



PARTICIPANT'S GUIDE

EXTERNAL QUALITY ASSESSMENT SCHEMES (EQAS)

CENTRE DE TOXICOLOGIE DU QUÉBEC



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This document contains information on policies and instructions that apply to External Quality Assessment Schemes (EQAS) offered by the *Centre de toxicologie du Québec* (CTQ). The guide's content has been approved by the scheme coordinator listed in subsection 8.5 herein.

1. EXTERNAL QUALITY ASSESSMENT SCHEMES OFFERED BY THE *CENTRE DE TOXICOLOGIE DU QUÉBEC*

- AMAP: AMAP Ring Test for Persistent Organic Pollutants in Human Serum, since 2001
- Creatinine: Inter-laboratory Comparison Program for Measurement of Serum Creatinine (provided in collaboration with the SQBC), since 2013
- Dioxin & Furans: Inter-laboratory Comparison Program for Dioxin & Furans in Serum, since 2014
- PCI: Inter-laboratory Comparison Program for Metals in Biological Matrices, since 1979
- QMEQAS: Quebec Multielement External Quality Assessment Scheme, since 1996
- OSEQAS: External Quality Assessment Scheme for Organic Substances in Urine, since 2015

The list of analytes available for each of the schemes is provided on the CTQ's EQAS Web site (refer to the link in paragraph 8.6.2).

2. ACCREDITATION

The CTQ's laboratory applies a quality management system accredited under the ISO/CEI 17043 standard applicable to EQASs (AMAP, PCI and QMEQAS).

3. INFORMATION REGARDING PARTICIPATION

3.1. CALENDAR OF ROUNDS

The annual schedule of EQASs is e-mailed at the beginning of the year and may be consulted at any time on the CTQ Web site under "Schedule", on each scheme page. **It contains the various shipment dates and reporting deadlines for every round of a given year.** If you do not receive your proficiency testing materials (PTM) within two weeks of the shipment date



specified in the schedule, please notify us as soon as possible (see contact information provided in subsection 8.5).

3.2. SUBSCRIPTION

Laboratories interested in participating in the EQASs offered by the CTQ may do so by completing the form entitled “Registration form” which is available on our website (see link at sub-section 8.6.2). Once the request has been received and approved, the person in charge of the participant account will receive a username and a temporary password to be used to log in to the system. The password will need to be changed after the first login.

3.3. PARTICIPANT ACCOUNT AUTHORITY AND SUBSCRIPTION AUTHORITY

Participant account authorities have access to all active subscriptions to the CTQ’s EQAS for their laboratory. They may either designate one or more authorities for each EQAS subscription or manage them themselves. **This request must be sent to us by e-mail.** Each subscription authority has his/her own username and password.

To retrieve a lost or forgotten password, or to request a new one, go to <http://paqe.inspq.qc.ca/> and click “Forgotten password”. Enter your username, last and first names, and e-mail address. Your username is made up of the first three letters of your last name and the first three letters of your first name followed by 01. For example, David Bisson’s username is bisdav01. If you have trouble with this procedure, please contact us (see contact information provided in subsection 8.5).

3.4. MANAGING THE PARTICIPANT ACCOUNT

Participants may access and manage their participant account at any time through the EQAS management system, whether for changing their mailing or e-mail address; viewing invoices; selecting PTM groupings, the number of tubes and the associated analytical methods; indicating the preferred units for reporting results; and printing comprehensive and individual reports.

A number is attributed to each participant account created. Every scheme subscription for this participant account is assigned a random unique subscription number. This number is used to identify participants in reports.

3.5. CONFIDENTIALITY

Every scheme subscription is identified by a unique subscription number. The CTQ safeguards the confidentiality of participants' identities.

All results obtained from participants remain confidential and are associated solely with the unique subscription number. However, results stripped of all



identifying information may be used in reports and publications, as agreed by participants when they subscribe.

3.6. COLLUSION, FORGERY AND SUBCONTRACTING

Participants bear full responsibility for preventing collusion, as well as the forgery and subcontracting of analyses.

3.7. PARTICIPATION CERTIFICATES

A participation certificate is issued at the end of the year to all participants who have submitted at least half the results for at least one analyte. The calculation is done yearly. Non-numerical results are excluded from the calculation. Results not submitted do not affect the calculation of the annual score.

