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Guidance for sampling and analysis of toxic gases and vapours in fire effluents using Fourier Transform Infrared (FTIR) spectroscopy

Lignes directrices pour l'analyse des gaz et des vapeur dans les effluents du feu par spectroscopie infrarouge à transforée de Fourier (IRTF)

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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 WTO principles in the Technical Barriers to Trade (TBT), see the following URL: Foreword — Supplementary information.

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

This second edition cancels and replaces the first edition (ISO 19702:2006), which has been technically revised.

Introduction

Sampling and analysis of fire effluents is required for a variety of applications in life threat[4][11][26] and environmental impact from fires[6] assessments. The end result of these analyses is a list of chemical species and their concentrations in the effluent at a specific time or over a time interval and at a specific location, during (and possibly after), the period of generation of the effluents. Depending on the end use of these data, the requirements may range from a highly detailed, time-resolved, quantified, and validated list of chemical species to a simple estimate of a single compound or small range of compounds.

Although occasionally employing methods used in other fields (e.g. atmospheric pollution), obtaining relevant data often requires specialized sampling and analysis techniques, due to the complexity, reactivity and generally "hostile" nature of typical fire effluents, as well as the commonly observed rapid changes in concentrations with time and distance from the fire source.

The following typical properties of fire effluents render more "traditional" methods of sampling and analysis inappropriate:

— high temperatures of 1 000 °C or higher;

— presence of aerosols (i.e. solid and liquid particulates) with a wide range of particle sizes and distribution, together with adsorbed and absorbed chemical species;

— presence of condensable organic and inorganic vapours (e.g. water);

— high turbulence, with spatially and temporally variable concentrations;

— a very wide range of species and their concentrations, typically varying rapidly with time and location with respect to the fire source (or heating zone in the case of a "bench-top" physical fire model);

— presence of acidic/corrosive species;

— presence of water soluble species and/or or highly reactive species resulting in sampling losses.

The identification of these factors has led to the development of new methods or the adaptation of existing methods for the sampling and analysis of the gases and vapours in the effluent from fires and physical fire tests.

Common methods have emerged in recent years, and in some cases, standards have been published for selected gases and vapours. Much of this information is provided in ISO 19701, which presents a variety of methods for the sampling and analysis of individual gases of toxicological importance. Several methods are often needed to determine all the species of interest for fire hazard analysis.

Fourier Transform Infrared (FTIR) spectroscopy offers an improved procedure, principally through:

— single-method measurements of gases and vapours relevant to fire toxicology;

— time-resolved measurements over relatively short periods (i.e. concentrations of chemical species of interest), enabling the monitoring of chemical species development and decay throughout the fire or physical fire test; and

— relevant data concerning the presence of a toxicant which may be found in the stored FTIR spectra, in case a new toxicant should later be identified as important.

Although when published, ISO 19701 summarized the technique and some applications of FTIR in fire gas analysis, the method has since undergone considerable development and the requirements for obtaining reliable results have been established, using "best practice" procedures. This International Standard is developed by ISO TC 92, SC 3 to provide the requirements, which will include additional information.

FTIR can be used to analyse fire effluents using these two methods:

a) open path analysis, where the infrared beam is directed across the effluent within and/or outside the fire test apparatus;

b) extractive analysis, where a fraction of the effluent from a fire test apparatus is drawn continuously through a heated sampling system through the gas cell of the FTIR instrument, enabling remote measurement (e.g. IMO Resolution MSC.307(88)[9]).

Both procedures (and variants) have been successfully applied although the extractive analysis technique is far more common in fire effluent analysis.

Of particular relevance in the development of FTIR as a practical tool in fire gas analysis is SAFIR (Smoke Gas Analysis by Fourier Infrared Spectroscopy), a European Union-funded project[18][19] which focused on the testing and validation of an extractive FTIR method when used in a variety of situations. The results of this project formed the basis for the first version of this International Standard. This revised version has been updated with more recent information, e.g. References [8], [15], [21], [25] and [27].

It should be appreciated that any chemical analysis is selective in terms of chemical species determined and the accuracy and precision of quantitative measurements. Some chemical analytical methods may be appropriate for accurate determination of some species but less appropriate for other species. Thus, despite the ability of FTIR to measure a wide range of chemical species of interest in the field of life threat from fire, additional methods may also be required to determine all the species of interest for a particular application. However the use of FTIR analysis alone can provide data of sufficient quality to identify and calculate the concentrations of many of the chemical species that are important in toxic hazard assessment.

Guidance for sampling and analysis of toxic gases and vapours in fire effluents using Fourier Transform Infrared (FTIR) spectroscopy

1 Scope

This International Standard specifies requirements and makes recommendations for sampling systems for use in small and large-scale fire tests, for the selection of parameters and use of the FTIR instrument itself and for collection and use of calibration spectra.

The primary purpose of the methods is to measure the concentrations of chemical species in fire effluents which may be used to

a) provide data for use in combustion toxicity assessment without requiring biological studies,

b) allow the calculation of yield data in fire characterisation studies,

c) provide data for use in mathematical modelling of hazard to life from the fire effluent by characterising the effluent composition generated by physical fire models,

d) characterise the effluent composition of small scale physical models and larger scale fires for comparative purposes,

e) assist in the validation of numerical fire models,

f) set the conditions for exposure in biological studies if required,

g) monitor biological studies where used, and

h) assist in the interpretation of biological studies where used.

This International Standard specifies principles of sampling and methods for the individual analysis, in fire effluents, of airborne volume fractions of carbon monoxide (CO), carbon dioxide (CO_2), hydrogen cyanide (HCN), hydrogen chloride (HCl), hydrogen bromide (HBr), nitric oxide (NO), nitrogen dioxide (NO_2), and acrolein (CH_2CHCHO).

In most common cases, a wide concentration range may be measured by an FTIR instrument. Typically, it is in the range from few µl/l to thousands of µl/l for HCl, HBr, HF, SO_2, NO_x, and HCN, and up to few per cent for CO, CO_2 and H_2O. This list is only indicative and many other species could be added.[27] Although not specifically defined in this International Standard, as they were not specifically studied in the SAFIR project,[18] the method presented is also suitable for analysis of other gaseous species, including e.g. hydrogen fluoride (HF) and sulfur dioxide (SO_2) with appropriate sampling methods.

Calibration methods are provided in this International Standard. Guidance is also given on the recommended cleaning, servicing and operating checks and procedures to be carried out on the FTIR instrument and the sampling systems which are considered essential to maintain the instrument in a suitable condition for use in fire effluent analysis.

Sampling is considered to be an integral part of the whole FTIR measurement methodology and recommendations are made for the design, maintenance and operation of suitable systems.

Conformance with this International Standard implies that:

— The sampling procedure used is in accordance with current internationally accepted “best practice” for the applications described.

— The analytical procedure has been carried out with due regard to the restraints imposed by the nature of the fire effluent atmosphere and the limitations of the FTIR methodology itself.

