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**Toxicity testing of fire effluents —
Guidance for analysis of gases and
vapours in fire effluents using FTIR gas
analysis**

*Essais de toxicité des effluents du feu — Lignes directrices pour
l'analyse des gaz et des vapeurs dans les effluents du feu par
spectroscopie infrarouge à transformée de Fourier (IRTF)*

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Case postale 56 • CH-1211 Geneva 20
Tel. + 41 22 749 01 11
Fax + 41 22 749 09 47
E-mail copyright@iso.org
Web www.iso.org

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Foreword

ISO (the International Organization for Standardization) is a worldwide federation of national standards bodies (ISO member bodies). The work of preparing International Standards is normally carried out through ISO technical committees. Each member body interested in a subject for which a technical committee has been established has the right to be represented on that committee. International organizations, governmental and non-governmental, in liaison with ISO, also take part in the work. ISO collaborates closely with the International Electrotechnical Commission (IEC) on all matters of electrotechnical standardization.

International Standards are drafted in accordance with the rules given in the ISO/IEC Directives, Part 2.

The main task of technical committees is to prepare International Standards. Draft International Standards adopted by the technical committees are circulated to the member bodies for voting. Publication as an International Standard requires approval by at least 75 % of the member bodies casting a vote.

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.

ISO 19702 was prepared by Technical Committee ISO/TC 92, *Fire safety*, Subcommittee SC 3, *Fire threat to people and environment*.

This corrected version of ISO 19702 incorporates the following corrections:

- 5.2.2.1: subclauses, which were numbered 4.2.2.1.1 to 4.2.2.1.4, have been renumbered to 5.2.2.1.1 to 5.2.2.1.4, respectively;
- Annex A, paragraph before Figure A.2, fourth sentence: “A coil of 0,6 cm (¼ in) od tubing...” has been changed to “A coil of 0,6 cm (¼ in) outside diameter (OD) tubing...”;
- Bibliography: The number of reference [4] reference has been changed from ISO/CD 21489 to ISO 21489.
- Bibliography: The number and title of reference [5] have been modified to the following:

IEC/TS 60695-7-50, *Fire hazard testing — Part 7-50: Toxicity of fire effluent — Estimation of toxic potency — Apparatus and method*

Introduction

During recent years, analytical techniques have been used widely for the measurement of the concentrations of specific volatiles generated during both laboratory studies and real fires.

The analysis of gases in fire effluents, whilst occasionally needing to rely on methods perfected in other fields (e.g. atmospheric pollution), represents a very specialized field of study due to the complexity and reactivity of the gas mixtures and the possibility for a rapid change in concentration with time. This has led a number of scientists from different countries developing new, or adapting existing methods for the analysis of the gases present during combustion, in accordance with their own requirements.

In some cases, common lines of analysis have emerged, and there is now sufficient expertise and experience to define standard methods for analysing selected gases. Much of this information is provided in ISO 19701, which presents a variety of chemical methods for the determination of individual gases of toxicological importance. Typically, multiple methods are needed to determine all the species of interest for fire hazard analysis.

Fourier transform infrared (FTIR) spectroscopy is different from other techniques in that

- a single method can be used to determine a variety of gases;
- FTIR measurements can be time-resolved, enabling the monitoring of how species develop throughout the fire;
- if a new toxicant should later be identified as important, relevant data concerning the presence of that toxicant might be found in the stored FTIR spectra from previous experiments.

ISO/TC 92 SC 3 has therefore developed ISO 19702 as a separate document.

There are two distinct ways in which FTIR has been used to characterize fire effluent:

- open path analysis, in which the infrared beam is directed across the effluent within the test apparatus;
- extractive analysis, in which a fraction of the apparatus environment is continuously flowed to a sample cell for remote measurement (e.g. IMO resolution MSC 61(67), part 2 toxicity analysis).

Fire scientists have successfully applied variants of both approaches; although, the latter is the more common.

In particular, a European Union funded project (SAFIR) focused on the testing and validation of an extractive FTIR method for use in fire testing. The results of this project form the basis for ISO 19702.

In this International Standard, specific recommendations for sampling systems for use in small-scale and large-scale measurements, for spectral resolution, and for collection and use of calibration spectra are provided. Spectral information is provided for the gases studied specifically in the SAFIR project as an aid to users to determine spectral regions of interest. Finally, applications of the analytical method are discussed.

The primary purpose of the analytical method presented here is to measure the concentration of toxic species to aid in

- a) characterizing physical fire models;
- b) validating numerical fire models;
- c) setting the conditions for exposure in biological studies;

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- d) monitoring of biological studies;
- e) interpreting biological studies;
- f) providing data for use in combustion toxicity assessment without requiring biological studies.

The methods are also generally applicable to the analysis of fire effluents in many situations including real fires.

Any chemical analysis is selective.

Chemical analytical methods are usually appropriate for accurate determination of some species, less for others. Thus, multiple methods can be needed to determine all the species of interest.

In most cases, FTIR can provide the concentration data needed to calculate the yields of the chemical species that are important as input to toxic hazard assessment.

The general recommendations given are based on work conducted using a number of small- and large-scale standard test methods. It is important that this International Standard be read together with the following standards:

- ISO 9705;
- ISO 5660-1:2002;
- ISO/CD 21489:—;
- IEC 60695-7;
- EN 13823:2002;
- ISO 5725.

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Toxicity testing of fire effluents — Guidance for analysis of gases and vapours in fire effluents using FTIR gas analysis

1 Scope

This International Standard specifies methods for the individual analysis of airborne concentrations of carbon monoxide (CO), carbon dioxide (CO₂), hydrogen cyanide (HCN), hydrogen chloride (HCl), hydrogen bromide (HBr), nitric oxide (NO), nitrogen dioxide (NO₂), and acrolein (CH₂CHCHO). Although not specifically defined in this International Standard, as they were not specifically studied in the SAFIR project, the method presented is suitable for most gaseous species able to be analysed using the FTIR technique, including hydrogen fluoride (HF) and sulfur dioxide (SO₂).

2 Normative references

The following referenced documents are indispensable for the application 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 5660-1:2002, *Reaction-to-fire tests — Heat release, smoke production and mass loss rate — Part 1: Heat release rate (cone calorimeter method)*

ISO 5725 (all parts), *Accuracy (trueness and precision) of measurement and results*
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3 Terms and definitions

For the purposes of this document, the following terms and definitions apply.

3.1

spectrometer

instrument used to disperse radiant energy into a spectrum and measure certain properties such as wavelength, mass, energy, or index of refraction

3.2

spectroscopy

study of spectra, especially to determine the chemical composition of substances and the physical properties or concentration of molecules, ions, and atoms

3.3

Fourier transform Infra-red spectroscopy

FTIR

technique for measuring concentrations of multiple species simultaneously using the mathematics of Fourier transforms

3.4

resolution

full width at half height of the instrument line shape function

NOTE This is expressed in units of per centimetre and is the smallest spacing between absorption peaks that can be resolved.

3.5
interferogram

modulated component of the IR beam at the detector measured versus mirror position

3.6
specimen

representative piece of the sample prepared to be tested

3.7
products of combustion

solid, liquid, and gaseous materials resulting from combustion

[ISO 13943]

3.8
minimum detection limit
MDL

theoretical lowest measurable concentration of each measured gas

4 Principle

Numerous different methods of analysis of fire gases are used internationally with acceptable results. Some of the more common alternative standard methods are outlined in ISO/TR 9122-3.

The analysis of gases in fire effluents is very complex due to the great number of different organic and inorganic chemicals potentially present in representative atmospheres. This point is discussed in more detail in conjunction with the presentation of the analysis method.

Conformance with this standard implies that [ISO 19702:2006](https://standards.iteh.ai/catalog/standards/sist/5e2dc1cd-31e9-4219-88ff-906101000000/iso-19702-2006)
[https://standards.iteh.ai/catalog/standards/sist/5e2dc1cd-31e9-4219-88ff-](https://standards.iteh.ai/catalog/standards/sist/5e2dc1cd-31e9-4219-88ff-906101000000/iso-19702-2006)

- the analysis of sampled gases has been carried out by standard procedures;
- the sampling procedure is in accordance with the general recommendations given and with due consideration to the reactive nature of the species analysed.

The sampling system is an integral part of the whole measurement methodology. Recommendations will be made separately for the various parts of the sampling system.

5 Test procedure

5.1 Principle

The effluent from the fire test or physical fire model for the FTIR analysis is taken either from a gas sampling system, such as a flue, or directly from the fire gases. The gas sample is drawn continuously through a heated sampling line to the heated IR absorption cell of the FTIR spectrometer. An interfered IR beam is directed through the gas cell and at chosen intervals interferograms are obtained and, either after the test or on-line, converted into absorption spectra. The concentrations of the gases are calculated by analysis of the absorption spectra using one or more of a variety of methods discussed in Clause 7. The concentration-time relationship of the gases can be evaluated from successive spectra at sufficiently frequent intervals.

FTIR is based on infrared absorption. Specific to FTIR is conversion of regular irradiance from an IR source into interfered irradiance and conversion of an interferogram into a conventional wavelength spectrum containing information over a wide range of wavelengths. In this method, the spectrum is usually presented as absorbance as a function of radiation in wave numbers.

Molecules with a dipole moment have absorption in the infrared region. Thus, only molecules that show sufficient asymmetry can be sensed by their infrared spectrum (e.g. symmetric molecule like oxygen cannot be studied by infrared). There is a large range of absorption strengths among IR-absorbing molecules. Thus, some weakly absorbing species can be “lost” if the user sets the scale for a species of high absorption strength. Conversely, strongly absorbing species can saturate the spectrometer if the user sets the instrument to measure weakly absorbing species. Concentrations are related to intensities of absorption. This is discussed in greater detail in Clause 7 below.

5.2 Sampling system

Recommendations for the filters, sampling line, pump speed, temperature, pressure and response of the sampling system are the same for both large-scale and small-scale testing. Thus, these are made for both small and large scale at the end of this section. The Annex A gives example of sampling systems.

The choice of volumetric sampling speed depends on a variety of parameters, including: the size of the absorption cell, the degree of turbulence within that cell, the temperature of the effluent, the rate at which the concentrations of the species changes during the experiment, the efficiency of the soot filtration system, the length of the sampling line (to control axial diffusion effects), etc. The diameter of the sampling line also should be adjusted based on the above, at least to avoid significant pressure drops in long lines. The sampling rate shall also be selected so as not to perturb the experiment. Thus, there can be differences between sampling conditions for different apparatus, even at the same scale.

The recommendations for the probe are somewhat dependent on the type of measurement and are treated separately for the small and large scale experiments.

IMPORTANT — The fire gases from the FTIR gas cell shall be returned to the exhaust duct of the fire test instrument or otherwise disposed of in a safe way that does not endanger personnel and at a location that does not disturb measurements.

5.2.1 Temperature

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The temperature of the sampling system shall be kept as high as practically possible to reduce the risk of condensation and subsequent washing of soluble fire gases out of the sample. The whole system shall be kept at a minimum temperature of 150 °C, although the recommended temperature is 180 °C.

The temperature throughout the sampling system should be homogeneous, or slightly increasing along the sampling system from the probe to the gas cell, to avoid cold points that could act as a condensation point for water and soluble gases.

5.2.2 Probe

5.2.2.1 Small scale

Sampling the gases from small-scale tests depends on the fire model (e.g. smoke box as in ISO 5659, tubular furnace, cone calorimeter as in ISO 5660-1). The best choice of a probe and its position are closely related with the fire model. Only recommendations are given in this International Standard.

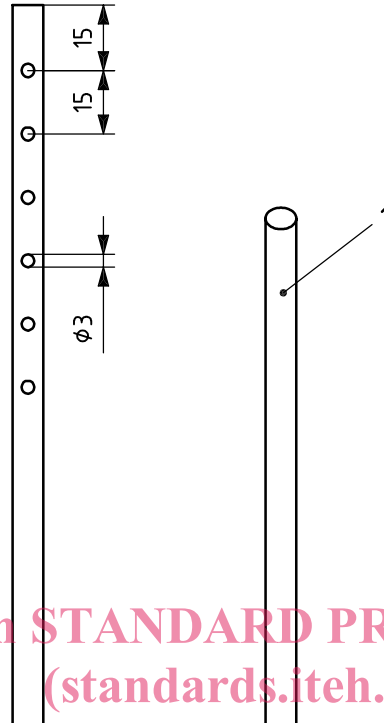
5.2.2.1.1 Different types of probes can be used, i.e. a single-hole or multi-hole probes. The choice will depend directly on the fire model considered. In order to obtain a representative mixture of effluent; when stratification effects are suspected, a multi-hole probe is preferred. An example of the different types of probes is shown in Figure 1.

5.2.2.1.2 The probe shall be made of material resistant to corrosion, stainless steel is recommended, with a minimum hole size of 3 mm in diameter.

5.2.2.1.3 In the case of a tube furnace type of test, the extraction probe takes a portion of the total flow from the furnace to the FTIR (generally by dividing the exhaust flow). In this case, the internal diameter of the extraction probe should not be less than 3 mm, in the case of a single-hole probe.

5.2.2.1.4 Samples from the exhaust duct of small-scale tests can be extracted using a probe placed in the exhaust duct of the particular test. In this type of situation, a multi-hole probe, inserted perpendicular to the flow of the fire gases, with the holes facing downstream from the gas flow, is recommended.

