PROFICIENCY TESTING SCHEME PROTOCOL

Ambient-air –Measurement of total carbon, organic carbon and elemental carbon

in PM2.5 deposited on filters

JRC-ERLAP

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 (2008/50/EC). 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 (JRC) of the European Commission has been supporting the quality of 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.

CONTENTS

1   SCOPE OF THE PROFICIENCY TESTING SCHEME

The overall scope of this proficiency testing (PT) scheme is to enhance the comparability and determine the uncertainty of the TC, OC and EC atmospheric concentration data produced across Europe.

Measurands of this PT 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 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.

By taking part in the OC&EC PT scheme, 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.

By principle, this PT scheme does not address any other step of the determinations 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.

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

JRC-ERLAP has the 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 the PT scheme (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.euroropa.eu;
-   Jean-Philippe Putaud (preparing test 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 schemes 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.

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

1-   ACTRIS National Facilities performing OC and EC analyses, as a result of an agreement 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.

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

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

After a possible selection process, applicants receive an automatic message either accepting or rejecting their application.

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

4 SEQUENTIAL STEPS OF THE PT SCHEME

Access to the PT schemes provided by JRC-ERLAP is provided through https://erlap-intercomparison.jrc.ec.europa.eu , the ERLAP-JRC Proficiency Testing Data Acquisition Platform (PT-DAP). Typical PT scheme timetable is described in Section 5;

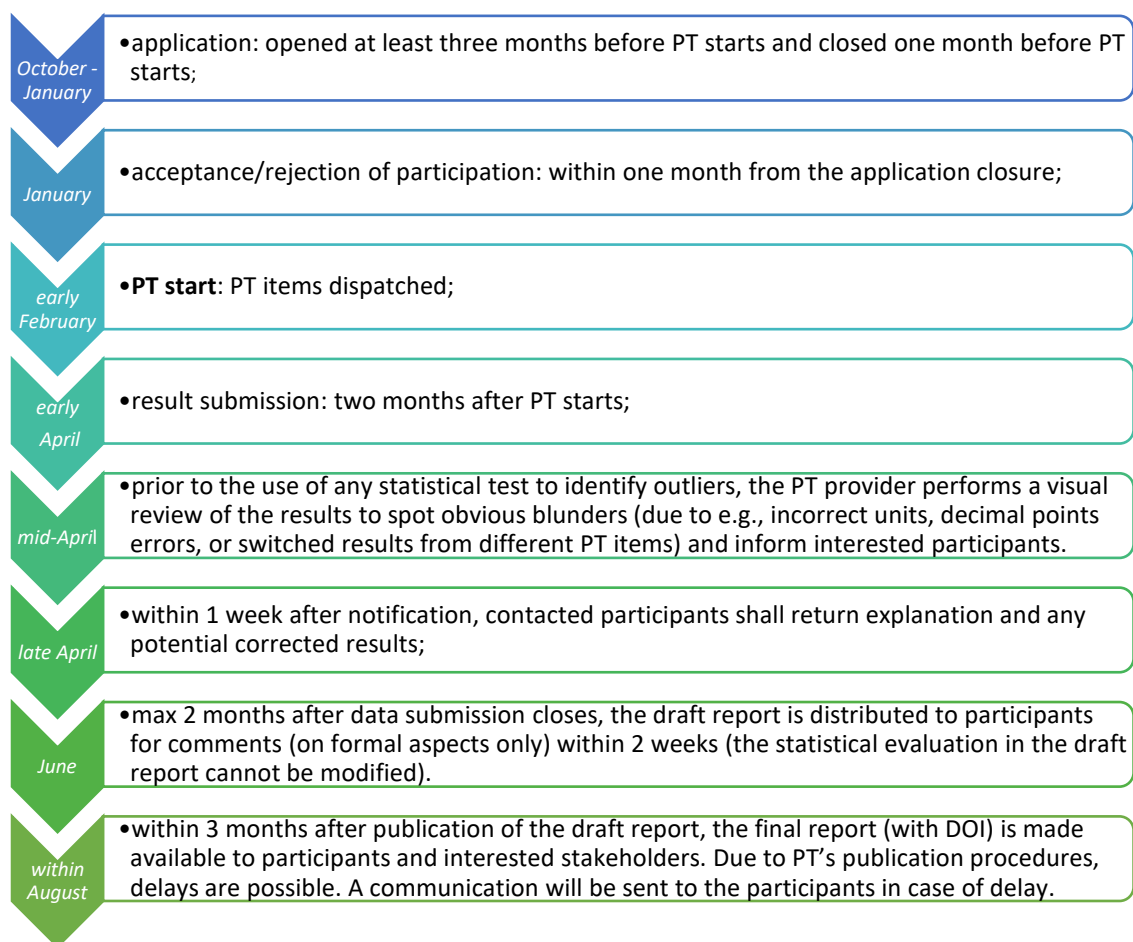The sequential steps of the PT scheme are listed below (web application details in par.6):

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

- applicants subscribe to PT-DAP (one time, two-step procedure), i.e.:

> 1) create an EU login account via a self-authentication page (authentication phase);
> 2) fill in a subscription form to access to the PT-DAP (subscription phase);

- applicants express their interest for participation in the OC&EC PT scheme (application phase), i.e.:

> duly fill in an application form (details on participant, shipping, measurement instrument and method, observational site and network membership);

- applicants receive a notification of successful application;

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

- participants receive a notification on PT items dispatch;

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

- participants process PT items in the same manner as the routine samples, including handling and storage;

- participants observe the analytical procedure they usually apply;

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

- participants submit their results and metrology information, via PT-DAP, i.e.:

> i. report in a single file TC, OC and EC loading values (unit format $\mu g/cm^2$ as instrument output) with three significant digits[2] from triplicate analyses for each PT item (format .csv file);
>
> ii. upload the temperature recording from the data logger (format .pdf file);
>
> iii. duly fill in the questionnaire (details on integration options);

- participants receive a notification of successful data submission;

- participants receive the report including the statistical evaluation, together with indicators of their laboratory performance;

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

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 scheme is following (*the timing assumes PT starts in February*):

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[2] 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.

October - January	• application: opened at least three months before PT starts and closed one month before PT starts;
January	• acceptance/rejection of participation: within one month from the application closure;
early February	• **PT start**: PT items dispatched;
early April	• result submission: two months after PT starts;
mid-April	• prior to the use of any statistical test to identify outliers, the PT provider performs a visual review of the results to spot obvious blunders (due to e.g., incorrect units, decimal points errors, or switched results from different PT items) and inform interested participants.
late April	• within 1 week after notification, contacted participants shall return explanation and any potential corrected results;
June	• max 2 months after data submission closes, the draft report is distributed to participants for comments (on formal aspects only) within 2 weeks (the statistical evaluation in the draft report cannot be modified).
within August	• within 3 months after publication of the draft report, the final report (with DOI) is made available to participants and interested stakeholders. Due to PT's publication procedures, delays are possible. A communication will be sent to the participants in case of delay.

Participants shall provide the PT provider with feedback regarding all aspects of the PT scheme round using the form in Annex 1.

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

6 WEB APLLICATION

EU Login is the European Commission's user authentication service.
It allows authorised users to access a wide range of European Commission web services and/or systems- using a single username (i.e. email address) and password- among which the JRC-ERLAP platform for proficiency testing scheme and data acquisition (PT-DAP).

Authentication: EU login

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

Subscription to the JRC-ERLAP PT-DAP:

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

Application to the OC&EC PT scheme round:

- o duly fill in the application form (details on participant, shipping, measurement instrument and method, observational site and network membership);
- o accept all procedures, terms and conditions as described in the PT plan.
- o you receive a notification of successful application;
- o you receive a notification either accepting or rejecting your application.

Submission of results:

- o browse to: OC&EC PT scheme in the PT-DAP and click "result submission";
- o download the .csv file template, report TC, OC and EC concentration values, following the instructions, and upload it;
- o upload the temperature recording from the data logger (format .pdf file);
- o duly fill in the questionnaire;
- o you receive a notification of successful submission.

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.
To provide permanent and public access to the report, a digital object identifier (DOI) is included.
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.

8   COLLUSION AND RESULTS FALSIFICATION

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

The PT provider conducts its program in the belief that participants perform the analysis and report results with scientific rigor. By expressing its own interest of participation, each applicant commits himself/herself not to falsify the results which were obtained and refrains from any collusion with other participants.
In case of a suspected event of falsification of results 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 TEST ITEM

10.1   PRODUCTION AND DISTRIBUTION OF PT ITEMS

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

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

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

PT items are dispatched to all participants via courier at ambient temperature. A single use USB temperature-data logger is included to 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. Participants shall treat PT items in the same manner

as routine samples, including handling and storing and stop the temperature record, from the USB temperature-data logger, only at completion of PT item analyses.

10.2 HOMOGENEITY OF PT ITEMS

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 circulation of proficiency test samples to evaluate possible impacts of inhomogeneity on the measurands.