This International Standard only provides general recommendations for the sampling and analysis of fire effluents, based on best practice as determined from a wide variety of small- and large-scale standard and ad hoc fire test studies. The Standard may not be wholly applicable for use in specific published fire test methods where FTIR may be specified as a requirement for effluent sampling and analysis in that particular test. In these cases, the specific requirements for the sampling and analysis by FTIR may be published within the standard test procedures and should be followed. However, if such specific requirements have not been published, this edition of this International Standard may be used as a basis for acceptable results.

2 Normative references

The following documents, in whole or in part, are normatively referenced in this document and are indispensable for its application. For dated references, only the edition cited applies. For undated references, the latest edition of the referenced document (including any amendments) applies.

ISO 6286, *Molecular absorption spectrometry — Vocabulary — General — Apparatus*

ISO 6955, *Analytical spectroscopic methods — Flame emission, atomic absorption, and atomic fluorescence — Vocabulary*

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

ISO 13344, *Estimation of the lethal toxic potency of fire effluents*

ISO 13571, *Life-threatening components of fire — Guidelines for the estimation of time to compromised tenability in fires*

ISO 13943, *Fire safety — Vocabulary*

ISO 19701, *Methods for sampling and analysis of fire effluents*

3 Terms and definitions

For the purposes of this document, the terms and definitions given in ISO 13943, ISO 6286, and ISO 6955, as well as the following apply.

3.1
apodisation
mathematical process to correct deviations from the theoretical interferogram obtained in FTIR spectroscopy

Note 1 to entry: This process widens absorption bands and therefore lowers the resolution.

3.2
interferogram
pattern of variable radiation intensity resulting from the interaction of (usually) two beams of monochromatic electromagnetic radiation of the same wavelength when the beams have travelled over a different path length before combining

3.3
resolution
capacity of a spectrophotometer to distinguish between two adjacent frequencies (or wavenumbers), mathematically defined as that separation which produces two bands which are separated by at least half the intensity of one of them

Note 1 to entry: In infrared spectroscopy, two consecutive bands often have a different intensity. Then, resolution is generally expressed as the width at half height of a single absorption band recognized as “isolated and thin”.

Note 2 to entry: This is commonly expressed in units of cm^{-1} and is the smallest spacing between absorption peaks that can be resolved.

[SOURCE: ISO 6286]

3.4
spectrophotometer
instrument used to disperse electromagnetic radiant energy into a spectrum and measure certain properties such as wavelength, energy, or index of refraction, for example, as the basis for the qualitative and quantitative determination of chemical species which interact with the radiant energy in selective ways dependent on the species

3.5
trueness in wavelength
ability of a given spectrophotometer to provide an accurate radiant flux at a specific wavelength or wavenumber

[SOURCE: ISO 6286]

3.6
wavenumber
inverse of the wavelength (λ) of electromagnetic radiation

Note 1 to entry: $\nu = \frac{1}{\lambda}$

where ν (wavenumber) is expressed in reciprocal centimetres (cm^{-1}) and λ is normally expressed in µm. This entails a conversion factor of 10 000 in the calculation of wavenumber from wavelength.

3.7
zero filling
correction technique applied to sparse data to enable intermediate data points to be generated by a mathematical regression

4 Principles

A system for measuring concentrations of gases and vapours in fire effluent by the extractive FTIR technique consists of a sampling system, a "flow-through" optical cell, an infrared light source, an interferometer and an optical detector. Software is required to extract species identification and concentrations from the collected signals.

The sampling system is designed to deliver a gas flow to the FTIR optical cell that is as true a representation as possible of the effluent in a known region from which the sample is extracted. Inaccuracies, caused for example, by condensation or adsorption losses in the sampling tubing must be understood, quantified and applied to the final results.

A detailed description of the principles of infrared spectroscopy and FTIR is provided in many texts including References [12], [16] and [28]. Annex A gives the general outline of this principle.

The mathematics by which an FTIR spectrophotometer generates species concentrations is typically proprietary and varies among manufacturers and models. Obtaining accurate concentrations requires calibration, examination of the spectroscopic peak shapes and separations, and perhaps verification of some concentrations using a second analytical technique.

5 Sampling

5.1 General

The requirements for the sampling systems given in this International Standard are in most cases generally applicable both for large-scale and small-scale testing but details of sampling requirements

for specific tests are not included. This detail is to be provided with the Standards which describe these specific tests. Parts of the sampling system to be designed for a specific test apparatus or sampling location within that apparatus include the sampling probe and the filter, the length and maintained temperature of the sampling line and the sample flow. These sampling parameters are normally specified to match the volume and geometry of the optical cell in the FTIR spectrometer.[18][19][25][27] Examples of sampling systems are given in Annex B.

The sampling probe is designed to extract fully representative samples from the test apparatus and/or the fire effluent stream and be constructed from material/s which will be inert to the effluents being measured. Guidance for probe design is provided in 5.4.

The filter in the sampling train shall capture particles to avoid deposits on mirrors in the FTIR cell. Guidance for the selection of filters is provided in 5.3.

The design of the sampling line and the flow characteristics affect the time of the concentration measurements. Guidance for sampling line design and sampling flow selection are provided in 5.5 to 5.7.

The cell volume and geometry set restrictions on the sample flow used and thus on the time resolution of the measurements and uniformity of the gas in the optical cell. Guidance for cell selection is provided in 5.8.

For safety reasons, the extracted and analysed gases are to be returned to the exhaust duct of the fire test fixture or otherwise disposed of in a safe way that does not endanger personnel and to a location that does not disturb measurements. With a standard test which has a requirement or option to use FTIR gas analysis, it is anticipated that this International Standard will provide specific requirements for the safe disposal of the effluent stream after measurement (e.g. whether the effluents will be recirculated or safely discharged elsewhere).

The requirement for each part of the sampling system is described separately in the following subclauses. Annex M gives examples of proprietary FTIR equipment and sampling systems that have been proved to be suitable for fire effluent analysis.

NOTE Sampling in large-scale tests such as in ISO 9705 and in large open calorimeters (ISO 24473) is described in Reference [3].

5.2 Temperature of the sampling system

5.2.1 The sampling system shall be heated to a temperature which shall be set between 150 °C and the temperature of the gas cell (recommended maximum 190 °C).

5.2.2 The temperature of the entire sampling system shall be kept at an even temperature and not be higher than the gas cell temperature to avoid condensation in the cell.

NOTE 1 It is important that the gas in the sampling system is heated to a temperature as close as possible to the set-temperature of the sampling system. A procedure for checking the gas temperature in the optical cell is given in F.1.

The temperature of the system should optimally be even but the most important condition is that the temperature of the gas cell is the highest in the sampling system.

The temperature shall be high enough to prevent condensation and losses due to the dissolving of soluble fire gases from the sample. The whole sampling system shall be kept at a minimum temperature of 150 °C, although the recommended temperature is 180 °C.[18][19]

NOTE 2 The temperature must not exceed 200 °C at any point between sampling point and gas cell, as chemical reactions between components of the sampled fire effluents could lead to a modification of gas composition above this temperature. Nitrogen oxides are particularly sensitive to this parameter.

5.3 Filter systems

5.3.1 A gas cell with internal mirrors shall be protected from soot/particle deposition from the sampled effluent, with a particulate filter.

5.3.2 The filter shall normally be placed directly after the sampling probe and prior to the heated sampling line.

5.3.3 The filter shall be uniformly heated in a housing to prevent condensation of liquids

NOTE 1 Correct placement of filters in the sample train is important, since incorrect filter placement can result in significant sample losses (e.g. through gas adsorption on particles) which leads to distorted concentration/time profiles of the measured species.

NOTE 2 For certain designs of filter and housing, placing the filter directly between the probe and the sample line can in some cases cause problems in the early stages of a compartment fire test. The filter medium, even though heated externally may be cooled internally by the cool sample gas stream. A significant temperature differential may then develop between the internal filter medium and the heated filter housing. This creates conditions favourable for the condensation of water, water-soluble acid gases and as well as high boiling point vapours within the filter medium. The trapped gases may be released as the filter medium temperature increases, further distorting the concentration histories. To avoid this, a sufficiently long sample line, with the appropriate number of heated segments can be used to preheat the sample gases to the intended sample line temperature prior to contact with the filter medium.

5.3.4 The filter shall be heated to a temperature which shall be set between 150 °C and the temperature of the spectrometer gas cell.

NOTE The recommended maximum temperature of the spectrometer gas cell is 190 °C.

5.3.5 The type of filter recommended is a cylindrical filter as opposed to a plane filter.

NOTE A cylindrical filter has a large area which gives a high filtration capacity and this is especially important for the primary or pre-filter. Cylindrical ceramic filters with a length of 75 mm, a diameter of 31 mm and a porosity of 2 µm have been successfully used in various types of fire tests.[13][14][18] Alternative materials for cylindrical filters are polytetrafluoroethylene (PTFE), glass fibre, and stainless steel.

Glass wool, ceramic, and stainless steel filters could induce losses of hydrogen fluoride and should be avoided in the sampling train when hydrogen fluoride is likely to be present in the effluent stream.

The porosity and size of the filter shall be chosen as a compromise between sufficient entrapment of soot and other particles without premature clogging of the filter, using the above recommendations as a guide.

5.3.6 Plane surface filters may alternatively be used.

NOTE 1 Plane surface filters generally have a lower filtration capacity compared to cylindrical filters with more likelihood of early blockage occurring. These can, however, be used effectively as secondary filters following a cylindrical pre-filter.

NOTE 2 Where no pre-filter is used, a 1 µm porosity, 47 mm to 75 mm diameter filter is the best compromise for plane surface filters (compared to 0,45 µm and/or 5 µm for PTFE), although other porosities and diameters may be successfully used.[18] Alternatively, 1µm or 2 µm stainless steel filter has been reported to be successful. Stainless steel filters can be cleaned and regenerated by calcinations. References [15] and [21] provide details on filters selection.

5.3.7 Filters shall be analysed for the presence of acid gases if these are to be measured and losses in the filter can be expected.

NOTE 1 Acid gas losses in the filter are due to adsorption onto the soot and or liquid particles in the fire plume or onto the soot retained by the filter. The adsorption losses are especially important when measuring low concentrations of acid gases or when sampling over a short time period. Under these conditions acid gases may initially be removed from the sampled effluent stream until the adsorption sites in the filter become saturated. After this stage most of the acid gas component will be passed on to the sampling line. This results in a spurious release of acid gas from the filter over time which does not accurately follow the release of the acid gases from the sampled atmosphere. To estimate these losses, a procedure to analyse the gases retained on the filter is given in Annex C.

NOTE 2 Analysis of losses of hydrogen chloride (HCl) in filters was made in the SAFIR project.[18] The chemical analysis of the filters in door opening measurements in ISO 9705 test chamber experiments showed that there were low losses (losses of between 0,4 %and 1,3 % relative to the total sampled amount) of HCl in cylindrical ceramic filters. A slightly greater retention of HCl was seen for a planar glass fibre filter (losses of between 1,1 and 5,8 relative per cent). In both cases the higher relative losses of HCl were found when the measured concentration of HCl was low.

The kinetics of absorption onto the filter has not been characterized and it is therefore difficult to establish a true time/concentration profile of the acidic species in the sampled fire atmosphere. However, when the total amount of gas produced during the combustion is required, the quantity measured on the filter should be added to the total amount measured by FTIR (see Annex C). It is stressed 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 required, information on gases analysed on the filter should be considered in order to estimate the potential effect on the concentration/time data.

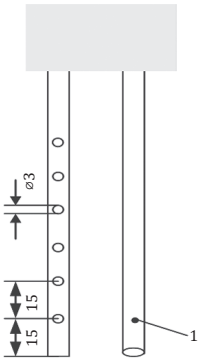
5.3.8 It should be noted that some filter materials can contain chlorine. The chlorine content of a clean unused filter should be measured to provide a baseline for the determination of the level of adsorbed chlorine from the fire gases.

5.4 Sampling probes

5.4.1 General

Two types of probes can be distinguished: "single-hole" and "multi-hole". The choice depends on the physical fire model from which the sample is being extracted in order to obtain a representative mixture of effluent. Examples of the two types of probes are shown in Figure 1.

Dimensions in millimetres



Key

1 inner diameter

NOTE An inner diameter of a single-hole probe of 4 mm has been shown to work effectively.[18]

Figure 1 — Schematic of multi-hole and single-hole probes for sampling in an exhaust duct

5.4.1.1 The probe shall be made of material resistant to corrosion and must not otherwise react significantly with the gases to be analysed.[18][19]

NOTE 1 PTFE or perfluoroalkoxy polymer (PFA) is recommended as the contact material for the effluent stream.

NOTE 2 A probe of PTFE is generally inert and would have a low potential for causing losses. The flexibility of the material could be a disadvantage in certain applications, for example where precise positioning is necessary. A further disadvantage is that PTFE is not suitable for higher temperatures, as high temperatures influences the material properties and at sufficiently high temperatures thermal degradation occurs.

NOTE 3 Quartz and/or stainless steels can be used for some effluents, but react with hydrogen fluoride (HF).

NOTE 4 A stainless steel probe placed in a position with initially a temperature lower than the sampled effluent may cause condensation of products including water. This will lead to sample losses, an important example of a gas species prone to losses being hydrogen chloride (HCl).

NOTE 5 A practical probe can be constructed using stainless steel tubing lined with a narrower-bore PTFE tube or lined with epoxy resin. The stainless steel tube will facilitate direct ohmic heating (i.e. passing a low voltage electric current through the metal tube) and the PTFE or epoxy lining will further reduce losses on the probe surfaces.

5.4.1.2 The probe shall be cleaned before each test to ensure that the holes do not become partially or wholly blocked

5.4.2 Single hole probes

5.4.2.1 Where the effluent stream is likely to be well mixed/homogenous a single-hole probe is appropriate

5.4.2.2 In the case of a flow-through type of physical fire model (e.g. a tube furnace[7]), the extraction probe takes a proportion of the total homogenous flow from the apparatus and directs it to the FTIR spectrometer. A single-hole probe is therefore appropriate for such applications

5.4.2.3 The internal diameter of the extraction probe shall not be less than 3 mm

NOTE A single-hole probe is used in many standardized test procedures where the effluent stream is assumed well mixed and homogenous e.g. Reference [9]. However, due to stratification effects in fire chambers and in extract ducts where laminar flow is present, (i.e. leading to poor mixing) the gas concentration may not be uniform over the chamber or duct volume and the measured gas concentration is thus dependent on the position of the single-hole probe. In these situations the use of a multi-hole probe is appropriate where the non-uniform gases can sampled over a more representative area.

5.4.3 Multi hole probes

5.4.3.1 When stratification is present in the effluents from the fire, a multi-hole probe is preferred to obtain a representative sample from across the stratified layer.

5.4.3.2 A minimum hole diameter of 3 mm is recommended for multi-hole probes for most applications.

5.4.3.3 The holes in a multi-hole probe shall be directed downstream in the effluent stream to avoid direct impingement of soot particles and thus reducing the possibility of blocking of the holes.

5.4.4 Probe positioning

5.4.4.1 In order to avoid perturbation in the effluent, the rate of volumetric sampling shall be a small fraction (<25 %) of the total flow rate in flow-through apparatus or the total volume in a fixed volume apparatus.

5.4.4.2 A single hole probe shall be positioned where the flow of effluent is not turbulent (but where the effluents are well mixed). Positioning of the probe shall be considered for each physical fire model, taking into account the effect of stratification and/or the velocity profile in flow tubes in addition to the end use of the data, which in some cases may require sampling from the effluent stream close to and/or at a distance from the effluent source.

5.4.4.3 With a multi-hole probe a gradation of hole sizes along the length of the probe and placement of the probe such that it crosses the fire gases monitored can be used in large scale fire tests. A simpler but less precise method is to place a single-port probe in a well-mixed location in the relatively well-mixed upper layers of the effluent. For detailed information of sampling in large-scale tests, see Reference [3].

NOTE 1 Measurement of the volumetric exit flow is necessary whatever probe type is used in order to convert measured concentrations to total flow of gas species from a test enclosure. The exit flow can be measured using traditional velocity probes such as pitot tubes, McCaffrey probes[23] or more advanced optical methods e.g. particle image velocimetry. An alternative method is to calculate the exit flow based on the pressure difference between the test enclosure and outside and the height of the neutral plane (i.e. a virtual horizontal plane separating the outgoing effluent from the clean incoming air) in the stratified case. An example of this method is given in Reference [22] and more details can be found in Reference [20].

NOTE 2 The exit flow in enclosure fire tests varies during a test. The rate of the exit flow grows with increasing fire intensity and the position of the neutral plane may stabilize during the "steady-state" period where the fire growth is relatively stable (e.g. due to ventilation control of burning rate rather than fuel involvement control of burning rate).

NOTE 3 It is often not possible to directly measure the exit flow using velocity probes as the pressure difference over the opening is relatively small and the often turbulent outflows in the opening have velocity components in directions other than the normal direction to the exit plane.

5.5 Sampling line

5.5.1 The sampling line shall be non-reactive with the gases to be analysed.

5.5.2 A readily replaceable sampling line is preferred.

NOTE 1 Various materials such as PTFE, PFA, and PTFE-lined stainless steel have been found suitable for sampling lines.

NOTE 2 A heated gas sampling line with a fluorocarbon such as PTFE or PFA offers the best resistance to acid gases. An inner diameter of 3 mm to 4 mm is suitable. The length should be as short as possible, yet should be long enough to preheat the sample gas to the cell temperature. Sample line lengths between 4 m and 20 m have been used successfully[3][25] although sampling problems due to the adsorption of gases, particularly acid gases, onto the walls of the sampling line, together with soot build up is more likely with a longer sampling line. Another disadvantage with a long sampling line is the back-pressure that increases with the length.

NOTE 3 Saturation behaviour for adsorbed species within the sample line is also possible as described for the filtration systems. This implies that a sampling line which has been pre-aged with acid gases will adsorb less acid gases during sampling than a pristine line. However this behaviour has not been characterized and thus a recommended method of ageing the line is not available.

NOTE 4 Multiple heating circuits are recommended for fire effluent sampling where the temperature of the sampled gases changes as a fire develops. Separate heating circuits are needed for each section of a heated sample line to maintain the desired temperature profile along the entire length. The controlling thermocouple/s should be positioned in the centre of each thermostatted section. If only one heating circuit is used, the upstream end of the line will be significantly colder than the mid-section when sampling cool air in the early stage of fire development. As the fire develops; the hot point of the heated sample line moves downstream. For a multi thermostatted heating line, the amount of heat applied to each circuit per foot of sample line is dependent on the temperature of the gases being sampled. The thermostatted section of the heated sampling line furthest upstream line (i.e. close to the sampling probe where fitted) should be no longer than 1 m, as significant acid gas losses can occur over even a very short section of poorly heated sample line.

5.5.3 The sampling line shall be cleaned with a frequency depending on tests performed.

NOTE 1 The need for cleaning the sampling line is based on two performance criteria: 1) the flow performance of the line, i.e. the observation of increased back-pressure from the line and consequent reduction in flow rate; and 2) the contamination level of the line which is monitored by background measurement of the measurement system.

NOTE 2 The following procedures have been found effective for cleaning sampling lines:

a) Connect a pressurized 150 psi nitrogen or air supply to the end of the sampling line and "back-flush" (i.e. with the flow in the reverse direction to the normal sampling direction) to remove collected particulate matter. Due attention must be given to the safety issues surrounding the use of high pressure gas lines. It has been found that a small crumpled spherical pellet of paper ("spitball"), with an outside diameter smaller than the sample line, inserted into the tube can assist this process by scraping the walls of the tube as the paper passes along it. This method is also effective in clearing completely blocked lines.[25]

b) If the spitball method is not effective, back-flush the line for a first time with deionized water, if the line is very blocked. A large Luer-tipped syringe with an appropriate adapter may be used.

Alternatively: 1) let the line stand with the water inside for at least 1 min; 2) then purge it with fresh water; 3) wash the line for a second time with a solution of 50 % ethanol in water; 4) wash the line a third time with a solution of 50 % acetone in water; and 5) dry the line with a flow nitrogen or air.

5.5.4 The sampling line shall be heated to a temperature which shall be set between 150 °C and the temperature of the gas cell (recommended maximum 190 °C).

NOTE 1 Multiple thermostatted heated line segments controlled by the same number of temperature controllers may be needed to keep each section of the sample line within the recommended temperature range.[25]

NOTE 2 The temperature profile along the sampling train can be measured as follows:

a) Insert a thermocouple at the open end of the sample line to allow it to reach the entire length of the line.

b) Start the sampling pump at the specified flow rate and wait until the system stabilizes.

c) Note the temperature through the length of the sample line and adjust the temperature set point of each temperature controller as required.

