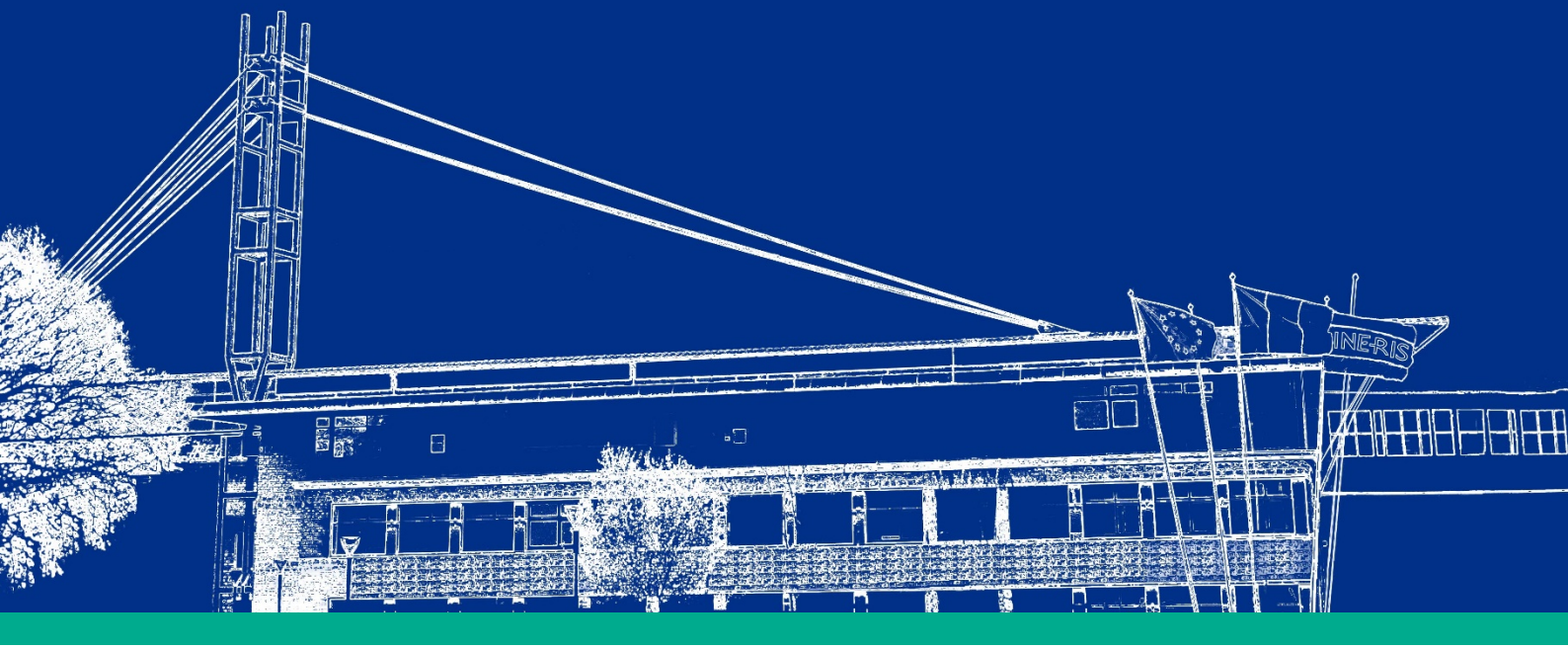

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22 février 2023

EMPIR Heroes Project Deliverable D4 Summary report on the scientific evidence base used to derive recommended uncertainty requirements to extend the application of EN1911 to low HCl emitting processes regulated via BAT conclusions

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controlling risks for sustainable development

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Partner in charge of the deliverable: INERIS

Date: January 2023

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Division responsible for the report: DIRECTION MILIEUX ET IMPACTS SUR LE VIVANT

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Abstract

The objective of the HEROES study was to assess whether the standardized reference method, applied for periodic HCl monitoring of industrial installations and calibration of continuous monitoring equipment for this compound (reference method described in standard EN 1911), remains suitable in a context of lowering emission limit values and therefore emitted concentrations.

The method described in EN 1911 is a manual method including a sampling phase on site, then an analysis phase of the samples (absorption solutions) in an analytical laboratory. During the HEROES study, different actions were proposed by the partners, in order to evaluate the factors that could have an impact on the measurement and therefore on its measurement uncertainty, and the ability of the method to respect at low concentration levels, the measurement uncertainty criterion set in the standard. The tests led to the identification of method limitations, and recommendations or requirements to be included in the revision of the standard to improve the performance of the method and to adapt it to future ELVs.

The report summarizes the work done and the main conclusions. These data have been compiled in order to make them available to the community via a data sharing platform.

Use the link provided below for quotations:

French national institute for industrial environment and risks (Ineris), EMPIR Heroes Project Deliverable D4 Summary report on the scientific evidence base used to derive recommended uncertainty requirements to extend the application of EN1911 to low HCl emitting processes regulated via BAT conclusions, Verneuil-en-Halatte : Ineris - 205486 - v1.022 février 2023.

Keywords:

Manual standardized reference method, HCl periodic monitoring, performance characteristics of the method, scientific base of tests implemented

1 Introduction

One of the objectives of the project was to evaluate the capability of the standardized reference method described in EN 1911 (Stationary source emissions - Determination of mass concentration of gaseous chlorides expressed as HCl - Standard reference method), to be in accordance with the requirement of uncertainty criteria of the standard, in a context of lowering emission limit values and therefore emitted concentrations.

The measurement method includes a sampling phase and an analysis phase.

This report summarizes actions that were proposed by the partners, to evaluate the factors that could have an impact on the measurement and therefore on its uncertainty, related to the different steps of the measurement procedure or to the equipment.

Tests of sampling equipment, analytical interlaboratory comparison (ILC), measurement interlaboratory comparison, measurement on industrial sites and evaluation of the impact of the stack configuration by modelling were implemented.

The objective was to evaluate the ability of the method to respect the measurement uncertainty performance set in the standard at low concentration levels, and if necessary, to identify recommendations or requirements to be included in the revision of the standard to improve the performance of the method to reduce uncertainties, and to adapt it to the future ELV.

Data related to the actions, have been compiled in order to make them available to the community via a data sharing platform.

2 Evaluation of the implementation of the analytical step of the EN 1911 during an ILC

2.1 Metadata

Analytical ILC for the analysis of chlorides in absorption solutions, were implemented by NPL. Metadata about organisation of the ILC are given in Table 1.

