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Validation methods for fire gas analyses —

Part 2: Intralaboratory validation of quantification methods

Méthode de validation des analyses de gaz d'incendie —

Partie 2: Validation intralaboratoire des méthode de d'analyse

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Foreword

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The procedures used to develop this document and those intended for its further maintenance are described in the ISO/IEC Directives, Part 1. In particular the different approval criteria needed for the different types of ISO documents should be noted. This document was drafted in accordance with the editorial rules of the ISO/IEC Directives, Part 2 (see www.iso.org/directives).

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For an explanation on the meaning of ISO specific terms and expressions related to conformity assessment, as well as information about ISO's adherence to the World Trade Organization (WTO) principles in the Technical Barriers to Trade (TBT) see the following URL: www.iso.org/iso/foreword.html.

The committee responsible for this document is ISO/TC 92, *Fire safety*, Subcommittee SC 3, *Fire threat to people and the environment*.

A list of all parts in the ISO 12828 series can be found on the ISO website.

Introduction

The reduction of human tenability from fire effluent has long been recognized as a major cause of injury and death in fire. The composition and concentration of the effluent from a large fire are also clearly key factors in determining the potential for harm to the environment. The harmful components of fire effluent can be determined from both large-and small-scale tests of materials and finished products. Equations have been developed for quantifying the effects of the effluent components, for example, to estimate the available safe egress time (ASET). Related documents are also being developed in ISO TC92 SC3 which deal with environmental threats from fire effluent.

These advances in fire science and fire safety engineering have led to an increasing demand for quantitative measurements of the chemical components of the fire effluent. Characterizing these measurements is a key factor in evaluating the quality of the quantitative data produced. Such a characterization is developed over four items.

Item 1: Define the objective of the analysis. Before undertaking a chemical analysis of fire effluent, the final objective of the analysis should be established. For example, the objective might be part of a fire safety engineering design of a building, validation of a numerical fire model, or determination of the toxic potency of the effluent from a particular combustible item.

Item 2: Determine the degree of accuracy and precision required from the analysis. Accuracy is dependent on a combination of the physical fire model being used, the sampling of the effluent and the analytical chemical technique. Precision means the tolerable uncertainty in the measured result. For example, in an FED (Fractional Effective Dose) calculation, where the individual contribution of a range of different species to the overall toxic potency of a fire effluent is estimated, interest might range from concentrations which might incapacitate people of average sensitivity to the effluent, to concentrations which show negligible toxic effect over a long exposure period.

Item 3: Select the appropriate chemical analytical methods, considering specificity, i.e. the other gases present. Guidance on options for measuring a wide variety of chemical species is provided in ISO 19701 and ISO 19702.

Item 4: Evaluate the suitability of the chosen method considering specificity. For chemical analyses, as with any other measurement, it is important to evaluate a specific methodology for its ability to provide appropriate, sufficient, and adequate data for a particular application. This evaluation normally has to consider a range of factors, including repeatability, reproducibility, and a measurement of uncertainty, especially for laboratories working under ISO 17025 rules. For fire effluent toxicity, these properties are discussed in ISO 19706.

Different methods may be deemed suitable for the particular application and for consistency in the interpretation of results from these different methods, it is also important to be able to compare the validity of the analytical technique used. In the field of fire effluents, many factors can affect the trueness and the fidelity of a measurement technique.

Validation methods for fire gas analyses —

Part 2:
Intralaboratory validation of quantification methods

1 Scope

This document describes tools and techniques for use in validating the analysis of fire gases when an analytical method is developed in a laboratory. It complements ISO 12828-1, which deals with limits of quantification and detection.

The tools and techniques described can be applied to the measurement of quantities, concentrations (molar and mass), volume fractions, and concentration or volume fraction versus time analyses. Fire effluents are often a complex matrix of chemical species, strongly dependent on the materials involved in the fire, but also dependent on fire scenario parameters (see ISO 19706). With such a wide variety of conditions, the analytical techniques available will differ in terms of the influence of the matrix on the methods and on the concentration ranges which can be measured. The analytical techniques available are likely to differ significantly in several respects, such as their sensitivity to the matrix and the range of concentrations/volume fractions which can be reliably measured. For these reasons, a unique reference analytical technique for every fire effluent of interest is, in practical terms, difficult or impossible to achieve. The tools in this document allow verification of the reliable measurement ranges and conditions for the analysis of fire effluents, thereby enabling a comparison among various analytical techniques.

Examples of existing International Standards where the information contained in this document can be used are the analytical chemical methods in ISO 19701, ISO 19702, ISO 5660-1, and the chemical measurements in the methods discussed in ISO/TR 16312-2, ISO 16405, or their application to fire toxicity assessment using ISO 13571 and ISO 13344.

NOTE 1 The variable “concentration” is used throughout this document, but it can be replaced in all places with “volume fraction” without altering the meaning. This does not apply to the Annexes.

NOTE 2 Concentration can be calculated from volume fraction by multiplying by the density of the relevant gas at the relevant temperature and pressure.

2 Normative references

The following documents are referred to in the text in such a way that some or all of their content constitutes requirements of this document. For dated references, only the edition cited applies. For undated references, the latest edition of the referenced document (including any amendments) applies.

ISO 12828-1:2011, *Validation method for fire gas analysis — Part 1: Limits of detection and quantification*

ISO 5479, *Statistical interpretation of data — Tests for departure from the normal distribution*

3 Terms and definitions

For the purposes of this document, the terms and definitions given in ISO 13943, ISO 5725-1, ISO 2854, ISO 2602, ISO 13571 and the following apply.

ISO and IEC maintain terminological databases for use in standardization at the following addresses:

— IEC Electropedia: available at http://www.electropedia.org/

— ISO Online browsing platform: available at https://www.iso.org/obp/

3.1
matrix (of fire effluents)
mixture of fire effluents in which the analyte of interest is present

Note 1 to entry: This includes all other species, solid, liquid and gas phases. It constitutes all components that could affect analysis, such as interfering species.

4 Symbols and abbreviated terms

y_0	Actual concentration of an analyte in a fire effluent
y_1	Concentration just after extraction by the sampling probe
y_2	Concentration after transportation to the conditioning system
y_3	Concentration at the entrance of the sensor
y_4	Concentration read by the sensing apparatus
$X_1 = y_0/y_1$	Sampling ratio; Because of the effectiveness of the sampling probe, X_1 might be more than 1 (see 6.2 for details)
$X_2 = y_1/y_2$	Transportation ratio (see 6.3 for details)
$X_3 = y_2/y_3$	Conditioning ratio; X_3 might be more than 1 (see 6.4 for details)
$X_4 = y_3/y_4$	Analysis ratio; X_4 might be more than 1 (see 6.5 for details)
y_m	Reported concentration of an analyte in the gas phase
y_i	One of a number of y_m values in a group
b_0	Zero order coefficient term in a regression; For a linear regression, b_0 is the intercept
b_1	First order coefficient term in a regression; For a linear regression, b_1 is the slope
b_2	Second order coefficient term in a regression.
$\hat{y}_i$	Predicted value for y_i, given by application of a regression model
$\bar{y}_i$	Mean value for y_i
p	Total number of measurements
df	Degrees of freedom; According to the context, several degrees of freedom could be defined
SCE	Sum of squares of deviations between measured values y_i and mean value $\bar{y}_i$
MS	Median square, corresponding to SCE divided by df

5 General considerations

5.1 Actual concentration and measured concentration

The objective of every chemical analysis used in fire science is to approach the actual concentration of an analyte, y_0, in fire effluents. The value of y_0 is unknown, as the only value measured is the concentration

y_m. The concentration y_m is affected by the measurement trueness and precision (uncertainty) of the chosen analytical technique

The difference between y_0 and y_m could be significant, depending as it does, on the measurement technique chosen. For fire gas analyses, there could be many alternative analytical techniques available, (see ISO 19701 and ISO 19702 for examples). Stages of the analytical procedure which could affect the measurement are sampling (e.g. probe design and temperature), transportation (e.g. size, length and temperature of sampling lines), conditioning of sample (e.g. filtration, drying), and the analysis efficiency. This last factor could be integrated in the trueness of the analytical technique. The different steps of this analytical process of fire effluents and the associated efficiencies are presented in Figure 1.

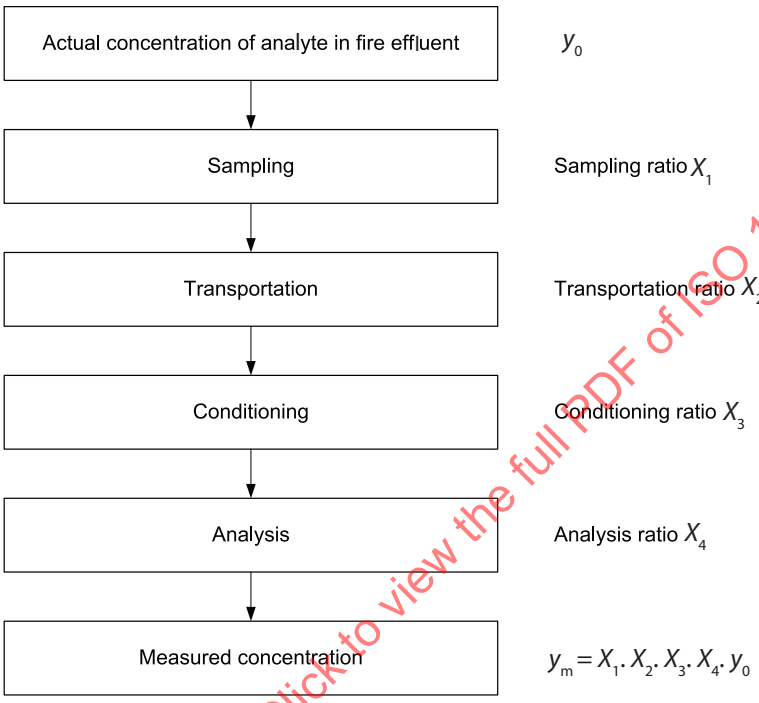

Figure 1 — Measurement ratios

5.2 Selection of analytical methods with respect to the physical fire model used

The selection of a physical fire model has an influence on the composition of the effluent, the concentration of individual components in the effluent and variations of effluent concentration with time. These parameters imply that the choice of an analytical method for fire effluents will depend on the physical fire model that produced the effluent. An analytical method validated by using a given physical fire model may therefore be of limited use with another physical fire model. See ISO 19706 and ISO 16312-1 for further details on the selection of physical fire models.

5.3 Validation of analytical techniques

Fire effluent from accidental fires is typically very specific matrix, characterized by a constantly changing and very wide range of chemical species and their concentrations. Some analytical techniques commonly used for combustion gas analysis are not suitable in the case of accidental fires. The selection of a technique with a wrong selectivity for example could lead to erroneous conclusions in a safety assessment. For example, the measurement of incinerator stack composition using solid-state detection techniques would be too limited in selectivity for use in a fire atmosphere safety assessment.

The conditions under which the analytical method is used in practice shall not differ from the conditions used to validate the method. This document proposes different steps to be followed and different techniques from those used in combustion gas analysis in order to validate that an analytical technique

could be applied specifically and meaningfully to fire effluents. The validation is therefore limited to the specific nature of a matrix and range of concentrations within the matrix.

Due to the variety of physical and chemical principles used in the analysis of fire effluents (see ISO 19701 and ISO 19702), the technique and its range of application shall be rigorously defined and selected. Figure 2 illustrates the different steps required to validate an analytical technique. Figure 3 illustrates the different steps required to compare two analytical techniques.

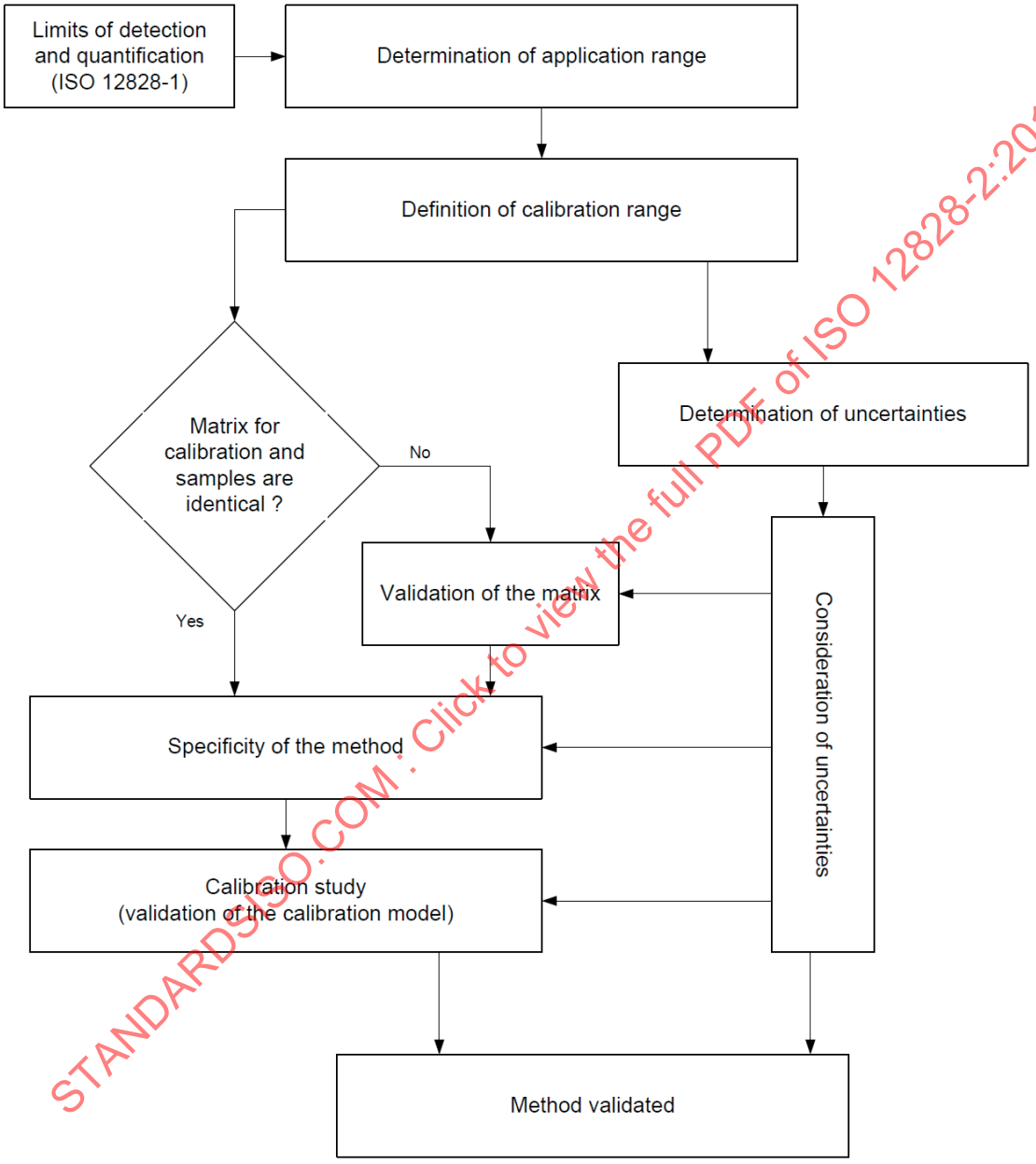

Figure 2 — Steps in validating an analytical technique

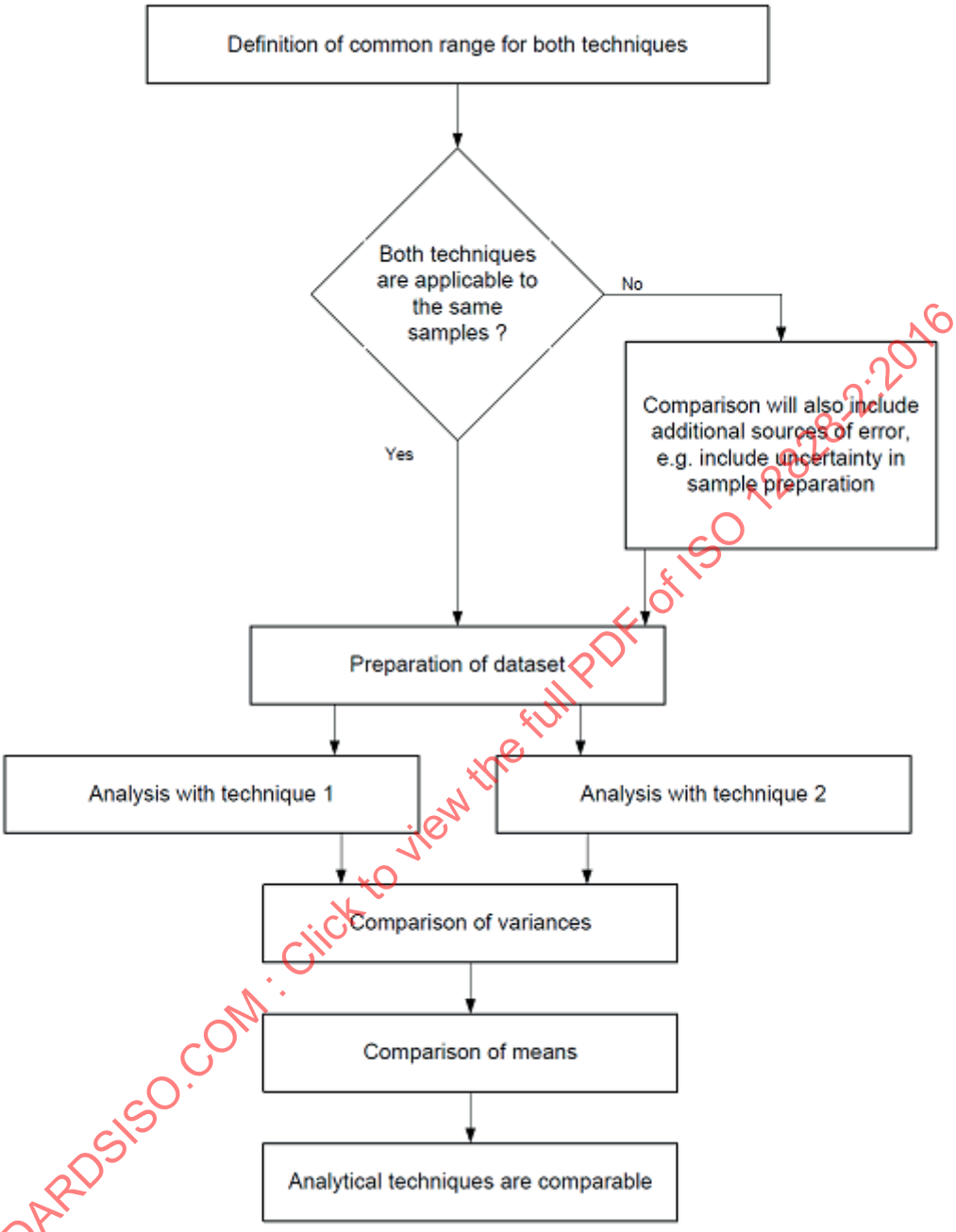

Figure 3 — Steps in comparing two analytical techniques

6 Sampling and measurement effectiveness

6.1 General considerations

Fire gases are a complex mixture of water, reactive/corrosive species, condensable species, aerosols, hygroscopic components and are usually in the presence of solid particles which may adsorb or absorb gases to a varying degree. The gases may be at temperatures between ambient and over 1 000 °C at the sampling point. This makes the sampling and analysis of fire effluents generally a difficult process requiring much attention to best practice procedures (e.g. as provided in ISO 19701).

The analysis can be performed *in situ* or with an extractive sampling technique. Quantification can be time-resolved or cumulative, depending on the end-use requirements for the data.

For the purposes of quantification, it should be recognized that in such a mixture, there is much scope for losses from a variety of causes. In any validation process of an analytical method, great care should be exercised to ensure that these losses are properly taken into account especially where there is a chemical or physical modification of the analyte between sampling point and analysis point. This is of particular importance with extractive sampling methods.[9]

6.2 Sampling probe

Sampling of fire effluents prior to their analysis should be carefully considered to ensure a representative sample is ultimately delivered to the analyser. The first part of a typical sampling system is the sampling probe, positioned in the effluent. The design of a sampling probe for fire gas analysis should allow the required portion of the effluent to be passed on to the sampling line. The probe may be a simple open-ended tube where the effluent stream is homogenous or may require holes along its length to allow for non-homogeneity. The location and diameter of the holes are supposed to be designed so that the sampling is indicative of the full effluent flow. Since the temperature, density and mixing of the flow can vary during a test, the assumption of representative sampling has limitations.

In general, to limit flow disturbances, the sampling flow rate shall be low in comparison with the effluent flow rate, and shall limit added turbulence. Some bench-scale systems require a complete sampling of the effluent.

Ideally, the sampling point will be in a known position with respect to the fire source in a location where temperature conditions are measured and where the effluent flow is as homogenous and representative as possible. Clearly, these conditions will sometimes not be met. In some cases, the sampling probe may have to be heated to avoid or reduce condensation. It could also be designed to limit soot particulate deposits (e.g. by incorporating a microcyclone device). Where an extractive method is used for aerosol sampling, isokinetic techniques shall be used (i.e. with the sampling velocity made equivalent to the aerosol flow velocity, see ISO 29904).

However, all these systems will have a limited efficiency, and technical choices are made in order to have X_1 close to 1.

6.3 Transportation of effluent from sampling probe to analysis system

Between sampling point and analysis point, effluent may be transported along a sampling line, trapped in a gas bag or passed through trapping solutions or solid adsorbates. The materials in contact with the sample should be carefully chosen to reduce losses, for example, through chemical reactivity, and the temperature conditions in the sampling line should be carefully chosen to avoid losses through condensation and/or further chemical reaction. The flow velocity shall be as high as possible (consistent with an extraction rate which will not disturb the effluent stream) to minimize losses due to adsorption on surfaces.

For example, some species such as HBr have an important tendency to be physically trapped and released by surfaces of sampling lines. This affects the kinetics of the analysis, and can result in prolonged delivery of the species to be analysed with a consequent spreading of detector response. Materials such as stainless steel, epoxy-lined stainless steel, glass (not where HF is present) or PTFE are often used.

With sampling line temperatures, the main factors to consider are the temperature of the gas itself and the temperature of the sampling line surfaces. Temperature is often chosen high enough to limit condensation of water, but also of other condensable species such as formaldehyde. Nevertheless, a too high temperature will affect the composition of the transported gas, as it is a reactive mixture, and increases in temperature will accelerate many reactions. A range from 150 °C to 200 °C has been found suitable for the large majority of extractive gas analysis methods used with fire effluents (ISO 19701, ISO 19702), but analysis of some non-hygroscopic gases such as NO, CO or CO_2 could be performed with sampling lines at ambient temperatures.

Because of transportation delay and the thermodynamic conditions, effluent could also react between the sampling point and the analyser and its composition could be modified. This phenomenon is particularly sensitive for gas bag sampling, and for species such as NO_x. The main influencing parameters here are temperature and time. It should be appreciated that the validation of various sample transportation methods is only valid where the sampling systems have similar intervals between times between sampling and analysis and are at similar temperatures.

6.4 Conditioning of the effluent

Effluent is often conditioned between the sampling point and the analysis point. The sampling line may be placed either before or after the conditioning procedure, or the conditioning could be performed in various steps, e.g. pre-filtration before the sampling line then final filtration after the sampling line.

Depending on the analytical technique used (See ISO 19701 and ISO 19702), conditioning may consist of filtration to remove soot from the effluent and/or a water trap. The water trap could be based on physical drying (i.e. through cooling) or chemical drying (e.g. calcium chloride, silicone oxide). Other gas traps could be used, such as a CO_2 remover (e.g. sodium hydroxide).

Some conditioning systems also include procedures to remove specific species, which could interfere with the analysis technique, but care should be exercised to ensure that other (wanted) species are not affected. For example, chemiluminescence analysers use converter ovens to convert NO_2 into NO before analysis. This operation has a limited efficiency, depending on the technique and design of the oven. For a suitable analysis of the NO_2 fraction in a NO_x mixture, the efficiency of the oven should be determined.

All conditioning systems have a limited and variable efficiency. For example, a gas of interest could be partially adsorbed on filters. The filter could be analysed after test (see ISO 19702), but the kinetic information is partially lost. Hygroscopic gases (HCl, HBr, HF, SO_2, NO_2) and gases with a high reactivity are particularly sensitive to such losses.

Conditioning systems should, therefore, be studied before use to determine the effects on the quantification of each analyte of interest. In addition, it is essential to check how the conditioning system modifies the effluent as a whole. This also includes the effects the conditioning system may have on the sampling flow rate. A quantification of the mass loss in the effluent stream from sampling point to analyser shall be determined.

6.5 Measurement technique

No measurement technique is perfect. Analysers are selective with variable sensitivity depending on the mix of species present. Calibration with “pure” gases may not take into account the effects of the other species in the matrix of compounds in the effluent being measured.

In addition to these effects, the response time from the sampling point to the end of the analysis has to be considered. This response time is an important characteristic of the system. In a dynamic measurement system, the transfer function of the system (i.e. a measure of the time required to achieve a given proportion of the species of interest at the analyser) could be a crucial parameter. A simple way to approach it is the time needed between 10 % and 90 % of the value for a single concentration measurement, as described for FTIR in ISO 19702. However, this parameter is not sufficient to fully characterize the response time in dynamic analysis conditions, as it doesn’t cover the transfer function of a particular apparatus.

7 Validation steps

7.1 General

Details on the different validation techniques outlined in this document are available in References [11], [12] and [13]. Figure 4 gives indications on validation sequence and related clauses.

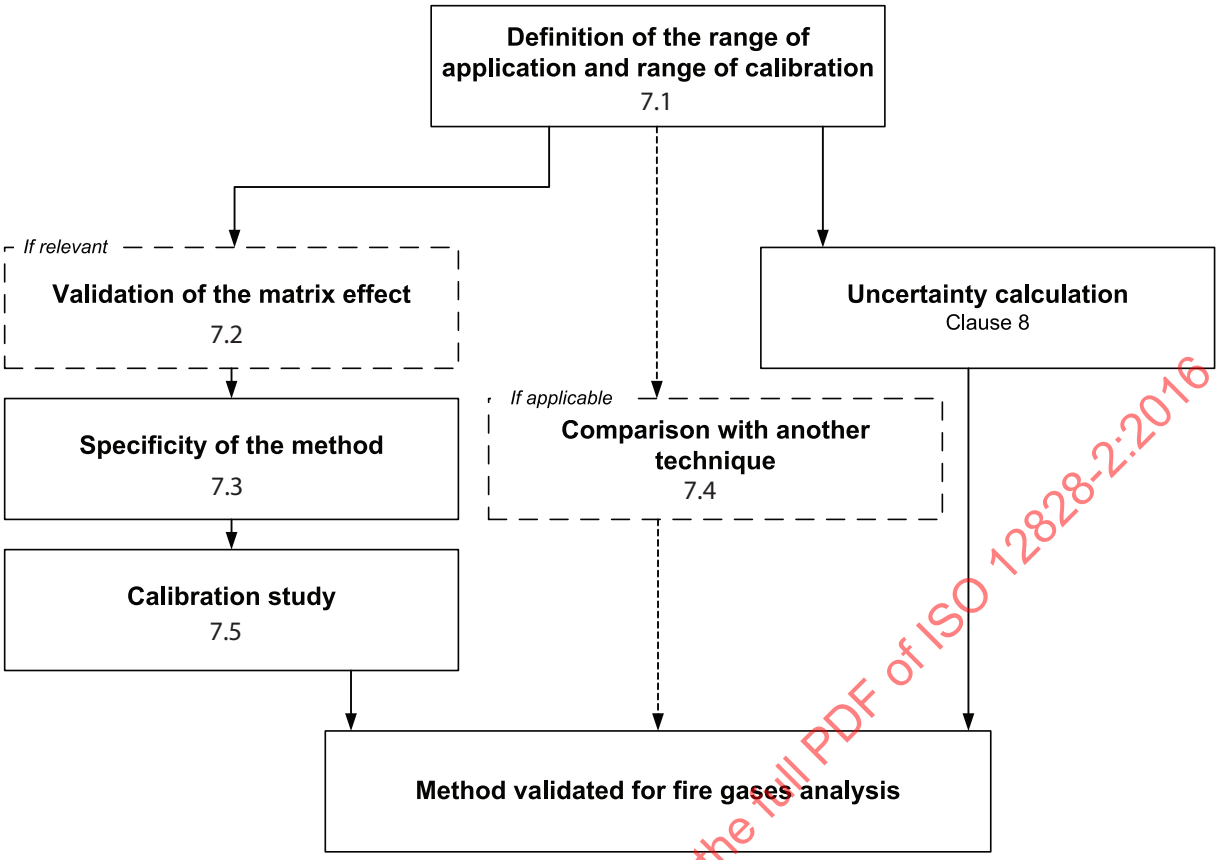

Figure 4 — Guidance on validation steps

7.2 Definition of the range of application and range of calibration

An analytical technique is only applicable over the range of conditions used for calibration – and then only when the tests for calibration validity have been successfully carried out.

The lower limit of the range of application shall be determined according to ISO 12828-1. ISO 12828-1 describes various techniques for use in different applications. Methods described in ISO 12828-1:2011, 6.2 and 6.3 allow the determination of the physical limits of detection and quantification of an analyte. The method described in ISO 12828-1:2011, 6.4 provides a check on whether a given value is within an acceptable range. For example, this method is suitable for validating the lowest value of a set of calibration data, confirming it is a fully quantifiable value.

The highest value of a set of calibration data often provides the upper quantification limit of the analytical device. No measurements higher than this value shall be performed. The upper limit of a range of calibration is fixed by the sensitivity of the analytical method. Some analytical instruments exhibit spurious behaviour with high concentrations of analyte. An example is where the detector becomes progressively saturated leading to a loss of sensitivity and possibly a complete lack of response as the concentration of the analyte increases further. Beyond these points, the calibration model becomes unusable and the tests given in 7.6 shall be used to determine if the upper point of the calibration is still suitable.

NOTE The calibration points are selected on the basis of the characteristics of the measuring instrument and the practical technique used. In general, a data set consisting of 5 to 10 different analyte concentrations distributed uniformly over the required measurement range is suitable. This distribution can be chosen in the absence of knowledge of the actual calibration model to be used. For analytical instruments whose calibration model is known, e.g. where a perfectly linear relationship between concentration and detector output exists over the calibration range, a data set consisting of low and high values plus checkpoints for intermediate values is statistically more appropriate.

It is recommended that analysis is confined within the limits of 10 % to 90 % of the calibration range.

7.3 Validation of the independence from the matrix effects

The matrix on which the analyte of interest is present may influence the concentration measured. A simple technique to evaluate the influence of the matrix is to test several different matrixes containing the analyte, and to compare the results obtained.

An example of procedure is as follows.

— Produce several blank samples – i.e. various typical matrices but without the species of interest being present.

— For each matrix, add a known quantity of the analyte of interest. Repeat so as to produce a range of added quantities.

— The added quantities shall be the same, within acceptable limits, for each matrix.

It shall be emphasized that the blank matrixes shall have no trace of the analyte of interest, but shall retain a similar mix of species apart from the analyte of interest. Such a suitable blank can be difficult to obtain.

An example of determination of the specificity of the chosen method is given in A.2.

7.4 Validation of the specificity of the chosen method

7.4.1 General

Fire effluents may contain hundreds of chemical species, some of which are very similar chemically to others, e.g. aldehydes, and ketones. Depending on the analytical method used, some species could have a positive or negative interference on the measured quantities of similar species. The analytical method selected should, therefore, be chosen to be specific to the analyte required. To ensure such specificity, a range of analytical techniques may have to be studied.

An example of determination of the specificity of the chosen method is given in A.3.

7.4.2 Simple method

A simple technique to validate the specificity of the method is as follows.

— First, produce a representative sample of fire effluent, e.g. smoke from a physical fire model or in a trapping solution obtained from a fire test.

— Second, analyse it for the species of interest and then separate the sample in two parts.

— Third, add known quantities of the species of interest in one of these two parts, then analyse these samples for the species of interest. The difference between measurements shall be equal to the quantity added, allowing for experimental error.

— Fourth, add various quantities to the other part of the matrix of chemical species that could also be encountered and that could interfere. The selection of these interfering species shall be done with regard to the application, the expected species present in the smoke, and the limitations of the analytical technique chosen. The influence of these interfering species is evaluated as a sensitivity factor on the variation observed for analysis of the species of interest. Note that interference could be positive or negative.

NOTE ISO 19701:2013, Annex A gives a list of analytical techniques that are not suitable with fire effluents, even if they are commonly used for combustion gases.

7.4.3 Quantitative method

7.4.3.1 Quality of separation

For chromatographic methods, such as described in ISO 19701, the quality of separation between two analytes can be expressed as a specific resolution between two adjacent peaks. The resolution for each set of two consecutive peaks shall be calculated according to Formula (1). If the resolution is higher than or equal to 0,6, then a qualitative analysis is possible. If the resolution is higher than or equal to 1,5, then a quantitative analysis is possible.[13]

$$R_s = 1{,}18 \times \left(\frac{t_2 - t_1}{w_2 - w_1} \right) \quad (1)$$

where

R_S resolution of the chromatographic method for two consecutive analytes (i.e. adjacent peaks);

t_1 and t_2 retention times for the two consecutive analytes;

w_1 and w_2 width at half height retention times for the peaks given from two consecutive analytes.

7.4.3.2 Determination of degree of specificity

The goal of this step is to check that the method has a sufficient specificity for the selected component to be analysed. The study of specificity is carried out with samples representative of the usually analysed samples.

For each analyte, the analytical instrument is first calibrated. Then, a series of samples containing increasing concentrations of the analyte is prepared. This series shall cover the whole range of expected concentrations for the particular application. The best straight line $r_i = f(v_i)$ is plotted, where r_i is the analytical result for samples of a known concentration v_i. This equation is a linear regression of the form $r_i = b_1 * v_i + b_0$. Statistical tools then allow a check to establish if $b_1 \approx 1$ and $b_0 \approx 0$. If these two conditions are simultaneously met, then the selectivity for the analyte is acceptable.

The calculations to be performed are given in Formula (2) for the residual standard deviation $s(e)$, in Formula (3) for $s(b_1)$, the standard deviation on b_1 and in Formula (4) for $s(b_0)$, the standard deviation on b_0. p is the total number of measurements performed.

$$s(e) = \sqrt{\frac{\sum_{i=1}^{p} \left(r_i - \hat{r}_i \right)^2}{p - 2}} \quad (2)$$

$$s(b_1) = \sqrt{\frac{s^2(e)}{\sum_i \left(v_i - \bar{v} \right)^2}} \quad (3)$$

$$s(b_0) = \sqrt{s^2(e) \left(\frac{1}{p} + \frac{\bar{v}^2}{\sum_i \left(v_i - \bar{v} \right)^2} \right)} \quad (4)$$

The test performed to check if b_1 is sufficiently close to unity is a unilateral Student's t-test for 3° of freedom with a 95 % confidence, according to Formula (5).

For an acceptable result, t_{obs} shall be less than the t value.

$$t_{obs} = \frac{|b_1 - 1|}{s(b_1)} \quad (5)$$

The test performed to check if b_0 is sufficiently close to zero is a unilateral Student's t-test for 3° of freedom with a 95 % confidence, according to Formula (6).

For an acceptable result, t'_{obs} shall be less than the t value.

$$t'_{obs} = \frac{|b_0|}{s(b_0)} \quad (6)$$

7.5 Influence of the measurement technique on results

7.5.1 Generalities

A species of interest could be suitably measured by different analytical techniques, based on various physical and chemical principles. As an example, ISO 19701 proposes two or three techniques for a large number of species of interest (see ISO 19701:2013, Table 1). In addition, several of these gases could also be analysed with FTIR according to ISO 19702.

For a given analytical species and a given application (e.g. physical fire model), these techniques are not, however, equivalent in terms of scope or response, or may have a different concentration range of application.

Sometimes, a technique is also referred to as "reference technique," usually perceived as the best method for a particular species in terms of specificity and quantitative accuracy. Tools are then needed to validate an alternative technique (which may be easier and/or cheaper to operate), by comparison with the reference technique.

Figure 5 details validation steps for the comparison between analytical techniques. Examples of the influence of the measurement technique on the analytical result according to various techniques presented hereafter are detailed in A.4.

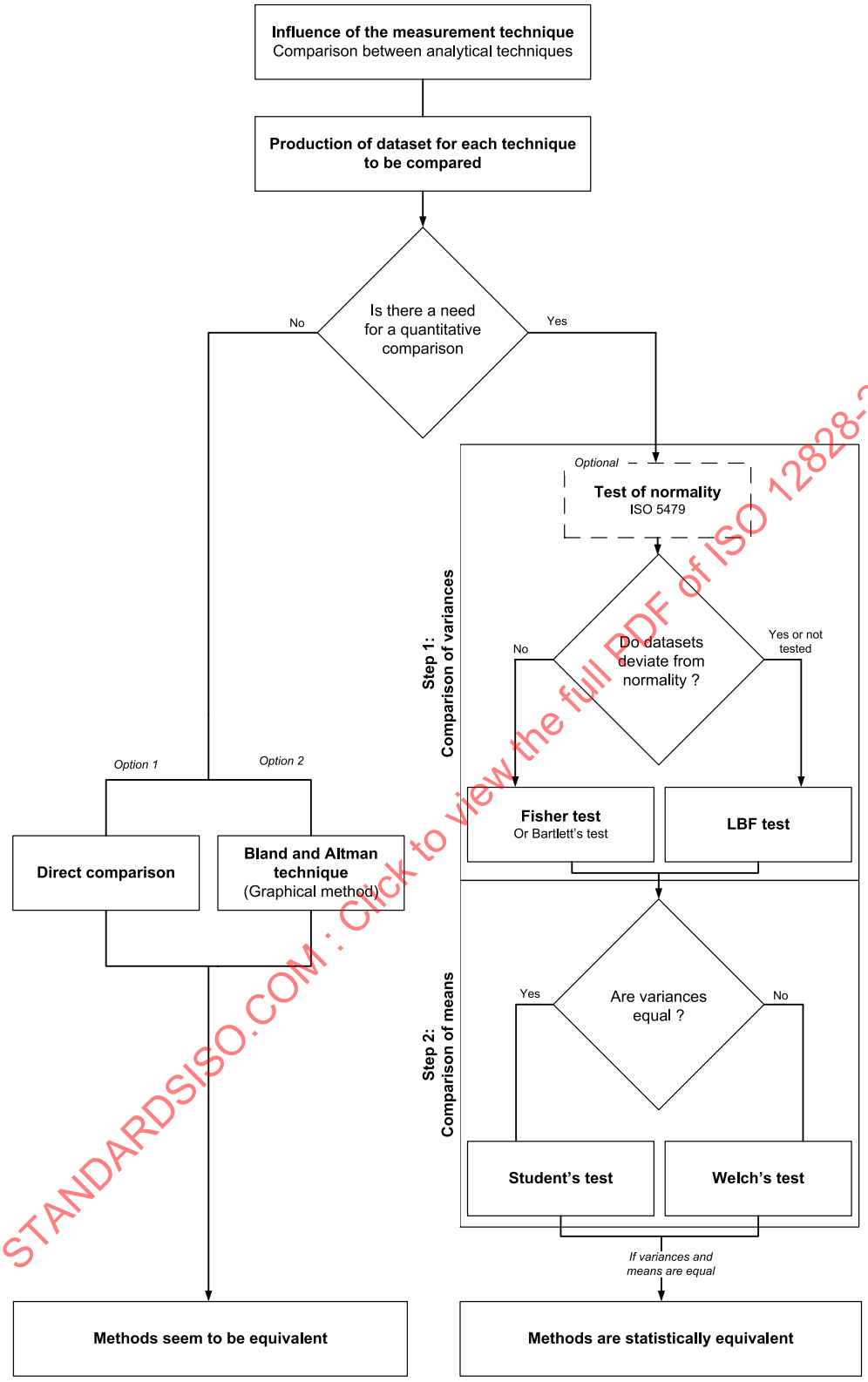

Figure 5 — Guidance on comparison between analytical techniques

7.5.2 Simple methods

7.5.2.1 Direct comparison

The following method is suitable for checking the influence of the measurement technique on results.

— First, select the two analytical techniques to be compared and calibrate the corresponding instruments. It is recommended that the techniques chosen are based on different properties of the analyte. Analytical techniques are normally only capable of measuring different samples in the same phase. A comparison of a gas-phase technique and a solution-based technique using the same equipment is therefore difficult with this method.

— Second, prepare at least five samples of increasing quantities in a representative matrix. The samples have to cover the range of concentrations capable of being measured by the two analytical techniques

— Third, analyse samples on both instruments. The values shall be the same within experimental error.

Results of both devices could be presented as a graph of measurement from analytical technique 1 vs. measurement from analytical technique 2. The linear regression of these data shall have a slope of 1 and an intercept of 0 if the two techniques are to be considered equivalent. Statistical tests proposed in 7.4.3 could be used to demonstrate that slope and intercept are statistically 1 and 0, respectively. An example of application is presented in A.4.2.

7.5.2.2 Graphical method of Bland and Altman

Reference [14] proposes a graphical technique to evaluate the differences between two series of data.

— Proceed as described in 7.5.2.1 to obtain two series of data for each measurement technique to compare, designated as $y_{a,i}$ and $y_{b,i}$.

— Calculate from both series the average of each pair of values, $\bar{y}_i = \left(y_{a,i} + y_{b,i}\right)/2$ and the difference between each pair of values, $d_i = y_{a,i} - y_{b,i}$.

— Calculate the average value $\bar{d}$ and its standard deviation σ_d.

— Plot d_i as function of $\bar{y}_i$ and add to the graph the lines corresponding to $\bar{d}$ and $\bar{d} \pm 2\sigma_d$.

An example of application is presented in A.4.3.

7.5.3 Quantitative method

7.5.3.1 Technique and statistical method

To determine whether two sets of analyses performed with two different techniques are equal or different, statistical tests are carried out, which require the mean value, the standard deviation and the variance to be calculated. Two series of data are then obtained, one for each analytical technique to be compared. Two tests shall then be carried out to verify the equivalence of the two techniques by comparing the variances and the mean values for each.

For comparison of variances, several statistic tests can be used.

— Fisher *F*-test[15] is the most known and simple statistical test for comparison of variances. This test supposes that variables are normal. However, checking normality (see ISO 5479) requires a large number of data, which is difficult to obtain for many fire tests.

— Alternate tests as Levene[15][16] or Brown-Forsythe tests[15][17] are less sensitive to deviations from normality, and might be used. These tests are recommended when fewer data are available.

For comparison of means, several statistic tests can be used.

— Student's *t*-test[15] is the most known statistical test for comparison of means. This test supposes that equality of variances have been previously demonstrated. This test is successive to a variance test and only valid if variances are equal.

— Alternate tests such as Welch's *t*-test[15][18] are independent from any hypothesis on variances. These tests are recommended and may be used in parallel to comparison of variances.

— Wilcoxon's rank sum test[15] and Bayesian data analysis might be used as alternatives (not detailed in this document).

Results are sometimes reported as *p*-values instead of test statistics. The *p*-value is the probability of observing a difference at least as large as observed due to the vagaries of sampling alone, and that therefore there is no real difference. Small *p*-values, typically 0,05 or less, suggest that there is a statistically significant difference compared to a given limit.

7.5.3.2 Comparison of variances

7.5.3.2.1 Method 1: Fisher *F*-test

The Fisher *F*-test is extremely sensitive to deviations from normality. If data are not normal, this test shall not be used. ISO 5479 proposes methods to check the normality of data.

The variances are statistically compared with an *F*-test. In this test, the ratio of the two variances ($F_{observed}$) is compared to a theoretical F-ratio (F_{theory}). The statistics are calculated according to Formula (7).

In this case, F_{theory} values are tabulated for different levels of probability.[15] It is then necessary to refer to the Fisher-Snedecor table at e.g. 1 % or 5 % of significance, in order to get the value of F_{theory}.

If $F_{observed} < F_{theory}$, then the variances are considered as equal. If not, analytical techniques are significantly different in terms of variances.

$$F_{observed} = \frac{{s_1}^2}{{s_2}^2} \tag{7}$$

where

s_1 standard deviation of series 1;

s_2 standard deviation of series 2;

$s_1 > s_2$ so that $F_{observed} > 1$.

NOTE The Bartlett test[15] is an alternative to the Fisher *F*-test, with the same assumption of normality of data.

A strong deviation from a normal distribution may indicate a problem in the data and would suggest that further investigation is needed.

7.5.3.2.2 Method 2: Levene and Brown-Forsyth (LBF) tests

Levene's test[15][16] is a statistical test for the equality of variances calculated for two or more groups. Equal variances across samples are called homogeneity of variance. Analysis of variance assumes that variances are equal across groups or samples. The Levene test can be used to verify that assumption. The Levene test is less sensitive than the Fisher *F*-test or the Bartlett test[15] to departures from normality. If there is strong evidence that data do in fact come from a normal, or nearly normal, distribution, then

Bartlett's test[15] is more appropriate. The Levene test statistic W is defined according to Formula (8). The variables are transformed to measure the spread in each group.

$$W = \frac{(N-k)}{(k-1)} \frac{\sum_{i=1}^{k} n_i \left(z_{i.} - z_{..}\right)^2}{\sum_{i=1}^{k} \sum_{j=1}^{n_i} \left(z_{ij} - z_{i.}\right)^2} \tag{8}$$

where

W is the result of the test;

k is the number of different groups to which the sampled case belong;

N is the total number of cases in all groups;

n_i is the number of cases in the group i;

$z_{ij} = \left| y_{ij} - \bar{y}_i \right|$ considering y_{ij} as the value of the measured variable for the j case from the i-th group and $\bar{y}_i$;

$z_{..}$ is the general mean of all z_{ij};

$z_{i.}$ is the mean of the z_{ij} values for i-th group.

The significance of W is tested against F_{theory} as defined in 7.5.3.2.1 with $k - 1$ and $N - k$ its degrees of freedom at e.g. 1 % or 5 % of significance.

Brown and Forsythe[15][17] extended Levene's test to use either the median or the trimmed mean instead of the mean (LBF test).

$z_{ij} = \begin{cases} \left| y_{ij} - \tilde{y}_i \right| \\ \left| y_{ij} - \bar{y}'_i \right| \end{cases}$, considering y_{ij} as the value of the measured variable for the j case from the i group, $\tilde{y}_i$ and $\bar{y}'$, respectively as the median and the 10 % trimmed mean of the i-th group.

The three choices for defining z_{ij} determine the robustness and power of the different tests. Robustness means the ability of the test to not falsely detect unequal variances when the underlying data are not normally distributed and the variables are in fact equal. Power means the ability of the test to detect unequal variances when the variances are in fact unequal. Using the mean provides the best power for symmetric, moderate-tailed, distributions. Although the optimal choice depends on the underlying distribution, the definition based on the median is recommended as the choice that provides good robustness against many types of non-normal data while retaining good power. If the underlying distribution of the data is known, this may indicate using one of the other choices.

7.5.3.3 Comparison of mean values

7.5.3.3.1 Method 1: Student's *t*-test

The application of Student's test to compare mean values supposes that variances are equal. If equality of variances has not been demonstrated earlier, or if the data failed comparison of the variances test, then another technique should be used.

The statistical parameters used to compare mean values are the pooled standard deviation s_p according to Formula (9) and the value of t_{observed} according to Formula (10). This value t_{observed} is compared with the value of the Student's table t_{student} at a degrees of freedom $n = n_1 + n_2 - 2$. If $t_{\text{observed}} < t_{\text{student}}$,

the mean values are regarded as equal. If not, analytical techniques are significantly different in terms of values.

$$s_p = \sqrt{\frac{(n_1 - 1){s_1}^2 + (n_2 - 1){s_2}^2}{n_1 + n_2 - 2}} \tag{9}$$

$$t_{\text{observed}} = \frac{\left|\bar{y}_1 - \bar{y}_2\right|}{s_p} \sqrt{\frac{n_1 \times n_2}{n_1 + n_2}} \tag{10}$$

where

n_1 and n_2 number of values in groups 1 and 2;

$\bar{y}_1$ and $\bar{y}_2$ mean values of groups 1 and 2.

7.5.3.3.2 Method 2: Welch's *t*-test

Welch's *t*-test[18] is an adaptation of Student's *t*-test, and is intended for use when the two samples have possibly unequal variances. Welch's *t*-test defines the statistic *t* by the Formula (11). Unlike in Student's *t*-test, the denominator is not based on a pooled variance estimate.

$$t_{\text{observed}} = \frac{\bar{y}_1 - \bar{y}_2}{\sqrt{\frac{s_1^2}{n_1} + \frac{s_2^2}{n_2}}} \tag{11}$$

The degrees of freedom ν associated with this variance estimate is approximated using the Welch–Satterthwaite Formula (12):

$$\nu \approx \frac{\left(\frac{s_1^2}{n_1} + \frac{s_2^2}{n2}\right)^2}{\frac{s_1^4}{n_1^2 \nu_1} + \frac{s_2^4}{n_2^2 \nu_2}} \tag{12}$$

$\nu_i = n_i - 1$ is the degrees of freedom associated with the *i*-th variance estimate.

Once t_{observed} and ν have been computed, these statistics can be used with the t-distribution to test the null hypothesis that the two population means are equal.

If the population variances are equal, or if the samples are rather small and the population variances can be assumed to be approximately equal, it is more appropriate to use Student's *t*-test.

7.6 Calibration studies

7.6.1 General

Analytical techniques use a calibration model to compare the concentration of the analyte with the value of a detector. This model is often linear, but not usually for all conditions. The regression coefficient r^2 given for many regression calculations is not sufficient to characterize the capability of the model to represent data: it is often not representative of the error due to the model for small values, as its calculation favours high values.

An example of a calibration study is given in A.5.

To study the capability of the chosen calibration model to represent data, a calibration curve with p different levels of concentration is constructed for each analyte. Each solution is prepared several times and consists of a series of n values of y. The study of the calibration model then consists in checking that the model represents the data. The study could start with a linear regression model as the simplest form If this model does not explain the data, then a second degree polynomial model is used. The calculation of global mean and associated standard deviation are detailed in Formulae (13) to (14).

$$\bar{y}_i = \frac{\sum_{i=p}^{i=1} y_i}{p} \tag{13}$$

$$S_{Y_i} = \sqrt{\frac{\sum_{i=p}^{i=1} (y_{i-} \overline{y_n})^2}{p-1}} \tag{14}$$

where

$\overline{y_i}$ is the global mean;

p is the total number of measurements performed;

S_{Y_i} is the global standard deviation.

The coefficients of the model are calculated according to least-squares models. For a linear model, coefficients are calculated according to Formulae (15) and (16). Formula (17) calculates the response of the model $\hat{y}_i$. The non-linearity residuals correspond to $\bar{y}_i - \hat{y}_i$ and the repeatability residues to $y_i - \bar{y}_i$.

$$b_0 = \frac{\sum\left(x_i - \overline{x_i}\right)\left(y_i - \overline{y_i}\right)}{\sum\left(x_i - \overline{x_i}\right)^2} \tag{15}$$

$$b_1 = \overline{y_i} - b_1 \times \overline{x_i} \tag{16}$$

$$\hat{y}_i = b_1 \times x_i + b_0 \tag{17}$$

The sum of the squares of the deviations SCE at y_i level is given by Formula (18). Then, the median square (MS) is calculated according to Formula (19). Various MS are calculated as function of various SCEs and degrees of freedom df as defined hereafter.

The model chosen is the one that minimizes a suitable model selection criterion. Several statistical techniques could be used to quantify the quality of the calibration model studied:

— Fisher statistic;

— BIC (Bayesian Information Criterion)[20];

— AICc (Akaike's Information Criterion with finite sample size correction)[21].

7.6.2 Analysis of calibration model using the Fisher statistic

The Fisher statistic observed for explained values $F_{\text{obs Explained}}$ is given by Formula (20), considering $df_{\text{Explained}} = df_{\text{Model}}-1$ for the calculation of $MS_{\text{Explained}}$ and $df_{\text{residual}} = np - p$ for the calculation of MS_{residual}.

The Fisher statistic observed for nonlinearity, $F_{\text{obs, Non linearity}}$, is given by Formula (21), considering $df_{\text{nonlinearity}} = p-2$ for the calculation of $MS_{\text{Nonlinearity}}$ and $df_{\text{Total}} = np - 1$ for the calculation of MS_{Total}.

$$SCE_{y_i} = \sum (y_i - \overline{y_i})^2 \tag{18}$$

$$MS = \frac{SCE}{df} \tag{19}$$

$$F_{\text{obs Explained}} = \frac{MS_{\text{Explained}}}{MS_{\text{residual}}} \tag{20}$$

$$F_{\text{obs Non linearity}} = \frac{MS_{\text{Non linearity}}}{MS_{\text{Total}}} \tag{21}$$

The first step of the analysis is the validation of the regression. $F_{\text{obs Explained}}$ shall be strictly superior to $F_{95\,\%}$, the Fisher F-statistic at 95 % confidence.

The second step is the validation of the linearity. $F_{\text{obs Nonlinearity}}$ shall be strictly inferior to $F_{95\,\%}$.

7.6.3 The BIC (Bayesian Information Criterion)

The BIC (Bayesian Information Criterion)[20] may be used to compare different calibration models. The BIC is defined according to Formulae (22) and (23).

$$BIC = k \ln(n) - 2 \ln(L) \tag{22}$$

if the errors are normally distributed:

$$BIC = k \ln(n) + n \ln(MSE) \tag{23}$$

where

k is the number of parameters of the model, e.g. two for a linear one;

n is the number of data;

L is the likelihood of the model, see Reference [15];

MSE is the Mean Squared Error defined as $MSE = \frac{1}{n}\sum_{i=1}^{n}\left(\hat{y}_i - y_i\right)^2$.

The best regression model is the one that minimizes the BIC value.

7.6.4 Analysis of calibration model using the AICc (Corrected Akaike Information Criterion)

The AICc (Akaike's Information Criterion with finite sample size correction)[21] is an alternative to the Fisher statistic to compare different calibration models. The AICc is defined according to Formulae (24) and (25) with the parameters defined in 7.6.3.

$$AICc = 2k - 2\ln\left(L\right) + \frac{2k\left(k+1\right)}{n-k-1} \tag{24}$$

Or, if the errors are normally distributed:

$$AICc = 2k + n\ln\left(MSE\right) + \frac{2k\left(k+1\right)}{n-k-1} \tag{25}$$

The best regression model is the one that minimizes the AICc value. The AICc is recommended if n is small or k is large. Degrees of freedom of the model affects the AICc criterion less than it does the BIC.

8 Determination of uncertainties

The objective of an analytical method is to try to determine the real concentration of analytes of interest at the sampling point in a fire atmosphere. Appreciation of the factors discussed in Clause 6 can help to reduce the uncertainty of analyte measurement, and the validation methods discussed in Clause 7 can be used to establish effective calibration and to check the influence of the measurement technique on results.

Uncertainties are calculated according to ISO/IEC Guide 98-3. The repeatability (R) and the reproducibility (r) of an analytical method for fire effluents could be determined according to the ISO 5725 series. However, for fire atmosphere analytical methods, this determination shall specify if the repeatability and reproducibility of the physical fire model is included in the final results. In many cases, a lack of repeatability and reproducibility could be due to the physical fire model (i.e. variations in ignition time, effects of sample homogeneity, etc.) instead of the analytical method itself, when results analysed are issued from combustion plus analysis process.

An example of uncertainty calculation according to ISO/IEC Guide 98-3, including repeatability considerations, is presented in Annex B.

Annex A
(informative)

Example of application of validation steps: Analysis of hydrogen chloride and hydrogen bromide from trapping solutions

A.1 General

The example given here is for the analysis of hydrogen chloride and hydrogen bromide according to the technique presented in ISO 19701:2013, 5.5.2. In the example, hydrogen chloride and hydrogen bromide are trapped in a liquid phase as halide ions using impingers, as described in NF X 70-100-2[22]. Chloride and bromide ions are then analysed using Ion-Liquid Chromatography (ILC) with a conductimetric detector. The standard protocol stated in ISO 19701, has been modified for this example by use of a trapping solution of deionised water containing 3 % of hydrogen peroxide. The addition of hydrogen peroxide allows the simultaneous trapping of sulfur dioxide.

This example is detailed in References [23] and [24]. The analytical system used includes the following:

— ion Liquid chromatograph type Dionex DX500;

— ion exchange column AS 14 (silica grafted with quaternary ammonium functional groups) and pre-column AG14;

— suppressor type ASRS Ultra 4 mm;

— detector ED40 (used in conductimetric mode);

— mobile phase: solution of 3,5 mmol/l Na_2CO_3 and 1 mmol/l $NaHCO_3$;

— flow rate of the mobile phase: 1,5 ml/min;

— autosampler with injection loop volume of 50 µl;

— organic filtration (Varian JR-C18 500mg) and mechanical filtration (PTFE 0,2 mm) of samples.

The instrument is calibrated using six standards for both ions. The concentration range for both ions is from 1 mg/L to 20 mg/L.

A.2 Validation of the non-influence of the matrix

CO and CO_2 are measured by NDIR according to ISO 19701:2013, 5.1 and 5.2. Prior to these gas analysers, other species of interest are adsorbed using two different trapping solutions: deionized water and deionized water containing 3 % of hydrogen peroxide. Deionized water has been previously validated as having no influence on the quantity of CO and CO_2 analysed. A series of tests is performed to validate that the second trapping solution has no influence either.

Two configurations are successively compared, at several volume fractions:

— impingers filled with deionized water (standard defined solution);

— the same impingers, filled with the alternate solution containing hydrogen peroxide.

As the only difference is the composition of the trapping solution, any difference between the data obtained with the alternate solution, and the data obtained with the standard defined solution, will

then be solely due to the difference of trapping solution. The measurements are carried out at three different volume fractions:

— low volume fraction: about 1 % CO and 4 % CO_2;

— medium volume fraction: about 3 % CO and 12 % CO_2;

— high volume fraction: about 5 % CO and 20 % CO_2.

All measurements are then compared, in order to determine the influence of the trapping solution. Typical results are presented in Table A.1. For contents from 0 % to 5 % of CO and 0 % to 20 % of CO_2, no difference in results is noted. The trapping solution has no influence on the measurement of the amount of CO and CO_2 after the adsorbers.

Table A.1 — data obtained to validate the non-influence of the matrix (in %)

	CO		CO_2	
	Standard defined solution	Alternative solution	Standard defined solution	Alternative solution
Low volume fraction	0,91 %	0,91 %	3,65 %	3,64 %
Medium volume fraction	3,00 %	3,00 %	11,80 %	11,81 %
High volume fraction	4,54 %	4,54 %	17,38 %	17,38 %

A.3 Specificity of the method

A.3.1 Quality of separation

In order to have a blank sample representative of the solutions to be analysed, the combustion of a material is carried out. This material has been chosen to produce a similar matrix of compounds in the effluent, but without the presence of chloride and bromide. This is checked using a titrimetric method. One ml of the solution used to trap this effluent, (termed "combustion matrix"), is mixed with 1 ml of a standard poly-anion solution containing: F^- (10 mg/l), Cl^- (20 mg/l), NO_2^- (20 mg/l), Br^- (20 mg/l), NO_3^- (20 mg/l), PO_4^{3-} (20 mg/l) and SO_4^{2-} (30 mg/l). The analysed ions are F^-, Cl^-, NO_2^-, Br^-, NO_3^-, PO_4^{3-}, SO_4^{2-} and CH_3COO^-, which is not quantified. All these anions could be present in the trapping solution obtained by sampling from a fire test.

Determination of the quality of separation is achieved through the calculation of the resolution as proposed in 7.4.3. The resolution for each set of ions has been calculated as shown in Table A.2. When both acetate and fluoride ions are present, a precise quantitative analysis of these ions is impossible, as peaks overlap. All other ions in solution can be successfully analysed and the resolutions calculated for the bromide and chloride ions are high enough to allow a quantitative analysis of both these ions.

Table A.2 — Quality of separation in ILC

Ion	Retention time (min)	Width at middle height (min)	Resolution with previous ion
Fluoride (F^-)	2,33	0,07	—
Acetate (CH_3COO^-)	2,57	0,16	**1,23**
Chloride (Cl^-)	3,27	0,09	3,30
Nitrite (NO_2^-)	3,83	0,11	3,30
Bromide (Br^-)	4,73	0,14	4,25
Nitrate (NO_3^-)	5,49	0,17	2,89
Phosphate (HPO_4^{2-})	7,12	0,25	ND
Sulfate (SO_4^{2-})	8,53	0,27	3,20

In fire effluents, a large quantity of hydrogen chloride could be released from materials containing chlorine. In these conditions, it may be difficult to analyse hydrogen bromide as in solution, a large quantity of chloride ions can mask the bromide ions. A solution originating from the combustion of PVC material, containing 1000 mg/L of chloride ions, is used. To this solution, 2,5 mg/L of bromide ions are added. Analysis is performed three times and the resulting concentration is (2,0 ± 0,11) mg/L. These results show that even the highest concentration of Chloride ions do not prevent weak concentrations of Bromide ions from being correctly measured in these conditions.

A.3.2 Determination of specificity

For chloride and bromide ions, five solutions with concentrations from 1 mg/L to 20 mg/L are used. The ions are added over the concentration range to be expected in the matrix from a fire study. For example, for a fire matrix with 5 mg/L of chloride ions, an addition of 5 mg/L of chloride ions is used.

The analytical instrument is first calibrated. Each solution is initially analysed to obtain the analyte concentration. Then, the additions are carried out using the standard solutions. In this way, the added concentration is accurately known, and is called the "real" addition (v_i). The resultant solution is then analysed. Since the initial concentration is known, the addition is measured (r_i). Five sets of data are obtained for the chloride and bromide ions. Results of calculations described in 7.4.3 are given in Table A.3. For both ions, b_0 can be considered as equal to 0 with a 5 % error. For chloride, b_1 can be considered as equal to 1 with a 5 % error. This error is 1 % for Bromide. Consequently, the method is specific for the measurement of chloride and bromide ions in such a matrix.

Table A.3 — Results of selectivity test

Ion	Chloride	Bromide
$S(e)$	$4{,}54 \times 10^{-1}$	$2{,}03 \times 10^{-1}$
B_1	1,039	1,111 2
$S(b_1)$	$3{,}37 \times 10^{-2}$	$3{,}32 \times 10^{-2}$
B_0	0,34	−0,151 6
$S(b_0)$	0,32	0,16
t_{obs}	1,18	3,35
t'_{obs}	1,06	0,94
$t_{student\ (95\ \%)}$	*3,18*	*3,18*
$t_{student\ (99\ \%)}$	*5,84*	*5,84*

A.4 Influence of the measurement technique

The ILC method is then compared to the titrimetric method described in ISO 19701:2013, 5.5.3.

A.4.1 Simple methods

The two techniques are compared using a wide range of concentrations in solutions obtained from the combustion of polymeric materials. Results are presented in Table A.4 and Table A.5 respectively for hydrogen chloride yield and hydrogen bromide yield, obtained from the combustion of a series of materials.

Table A.4 — Comparison of methods (concentration in liquid for hydrogen chloride)

Material	HCl yield (mg/g) with titrimetry		HCl yield (mg/g) with ILC		Deviation between mean values	
	Mean value	Std. dev.	Mean value	Std. dev.	(mg/g)	(%)
A1	4,20	1,18	4,18	0,93	0,02	0,5
B1	8,34	1,01	8,10	1,09	0,24	3,0
C1	14,4	1,69	13,9	1,44	0,47	3,4
D1	134	7,83	133	9,14	0,91	0,7
F1	162	5,67	152	11,72	10,7	7,0
G1	249	1,10	232	3,53	16,6	7,1
H1	575	8,90	523	9,12	51,6	9,9

Table A.5 — Comparison of methods (concentration in liquid for hydrogen bromide)

Material	HBr yield (mg/g) with titrimetry		HBr yield (mg/g) with ILC		Deviation between mean values	
	Mean value	Std. dev.	Mean value	Std. dev.	(mg/g)	(%)
A1	33,5	2,93	33,2	2,56	0,35	1,1
B1	59,5	3,21	56,3	3,07	3,19	5,7
C1	9,52	1,82	7,84	1,46	1,69	21,6

For all materials releasing HBr and those releasing HCl between 4,12 mg/g and 157 mg/g, calculations show that there is no influence of the technique on the results. For the two materials releasing a higher amount than 157 mg/g for HCl, amounts measured by ILC are approximately 10 % lower than those measured by titrimetry. For one material, the two sets of results have unequal variances and mean values. For one material (H1), the variances are comparable but the mean values are unequal.

A.4.2 Graphical representation

The results are plotted as Figure A.1 for hydrogen chloride data.

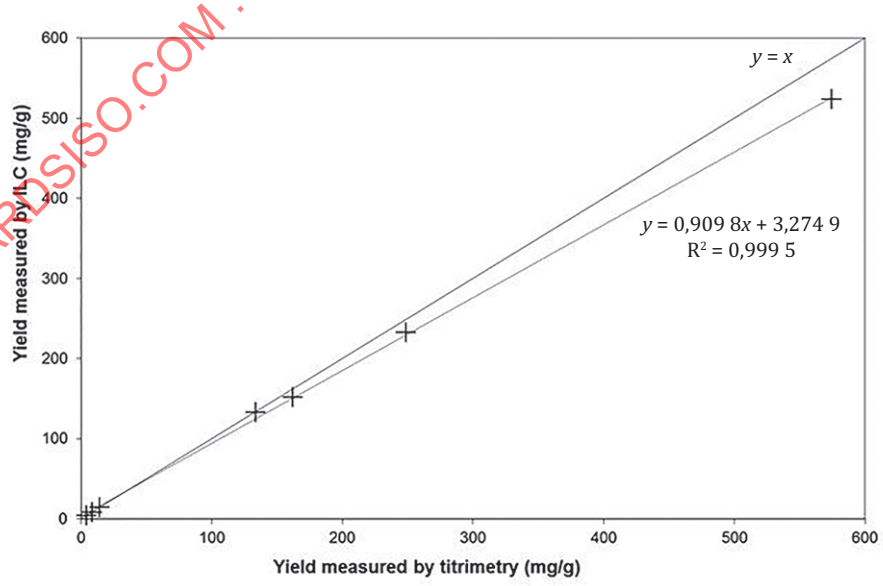

Figure A.1 — Graphical representation of results (case of hydrogen chloride)

A.4.3 Bland and Altman graphical method

The results of the Bland and Altman method are plotted as Figure A.2 for hydrogen chloride data. It confirms the observation of a problem with data corresponding to H1 material.

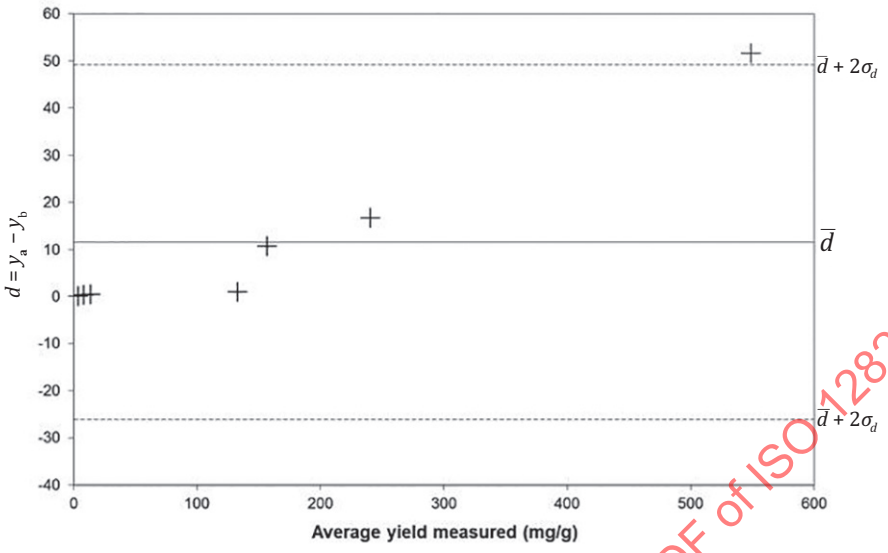

Figure A.2 — Bland and Altman graphical method results (case of hydrogen chloride)

A.4.4 Quantitative method

A.4.4.1 Comparison of variances

A.4.4.1.1 Using the Fisher *F*-test

The quantitative technique using the Fisher *F*-test has been applied to the data shown in Table A.4 and Table A.5. Results of the comparison of variances are given in Table A.6 and Table A.7 respectively for hydrogen chloride and hydrogen bromide. One single case of non-equivalence of variances is observed for hydrogen chloride for the material G1. Equivalence is established for this point at the level of 1 % ($F_{\text{theory, 1 \%}}$ = 15,98 for n = 5).

NOTE The Fisher test is performed using a low number of observations. This yields to a low power of the test, i.e. a low capacity for the test to detect any difference between the variances, unless the difference is very large.

Table A.6 — Comparison of variances using the *F*-test — Results obtained for the yield of hydrogen chloride

Material	Number of tests $n_1 = n_2$	Comparison of variance	
		F_{observed}	$F_{\text{theory, 5 \%}}$
A1	5	1,61	6,39
B1	3	1,18	19,0
C1	3	1,37	19,0
D1	3	1,36	19,0
F1	5	4,28	6,39
G1	5	**10,4**	6,39
H1	5	1,05	6,39

Table A.7 — Comparison of variances using the *F*-test — Results obtained for the yield of hydrogen bromide

Material	Number of tests $n_1 = n_2$	Comparison of variances	
		$F_{observed}$	$F_{theory,\ 5\ \%}$
A1	5	1,31	6,39
E1	5	1,09	6,39
F1	5	1,56	6,39

A.4.4.1.2 Using the Levene test as modified by Brown-Forsyth (LBF)

Results of the comparison of variances using the LBF test are given in Table A.8 and Table A.9 respectively for hydrogen chloride and hydrogen bromide. The results indicate that variances are homogeneous for all materials and for both HCl and HBr. Comparison of variances using LBF highlights no significant deviation at the 5 % level (no *p*-value inferior to 0,05).

Table A.8 — Comparison of variances using the LBF test — Results obtained for the yield of hydrogen chloride

Material	Number of tests $n_1 = n_2$	Comparison of variance		
		W	$F_{theory,\ 5\ \%}$	p-value
A1	5	0,206	6,39	0,66
B1	3	0,004	19,00	0,95
C1	3	1,014	19,00	0,37
D1	3	0,046	19,00	0,84
F1	5	0,770	6,39	0,41
G1	5	0,872	6,39	0,38
H1	5	0,037	6,39	0,85

Table A.9 — Comparison of variances using the LBF test — Results obtained for the yield of hydrogen bromide

Material	Number of tests $n_1 = n_2$	Comparison of variances		
		W	$F_{theory,\ 5\ \%}$	p-value
A1	5	0,034	6,39	0,86
E1	5	0,003	6,39	0,15
F1	5	0,276	6,39	0,15

A.4.4.2 Comparison of means

A.4.4.2.1 Using Student's *t*-test

Results of the comparison of means are given in Table A.10 and Table A.11 respectively for hydrogen chloride and hydrogen bromide. In the case of hydrogen chloride, the results highlight that the two techniques are not equivalent for higher concentrations in terms of mean values. They are equivalent for the determination of yields up to 160 mg/g.

Table A.10 — Comparison of means — Results obtained for the yield of hydrogen chloride

Material	Number of tests $n_1 = n_2$	Comparison of means	
		$t_{observed}$	t_{theory}
A1	5	0,01	2,31
B1	3	0,15	2,78
C1	3	0,22	2,78
D1	3	0,09	2,78
F1	5	1,28	2,31
G1	5	**6,24**	2,31
H1	5	**6,32**	2,31

Table A.11 — Comparison of means — Results obtained for the yield of hydrogen bromide

Material	Number of tests $n_1 = n_2$	Comparison of means	
		$t_{observed}$	t_{theory}
A1	5	0.13	2.31
E1	5	1.04	2.31
F1	5	0.87	2.31

A.4.4.2.2 Using Welch's *t*-test

Results of the comparison of means using Welch's test are given in Table A.12 and Table A.13 respectively for hydrogen chloride and hydrogen bromide. The results indicate that means are different for materials C1, G1 and H1 in the case of hydrogen chloride (*p*-values inferior to 0,05).

Table A.12 — Comparison of means using the Welch's test — Results obtained for the yield of hydrogen chloride

Material	Number of tests $n_1 = n_2$	Comparison of means			
		$t_{observed}$	t_{theory}	ν	*p*-value
A1	5	0,03	2,31	7,59	0,97
B1	3	0,28	2,78	3,97	0,79
C1	3	**12,4**	2,78	2,36	**0,00**
D1	3	0,13	2,78	3,91	0,90
F1	5	1,83	2,31	5,77	0,12
G1	5	**10,0**	2,31	4,76	**0,00**
H1	5	**9,05**	2,31	7,99	**0,00**

Table A.13 — Comparison of means using the Welch's test — Results obtained for the yield of hydrogen bromide

Material	Number of tests $n_1 = n_2$	Comparison of means			
		$t_{observed}$	t_{theory}	ν	*p*-value
A1	5	0,20	2,31	7,86	0,85
E1	5	1,61	2,31	7,98	0,15
F1	5	1,61	2,31	7,63	0,15

A.5 Calibration study

The calibration study of ILC for chloride ion is carried out according to techniques presented in 7.6. The calibration data set is made from 25 solutions: 5 standards are analysed at 5 concentrations, ranging from 1 mg/L to 20 mg/L. The analysis uses the area under the peak *y,* vs. concentration *x*.

As the model uses data from a detector based on a specific physical measurement principle, the choice of the model's mathematical form has to be driven by the physics of the detector principle. For example, an ILC (Ion Liquid Chromatography) measurement with a conductimetric detector, as proposed for chloride or bromide ions in ISO 19701 corresponds to a resistor-capacitor (RC) equivalent alternating current (AC) electric circuit dependent on ion mobility. When concentration increases, ion mobility decreases so the linear model is not applicable to concentrated solutions or to a wide range of concentrations. It is nevertheless possible to use such a model for diluted concentrations and with a narrow range of concentrations. When the range increases, another model such as a second degree polynomial relation is more appropriate to represent the data. See Reference [19] for more details.

Figure A.3 presents graphically the data and both regression models. Figure A.4 presents the residues for both models.

Table A.14 and Table A.15 present results obtained using a linear regression model. As a first step, the regression is validated as $F_{\text{explained}} > F_{1\ \%}$. The model is therefore acceptable as it fits the data. As a second step, linearity is not verified, as $F_{\text{non linearity}} > F_{1\ \%}$. The residuals which cannot be explained are deemed excessive. A model of second order is therefore tested.

Table A.14 — Results of a regression calculation for the case of a linear model

Model	$y = b_1.x+b_0$
Slope b_1	$1{,}74 \times 10^5$
Standard deviation on slope $s(b_1)$	$1{,}87 \times 10^4$
Intercept b_0	$-1{,}03 \times 10^5$
Standard deviation on intercept $s(b_0)$	$1{,}92 \times 10^5$
Regression coefficient r^2	0,997
Sum of residuals	$6{,}48 \times 10^4$
F-statistic	$8{,}69 \times 10^4$
Degrees of freedom	23
Sum of explained squares SCexp	$3{,}65 \times 10^{13}$
Sum of residuals SCres	$9{,}67 \times 10^{10}$

Table A.15 — Results of a Fisher test for calibration for the case of a linear model

Origin of variation	Sum of the squares of the deviation (*SCE*)	Degrees of freedom	Mean square (*MS*)	F_{obs}	$F_{(5\ \%)}$	$F_{(1\ \%)}$
Explained	$3{,}65 \times 10^{13}$	1	$3{,}65 \times 10^{13}$	$3{,}33 \times 10^5$	4,4	8,1
Non linearity	$9{,}45 \times 10^{10}$	3	$3{,}15 \times 10^{10}$	**288**	3,1	4,9
Residuals	$2{,}19 \times 10^9$	20	$1{,}10 \times 10^8$	—	—	—
Total	$3{,}66 \times 10^{13}$	24	—	—	—	—

Table A.16 and Table A.17 present results obtained for a second-order model. As a first step, regression is validated as $F_{explained} > F_{1\ \%}$. The model is therefore acceptable as it fits the data. In the second step, linearity is verified, as $F_{non\ linearity} < F_{1\ \%}$.