Dimensions in millimetres



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Key
1 inner diameter

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Figure 1 — Schematic of probes for sampling in exhaust duct

Care shall be taken to ensure representative sampling. In order to avoid perturbation in the effluent, volumetric sampling shall be a small fraction of the total flow through the duct. The probe shall be positioned such that the flow of effluent is not turbulent (effluents well mixed) and as near as possible to the fire source (in order to limit the condensation or secondary reaction of gases). Positioning of probe shall be considered for each fire model: taking into account the effect of stratification and/or the velocity profile in flow tubes.

The probe shall be cleaned regularly to ensure that the holes do not become blocked, as this will reduce the reliability of the sampling.

5.2.2.2 Large scale

The type of probe recommended above for duct extraction in small scale tests is suitable for measurements in the duct of a large-scale test such as the ISO 9705 room or SBI apparatus.

When sampling directly from inhomogeneous fire gases, however, a representative sample should be taken over the whole of the fire gases being monitored. In order to accomplish this, it is necessary to have a gradation of hole sizes along the length of the probe and to place the probe such that it crosses the fire gases monitored. An example of a suitable probe is given in Table 1. This probe has been successfully applied to measurements taken in the door of the ISO 9705 room, where the top of the probe (closest to the pump) was placed at the top of the ISO 9705 door and the probe traversed the door diagonally, finishing 30 cm below the top of the doorway.

Table 1 — Example of a probe suitable for sampling fire gases from the door of the ISO 9705 room

Probe characteristics ^a	
Hole number	Hole diameter mm
1 (closest to end)	5
2	3,2
3	2,5
4	2,1
5	1,8
6	1,6
7 (closest to pump)	1,5

^a This probe has an internal diameter of 6 mm and the holes are placed 10 cm apart. The end of the probe is sealed.

This probe is placed such that it crosses the top of the door opening with the lowermost hole 30 cm below the top of the door. The holes are facing downstream from the fire gases.

5.2.3 Gas cell

The gas cell should be composed of inert material that is resistant to the fire gases measured (e.g. nickel coated aluminium or synthetic silica are often used).

It has been shown that nickel-coated aluminium can fail rapidly unless it is ensured that the coating is of sufficient thickness. Caution shall be taken using that type of equipment.

The volume and the path length of the gas cell are critical for the response time of the total measurement system, and a gas cell volume of between 0,2 to 2 l is normally recommended in fire testing. The path length could vary with the volume of gas cell. A path length between 2 m and 10 m has been found suitable for fire effluent analysis. The volume and the path length of the gas cell shall be adapted with regard to the desired detection limit and the fire model considered.

The gas cell should be heated to a minimum of 150 °C and both the temperature and pressure in the cell should be monitored throughout the fire test. It is recommended that both the pressure and temperature be kept constant as this effects the intensity of the spectral band (see Annex A). If the temperature or pressure in the fire test cannot be maintained at the same value as that used when collecting calibration spectra, then a correction should be made for this difference when calculating species concentrations. However, the correction is valid only for limited variation in pressure and temperature. This correction can be made using the universal gas law. This correction might not be completely effective in every case due to non-linear changes in the shape of spectra with pressure and temperature.

5.2.4 Filter

The gas cell (internal mirrors) shall be protected from the intrusion of soot from the fire gases.

NOTE This is always true unless a so called "dirty cell" is being used. In this case, soot is allowed to enter the gas cell. These cells are, however, only suitable when small amounts of soot are expected and are not recommended for the study of fire tests.

A filter or filters may be placed either between the probe and sample line or after the sample line. Both positions have advantages and disadvantages.

Placing the filter between the probe and sample line protects the sample line from build-up of soot, which may adsorb acid gases. The disadvantage of this filter position is that during the early stages of a fire, the filter medium may be cooled by the sample gas stream. A large temperature differential may develop between the geometric centre of the filter medium and the heated filter housing. This creates a condition favourable for the retention of water and water-soluble acid gases in the filter medium. Care shall be taken to use a sufficiently long heated probe to preheat the sample gases prior to contact with the filter medium, and/or a heated filter housing of sufficiently small diameter to allow the filter housing to more effectively heat the core of the filter medium. Decreasing the diameter of a membrane filter has the benefit of lowering the absorption of acid gases on the filter.

Placing the filters downstream of the heated sample line preheats the sample gas prior to reaching the filters, ensuring that the filter medium is too hot to contain moisture. This minimizes the loss of acid gases on the filter medium.

