INTER-LABORATORY COMPARISON PROGRAMME
Emissions - metals
ROUND EM/1/2019
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1. Programme Objective
Assessment of proficiency of laboratories measuring metals in samples of emission dusts.

2. Organiser of the Programme
The organiser of inter-laboratory comparisons is the Quality Research Center [Centrum Badań Jakości] sp. z o.o. is an organisation operating within the structures of KGHM Polska Miedź S.A. All laboratories of the Company have implemented and certified Quality Management System compliant with the requirements of ISO 9001:2015 and implemented elements of the information security management system (PN-ISO/IEC 27001). In addition, since January 2003 the Company has been accredited by the Polish Centre for Accreditation for compliance with the requirements of the PN-EN ISO/IEC 17025:2005 standard (Accreditation Scope No. AB 412).

The inter-laboratory comparison programme is organised on the basis of the requirements of PN-EN ISO/IEC 17043:2011 “Conformity assessment. General requirements for proficiency testing” and ISO 13528:2015 “Statistical methods for use in proficiency testing by inter-laboratory comparison” and the IUPAC Technical Report “The international harmonised protocol for the proficiency testing of analytical chemistry laboratories”.

The organiser will not use subcontracting as part of an inter-laboratory comparison. All stages of the inter-laboratory comparison, beginning with the preparation of the test facility, statistical evaluation to the issuance of the report, are performed by the Organiser on the basis of the experience and competence of the employees of the Quality Research Center [Centrum Badań Jakości] sp. z o.o.

The following coordinators are responsible for the implementation of the inter-laboratory comparison programme:

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3. Participation criteria
The inter-laboratory comparison is open. Laboratories routinely performing tests on metals/non-metals in samples of emission dusts, having accreditation or applying for it, may participate in the comparison.

In order to participate in the inter-laboratory comparison it is necessary to send a completed and signed Application Form to the Coordinator within the deadline specified in the Schedule (item 4 of the Inter-laboratory Comparison Programme).

The Organiser reserves the right to cancel the inter-laboratory comparison round in case of insufficient number of Participants.

Participation in the inter-laboratory comparison is payable. Information on costs can be found in the Application Form available on the Organiser's website, i.e. www.cbj.com.pl

4. Schedule
The Organiser reserves the right to change any of the dates or, in the event of insufficient number of participants, to cancel the inter-laboratory comparison round, after prior notification (via e-mail) of the Participants.

As part of the inter-laboratory comparison programme, one round per calendar year is planned according to the following schedule:
1 – sending the Application Form to the Coordinator - by 24/05/2019.
3 – sending the Test Subject Delivery Protocol back to the Coordinator – up to 3 days from the receipt of the test subject.
4. – sending the Test Results Sheet back to the Coordinator - by 28/06/2019.
5. – providing the participants with the Inter-laboratory Comparison Report – by 09/08/2019.

5. Confidentiality

All information obtained as part of the organisation of the inter-laboratory comparison shall be confidential information. Laboratories participating in the inter-laboratory comparison will not be informed about other Participants, and each Participant will receive a unique identification code (randomly assigned), known only to the Coordinators and the Participant to whom this code has been assigned.

Each Participant of the inter-laboratory comparison shall avoid collusion and falsification of results involving passing on the obtained results to other Participants whose participation in the inter-laboratory comparison is known from other sources. When collusion is suspected and the results are falsified, the entire inter-laboratory comparison programme is invalidated.

6. Potential main sources of errors

Potential main sources of errors occurring in relation to the proposed inter-laboratory comparison are:
- heterogeneity and/or instability of the test subject,
- identifying collusion or falsification of results among participants,
- differences between the testing methods used.

7. Test subject

The subject of the proficiency test is an actual sample of emission dust taken from the place of its occurrence. The Organiser ensures that the preparation of the test subject is carried out in accordance with established testing methods applicable in an accredited laboratory, which has the above mentioned inter-laboratory comparison subject within the scope of accreditation. At each stage of the Inter-laboratory Comparison Programme, the test subject shall be stored in a manner which guarantees its stability.
Determination of Cd, Cr, Cu, Ni, Zn and V content shall be carried out according to laboratory procedures, using any spectrometric technique. The Organiser undertakes to provide the laboratories participating in the inter-laboratory comparison with the following information:
- the manner of handling the test subject prior to mineralisation,
- the weighed amount of the test subject ensuring the homogeneity of the sample.