The annual score (%) is calculated based on the total points accumulated, with a maximum total of three (3) points per result. The score is calculated using the absolute value of the z'-score:

- 3 points if $0.0 < |z'\text{-score}| \leq 1.0$
- 2 points if $1.0 < |z'\text{-score}| \leq 2.0$
- 1 point if $2.0 < |z'\text{-score}| < 3.0$
- 0 point if $|z'\text{-score}| \geq 3.0$

Scores falling under the pass threshold appear under the pass threshold line and indicate unsatisfactory performance.

The pass threshold has been set at 65%.

4. COSTS, INVOICING AND PAYMENT

Scheme subscriptions are renewed in November. However, a participant may subscribe to a scheme at any time during the year, in which case the subscription fees are prorated for the remaining rounds.

Participation in the CTQ's EQASs is a prepaid service. Annual subscription fees, including fees for selected PTM, are payable within 30 days after the reception of the invoice for the following year. Reimbursements are not issued for cancellations received after the second round for all schemes, except for the PCI scheme which will be after the third round.

For each scheme, you will find the number of rounds and annual PTM, the subscription fees, the cost of each PTM grouping and the cost of additional PTM on the CTQ's EQAS Web site (see link at sub-section 8.6.2).



You may view your invoices online on the “Billing” tab of your participant account. Please note that we do not send any invoices by post, and that all amounts are in Canadian dollars.

You may pay your invoice in three ways:

- by cheque (payable to: Centre de toxicologie du Québec);
- via bank transfer (refer to Appendix 1 for information);
- via the online credit card payment system (Visa or MasterCard) on the Web site (refer to paragraph 8.6.2 for details).

5. INFORMATION REGARDING PROFICIENCY TESTING MATERIALS (PTM)

5.1. CODING SYSTEM

Standard PTM numbering is used for all EQASs. The identification code consists of the following characters (refer to the table in Appendix 3 for detailed explanations):

- The first two letters of the scheme;
- One letter identifying the matrix (B=blood, S=serum, U=urine, H=hair);
- One letter representing the analytes;
- The last two digits of the year;
- A PTM sequence number.

For example, the first serum aluminum PTM for the PCI in 2014 will have the following code: PC-S-A1401.

5.2. PREPARATION AND VERIFICATION

The PTM are prepared in our laboratory using biological matrices obtained from non-exposed donors. When needed, analytes are added to each matrix. Homogeneity and stability are verified in conformance with the ISO 13528:2005⁽¹⁾ standard, or an ANOVA analysis (for AMAP, Creatinine, OSEQAS and Dioxins & Furans schemes homogeneity). The PTM are stored frozen at -20 °C until shipped to participants.

5.3. RECEIPT

Please notify us of any discrepancies between the shipping list and the PTM received, including any damaged items. Missing or damaged PTM will be replaced as soon as possible. Follow the storage instructions printed on the shipping list.

5.4. REPLACEMENT PTM

In case of mishaps, lab accidents or analytical problems, additional PTM for the current round are available. To order replacements, please contact us.



Additional fees will apply to cover the cost of the PTM, as well as shipping and handling. Depending on availability, PTM for previous rounds may be purchased through the Web site's virtual store (refer to the details in paragraph 8.6.3).

5.5. HANDLING AND ANALYSIS

Biological matrices consisting of blood and serum are tested for hepatitis B and C, HIV and syphilis. However, no known test is able to guarantee that human blood products are completely free of infectious agents.

PTM must be considered as routine samples and therefore submitted to the same analytical procedures as any routine sample.

PTM must be handled as potentially infectious. PTM must be disposed of in accordance with the same methods used for other human biological matrices. Prior to analysis, bring the PTM to room temperature and stir thoroughly.

6. INFORMATION REGARDING ANALYTICAL RESULTS

6.1. REPORTING RESULTS

All results must be reported through the participant account in the EQAS management system. For the AMAP, OSEQAS and the Dioxins & Furans schemes, results must be reported in conventional units. For the PCI and QMEQAS schemes, the preferred units (conventional or SI) must be specified at the beginning of the year. All PCI and QMEQAS results will be converted into SI units before being published in the reports. For the Creatinine scheme, the results must be transmitted in SI units.

The deadline for the transmission of results is 7 weeks after the shipment of PTM, except for the PCI programme, where the deadline is 6 weeks after shipment of PTM.

The results submitted by participants must be precise to a minimum of three significant digits or to a different precision level dictated by their method.

No extension is granted for the reporting of results, as the EQAS system will automatically block results reporting as of midnight (Eastern Standard Time) on the specified reporting deadline date.