Either planar membrane filters or cylindrical filters are recommended. The planar filters should optimally have a porosity of 5 μm and a diameter of 47 mm, although other porosity and diameters may be used. Placing a high-capacity, high-porosity filter upstream of this low-porosity filter prolongs the service life of the downstream filter. Glass fibre, ceramic, and PTFE coated filters have been found suitable. Care shall be taken when working with heated filters, in particular close to the high working temperature limit, as the filter is required to function at temperatures above 150 °C for a long period of time.

Glass wool filters cannot be used for fluorine analysis. The porosity of the filter shall be chosen as a compromise between sufficient entrapment of soot without premature clogging of the filter.

The filter housing should be made of stainless steel (although in certain cases PTFE can be used) and the filter temperature should not be less than 150 °C.

More important than the specific choice of filter material and porosity is that the filters used are analysed for the presence of acid gases if these are measured. This is due to the fact that acid gases can adsorb onto the soot particles in the fire plume or onto the soot retained by the filter in an unpredictable way. This adsorption behaviour is especially important when measuring low concentrations of acid gases as some saturation behaviour is expected, i.e. the amount adsorbed onto the filter decreases as the filter becomes saturated with acid gases. An example of a procedure to analyse the gases retained on the filter is given in Annex B.

It should be noted that some filters contain chlorine. Care shall be taken if the filter is washed to collect the gases retained on soot or condensed with the water coming from combustion to determine the chlorine content without fire gases to provide a baseline for the determination of the level of adsorbed chlorine from the fire gases.

The kinetics of absorption onto the filter has not been characterized. However, when the total amount of gas produced during the combustion is needed, the quantity measured on the filter should be added to the total amount measured by FTIR. It shall be noted that the adsorption on the filter has an effect on the accuracy of the time-dependent measurement of the gases evolved during combustion. When a time-dependent measurement is needed, information on gases analysed on the filter shall be considered in order to identify the potential effect on the concentration/time curves.

Soot deposition on the cell optics can be minimized by selecting a FTIR system with the gas cell mirrors and cell windows mounted in a vertical position.

5.2.5 Sampling line

A gas sampling line of PTFE offers the best performance. This line should be kept at a constant temperature of at least 150 °C. An inner diameter of 3 mm to 4 mm is suitable. The length should be as short as possible and 4 m has been found to work well. Problems due to the adsorption of gases, particularly acid gases, onto the walls of the sampling line become more pronounced for the longer sampling line.

Saturation behaviour is expected for the sampling line as described for the filters above. This implies that a pre-aged line will adsorb less acid gases than a new line. This behaviour has not been characterized and thus a recommended method of ageing the line is not available.

Various materials such as synthetic, high-purity silica, PTFE and stainless steel have been found suitable for sampling lines. Their use depends on the type of gases to be analysed.

5.2.6 Pump speed

The sampling flow rate should be as high as possible without incurring problems due to clogging of filters. A minimum pump flow of 3,5 l/min is recommended, although this does depend on the cell volume and required response time. In the case of tubular furnace, for example, a lower flow rate is usually sufficient.

5.2.7 Response time of the sampling system

It is difficult to recommend a single experimental set-up for FTIR measurements, as different laboratories will have different equipment. In order to correctly interpret the FTIR results and compare them to other measurements in the same experiment, it is important that the response time for the system be known. A protocol for the determination of the response time for the whole sampling system is summarized in Annex C.

In general, the FTIR gas cell is responsible for most of the response time. An approximate response time can be calculated using an estimate of the total volume of your sampling system plus gas cell to divide by the flow rate in your system. This does not take into account the effect of the geometry of the sampling system, but is generally greater than 70 % of the full response time

6 Spectrometer parameters

The spectrometer should be located in a suitable environment to ensure correct function of the equipment, keeping in mind that some parts of the equipment are susceptible to moisture.

The spectrometer parameters are described in more detail in Annex E.

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6.1 Detectors <https://standards.iteh.ai/catalog/standards/sist/5e2dc1cd-31e9-4219-88ff-34b00c9f7001/iso-19702-2006>

Different type of detectors can be used, e.g. DTGS or MCT (see Annex E).

6.2 Resolution

A resolution in the range 0,5 cm⁻¹ to 4 cm⁻¹ is recommended for most requirements in fire experiments. This allows the collection of several measurements every minute while still retaining an acceptable sensitivity.

The resolution should be the same for calibration spectra and testing. Indeed, some software does not allow calibration spectra and spectra from tests to have different resolution.

6.3 Minimum detection limit (MDL)

Table 2 shows some examples of how the combination of resolution and number of scans that are being averaged effects the minimum detection limit of CO.

Table 2 — The effect of resolution and number of scans on the MDL of CO

Resolution cm ⁻¹	Number of scans	MDL μ/l
1	1	16
	4	8
4	1	15
	4	7