Table 1: Metadata related to the ILC on chloride analysis

Origin of the data	
Institut/company/laboratory	NPL
Country	UK
Contact	Thomas Smith
Mail contact	thomas.smith@npl.co.uk
Date of transmission data	January 2023
Purpose of the ILC	
Demonstrate laboratory performance and stated uncertainties for EN 1911 at low HCl levels.	
How the data was obtained	
Interlaboratory comparison: distribution of sample solutions to participants	Samples generated in the laboratory with known concentration: by dissolving NaCl in deionised water and further samples from a stack simulator were split into equal samples and sent out to a selection of accredited laboratories ISO 17025 for the required analysis in EN 1911, as normal stack samples (blind ILC).
Conditions for the implementation of ILC	
Date of trials	June-August 2021
Number of participants	6 accredited laboratories for synthetics samples 3 accredited laboratories for real samples

Number of samples	- Synthetic samples: preparation of 5 solutions; each of the 5 solutions was split into 24 samples; each of the 6 accredited laboratories then received 4 samples at each concentration level for a total of 20 tests per laboratory. - Real samples: 34 solutions in the 0-15 $mg.m^{-3}$ range were prepared by generating representative stack gas matrices in the NPL Stack Simulator Facility.
Characteristics of the samples	- Synthetic samples: NaCl dissolved in de-ionised water to create chloride solutions of 5 concentrations: 1.9, 3.9, 5.9, 7.7 & 9.8 $mg.m^{-3}$. - Real samples: 52 stack Sim samples were taken from stack simulator, although only 34 in the 0-15 $mg.m^{-3}$ range were used for ILC with concentrations < 10 $mg.m^{-3}$ for 26 solutions and < 4.5 $mg.m^{-3}$ for 17 solutions. Matrix generated to prepare samples: HCl: 0-60 $mg.m^{-3}$; SO_2: 0-290 $mg.m^{-3}$; CO: 0–100 $mg.m^{-3}$; NO: 0-300 $mg.m^{-3}$; H_2O: 0-14%vol. Other species were included at fixed concentrations: NH_3: 15 $mg.m^{-3}$; NO2: 30 $mg.m^{-3}$; VOC mixture (CH_4: 9 $mg.m^{-3}$ /C_2H_6: 8 $mg.m^{-3}$/C_3H_8: 8.5 $mg.m^{-3}$); CO_2: 10% vol and O_2: 10% vol. The simulator was operated at 180°C and a recirculating gas velocity of 12 $m.s^{-1}$
Data processing	Concentration (mg/m^3) calculation from analysis results (mg/l) & ISO 5725-6
Type of results	HCl concentration taken as assigned values for comparisons: reference concentration for synthetics samples, mean of the participant's measurements for real samples Relative deviations of analytical laboratories from assigned values Comparisons of the deviations to the permissible uncertainty required in EN 1911: calculation of permissible deviation for analytical step based on the required measurement uncertainty (30%) and an estimated sampling uncertainty (7.2%, based on the performance criteria to be met for sampling step)

2.2 Main conclusions

Across a 0–10 $mg.m^{-3}$ HCl concentration range, it was found that for the real samples 42.3% of the measurements deviated from the mean in excess of the uncertainty quoted by the respective laboratory, whereas the analogous result for the synthetic samples was 5.8%. This contrast showed that national proficiency testing schemes based on synthetic samples may be providing an overly optimistic view of the level of uncertainty that can be routinely achieved following the analytical element of EN 1911.

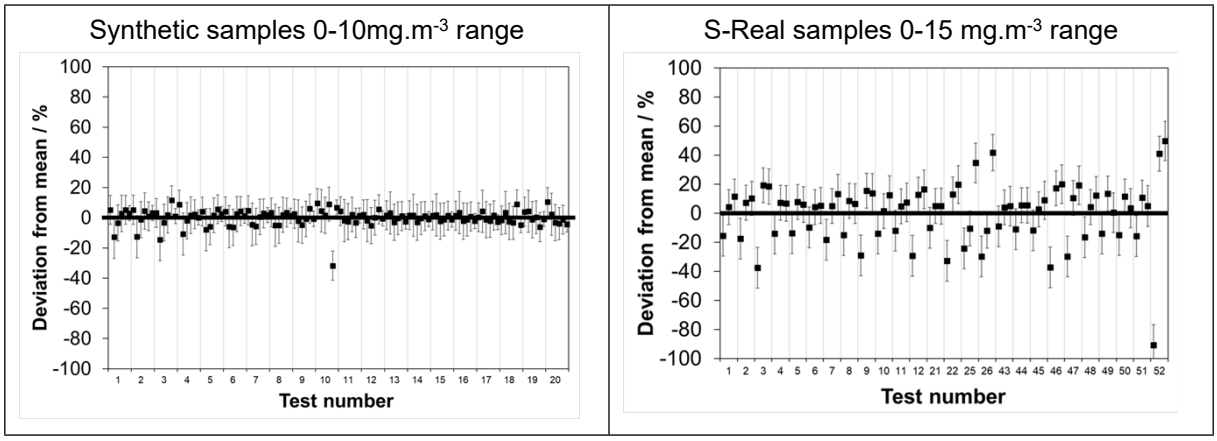


Figure 1: Relative deviations from the assigned value

It was also found, by estimating the contribution to the measurement uncertainty of the sampling phase, based on the sampling performance criteria required in the standard, that almost 10% of the measurements for installations regulated by the IED Directive (10 $mg.m^{-3}$ emission limit, 0-15 $mg.m^{-3}$ measurement range) and almost 20% of the measurements for installations that should comply with BAT conclusions (3 $mg.m^{-3}$ emission limit, 0-4.5 $mg.m^{-3}$ measurement range) would not comply with the overall uncertainty criterion fixed in EN 1911. These observations raise questions on the capability of the EN 1911 standard for the periodic monitoring of the atmospheric emission as well as for the calibration of analysers (AMSs) used for continuous monitoring, with the lowering of the emission limit values.

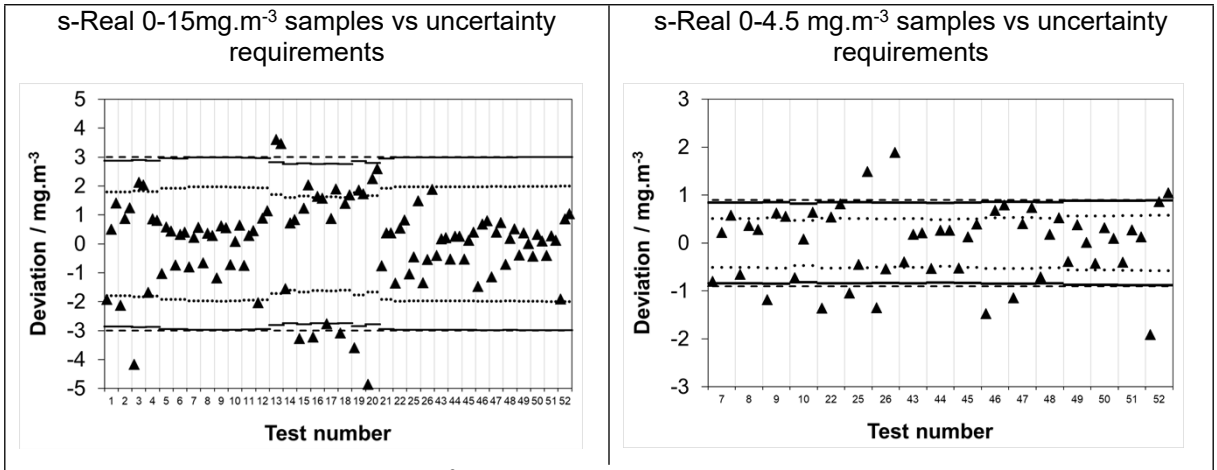


Figure 2: Comparison of deviations to uncertainty requirements

Analysis uncertainty will therefore have to improve to achieve lower global measurements uncertainty limits. Currently, EN 1911 does not consider the analytical step of the method as thoroughly as the sampling step. For the analysis only a repeatability criterion is imposed. It is necessary, when revising the standard, to impose an assessment of the uncertainty of analysis considering the various factors that have an influence on the result, and not only of repeatability. his will also allow laboratories to identify the factors having the greatest impact and the improvements to be made.

3 Testing of the implementation of part of the sampling equipment used for EN 1911 in lab

3.1 Metadata

Testing of different types of impingers and at different sampling volume flow were implemented by VTT. Metadata about tests implemented are given in Table 2.

Table 2: Metadata related to the tests of impingers implementation for HCl measurements

Origin of the data	
Institut/company/laboratory	VTT Technical Research Centre of Finland
Country	Finland
Contact	Tuula Pellikka, Tuula Kajolinna
Mail contact	tuula.pellikka@vtt.fi; tuula.kajolinna@vtt.fi
Date of transmission data	January 2023
Purpose of the tests	
Aim was to make tests using four different glassware tips of impigners and assess if there is statistical differences between the results.	
How the data was obtained	
Tests in laboratory at VTT	
Conditions for the implementation of tests	
Date of trials	Flowrate tests on May 2020 Tip tests 1-9 on June 2020 and tests 10-15 on February 2021
Glassware tests: Number of glassware tips tested Number of tests Number of measurements	 4: Size 200 ml, volume of absorption liquid 80 mL/impinger, 4 different impinger tips: ”straight”, ”normal”, ”sugar”, ”bottom” (see Figure 2) 15 60
Flowrate tests: Number of flowrates tested Number of tests Number of measurements	 2 : 1.5 and 8 L/min 10 20
Duration of each test	30 min
Other results	Absorption efficiency from one test per campaign
Charactéristics of the matrix	Liquid vapourized to gas flow with Hovacal (incl. scale). Gas: N_2 10 Lpm, HCl liquid: 1 mmol/L, HCl concentration target 2 $mg.m^{-3}$ (dry, NTP), Water vapour 6.4 vol-%. NTP=273.15 K and 101325 Pa Measurement of HCl concentration with FTIR
Data processing	In accordance with ISO 13528 / ISO 5725-2. Average, repeatability, between-laboratory variance, reproducibility
Type of results	HCl concentrations, $mg.m^{-3}$, NTP (0 °C, 101,3 kPa), dry

3.2 Main conclusions

3.2.1 Testing of influence of the types of impingers

Four different impinger tips presented in the figure were implemented over a set of 15 trials, at a HCl concentration level of about 2 mg/m^3, to evaluate the influence of the impinger configuration on the absorption efficiency.

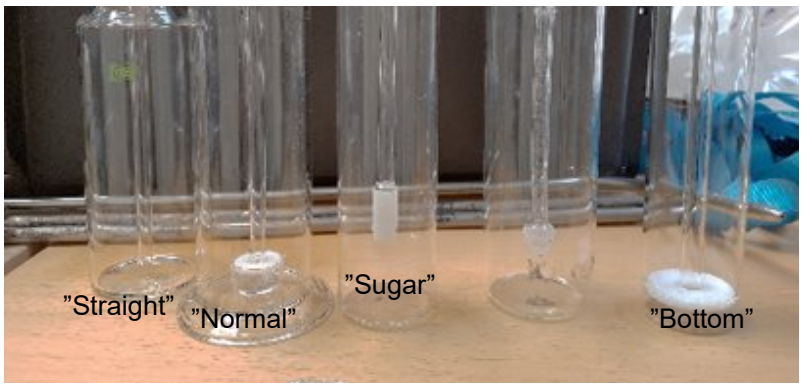
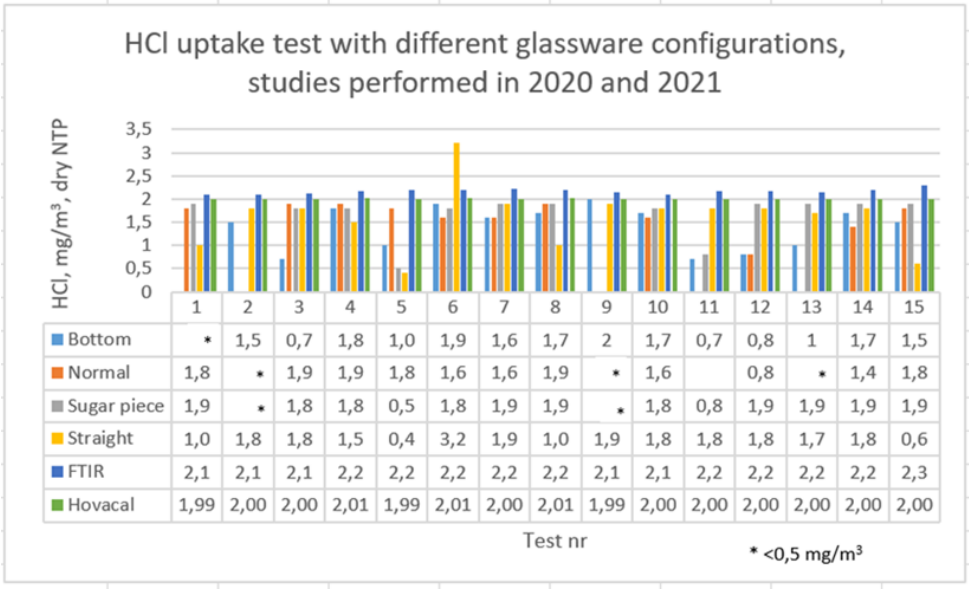


Figure 3: Type of glassware tested

Concentrations of HCl measured are summarized in the Figure 4. Values below LoQ (Limit of Quantification = 0.2 mg/L ≈ 0,5 mg.m^{-3}) were not considered.



	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15
Bottom	*	1,5	0,7	1,8	1,0	1,9	1,6	1,7	2	1,7	0,7	0,8	1	1,7	1,5
Normal	1,8	*	1,9	1,9	1,8	1,6	1,6	1,9	*	1,6		0,8	*	1,4	1,8
Sugar piece	1,9	*	1,8	1,8	0,5	1,8	1,9	1,9	*	1,8	0,8	1,9	1,9	1,9	1,9
Straight	1,0	1,8	1,8	1,5	0,4	3,2	1,9	1,0	1,9	1,8	1,8	1,8	1,7	1,8	0,6
FTIR	2,1	2,1	2,1	2,2	2,2	2,2	2,2	2,2	2,1	2,1	2,2	2,2	2,2	2,2	2,3
Hovacal	1,99	2,00	2,00	2,01	1,99	2,01	2,00	2,01	1,99	2,00	2,00	2,00	2,00	2,00	2,00

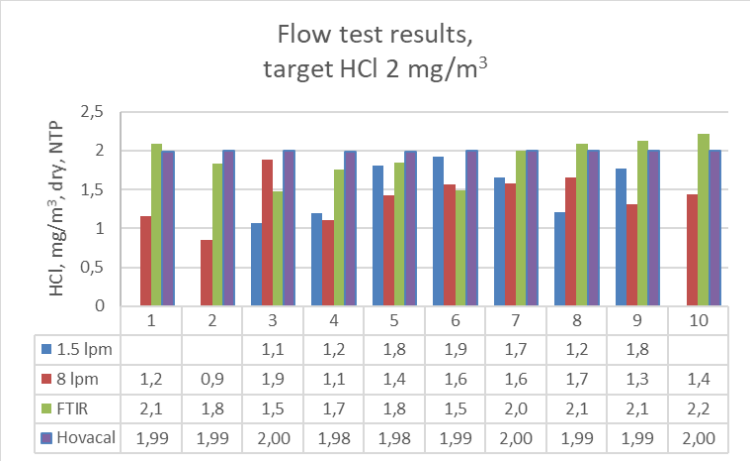
Figure 4: Concentration measured with the four types of impingers tested

The variability between the results obtained with the different types of impinger types is not significant with respect to the repeatability of concentrations measured with each type of impinger.

3.2.2 Testing of influence of the sampling flow rate

Tests were implemented at two levels of sampling flow rates: about 1.5 and 8 L/min, to evaluate the absorption efficiency in both sampling conditions, over a set of 10 trials, at a HCl concentration level of about 2 mg.m^{-3}. Level of concentration was about 2 mg.m^{-3}.

Results of measurements are summarized in Figure 5.



	1	2	3	4	5	6	7	8	9	10
1.5 lpm			1,1	1,2	1,8	1,9	1,7	1,2	1,8	
8 lpm	1,2	0,9	1,9	1,1	1,4	1,6	1,6	1,7	1,3	1,4
FTIR	2,1	1,8	1,5	1,7	1,8	1,5	2,0	2,1	2,1	2,2
Hovacal	1,99	1,99	2,00	1,98	1,98	1,99	2,00	1,99	1,99	2,00

Figure 5: Concentration measured for two levels of flow rate tested

The variability between the results obtained with both sampling flow rates is not significant with respect to the repeatability of concentrations measured with each sampling flow rate.

Based on these calculations, the statistical difference for both repeatability and reproducibility is negligible, both for:

- Different impinger tips and
- Different flow rates (1.5 L/min and 8 L/min)

The variability related to this element of the measurement sampling train is non-significant, even at low concentration.

Demonstrating the equivalence of these variables is an important finding that provides added confidence in the performance of the equipment implemented for the EN 1911 method.

4 Evaluation of the contribution in the measurement uncertainty of the isokinetic sampling in case of droplets in the matrix

The EN 1911 standard requires isokinetic sampling when the occurrence of droplets is suspected or known in the gas to be analysed, because droplets may have a high chloride content (dissolved chlorides or/and HCl).

It was therefore studied the influence of an isokinetic sampling on the HCl measurement, considering the following parameters:

- The variability of the calibration of a S-type Pitot tube when associated with different types of probes for isokinetic sampling
- The configuration of the duct which opens in the stack and the matrix (size and concentration of the droplets).

4.1 Calibration on S-type Pitot tube

4.1.1 Metadata

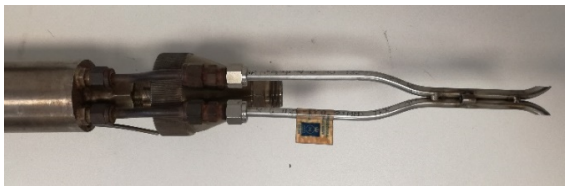
The S-Pitot tube can be associated to probes with different configurations. It can happen that the laboratory calibrates its pitot tube in a configuration and then uses it in other different configurations if it has different types of sampling probes. Indeed, most of the time, the calibration is annual and the Pitot tube is calibrated alone or with only one type of probe.

The objective of the tests implemented in laboratory by CMI, was to evaluate if the type of probe associated to the S-type Pitot tube can have an impact on the K coefficient of the tube.

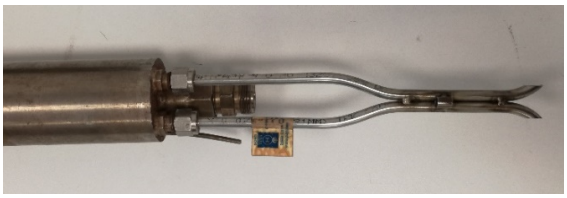
Metadata about tests implemented are given in Table 3.

Table 3: Metadata related to the tests of S-type Pitot tubes calibration

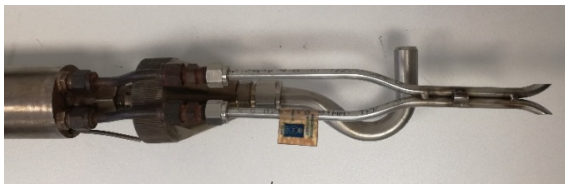
Origin of the data	
Institut/company/laboratory	Czech Metrology Institute
Country	Czech Republic
Contact	Jan Geršl
Mail contact	jgersl@cmi.cz
Date of transmission data	January 2023
Purpose of the tests	
To determine a calibration coefficient of the S-type Pitot tube in several configurations with various sampling probes and to identify the influence of the sampling probe installation to the calibration coefficient.	
How the data was obtained	
Tests in laboratory at CMI	Tests have been performed in the wind tunnel laboratory of CMI. The wind tunnel has an open test section with a diameter of 45 cm and it uses a Laser Doppler Anemometer (LDA) as an air speed reference. Indication of the air speed sensor which is a part of the isokinetic probe (S-type Pitot tube) was compared with the reference LDA in several configurations with various sampling probes.
Conditions for the implementation of tests	
Date of trials	September 2021
Number and types of configurations tested	36 See tested configurations in Figure 6
Duration of each test	10 min
Data processing	Evaluation using an excel calibration template of CMI
Type of results	Calibration data: calibration coefficient K, expanded uncertainty



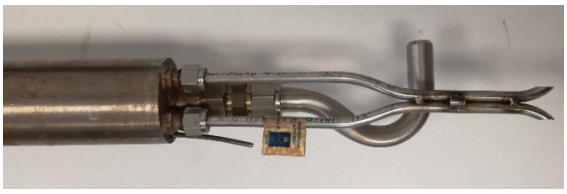
Filter holder with no probe



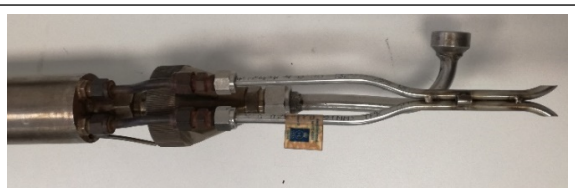
No probe with no filter holder



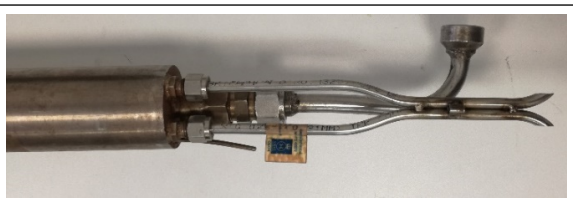
Filter holder with swan neck



Swan neck with no filter holder



Filter holder with nozzle arm



Nozzle arm with no filter holder

Figure 6: Tested configurations of S-type Pitot tube

4.1.2 Main conclusions

The values of the calibration coefficient determined during the different tests are given in Figure 7.

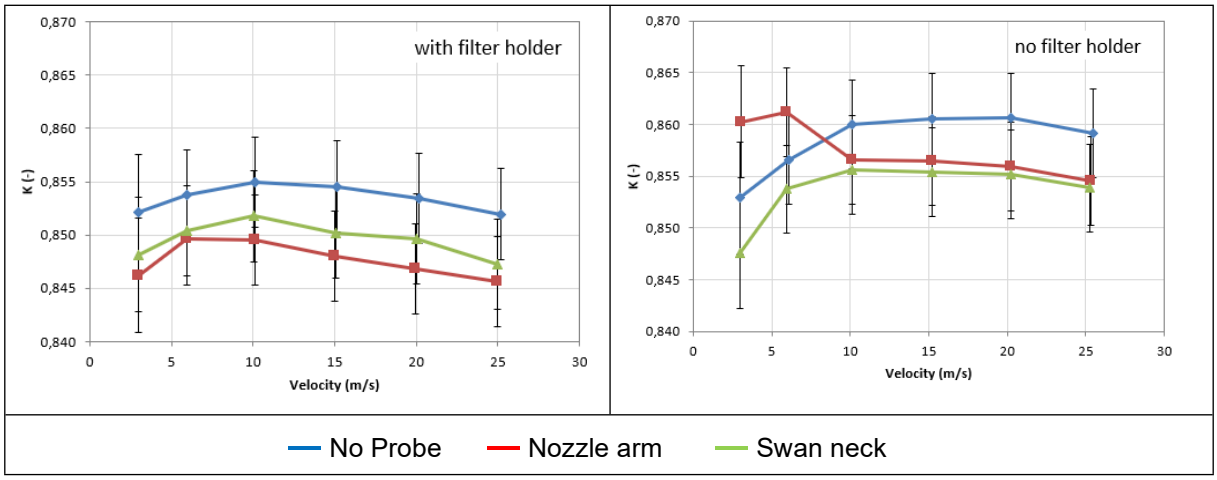


Figure 7: Results of K coefficient for the different S-type Pitot tube configurations

Maximal deviation in the calibration factor K was observed between the configurations "filter holder with nozzle arm" and "no filter holder with no probe" and its value was 1.6 %.

The calculation of velocity is given by equation: $V = K\sqrt{\frac{2\Delta p}{\rho}}$.

Where V: velocity
K: calibration coefficient K
ΔP: differential pressure measured with Pitot tube
ρ: gas density

A deviation on the calibration coefficient can thus lead at most to a deviation of velocity and thus of isokineticism of 1.6% for the type of Pitot tubes configurations tested. The impact on the measured mass concentration depends on the droplet size: it increases with the particle size, and whether this leads to under- or over-isokinetic sampling: according to the EN 13284-1 standard (*Determination of low range mass concentration of dust - Part 1: Manual gravimetric method*), under-isokinetic sampling leads to an overestimation of the concentration and over-isokinetic sampling to an underestimation.

Based on the reference by Belyaev and Levin [*S. P. Belyaev and L. M. Levin, Techniques for collection of representative aerosol samples, J. Aerosol Science 5(1974) p. 325*], the relation between the relative error of the concentration measurement and the relative deviation of the suction velocity from an undisturbed gas stream, leads to the conclusion, that if this deviation is small, the deviation from isokinetic sampling due to an error in calibration coefficient of the Pitot tube should cause a deviation in concentration measurement below 1.6% for the configurations tested.

4.2 Evaluation by modelling on effect of configuration on a supply pipe

4.2.1 Metadata

The configuration of an installation can lead to a non-uniform flow, and thus in case of presence of droplets, to a non-homogeneous distribution of these droplets on the measuring section.

The objective of the modeling tests was to evaluate the effect on the HCl measurement, of the location of the measurement section and the number of sampling points provided by the EN 15259 standard,

- According to the configuration of the duct leading into the chimney (without elbow, with one elbow, with 2 elbows)
- According to the size and concentration of the particles/droplets.

Metadata about tests implemented are given in Table 4.

Table 4: Metadata related to the tests of S-type Pitot tubes calibration

Origin of the data	
Institut/company/laboratory	Czech Metrology Institute
Country	Czech Republic
Contact	Jan Geršl
Mail contact	jgersl@cmi.cz
Date of transmission data	January 2023
Purpose of modelling	
To asses the measurement uncertainty of mass concentration caused by sampling section and sampling points located under the standard EN 15259:2007, for different duct configurations and matrices with different droplets/particulates size.	
How the data was obtained	
Modelling	Data obtained by simulations done in open source software OpenFOAM 5.x
Model and assumptions considered	Computational Fluid Dynamic (CFD) based models using the OpenFOAM software CFD modelling used to analyse particle distributions in dependence on type of stack supply pipe and for different emission particles size and different inlet concentrations.
Conditions for the implementation of the model	
Stack	Diameter: 0.75 m, heigh approximative: 10m
Particle size and density	10, 20 and 50 µm, 2300 $kg.m^{-3}$
Inlet emission concentration	0.1, 1 and 10 $mg.m^{-3}$
Fluid properties	kinematic viscosity 10cSt

4.2.2 Main conclusions

The developed model has been used for:

- Simulation of particle distributions in stacks for different geometrical and physical conditions (see Figure 8);
- Modelling of a concentration measurement in predefined sampling points, and determining the mass concentrations of the particulate matter passing through the selected sampling points;
- Determining deviations from the average concentration value, when the sampling on the measurement section is carried out, at the points specified in the EN 15259 standard.

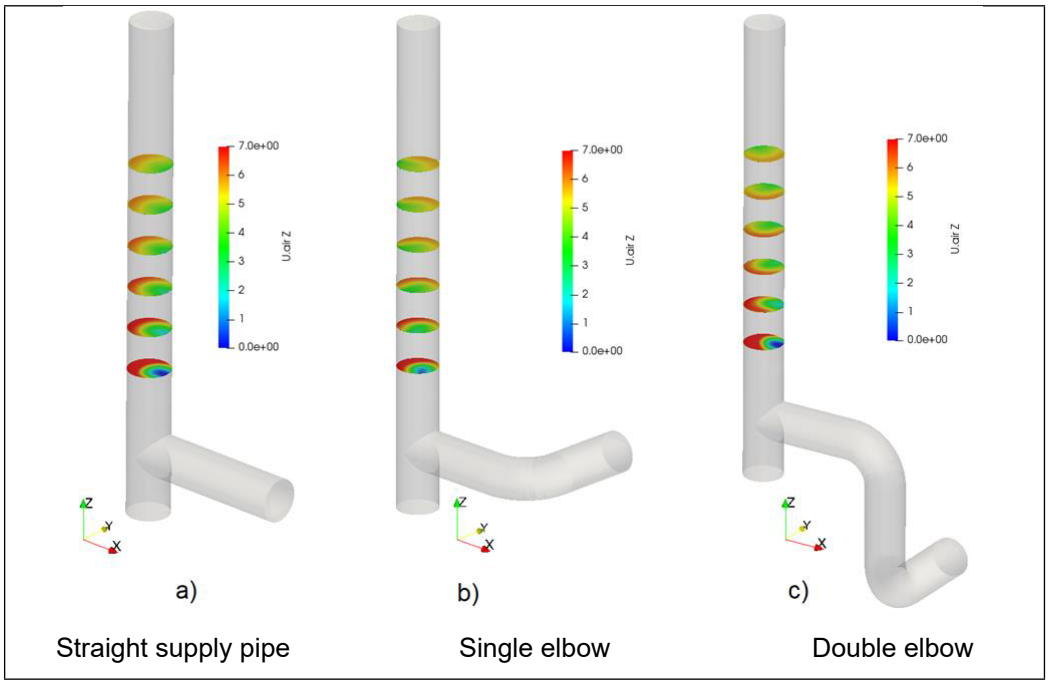
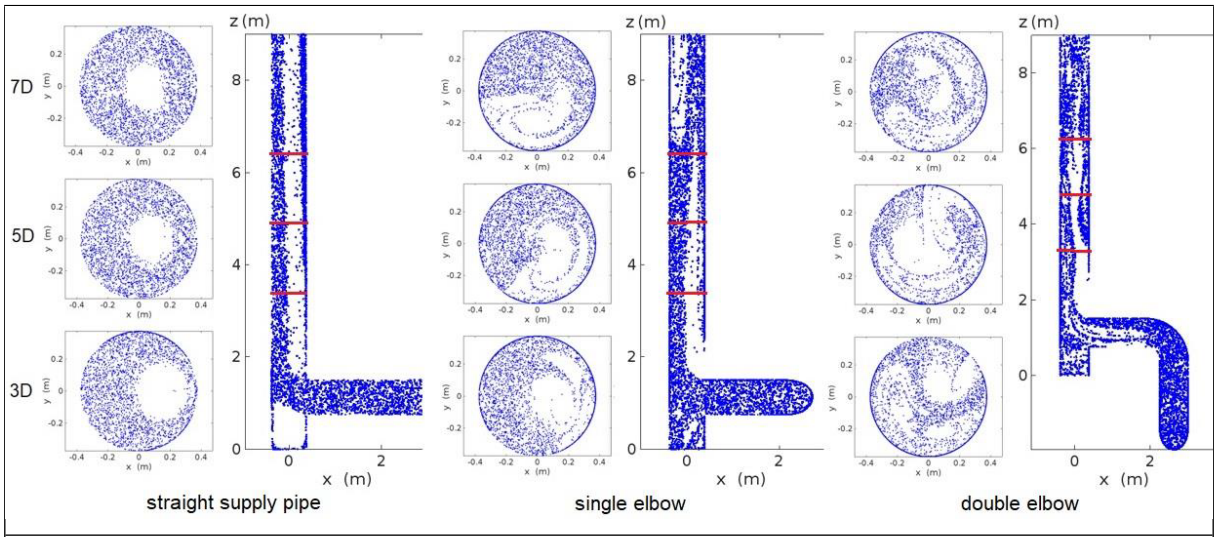


Figure 8: Distribution of axial velocity component in horizontal cuts
for the 3 studied geometrical configurations of the supply pipe

It was shown that flow patterns which are typical for stacks can lead to significant particle redistributions and inhomogeneities in particle concentrations in stacks: example for inlet concentration of 1 mg/m3 in Figure 9. The larger the particles are the more significant the effect is. Concentrations in specific sampling points which are prescribed for isokinetic sampling, can then be non-representative for the overall average concentration leading to measurement errors up to 50%. The results have been summarised in a paper which is going to be submitted to Journal of the Air & Waste Management Association.