NOTE 3 Various methods have been found suitable for heating, including direct ohmic heating (i.e. with stainless steel tubing, passing a current directly through the tube at low voltage), proprietary heating tape and heating tracer wire. These heating lines will have an external layer of thermal insulation (e.g. glass wool and glass fibre tapes, flexible ceramic cloth tubing and/ or ceramic cloth lined silicon-coated tubing). Custom heating line options are available commercially that are PTFE-lined, flexible, insulated, with a weatherproof, thermally robust covering. The whole system can be controlled by commercially available temperature controllers.

5.6 Pump selection, position, and flow rate

5.6.1 The sampling pump can be of "pushing" or "pulling" type.

A pump can either push or pull the gas sample through the FTIR gas cell. Examples of the two main approaches to sampling system design (i.e. pump "pushing" or pump "pulling") are presented in Annex B. Pushing enables the use of an analyser bypass loop with a bypass regulator, which ensures a constant cell pressure resulting in more accurate concentration measurements and a constant flow rate through the sample cell throughout the life of the filter, resulting in more accurate gas concentration histories. Alternatively if the gases are pulled through the FTIR gas cell, the gas cell pressure will drop during the life of the filter, if the pump flow rate is maintained. This can be a major source of error, particularly for gases with nonlinear calibrations. In both cases leakage is possible particularly between a clogging filter and the pump, so pressure tests should be performed after each filter change.

A motor-driven high temperature bellows-type pump should be selected for pushing sampled air to the gas cell. These pumps will not contaminate the sample and the pump "head" can be placed in a thermostatted chamber with the driving motor positioned external to the thermostatted chamber.

5.6.2 The pump flow rate shall be selected based on the specific measurement system and the test requirements.

NOTE 1 The volumetric flow of the sample gas through the FTIR is selected after consideration of a variety of parameters, including: the volume of the cell, the degree of turbulence within the cell, the temperature of the sample gas, the rate at which the concentrations of the species changes during the experiment, the efficiency of the soot filtration system and the length and volume of the sampling line.

NOTE 2 The diameter of the sampling line is chosen based on the parameters mention above, to avoid significant pressure drops in long lines and to reduce blockages.

5.6.3 The flow rate of the extracted effluent shall not perturb the studied test or experiment and shall be low enough not to affect the gas concentration in the test apparatus.

NOTE With respect to 5.6.3, the flow rate of the combustion gases drawn into the system must be high enough to achieve the desired time of 90 % response, from sampling probe to analyser, termed "t_{90}". This is a function of the flow rate and the internal volumes of the filters, tubing and gas cell. See Annex D for the procedure to determine response times.

5.7 Response time of the sampling system

5.7.1 A small volume gas cell is generally desirable for time-resolved combustion and fire gas analysis to ensure rapid throughput and measurement.

NOTE 4 m long path length cells are available with internal volumes as small as 160 ml on commercial FTIR instrumentation; 2 m long path length cells are available with internal volumes as small as 90 ml. Even smaller volume custom cells can be obtained while maintaining long path lengths.

5.7.2 The response time for the sampling system shall be determined.

NOTE 1 A protocol for the empirical determination of the response time is summarized in Annex D.

NOTE 2 Different equipment in different laboratories makes it impractical to specify a single experimental set-up for ensuring acceptable response time for FTIR measurements.

NOTE 3 Factors influencing the response time are: 1) the length and internal diameter of the heated sampling line; 2) the internal volume of the measuring cell and filtering element(s); 3) the geometry of the cell and filtering element(s); 4) the sample flow rate; and 5) the presence of any cold spots in the sample train.

5.8 Optical cell

5.8.1 The gas cell shall have an internal volume that gives an acceptable response time.

NOTE See Annex D for response time and Annex E for considerations for optical cell performance.

5.8.2 The gas cell shall have an optical path length that allows acceptable detection limits.

NOTE See Annex E for the influence on detection limits from the optical path length.

5.8.3 The gas cell shall be made of inert material that is resistant to the fire gases measured.

NOTE 1 Nickel or synthetic silica is often used as internal coating of a cell body made of aluminium. However, it has been shown that nickel-coated aluminium can fail rapidly unless it is ensured that the coating is of sufficient thickness. Caution and frequent checking have to be taken using this type of equipment.

NOTE 2 Potassium bromide (KBr) cell windows are not appropriate for fire gas analysis as they are sensitive to moisture. Zinc selenide (ZnSe) has a high thermal resistance and is transparent over a usable spectral range of 650 cm^{-1} to 4 500 cm^{-1} and is resistant to water. ZnSe cell windows are available with additional coatings to make these windows even more resistant to water.

5.8.4 The gas cell shall be heated to a minimum of 150 °C.

NOTE A recommended maximum cell temperature is 190 °C as fittings and gaskets can be degraded over time at higher temperatures.

5.8.5 The temperature and pressure in the gas cell shall be recorded throughout the fire test and corrections made for any changes that take place during the fire test. See Annex F for detailed requirements.

5.8.6 It is essential that calibrations are made at cell temperatures, pressures and flow rates as close as possible to those used for measurements in the fire tests. See Annex F for detailed requirements.

NOTE 1 Some FTIR software programs allow the logging of the cell temperature and pressure with each acquired spectrum and correct the concentrations for pressure and temperature.

It is important that both the cell pressure and temperature are kept constant (see Annex F) as these affect the intensity and shape of the spectra. If the temperature or pressure in the gas cell during measurements in a fire test cannot be maintained at the same value as those used when collecting calibration spectra, then a correction should be made for this difference when calculating species concentrations. This correction can be made using the universal gas laws. However, the correction is valid only for limited variation in pressure and temperature. This correction might not be completely effective in every case due to nonlinear changes in the shape of spectra with pressure and temperature, see Reference [17].

5.8.7 The gas cell shall be well maintained to keep its optical performance.

NOTE Procedures for maintaining the gas cell are given in Annex F.

6 The FTIR spectrophotometer

6.1 Spectrophotometer environment

The spectrometer must be located in a suitable environment to ensure correct and stable operation. The location must be free from vibration, extremes of ambient temperature and humidity. Access to all parts should be unobstructed.

NOTE General information on an acceptable FTIR spectrometer location and installation can be found in Reference [10].

6.2 Detector

The choice of the detector depends on the requirements of sensitivity, response time and limit of detection.

NOTE Mercury cadmium telluride (MCT) detectors are faster and can provide a sensitivity of up to 10 times that of a Deuterated tri-glycine sulfate (DTGS) detector. However, MCT detectors are more nonlinear than DTGS detectors. See Annex G for details.

6.3 IR-source

Two types of source are frequently used, the “Nernst” source or the “Globar” source. Both types can be used for the purpose of this International Standard.

6.4 Mirror alignment and cleanliness

In order to maximize the sensitivity of the spectrophotometer-cell combination the mirrors shall be properly aligned and the internal mirrors and optical window at the entrance of the IR beam should be kept clean and in good condition.

NOTE Auto-alignment systems that optimize the gain through the optics, are often provided by the manufacturer.

