BS ISO 12828-2:2016

BSI Standards Publication

Validation methods for fire gas analyses

Part 2: Intralaboratory validation of quantification methods

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National foreword

This British Standard is the UK implementation of ISO 12828-2:2016.

The UK participation in its preparation was entrusted to Technical Committee FSH/16, Hazards to life from fire.

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Validation methods for fire gas analyses —

Part 2: Intralaboratory validation of quantification methods

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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).

Attention is drawn to the possibility that some of the elements of this document may be the subject of patent rights. ISO shall not be held responsible for identifying any or all such patent rights. Details of any patent rights identified during the development of the document will be in the Introduction and/or on the ISO list of patent declarations received (see www.iso.org/patents).

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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.

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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.

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INTERNATIONAL STANDARD ISO 12828-2:2016(E)

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/

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— 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

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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.

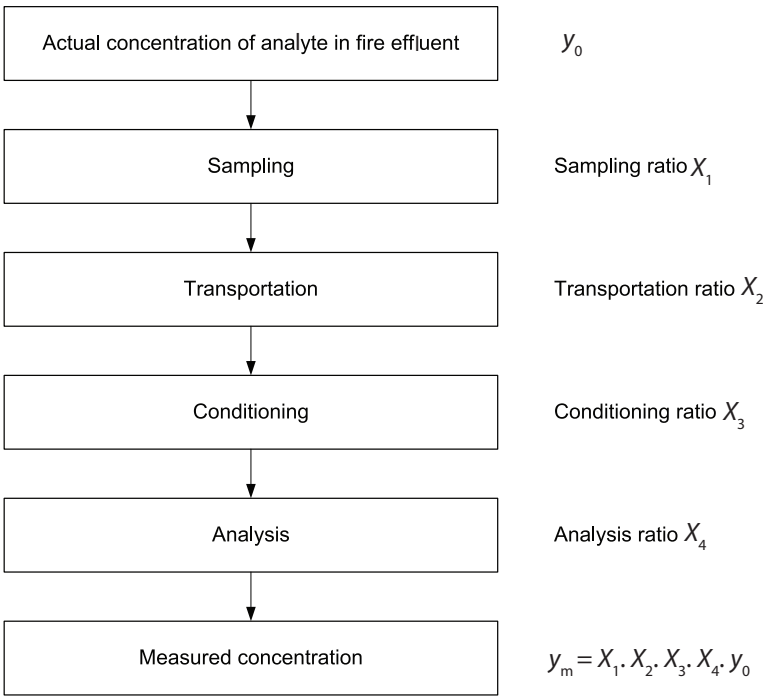

Figure 1 — Measurement ratios

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

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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.

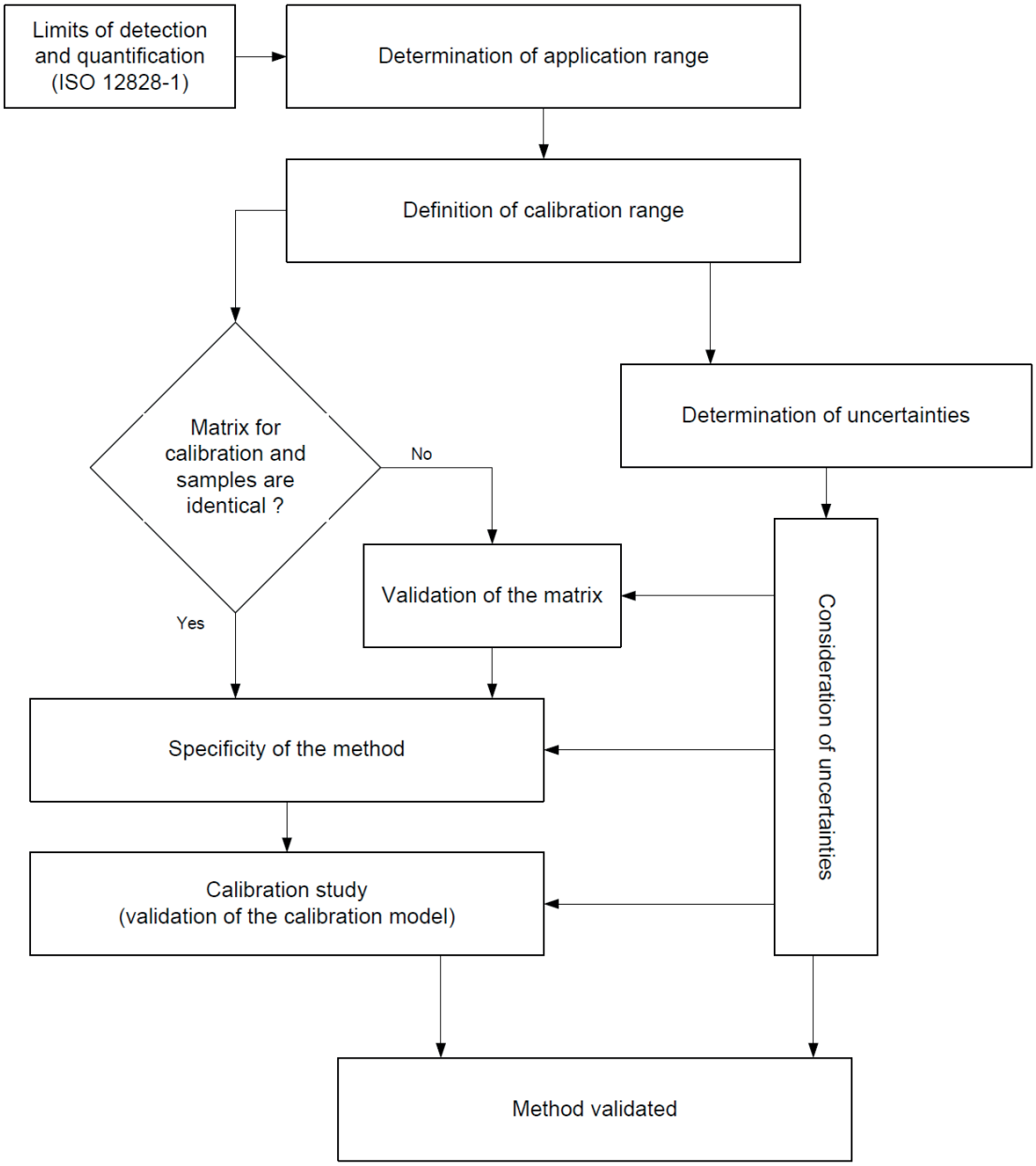

Figure 2 — Steps in validating an analytical technique

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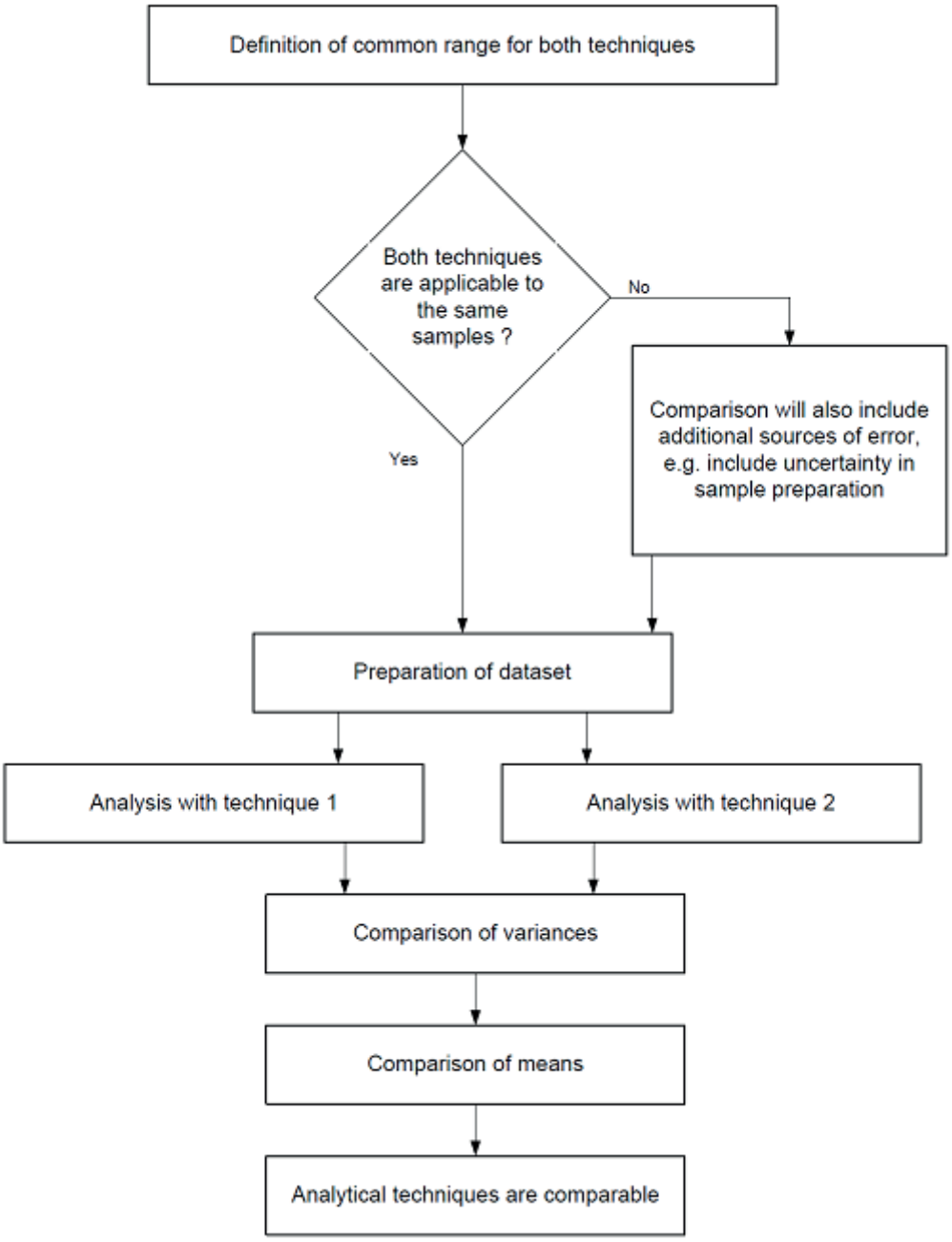

Figure 3 — Steps in comparing two analytical techniques

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).

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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.

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