ORGANISATION OF INTERCOMPARISON EXERCISES FOR GASEOUS AIR POLLUTION FOR EU NATIONAL AIR QUALITY REFERENCE LABORATORIES AND LABORATORIES OF THE WHO EURO REGION.

1 General

1.1 Background and objectives

The European Commission's Joint Research Centre in Ispra, European Reference Laboratory for Air Pollution (ERLAP) has been organising intercomparison exercises (IEs) for European National Air Quality Reference Laboratories (NRLs) since the early '90s. The first of these IEs were dedicated to single pollutants, but for some years several pollutants have been tested during each exercise. These IEs are organised with a view to harmonizing European air quality measurements and for checking the status of the implementation of Air Quality directives by the responsible bodies in the EU Member States.

The World Health Organization (WHO) is carrying out similar activities, but with a view to obtaining harmonised air quality data for health related studies, and integrating their programme within the WHO EURO Region, which includes public health institutes and other national institutes - especially from the Central Eastern Europe, Caucasus and countries from Central Asia.

This document discusses bringing together the efforts of both these organisations, and coordinating their activities as far as possible, in order to optimize resources to reach greater international harmonisation.

The intercomparison exercises will thus have two purposes:

1) Quality control of air pollution measurements of the EU NRLs.
2) Harmonisation of Air Quality (AQ) measurements made by public health and environmental institutes in the WHO EURO Region.

The NRLs, representing the EU Member States, are required to participate in the IEs. These IEs are carried out in order to compare calibration standards and measurement capabilities, and to facilitate exchange of technical information amongst the national experts. The basis for the organization of these IEs is laid down in the FWD 96/62/EC, in which Article 1 mentions the assessment of air quality on the basis of common methods and criteria, Article 3 mentions the Community wide quality assurance programmes organized by the EC, and Article 4 specifies criteria for reference measurement and sampling techniques.

In case of the WHO, laboratories in Member States of the WHO EURO Region are invited to participate by the WHO Collaborating Centre for Air Quality Management and Air Pollution Control, Berlin (WHO CC). In some cases these laboratories will also be NRLs.

The objectives of this initiative are to merge these activities and therefore to:

- prevent duplication of participation,
- optimize the value of the IEs to the participants,
- ensure the comparability and accuracy of results obtained beyond the current EU borders and
- optimize the technical capabilities of the participating laboratories.

1.2 IE procedure

These IEs are carried out according to the principles of ISO Guide 43-1[1] (1997).

1.3 Organiser and participants

The IEs are organized by the European Commission's, DG JRC, European Reference Laboratory for Air Pollution (ERLAP), in collaboration with the WHO European Centre for Environment and Health (WHO/ECEH, Bonn Office) and WHO CC.

2 Reference documents

Registration form
Questionnaire
Reporting form
Complaint form (LAB-REC-0310)

3 Frequency, place, time

The IEs are usually organised twice a year. All NRLs are required to participate at least once every three years. The same is recommended for the other laboratories.

The duration of an IE is about 3 days. However, additional time is needed for installation, warming up and dismantling of the equipment.

Three IE facilities are currently available:

1) ERLAP
Joint Research Centre – IES, T.P. 441, I – 21020 Ispra (VA)
Contacts: Annette Borowiak (annette.borowiak@jrc.it)
Friedrich Lagler (friedrich.lagler@jrc.it)

2) LANUV NRW, Wallneyer Str 6, D – 45133 Essen
Contacts: Ulrich Pfeffer (ulrich.pfeffer@lanuv.nrw.de)

3) UBA, Paul-Ehrlich Str 29, D – 63225 Langen
Contacts: Volker Stummer (volker.stummer@uba.de)
Hans-Guido Muecke (hans-guido.muecke@uba.de)

[1] *ISO/IEC Guide 43-1:1997, Proficiency testing by interlaboratory comparisons - Part 1: Development and operation of proficiency testing schemes, ISO, Geneva, Switzerland.*

4 Invitation, measurements, communication, reporting and deadlines

An IE will be announced 6 months in advance to the AQUILA group and WHO CC representative. The JRC will invite the NRLs, and the WHO CC will invite the other laboratories. The compounds to be measured and their rough concentration levels will be communicated in this announcement. The laboratories must confirm their interest in participating within 6 weeks of this announcement. A selection process may then be required - depending on the number of applicants. A formal invitation with technical details will then be sent to the participating laboratories at the latest 2 months in advance of the exercise.

Indicative time table

1. JRC & WHO CC: Announcement of IE (6 months before IE)
2. NRLs and WHO contacts: Expression of interest (4,5 months before IE)
3. JRC & WHO CC: Formal invitation to selected laboratories with registration form for the actual participants (4 months before IE)
4. Participants: Registration (3 months before IE)
5. JRC & WHO CC: Formal invitation to participants with technical details (2 months before IE)
6. Intercomparison exercise
7. Participating laboratories**:** Deadline for reporting results and questionnaires to JRC (0,5 month after IE)
8. JRC: Contacting laboratories which results were identified as statistical outliers (1,5 months after IE)
9. Outlying laboratories: Return explanation and any potential corrected results (2 months after IE)
10. JRC**:** Deadline for distributing draft report to participating laboratories, corrections by participants are no more allowed. No anonymous treatment is foreseen. (4,5 months after IE)
11. Participating laboratories**:** Deadline for commenting on the draft report. Reasonable comments can be included in the final report (5 months after IE)
12. JRC**:** Deadline for issuing the final report of IE and distribution of pdf copy to participants , Directorate General Environment and WHO/ECEH (6 months after IE)

5 Measurements

The measurement methods to be used by the NRLs are those specified as reference methods in the AQ Directives (or in alternative the ones that have formally been recognized as equivalent). For the other laboratories, national measurement methods may be used, but reference methods are recommended.

The participants must bring their own complete measuring equipment that is needed for the analysis and data acquisition of the test gases, including, where possible calibration facilities.

5.1 Generation of test gases

It is possible that not all the compounds listed below will be tested at each IE.

At least three concentration steps will be generated per compound.

The following table indicates the concentration ranges of interest for the intercomparison exercise (chosen as 75 % of the measurement ranges defined in the EN standards[2]):

Compound	SO_2	NO	NO_2	CO	O_3	Benzene
Conc. min	0 µg/m^3	0 µg/m^3	0 µg/m^3	0 mg/m^3	0 µg/m^3	0 µg/m^3
Conc. max	750 µg/m^3	900 µg/m^3	375 µg/m^3	75 mg/m^3	400 µg/m^3	50 µg/m^3

Each concentration level will be normally generated for a minimum of 2 hours. Shorter durations may apply for particular studies. During an IE, the organiser may also introduce interferences into the test gas, i.e. to check for compliance of equipment according to the EN standards. Other tests regarding certain performance characteristics may also be performed during the IE. These possible tests will be detailed into the invitation to participate to IEs.

5.2 Reporting of the measurement results

Each participating laboratory is required to deliver three 30-minute averaged values (in nmol/mol for NO, NO_2, NOx, SO_2, O_3 and benzene while in µmol/mol for CO) and their associated uncertainty (obligatory for NRLs and recommended for others) for each compound and concentration.

Each participating laboratory is also required to complete the questionnaire inquiring on traceability, implemented practice concerning calibrations, measurements and uncertainty evaluation. Further reporting requirements may be sent with the invitation.

6 Evaluation scheme

6.1 General

The evaluation of the results of the IE will be carried out according to the ISO Guide 43-1 and ISO 13528. Proficiency of participating laboratories will be evaluated by two methods:

1. The z'-score method[3] will be used to demonstrate the capacity of NRLs to comply with the uncertainty requirements for calibration gases stated in the relevant EN standards (which are consistent with the data quality objective DQO of the European Directives). Other criteria may apply to laboratories other than NRLs. The z'-score will be evaluated for all participants of the IE and for all runs having a reference value. For example the interference tests (see hereafter) may

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[2] *EN 14212 (2005), Standard method for the measurement of the concentration of sulphur dioxide by ultraviolet fluorescence*
EN 14211 (2005) Standard method for the measurement of the concentration of nitrogen dioxide and nitrogen monoxide by chemiluminescence
EN 14625 Standard method for the measurement of the concentration of ozone by ultraviolet photometry
EN 14626 Standard method for the measurement of the concentration of carbon monoxide by nondispersive infrared spectroscopy
EN 14662-3 (2005) Ambient air quality - Standard method for measurement of benzene concentrations - Part 3: Automated pumped sampling with in situ gas chromatography;

[3] *ISO 13528 (2005) Statistical methods for use in proficiency testing by interlaboratory comparisons. ISO, Geneva, Switzerland.*

not have reference values and therefore cannot be treated using the z'-score method.

2. The En-number method[1,3] will be used to demonstrate that the difference between participating laboratories' results and assigned values remains within participating laboratories' claimed uncertainties and the uncertainty of assigned values. The En-numbers are calculated for all participants reporting uncertainty of measurements, this latter parameter being mandatory for NRLs.

Beside proficiency of participating laboratories also repeatability and reproducibility of standardized measurement methods will be evaluated according to ISO 5725-2[4]. This group evaluation will be used as an indicator of the trend of the quality of measurements from one IE to other ones (ISO 13528 § 6.7).

In some IEs, tests of interference on the response of analysers will be performed. The reporting of results of these tests is only informative and is not foreseen is this document.

6.2 Assigned values for proficiency evaluation

Generally the measurements of ERLAP will be used as assigned values (X) of IEs. The assigned values of tested concentration levels will be derived from a calibration against the certified reference values of the CRMs (ISO 13528 §. 5.4) and will be confirmed by comparison to robust averages (ISO 13528 § 5.7). If ERLAP measurements fail to pass this conformation test or if the IE will take place far from Ispra and ERLAP will not be able to implement its optimum measurement capability, the assigned values will be calculated as the robust averages (ISO 13528 § 5.5) from a subset of expert NRLs. As expert NRLs will be regarded laboratories that participate to BIPM CCQM GAWG key comparisons and/or are accredited with appropriately small uncertainty. For each IE the list of participating expert NRLs will be given in step 5 of indicative time table (§ 4).

The uncertainty of the assigned value will be calculated as combined uncertainty of the ERLAP measurement uncertainty and the possible lack of homogeneity among the different position on the testing bench. However, if the assigned value is calculated according to (ISO 13528 § 5.5) instead of using ERLAP's value then the uncertainty will be calculated with the equation 1 (ISO 13528 § 5.5.2):

$$u_X = \frac{1.25}{p}\sqrt{\sum u_i^2} \qquad (1)$$

where p is the number of expert NRLs and u_i are their standard uncertainties.

The calculation of the assigned value and its uncertainty will be documented and made available in an annex to the report of the IE.

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[4] *ISO 5725:1994, 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, ISO, Geneva, Switzerland*

6.3 z'-score

The z'-score will be calculated as follows:

$$z' = \frac{x_i - X}{\sqrt{\sigma_p^2 + u_X^2}} \quad (2)$$

where x_i is a participant's value, X is the "assigned value", σ_p is the fitness-for-purpose-based "standard deviation for proficiency assessment" and u_X is the standard uncertainty of the assigned value.

In the NO_2, SO_2, CO and O_3 EN Standards the uncertainties for calibration gases used in ongoing quality control are prescribed. In fact, it is stated that maximum permitted expanded uncertainty for calibration gases at the calibration point (75% of calibration range) is 5% and that 'zero gas' shall not give instrument reading higher than the detection limit. However no criteria for detection limits are prescribed. The 'standard deviation for proficiency assessment' (σ_p) [3] is derived in a fitness-for-purpose manner from requirements given in the EN standards, where in place of detection limits criteria the specifications for purity of zero gas used in type approval as defined in EN Standards are taken. This general reference to the EN standards can not be made for benzene, where measurement method used by NRLs for verification purposes can differ from the method used at IE. Therefore for benzene σ_p is set to 6% at the calibration point.

Over the whole measurement range, σ_p is calculated by linear interpolation between the value at the calibration point and zero. The linear function parameters (a,b) of σ_p are given in Table 1. Figures 1 to 6 give the absolute and relative values of σ_p over the concentration range for each compound.

	σ_p (zero)	σ_p (calibration point)	$\sigma p_{nmol/mol} = a \cdot [\text{Assigned value}]_{nmol/mol} + b$	
			a	b
	nmol/mol	nmol/mol		nmol/mol
SO_2	1	7.1	0.022	1
CO	100	1613	0.024	100
O_3	1	4.7	0.020	1
NO	1	18.0	0.024	1
NO_2	1	4.9	0.020	1
Benzene	0.04	0.7	0.057	0.04

Table 1 : Standard deviation for proficiency assessment σ_p.

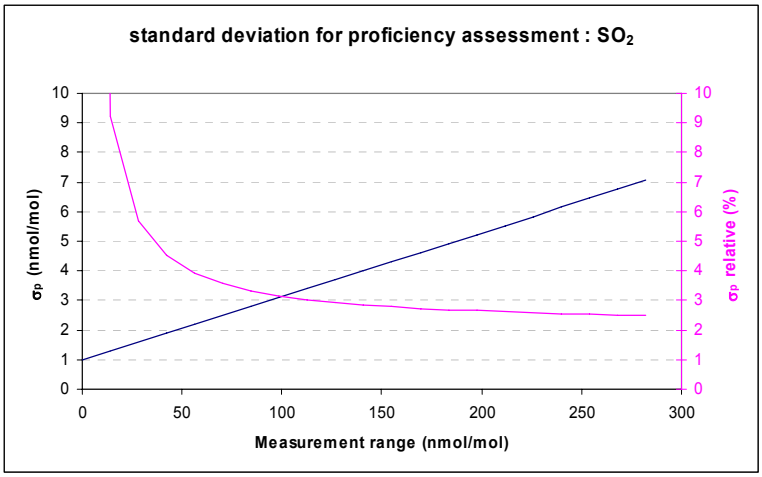

Figure 1 Absolute and relative representation of SO_2 σ_p over the IE testing range.

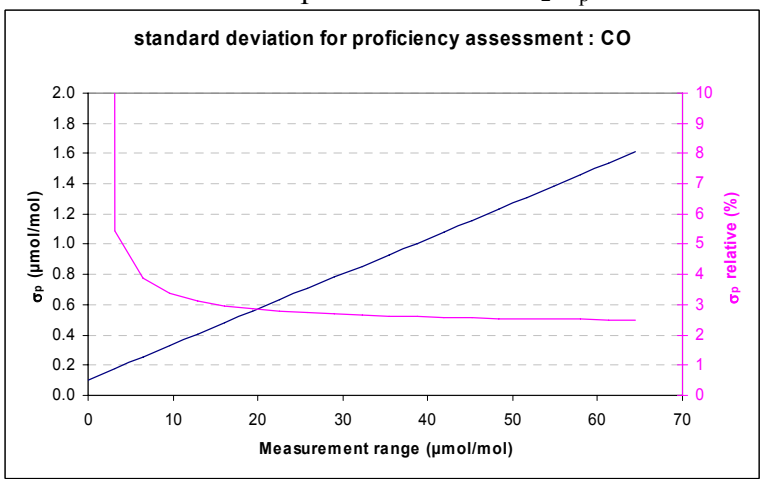

Figure 2 Absolute and relative representation of CO σ_p over the IE testing range.

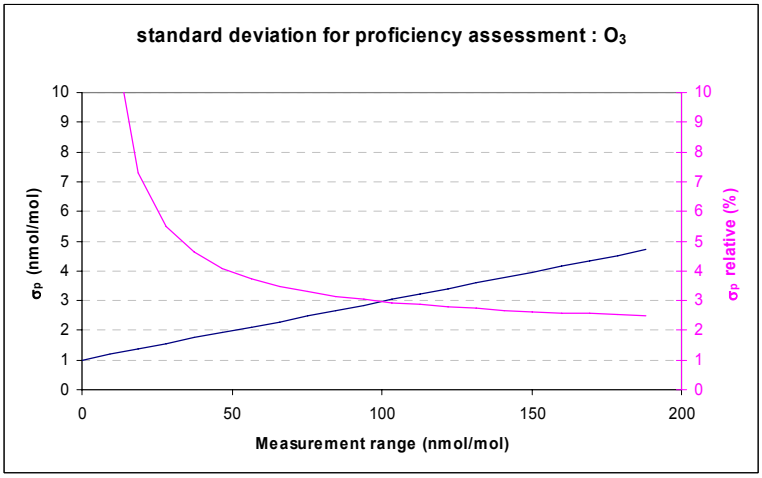

Figure 3 Absolute and relative representation of O_3 σ_p over the IE testing range.

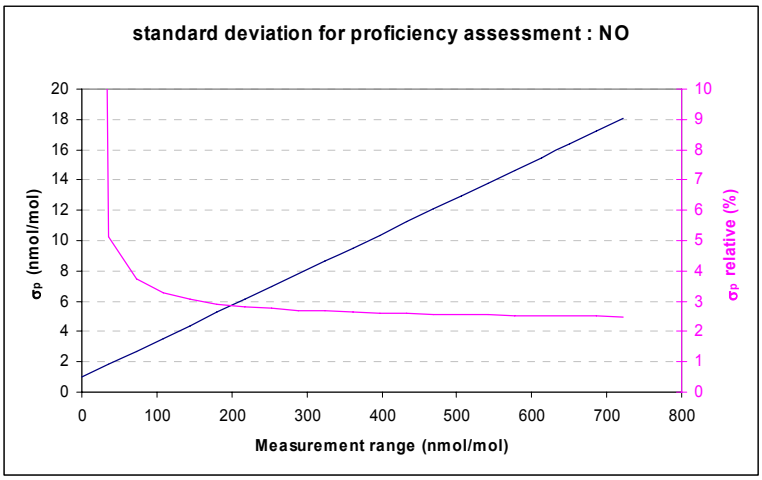

Figure 4 Absolute and relative representation of NO σ_p over the IE testing range.

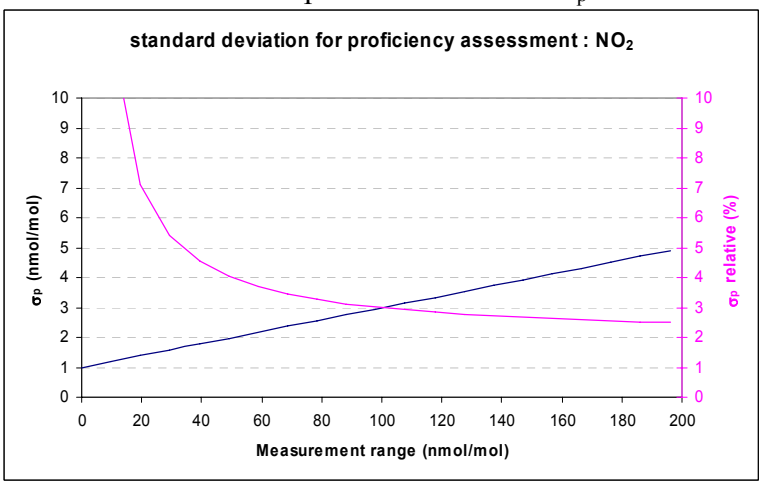

Figure 5 Absolute and relative representation of NO_2 σ_p over the IE testing range.

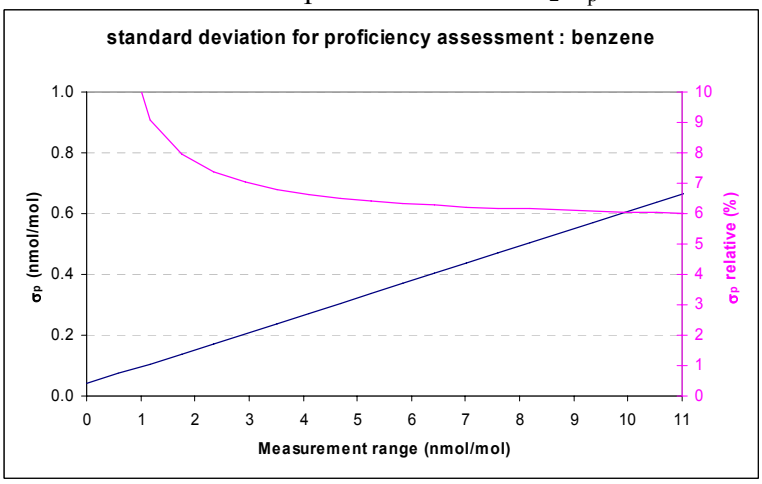

Figure 6 Absolute and relative representation of benzene σ_p over the IE testing range.

6.4 En-number

The normalized deviations, according to ISO Guide 43-1 (ISO, 1997), will be used to evaluate whether the differences between the results of laboratories that reported expanded measurement uncertainty together with their measurement results and the IE reference value remained within the stated uncertainties. The normalised deviations are calculated using the following equation:

$$E_n = \frac{x_i - X}{\sqrt{U_x^2 + U_X^2}} \quad (3)$$

where: x_i is the results of a participating laboratory with stated expanded uncertainty U_x while X is the assigned value with expanded uncertainty U_X, determined according to 4.1. E_n values will be presented by plotting $(x - X) \pm (U_x^2 + U_X^2)^{1/2}$ for each concentration level.

6.5 Group evaluation/evaluation of precision of standardized measurement method

The procedure laid down in ISO 5725-2 will be implemented in order to evaluate the repeatability and reproducibility of the measurement methods. Data consistency and outlier tests will be performed and relationship between r and R and the concentration levels of the IE test will be investigated.

7 Assessment

The z'-score evaluation allows the following criteria to be used for the assessment of the results:

- $-2 \leq z' \leq 2$ are designated satisfactory. Approximately 95 % of z-scores should fall between –2 and +2.
- $-3 \leq z' < -2$ or $2 < z' \leq 3$ are designated questionable. They are expected about 1 time out of 20.
- $z' < -3$ or $z' > 3$ are designated unsatisfactory. Scores falling in this range are very unusual and are taken to indicate that the cause of the event should be investigated and remedied.

The En evaluation allows evaluating whether the differences between participating NRLs and the assigned value would remain within the assigned uncertainty and NRL uncertainty provided that $-1 \leq En \leq 1$. In bar plot representation all results that touch or cross x-axis are satisfactory.

Further details concerning the standard deviation of the repeated measurements at the same concentration will be given as additional information to each participant.

8 Measures

The IEs are organized in order to provide the NRLs with the possibility of comparing their results and test their proficiency. As the quality of the NRLs measurement is connected to the data quality of the Member State, the European Commission requires satisfactory results within the data quality objectives to be obtained. In the case of NRLs overall unsatisfactory results of z'-score evaluation (one unsatisfactory or two questionable results per parameter (ISO 13528 § 7.4.2)) the EC requires to repeat participation to the next IE in order to demonstrate remediation measures. In case of failing participation to the IEs for more than 3 consecutive years, the JRC will inform DG-Env.

9 Complaints

Should be sent in writing to the organiser of the IE within 5 months of its completion (annette.borowiak@jrc.it or friedrich.lagler@jrc.it).

10 Costs

The costs of participation by the NRLs in the IEs will be covered by the NRLs themselves. Other laboratories may apply to the WHO CC or the JRC for financial assistance.