6.5 Spectrophotometer compartment

The intensity of the IR beam generated by the interferometer is subject to attenuation by the atmospheric carbon dioxide (CO_2) and water vapour in the surrounding environment which could change during use. To limit this effect, instruments may be purged with nitrogen.

NOTE A filter can be added to remove remaining trace concentrations of water and CO_2 in the nitrogen purge gas.

6.6 Spectral range limits

The spectral range used determines which species can be identified and quantified. A wavenumber range of 650 cm^{-1} to 4 500 cm^{-1} is recommended.

NOTE 1 In practice, the range is limited by transparency properties in the infrared beam splitter and gas cell window, and also by the detector sensitivity. The use of ZnSe windows to the gas cell gives a useful wavenumber range of 650 cm^{-1} to 4 500 cm^{-1}.

NOTE 2 For quantitative analysis, calibration spectra are collected using the same spectral range as for experimental spectra. For details of calibration techniques, see Clause 7, Annex I, and Annex J.

6.7 Resolution

A resolution of 0,5 cm^{-1} or finer is recommended for minimization of interferences in fire gas analysis, although a coarser resolution (>0,5 cm^{-1}) is allowed as long as spectral interference from overlapping compounds are identified and corrected for by the software.

It is the responsibility of the operator to ensure that the resolution of the FTIR instrument is adequate for the analysis undertaken. This shall be confirmed by the use of a separate quantitative analytical measurement of the effluent, according to ISO 19701.

The resolution, sample gas temperature, cell temperature, cell pressure and apodisation function should be the same for calibration spectra and experimental spectra.

NOTE See Annex G for details regarding resolution.

7 Calibration

7.1 Background noise

7.1.1 Excessive background noise could be produced from a number of sources such as the IR source, the detector or a poor optical path alignment. It can also be caused by electronic sources in the FTIR instrument circuitry. It is also a function of resolution, apodisation function, and use of zero filling as well as the speed of the moving mirror.

7.1.2 The background noise shall be determined in various positions in the spectrum to be used.

NOTE A procedure for the determination of background noise is given in Annex G.

7.2 Limits of detection and of quantification (L_D and L_Q)

7.2.1 The cell path length and signal-to-noise ratio of the output from the FTIR instrument determine the limit of detection (L_D) and the limit of quantification (L_Q) of the method.

7.2.2 L_D and L_Q shall be determined for the FTIR instrument.

NOTE 1 ISO 12828-1 describes different methods to estimate these limits. The method adapted for this FTIR standard is the determination from a data matrix of blank samples, fully described in ISO 12828-1:2011, 6.2.

NOTE 2 A practical procedure for the determination L_D and L_Q is given in Annex G.

7.3 Calibration methods

7.3.1 The FTIR instrument shall be calibrated with a specific traceable method for each gas species that is measured and reported as described in Clause 9.

NOTE Information on appropriate calibration methods are given in Annex J.

7.3.2 The calibration is specific to a particular gas cell at a given temperature, path length, and pressure. The calibration is also specific to the resolution, apodisation, phase correction and gain of the specific spectrometer. If any of these parameters change, a new calibration must be carried out.

7.4 Acquiring and collecting calibration standards

7.4.1 Gas mixtures of known and traceable concentrations shall be used as reference gases for calibration.

NOTE Information on methods to produce and use calibration gases are given in Annex I.

7.4.2 Calibration spectra shall be collected using the same FTIR arrangement as used for fire gas analysis.

NOTE Information on recording reference spectra for calibration and building the calibration set are given in Annex K.

8 Measurement procedure

8.1 General

It is important that the limits of detection and quantification are appropriate to the species being measured. Each species required for the measurement, as specified in ISO 13344, ISO 13571, or a specific test procedure, shall be within the limits of quantification and detection at concentrations of toxicological significance.

NOTE To ensure optimal detection limits the optical bench of the FTIR instrument must be nitrogen purged. A long purge may be required to minimize water vapour interferences. It may need to be initiated a day or two in advance.

8.2 Daily checks and controls

8.2.1 General

All the following operations shall be performed at the beginning of each day of operating. The instrument shall be set up and used under the same conditions as those for calibration measurements, in terms of resolution, number of scans, iris aperture, gain and mirror scan speed apodisation and phase correction.

Before being used to analyse fire effluents, the sampling system and gas sampling cell shall be heated to their chosen working temperatures. If an MCT detector is used, this shall be cooled to the required temperature. Ample time should be allowed for temperature equilibration of the whole sampling system.

8.2.2 Control of calibration method

The calibration of an FTIR spectrophotometer normally remains stable provided no major changes are made to the instrument and associated equipment. Nevertheless, parameters such as shocks or unexpected variations with the interferometer, or ageing effects, could lead to a deviation from the calibration.

"Control calibration" shall be performed with a control gas. The reference concentrations of the control gases shall have a precision of at least 1 %. When measured with the FTIR instrument, the deviation from the nominal concentration shall not exceed 5 %. If these values are not possible to obtain, the verification procedures stated in Annex F shall be performed.

The control gas shall be standard certificated gases in pressurized cylinders. Ideally, the control gas is a mixture of gases which are stable over time and absorb IR radiation over a spread of wavenumbers which are exclusive to each gas. A mixture of CO, CO_2, C_2H_4 and CH_4 has been found suitable for daily calibration control.

8.2.3 Spectrophotometer sensitivity measurements

With no sample in the gas cell, the signal attenuation and the beam aperture needed to produce a normal signal from the FTIR detector shall be noted. These parameters are then compared to the initial values obtained after the qualification procedures of Annex H have been carried out (i.e. the "nominal values").

If the signal attenuation obtained is under 50 % of the nominal value, proceed to the cleaning of mirrors as described in Annex F. If this operation does not lead to a strong reduction of attenuation, check the windows and change them if needed. If all these operations are insufficient to decrease the attenuation, there may be a further technical problem with the interferometer.

NOTE Dedicated software may be provided from the manufacturer of the FTIR allowing a check of the spectrometer sensitivity.

8.2.4 Sampling system tests

The sampling system shall be tested for leaks.

NOTE 1 Leaks developing in the sampling train may allow dilution of the sample or losses of sample depending on whether the pump is "pulling" or "pushing" the sample. This will affect the calibration parameters of the FTIR.

NOTE 2 To check the sampling system for leaks with a sample pump of "pulling" type, block the opening/s of the sampling probe or the end of the sampling line with no probe fitted, with the sample pump operating, until the pressure indicator reaches 100 Torr. If this value cannot be achieved or held when the pump is switched off there are leaks in the sampling system and all parts have to be checked and where necessary repaired. Leaks can also be checked by installing shutoff valves at key positions on the sampling train (e.g. upstream and downstream of the filters and the pump), along with a pressure/vacuum gauge and a 3-way valve to introduce nitrogen. Pressurize to 10 psi and check if the system holds pressure (see Reference [25] and Figure B.2).

8.2.5 Control of the sampling flow rate

The method for controlling the sampling flow rate is dependent on if the sampling system is of "pulling" or "pushing" type.

NOTE 1 A calibrated rotameter (float-type flowmeter) can be used in both cases. A reference flowmeter (a mass flowmeter, a bubble flowmeter or a dry meter) can be used to calibrate the rotameter.

For a sampling system of the "pulling type", i.e. when the pump is placed after the sample cell, the flowmeter shall be positioned at the sampling point of the system.

NOTE 2 The open-path rotameter is positioned at the sampling point, i.e. before the primary filter and the sampling line in order for the flow measurement not to be biased by back-pressure effects. The other side of the flowmeter shall experience atmospheric pressure (see B.1). The flow is controlled downstream at the vacuum pump. The flow should be measured before and after each test. The disadvantage of a "pulling" type sampling system is that the cell vacuum will increase as the soot builds up in the filters if not regulated for. This can pose major errors, particularly for quantification of gases in nonlinear calibration ranges.

For a sampling system of the "pushing type", i.e. when the pump is placed before the sample cell, a needle valve shall be positioned upstream of the sample cell to control the flow to the cell. The open

rotameter (no needle valve) shall be positioned downstream of the sample cell, resulting in no cell back-pressure (see B.2 and Figure B.2).

NOTE 3 When using a bypass pressure regulator to bypass flow to the sample cell, position a needle valve upstream of the sample cell to control the flow to the cell (see Reference [25], B.2, and Figure B.3). Use an open path (i.e. open to atmosphere) rotameter downstream of the sample cell, which will produce no cell back-pressure. The back-pressure regulator ensures that the pressure at the needle valve is constant, resulting in a constant flow rate through the cell as soot builds up in the sample filters. A constant flow through the sample cell provides more accurate time histories.

A rotameter placed at the downstream end of the sample cell is a convenient visual way to monitor the flow during tests. The rotameter is generally calibrated for 1 atm and the pressure at the sample cell output should be very close to atmospheric pressure. The needle valve should be upstream of the sample cell to control flow to the cell, without affecting the cell pressure.

8.3 Preparation for sampling and analysis

8.3.1 Select a filter material which is chemically inert to the expected effluents and of suitable porosity.

NOTE If the test specimen is thought, or known, to contain fluorine, use PTFE or ceramic filters.

8.3.2 The filter shall be changed after at least every three tests and every time the fuel types in the test are changed. The filter shall also be changed if the pressure in the gas cell cannot be maintained due to back pressure in the sampling system.

A new or clean filter should be used when determining acid gases as specified in 5.3 and in Annex C.

8.4 Initial procedures immediately before a test

8.4.1 Collect a background spectrum.

Collect a background spectrum before starting the sample flow from the fire effluent. It is recommended to collect a minimum of 30 scans for the background spectrum. The background spectrum should be made with a non-IR absorbing gas such as moisture-free nitrogen. The background spectra should not be collected until the water absorbance is minimized.

NOTE 1 The optical bench can be purged with a non-IR absorbing gas such as moisture-free nitrogen for a sufficient duration to minimize water and CO_2 absorbance.

NOTE 2 Collect the background spectra using the same spectral resolution as to be used during the subsequent measurements in the test.

8.4.2 Start acquiring spectra and record the timing of scans.

NOTE The number of scans per spectra is a determining factor for the time resolution of the measurement and for the noise level.

8.5 Procedures during sampling from a test

8.5.1 Note the start time of the test relative to the time of the FTIR spectra collection.

8.5.2 Carefully monitor and record the cell pressure and cell temperature throughout the test.

The temperature and pressure shall ideally not vary during the test period.

NOTE 1 Most FTIR instruments are equipped to monitor the cell pressure and cell temperature and have software to record these readings for every spectra stored.

NOTE 2 The acceptable cell pressure variation depends on the degree of nonlinearity of the calibration. Small variations on cell pressure during a test can be corrected using the universal gas laws. See Annex F for requirements.

8.6 Procedures after a test

8.6.1 When the test has ended, stop spectra collection and purge the whole sampling train with clean air or nitrogen for at least 5 min.

NOTE 1 Purging with dry air or nitrogen has the advantage of more quickly removing corrosive acid gases from the sampling system.

8.6.2 Check all filters and change or clean them if needed before the next test.

8.7 Data reduction

Data reduction is often performed automatically by the software supplied with the FTIR instrument. The process results in a collection of spectra which are then presented as plots of individual species versus time. However, the effluent could contain interfering species that were not included in the calibration mix or matrix and may therefore be misinterpreted by the data reduction software. The data shall be checked for interfering species that can produce errors in the results. Procedures for checking data in this respect are given in Annex J.

9 Test report

Presentation of results is an important aspect of the procedure for measurement of gases and vapours using FTIR spectroscopy. The format for presentation will vary depending on the end use of the results but for comparative purposes (e.g. during reproducibility and repeatability studies) it is important that this format is identical for every test. Typically, the content would include tabular and graphical representations of concentration with time with the following as a minimum list of parameters to be included:

— sampling system design;

— name of operator;

— date and time of the fire test;

— notes of any sampling problems during the test;

— notes of any data collection problems during the test;

— notes and times of important occurrences in the fire test (e.g. start of test, ignition, extinction etc.);

— spectrophotometer parameters: resolution, iris aperture, gain and mirror speed used;

— FTIR gas cell used: reference, path length, temperature, pressure, volume;

— type of detector used;

— calibration method(s) employed;

— number of scans for background;

— number of scans per spectra;

— time resolution between each spectrum acquired and number of spectra in the collection;

— wavenumber(s) or region(s) used for quantification;

— estimated overlapping gases in the selected wavenumber region;

— time of measurement of maximum concentration during the test;

— whether evaluated concentrations lie in the range defined by calibration data or are based on extrapolation outside of this range; and

— concentration versus time for each chemical species of interest.

10 Precision and accuracy

10.1 General

Precision and accuracy shall be determined for each calibration gas with multiple measurements covering each selected concentration range.

10.2 L_D and L_Q

The results shall be analysed by taking into account the limit of detection (L_D) and limit of quantification (L_Q), as described in ISO 12828-1.

NOTE 1 Information for the determination of L_D and L_Q are given in 7.2 and Annex G.

NOTE 2 The precision of FTIR smoke gas data is influenced by several factors, including the sample flow rate the gas cell pressure control, sampling system temperature, filter and sampling system efficiency and the quality of the calibration model used.

10.3 Repeatability and reproducibility

The repeatability of the measurement with the specific FTIR system used shall be determined.

NOTE An example of a repeatability and reproducibility study is presented in Annex L.

Annex A
(informative)

FTIR theory

For the purposes of this International Standard and its proper use, a general outline of the principles of operation of an FTIR spectrometer is given here. Molecules which contain a "dipole" (i.e. residual positive and negative charges at each end of a chemical bond) can interact with infrared radiation (IR) by virtue of the electromagnetic field set up as the dipole rotates, vibrates, stretches, translates (i.e. moves as a body) through natural thermal effects. This interaction manifests itself as absorption of specific wavelengths of the radiation by specific dipole groups within the molecule and this is used as the basis of qualitative and quantitative measurements on samples placed in the IR beam. It is also possible to obtain IR spectra with certain species which do not contain such a dipole but are capable of obtaining one through the effect of infrared radiation. This is then termed "Raman" spectroscopy.