Subsamples (≥ 10) of 3.6 cm x 1.8 cm are randomly taken from specific filter sample across an area corresponding to the punched one in the PT items; three replicates of TC, OC and EC measurements are performed on each subsample. The filter homogeneity is assessed as estimate of the between-sample standard deviation, calculated using 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 filter samples have a similar homogeneity.

In previous rounds 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.

The homogeneity is considered as a component of the uncertainty associated with the assigned value of the PT item and 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.

10.3 STABILITY OF PT ITEMS

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 during transport and storage on the measurands.

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 scheme rounds), subsamples (≥3), from specific filter samples (≥1) are exposed to a temperature of 25 °C ± 0.5 for a period of 6 weeks. The effect of temperature condition during storage and transport is assessed by comparing, over time, each stability monitoring result (i.e. at t_1= after 1 week and t_2 = after 6 weeks) to the initial value (t_0= in refrigerator at T of 3±2 °C) for each measurand. Three replicates of TC, OC and EC measurements are performed on each subsample. PT items' stability is assessed by determining if the difference of the means of the measurements performed over time are statistically (t-test) different from zero.

The stability is considered as a component of the uncertainty associated with the assigned value of the PT item and taken into account in the evaluation of participants' 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. These two variables are more powerful to diagnose the source of possible under-performance than OC and/or EC. The repeatability and reproducibility standard deviations of the thermal-optical method described in EN16909 are also determined.

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 ASSIGNED VALUE AND ITS STANDARD DEVIATION

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

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).

The standard deviation for proficiency assessment (σ*) is calculated using the repeatability ($σ_r$) and reproducibility ($σ_R$) standard deviations derived from previous PT scheme rounds for the determination of TC loading and EC/TC ratio, as follows:

$$\sigma_{pt} = \sqrt{(\sigma_R^2 - \sigma_r^2 \, (1 - 1/m))}$$

where *m* is the number of replicate measurements in the PT scheme round.

On the basis of the results of previous PT scheme rounds, the repeatability and reproducibility standard deviations for the determination of TC loading are dependent on the mean TC loading value; functional relations are derived (according to ISO 5725-2) and used to calculate the repeatability and reproducibility standard deviation and the standard deviations for proficiency assessment for the assigned values.
On the basis of previous PT scheme round results, the repeatability and reproducibility standard deviations for the EC/TC ratio are not dependent on the mean value of the EC/TC ratio; the repeatability and reproducibility standard deviation medians for EC/TC ratio are derived from previous PT scheme round results, and used to calculate a single standard deviation for proficiency assessment for all assigned values.

To verify the robustness of the assigned value and its standard deviation, the Q/Hampel method is applied using the available web application https://quodata.de/en/web%C2%ADservices/QHampel.html (ISO 13528:2015 (E) par. C.5.4).

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

z = (x_i-X) / $σ_{PT}$

where x_i is the result from the participant i; X is the assigned value for the PT item; and $σ_{PT}$ 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 large (|z-scores|> 2) and/or systematic biases shall carefully examine their measurement procedure and identify appropriate corrective actions that are likely to prevent the recurrence of such results in the future.

12   REPEATABILITY AND REPRODUCIBILITY
The determination of the precision (in terms of repeatability and reproducibility standard deviations) 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 test items separately;
- establishment of a relationship between precision and the means.

Relevant references:

1) Directive 2008/50/EC of the European Parliament and of the Council of 21 May 2008 on ambient air quality and cleaner air for Europe, L 152, 11.06.2008 and Directive 2015/1480/EC, 28.08.2015.

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: FEEDBACK/APPEAL/COMPLAINT FORM

During a PT scheme round, any concerns, suggestions or suspected errors should be reported to the PT provider.

This form should be delivered as soon as possible to the PT provider team.

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

Laboratory and participant name:

PT scheme: OC&EC YYYY-n

General Feedback:

Timelines	Below expectations	Met expectations	Above expectations	N/A
Respect of timeline	☐	☐	☐	☐
Deliverable	Below expectations	Met expectations	Above expectations	N/A
Respect of requirements	☐	☐	☐	☐
Form	☐	☐	☐	☐
Content	☐	☐	☐	☐
Overall Quality	☐	☐	☐	☐
Information/ Communication	Below expectations	Met expectations	Above expectations	N/A
Interaction with PT provider team	☐	☐	☐	
Comments				
Any additional general comment (especially for explaining the reasons for "below expectations")				

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

Description of Appeal/Complaint:

Date: Name and Function: Signature: