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Validation method for fire gas analysis —

Part 3:
Considerations related to interlaboratory trials

Méthode de validation pour l'analyse des effluents du feu —
Partie 3: Considerations relatives aux essais inter laboratoires avec les analyses chimiques des effluents du feu

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ISO copyright office
CP 401 • Ch. de Blandonnet 8
CH-1214 Vernier, Geneva
Phone: +41 22 749 01 11
Fax: +41 22 749 09 47
Email: copyright@iso.org
Website: www.iso.org

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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 of the voluntary nature of standards, 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 www.iso.org/iso/foreword.html.

This document was prepared by Technical Committee ISO/TC 92, *Fire safety*, Subcommittee SC 3, *Fire threat to people and environment*.

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

Any feedback or questions on this document should be directed to the user’s national standards body. A complete listing of these bodies can be found at www.iso.org/members.html.

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 escape time (ASET)[1]. Related documents are also being developed in ISO/TC 92/SC 3 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 described in ISO 12828-2. Comparing results from one laboratory to another and giving a global confidence in any measurement technique, independently from the user and the conditions of use, are described in this document.

Validation method for fire gas analysis —

Part 3:
Considerations related to interlaboratory trials

1 Scope

This document describes tools and gives guidance concerning interlaboratory trials related to fire effluent analyses. It explains the relative contributions from the physical fire model and analytical techniques to evaluate trueness and fidelity. It also explains the difficulties involved with the interpretation of round-robin data and with the evaluation of trueness in fire effluent analyses.

This document complements ISO 12828-1, which deals with limits of quantification and detection and ISO 12828-2, which deals with interlaboratory validation of analytical methods. It is a toolbox useful in the framework of ISO/IEC 17025 assessment of any fire laboratory.

Examples of existing standards where the information contained in this document can be used are the analytical chemical methods in ISO 19701[2], ISO 19702[3], ISO 5660-1[4], and the chemical measurements in the methods discussed in ISO/TR 16312-2, ISO 16405[6], ISO/TS 19021[7], or their application to fire toxicity assessment using ISO 13571[1] and ISO 13344[8].

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 5725-1, *Accuracy (trueness and precision) of measurement methods and results — Part 1: General principles and definitions*

ISO 5725-2, *Accuracy (trueness and precision) of measurement methods and results — Part 2: Basic method for the determination of repeatability and reproducibility of a standard measurement method*

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

ISO 12828-2, *Validation method for fire gas analysis — Part 2: Intralaboratory validation of quantification methods*

ISO 13943, *Fire safety — Vocabulary*

ISO 19706, *Guidelines for assessing the fire threat to people*

3 Terms and definitions

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

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

- ISO Online browsing platform: available at https://www.iso.org/obp
- IEC Electropedia: available at http://www.electropedia.org/

3.1

accuracy

closeness of agreement between a measured quantity value and a true quantity value of a measurand

[SOURCE: ISO/IEC Guide 99:2007, 2.13, modified — NOTES 1 to 3 have been removed.]

3.2

k-score

score that characterizes the fidelity of a laboratory, defined by:

$$k_i = \frac{s_w}{s_r}$$

3.3

precision

closeness of agreement between indications or measured quantity values obtained by replicate measurements on the same or similar objects under specified conditions

[SOURCE: ISO/IEC Guide 99:2007, 2.15, modified — NOTES 1 to 4 have been removed.]

3.4

trueness

closeness of agreement between the average of an infinite number of replicate measured quantity values and a reference quantity value

[SOURCE: ISO/IEC Guide 99:2007, 2.14, modified — NOTES 1 to 3 have been removed.]

3.5

z-score

score that characterizes the bias and thus the trueness of a laboratory, assuming the real value is the general mean and the real dispersion is the overall standard deviation s, defined by:

$$z_i = \frac{\bar{y}_i - m}{s}$$

4 Symbols

b	laboratory component of bias under repeatability conditions
e	random error occurring in repeatability conditions
m	general mean, sometimes expressed as the level of the test
n_i	number of laboratories
s_L	between-laboratory standard deviation
s_r	estimate of the repeatability standard deviation
s_R	estimate of the reproducibility standard deviation
s_w	within-laboratory standard deviation for the laboratory i
$\bar{y}_i$	mean value from laboratory i
$\bar{\bar{y}}_i$	mean value from all laboratories

5 General considerations

5.1 Trueness and fidelity

A test result is described by the model $y = m + b + e$. In this expression, the measured value is the real value affected by the bias (trueness error) and the random error (fidelity error).

5.1.1 Trueness

In the context of fire effluent analysis, trueness is the correspondence between the real (theoretical) value of an analyte and the measured value (see ISO 19703). Depending on the existence and knowledge of the real value, bias b, characterizing trueness is sometimes partially characterized by Z-score. Bias expresses the deviation to a real value, where Z-score supposes that the general mean corresponds to the real value; this last assumption is questionable in several cases for fire gases analysis. The Z-score could be interpreted as follows:

- $|z_i| \leq 2$ means that the trueness performance of the laboratory is in the 95 % range of more probable values;
- $2 < |z_i| \leq 3$ means that the trueness performance of the laboratory is questionable, in the range of the next 4,7 % less probable values;
- $|z_i| > 3$ means that the trueness performance of the laboratory is unsatisfactory, in the range of the remaining 0,3 % of the least probable values.

There are several ways to determine trueness in fire gas analysis:

- Case 1): Physical fire model included. General principle is combustion of standard materials then mass balance. A real value could be assumed and bias calculated for several mass balances, including:
  - Halogenated acids, assuming 100 % mol/mol of X (often chloride) in the initial material is converted into HX;
  - Carbon, considering CO_2, CO and other carbonaceous compounds represent the large majority of carbon initially present, preferably in well ventilated conditions;
  - Sulfur released as SO_2 in well ventilated conditions (stage 2 according to ISO 19706).

  This kind of mass balance corresponds to a global validation of trueness and fidelity due to the fire model itself plus the analysis as the related error sources cannot be separated. It is not possible to do so with some other elements such as nitrogen.
- Case 2): Physical fire model excluded
  - Sub-case 2a): Use of standard gases injected at the point of emission in normal use, e.g. at the location of the material in combustion tests. This checks the sampling and analysis trueness and fidelity, but not the possible variation due to combustion process itself.
  - Sub-case 2b): Use of standard gases or standard solutions (see ISO 12828-1) in realistic matrix. This checks the trueness and fidelity of the analysis.

EXAMPLE 1 Cases where the theoretical value is known.

The analyte studied is hydrogen chloride. The analytical method is high performance ion chromatography according to ISO 19701:2013, 5.5.2. To determine the trueness of the method:

- Case 1): Unmodified PVC is burnt according to an appropriate fire model. Suitable solution traps are used to capture the hydrogen chloride gas from the effluent. The solution is then analyzed. Chlorine comprises 56,8 % by mass of PVC and the theoretical yield of HCl is 0,584 g/g.

— Cases 2a) and 2b): A known quantity of HCl gas is introduced at an appropriate point in the fire test apparatus. For example, a flow of 0,5 L/min under standard pressure and at 20 °C at a volume fraction of 1 000 µL/L for a period of 5 min. This results in a theoretical quantity of 3,80 mg.

EXAMPLE 2 Cases where the theoretical value cannot be evaluated:

— The analyte studied is nitrogen dioxide. The analytical method is chemiluminescence for all laboratories. The estimate of the real value is the general mean from all laboratories, excluding outliers.

— Analyte studied is Nitrogen dioxide. A method is supposed to be the reference one, e.g. High Performance Liquid Chromatography. A method is used to be compared to this one.

5.1.2 Fidelity (precision)

Fidelity with respect to repeatability corresponds to the dispersion of a measurement by a single laboratory. Fidelity with respect to reproducibility corresponds to the dispersion of a measurement by a group of laboratories. Laboratories joining an interlaboratory comparison of testing should follow ISO/IEC 17043 for the development and operation of interlaboratory comparison schemes. Repeatability r is often expressed as a standard deviation S_{r} and reproducibility R, is often expressed as a standard deviation S_{R}. These two values are linked as follows:

$$s_R^2 = s_L^2 + s_r^2$$

where

s_L^2 represents the between-laboratory variance;

s_r^2 is the estimate of the repeatability variance. It is given as the arithmetic mean of the within-laboratory variance s_w^2 after tests to exclude outliers;

s_R^2 is the estimate of the reproducibility variance.

k-score is a way to assess the fidelity and can be interpreted after removal of outliers (using statistical tests described in ISO 5725-1 and ISO 5725-2) as follows:

— $k_i \leq 2$ means that the precision performance of the laboratory is in the 95 % range of more probable values;

— $2 < k_i \leq 3$ means that the precision performance of the laboratory is questionable, in the range of the next 4,7 % less probable values;

— $k_i > 3$ means that the precision performance of the laboratory is unsatisfactory, in the range of the remaining 0,3 % of the least probable values.

5.1.3 Summary

Table 1 presents an overview of the parameters expressed in Clause 5.

Table 1

Case	Assessment	Trueness	Fidelity
1)	Fire model (combustion process) + sampling + analysis	Mass balances: — Hydrogen halides — Carbon (well-ventilated mainly) — Sulfur (well-ventilated only)	Interlaboratory trial according to ISO 5725-1 and ISO 5725-2
2a)	Sampling + analysis		
2b)	Analysis		

When values of bias, repeatability and reproducibility are compared between two round-robins, it is important that values have been determined under the same conditions.

5.2 Deviation sources independent from analytical technique

5.2.1 Deviation sources from the material or product tested

Several sources of error can be generated from variations in the material tested.

One of the most important parameters is material homogeneity. Lack of homogeneity is a frequent source of error in round robins and the selection of materials and products suitable for an interlaboratory trial has to be performed carefully. Materials shall be traceable and be readily available for a long period of time. Typically, polymers from a similar batch, with a reduced number and quantity of additives and resistant to ageing are suitable for such purposes. Otherwise results from round-robins cannot be compared. ISO 17034 [10] gives advice concerning the production of reference materials.

EXAMPLE 1 Pellets of polyamide 6-6 are an example of a suitable material. It could generate carbon oxides in known quantities for the purposes of a carbon mass balance. It will also generate nitrogen-containing species such as HCN, depending on the combustion conditions.

EXAMPLE 2 PMMA is also often used in round-robins as a carbon mass balance is easy to perform. This is because in well-ventilated conditions carbon is converted mainly to CO_2 and CO with very little soot formation. It is important to make sure that all the PMMA samples are equivalent — there are many different grades of PMMA having different properties.

For several materials and products, test conditions and conditioning may be of great importance. However, these conditions are not necessarily specified in the related testing methods. Some materials are very sensitive to moisture, and water content can affect their burning behaviour. Examples are cellulosic materials or polyamide-10.

5.2.2 Deviation sources from the physical fire model used

ISO 16312-1 and ISO TR 16312-2 describe the different apparatuses that may be used to generate fire effluents for gas analysis. Independently from the material tested and the combustion conditions expected from ISO 19706, the different test methods could generate a source of error. The ignition model, the radiative heat flux homogeneity, the presence/absence of a pilot flame and the mixing conditions of fuel/air are examples of parameters that can affect the results.

EXAMPLE ISO 5660-1[4] and ISO 12136[5] are two test apparatus able to produce effluents from well-ventilated fire conditions with small-scale samples using the same level of irradiance. However, results are not comparable in trueness and in fidelity. Parameters that affect fidelity are not fully identified, but could concern radiative spectral sensitivity of the sample tested and of the heating source, and different air/fuel mixing conditions.

5.3 Deviation sources due to analytical technique

Sometimes a single round-robin may include results aggregated from several analytical techniques. In this case, some of the requirements of ISO 5725-1 and ISO 5725-2 are not satisfied. This kind of round-robin shall be interpreted carefully. Where different analytical techniques are used, they shall be reported. ISO 5725-2 shall be used to analyze data of each group of analytical technique, then for the data as a whole. Tools described in ISO 12828-2 shall be used to compare the data between the different groups.

EXAMPLE A round-robin is organized to compare results from different laboratories in emission yields for NO_2. Several laboratories use wet chemistry (as described in ISO 19701), some use FTIR (as described in ISO 19702) and some use chemilumiescence (as described in ISO 19701). The results obtained in Z-score and fidelity are of importance, but they are not determined under the conditions of ISO 5725-1 and ISO 5725-2.

6 Different kinds of round robins

6.1 Sources of error

In the different round-robins, several sources of error can be identified as follows according to the analysis process:

Parameter		Fire model →	Sampling →	Conditioning →	Analysis
Trueness	**bias b**	$b_{\text{Fire model}}$	b_{sampling}	$b_{\text{conditioning}}$	b_{analysis}
Fidelity	within laboratory variance s_w^2	$s^2_{\text{Fire model}}$	s^2_{sampling}	$s^2_{\text{conditioning}}$	s^2_{analysis}
	repeatability estimate variance s_r^2	$s_r^2 = \dfrac{\sum\left(s_w^2\right)_i}{n_i}$ (after excluding outliers)			
	reproducibility estimate variance s_R^2	$s_R^2 = s_L^2 + s_r^2$ with $s_L^2 = \dfrac{\left(\bar{y}_i - \bar{\bar{y}}_i\right)^2}{n_i - 1}$			

6.2 Fire model + sampling + conditioning + analysis

For several analytical techniques, thermal degradation, sampling and conditioning could not be separated from the analytical technique. This is the case of time-resolved gas analysis techniques such as NDIR according to ISO 19701 or FTIR according to ISO 19702. This is also the case when round-robin organizers distribute the same material to all participants for realization of the whole process from combustion to analysis.

In this case, separation between errors from the thermal degradation, from sampling and from the analysis are difficult to assume.

It means that:

— for trueness, bias $b = b_{\text{Fire model}} + b_{\text{sampling}} + b_{\text{conditioning}} + b_{\text{analysis}}$

— for fidelity, within-laboratory variance $s_w^2 = s^2_{\text{Fire model}} + s^2_{\text{sampling}} + s^2_{\text{conditioning}} + s^2_{\text{analysis}}$

EXAMPLE Results from trueness, repeatability and reproducibility on carbon dioxide stated in ISO 19701:2013, 5.2.10, are obtained using: tube furnace as fire model, sampling and filtration through a silica wool stamp and water impingers. Gas is then dried using calcium chloride and analyzed through NDIR. The bias and the fidelity obtained cover all errors from the thermal degradation to the analysis.

6.3 Analysis alone

For several analytical techniques such as wet chemistry, one laboratory could realize thermal degradation and sampling of the effluents, and imping fire effluents to produce a representative solution. This solution is then split into several parts and sent to all participating laboratories for analysis. In this case, bias covers all sources but within-laboratory variance only comes from the analysis.

It means that:

— for trueness, bias $b = b_{\text{Fire model}} + b_{\text{sampling}} + b_{\text{conditioning}} + b_{\text{analysis}}$

— for fidelity, within-laboratory variance $s_w^2 = s^2_{\text{analysis}}$

The analysis has to be performed as quickly as possible and in the same time frame for all participants.

EXAMPLE Results from trueness, repeatability and reproducibility on the analysis of hydrogen chloride, as stated in ISO 19701:2013, 5.2.10, are obtained using: a tube furnace as the fire model, sampling and filtration through silica wool and water impingers. The solution is then analyzed using high performance ion chromatography to determine the chloride content. The bias obtained comprises all errors from the thermal degradation to the analysis. The fidelity obtained is only for the analysis.

6.4 Comparison between techniques

An interlaboratory trial could be performed to compare two different analytical techniques.

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 trueness and fidelity. 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.

In this case, ISO 12828-2:2016, 7.5 is suitable to compare two groups of results obtained from the two analytical techniques, in trueness and in fidelity. Such conditions are out of repeatability conditions of the ISO 5725 series. ISO 29903-1 describes general principles of comparison.

Annex A
(informative)

Examples of application in existing standards

A.1 Examples of trueness determinations

Comparison with a real value

Table A.1 shows comparisons of some measured quantities with the corresponding theoretical quantities.

Table A.1

Species	Analytical technique (thermal degradation)	Quantity measured (level)	Theoretical quantity	Trueness compared to theory	Thermal degradation	Analysis	Source
CO_2	NDIR (tube furnace)	0,149 kg/kg	0,160 kg/kg	7,3 %	X	X	ISO 19701:2013, 5.2.10.1
HCl	ILC (tube furnace)	0,578 kg/kg	0,584 kg/kg	1,1 %		X	ISO 19701:2013, 5.5.2.11
	FTIR (smoke density chamber)	0,514 kg/kg	0,529 kg/kg	2,7 %	X	X	ISO/TS 19021:2018, B.2.2
SO_2	FTIR (smoke density chamber)	0,045 kg/kg	0,037 kg/kg	19,8 %	X	X	ISO/TS 19021:2018, B.2.1
		0,532 kg/kg	0,533 kg/kg	0,2 %			

Comparison between techniques

Table A.2 shows comparisons between different analytical techniques.

Table A.2

Species	Analytical technique (thermal degradation)	Quantity measured (level)	Theoretical quantity	Trueness by comparison	Thermal degradation	Analysis	Source
CO_2	FTIR compared to NDIR	50 – 100 000 µL/L (fixed concentrations)	?	<5 %		X	[9]
CO_2		0 – 22 000 µL/L (tube furnace)	?	<20 %	X	X	[9]
CO	FTIR compared to NDIR	50 – 5 000 µL/L (fixed concentrations)	?	<5%		X	[9]
		0 – 500 µL/L (tube furnace)	?	>20 %	X	X	[9]
HCN	Spectro-colorimetry with picric acid	8 mg/L	Supposed to be ILC	<13 %		X	ISO 19701:2013, 5.4.11
	Compared to ILC (primary technique)	32 mg/L		<4 %			
	FTIR compared to spectro-colorimetry	5,23 mg/g	Supposed to be spectro-colorimetry	7,8 %		X	[9]