Horizontal cuts at 3 heights corresponding to the red lines
Vertical central cut through the stack
Inlet concentration 1 mg.m^{-3}, particle diameter 20 µm

Figure 9: Graphical representation of the particle distributions:

5 Testing of the implementation of the measurement method EN 1911 during an ILC on a test bench

5.1 Metadata

Measurement ILC was organized by Ineris on a bench test. Metadata about organisation of the ILC are given in Table 5.

Table 5: Metadata related to the ILC HCl measurement organized on Ineris bench test

Origin of the data	
Institut/company/laboratory	Ineris
Country	France
Contact	Cécile RAVENTOS
Mail contact	cecile.raventos@ineris.fr
Date of transmission data	January 2023
Purpose of the ILC	
To test the capability of the EN 1911 to measure new ELVs with acceptable uncertainty	
How the data was obtained	
ILC on Ineris test bench (see Figure 6)	
Conditions for the implementation of ILC	
Date of trials	27 to 29 April 2021
Number of participants	9
Number of tests	15
Duration of each test	60 min
Number of measurement lines	2 independent sampling systems implemented by each participant => 18 sampling lines
Number of measurements and samples	15 x 2 = 30 measurements by each participant 9 x 2 measurements for each trial Duplicate analysis of each sample under repeatability conditions 15 x 2 x 2 x 9 = 540 results In fact 540 + 60 results = 600 results because 1 participant doubled his sampling lines to send his samples to 2 different analytical laboratories
Characteristics of the matrix	HCl concentration: 2.4 to 12.9 $mg.m^{-3}$ at 273.15 K / 101325 Pa/dry Oher doping: NH_3/SO_2
Data processing	- In accordance with standards ISO 13528 / ISO 5725-2 / ISO 5725-5 Assigned value = reference value for each trial: robust mean calculated from the participants' results and according to ISO 5725-5 Calculation of half confidence intervals and biases of participants - In accordance with Statistical treatment based on Eurachem Guide/Citac “Measurement uncertainty arising from sampling“. Evaluation of the sampling and the analysis contributions in repeatability

Type of results	For each trial: - Robust mean - Half confidence interval of repeatibility - Half confidence interval of reproducibility - Biases for ech trial and each sampling line of each participant - For each participant, the sampling and the analysis contributions in repeatability on average, for 15 trials Other data: - Field blanks, absorption efficiency - Metadata: > description of sampling lines > analysis method of solutions > analysis and measurement LoQ of each sampling and analytical laboratory > analysis and measurement uncertainties of each sampling and analytical laboratory analysis calculated by budget uncertainty approach
Other information	Each participant sent their samples to the analytical laboratory they usually work with

Figure 10: Ineris test bench

5.2 Main conclusions

- Temperature is a parameter that has a strong influence on the results in case of the presence of compounds that can lead to the formation of salts like NH_3. The temperature chosen should consider the risk of salt formation that could lead to measurement bias, and it is important to avoid any cold spots in any part of the sampling system that is not flushed.
- Comparison of expanded uncertainties provided by participants from GUM approach and calculated from ILC (1/2 half confidence interval of reproducibility):
  - GUM approach leads to expanded uncertainties that comply with the standard's criterion: < 30 % of concentration.

    Whereas ILC approach leads to ½ IC95 > 30 % of concentration: see Figure 11.

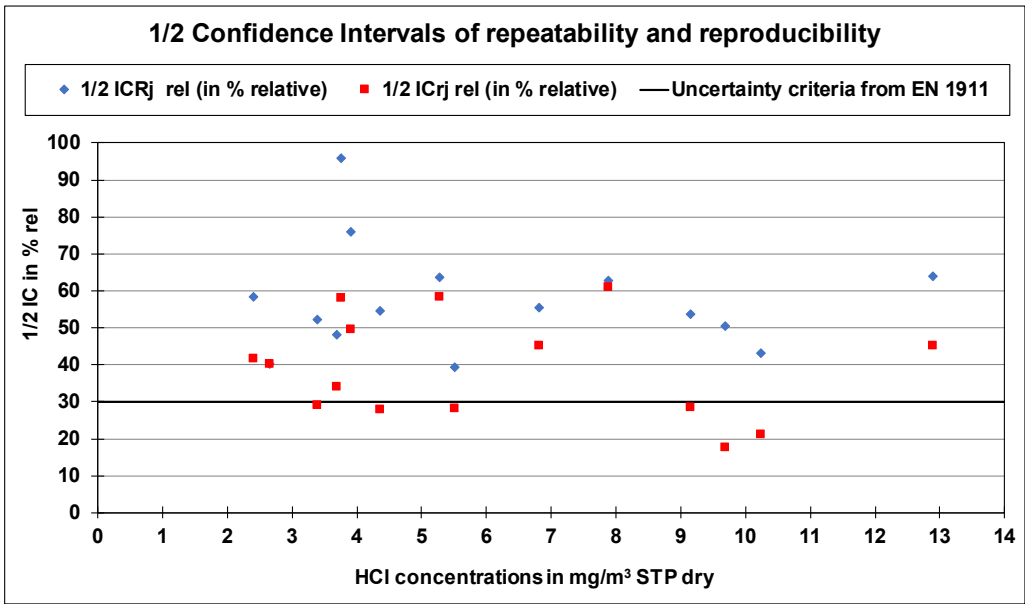


Figure 11: Half confidence intervals of repeatability and reproducibility

- Some uncertainty components are not modelled in the GUM approach: e.g. human factor.

  Some implementation biases are not modelled in the GUM approach: e.g. risk of salt formation in the presence of ammonia, loss in case of condensation.
- The GUM approach evaluates uncertainty for one measurement / implemented by one measurement laboratory / using one equipment / with analysis of the solutions by an analytical laboratory: configuration corresponding to the one implemented during periodic monitoring,

  whereas the ILC approach evaluates the variability for one measurement / implemented by several measurement laboratories, using different equipment's with variable performance / with analysis of the solutions by several analytical laboratories: configuration which does not quite correspond to the implementation of an on-site control.
- Analyses uncertainties declared by participants were equal for the 15 tests for most participants: one can wonder if that was really the case.

  Analyses uncertainties need to be refined to improve the estimation of measurement uncertainties, as already noted in §2.2.
- In the GUM approach, contribution of analysis in measurements uncertainties varies between participants. The ILC approach seems to show that for HCl this contribution of analysis to the repeatability is limited and that the measurement bias is more related to sampling.

- Need to estimate the uncertainty for the analysis step, and not just repeatability as required in actual EN 1911.

  Moreover, in France, analytical laboratories shall estimate the analytical uncertainty at least three concentration levels of the validated concentration range [$LoQ_{analysis}$ - C_{max}].
- Setting an uncertainty criterion only in relative terms is not appropriate for the lowest concentrations as some sources of uncertainty are not proportional to concentration. In the French Standard NF X 43-551, a concentration threshold below which the uncertainty criterion is expressed in $mg.m^{-3}$ and is therefore constant; has been defined: if concentration is < 5 $mg.m^{-3}$, expanded uncertainty criterion is < 1.5 $mg.m^{-3}$.

6 Testing of the implementation of the measurement method EN 1911 on industrial site

6.1 Metadata

Measurement tests tests of implementation of the EN 1911 method on industrial, was organized by VTT. Metadata about organisation of the ILC are given in Table 6.

Table 6: Metadata related to the implementation of the EN 1911 method on industrial site

Origin of the data	
Institut/company/laboratory	VTT Technical Research Centre of Finland
Country	Finland
Contact	Tuula Pellikka, Tuula Kajolinna
Mail contact	tuula.pellikka@vtt.fi; tuula.kajolinna@vtt.fi
Date of transmission data	January 2023
Purpose of the tests	
Aim was to measure on real field circumstancies the HCl concentrations using two lines of EN1911 and two lines of P-AMS FTIR (Gasmet Dx4000), and to compare the results	
How the data was obtained	
Tests on industrial site: plant localized at Southern Finland	
Conditions for the implementation of tests	
Date of trials	20 to 22 April 2021
Number of sampling lines	4 : 2 for EN 1911 and 2 for P-AMS FTIR
Characteristics of sampling lines	- Non-isokinetic sampling - “Main stream” approach - Heated probe (20°C above the stack gas temperature) - Out-stack filter, quartz filter, 47 mm - After the heated probe, non-heated PTFE-lines were used. These lines were rinsed after each sampling and the rinse was added to the first impinger - Absorber type: ”normal”, volume of the absorption solution used ~80 ml
Number of tests	8
Duration of each test	30 min (EN1911 sampled gas volume ~ 120 l)
Number of measurement lines	2 independent sampling systems implemented by each participant => 18 sampling lines
Number of samples/measurements	8 tests x 4 lines/test = 32 samples (+ efficiency tests of EN 1911)
Characteristics of the matrix	Fluegas:. Fuel 70% biomass + 30% coal and peat Temperature ~140°C HCl concentration measured: 4-11 $mg.m^{-3}$ Ammonia was not present in the flue gas SO_2 levels: ~35- 40 ppm Moisture: 19-20 % O_2: 4,5- 5,1 % (dry)
Type of results	HCl concentration as $mg.m^{-3}$ at NTP dry (NTP 101.3 kPa, 0°C)
Other information	For EN1911 the sampling flowrate between 3 and 5 l/min was used. Sampling flowrate to each P-AMS was 4 l/min

6.2 Main conclusions

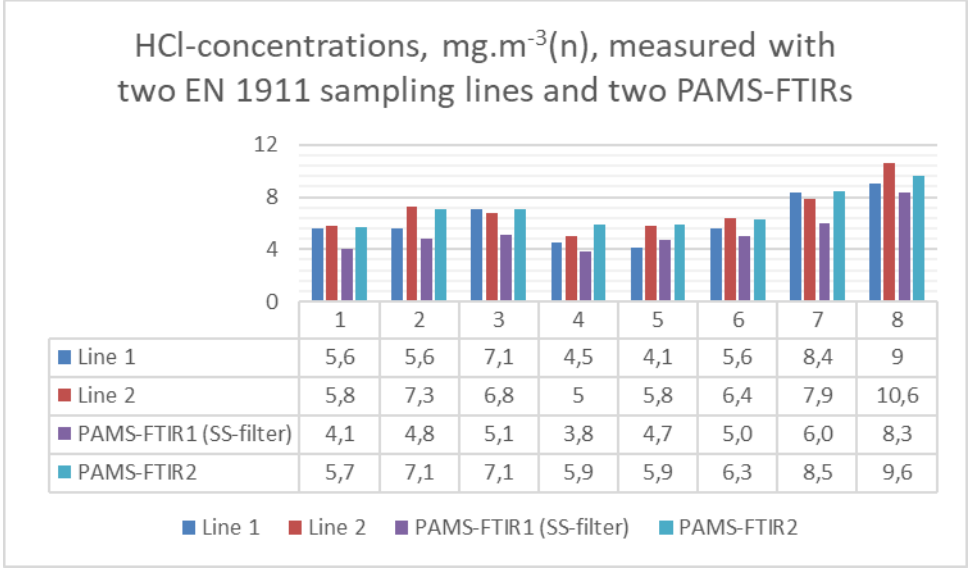
Conditions of implementation of EN 1911 method and quality controls:

- Same impingers and sampling lines were used one day, then changed to new ones.
- Leak tests were performed before the measurements and also, during the sampling, by measuring O_2 at the end of the sampling line.
- Field blanks were taken before and after the measurements in order to test if any HCl was left in the impingers.

  There were below LoQ both before and after the sampling which means that the rinsing efficiency was good: according to chapter 5.3.3.3 in EN 1911, the glassware can be re-used after rinsing.
- Absorption efficiency was checked once during the measurement campaign.

  For both lines, the last absorber concentrations were < LoQ: results were in conformity with the criterion of the EN 1911 standard.
- Measurement uncertainties:
  - Measurement uncertainty for chloride analysis (by EN ISO/IEC 17025 accredited laboratory) was 22 %, with the 95 % confidence level (k=2)
  - EN 1911 measurement uncertainties during field measurements were ~ 45 %, calculated for the measured concentrations
  - If ELV would be 8 mg.m^{-3}, the criteria set at EN 1911 for the measurement uncertainty (max. 30 %) is not filled anymore.

Measurement results of EN 1911 method and of FTIR are summarized in Figure 12.



	1	2	3	4	5	6	7	8
Line 1	5,6	5,6	7,1	4,5	4,1	5,6	8,4	9
Line 2	5,8	7,3	6,8	5	5,8	6,4	7,9	10,6
PAMS-FTIR1 (SS-filter)	4,1	4,8	5,1	3,8	4,7	5,0	6,0	8,3
PAMS-FTIR2	5,7	7,1	7,1	5,9	5,9	6,3	8,5	9,6

SS: stainless steel

Figure 12: Measurements results

Based on this data sets, both sampling lines for EN 1911 seem to give uniform results.

7 Data repository

The data from the work presented in the previous chaptersare available in the Zenodo repository and can be accessed through the following location DOI: 10.5281/zenodo.7576450.

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