

FRENCH INTERLABORATORY COMPARISONS (ILCs)
Emission measurement of pollutants at chimneys including sampling and analysis

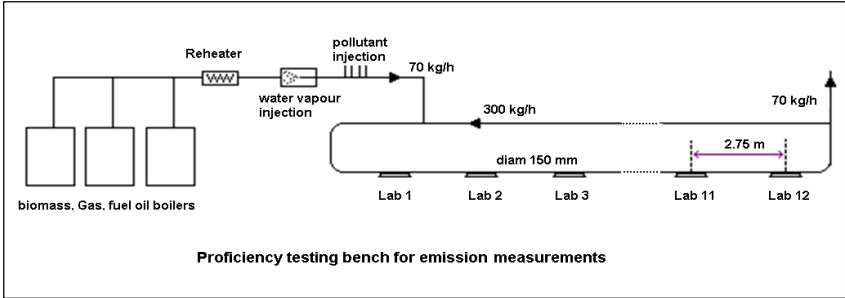
INERIS Test Bench – Design, objectives and results

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A bench which generates real gaseous effluents



Proficiency testing bench for emission measurements

- The bench is designed to deliver gaseous effluents of identical composition at each of the 12 available sampling ports of the testing loop
- Flue gases are generated by domestic combustion facilities fueled with gas, light fuel oil or biomass
- At each trial, concentration of each pollutant in the gas matrix can be increased by the controlled injection of additional gases : CO, NO, SO₂, HCl, CH₄, C₃H₈, etc. or by stripping liquids: specific VOCs. Water vapor content can also be added.
 - possibility to generate a lot of types of combustion or incineration flue gases.

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A bench to simulate real effluents

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A bench which generates real gaseous effluents

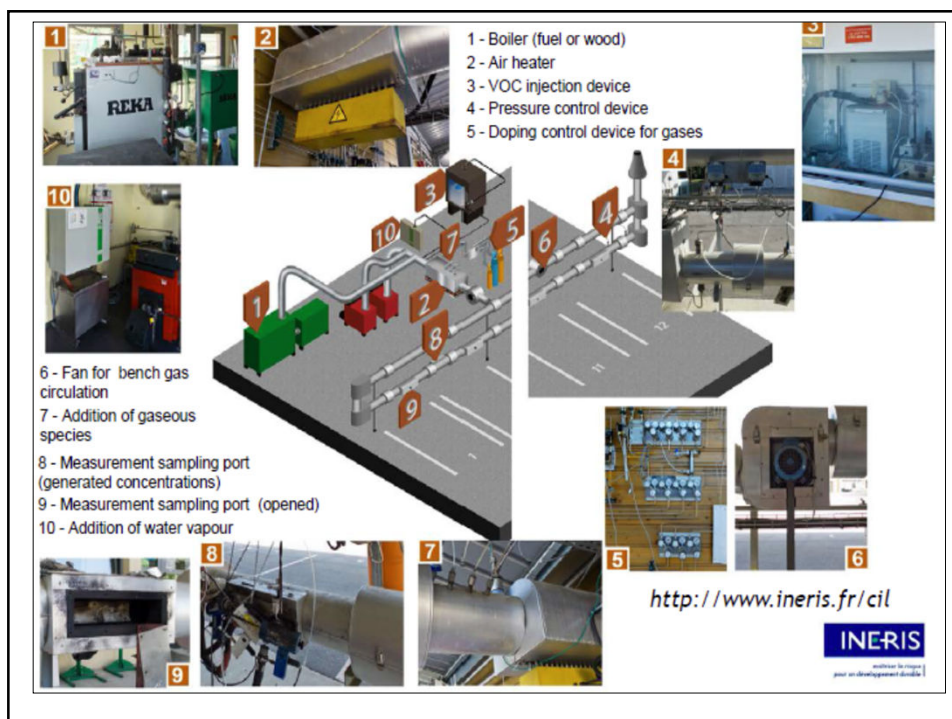
The design of a bench with real gaseous effluents has been preferred to a bench where mixtures of calibration gases in dry, and cold air are generated.

Pros and cons of a bench with real gaseous effluents

	Pros	Cons
Detection of sampling issues	Sampling is the highest contributor to the uncertainty → ILCs highlight temperature issues – deposit / adsorption on materials... ILCs assess that sampling systems are suitable to sample wet, hot and dusty flue gases	
Reference value		Not known exactly → assigned value = robust average value of participants
Estimation of the uncertainty	Realistic estimations of the fidelity of the method Fruitfull tool for the legislator for : <ul style="list-style-type: none"> the interpretation of measurement results (conformity of a plant or a measuring system) and to fix achievable uncertainty requirements in connection with the level of concentration 	

The level of concentration is controlled continuously by a FTIR for gaseous compounds and by a TEOM for dust.

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Objectives

The aim of these interlaboratory comparisons, **for participants** is to confirm :

- the **accuracy of their results compared to the assigned value** (value taken as the "reference");
- the **on-site repeatability** of their measurements by **simultaneous implementation of two measurement equipments**, complying with the standard reference methods (SRMs) applied.

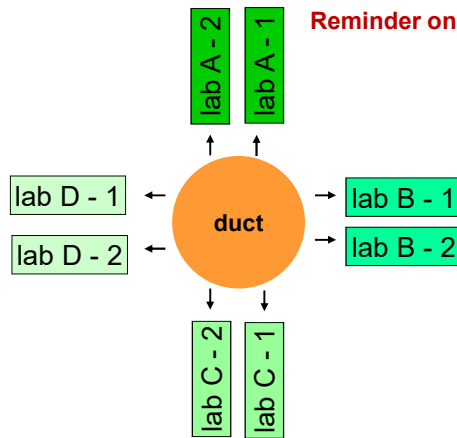
The participation to the INERIS ILCs is useful for laboratories to demonstrate their proficiency with respect to the SRMs' implementation

- recommended for accreditation according to EN 17025,
- compulsory to obtain the « agréments » from the Ministry of Environment to perform regulatory controls in France on classified installations (Rules of participation are described in « decree of 11 March 2010 »)

Objectives

For authorities and for participants, ILCs allow:

- to determine repeatability and reproducibility (quantities to qualify the fidelity of a method according to ISO 5725)



Reminder on the fidelity of a method (ISO 5725)

→ Reproducibility standard deviation

$$s_R = \sqrt{s_F^2 + s_L^2}$$

Interlaboratory variance (pointing to s_F^2)
Variance of repeatability (pointing to s_L^2)

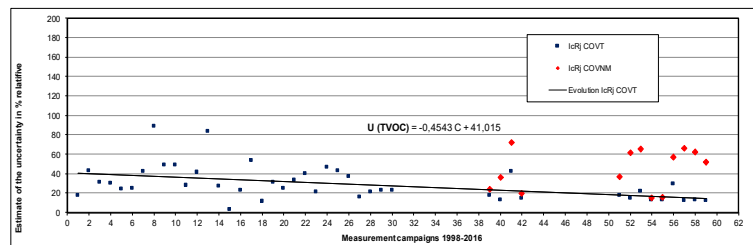
→ Estimation of the uncertainty
 $U = 2 \cdot s_R$

Objectives

For authorities and for INERIS, ILCs allow:

- to track, year after year, the progress of implementation of standardized procedures ⇒ Choice was made to work with real matrices

Evolution of the estimate of uncertainty according to ISO 5725 from 1998 to 2016



Campaign	1	2 à 5	6 à 8	9 à 13	14 à 18	19 à 22	23 à 26	27 à 30	31 à 42	51 à 63	54 à 66	57 à 69
Year	1998	2000	2001	2002	2003	2004	2005	2006	2008	2013	2014	2015

Certification and standards

ILCs are organized every year, by INERIS, on a bench which can provide tests on the following parameters:

- measurement of gaseous compounds contents: O₂, CO₂, NO_x, CO, TVOC, CH₄, nMVOC, HCl, SO₂, NH₃, and water vapor;
- measurement of dust content.

INERIS is accredited by COFRAC (n° 1-2291) for the organization of inter-laboratory campaigns according to ISO CEI 17043



The Statistical plan is set in accordance with standards ISO 13528 and ISO 5725-5

Context and Programs

- Each laboratory approved by the French Ministry of Environment must participate periodically to ILCs (decree of march 11th 2010). ⇒ The frequency is set by regulation depending on the size of the laboratory.
- Registration is also open to all laboratories implementing EN standards
- A new program is submitted every 3 years:
 - 2010 / 2012 : implementation of manual methods (HCl, SO₂, NH₃, water vapour),
 - 2013 / 2015 : implementation of automatic methods (O₂, CO, CO₂, TVOC, CH₄, NMVOC, SO₂, NO_x),
 - 2016 / 2018 : Determination of low mass concentrations of dust (EN 13284-1).
- Several auditors are mandated to observe the practice of each participant during the 3 days of ILCs in order to ensure that all QA/QC procedures are well implemented.
Any deviation from the procedure or anomalies in the design of the sampling lines are highlighted to be treated by the participant.
- **To avoid collusion** between the 12 participants,
 - the teams of the same company don't participate to the same campaign
 - Some key operating and measurement data are collected at the end of the campaign and entrusted to the ILCs 'organizer

Quality checks

- Homogeneity of flue gases is checked once for each compound at different concentration levels.
- Every year, a check of the good shape of the installation is controlled through an homogeneity test conducted with HCl and NH₃ (the most reactive compounds)
- During the measurement campaign, criteria are fixed to ensure the homogeneity of the distributed gas:
 - The difference of temperature along the bench must not exceed 10 °C
 - The gaz pressure after the sampling port # 12 must not exceed 7 Pa, to guarantee an overpressure along the loop
 - The difference between O₂ contents measured at the beginning and at the end of the loop must be < 0.3 % vol.

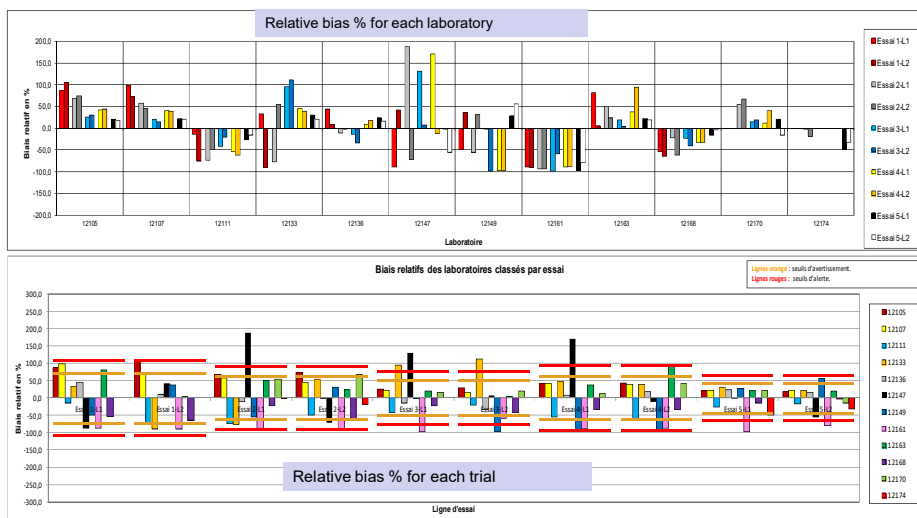
Accuracy of the results - Performance Test

1. Determination of the assigned value by applying the robust data analysis method (Algorithm A) **the assigned value = robust average value**
 - procedures described in Standards ISO 13528 and ISO 5725-5
2. Criteria for evaluation of performance based on 2 alarm and warning thresholds
 - The bias of the laboratory are assessed from thresholds corresponding to an alarm signal or an action signal, calculated on the basis of the standard deviation for the aptitude assessment.

Standard deviation for the aptitude assessment : 2 options :

 - on the basis of the results of the participants ⇒ equal to the robust standard deviation estimated by applying Algorithm A
 - on the basis of a fixed value ⇒ the uncertainty stipulated in the Standard describing the reference method when it exists, otherwise deduced from the uncertainty stipulated in the Directives for AMS.

Accuracy of the results ie - thresholds based on the results of the participants



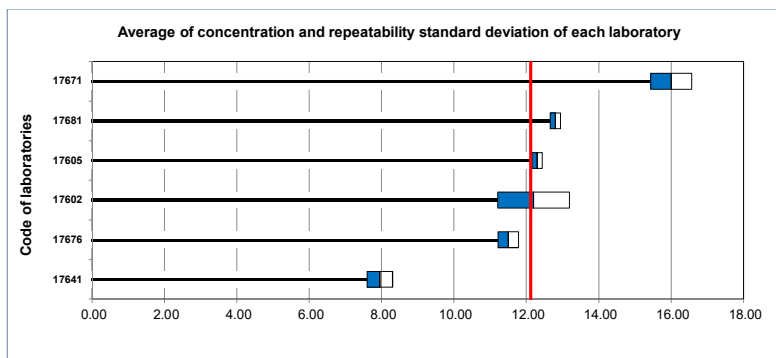
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On-site repeatability

Another graphic of presentation of bias and repeatability of the laboratories
Repeatability is determined by a robust estimation following the procedure described in Standard ISO 5725-5



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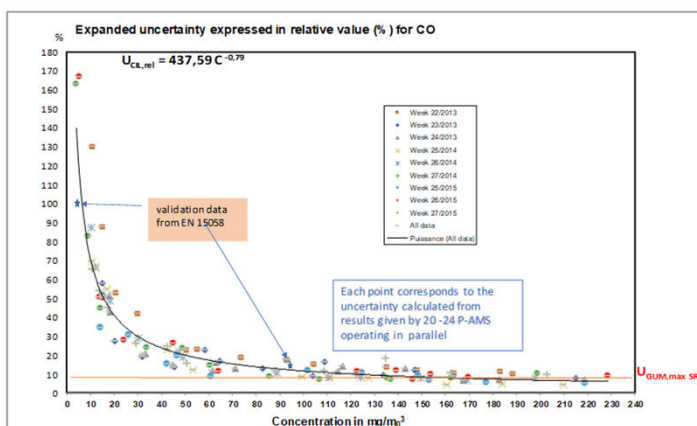
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Reproducibility confidence intervals

Uncertainty increases when the concentration decreases:

- EN 15058 requirement à la VLE $U_{thSRM} < 6\%$ (conformity assessed with an uncertainty budget)
- In practice U_{SRM}
 - 10% - 22% at 50 mg/m³
 - 75% - 100% at 10 mg/m³

CO



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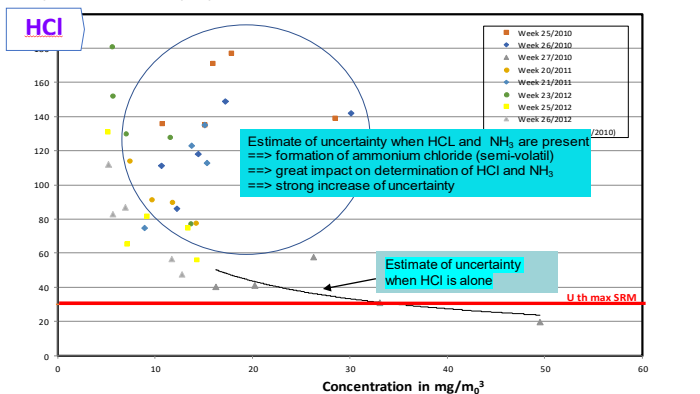
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Reproducibility confidence intervals

Uncertainty strongly increases when NH₃ is present:

- EN 1911 requirement at ELV à la VLE $U_{thSRM} < 30\%$ (conformity assessed with an uncertainty budget)
- In practice U_{thSRM}
 - 45% at 20 mg/m³ when HCl is alone
 - 50% - 180% at 5 - 20 mg/m³ when NH₃ is present

Expanded uncertainty expressed in relative value (%) for HCl



ILCs can be an opportunity to test the impact of influence factors on the dispersion of results and to improve the procedure of reference methods

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Conclusion

The Intercomparison bench is a very useful tool, which allows to :

- Consider all the steps of the reference methods (sampling, gas conditioning and analysis) in ILCs; Sampling is the major source of uncertainty despite the QA checks required by the reference methods
- Organize ILCs in real conditions, with real matrices (gases, dust, semi volatile species, water vapour, temperature...) provide realistic uncertainty estimates
 - better identify procedure or implementation issues
 - improve the procedures in standards
 - for gaseous compounds, the evolution trend in standardization and regulation is to replace or to propose automated methods as alternatives to manual Reference Methods (better fidelity, lower uncertainty).
 - validate standards for different gas matrices and ranges of concentration
 - compare one method to another one according to EN 14793.

Conclusion

The Intercomparison bench is a very useful tool, which allows to :

- Bring to light the progress done on the implementation of the reference methods
- Bring data to the regulators and to the European Commission on the actual uncertainty that can be reached by the existing measurement methods at different concentrations
 - So that they propose in the future, uncertainty requirements adapted to the level of concentration.

Thank you for your attention !