frac{\left(J \cdot \sum_{j=1}^{J} A_j \cdot \overline{x_j} - \sum_{j=1}^{J} A_j \sum_{j=1}^{J} \overline{x_j} \right)^2}{J \cdot (J-2) \cdot \left(J \cdot \sum_{j=1}^{J} A_j^2 - \left(\sum_{j=1}^{J} A_j \right)^2 \right)} \right)}. \quad \text{(G.3)}$$

G.4 Formula for calculation the standard uncertainty $u(\beta)$ of the term β of the reference dependence

$$u(\beta) = \sqrt{\frac{J}{\left(J \cdot \sum_{j=1}^{J} A_j^2 - \left(\sum_{j=1}^{J} A_j \right)^2 \right)} \cdot \left(\frac{\sum_{j=1}^{J} \overline{x}_j^2}{J-2} - \frac{\left(\sum_{j=1}^{J} \overline{x_j} \right)^2}{J \cdot (J-2)} - \frac{\left(J \cdot \sum_{j=1}^{J} A_j \cdot \overline{x_j} - \sum_{j=1}^{J} A_j \sum_{j=1}^{J} \overline{x_j} \right)^2}{J \cdot (J-2) \cdot \left(J \cdot \sum_{j=1}^{J} A_j^2 - \left(\sum_{j=1}^{J} A_j \right)^2 \right)} \right)}. \quad \text{(G.4)}$$

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INFORMATION DATA

COOMET Recommendation R/RM/29:2016

1. Coordinating organization:
   COOMET TC 1.12 "Reference Materials"
   Ural Research Institute for Metrology (UNIIM)

2. COOMET project KOOMET:
   498/RU/10

3. The Recommendation is approved:
   at the 26th meeting of COOMET Committee

4. Information on the use of the Recommendation by COOMET member-organizations:

As COOMET Recommendation is of organization and methodical nature and reflects legal and procedural issues, to be followed by all COOMET structural bodies when conducting comparisons within COOMET, this Recommendation is used by all COOMET member- organizations, including national metrological institutes,