# INTER-LABORATORY COMPARISONS
## YEAR *2024*

## "Workplace exposures to chemical agents"

# Inorganic acids, aldehydes, ammonia, BTEX, mercury, metals, and methanol

*MIV – 227297 - 2788504 - v1.0*

*10/01/2024*

*Organizer: Ineris – Environmental Characterisation and Impacts on Human and Biodiversity Department*


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## 1. CONTEXT

Ineris organizes an Inter-Laboratory Comparison relating to the analysis of some parameters in workplace atmosphere. This Inter-Laboratory Comparison allows accredited laboratories to meet the requirement to monitor their proficiency.

Participation in Inter-Laboratory Comparisons is indeed an essential tool for analytical methods implementation monitoring. It is the subject of accreditation requirement and it leads to checks of the proper fulfillment in audit.

This document gathers all the necessary information for an Inter-Laboratory Comparison (ILC) registration.

It contains :

- The terms of participation;
- The description of the Inter-Laboratory Comparison.

## 2. OBJECTIVE

An Inter-Laboratory Comparison participation enables laboratory:

- to compare its results with those of other laboratories carrying out same type of analysis;
- to assess skills of the operators in a given technique;
- to evaluate a quantification method in a given matrix;
- to meet the requirements of quality references;
- to improve its measurement quality;
- to demonstrate its measurement proficiency in a given environment in order to meet the regulatory requirements to obtain, for an example, an approval or an accreditation.

The achievement of these objectives is evaluated with a performance score (z-score or z'-score) enabling participants to estimate the closeness of their results from an assigned value known as reference value, calculated by proven statistical algorithms.

## 3. DESCRIPTION OF THE PROGRAM

The purpose of the program is to implement and to carry out **two** Inter-Laboratory Comparisons campaigns, scheduled for **March** and for **September**, dealing with the analysis of the following parameters:

- ✓ Inorganic acids (HF, HBr, HCl, $HNO_3$, $H_2SO_4$, $H_3PO_4$),
- ✓ Aldehydes (formaldehyde, acetaldehyde),
- ✓ BTEX (benzene, toluene, ethylbenzene, xylenes),
- ✓ Metals (Cd, Cr, Cu, Ni, Pb).

For the following parameters, **only one** campaign is scheduled:

- ✓ Ammonia ($NH_3$) in September 2024,
- ✓ Mercury (Hg) in September 2024,
- ✓ Methanol (MeOH) in September 2024.

***A test may be deferred or canceled if the number of participants for a program is less than 10.***

### 3.1. INORGANIC ACIDS

The samples shall consist of membranes impregnated with sodium carbonate and spiked with fluoride, chloride, bromide, nitrate, phosphate and sulphate. The spiking shall be carried out by depositing a solution with known levels.

Only the soluble fraction of fluoride will be studied.

Only one concentration will be studied.

Two blank filters will be provided.

### 3.2. ALDEHYDES

The samples shall consist of silica gel tubes impregnated with 2,4-DNPH (S10 Supelco type) and then spiked with formaldehyde and acetaldehyde. The spiking shall be carried out by adding solutions with known levels.
These tubes shall be analyzed within 8 days of the date of preparation of these test materials.

Only one concentration will be studied.

A blank tube will be provided.

### 3.3. AMMONIA

The samples shall consist of membranes impregnated with sulfuric acid and spiked with ammonium. The spiking shall be carried out by depositing a solution with known levels.

Only the soluble fraction will be studied.

Only one concentration will be studied.

One blank filter will be provided.

### 3.4. BTEX

The samples shall consist of dual-zone activated carbon tubes spiked with benzene, toluene, ethylbenzene and xylenes. The spiking shall be carried out by adding a solution with known contents.
These tubes shall be analyzed within 14 days of the date of preparation of these test materials.

Only one concentration will be studied.

A blank tube will be provided.

### 3.5. MERCURY

The samples shall consist of mercury-spiked hopcalite tubes. The spiking shall be carried out by adding a solution with a known content.
They shall be analyzed until 10 days from the date of preparation of these media.

Only one concentration will be studied.

A blank tube will be provided.

### 3.6. METALS

The samples shall consist of quartz fiber membranes spiked with cadmium, chromium, copper, nickel and lead. The spiking shall be carried out by depositing a solution with known levels.

Only one concentration will be studied.

Two blank filters will be provided.

### 3.7. METHANOL

The samples shall consist of silica gel tubes impregnated and then spiked with methanol. The spiking shall be carried out by adding solutions with known levels.
They shall be analyzed until 8 days from the date of preparation of these media.

Only one concentration will be studied.

A blank tube will be provided.

## 4. LABORATORIES CONCERNED

This Inter-Laboratory Comparison is specially designed for all laboratories undertaking analysis of samples derived from workplace air monitoring. Laboratories carrying out analyses in the field of indoor air on supports obtained by passive sampling may also participate.

# 5. GENERAL TECHNICAL REQUIREMENTS

## 5.1. REGISTRATION

Period for registration is set to:

**10 January 2024** to **23 February 2024**

by going to the website:

https://comparaisons-interlaboratoires.ineris.fr

For the **first connection**, the laboratory shall create his account for accessing to website utilities. For that, laboratory shall have the information below:

- Enterprise identification (SIRET, DUNS,…),
- VAT Intracommunity number (Europe only).

After validation of the account by Ineris, the laboratory will then be able to register to the proposed interlaboratory comparisons.

Online help is available on the website.

If the laboratory **account already exists**, the laboratory can go directly to the registration step described below.

During the **registration phase**, the laboratory shall have the information below:

- Enterprise identification (SIRET, DUNS,…),
- An **order.**

**Please note**: The BIPEA quote and the form available on the website are not accepted as valid orders.

A confirmation will be sent to the participant 15 days after the end of registration with his lab identification.

## 5.2. PRICE

| FEE SCHEDULE | | | |
|---|---|---|---|
| | **Amount in € before tax** | **20% VAT** | **Total amount in €, tax included** |
| **24-227297_Acids**** | 747.00 € | 149.40 € | 896.40 € |
| **24-227297_Aldehydes**** | 986.00 € | 197.20 € | 1183.20 € |
| **24-227297_$NH_3$*** | 344.00 € | 68.80 € | 412.80 € |
| **24-227297_BTEX**** | 843.00 € | 168.60 € | 1011.60 € |
| **24-227297_Hg*** | 344.00 € | 68.80 € | 412.80 € |
| **24-227297_Metals**** | 705.00 € | 141.00 € | 846.00 € |
| **24-227297_Methanol*** | 510.00 € | 102.00 € | 612.00 € |
| *** : 1 campaign ; ** : 2 campaigns<br>Prices are indivisible** | | | |

## PAYMENT CONDITIONS

Invoice is established **when sending samples from the second campaign**.

Payment by credit card is not accepted.

## 5.3. COMMITMENTS OF INERIS

Ineris undertakes to comply with standard ISO/CEI 17043 in the organization of its Inter-Laboratory Comparisons.

Ineris undertakes to ensure the confidentiality of information when returning the results online, and anonymity when sending the report by assigning a confidential code to each participant.

Ineris undertakes to preserve the confidentiality of the identity of each participant by limiting the access of the confidential code to a restricted number of persons collaborating in the coordination of the tests.

Ineris undertakes to promptly notify participants of any changes in the design or operation of the proficiency testing program.

Ineris undertakes to examine all claims and to take action if necessary. Claims must be submitted in writing to the attention of the coordinator.

## 5.4. COMMITMENTS OF THE PARTICIPANTS

At the time of registration, participants agree to:

- complete and return the Acknowledgment of Receipt IM-0223;
- respect, for each parameter, the method specified in Appendix 1 and completed in the instructions form IM-1541;
- return the results in good faith, without falsification or collusion;
  - In case of NO-COMPLIANCE, Ineris reserves the right not to take into account the data of the participant concerned and shall take the appropriate actions.
- submit the results according to the planned schedule, except for equipment failure reported before the deadline for return of the results;
- provide associated metadata as requested.

## 5.5. COMMUNICATIONS

The exchanges between Ineris and the participants will be mainly electronic. Ineris cannot be held responsible for the failure to receive an e-mail. The confidential code shall be quoted in all correspondence with the coordinator.

The documents relating to the test can be downloaded from the site dedicated to ILC Ineris **https://comparaisons-interlaboratoires.ineris.fr**

## 6. ANNEXES

| Annex no. | Title |
|---|---|
| 1 | Description of the program |
| 2 | General organization of an Inter-Laboratory Comparison |
| 3 | Statistical processing and return of the test |

## Annex no. 1: Description of the program

| Test | 24-227297_Acids | | 24-227297_Aldehyde | |
|---|---|---|---|---|
| Substances to be analyzed | HF, HBr, HCl, $HNO_3$, $H_3PO_4$, $H_2SO_4$ | | Acetaldehyde, formaldehyde | |
| Date of receipt | Campaign 1 | Campaign 2 | Campaign 1 | Campaign 2 |
| | Week 11 | Week 38 | Week 11 | Week 38 |
| Analytical methods | Metropol M-144, M-53 or equivalent (NIOSH 7907, 7908 for example) | | Metropol M-4, M-66 or equivalent (NIOSH 2016 for example) | |
| Matrices tested / Sampling medium | $Na_2CO_3$ Impregnated quartz filter | | Tube of 2,4-DNPH impregnated silica gel type SUPELCO S10 | |
| Level of concentration | 5 à 3000 µg | | 1 à 1000 µg | |
| Number of media | 2 + 2 blanks | | 2 + 1 blank | |
| Number of measurements per medium | 1 | | 1 | |
| Stability | Stable compound | | 8 days | |
| Refrigeration | No | | Yes | |
| Statistical processing implemented | Assigned value:<br>Robust average of all the results of the participants by application of algorithm A of standard ISO 13528 | | | |
| | Performance:<br>z-score except for a population < 8 after exclusion of missing or aberrant results => indicative value | | | |
| Monitoring of the homogeneity of test materials | Yes: Ineris | | | |
| Monitoring of the stability of test materials | No | | | |

| Test | 23-215496_BTEX | | 23-215496_Hg |
|---|---|---|---|
| Substances to be analyzed | Benzene, toluene, ethylbenzene, xylenes (m, p and o) | | Hg |
| Date of receipt | Campaign 1 | Campaign 2 | Campaign 2 |
| | Week 11 | Week 38 | Week 38 |
| Analytical methods | Metropol M-188 or equivalent | | Metropol M-114 or equivalent |
| Matrices tested / Sampling medium | Activated charcoal tube | | Hopcalite tube |
| Level of concentration | 10 à 10000 µg | | 0,1 à 20 µg |
| Number of media | 2 + 1 blank | | 2 + 1 blank |
| Number of measurements per medium | 1 | | 1 |
| Stability | 14 days | | 10 days |
| Refrigeration | No | | No |
| Statistical processing implemented | Assigned value:<br>Robust average of all the results of the participants by application of algorithm A of standard ISO 13528 | | |
| | Performance:<br>z-score except for a population < 8 after exclusion of missing or aberrant results => indicative value | | |
| Monitoring of the homogeneity of test materials | Yes: Ineris | | |
| Monitoring of the stability of test materials | No | | |

| Test | 24-227297_metals | | 24-227297_methanol |
|---|---|---|---|
| Substances to be analyzed | Cd, Cr, Cu, Ni, Pb | | MeOH |
| Date of receipt | Campaign 1 | Campaign 2 | Campaign 2 |
| | Week 11 | Week 38 | Week 38 |
| Analytical methods | Metropol M-120, M-121, M-122 or equivalent (NIOSH 7304 for example) | | Metropol M-26 or equivalent (NIOSH 2000 for example) |
| Matrices tested / Sampling medium | Quartz filter | | Silica |
| Level of concentration | 2 à 5000 µg | | 100 à 8000 µg |
| Number of media | 2 + 2 blanks | | 2 + 1 blank |
| Number of measurements per medium | 1 | | 1 |
| Stability | 4 weeks minimum | | 8 days |
| Refrigeration | No | | Yes |
| Statistical processing implemented | Assigned value:<br>Robust average of all the results of the participants by application of algorithm A of standard ISO 13528 | | |
| | Performance:<br>z-score except for a population < 8 after exclusion of missing or aberrant results => indicative value | | |
| Monitoring of the homogeneity of test materials | Yes: Ineris | | |
| Monitoring of the stability of test materials | No | | |

| Test | 23-215496-$NH_3$ |
|---|---|
| Substances to be analyzed | $NH_3$ |
| Date of receipt | Campaign 1 |
| | Week 38 |
| Analytical methods | Metropol M-13 or similar |
| Matrices tested / Sampling medium | $H_2SO_4$ impregnated quartz filter |
| Level of concentration | 200 to 10000 µg |
| Number of media | 2 + 1 blank |
| Number of measurements per medium | 1 |
| Stability | 2 months |
| Refrigeration | No |
| Statistical processing implemented | Assigned value:<br>Robust average of all the results of the participants by application of algorithm A of standard ISO 13528 |
| | Performance:<br>z-score except for a population < 8 after exclusion of missing or aberrant results => indicative value |
| Monitoring of the homogeneity of test materials | Yes: Ineris |
| Monitoring of the stability of test materials | No |

## Annex no. 2: General organization of an Inter-Laboratory Comparison

For each test, the chronology of events will be as follows:

- feasibility study to define the right conditions for the future test, if necessary;
- sampling, possible spiking, packaging;
- shipment (d = 0) of the test materials to the different participants by Ineris; reception by participants (d = +1);
- analysis of the test materials by the participants (d+1 to d+8, d+10, d+14 depending on the parameters); and reporting to Ineris, if relevant, on the homogeneity and stability of the test materials sent;
- entry of the results by the participants on the website https://comparaisons-interlaboratoires.ineris.fr;
- data processing and statistical exploitation by Ineris;
- dissemination of the final report accompanied by the satisfaction survey.

The general organization of the Inter-Laboratory Comparison is as follows:

### 1. Feasibility study of the test

Each test material is subjected to a feasibility study over several weeks. However, if homogeneity and stability have already been the subject of an earlier study on similar test materials (matrix, level of concentration) and prepared according to the same procedures, the feasibility study will not be repeated.

### 2. Announcement of the test

Ineris informs the laboratories of the organization of a test by transmitting the **Annual Program** IM-1540.

### 3. Registration of the participants

Ineris receives the registration requests and confirms the registration of each participant by mail by communicating its laboratory identification.
The **Instructions Form** IM-1541 is communicated to the participants before or/and upon dispatch of the test materials, in order to provide them the instructions to follow (substances to be dosed, preservation means used, type of flask used, etc.) and the deadlines to meet. It may also be posted on the website https://comparaisons-interlaboratoires.ineris.fr

### 4. Preparation of the test materials

The test materials are prepared and packaged by Ineris, in compliance with the requirements of the analysis standards. These requirements relate in particular to the nature of the matrix used, the level of concentration and mainly the preparation of the test materials in order to ensure their quality in terms of stability and homogeneity.

The dispatch of the test materials is carried out in disposable packaging by Ineris.

## 5. Routing of the test materials

The test materials are shipped via express delivery service. The quality of the service is monitored by Ineris.

The following documents will be attached to the test materials:

- **Acknowledgement of Receipt** IM-0223: **upon receipt of the packages**, the participant shall send this document duly completed to Ineris;
- Instructions Form IM-1541.

The test materials will preferably be shipped at the beginning of the week in order to allow the participants to start the analytical process before the end of the week.

Result entry forms are available on the site https://comparaisons-interlaboratoires.ineris.fr.

## 6. Reception and analysis of the test materials by the participant

Upon opening the package, the participant:

- shall perform a temperature check in case of a refrigerated packaging. It shall report the result of its measurement on the Acknowledgment of Receipt IM-0223;
- shall check the condition of the package as well as its composition and record its findings on the Acknowledgment of Receipt IM-0223;
- shall immediately implement appropriate conservation measures;
- shall promptly inform Ineris of the receipt of the packages and their condition by return of the Acknowledgment of Receipt, duly completed, by fax or mail.

The participant shall begin the analytical process by applying the specified methods.

## 7. Monitoring of the test materials by the organizer

Monitoring of the test materials sent will be carried out during the analysis phase by the participants. Ineris shall ensure that the test materials are stable and homogeneous by carrying out tests on several samples during the analysis phase.

Some materials may be exempted from this control if previous data have shown that the preparation procedures allow for sufficient homogeneity and stability.

## 8. Return of test data

The participant has a limited time to conduct analyzes and return its results. This period is usually 3 to 4 weeks.

The results will be transmitted by the participant via the https://comparaisons-interlaboratoires.ineris.fr.site with his personal account.

For some tests, a complementary form may be submitted to the participants. In this case, the entry of the results will be validated only after having completed it.

Assisted data entry is available online to help the participant use this entry software package.

A participant may, for reasons of its own, not perform the analysis of one or more substances. Incomplete analysis reports are accepted.

In all cases, the results not considered in statistical processing are:

- returned values below the limit of quantification*;

- values entered as null "0";
- values for which an error of dilution or return in the imposed unit is highlighted (e.g. a factor of 1000)

*The methodology will be as follows:

**Return of 2 values**

| | Received data | Data taken into account |
|---|---|---|
| **1st case** | C, C | C, C |
| **2nd case** | C, <LQ | Aucune |
| **3rd cas** | <LQ, <LQ | Aucune |

## Annex No. 3: Statistical processing and return of the test

### 1. Statistical processing

Statistical processing of the results shall meet standard NF EN ISO/CEI 17043. It shall be carried out by Ineris in accordance with the requirements of:

- Standards 1, 2 and 5 of the NF ISO 5725 series: "Accuracy (trueness and precision) of the results and methods of measurement,"
- Standard NF ISO 13528 (2015): "Statistical methods for use in proficiency testing by Inter-Laboratory Comparisons,"
- Standard NF X 06-050 "Application of statistics - Study of the normality of a distribution."

The assigned value shall be based on the consensus of the results of the general population participating in the test. It shall be calculated using robust statistical methods.

The benefit of robust analysis is that the calculations of the assigned value (benchmark), confidence intervals, and performance statistics are not affected by the judgment of the data analyst. **The results of the participants are processed impartially and transparently.**

The standard deviation for the evaluation of the chosen proficiency $\sigma_{pt}$ is equal to the robust standard deviation $s^*$. It is determined from the results of the participants by applying Algorithm A of standard NF ISO 13528 (2015). However, if regulatory or normative requirements exist regarding uncertainty, $\sigma_{pt}$ may be set.

The performance evaluation shall be carried out using the z-score. Thus, each participant can position itself in relation to the assigned value.

The search for suspicious values or outliers in the participants' values (even if data processing by application of robust statistics does not require a preliminary identification of the suspicious values by statistical tests) shall be carried out using the Cochran, Grubbs and coherence tests so that the participants and the organizer, in a process of improvement, can take advantage of research into the causes that led to the attainment of these values.

## 2. Return of the test

The return of the test shall be carried out in two stages:

- Submission of a Preliminary Test Report, one month after the closing date for the online data entry for each campaign. This report shall collect the raw results of all participants, the mean, the standard deviation of repeatability, the coefficient of variation of repeatability and the performance of each participant for each parameter and each test material. At this stage, **no detailed analysis of the data is carried out**. This preliminary report will provide participants with a first feedback on the test results.
- Submission of the Final Test Report three months after the end of the second campaign. Said report shall include several types of information and relate to each test material:
  - The raw data,
  - the values deviating from the data set;
  - the mean and standard deviations after statistical processing;
  - the distribution curve for the mean of all participants;
  - a histogram plotting laboratory performance on the same graph;
  - the assessment of zeta score performance (in case of certified materials);
  - Mandel k (intra-laboratory variability) coherence statistics, if relevant;
  - general and individual opinions and interpretations.

The distribution of the Final Test Report will be **restricted**. It will be sent in digital format to the participants.

A satisfaction survey will be sent along with the final test report.