OC/EC:PT protocol for participants

This document has been edited by Fabrizia Cavalli. He will keep it up to date and will inform the quality officer about changes. The quality officer will then do the necessary to update and distribute the modified document.

REFERENCES :

Upstream	LAB-REC-9031 PT planning form
Downstream	RES-SOP-9713 OC/EC PT item homogeneity&stability LAB-SOP-0750 Application of EN 16909: Ambient air — Measurement of elemental carbon (EC) and organic carbon (OC) deposited on filters

Distribution list
Classifier SOPs

SUBJECT, SCOPE OF APPLICATION

This procedure is describing the protocol used in ERLAP for the OC&EC Proficiency testing scheme.

CONTENTS:

This document specifies in the ANNEX the objectives, purpose and basic design of the proficiency testing scheme including the following information:

a) the name and address of the proficiency testing provider; the personnel involved in the design and operation of the proficiency testing scheme;
b) criteria to be met for participation;
c) the number and type of expected participants in the proficiency testing scheme;
d) selection of the measurand(s);
e) a description of the range of values to be expected for the proficiency testing items;
f) requirements for the production, quality control, storage and distribution of proficiency test items;
g) actions to be taken in case of lost or damaged PT items;
h) reasonable precautions to prevent collusion between participants or falsification of data, and procedures to be employed if collusion or falsification of data is suspected;
i) the time schedule for the various phases of the proficiency testing scheme;
j) any information on methods or procedures which participants need to use to handle and store the test items and perform the measurements;
k) procedures for assessing the homogeneity and stability of proficiency testing items;
l) preparation of any standardized reporting formats to be used by participants;
m) a detailed description of the statistical analysis to be used;
n) the treatment of data from different measurement method;
o) the origin, metrological traceability and measurement uncertainty of any assigned values;
p) criteria for the evaluation of performance of participants;
q) a description of the data, reports or information to be returned to participants;

r) a description of the extent to which participant results, and the conclusions that will be based on the outcome of the proficiency testing scheme, are to be made public.

ANNEX

PROFICIENCY TESTING OC&EC SCHEME PROTOCOL

Ambient-air –Measurement of total carbon, organic carbon and elemental carbon in PM2.5 deposited on filters

(PT OC&EC-2025-1)

EC - JRC

OC/EC:PT protocol for participants

INTRODUCTION

Organic carbon (OC) and elemental carbon (EC) are key components of $PM_{2.5}$, the fine fraction of the air-suspended particulate matter. Their measurement is required by the European Air Quality Directive (2024/2881). OC and EC concentrations are also part of the core variables listed by the co-operative programme for monitoring and evaluation of the long-range transmission of air pollutants in Europe (EMEP) and the European Research Infrastructure Consortium (ERIC) ACTRIS (Aerosol, Clouds, Trace Gases Research Infra-Structure).
The Joint Research Centre of the European Commission (EC DG JRC) has been supporting the quality assurance process for total carbon (TC = OC + EC), OC and EC measurement data across Europe for almost 2 decades. In particular, it has been organising, running, analysing, and reporting about yearly inter-laboratory comparisons for the measurement of TC, OC and EC in $PM_{2.5}$ samples deposited on filters for more than 15 years. These ILCs involved the scientific community, members of international and national monitoring networks, National Reference Laboratories, and instrument manufacturers.

This document describes the proficiency testing scheme for the measurement of TC, OC and EC in $PM_{2.5}$ deposited on quartz fibre filters, as performed by the European Reference Laboratory for Air Pollution (ERLAP) of the JRC, according to the requirements of the ISO/IEC 17043:2023 standard.

OC/EC:PT protocol for participants

CONTENTS

OC/EC:PT protocol for participants

1 SCOPE OF THE PROFICIENCY TESTING SCHEME

The overall scope of this inter-laboratory exercise (ILC) is to enhance the comparability and determine the uncertainty of the TC, OC and EC atmospheric concentration data produced across Europe.

Measurands of this ILC scheme are total carbon (TC), organic carbon (OC) and elemental carbon (EC) (in unit format µg cm^{-2}) in $PM_{2.5}$ deposited on quartz fibre filters, in the concentration range for the applicability of the EN 16909:2017 standard (1.8-49 µg cm^{-2} and 0.2-38 µg cm^{-2} for OC and EC, respectively).

The primary goal is to assess participants' performance (i.e. proficiency testing, PT) in determining the TC loading and the EC/TC ratio, to evaluate the accuracy of the instrument response throughout the analysis and the optical correction for charring.

The repeatability and reproducibility standard deviations of the thermal-optical method described in EN16909:2017 are also determined for informative purposes only.

By taking part in the exercise, participants can detect possible problems in their analytical chain and take remedial actions (if necessary), or else prove the reliability of their analyses. To fully benefit from their partaking, participants are recommended to observe the analytical procedure they usually apply [Note: The European Air Quality Directive (2024/2881) indicates as reference method for the measurement of OC and EC in ambient air that described in the EN 16909:2017].

By principle, this PT scheme does not address any other step of the determination of TC, OC and EC atmospheric mass concentrations such as sampling and upscaling processes.

2 PT PROVIDER

The European Reference Laboratory for Air Pollution of the EC DG JRC (via E. Fermi 2749, I-21027 Ispra (VA)) takes the legal responsibility for all activities of the proficiency testing scheme.

JRC-ERLAP does not make use of any externally provided products and/or services for any of the operations involved in the PT OC&EC scheme.

JRC-ERLAP has the authorized competence and impartiality to run inter-laboratory comparisons (according to ISO/IEC 17043:2023), and the expertise and experience to perform measurement of ambient airborne TC, OC and EC collected on filters (according to the European standard EN16909 and the requirements of ISO/IEC 17025:2018).

JRC-ERLAP participates in this ILC (and carries out measurement of ambient airborne TC, OC and EC collected on filters) according to the European standard EN16909 and the requirements of ISO/IEC 17025:2018.

Personnel:

- Fabrizia Cavalli (PT coordinator and statistician) – fabrizia.cavalli@ec.europa.eu; jrc-erlap@ec.europa.eu;
- Jean-Philippe Putaud (PT items –from sampling to dispatch–, stability and homogeneity determination and testing).

3 PARTICIPANTS

In order to meet the specific requirements of the applied statistical method (i.e. to limit the standard uncertainty of the assigned values), the minimum number of participants is twelve (12). PT exercises will be delayed until this minimum number of participants is reached.
Because PT items are punched out from a 20.32 cm x 25.4 cm filter, the maximum number of eligible participants is limited by the dimensions of the filter itself. Typically, around 40 requests of participation can be accepted at maximum, generally with a single instrument.

Participation in the PT scheme exercise will be granted in priority to:

1- ACTRIS National Facilities performing OC and EC analyses, as a result of the contract JRC N°36775 signed with TROPOS (the leading institution of the ACTRIS Thematic Centre for aerosol in-situ);

2- EMEP observatories, considering their essential role under the CLRTAP[1] Gothenburg protocol;

3- National Reference Laboratories, as key stakeholders in the implementation of the European Air Quality Directives.

Entities in categories 1 and 2 are required to participate by the networks they contribute to.
Any other laboratory is welcome to apply for participating.

When the number of applications is greater than 40, priority ranking among the requests from these other laboratories will be based on the poor performance in previous inter-laboratory exercises, instrument novelty, date of last participation, and private sector belonging.

In case the number of applications that could not be accepted is greater than 12, another PT exercise will be organised, starting in September.

4 SEQUENTIAL STEPS OF THE PT OC&EC EXERCISE

Access to the PT OC&EC exercise is provided through the Proficiency Testing Data Acquisition Platform (PT-DAP) of the ERLAP–JRC, https://erlap-intercomparison.jrc.ec.europa.eu.

Typical PT OC&EC exercise timetable is described in paragraph 5;

The sequential steps of PT OC&EC exercise are listed below and described in details in par.6:

- applicants open https://erlap-intercomparison.jrc.ec.europa.eu;

- applicants

  subscribe to PT-DAP (one time, two-step procedure), in case of new users;

  and/or directly log in using their EU Login credential;

- applicants express their interest for participation in the PT OC&EC exercise;

- applicants receive a notification of successful application; if not, applicants contact PT coordinator; applicants may also *delete* their application;

- applicants receive a notification stating either acceptance or rejection of their application (within a month from the date of application closure);

- participants receive a notification on PT items dispatch;

- participants reply to PT coordinator confirming PT item receipt and report on their integrity;

- participants process PT items in the same manner as the routine samples, including handling, storage and disposal and observe the analytical procedure they usually apply [Note: The European Air Quality Directive (2024/2881) indicates as reference method for the measurement of OC and EC in ambient air that described in the EN 16909:2017].

- participants stop the transport&storage temperature recording, on the USB temperature data logger, pressing "STOP" only at completion of PT item analyses;

- participants submit their data (*uncertainties not required*) and metadata, via ERLAP–JRC PT-DAP;

- participants receive a notification of successful data submission; participants may manage their data any time before the "data submission" closure;

- participants may also withdraw their participation;

- participants receive a notification when the PT report is available for comments (only formal aspects); the report will be officially published on JRC Publications Repository (the URL to the record will be distributed, when available);

- participants shall provide feedback on the provided service, preferably at the completion of the PT exercise;

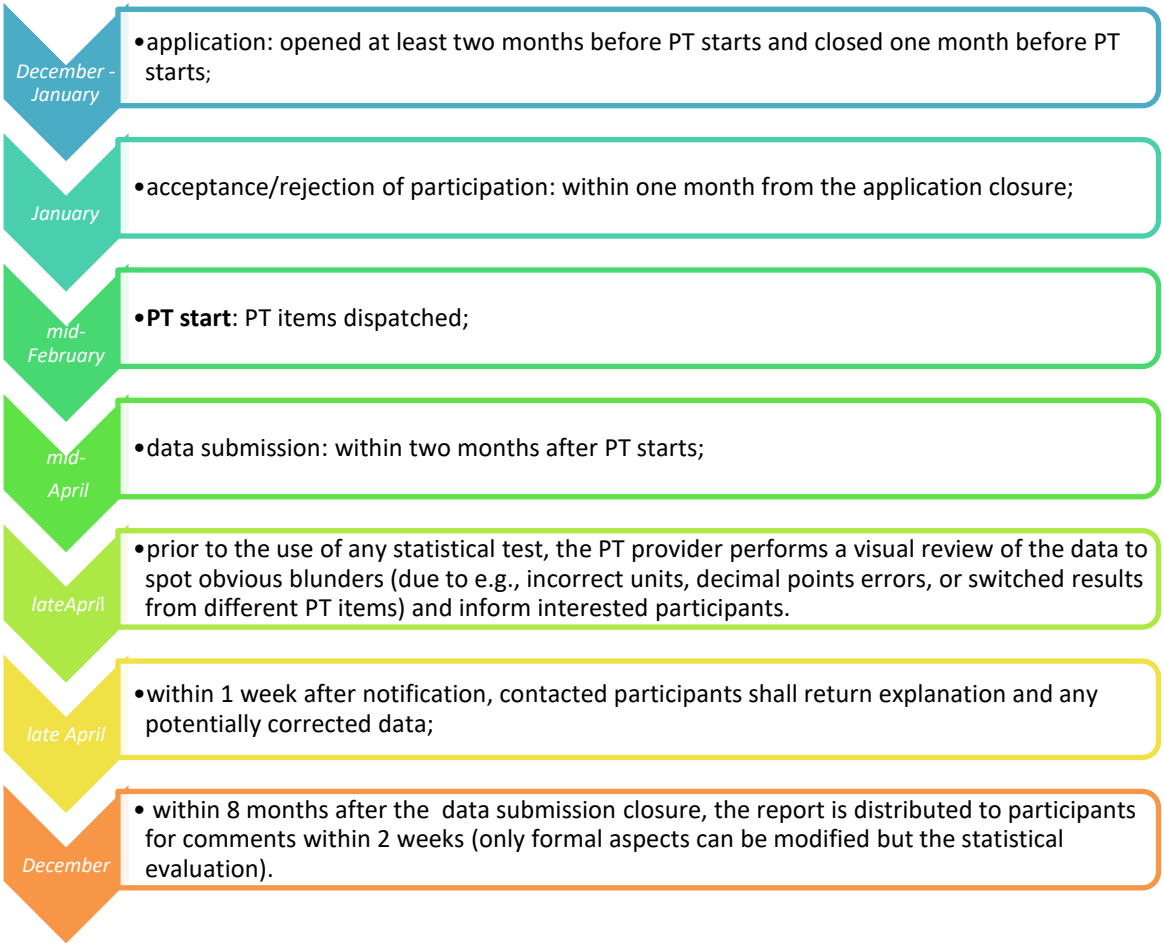
[1] United Nations Convention on Long-Range Transboundary Air Pollution

- participants may use the form in Annex 1 to communicate complaints and appeal to the PT provider.

5 TYPICAL TIMETABLE

The PT is normally organised once a year starting, typically, in February and possibly in September for the second one.

A timetable summary of this PT OC&EC exercise is following (*the timing assumes PT starts in February*):



6 WEB APPLICATION

The JRC–ERLAP platform for proficiency testing scheme and data acquisition, PT-DAP, is a web application that allows stakeholders/users to access PT schemes organised by JRC-ERLAP for variables of air quality relevance.

This web application adopts the European Commission's identity and access management service, EU Login.

Authentication: EU login account

- open https://erlap-intercomparison.jrc.ec.europa.eu Proficiency Testing Data Acquisition Platform (PT-DAP) and click "*SUBSCRIBE*";
- if you are a new user and do not have an EU Login account yet, create an account;
- fill in all mandatory fields (i.e. First name, Last Name, e-mail, confirm e-mail and e-mail language) and acknowledge the privacy statement, then click on "Create an account";
- you can now sign in using your e-mail and password.

Subscription to the JRC-ERLAP PT-DAP:

- fill in the subscription form, accept the privacy statement, enter the verification code and send;
- you receive an e-mail; click on the "validation link" to confirm your e-mail and access the JRC-ERLAP PT-DAP;

Application-Registration to the OC&EC PT exercise:

- select the OC&EC scheme section and apply for the available exercised;
- duly fill in the application form (details on applicant, shipping, measurement instrument and method, observational site and network membership); and express the interest in possibly participating with an additional instrument;
- accept all procedures, terms and conditions as described in the PT plan;
- you receive a notification of successful application; if not, contact PT coordinator (Par.2);
- you receive a notification either accepting or rejecting your application;
- you may also delete your application.

Submission of data and metadata:

access the DAP OC&EC section, select the relevant PT-OC&EC exercise:

- click *SUBMIT* to submit your data (corresponding uncertainties are not required) and metadata:
  - from the drop down list, *SELECT* one measurand (i.e., OC, EC and TC loading) and the measurement instrument serial number;
    - upload the CSV file with the data from triplicate analyses for each PT item (i.e. 1, 2, …8) with unit format µg/cm² (as instrument output) and three significant digits. Leading zeros (for instance in 0.08) are not significant digits. In contrast, a zero after a decimal (e.g., 7.60) is significant. The use of the scientific notation with 2 decimal places (e.g., 5.43 E-2) is recommended;
    - the CSV file is automatically verified for format and completeness issues; in case of a well formed file, data are shown in a table (cells highlighted in yellow indicate missing entries, left intentionally or mistakenly empty); otherwise, error details are provided;
  - repeat it for each measurand;
  - upload the transport&storage temperature recording from the data logger (format .pdf file).

  you receive a notification of successful data submission, if not, contact PT coordinator (Par.2);

  you may manage your data any time before the "data submission" closure, accessing the PT OC&EC exercise.

- or click *WITHDRAW* to withdrawn your participation from the PT exercise.

Feedback

- At the completion of the PT exercise, preferably, leave your feedback on the provided service (fit for the purpose, respect of timeline, deliverable quality and communication with the PT provider team)

The web application and the database are hosted and maintained at the JRC-ERLAP in Ispra (IT). The use of the web application and database is regulated by European Commission Legal Notice and JRC Privacy Statement.

7 CONFIDENTIALITY

For the purpose of discussion and mutual assistance (e.g. to improve participant performance), results and performance are reported together with the identity of participants.

Instead, personal data (e.g. address, e-mail address, telephone number) are confidential and cannot be disclosed to third parties, according to the European Commission Legal Notice and JRC Privacy Statement.
By expressing its own interest in participation, each applicant agrees on the above privacy and confidentiality policies.
To provide permanent and public access to PT results, a digital object identifier (DOI) is associated to the report.

8 COLLUSION AND DATA FALSIFICATION

Collusion between participants and falsification of data are contrary to professional ethics. Such conduct annuls the benefit of PT exercises for participants and provider. It defeats the objective of taking part in PT exercises if participants are not returning genuine data.

The PT provider conducts its program in the belief that participants perform the analysis and report data with scientific rigor. By expressing its own interest of participation, each applicant commits himself/herself not to falsify the data which were obtained and refrains from any collusion with other participants.
In case of a suspected event of falsification of data and/or collusion among participants, and if evidences of it are confirmed, the participants involved will be excluded from the PT data evaluation.

9 FEES

No fees are charged to participants.

10 PT ITEM

10.1 PRODUCTION

Any sampler which can accommodate filters whose dimensions are sufficient to produce the necessary number of PT items can be used.
Sampling can be performed anywhere, any time and for any duration. Filters shall be in binder-free quartz fibre.

In this PT exercise, ambient (outdoor) $PM_{2.5}$ aerosol is collected with a high-volume sampler (namely a on quartz fibre filters (Pallflex, Tissuquartz-2500QAT-UP binder free; 20.32 x 25.4 cm) at the regional background site of Ispra, Italy. Filter samples (i.e. PT items) are preferably stored in a refrigerator at temperature of 3±2 °C.

10.2 SELECTION AND DISTRIBUTION

Selection, distribution and dispatching of the PT items are conducted by the PT provider making use of its facilities and laboratories.

Filter samples are selected so that their TC, OC and EC loadings (µg/cm²) are within the range of applicability of EN16909:2017 (i.e., 1.8-49 µg cm^{-2} and 0.2-38 µg cm^{-2} for OC and EC, respectively).

Aliquots (according to participants needs to triplicate measurements) are punched out from 8 filter samples (1, 2, 3, …8); the PT items are then packaged in closed petri dishes, securely labelled, and randomly distributed among participants.

A sufficient number of PT items is prepared also to allow for the need to replace any such PT items lost or damaged during distribution or the use after the participant performance evaluation (particularly in case of underperformance). PT items will be retained for one year from their distribution.

PT items are dispatched to all participants via courier (limiting to a max of 3 days the time needed for transport) at ambient temperature. A single use USB temperature-data logger is included to qualitatively monitor the temperature experienced by the PT items from dispatchment to analysis.

Participants, notified about PT item dispatch by e-mail, shall reply to the PT coordinator confirming their receipt, expected within a few days, and report on their integrity. In the case of lost, delayed or damaged PT items, participants shall promptly inform the PT coordinator, who shall organize a new dispatchment.

Participants shall treat PT items in the same manner as routine samples, including handling, storing and disposal, and stop the temperature record, from the USB temperature-data logger, only at completion of PT item analyses.

10.3 HOMOGENEITY

The homogeneity of the PT items is assessed by the PT provider on the basis of the recommendations listed in ISO 13528:2022, informative Annex B, for all measurands, i.e. TC, OC and EC. Measurement of TC, OC and EC are performed according to the European standard EN16909:2017.

Studies are conducted prior to the circulation of PT items to evaluate possible impacts of inhomogeneity on the measurands' loadings (µg/cm²).

Subsamples (≥ 10) of 3.6 cm x 1.8 cm are randomly taken from a specific filter sample across an area corresponding to that used to produce all aliquots from the PT items; three measurements of TC, OC and EC are performed on each subsample.

The filter homogeneity is assessed as the estimate of the between-sample standard deviation, calculated using the analysis of variance, according to ISO 13528:2022 (E) Annex B, par. B.3.
If sampling occurs under repeatable conditions, it is reasonable to assume that all PT items have a similar homogeneity.

In previous exercises of this PT scheme, the homogeneity resulted better than 5% for TC, OC, and EC.
Because 5% represents also the accepted repeatability value for the measurement of TC, OC and EC (EN 16909:2017 (E)), a homogeneity of 5% shall be considered sufficient. In case this criterion is not met, the homogeneity assessment shall be repeated after cleaning of the sampling device and filter holder, and use of new batch of binder-free quartz fiber filters.

The homogeneity is considered as a component of the uncertainty associated with the assigned value of the PT item and is therefore taken into account in the evaluation of participants' performance.

To limit the contribution of localized heterogeneities and/or contaminations to the occurrence and recurrence of poor performance from a single participant, a random distribution of PT items is used among participants.

10.4 STABILITY

The stability of the PT items is assessed by the PT provider on the basis of the recommendations listed in ISO 13528:2022, informative Annex B, for all measurands (TC, OC and EC). Measurements are performed according to the European standard EN16909:2017.

Studies are conducted prior to circulation of PT items to evaluate possible impacts of temperature conditions over the duration of the PT exercise (including transport and storage) on the measurands' loadings (µg/cm²).

Based on the time and temperature limits for sample transport and storage in the EN16909:2017 (par. 7.2), and on the temperature conditions foreseeable during transport and storage at participants' premises (as determined from previous PT exercises), subsamples (≥3), from specific samples (≥1) are exposed to a temperature of 25 °C ± 0.5 for a period of ca. 6-7 weeks (i.e. duration of the PT exercise).

The effect of temperature condition during storage and transport is assessed by comparing, over time the assessment result at t_f (i.e. after 6-7 weeks) to the initial value t_0 (in refrigerator at T of 3±2 °C) for each measurand. PT items' stability is assessed by determining if the difference of the means of the measurements performed over time are statistically (i.e. t-test at the 99% level of confidence) different from zero. In case this criterion is not met, the stability assessment shall be repeated on particulate matter samples collected in periods where the contribution of the semi-volatile organic compounds to aerosol mass is lower. The PT items shall also be selected accordingly.

The stability is considered as a component of the uncertainty associated with the assigned value of the PT item and is therefore taken into account in the evaluation of participants' performance.

To qualitatively monitor the temperature conditions experienced by each PT item set during transport and storage at participant' premises, a single use USB temperature-data logger is also dispatched together with the PT items. The exposure to extreme temperature conditions (e.g. T > 25 °C for more than 500°C hour) are is taken into account in the case of participants' poor performance.

11 PERFORMANCE ASSESSMENT

The primary goal is to assess participants' performance in determining the TC loading and the EC/TC ratio in order to evaluate the accuracy of the instrument response throughout the analysis and of the optical correction for charring, respectively. These two variables are more powerful to diagnose the source of possible under-performance than OC and/or EC loadings themselves.

Participants' performance is determined in terms of z-scores, a measure of the participants' bias compared to an assigned value associated with its standard deviation.

11.1 DATA REVIEW

At an early stage of the evaluation of the PT exercise data and prior to use of any statistical procedure, the PT provider conducts a review of the entire dataset to identify obvious blunders (e.g. reporting results in incorrect units, switching results from different PT items, transcription/typing errors). If blunders are identified, the PT provider asks relevant participants for clarification and possible corrections.

11.2 EVALUATION OF PERFORMANCE

Participants are allowed to analyse the PT items using their routine measurement method [Note: The European Air Quality Directive (2024/2881) indicates as reference method for the measurement of OC and EC in ambient air that described in the EN 16909:2017]. Based on previous ILC exercises, the vast majority of participants (95-97%) apply the EUSAAR_2 thermal protocol. The results from different measurement method will be treated separately, only if sufficient in number to produce a statistically meaningful evaluation.

To calculate z-scores, an assigned value and its standard deviation shall be determined for each PT item.

