Proficiency Testing Protocol

Inorganic gaseous pollutants measurement

11-14 March 2024

18-21 March 2024

Joint Research Centre (JRC-ERLAP)
Ispra

INTRODUCTION

With the adoption of Directive [1] on ambient air quality and cleaner air for Europe, a framework for a harmonized air quality assessment in Europe was set.
As foreseen in the Directive, the Joint Research Centre (JRC) of the EC (European Commission) organizes proficiency testing (PT) to assess and improve the status of comparability of measurements of National Reference Laboratories (NRL) of the Member States of the European Union.
JRC-ERLAP (European Reference Laboratory for Air Pollution), with this proficiency testing (PT), evaluates the performance in the analysis of inorganic gaseous pollutants covered by European Air Quality Directives [1] (SO_2, CO, NO, NO_2 and O_3).

Contents

1 SCOPE OF PROFICIENCY TESTING SCHEME

ISO/IEC 17043:2010 [2] defines proficiency test as the evaluation of participant performance against pre-established criteria by means of PT. The demand for independent demonstration of competence, from regulatory bodies and customers, means that proficiency testing is relevant to all laboratories testing samples for quality and safety. PT is organised to harmonise air quality measurements across the EU made by public health and environmental institutes in the EU and WHO EURO Region. Measurands of this PT scheme are SO_2, CO, NO, NO_2 and O_3 in the concentration range for the applicability of the following standards methods:
EN 14211:2012-NO/NO_2,
EN 14212:2012-SO_2,
EN 14625:2012-O_3,
EN 14626:2012-CO

By taking part in this PT scheme, participants can detect possible problems in their analytical chain and take remedial actions (if necessary), compare calibration standards and measurement capabilities, facilitate exchange of technical information amongst the national experts.
To fully benefit from their participation in this test, participants are recommended to observe the analytical procedure they usually apply.

2 PT PROVIDER

JRC-ERLAP Laboratory is accredited for ISO/IEC 17025 and ISO 17043 for the pollutants measurement scope of this PT.
JRC-ERLAP takes the responsibility for all activities of the proficiency testing and as PT organizer does not make use of any externally provided products and/or services for any of the operations involved in the exercise.

JRC-ERLAP has the competence to run inter-laboratory comparisons, the expertise and the experience to perform measurement of inorganic gases.
PT provider staff are:

- Annette Borowiak (PT coordinator)
- Maurizio Barbiere (statistician);
- Claudia Tarricone (testing technician).

This protocol refers also to the document N37 [4] (draft version) presented and approved within the AQUILA network.

3 PARTICIPANTS

In JRC-ERLAP, the supply bench can host a maximum number of 11 laboratories (including the PT provider) measuring 4 inorganic gases (in case less pollutants are measured, this number might be increased).
JRC-ERLAP measurement is the reference value then the proficiency assessment is always possible also with only 1 participant but, for organizational reasons, a PT will be run for a minimum number of 5 participants.
The selection of participants is based on the following criteria:

1. Being NRL
2. Periodicity of participation to previous PT organized by JRC
3. Results of previous PT
4. The principle first come first served

After the selection process, the laboratories receive an automatic message either admitting or rejecting their request of participation.
Other public laboratories or those involved in the air quality metrology might be accepted only in case of vacancies.
Any excluded participant will be inserted into a waiting list and it will able to participate if any cancellation occurs. In case the waiting list includes an NRL who had unsatisfactory results or didn't participate in the PT for 3 years, a new unplanned PT could be proposed.

4 TYPICAL TIMETABLE

A timetable summary of the PT organization is following:

1. JRC-ERLAP & WHO CC: Announcement of PT (at least 3 months before PT)
2. Laboratories: Expression of interest (within the closing registration deadline proposed)
3. JRC-ERLAP confirmation to the expression of interest (after the closing registration deadline proposed)
4. Event Registration (2 weeks before PT)
5. Laboratories: deadline for reporting results and questionnaires to JRC-ERLAP (1 month after the end of PT)
6. JRC-ERLAP: Contacting laboratories in case of obvious anomalies in their results (3 months after the end of PT)
7. Laboratories: Return explanation and any potential corrected results (2 weeks after anomalies communication)
8. JRC-ERLAP: distributing final report to participating laboratories. (6 months after the end of the PT).

9. Laboratories: comments about the final report by email to PT Provider. (2 weeks after final report delivery). The statistical evaluation in the final report cannot be modified, but reasonable comments of the NRL may be added to the report. In case of approved modification requests the report will be reissued.
10. Laboratories: appeal or complaint submission (see annex1) (7 months after the end of the PT).
11. JRC-ERLAP: report publication on the JRC repository (https://publications.jrc.ec.europa.eu/repository/) will be available as soon as the JRC internal process is completed.

5 TYPICAL GAS MIXTURE GENERATION AND MEASUREMENT

In the following table 1 is shown the PT scheduling of the gas mix generation.

Table 1:Pt example program

Run	Component	day	start time	duration	NO	NO_2	O_3	SO_2	CO
				h	nmol/mol				µmol/mol
	/	1st - Mon	09:00		Installation and Calibration				
	/	2nd - Tue	08:00	3	Calibration				
0	NO-NO_2-O_3	2nd - Tue	11:00	1	Zero air				
1	NO-NO_2	2nd - Tue	12:00	2	X	X			
2	NO-NO_2	2nd - Tue	14:00	2	X	X			
1	O_3	2nd - Tue	16:00	2			X		
3	NO-NO_2	2nd - Tue	18:00	2	X	X			
4	NO-NO_2	2nd - Tue	20:00	2	X	X			
2	O_3	2nd - Tue	22:00	2			X		
5	NO-NO_2	2nd - Tue	00:00	2	X	X			
6	NO-NO_2	3rd - Wed	02:00	2	X	X			
3	O_3	3rd - Wed	04:00	2			X		
7	NO-NO_2	3rd - Wed	06:00	2	X	X		SO_2 value	
8	NO-NO_2	3rd - Wed	08:00	2	X	X		SO_2 value	
4	O_3	3rd - Wed	10:00	2			X		
9	NO-NO_2	3rd - Wed	12:00	2	X	X		SO_2 value	
10	NO-NO_2	3rd - Wed	14:00	2	X	X		SO_2 value	
5	O3	3rd - Wed	16:00	2			X		
0	CO-SO2	3rd - Wed	18:00	1	Zero air				
1	CO-SO_2	3rd - Wed	19:00	2				X	X
2	CO-SO_2	3rd - Wed	21:00	2				X	X
3	CO-SO_2	3rd - Wed	23:00	2				X	X
4	CO-SO_2	4th - Thu	01:00	2				X	X
5	CO-SO_2	4th - Thu	03:00	2				X	X
6	CO-SO2	4th - Thu	05:00	2				X	X
		4th - Thu	07:00	END - Zero air (not to be reported)					

The measurements have to be carried out continuously by the participating laboratories with their own automatic analyzers, calibrated with their own reference standards (including zero air). Measurement results have to be stored with participant's data acquisition systems.
The test mixtures are prepared by the dilution of gases from cylinders containing high concentrations of NO, SO_2 or CO using thermal mass flow controllers. O_3 is produced using an ozone generator and NO_2 is produced applying the gas phase titration method in a condition of NO excess.
Test gases will be dry matrix and free of particulate matter.

6 SUBMISSION OF RESULTS AND METROLOGY INFORMATION

The reporting of results, within the requested time scale and in the specified units, is part of the performance assessment.
The participants have to report the mean value on the request interval time, for each concentration level (run).
Participants have to submit their results and the uncertainties, combined and expanded, associated to each concentration level, including the zero concentration through a .csv template document, via the secure pages on our web site.
The uncertainty has to be reported in the same units as the result.
In case of missing measurements, the participant must leave the space in the .csv template blank.
The runs 0 are used for checking zero level. In this case the participant has to provide only one half an hour average measurement and the two uncertainties. For all the other span runs, three half hours average values of concentration and the two uncertainties should be submitted. The reported data should follow the rounding rules defined in table 2.

Table 2: Rounding rules

Value x	**Number of decimals**	**Example : before rounding**	**Example: after rounding**
$x \geq 10$	integer	17.83	18
$1 \leq x < 10$	1 decimal	2.345	2.3
$0.1 \leq x < 1$	2 decimals	0.865	0.87
$0.01 \leq x < 0.1$	3 decimals	0.0419	0.042
Etc…			

Submitted data are saved in a central database and subsequently used for calculations and comparisons. When all data are uploaded it will be possible to evaluate the

laboratory's measurement proficiency and writing the final report about the PT exercise.

6.1 Web application

EU Login is the European Commission's user authentication service.
It allows users to access a wide range of European Commission systems using a single username (i.e. email address) and password among which the Proficiency Testing Data Acquisition Platform (PT-DAP).

Authentication: EU login

- if you are a new user and do not have an EU Login account yet, create a new one following this link Create an account (europa.eu)
- 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";
- you can now sign in using your e-mail and password.

If you have already an EU Login account and you want to participate to one of JRC-ERLAP PT exercises, follow the procedure below:

- Proficiency Test Data Acquisition Platform (PT-DAP) and click "SUBSCRIBE";
- fill in the registration form, accept the privacy statement and click "send";
- you receive an e-mail; click on the "validation link" to confirm your e-mail and access the PT-DAP;

Select the desired PT scheme:

- duly fill in an application form (details related to participant, shipping, instrument, measurement method, observational site and network membership);
- accept all procedures, terms and conditions as described in the PT plan and send it.
- At the end of the closing date of the registration you'll receive a notification either accepting or rejecting your application.

Results submission:

- From your profile select the right inorganic gases PT scheme to upload your data;
- download the .csv file template, fill it in with inorganic gases results following the instructions, rounding rules and upload it;
- duly fill in the questionnaire
- you receive a notification of successful submission.

At the end of this protocol, in Annex 1, there is a feedback form to fill in and give to one of JRC-ERLAP team.

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

7 ASSIGNED VALUES AND EVALUATION SCHEME

The assigned values are derived from JRC-ERLAP's measurement process as defined in the ISO 13528 (§7.5) [6]. The uncertainty of the assigned value will be calculated as combined uncertainty of the JRC-ERLAP measurement uncertainty and the contribution of inhomogeneity among the different position on the testing bench.
The evaluation of the PT results will be carried out according to the ISO/IEC 17043 [5] and ISO 13528 [6]. Proficiency of participating laboratories will be evaluated with at least two performance indicators: z score or z' score method [6] and En score.

7.1 Performance indicator for gaseous pollutants

The z score or z' score method [6] will be used to demonstrate the capacity of NRLs to perform in accordance with the EN standard. When the uncertainty of assigned value ($u(x_{pt})$) has a similar order of magnitude of the standard deviation for proficiency assessment (σ_{pt}) i.e. $u(x_{pt}) > 0.3\sigma_{pt}$, then z' score is applied.

The z score/z' score will be calculated as described in ISO:13528 (§ 9.4, 9.5) [6]:

$$zi = \frac{(xi - Xpt)}{\sqrt{\sigma_{pt}^2}} \qquad (2)$$

$$z_i' = \frac{(x_i - x_{pt})}{\sqrt{\sigma_{pt}^2 + u^2(x_{pt})}} \qquad (3)$$

Where:

- z_i = *z score*
- z_i' = *z' score*
- x_i = participant average values
- x_{pt} = assigned value
- $u(x_{pt})$ = uncertainty of the assigned value
- σ_{pt} = Standard deviation for proficiency assessment

The E_n-score method [6] will be used to demonstrate that the difference between the participating laboratories' results and the assigned values remains within the participating laboratories' claimed uncertainties and the uncertainty of assigned values. The En-scores are calculated for all participants reporting uncertainty of measurements, this latter parameter being mandatory for NRLs.

$$E_n = \frac{x_i - x_{pt}}{\sqrt{U^2(x_i) + U^2(x_{pt})}} \qquad (4)$$

Where:
E_n = *E_n score*
x_i = participant average values
x_{pt} = assigned value
$U(x_i)$ = expanded uncertainty of the individual participants
$U(x_{pt})$ = expanded uncertainty of the assigned value

Other parameters may be used in addition to evaluate the laboratory's performances.

Beside the proficiency of participating laboratories, it is possible to evaluate the reproducibility of standardised measurement methods, according to ISO 5725-2 [7]. This group evaluation could be used as an indicator of the trend of the quality of measurements from one exercise to other ones (ISO 13528 § 8.7.2) or longer time series [6].
Tests of interference on the response of analysers might be performed. The reporting of results of these tests is only informative.
The calculation of the assigned value and its uncertainty will be documented and made available in an annex of the PT report. The *z score/z' score* will be calculated as described in equation 2 and 3, and in particular the σ_{pt} is obtained with the following equation

$$\sigma_{pt} = (a \ . \ x_{pt} + b) \qquad (5)$$

Where:
σ_{pt} = Standard deviation for proficiency assessment
x_{pt} = assigned value
a = slope see table 1
b = intercept see table 1

In fact, the 'standard deviation for proficiency assessment' (σ_{pt}) [6] is derived in a fitness-for-purpose manner from requirements given in the EN Standards [8, 9, 10, 11], where it is stated that the maximum permitted expanded uncertainty for calibration gases at the calibration point (75% of certification range) is 5%.
Over the whole measurement range, σ_{pt} is calculated by linear interpolation between the value at the calibration point and zero. For zero, instead of detection limit criteria, the specifications for purity of zero gas used in type approval as defined in EN Standards, are taken. Considering the measurement of NO_2 is obtained from the difference of concentration between NO_x and NO channels, its σ_{pt} considers the contributions of the two channels.
The linear function parameters (a, b) of σ_{pt} are given in Table 3.

Table 3: *Standard deviation for proficiency assessment σ_{pt}.*

	σ_{pt} (zero)	σ_{pt} (cal point)	$\sigma_{pt\ (nmol/mol)}$=a·[Assigned value]$_{nmol/mol}$+b		cal point
			a	b	
	nmol/mol	nmol/mol		nmol/mol	
SO_2	1	7.1	0.022	1	282.0
CO	100	1613	0.024	100	64500
O_3	1	4.7	0.020	1	187.5
NO	1	18.0	0.024	1	721.5
NO_2	1.4	6.9	0.028	1.4	195.8

8 REPORTING

Before finalizing the report, laboratories showing obvious anomalies (typo, blunders…) are requested to investigate the cause of discrepancies and eventually resend the data. Subsequently, data are considered definitive and the performance indicators are calculated. At the end of the statistical data evaluation, a final report version will be sent to the participants. At this stage, submitted data cannot be changed and only minor formal approved corrections, comments or reasonable suggestions are allowed. The report will be published and will be available for download at the https://publications.jrc.ec.europa.eu/repository/ .
All records and reports of any PT organized by JRC-ERLAP is kept for at least 4 years.

9 COLLUSION AND FALSIFICATION RESULTS

Although PT are used by participants to improve their performance, it is possible that someone 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 annuls the benefit of proficiency tests for participating laboratories and for the organizer. It defeats the objective of taking part in proficiency testing if participants are not returning genuine results. JRC-ERLAP conducts its program in the belief that participants perform the analysis and report results with scientific rigor. However, JRC-ERLAP will take steps to prevent collusion or falsification of results by participants. A member of the PT will always be in the laboratory whenever a participant is present.

Through this protocol every participant is informed about the consequences of a clear situation of collusion or falsification identified by the PT.

Collusion and falsification are unethical and constitute scientific fraud.

In case of a clear situation of collusion or falsification the laboratories involved will be contacted and if the evidences are confirmed they will be excluded from the PT data evaluation.

10 CONFIDENTIALITY

Results of the PT are published based on a non-confidentiality principle as agreed within the AQUILA network and reported in the document N37 [4].

During the PT, JRC-ERLAP ensures impartiality and confidentiality of the personal participant's information as follows: any administrative information provided by the laboratory is confidential and cannot be communicated to a third party.

Access to JRC-ERLAP facilities is allowed only to members of the Unit C5 and authorized persons (cleaning staff, maintenance staff, safety and security staff etc.)

Confidential password is released to access the web application for data submission and it allows access to the WEB data acquisition platform. Laboratories can change their password online.

The form LAB-REC-2000 (Confidentiality involvement form) is asked to be signed by the participants during their first participation to a PT organized by JRC-ERLAP.

11 PT ORGANIZATION

JRC-ERLAP organises the PT at the Joint Research Centre – Directorate C, Unit C05 T.P. 120, I – via E. Fermi 2749, 21027 Ispra (VA)

Contacts:

- Annette Borowiak (PT coordinator) office tel. +390332789956
- Maurizio Barbiere (statistician) office tel. +39 0332783057
- Claudia Tarricone (testing technician) office tel. +39 0332789573

For communication use the following email addresses: JRC-ERLAP@ec.europa.eu and in cc maurizio-giuseppe.barbiere@ec.europa.eu and claudia.tarricone@ec.europa.eu

11.1 Registration and accommodation

Due to peculiarities of the JRC Ispra site, all participants must register their presence at the PT also with the JRC REM (Register for Events Module) event registration system. The meeting will be inserted into the web application (REM) to be accessed via https://web.jrc.ec.europa.eu/remjrc/screen/meetings the page below will appear.

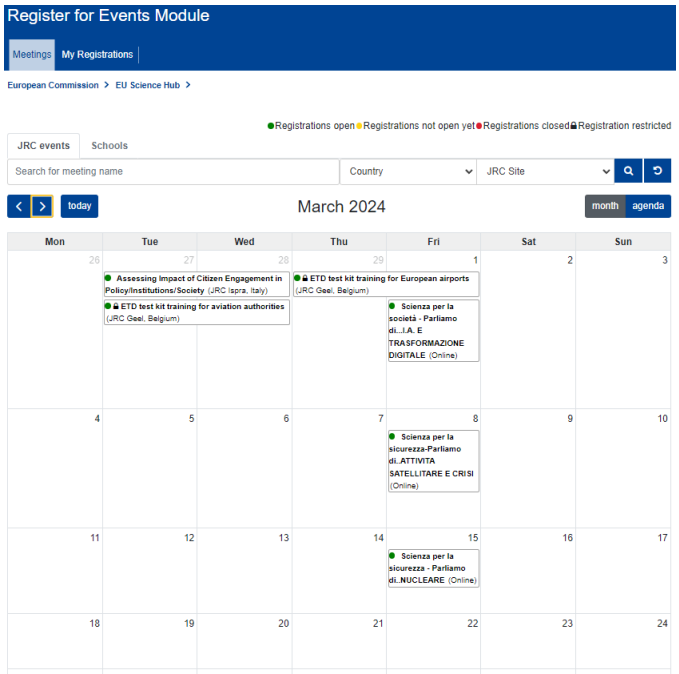


Figure 1: Register Event Module.

It is necessary to create a user account (if it has not been done for a previous visit to the JRC site) and then register for the appropriate meeting called "Proficiency Test SO2/NO/NO2/CO/O3: dd - dd mm YYYY".
The opening and deadline for the registration will be defined.
All non EU participants have to send their passports to the JRC-ERLAP Committee no later than 40 days before the PT.
Each participant (max. 2 people per laboratory) has to register on the website.
The entrance permit to the JRC-Ispra site for the participants will be prepared by JRC-ERLAP team based on identity document details given during the registration on the web. The entrance permit allows visitors to stay in the JRC from 8.00 am till 7.00 pm, but arrival and departure needs to be agreed with JRC-ERLAP team before.

It is not foreseen any reimbursement for travel expenses (flights, hotels, etc.) for participants or shipment costs for equipment.

11.2 How to reach Ispra

The closest and most convenient airport to Ispra is Milan Malpensa (MXP). By car, the closest motorway exit is Sesto Calende or Castelletto Ticino and then follow direction for Ispra-Euratom.

11.3 Accommodation

Due to limited hotel resources in the area, JRC-ERLAP usually pre-books the hotel. When registering the participation through the JRC web application REM, it is important to select the 'accommodation' check box, fill in the details and JRC-ERLAP will handle the booking (the PT participant has to pay for the accommodation at the hotel).
In case the PT participants prefer to have a different accommodation it can be organized personally, but it is kindly requested to fill in the online registration form accordingly.

11.4 Custom issues

All the equipment used during the PT has to go through the custom's control of the JRC.
Shipment: Equipment must be labeled with the address of the proficiency provider (see par. 11). When the equipment arrives at the customs office in Ispra from an EU–member state, a delivery note (list of goods) and a pro-forma invoice (value of goods) must be provided with the equipment and a note "MATERIAL FOR TEST" must be included in all documents.
Equipment arriving from outside the EU need a Carnet ATA to pass the custom.
When the equipment is shipped, please inform the reference persons of the PT in Ispra (**Maurizio Barbiere** and **Claudia Tarricone).**
JRC-ERLAP team is not responsible for any damage that happens to the equipment so it is suggested a particular care during the packing of the instruments. If any evident damage to the equipment package is noticed after the delivery to the JRC, the participant is informed by the JRC-ERLAP team. Inside the JRC the equipment is transported with suitable vehicles to the laboratory in Building 100. Any damage happened during the internal transport is covered by the JRC insurance. The package is only opened by the owner, JRC-ERLAP team is not allowed to check inside the pack.

Own transport: upon arrival, the participant has to go through the Customs entrance of the JRC (Opening hours Mon-Thu: 08:30 - 11:45 and 13:30 - 17:00, Fri: 08:30 – 11:45 and 13:30 – 15:45), which is about 500 m to the West of the main entrance.
For both (Shipment and Own transport) the list of goods and the pro-forma invoice must be prepared in advance, including a note "MATERIAL FOR TEST" that will be checked by the custom office.

Example:
-1 NO_x analyser
-1 SO_2 analyser
-1 CO analyser
-3 gas cylinders
-1 Notebook
Estimated value: 50.000 Euro

From the customs the participants can drive directly to the JRC-ERLAP laboratory in building 100. The papers received from customs (FATTURA PROFORMA) need to be kept for taking the equipment out of the JRC on the last day.
At the end of the exercise, before leaving, every participant who is shipping the equipment, has to pack and label them, indicating the destination and reference name, their equipment as requested by the delivery company.
The delivery company outside the JRC is chosen, contacted, and paid by the participant. The pick-up from our customs office has to be booked by the participants and the JRC-ERLAP team has to be informed 2 working days in advance and 5 working days for delivery with carnet ATA.

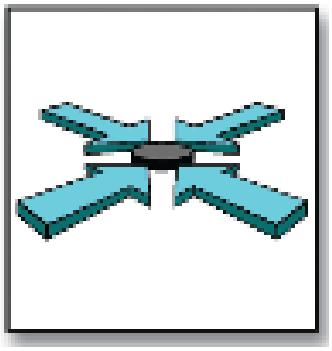
11.5 Safety

JRC Ispra Site has one emergency number: **+39 0332 78 9999**. We strongly recommend you to memorize the number on your mobile at the very beginning of the list, in order to have it when needed. It is for both medical and non-medical emergencies.
We would invite you not to walk around if you are not accompanied by JRC-ERLAP staff. It is forbidden.
At JRC Ispra premises, Italian legislation for Safety at Work (D.lgs. 81/2008) is implemented. Be sure you wear adequate work safety equipment, like work gloves and safety shoes.
Pay attention to signs:

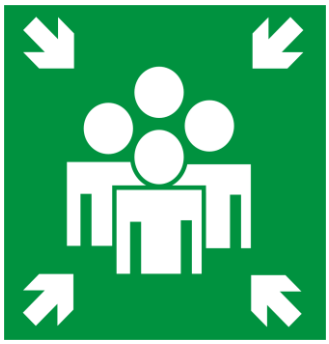
- any circular plate, with a red diameter, indicates a forbidden action
- any plate with blue background indicates a recommendation.

A fire extinguisher is placed at the entrance of the PT area.

We would invite you to respect JRC colleague's indications regarding safety and installation timing, to avoid too many people on place.
Below are shown the two meeting points (Figure 2: Emergency signs) in case of emergency. For **nuclear emergency** a **double siren tone** will be heard and everybody must go to the internal assembly point. In case of **non-nuclear emergency** the alarm will be **a single tone** sound and everybody is requested to go outside and stay close to the external assembly point.



- Posto di Raduno
- Internal assembly point
- In case of nuclear emergency
- (Double tone siren)



- Punto di Raccolta
- External assembly point
- In case of non-nuclear emergency
- (Single tone siren)

Figure 2: Emergency signs

11.6 During the PT

In the pictures below the facility available during an PT is illustrated.

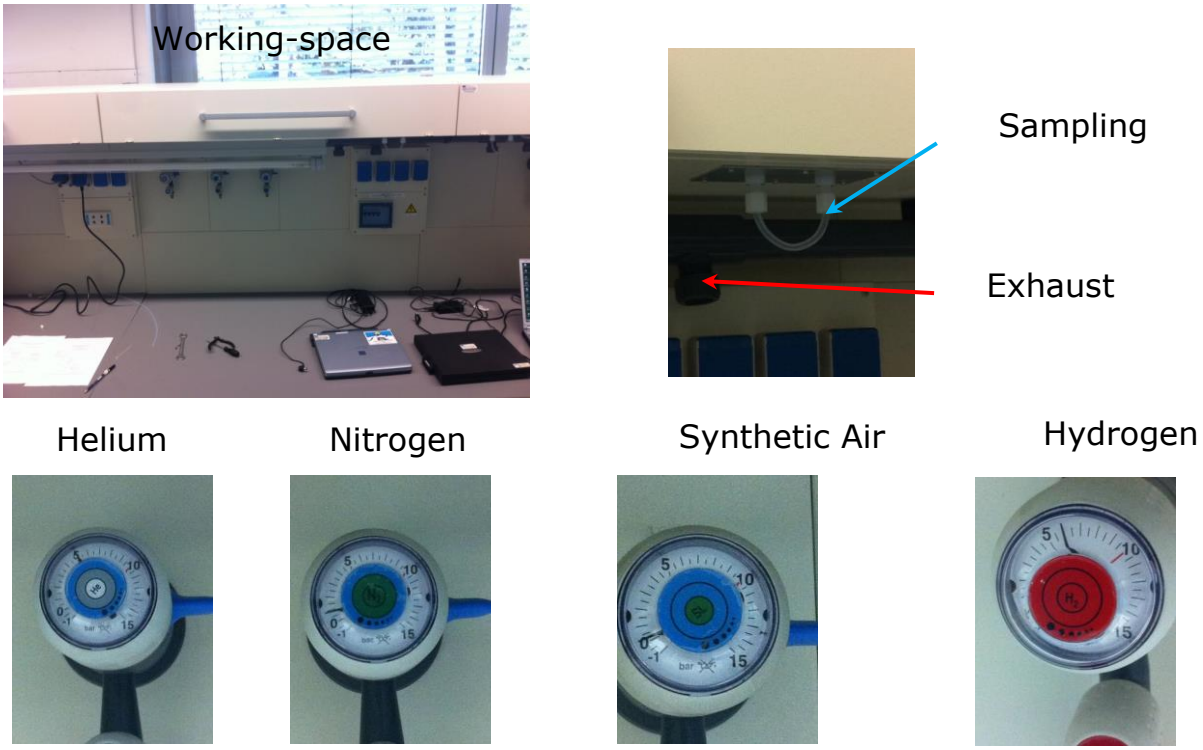


Figure 3: JRC-ERLAP laboratory facility for the PT.

Every participant will have a working area where the instrumentation can be installed. Electrical plugs and gas supply are available as well. As shown in Figure 3 there is a sampling line (white tube) to connect to the instrument for measurement during the PT.
The dark gray pipe is to connect the exhaust gas of the instrument. The sampling line must be closed when it is not used.
Time, temperature and line-voltage will be registered during the PT with proper devices. All data recorded are available on request to the participants of the PT.

12 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) ISO 17043:2023, Conformity assessment - General requirements for proficiency testing
3) ISO/IEC 17025:2017, General requirements for the competence of testing and calibration laboratories.
4) AQUILA protocol N 37: Organization of Inter-Comparison Exercises for gaseous air pollution for EU National Air Quality Reference Laboratories and Laboratories of the WHO EURO Region
5) ISO 13528: 2015, Statistical Methods for use in Proficiency Testing by Inter-Laboratory Comparisons
6) ISO 5725-2:1994, 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.

The following form has to be filled in and returned to a member of the PT provider before the end of the exercise.

ANNEX 1: FEEDBACK/APPEAL/COMPLAINT FORM

During an PT any concern, suggestions or errors should immediately be communicated to a member of JRC-ERLAP team. This form can be delivered as soon as possible to one of JRC-ERLAP team.

□ I have read the protocol. Signature

Participant and laboratory name: _____

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General Feedback				
Comments about the PT: **before** the event				
Comments about the PT: **during** the event				
Comments about the PT: **after** the event				
	Below expectations	Met expectations	Above expectations	N/A
General evaluation	□	□	□	□
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: