Evaluation of the suitability of the HCl reference measurement method for the increasingly stringent legislation on industrial plants

C. Raventos, H. Bautista, A. Dermigny, O. Feuger, I. Fraboulet, N. Karoski, J. Poulleau, C. Vancayseele (INERIS - France)
T. Pellika (VTT – Finland) – M. Coleman (NPL – United Kingdom)

INERIS

Context

To further reduce the impact of air pollution on environment and health in Europe, the regulations are constantly evolving, through the revision of the Best Available Techniques REFerence Documents. New atmospheric Emission Limit Values (ELV) are to be defined based on the emission levels associated with BAT (BAT-AEL).

Thus, in the case of HCl, a compound with high toxicity and impact on ecosystems, **the ELV defined today in Industrial Emission Directive (2010/75/EU) of 10 mg/m^3 will have to be lowered.**

Question: is the standard reference measurement method, imposed today for periodic monitoring by laboratories, capable of meeting the uncertainty requirements at level of future ELVs?
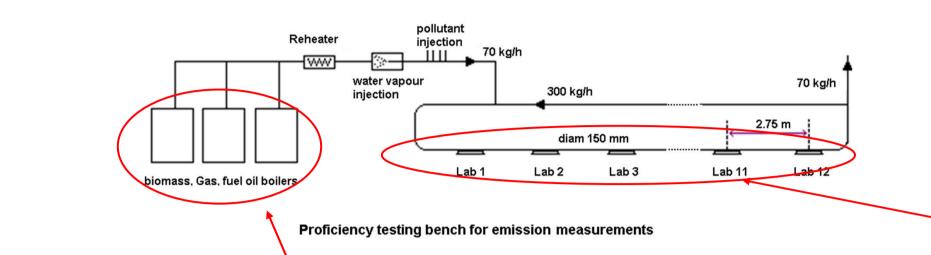
Examples of BAT-AEL for HCl

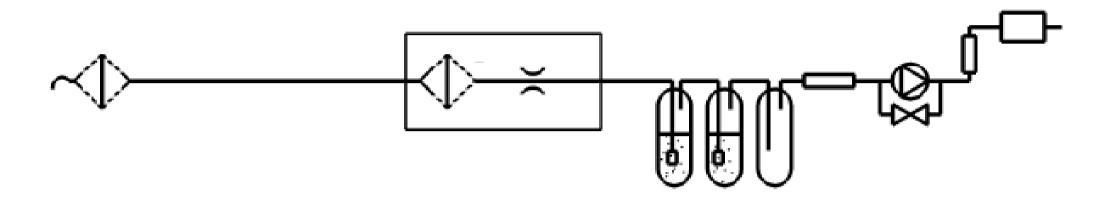| Type of plant	BAT-AEL
Waste Incineration plant (Decision 2019/2010)	2-6 (new plant)
Large Combustion plant (Decision 2017/1442)	1-12 to 1-35
Production of cement plant (Decision 2013/163/EU)	< 10
Iron and steel production (2012/135/EU)	< 1-3

HCl Standard Reference method: EN 1911 (2010)

Scope: measurement of all hydrogen chlorides expressed as HCl concentration: 1 to 5000 mg/m^3

Principle: « manual method » by absorption in solution combining:
1/ Sampling on site: extraction of a **known volume** of flue gas **through deionised water in 2 absorbers**, after filtration

Example of sampling equipment

2/ Analysis of solutions in laboratory: 3 possible analytical methods

Performance criteria:
Equipment: uncertainty criteria for volume gas meter, T and P measured at gas meter, and determination of volume of solution
Quality controls: leakage control, field blank, absorption efficiency
Standard deviation of analytical repeatability: ≤ 2,5 %

Relative expanded uncertainty of measurement: ≤ 30 %

ILC TO EVALUATE MEASUREMENT UNCERTAINTY OF EN 1911

Test bench

Proficiency testing bench for emission measurements

➢ Designed to generate gaseous effluents of identical composition for each of the 12 sampling ports
⇨ **12 "stack teams" can participate to ILCs simultaneously**
➢ Gas generated from boilers (natural gas, light fuel oil or biomass);
➢ Gas provided by the combustion can be heated, moistened and spiked ⇨ **simulate gas matrix like those of industrial plants**

Prerequisites for the organisation of ILC performed in June 2020
Validate the possibility of generating concentrations below 10 mg/m^3
Verify the homogeneity of concentration along the bench, i.e. between the 12 sampling ports

Program of ILC performed in April 2021
• 9 participants (i.e. logos at the bottom of the poster)
• 15 trials, 60 min each
• Variation of the compound of the matrix: concentration range of HCl: 3 to 16 mg/m^3 NTP; evaluation of the impact of the presence of NH_3 and SO_2: may lead to the formation of salts
• **2 independent sampling systems implemented by each participant**
• **Duplicate analysis of each sample under repeatability conditions**
• 3 field blanks and 2 absorption efficiency controls for each sampling line
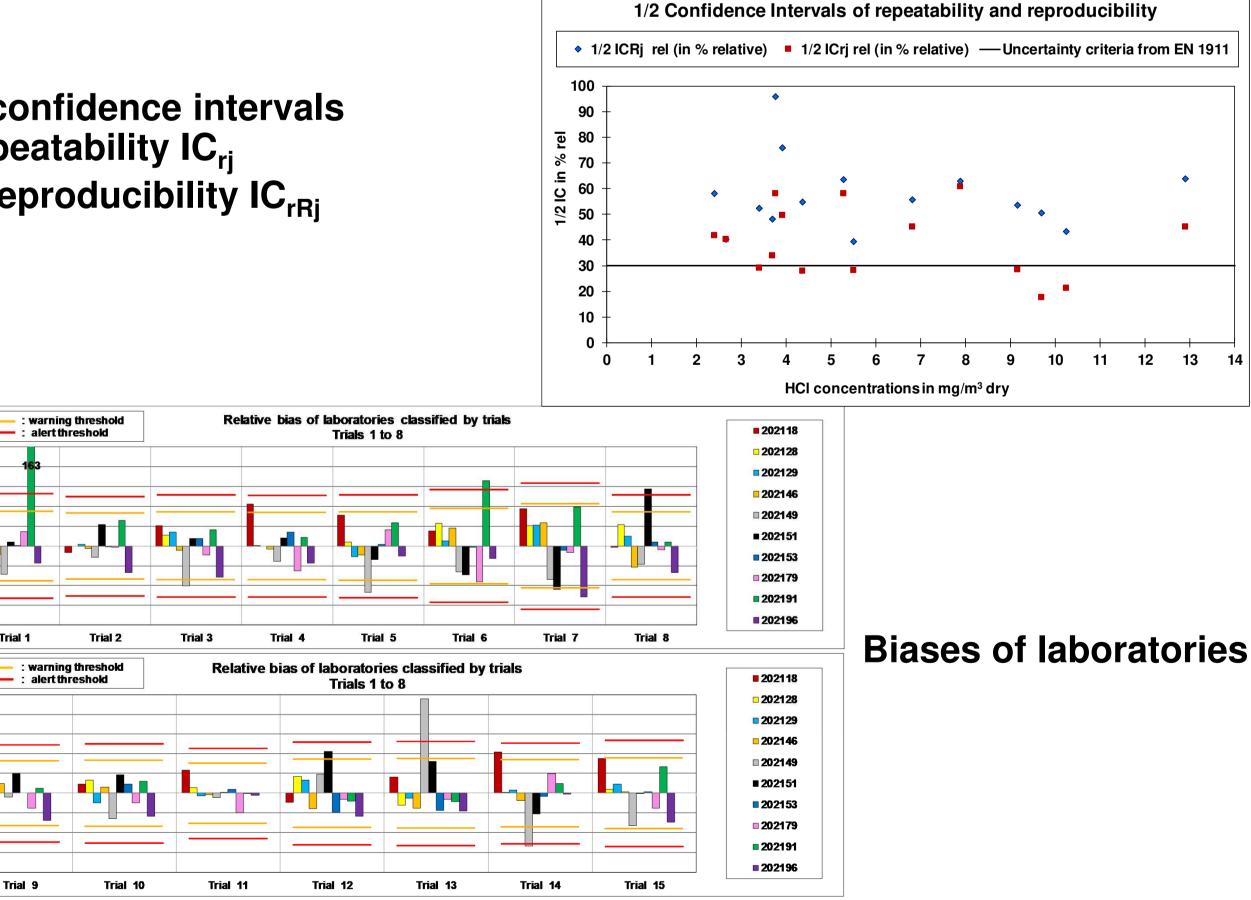
NEXT STEP : processing and analysis of data from ILC

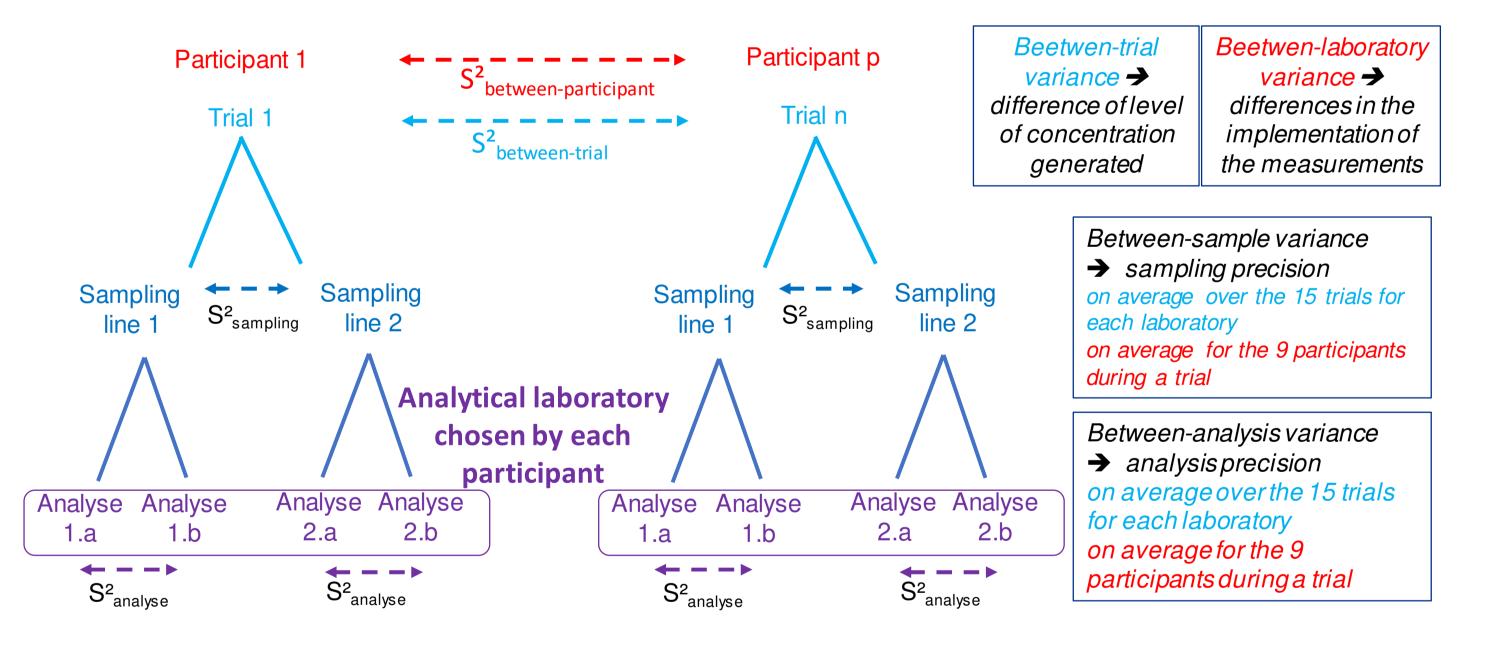**Equipments and quality controls metadata:**
▪ Type of absorbers
▪ Field blank, absorption efficiency, temperature of filtration
▪ **Analysis LoQ and measurement LoQ**
▪ **Analysis and measurement uncertainties** provided by analysis and control laboratories

Statistical treatment based on ISO 13528 (a) and ISO 5725-2 (b)

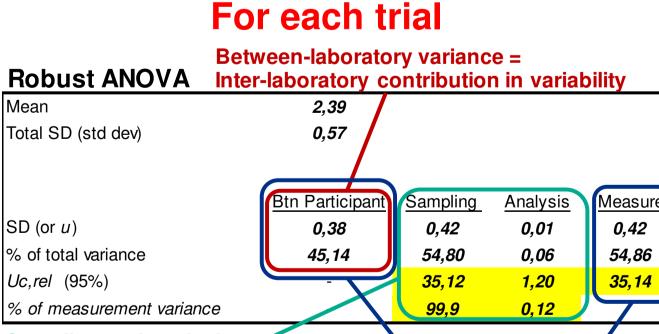Half confidence intervals of repeatability IC_{rj} and reproducibility IC_{rRj}

1/2 Confidence Intervals of repeatability and reproducibility

Relative bias of laboratories classified by trials Trials 1 to 8

Relative bias of laboratories classified by trials Trials 1 to 8

Biases of laboratories

Statistical treatment based on Eurachem Guide/Citac (c) applied:

For each participant & for each trial

Beetwen-trial variance ➔ difference of level of concentration generated
Beetwen-laboratory variance ➔ differences in the implementation of the measurements

Between-sample variance ➔ sampling precision on average over the 15 trials for each laboratory on average for the 9 participants during a trial

Between-analysis variance ➔ analysis precision on average over the 15 trials for each laboratory on average for the 9 participants during a trial

For each participant

Between-trial variance = Variability of concentrations generated

Robust ANOVA

		Sampling	Analysis	Measure
Mean	7,11			
Total SD (std dev)	4,42			
SD (or u)	4,42	0,23	0,11	0,25
% of total variance	99,67	0,26	0,07	0,33
Uc,rel (95%)		6,3	3,19	7,1
% of measurement variance	-	79,7	20,3	-

Uc: expanded relative uncertainty

Sampling and analysis contributions in repeatability of measurements

For each trial

Between-laboratory variance = Inter-laboratory contribution in variability

Robust ANOVA

		Btn Participant	Sampling	Analysis	Measure
Mean	2,39				
Total SD (std dev)	0,57				
SD (or u)		0,38	0,42	0,01	0,42
% of total variance		45,14	54,80	0,06	54,86
Uc,rel (95%)			35,12	1,20	35,14
% of measurement variance	-		99,9	0,12	-

Sampling and analysis contributions in repeatability of measurements

Comparison of the importance of intra-laboratory repeatability versus inter-laboratory variability

Perspectives

➢ *New database to assess the performance of the SRM in terms of uncertainty for concentrations below 10 mg/m^3 NTP*
➢ *Comparison of results with the LoQ and uncertainty requirements*
➢ *Assessment of the contribution of sampling and analysis to the repeatability component of the method*
➢ *Identification of parameters influencing the measurement, if possible*
➢ *Identification of possible ways of improving the measurement method and revision of the standard in 1911*

References
a) ISO 13528: Statistical methods for use in proficiency testing by interlaboratory comparison
b) ISO 5725-2: 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
c) Eurachem Guide/Citac - Measurement uncertainty arising from sampling