6.2. PROCEDURE FOR ENTERING RESULTS IN THE EQAS MANAGEMENT SYSTEM

6.2.1 DATA REPORTING

1. Log in to the participant account;
2. Click on “Results” tab;
3. Select the appropriate year and scheme;
4. Then click the PTM grouping and the PTM for which you wish to report results;
5. Type the result corresponding to the analyte in the “Result” box according to the specified unit, **indicating a minimum of three significant digits, or according to the precision level of the method**;
6. In the pull-down menus, select the instrumentation methods and other factors related to this result. Use the horizontal scroll bar to view all method categories. **Important:** The selected methods are automatically reproduced for the following rounds, in order to avoid having to enter them every time. The reliability of statistics by type of method is proportional to the number of participants who report the instrumentation methods related to their results;
7. Click **Save** at the bottom of the page before leaving the page;
8. Repeat this procedure for each PTM.

6.2.2 PRINTING RESULTS

The **Print** icon at the bottom of the page is used to print all results for the round as a single document. We strongly recommend that you keep a paper or electronic copy as proof that you have submitted your results.

6.2.3 QUESTIONS AND COMMENTS

You can send us your questions and comments in any of three ways:

1. Include a comment on the results page. Information in the “Comment” box applies to all PTMs in the current round. Specify the PTM or analyte to which the comment applies.
2. Send an e-mail message to ctq@inspq.qc.ca; remember to specify your unique subscription number.
3. Call 418-650-5115, extension 4649.

6.3. UNREPORTED RESULTS

Only numerical results reported are taken into account in the statistical treatment of the data. The only allowable non-numerical results are: <LD, <LQ or >LL. An unreported result will not lead to a penalty regarding the issuance of participation certificates (refer to subsection 3.7).



6.4. ANALYTICAL METHODS

For all schemes and for each PTM grouping, participants must specify which preparation, instrumentation and benchmarking methods were used in the analyses. This information will be used for the statistical analysis of the results by method group and to provide detailed statistics by analysis method in the reports. To participate in a scheme and to be assessed using two different analysis methods for the same analyte, please contact us.

7. INFORMATION REGARDING REPORTS

7.1. PROCESSING RESULTS

Results are processed for report production purposes after the reporting deadline. Reports are available on your participant account's "Reports" tab four weeks after the reporting deadline. Participants will be notified of the posting by e-mail. Please verify your results and promptly notify the program coordinator of any errors or discrepancies on the data contained in the report. **We will correct only those errors for which we are responsible.**

7.2. REPORT

Reports contain the following information:

- Results submitted by participants for each analyte/matrix in the scheme. Unless specified otherwise, aberrant results are not excluded unless the aberration can be explained by something like a unit or conversion error.
- Robust statistics calculated for all results combined and for subgroups of results (when there are at least three results) per type of analytical method.
- The assigned value (AV) derived from the consensus value calculated using the robust average of Algorithm A⁽¹⁾.
- The robust standard deviation based on Algorithm A⁽¹⁾.
- The AV's standard uncertainty.
- The arithmetic mean and standard deviation.
- The median and median absolute deviation (MAD).
- The coefficient of variation (CV) or variability.
- The proficiency standard deviation (σ_{apt}) modelled for each analyte/matrix using CTQ's EQAS data from recent years.
- The acceptable range based on the concentration of the analyte/matrix.
- The performance calculation: z'-score (including the AV's standard uncertainty).
- The graph of results in increasing order.



7.3. INDIVIDUAL REPORTS

- Bias (%) – deviation from the assigned value (AV) for the selected round.
- Summary of z'-scores for the selected round.
- Cumulative z'-score for the chosen number of rounds, including the round in progress.
- Cumulative reproducibility score for all rounds since the beginning of the year.
- Cumulative – RSZ and SSZ scores for the desired number of rounds, including the round in progress.

7.4. CRITERIA FOR INTERPRETING PERFORMANCE BASED ON THE OBTAINED Z'-SCORE

$ z'\text{-score} \leq 2.0$	Satisfactory
$2.0 < z'\text{-score} < 3.0$	Questionable
$ z'\text{-score} \geq 3.0$	Unsatisfactory

8. GENERAL AND ADMINISTRATIVE INFORMATION

8.1. COMMUNICATION

The success of any quality assessment scheme is highly dependent on the effectiveness of communication between participants and the scheme provider. To this end, we strongly encourage you to send your comments and suggestions to the scheme coordinator.

8.2. CHANGES TO SCHEMES DURING THE YEAR

You will promptly receive written notification of any major changes to the way schemes operate - addition of analytes, additional rounds, etc.

8.3. COMPLAINTS

Contact the scheme coordinator or the EQAS administrator regarding any complaints or comments about the scheme.

8.4. BUSINESS HOURS

Customer Service regarding the CTQ's EQAS is available weekdays from 8:30 a.m. to 4:30 p.m. Eastern Time, except on statutory holidays. After business hours, please write to us at ctq@inspq.qc.ca.



8.5. CONTACTS

EQAS Administrator: Alain LeBlanc
Telephone: 418-650-5115, extension 4648
E-mail: alain.leblanc@inspq.qc.ca

Schemes Coordinator: David Bisson
Telephone: 418-650-5115, extension 4649
E-mail: david.bisson@inspq.qc.ca

Technical Coordinator: William Molon Noblot
Telephone: 418-650-5115, extension 4035
E-mail: william.molon-noblot@inspq.qc.ca

EQAS Secretary: Annabelle Dubreuil
Telephone: 418-650-5115, extension 5254
Fax: 418-654-2148
E-mail: annabelle.dubreuil@inspq.qc.ca

8.6. COMMUNICATION TOOLS

8.6.1. TO ACCESS PARTICIPANT ACCOUNTS VIA THE EQAS MANAGEMENT SYSTEM
paqe.inspq.qc.ca

8.6.2. WEB SITE
www.inspq.qc.ca/en/ctq/eqas

8.6.3. TO PURCHASE REFERENCE MATERIALS
The virtual store at <http://ctqvente.inspq.qc.ca> offers a range of reference materials that can be ordered online at very competitive prices.

9. REFERENCES

- (1) ISO 13528, Statistical methods for use in proficiency testing by inter-laboratory comparisons, ISO, first edition, 2005-09-01



APPENDIX 1

BANKING DATA

Institution Name: Banque Nationale du Canada
1385 chemin Ste-Foy
Quebec (Quebec) G1S 2N2
Telephone: 418-684-0328
Fax: 418-684-0329

Institution (branch) number: 10641-006

Account number: 01-898-20

SWIFT address: BNDCCAMMINT

IBAN: CA006-10641 01-898-20

Company: Institut national de santé publique du Québec

Please e-mail the following information to ctq@inspq.qc.ca:

- the date of your bank transfer;
- the exact amount of your payment;
- the invoice number.

APPENDIX 2

EQAS PTM CODES

AMAP - Français	AMAP - English	AMAP - Español	Code - Código
BPC, Retardateurs de flamme, Pesticides organochlorés et Lipides sériques	PCB, Brominated flame retardants, Organochlorinated pesticides and Serum lipids	BPC, Retardantes de llama, Pesticidas organoclorados y Lípidos séricos	AM-S-W1601
Composés perfluorés	Perfluorinated compounds	Compuestos perfluorados	AM-S-Y1601
CRÉATINIE - Français	CREATININE - English	CREATININA - Español	Code - Código
Créatinine	Creatinine	Creatinina	MC-S-C1601
DIOXINS & FURANS - Français	DIOXINS & FURANS - English	DIOXINS et FURANS - Español	Code - Código
Dioxine	Dioxine	Dioxine	DF-S-1601
PCI - Français	PCI - English	PCI - Español	Code - Código
Aluminium sérique	Serum aluminum	Aluminio sérico	PC-S-A1601
Arsenic urinaire (Inorganique et Total)	Urine arsenic (Inorganic and Total)	Arsénico urinario (Inorgánico y Total)	PC-U-S1601
Cadmium sanguin	Blood cadmium	Cadmio sanguíneo	PC-B-C1601
Cadmium urinaire	Urine cadmium	Cadmio urinario	PC-U-D1601
Chrome urinaire	Urine chromium	Cromo urinario	PC-U-B1601
Cuivre et Zinc urinaire	Urine copper and zinc	Cobre y Zinc urinario	PC-U-R1601
Éléments essentiels sérique (Cuivre, Sélénium et Zinc)	Serum essential elements (Copper, Selenium and Zinc)	Elementos esenciales sérico (Cobre, Selenio y Zinc)	PC-S-E1601
Fluorure urinaire	Urine fluoride	Fluoruro urinario	PC-U-F1601
Iodure urinaire	Urine iodide	Yodo urinario	PC-U-I1601
Plomb sanguin	Blood lead	Plomo sanguíneo	PC-B-L1601
Plomb urinaire	Urine lead	Plomo urinario	PC-U-P1601
Manganèse sérique	Serum manganese	Manganeso sérico	PC-S-G1601
Mercuré sanguin	Blood mercury	Mercurio sanguíneo	PC-B-M1601
Mercuré urinaire	Urine mercury	Mercurio urinario	PC-U-H1601
Sélénium urinaire	Urine selenium	Selenio urinario	PC-U-N1601
QMEQAS - Français	QMEQAS - English	QMEQAS - Español	Code - Código
Multiéléments cheveux	Multielement in hair	Multielemento cabellos	QM-H-Q1601
Multiéléments sanguin	Multielement in blood	Multielemento sanguíneo	QM-B-Q1601
Multiéléments sérique	Multielement in serum	Multielemento sérico	QM-S-Q1601
Multiéléments urinaire	Multielement in urine	Multielemento urinario	QM-U-Q1601
OSEQAS - Français	OSEQAS - English	OSEQAS - Español	Code - Código
Substances organiques dans l'urine	Organic substances in urine	Sustancias orgánicas en la orina	OS-U-E1601
Code des matrices	Matrix code	Código de matrices	
B = Sang S = Sérum U = Urine H = Cheveux	B = Blood S = Serum U = Urine H = Hair	B = Sangre S = Suero U = Orina H = Cabello	

