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ET DE LA LUTTE CONTRE
LES CHANGEMENTS CLIMATIQUES

ANALYTICAL LABORATORY ACCREDITATION PROGRAM

PROTOCOL FOR PROFICIENCY TESTING OF ANALYTICAL LABORATORIES (DR-12-SCA-04-ENG)

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FOREWORD

The Centre d'expertise en analyse environnementale du Québec (hereinafter "the Centre d'expertise") administers the Analytical Laboratory Accreditation Program – *Programme d'accréditation des laboratoires d'analyse* (PALA)[1] **which stems from section 118.6 of the Environment Quality Act.** The Ministère de l'Agriculture, des Pêcheries et de l'Alimentation du Québec (MAPAQ) **and the Institut de recherche Robert-Sauvé en santé et en sécurité du travail (IRSST – Robert-Sauvé research institute in occupational health and safety) respectively provide technical support for the agricultural sector and air microbiology sector.**

Proficiency tests are an integral part of the PALA's quality control activities. Their purpose is essentially to determine, through interlaboratory comparisons, the proficiency of each accredited laboratory at producing **reliable** analytical results.

This document sets out the terms and conditions applicable to proficiency tests in which participation is mandatory for accredited laboratories.

INTRODUCTION

This document describes the steps of the proficiency test process for analytical laboratories, which are: planning, preparation, performance, information processing, data interpretation, report and follow-up.

The Centre d'expertise en analyse environnementale du Québec is accredited by the Standards Council of Canada as a proficiency testing provider. This accreditation, based on standard ISO/IEC 17043, confirms the competence of the Centre d'expertise to evaluate the performance of analytical laboratories both nationally and internationally.

The elements presented here are in line with the requirements of international standard ISO/IEC 17043:2010: *Conformity assessment – General requirements for proficiency testing*[(2)].

1 PLANNING

Schedules for proficiency tests under the Analytical Laboratory Accreditation Program – *Programme d'accréditation des laboratoires d'analyse* (PALA) are drawn up at the end of each calendar year. The analytical parameters are generally evaluated at least once per year. The preparation of schedules takes into account the previous year's planning, the determination of development needs, and various changes and adjustments needed for the continuous improvement of the accreditation program.

Participation in proficiency tests, at the frequency established and announced, is mandatory for all laboratories accredited by the Ministère de l'Environnement et de la Lutte contre les changements climatiques. **Government agencies** that are not accredited by the Ministère may also, under certain conditions, take part in proficiency tests. The management of proficiency tests for such laboratories is not discussed in the present document.

Proficiency test schedules are distributed to accredited laboratories before January 1 of each year, to inform them in advance of the dates and domains concerned. The necessary information on domains of accreditation is provided in document DR-12-CDA, *Champs et domaines d'accréditation en vigueur* (Current fields and domains of accreditation)[(3)]. This document is available on the website of the Centre d'expertise, along with the schedules. For administrative reasons, schedules may be modified. When this occurs, the website is updated and the laboratories concerned are promptly informed.

The Centre d'expertise prepares preliminary proficiency tests **when it receives new accreditation applications.**

Additionally, in response to needs expressed by its clients or partners, the Centre d'expertise organizes trial proficiency tests in which one or more laboratories may participate. These trials are conducted for the purpose of knowledge, comparison or improvement.

Since under the PALA participation in proficiency tests is mandatory for accredited laboratories, no minimum number of participants are required. Data processing methods are adapted to the number of participating laboratories.

2 PREPARATION

2.1 Instructions and related documents

Work instructions and an electronic form for submitting results are provided for each project, to standardize the process and ensure smooth operations. Among other things, the instructions cover the following:

- how samples should be stored;
- the date and time of analysis (if required);
- the procedure to be followed, if applicable;
- the return address for materials;
- the method and procedure for submitting information.

Unless otherwise indicated, proficiency test samples should be handled using routine methods. Any evidence that a laboratory has not followed standard procedures could lead to a subcontract notice and a repeat of the proficiency test.

Proficiency test results are verified during on-site assessments. The laboratory must show that the analyses were performed using routine methods for which validation data are available.

2.2 Proficiency test samples

The Centre d'expertise prepares samples similar to those routinely analyzed by participating laboratories. For agricultural analyses and the air microbiology sector, samples are prepared and validated in **collaboration with external organizations.**

For the environmental sector, samples are prepared in relation to concentrations specified in regulations and other normative documents, and in the media evaluated (drinking water, wastewater, soil, waste, air, etc.). Before samples are sent, the accuracy of concentrations is validated. For the agricultural and air microbiology samples, the content and concentration are chosen by the specialists in the areas concerned.

Besides validating concentrations, the Centre d'expertise makes sure of the homogeneity and stability of samples, to guarantee the success of proficiency tests. When storage time is critical, participating laboratories are informed of when the analysis must be done for the quality of samples to be preserved.

The shipping of proficiency test samples is done by a carrier capable of performing delivery within the required time. Particular attention is paid to maintaining sample stability. Appropriate packing materials are used, with refrigerants when necessary. At all times, the Centre d'expertise complies with the regulations in force with regard to shipping samples.

If samples are missing or containers are broken or leaking **when they are received by the participating laboratory**, the laboratory must inform its program officer within twenty-four hours. New samples will be sent to the laboratory free of charge.

3 PERFORMING ANALYSES

On receiving proficiency test samples, participating laboratories perform their analyses using the methods indicated in their accreditation file, in accordance with the instructions and time limits for proficiency tests.

If a problem arises in the course of analysis, the participating laboratory can report the difficulties encountered or any other problematic situation to its program officer. The information is filed using the forms for that purpose.

If an event occurs in the course of analysis requiring that a sample be replaced, a written request describing the situation must be sent to the program officer. When possible, a replacement sample or series of samples is sent to the laboratory and charged according to the fees for repeating proficiency tests (see *Tarification relative au Programme d'accréditation des laboratoires d'analyse* [Fee schedules for analytical laboratory accreditation programs], DR-12-PALA-TARIF [(4)]).

4 INFORMATION PROCESSING

The analysis results generated by proficiency tests go through a procedure that includes the following steps: data collection, data processing, sample rejection, and statistical presentations and trends.

4.1 Data collection

The analysis results of participating laboratories are entered on an electronic form developed for the proficiency test. The internal identification number of methods used by the laboratories must also be entered on the form.

Laboratories must respect the instructions for expressing results, including the number of significant digits corresponding to the precision of the method used, and the appropriate units.

The electronic form, with the name of the laboratory supervisor clearly indicated, must be emailed to the Centre d'expertise before the deadline. Results received after that date will be refused, and a subcontract notice will be sent to the laboratory in accordance with the terms of document DR-12-SCA-05, *Terms and conditions of accreditation*[(5)].

When the forms are received, laboratories are sent an acknowledgement of receipt and the forms are checked to verify that the information is complete. If it is not, a program officer will contact the laboratory concerned to collect the missing information.

4.2 Data processing

Quantitative analytical results may be processed in several ways. Generally, a consensus value is used to determine the expected value, and the following steps are applied:

- the data are arranged in ascending order;
- a brief assessment is done;
- one or more rejection tests are done to eliminate outlying results;
- the Shapiro-Wilk test is done to determine whether the results are in line with a normal distribution;
- the expected value is determined;
- the expected deviation is determined;
- the expected value and deviation are then used to calculate the Z-score.

4.2.1 Brief assessment of results

The results returned by each laboratory are compiled and quickly examined to check for the presence of questionable values. Such values are often eliminated before continuing the analysis.

4.2.2 Elimination of outlying results

Rejection tests are performed to eliminate outlying results by computation. By definition, an outlying result is one that differs from all the other data in a distribution. Such results can have considerable influence on the “average” and “standard deviation” parameters of a data distribution, while having none on the “median”.

The rejection test is applied with the following procedure:

- using the Dixon test, at a confidence threshold of 95%, outlying results are identified and rejected;
- the median and standard deviation are calculated from the remaining values;
- results beyond two standard deviations are eliminated;
- if the number of participants is greater than 40, a robust test such as Algorithm A is used (Appendix 1).

4.2.3 Shapiro-Wilk test

This test is used to determine the normality of a result distribution. It is applied to each series of results. The outcome determines whether the average or median is chosen as the expected value.

4.2.4 Determination of expected values

Expected values are determined by one of the methods below. Which one was used with a given proficiency test is indicated in the assessment report.

- **Certified reference materials**

  The expected value corresponds to a certified concentration of a substance of interest in a certified reference material (CRM) obtained from a recognized organization. The certificate issued by the supplier gives the expected values for each analytical parameter of interest in the material used for the assessment.

- **Consensus value**

  For a sample prepared by the Centre d'expertise, if there are 10 or more participants, the expected value is produced by a statistical treatment of all the results.

  In the presence of a normal distribution (based on the Shapiro-Wilk test), after applying the rejection tests described in 4.2.2, the expected value is the median of the remaining results from all the laboratories.

  In the presence of a non-normal distribution (based on the Shapiro-Wilk test), after applying the rejection tests described in 4.2.2, the expected value is the arithmetic mean of the remaining results from all the laboratories.

- **Preparation value**

  For a sample prepared by the Centre d'expertise, if there are fewer than 10 participants, the expected value will be the preparation value, as validated by analyses performed in the laboratories of the Centre d'expertise or another reference laboratory.

  In water and solid matter microbiology, the preparation value corresponds to the validation value produced by averaging the results of five replicates analyzed by the reference laboratory on the same day as the laboratories participating in the proficiency test.

4.2.5 Rounding of the expected value and expected deviation

Unless otherwise stated, expected values and expected deviations are rounded in the results report using the following table:

Number	Number of decimal places
> 0 to ≤ 0.001	5
> 0.001 to ≤ 0.1	4
> 0.1 to ≤ 1	3
> 1 to ≤ 10	2
> 10 to ≤ 50	1
> 50	0

4.2.6 Determination of expected deviations

Expected deviations (ED) are used to calculate a score for each sample analyzed in a proficiency test.

Expected deviations are determined by one of the following methods:

- **Relative difference criterion**

  The values used for calculating the relative difference criterion (RDC) are principally drawn from the statistical data from previous proficiency tests. For certain parameters, how the RDC is determined will depend on the conditions and requirements of analysis methods.

  In chemistry and toxicology, RDCs are estimated for each parameter evaluated, as presented in document DR-12-CVR, *Critères de variation relatifs*[6].

  In water and solid matter microbiology, regression equations are used to calculate the RDCs needed to evaluate results. These equations are also presented in document DR-12-CVR.

  For a series of analytical results, expected deviation is calculated with the following formula:

$$Expected\ deviation = Expected\ value \times RDC$$

- **Standard deviation of the distribution**

  The standard deviation is calculated from the series of results remaining after the application of rejection tests. The standard deviation so obtained corresponds to the expected deviation for that series of results. The standard deviation of the distribution is used when the sample provided for the proficiency test does not have the requisite homogeneity for RDCs to be used.

4.2.7 Calculation of Z-score

Z-score is calculated as follows:

$$Z\ score = \frac{X - EV}{ED}$$

where X : laboratory result;
EV: expected value;
ED: expected deviation.

Thus calculated, the Z-score provides a point system with which to score the performance of participating laboratories.

4.2.8 Performance evaluation

The performance of each participating laboratory is evaluated by calculating the points for each sample, using the following table:

Z-SCORE	POINTS
$\|Z\| \leq 1$	5
$1 < \|Z\| \leq 2$	4
$2 < \|Z\| \leq 3$	3
$\|Z\| > 3$	0

Then a percentage score is calculated, using the following formulas:

$$\text{Score per parameter (\%)} = \frac{\text{Total points}}{\text{Number of samples}} \times \frac{100}{5}$$

$$\text{Score per domain (\%)} = \frac{\text{Total points per parameter (\%)}}{\text{Number of parameters}}$$

For chemistry, a result of "0" is treated as if the laboratory had not sent in any results. It is therefore given a score of "0" for that sample. **If the value provided by the laboratory is preceded by the symbol** "<" **or** ">"**, the laboratory** also gets a score of "0" if the expected value is between the minima and maxima specified in document DR-12-CVR.

4.3 Processing of qualitative analytical results

The processing of qualitative results depends on the type of analysis, i.e. presence/absence methods or identification methods.

4.3.1 Presence/Absence methods

4.3.1.1 Brief assessment of results

The results returned by laboratories are compiled and quickly examined to check for the presence of outliers. Outlying results are evaluated to determine whether problems occurred in the preparation of test samples.

4.3.1.2 Determination of expected results

The expected result is determined by the preparation value, i.e. the addition or not of the parameter targeted in the sample. If all the participating laboratories get a result that is different from the preparation value for a given sample, an internal verification is done. If appropriate, the result returned by the laboratories could be used.

4.3.1.3 Point calculation

For each sample, 5 points are given when the result returned by the laboratory corresponds to the expected result, and 0 points when the result returned by the laboratory does not correspond to the expected result.

4.3.1.4 Performance evaluation

A percentage score is then calculated using the following formulas:

$$\text{Score per parameter (\%)} = \frac{\text{Total points}}{\text{Number of samples}} \times \frac{100}{5}$$

$$\text{Score per domain (\%)} = \frac{\text{Total parameter scores (\%)}}{\text{Number of parameters}}$$

4.3.2 Identification methods in air microbiology

4.3.2.1 Brief assessment of results

The results returned by the laboratories are compiled and quickly examined to check for the presence of outliers. Outlying results are evaluated to determine whether problems occurred in the preparation of test samples.

4.3.2.2 Determination of expected values

The expected values correspond to the genus and species of the selected microorganism sent to the laboratory for identification. If all the participating laboratories get a different result than the preparation value for a given sample, an internal verification is done. If appropriate, the result returned by the laboratories will be used.

4.3.2.3 Point calculation - Identification of microorganisms

Points are given for the accuracy of identification achieved by the laboratory, as follows:

- 10 points are given when the laboratory correctly identifies both the genus and species of the unknown microorganism submitted;
- 9 points are given when the laboratory returns an identification for only the genus of the unknown microorganism, but does so correctly;
- 8 points are given when the laboratory returns an identification for both the genus and species of the unknown microorganism, but only identifies the genus correctly;
- 0 points are given when the identification returned by the laboratory is incorrect for both the genus and the species.

4.3.2.4 Performance evaluation

$$\text{Score per parameter (\%)} = \frac{\text{Total points}}{\text{Number of samples}} \times \frac{100}{5}$$

$$\text{Score per domain (\%)} = \frac{\text{Total parameter scores (\%)}}{\text{Number of parameters}}$$

4.4 Sample rejection

In compiling the results of a proficiency test, a sample may be rejected for the calculation of a laboratory's final score. The reasons for doing so generally involve the stability of samples or inadequate mastery of analytical methods.

When **the Centre d'expertise makes the decision to reject a sample,** the reason is explained in the proficiency test report. The sample is not included in the final evaluation, but all values **from all participants** are presented in the report, accompanied by the expected values.

4.5 Statistical presentation and trends

Statistical presentation of the results of a proficiency test offers a quick overview of the performance of all the laboratories that participated in a proficiency test. Statistical presentations are used when needed to provide a visual representation of trends. The content of such graphic presentations could include:

- the coefficients of variation per sample;
- sum of all of the Z-scores;
- sum of all of the absolute values of Z-scores.

5 DATA INTERPRETATION

Data interpretation is primarily based on the statistical treatment described earlier. However, some of the results from proficiency tests could reflect problems that occurred when the samples were in transit, in storage, or being analyzed. In such cases, final interpretation of the data takes all of these factors into account.

6 REPORT

The proficiency test report is prepared when all information processing is complete and the data have been interpreted correctly. The report provides an overview of how all the participating laboratories have performed in each domain and for each parameter, anonymously. At the same time, each laboratory can see its own performance, as identified by a confidential number.

In the case of preliminary tests, the report is individualized and gives an appropriate interpretation.

Only the final version of the proficiency test report is provided to participating laboratories. No scores are released before the final report is sent out.

The proficiency test report is available within two months after the results are received from participating laboratories. However, when a laboratory does not meet the requirements of the accreditation program, it is notified as quickly as possible.

7 PROFICIENCY TEST FOLLOW-UP

The proficiency test report is a valuable tool in the management of accreditation programs.

Document DR-12-SCA-05 describes the criteria for passing proficiency tests by laboratories accredited under the accreditation program and the rules that apply in the event of failure.

7.1 Collusion between participants and falsification of results

Although proficiency tests are used by participants to improve their performance, it is possible that some may be tempted to give a false impression of their analytical capabilities.

Collusion between participants and falsification of results are contrary to professional ethics. Such conduct cancels the benefit of proficiency tests for participating laboratories and for the Centre d'expertise.

Consequently, accredited laboratories commit to respect the rules for proficiency tests by signing the commitment form when they apply for accreditation, and renew that commitment each time they complete and return the submission form for proficiency test results. Laboratories that fail to respect that commitment will be subject to the sanctions specified in document DR-12-SCA-05 (Terms and Conditions of Accreditation).

7.2 Review of proficiency tests

A review mechanism for the conclusions of proficiency test reports is available for participating accredited laboratories that feel wronged or incorrectly evaluated. In such cases, the laboratory must inform its program officer within thirty days after reception of the report. The program officer will take the necessary steps to verify matters and make the appropriate corrections, if any.

If the laboratory is not satisfied with the decision, a complaint may be addressed to the Director of Accreditation and Quality at the Centre d'expertise.

Laboratories are encouraged to make comments toward improving the proficiency tests. Both positive and negative comments on the proficiency test program will be considered during the management review, and action will be taken when necessary.

7.3 Proficiency test review committee

This ad hoc committee is composed of staff involved in the preparation of proficiency tests and from the *Division des programmes d'accréditation*. The committee reviews the results returned by participating laboratories for each set of proficiency tests.

The committee works to ensure that proficiency test programs always meet the needs for which they were intended. After examining and compiling the results of participating laboratories, the committee documents anomalies and particular situations encountered, regarding:

- the selection of parameters evaluated;
- the relative difference criteria;
- the identification of anticipated difficulties in preparing or obtaining homogeneous or stable samples;
- the evaluation of comments on any technical problem raised by participants.

DEFINITIONS

Accreditation: Recognition of a laboratory's proficiency and skill at performing analyses in a specific domain.

Analysis: Technical operation that consists of determining the concentration or presence of a substance in a medium.

Certified reference materials: Material or substance with one or more properties that are sufficiently well defined for it to be used to calibrate an apparatus, evaluate a measuring method, or assign values to materials.

Domain of accreditation: Designation given to **one or** a group **of** analysis parameters based on their analytical affinity, their complementarity**,** the medium studied **or the associated regulatory requirements**.

Field of accreditation: Designation given to a group of domains of accreditation based on the medium studied or the analytical sector.

Participating laboratory: Laboratory authorized to participate in proficiency test campaigns.

Proficiency test sample: Sample with predetermined characteristics (stability, homogeneity, etc.), and for which there are designated reference values, that is used in laboratory proficiency tests.

Proficiency test: Activity structured in programs (e.g. water microbiology, air chemistry) and campaigns (e.g. drinking water microbiology MEP, water toxicology TEU), that is used to verify the competence of laboratories through interlaboratory comparison.

Quality control activities: All of the means used under the analytical laboratory accreditation program (**on-site assessments and proficiency tests**) to verify a laboratory's proficiency at performing analyses within the scope of the Analytical Laboratory Accreditation Program.

Reference laboratory: Laboratory used to validate proficiency test samples.

REFERENCES

(1) CENTRE D'EXPERTISE EN ANALYSE ENVIRONNEMENTALE DU QUÉBEC. *Programme d'accréditation des laboratoires d'analyse : Normes et exigences*, DR-12-PALA, Québec, Ministère du Développement durable, de l'Environnement et des Parcs, 2012, 77 p.

(2) INTERNATIONAL ORGANIZATION FOR STANDARDIZATION. *Conformity assessment – General requirements for proficiency testing,* First edition, Geneva, ISO, 2010, 39 pages (International Standard ISO/CEI 17043).

(3) CENTRE D'EXPERTISE EN ANALYSE ENVIRONNEMENTALE DU QUÉBEC. *Champs et domaines d'accréditation en vigueur* (DR-12-CDA), Québec, Ministère de l'Environnement et de la Lutte contre les changements climatiques, 2019, 40 p.

(4) CENTRE D'EXPERTISE EN ANALYSE ENVIRONNEMENTALE DU QUÉBEC. *Tarification relative au Programme d'accréditation des laboratoires d'analyse* (DR-12-PALA-TARIF), Québec, Ministère de l'Environnement et de la Lutte contre les changements climatiques, 2020.

(5) CENTRE D'EXPERTISE EN ANALYSE ENVIRONNEMENTALE DU QUÉBEC. *Modalités d'accréditation* (DR-12-SCA-05), Québec, Ministère du Développement durable, de l'Environnement et des changements climatiques, 2017, 20 p.

(6) CENTRE D'EXPERTISE EN ANALYSE ENVIRONNEMENTALE DU QUÉBEC. *Critères de variation relatifs* (DR-12-CVR), Québec, Ministère de l'Environnement et de la Lutte contre les changements climatiques, 2019, 27 p.

BIBLIOGRAPHY

DIXON, W. J. "Processing data for outliers", in *Biometrics*, 1953, Vol. 9, No. 1, p. 74-89.

DIXON, W. J. "Simplified estimation from censored normal sample", *Ann. Math. Stat*., 1960, Vol. 31, p. 385-391.

APPENDIX 1 – ROBUST ANALYSIS: ALGORITHM A[1]

This algorithm gives robust values for the average and standard deviation of data to which it applies.

Designate the *p* elements of data, arranged in ascending order, by:

$x_1. x_2. .... x_i. .... x_p$

Designate by x^* and s^* the robust average and robust standard deviation of this data.

Calculate the initial values of x^* and s^* by:

x^* = median of x_i (i = 1, 2, …, p)

s^* = 1.483 median of $| x_i - x^* |$ (i = 1, 2, …, p)

Update the values of x^* and s* as follows. Calculate:

$$\delta = 1.5 s^*$$

For each value x_i (i = 1, 2, …, p), calculate:

$$x_i^* = \begin{cases} x^* - \delta, & \text{if } x_i \prec x^* - \delta \\ x^* + \delta, & \text{if } x_i \prec x^* + \delta \\ x_i, & \text{otherwise} \end{cases}$$

Calculate the new values of x^* and s^* by:

$$x^* = \sum x_i^* \Big/ p$$

$$s^* = 1{,}134 \sqrt{\sum \left(x_i^* - x^* \right)^2 \Big/ (p-1)}$$

Where the summation is done on i.

Robust estimates of x^* and s^* can be deduced by iterative calculation, i.e. by repeatedly updating the values of x^* and s^* using the modified data, until the process converges. We can assume that convergence is assured when the third significant digit of the robust standard deviation and the robust average no longer changes from one iteration to the next. The method is easily programmed on a computer.

[1] From ISO 13528:2015, *Statistical methods for use in proficiency testing by interlaboratory comparison*, Appendix C.3 Robust analysis: Algorithm A. [Translated from the French version.]

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