Among the available approaches for determining the assigned value (and in absence of a reference or certified reference material), the approach of the *"Consensus value from participant results"* is chosen. With this approach, the assigned value X for each PT item is the robust (i.e. resistant to asymmetric outlier distribution) average calculated, with the ISO 13528 Algorithm A, a recursive technique, from the results reported by all participants (See ISO 13528:2005(E), Annex C).

Among the available methods for determining the standard deviation for proficiency assessment (σ*), the approach of calculating σ* *from data obtained in a round of a proficiency testing scheme* was chosen. With this approach, σ* is the robust standard deviation calculated, with a recursive algorithm, from the results reported by all participants (See ISO 13528:2005(E), Annex C).

Overall, this approach is considered producing **reliable** assigned values and associated robust standard deviation for our PT scheme because of the large number of experienced and expert participants in the yearly ILCs, and the use of a single thermal-protocol. In addition, by experience from previous exercises, the robust standard deviations from all data in a exercise of PT scheme are in the range of the overall method precision (repeatability and reproducibility).

To verify the robustness of the assigned value and its standard deviation, the Q/Hampel method is applied (https://quodata.de/content/qhampel-webtool, as in ISO 13528:2015 (E) par. C.5.4).

For each participants and PT item, the z-score is calculated as:

$z = (x_i - X) / \sigma^*$

where x_i is the result from the participant i; X is the assigned value for the PT item; and σ^* is the standard deviation for proficiency assessment.

When a participant reports an entry that produces a bias greater than +3 z or less than -3 z (i.e. deviating from the assigned value for more than 3 standard deviations), this entry is considered to give an "action signal". Likewise, a participant bias above +2 z or below -2 z (i.e. deviating from the assigned value for more than 2 but less than 3 standard deviations) is considered to give a "warning signal". A participant bias between -2 z and +2 z indicates a satisfactory participant performance with respect to the standard deviation for proficiency assessment.

Participants showing three large |z-scores|(i.e. > 2) and/or systematic biases (i.e. for all PT items and larger than ± 5%), on average shall carefully examine their measurement procedure and identify appropriate corrective actions that are likely to prevent the recurrence of such performance in the future.

12 METHOD REPEATABILITY AND REPRODUCIBILITY

For informative purposes only, the data from this ILC exercise are also used to determine the repeatability and reproducibility of the standard measurement method in EN16909:2017, according to the ISO 5725-2:2019. The determination of the precision of the measurement method for TC and EC/TC determination involves, in brief, the following stages, according to ISO 5725:2:

- application of statistical tests (i.e. Cochran's test and Grubbs' test) to identify possible outliers;
- computation of means and precision for each PT item separately;
- establishment of a relationship between precision and the mean.

13 PT REPORT

The report describing the results of the statistical evaluation will be distributed to participants. This report is valid only in its entirety and not in parts. Reports including single participant performance only are not foreseen.

Relevant references:

1) Directive (EU) 2024/2881 of the European Parliament and of the Council of 23 October **2024** on ambient air quality and cleaner air for Europe, https://eur-lex.europa.eu/eli/dir/2024/2881/oj
2) EN 16909:2017, Ambient air – Measurement of elemental carbon (EC) and organic carbon (OC) collected on filters.
3) ISO/IEC 17025:2018, General requirements for the competence of testing and calibration laboratories.
4) ISO 5725-2:2019, Accuracy (trueness and precision) of measurement methods and results – Part 2: Basic method for the determination of repeatability and reproducibility of a standard measurement method.
5) ISO 13528: 2022, Statistical Methods for use in Proficiency Testing by Inter-Laboratory Comparisons.
6) ISO/IEC 17043:2023(E), Conformity assessment - General requirements for the competence of proficiency testing providers.

ANNEX 1: APPEAL/COMPLAINT FORM

This form should be addressed to the PT provider team.

Laboratory and participant name:

PT scheme: OC&EC YYYY-n

If you would like to file an appeal[§]/complaint, please use the box below:

Description of Appeal/Complaint:

Date: Name and Function: Signature:

[§]Errors made by the participants in data entry cannot be corrected after the report is issued and these errors are not grounds for appeal.