Signification du code **PC-S-A1401** :

PC = PCI, **S** = Serum, **A** = Lettre représentant l'analyte, **14** = l'année et **01** = numéro séquentiel

Meaning of the **PC-S-A1401**:

PC = PCI, **S** = Serum, **A** = Analyte code, **14** = year and **01** = sequence number

Significado del código **PC-S-A1401**:

PC = PCI, **S** = Suero, **A** = Analito código, **14** = año y **01** = número de secuencia

APPENDIX 3

Statistical Approach Used in Reports

1 Statistical Treatment

Statistical parameters are calculated for each set of data in the section « All methods ». Such parameters are also determined in different sections for a subset of data corresponding to a grouping of analytical methods, for schemes allowing the use of various analytical methods. A table describing the groupings of analytical methods included in each of them is presented in this report.

1.1 Outliers

For each PTM and for each analyte, the statistics are calculated after having removed, if required, outlying results. No outlier exclusion test is used since the assigned values are determined from robust statistics as recommended in the document ISO 13528:2005.

Results can be considered outliers and removed from the statistical treatment for several reasons such as:

- Wrong units reported;
- Wrong conversion factor used;
- Results entered for the wrong PTM (inversion with another PTM);
- All other reasons believed appropriate by the scheme coordinator.

Results having been identified and removed as outliers are indicated in ***bold italics*** in the report. For the statistical treatment per method type, the calculations are made from subsets of data corresponding to a grouping of analytical methods. Results considered outliers in the all methods category are the same as those for each grouping of analytical methods.

1.2 Assigned Value (AV)

The AV is determined by consensus of participants by calculating the robust average of Algorithm A, from the results reported by all the participants in the round, as described in ISO 13528:2005.



There may not always be consensus from the participants for the AV for the following reasons:

- Too few results (N too small);
- Abnormal distribution of results;
- Use of biased methods by some participants;
- Difficulty for some participants to measure specific chemical forms of the analyte;
- Difficulty for some participants to measure low level concentrations with acceptable reliability;

The AV may be determined using other methods, such as:

- Median;
- Arithmetic mean;
- Assigned value obtained by inclusion of the same PTM within another EQA scheme operated by the CTQ (Inter-program correspondence);
- AV obtained from participants that have demonstrated a good past performance;
- The theoretical concentration of the analyte in the PTM;
- Reference value obtained using a reference analytical method (ex.: ID-ICP-MS);

The selection of an AV other than the robust average of the Algorithm A is documented in the report, if necessary.

The method of calculation of the selected AV is indicated by a gray shaded background in the statistics page of each PTM.

1.3 Calculated Statistical Parameters

The following statistical parameters are provided for all results (for all methods) and for subsets of results per grouping of analytical methods (per method type).

Number of Results (N)

Non numerical results and results identified as outliers are listed in the table of results but excluded from the statistical treatment.

We calculate the statistical parameters for an analyte when we have a dataset of at least 3 results.

For each analyte, a minimum dataset of 20 results is necessary in order to obtain meaningful statistics. However, if fewer than 20 results are available, the statistics are still provided. When fewer than 20 results were considered for statistical treatment of all or a subset of results, the accuracy of statistical data may be questionable.



Robust Average (x^*) and Robust Standard Deviation (s^*) per the Algorithm A

This method of calculation is the default method used to generate the AV by consensus of all participants.

The robust analysis of the Algorithm A is performed by iterations based on estimations of the robust average (x^*) and the robust standard deviation (s^*) refreshed many times using the modified data up until the process converges. This process is assured when the third significant figure of the robust standard deviation no longer changes from one iteration to the other. To better understand the details of this method, please consult the ISO 13528: 2015 documentation.

Median

The median is the value, in a series of incremented results, located where the number of results preceding it is equal to the number of results following it.

- For a number of **odd results**, the median is the result of the rank $(n+1)/2$
- For a number of **even results**, the median is equal to $0.5 \times [\text{result of rank } n/2 + \text{result of rank } (n+1)/2]$

The median is considered robust, meaning that it is little affected by an outlier result.

Standard Deviation from MAD

The standard deviation associated with the median can be calculated from the median absolute deviation (MAD).

The MAD is obtained by considering the median of the absolute values of the deviations between the median and each result. The median of those deviations equals the MAD.

The standard deviation from MAD is estimated by $1.483 \times \text{MAD}$.

Arithmetic Mean

The arithmetic mean is the value corresponding to the sum of the N results divided by N.

For a perfectly normal distribution, the arithmetic mean, the median or the robust average of the Algorithm A coincide. Since outliers influence considerably the arithmetic mean, they must be removed prior to calculations.

Standard Deviation

The standard deviation is equal to the square root of the sum of the deviations between each result and the arithmetic mean squared and divided by $N-1$.

$$s = \sqrt{\frac{\sum_{i=1}^n (x_i - \bar{x})^2}{n - 1}}$$



Coefficient of Variation (CV) or Variability (%)

The % CV is equal to the standard deviation divided by the arithmetic mean multiplied by 100.

If the method of calculation for the AV is the robust average of the Algorithm A, the CV indicated is called Variability. The variability (%) indicated in the report is then calculated by replacing the standard deviation and the arithmetic mean with the robust standard deviation and the robust average of the Algorithm A.

Similarly, if the method of calculation of the AV is in fact the median, the standard deviation and the arithmetic mean are replaced by the standard deviation from MAD and the median to obtain the calculation of the variability (%).

Standard Uncertainty of the AV (μ_x)

The standard uncertainty of the AV can be calculated in several ways. However, it is always calculated according to the method used to calculate the AV. Since the default method used to calculate the AV is the robust mean according to the Algorithm A (1.3.2), the standard uncertainty of the AV will be default calculated according to the formula described in Section 1.3.8.1. If the AV has been determined using the median (1.3.3) or the arithmetic mean (1.3.5), the standard uncertainty of the AV will be calculated using the formulas in Sections 1.3.8.2 or 1.3.8.3.

AV Obtained Using the Algorithm A

If the selected AV is calculated using the Algorithm A, the standard uncertainty is calculated as:

$$\mu_x = 1,25 \times s^* / \sqrt{N}$$

where s^* is the robust standard deviation calculated using Algorithm A (1.3.2) and N the number of numerical results reported.

AV from the Median

If the selected AV is calculated from the median, the standard uncertainty is calculated as:

$$\mu_x = 1,25 \times \text{standard deviation from MAD} / \sqrt{N}$$

where the standard deviation from MAD is calculated according to the equation in Section 1.3.4.

AV from the Arithmetic Mean

If the selected AV is calculated from the arithmetic mean, the standard uncertainty is calculated as:

$$\mu_x = \text{standard deviation} / \sqrt{N}$$

where the standard deviation is calculated according to the equation in Section 1.3.6.



Kolmogorov-Smirnov (Lilliefors) Test

The Kolmogorov-Smirnov (Lilliefors) statistical test is a tool used to evaluate the normality of a distribution of results. The test can be performed with $N \geq 4$.

The power of the test increases rapidly with the number of observations. For a high N (> 30), the test will be sensitive to account for small deviations from normality even with the presence of only one outlier.

For a small sample size ($N \leq 10$), the hypothesis that the observations follow a normal distribution will generally be accepted. However, if normality is rejected for $N \leq 10$, this indicates that the observations are far from following a normal distribution and that one or more observations are most likely outliers.

When the normality hypothesis is rejected, the use of robust methods for the determination of the AV by consensus such as the Algorithm A allows to obtain a better estimation of the AV. Outliers are retained except if their deviation from the other observations can be clearly explained as indicated in section 1.1.

The normality hypothesis is rejected when the statistical value is too weak according to the Kolmogorov-Smirnov (Lilliefors) critical value table. The result of the normality of the distribution of each set of observations is provided in the report whether the test is "Accepted" or "Rejected" under the column labeled "KS (Lilliefors)"

Proficiency Standard Deviation (σ_{apt})

The standard deviation for proficiency testing is a measure of dispersion used in the evaluation of proficiency. It is established for any given concentration and based with regards to participants' performance prior to 2013.

For each EQAS operated by the CTQ and for each analyte-matrix combination, the Proficiency Standard Deviation (σ_{apt}) has been modelled using standard deviations of several PT rounds and according to corresponding AV.

For each analyte-matrix combination of each program, one or two equations representing a straight line describe the relationship between the proficiency standard deviation (σ_{pt}) and the concentration (or AV) according to the following parameters:

$$\sigma_{\text{apt}} = m \times x + \text{OAO}$$

where m is the slope of the straight line and OAO is the intercept point of the straight line.

2 Acceptable Range

The acceptable range is calculated by defining the outer limits from the AV using the following equation:

$$AV \pm 2 \times \sqrt{(\sigma_{\text{apt}})^2 + (\mu_x)^2}$$

3 Calculation of z'-score and Performance Criteria

The z'-score considers the standard uncertainty of the AV (μ_x) and the standard deviation for proficiency testing (σ_{pt}) at a given level of concentration.

For each result submitted by a participant, a z'-score is calculated from unrounded results.

The z'-score is defined as:

$$z' = (x - AV) / \sqrt{(\sigma_{\text{apt}})^2 + (\mu_x)^2}$$

The z'-scores should be interpreted using the same criteria as the z-scores and the same critical values, 2.0 and 3.0.

$ z'\text{-score} \leq 2.0$	Satisfactory
$2.0 < z'\text{-score} < 3.0$	Questionable
$ z'\text{-score} \geq 3.0$	Unsatisfactory

Performance is deemed satisfactory for results between ± 2.0 . A z'-score equal to ± 2.0 corresponds to a result at the limit of the acceptable range.

When the standard uncertainty of the AV is negligible, z'-scores are almost identical to z-scores.

z'-scores comprised between 2.0 and 3.0 are colored in blue in the report. Those above or equal to 3 are indicated in red.

4 Distribution Graph in Ascending Order

For each PTM, the distribution of results from participants is presented in ascending order. Outliers are not included in the graph.

5 References

- ISO 13528, Statistical methods for use in proficiency testing by inter-laboratory comparisons, ISO, first edition, 2005-09-01



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APPENDIX 4

Statistical Approach Used in the Individual Reports

BIAS (%) – DEVIATION FROM THE ASSIGNED VALUE (AV)

This chart is presented **for the selected round** for each analyte-matrix for which the participant has sent results.

The calculation of the bias (%) with the assigned value (AV) is as follows:

$$\text{Bias (\%)} = (\text{Result} - \text{rounded AV}) * 100 / \text{rounded AV}$$

Summary of z'-scores

This chart visually shows the z'-scores obtained **for the selected round** for each analyte-matrix for which the participant has sent results.

If a z'-score lies outside the range of -5.0 and +5.0, it will not be displayed on the chart.

If no result has been sent for that particular round for a given PTM, no z'-score will be displayed for that round, and the round number will not be indicated at the bottom of the chart.

Cumulative z'-scores

This chart is presented **retroactively for the desired number of rounds**, including the round in progress, for each analyte-matrix for which the participant has sent results.

Each z'-score is presented by an empty circle, and the average of z'-scores per round is presented by a full circle. A cumulative z'-score for all the rounds is calculated and indicated at the top of each chart.

The cumulative z'-scores **for all the rounds** is calculated as follows:

$$\text{Cumulative z'-scores} = \sum \text{z'-scores} / \text{Number of z'-scores for all the rounds}$$

If a z'-score lies outside the range of -5.0 and +5.0, it will not be displayed on the chart, but it will still be included in the calculation of the cumulative z'-scores.

If no result has been sent for a round for a given PTM, no z'-score will be displayed for that PTM, and the round number will not be indicated at the bottom of the chart.

Results that have not been sent for a PTM are excluded from the calculation. There is no penalty for a result that has not been sent.

Cumulative – Reproducibility Scores

This table is presented for all rounds since the beginning of the year, for each analyte-matrix for which the participant has sent results.

The calculation of the average deviation between the participant's result and the average AV is the following:

$$\text{Average deviation} = \frac{(| \text{AV source PTM} - \text{Result source PTM} | + | \text{AV Duplicate} - \text{Duplicate result} |)}{2}$$

where:

AV source PTM = rounded AV from the 1st PTM of the pair of PTM's

AV duplicate = rounded AV from the 2nd PTM of the pair of PTM's

Result source PTM = Participant's result from the 1st PTM of the pair of PTM's

Duplicate result = Participant's result from the 2nd PTM of the pair of PTM's

The granted mark is the total of points cumulated over a total maximum of 2 points for the analysis of the source and the duplicate PTM's.

The score is calculated by comparing the average deviation between the results and the average AV in absolute value according to σ_{apt} at the concentration of the average AV for this analyte-matrix:

- If Average Deviation $\leq \sigma_{\text{apt}}$ **2 points**
- If $\sigma_{\text{apt}} < \text{Average Deviation} < 2 \sigma_{\text{apt}}$ **1 point**
- If Average Deviation $\geq 2 \sigma_{\text{apt}}$ **0 point**

The total reproducibility score is equal to the sum of the scores for each pair of source PTM and its duplicate, converted to percentage.

Results not sent for a source PTM or its duplicate are excluded from the calculation of the reproducibility score. There is no penalty for a result that has not been sent.

Cumulative – RSZ and SSZ scores

This table is presented for the desired number of rounds, including the round in progress, for each analyte-matrix for which the participant has sent results.

For each analyte, the z'-scores are combined in order to produce the RSZ and SSZ, two complementary indicators of the overall performance.



The RSZ (Rescaled Sum of z) is defined as:

$$RSZ = \sum z'_i / \sqrt{n} \text{ (n = number of z'-scores)}$$

and uses the z'-score signs to evaluate the bias of the analytical system.

The SSZ (Sum of Squared z) is defined as:

$$SSZ = \sum z_i^2.$$

It uses the absolute values of the z'-scores to highlight the amplitude of the deviations compared to the assigned values.

These indicators are complementary and both must be calculated to evaluate the overall performance of a laboratory. Both indicators must be acceptable in order for a laboratory to be considered efficient.

The SSZ follows a chi-square distribution (χ^2) and is interpreted using the χ^2 table, as described in the following section.

In order to avoid undue influence of outliers, the z'-scores above +3.0 or below -3.0 are adjusted to 3.0.

The results not sent for a PTM are excluded from the calculation. There is no penalty for a result that has not been sent.

Criteria for the Interpretation of Performance Using the SSZ score

The SSZ increases according to the number of reported results. The χ^2 table at the confidence intervals indicated below allows to determine the acceptable limits according to the number of degrees of freedom (n-1) where n represents the number of reported results.

χ^2 Tables at Two Confidence Intervals (CI) for n= 2 to 45

n	CI 95 %	CI 99 %
2	6.0	9.2
3	7.8	11.3
4	9.5	13.3
5	11.1	15.1
6	12.6	16.8
7	14.1	18.5
8	15.5	20.1
9	16.9	21.7
10	18.3	23.2
11	19.7	24.7
12	21.0	26.2
13	22.4	27.7

External Quality Assessment Schemes (EQAS)



n	CI 95 %	CI 99 %
14	23.7	29.1
15	25.0	30.6
16	26.3	32.0
17	27.6	33.4
18	28.9	34.8
19	30.1	36.2
20	31.4	37.6
21	32.7	38.9
22	33.9	40.3
23	35.2	41.6
24	36.4	43.0
25	37.7	44.3
26	38.9	45.6
27	40.1	47.0
28	41.3	48.3
29	42.6	49.6
30	43.8	50.9
31	45.0	52.2
32	46.2	53.5
33	47.4	54.8
34	48.6	56.1
35	49.8	57.3
36	51.0	58.6
37	52.2	59.9
38	53.4	61.2
39	54.6	62.4
40	55.8	63.7
41	56.9	65.0
42	58.1	66.2
43	59.3	67.5
44	60.5	68.7
45	61.7	70.0



The SSZ for an analyte is compared to the values from the \square table at the chosen confidence intervals for n-1 degrees of freedom, according to the following table.

SSZ \leq \square (95 %)	Satisfactory
\square (95 %) < SSZ \leq \square (99 %)	Questionable
SSZ > \square (99 %)	Unsatisfactory

Criteria for the Interpretation of the Performance Using the RSZ score

The RSZ is interpreted using the same criteria as the z'-scores.

RSZ \leq 2.0	Satisfactory
2.0 < RSZ < 3.0	Questionable
RSZ \geq 3.0	Unsatisfactory