The information concerning the expected content of elements in the test subject can be found in the *Proficiency Test Information* available at www.cbj.com.pl and will be sent together with the test subject to the Participants.

The deadline for sending the samples and the execution of the comparison is the same for all Participants. All samples will be sent by a courier company.

The service provided by the Organiser is planned, supervised, monitored and approved in such a manner as to ensure the quality of the Inter-laboratory Comparison Programme. The Coordinators are responsible for the proper planning of the process of carrying out the Inter-laboratory Comparison Programme. Supervision is established over the implementation of each round of comparison from the moment of preparation of the test subject until the submission of the Inter-laboratory Comparison Report to the Participants.

The Inter-laboratory Comparison Programme shall be carried out by competent personnel in a manner established in standards and/or instructions, using compliant equipment, as specified in the management system documents and, if necessary, in legislation.

8. Statistical model

The statistical model used for the evaluation of results obtained from the laboratories participating in the inter-laboratory comparison and the criteria for the individual evaluation of laboratories comply with ISO 13528:2015 and PN-EN ISO/IEC 17043:2011, as well as with the IUPAC Technical Report.

The statistical analysis consists of the following steps:
- examination of homogeneity and stability,
- determination of the assigned value and its uncertainty,
- calculation of performance statistics.

The statistical methods used to analyse and evaluate the results of an inter-laboratory comparison shall be adapted to each situation and shall take into account the nature of the test subject, the number of subjects, the number of results obtained, the manner in which the assigned value is determined and information on the uncertainty of the results obtained.

8.1. Calculation of homogeneity and stability of the test subject
The assessment of homogeneity and stability shall be carried out according to the procedure described in Annex B of ISO 13528:2015.

8.1.1 Assessment of homogeneity of the test subject
According to ISO 13528:2015, not less than 10 samples shall be taken from a batch of material in the round of inter-laboratory comparison prepared for dispatch to assess homogeneity. In each sample, the selected parameter is determined twice under repeatability conditions. Next:

1) the Cochran test is performed on pairs of individual samples,
2) the standard deviation for repeated analyses is calculated $S_x$,
3) the standard deviation inside the samples (repeatability deviation of double-made samples) $S_w$,
4) inter-sample standard deviation $S_s$.

The Organiser shall consider the test subject to be sufficiently homogeneous if the following criterion is met:

$$S_s \leq 0,3\sigma_{pt}$$

where:
\( \sigma_{pt} \) – standard deviation of inter-laboratory comparisons

In particular situations where it is not possible to obtain a homogeneous test subject, the value of the inter-sample standard deviation will be included in the standard deviation for inter-laboratory comparisons according to the following equation:

\[
\sigma_{pt} = \sqrt{\sigma_{pt}^2 + S_s^2}
\]

In the case of the above situation, the Organiser undertakes to inform the Participants of the inter-laboratory comparison.

### 8.1.2 Test subject stability assessment

The Organiser shall assess the stability of the test subject throughout the duration of the inter-laboratory comparison round, taking into account the impact of transport on the test subject.

The test subject shall be considered stable if the following criterion is met:

\[
|\bar{y}_1 - \bar{y}_2| \leq 0.3 \sigma_{pt}
\]

where:

\( \bar{y}_1 \) - the mean value of the parameter to be determined for individual samples obtained during the homogeneity test,

\( \bar{y}_2 \) - the mean value of the parameter to be determined for individual samples obtained during the stability test.

If the stability criterion is not met, the Organiser shall estimate the impact of instability on the value attributed to the test subject.

### 8.2 Determination of the assigned value and its uncertainty

In the case of occurrence of outliers, the Organiser shall proceed in accordance with item B.2.5 of EN ISO/IEC 17043:2011 and the ISO 13528:2015 standard. The Hampel test
shall be used to identify deviating values. The Organiser also checks the normality of the results distribution.

The assigned value $x_{pt}$ is the value agreed on the basis of the Participants' results obtained in a given round of inter-laboratory comparison, using one of the robust methods described in Appendix C of ISO 13528:2015 and Appendix D, in the case of a small number of inter-laboratory comparison Participants. The robust methods described in the above mentioned Appendices of the standard in question are also used to determine the standard deviation for proficiency assessment $\sigma_{pt}$.

The uncertainty of assigned value $u(x_{pt})$ shall be calculated using the expression described in ISO 13528:2015, item 7.7.3:

$$u(x_{pt}) = 1,25 \times \frac{s^*}{\sqrt{p}}$$

where:

$s^*$ - standard deviation determined by the robust method,

$p$ - number of results obtained in the inter-laboratory comparison,

$1,25$ - a constant representing the maximum ratio of the median standard deviation to the arithmetic mean standard deviation for normal distribution data.

8.3 Calculation of performance statistics (parameters of individual statistics)

The results obtained in the process of inter-laboratory comparisons shall be assessed using the following parameters, taking into account the number of Participants and the number of determination results obtained.

Before choosing an appropriate performance evaluation indicator from among those proposed in ISO 13528:2015, the Organiser checks the the following condition:

$$u(x_{pt}) \leq 0,3\sigma_{pt}$$

If this criterion is met, the indicator for the evaluation of performance statistics need not take into account the uncertainty of the assigned value. Otherwise, an indicator taking into
account the uncertainty of the assigned value will be used to calculate the performance statistics.

Where the \( u(x_{pt}) \leq 0.3\sigma_{pt} \) condition is met, the parameter used to evaluate individual statistics will be: z-score

\[
z_i = \frac{(x_i - x_{pt})}{\sigma_{pt}}
\]

where:
- \( x_i \) - the result obtained by the Participant,
- \( x_{pt} \) - the value assigned to the test subject,
- \( \sigma_{pt} \) - standard deviation of inter-laboratory comparisons

If the \( u(x_{pt}) \leq 0.3\sigma_{pt} \) condition is not met, the parameter used to evaluate individual statistics will be: z′-score

\[
z' = \frac{x_i - x_{pt}}{\sqrt{\sigma_{pt}^2 + u^2(x_{pt})}}
\]

where:
- \( u(x_{pt}) \) - the standard uncertainty of the assigned value.

In order to assess the uncertainty of the testing method estimated by the Participants, the Organiser shall apply the zeta-scores \( \zeta \)

\[
\zeta_i = \frac{x_i - x_{pt}}{\sqrt{u^2(x_i) + u^2(x_{pt})}}
\]

where:
- \( u(x_i) \) - standard uncertainty of the Participant's result.
The zeta indicator should not be treated as a parameter which serves to individually assess the Participant. The indicator makes it possible to improve the work of the laboratory.

8.4 Acceptance criteria for the results of performance statistics

I. for z-score:
   \[ |z| \leq 2.0 \] satisfactory result
   \[ 2.0 < |z| < 3.0 \] doubtful result
   \[ |z| \geq 3.0 \] unsatisfactory result

II. for \( z' \)-score
   \[ |z'| \leq 2.0 \] satisfactory result
   \[ 2.0 < |z'| < 3.0 \] doubtful result
   \[ |z'| \geq 3.0 \] unsatisfactory result

III. for zeta-scores
   \[ |\zeta| \leq 2.0 \] satisfactory result
   \[ 2.0 < |\zeta| < 3.0 \] doubtful result
   \[ |\zeta| \geq 3.0 \] unsatisfactory result

9. Report of the statistical assessment of the inter-laboratory comparison

The Organiser provides the results of the statistical assessment to the Participants on the form entitled “Inter-laboratory comparison report”, which contains all the information required by the PN-EN ISO/IEC 17043:2011 standard.

The reports are sent to the Participants of the inter-laboratory comparison by e-mail in the form of a PDF file or sent via the Polish Post Office.

The Organiser reserves the copyrights to all issued Inter-laboratory comparison reports.

10. List of forms

I. Participation Application Form
II. Test Subject Delivery Protocol
III. Test Results Sheet
IV. Inter-laboratory Comparison Report

11. Withdrawal from participation

Each participant of an inter-laboratory comparison has the right to withdraw from participation in the comparison by sending written information to the Coordinator's e-mail address no later than 7 days prior to sending the test subjects, according to the current schedule.

12. Complaints

In order to submit a complaint regarding the organisation of the inter-laboratory comparison programme, a written notification should be sent to the Organiser's address no later than 14 days after receiving the electronic version of the Inter-laboratory comparison report. The Organiser shall, within 30 days from the date of acceptance of the complaint, conduct an investigation and provide a written information on the decision, within 90 days from the date of acceptance of the complaint.