The infrared region of the electromagnetic spectrum is usually divided into three parts; the near-, mid- and far-infrared:

— Near-IR — approximately 14 000 cm^{-1} – 4 000 cm^{-1} wavenumbers (0,7 µm – 2,5 µm wavelength) corresponding to overtone or harmonic vibrations within the irradiated molecule.

— Mid-IR — approximately 4 000 cm^{-1} – 400 cm^{-1} wavenumbers (2,5 µm – 25 µm wavelength) corresponding to fundamental vibrations and associated rotations and-vibrations within the irradiated molecule.

— Far-IR — approximately 400 cm^{-1} – 10 cm^{-1} wavenumbers (25 µm – 1 000 µm wavelength), corresponding to the rotation of the irradiated molecule.

With classical "dispersive" Infrared Spectroscopy, an infrared source is resolved into its component wavelengths by an optical grating. The instrument is so arranged that the range of wavelengths can be successively passed through the sample (or "scanned"). A detector in the IR beam placed after the sample gives a trace of the intensity of the various wavelengths (or wavenumber) with time as the sample is scanned and results in a number of absorption "peaks". The position of the peaks and the extent of absorption is used to qualify and quantify respectively, the species in the sample. Such a scan typically requires several minutes to complete, and therefore severely limits this technique for "on-line" fire gas analysis.

Fourier transform infrared (FTIR) spectroscopy refers to a general technique used to obtain an infrared spectrum of absorption, emission or Raman scattering of a solid, liquid or gas. An FTIR spectrophotometer simultaneously collects spectral data over a wide IR spectral range, in the form of an interferogram (i.e. all wavenumbers are collected simultaneously), as distinct from classical dispersive spectroscopy, (which collects data at each wavelength sequentially). The Fourier transform is a mathematical algorithm used to convert the raw interferogram data into a practical spectrum, analogous to the spectrum resulting from a slow scanning classical dispersive method.

NOTE 1 In practice, the infrared beam is generated by a polychromatic IR-source. The radiation enters a "Michelson interferometer" (see Figure A.1) that allows some wavelengths to pass through, but blocks others due to wave interference. The beam is modified for each new data point by moving one of the internal mirrors and therefore changing the length of one or both beams of the interferometer. This changes the set of wavelengths that pass through. A laser is used to determine the accurate position of the mirror, for the wavelengths studied. Computer processing by Fourier Transform is required to convert infrared absorption for each mirror position (the interferogram) into a spectrum, i.e. infrared absorption for each wavelength.

NOTE 2 It is important to understand the function of the laser in determining wavenumber accuracy, which is related to the registration and drift of wavenumber accuracy that can occur for various reasons. In an FTIR-Michelson interferometer, radiation from the polychromatic infrared source is collimated and directed to a beam splitter. One half of the radiation is reflected towards a fixed mirror and one half is transmitted towards a moving mirror. Radiation is reflected from the two mirrors back to the beam splitter and 50 % of the original radiation is focused on the sample and then onto the detector. The difference in optical path length between the two beams of the interferometer is called "retardation". It defines the "amplitude" and resolution of the spectrophotometer. The interferogram is obtained by varying the retardation and recording the signal from the detector. The shape of the interferogram when no sample is present depends on the splitter and on the "couple source" (i.e. a diaphragm used to limit illumination). This leads to a typical interferogram shape with a maximum at zero retardation (constructive interference at all wavelengths), with, on either side, a series of lower intensity peaks from destructive interference.

The use of an interferometer provides two main advantages in comparison with the traditional dispersive spectroscopy: First, as all wavelengths are collected simultaneously, the signal resolution (in intensity) is increased. Second, the interferometer throughput is determined only by the diameter of the collimated beam coming from the source and not affected by the instrument itself (as it is where if a monochromator diffraction grating is used in a dispersive instrument). In modern instruments the moving mirror of the interferometer turns at a constant velocity, and sampling of the interferogram is triggered by finding zero-crossings in the fringes of a secondary interferometer irradiated by a helium-neon laser. This confers high wavenumber accuracy on the resulting infrared spectrum and limits wavenumber calibration errors (a trueness around 0,01 cm^{-1} can be reached).

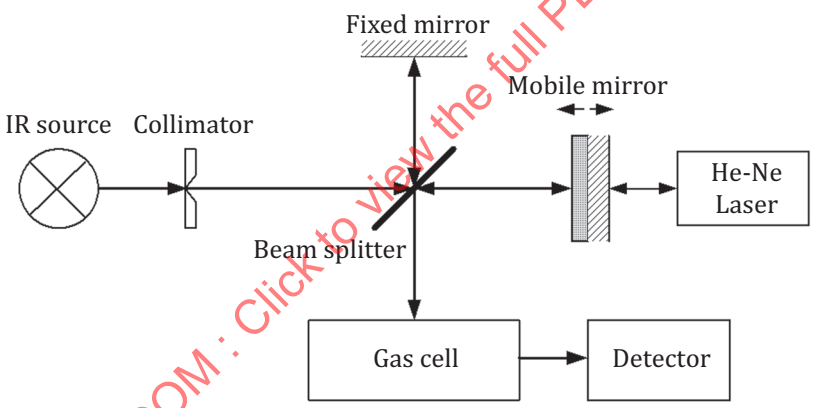


Figure A.1 — FTIR interferometer principle

Annex B
(informative)

FTIR sampling systems

B.1 Example of a “pulling” sampling system

An optimized sampling method was proposed in the SAFIR project.[18][19] Figure B.1 gives a schematic diagram of such a “pulling” sampling system.

— The point for gas collection in the exhaust duct connected to a fire chamber is placed at a distance where the gaseous mixture is homogeneous and the gas flow is not disturbed, i.e. laminar flow.

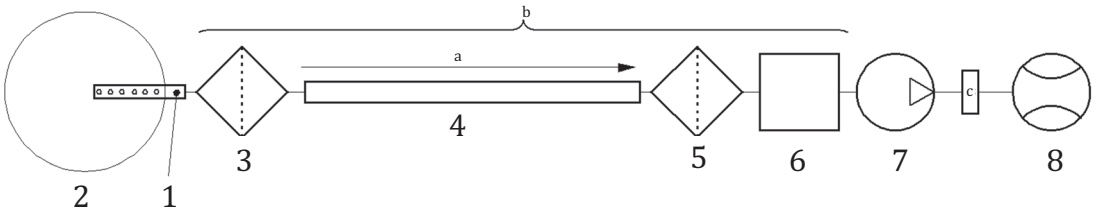
— The distance between the fire source and the sampling probe should be as short as possible (consistent with a homogenous and laminar flow) to maintain the probe at an elevated temperature. This will assist in reducing condensation in the probe.

— The filter is placed between the probe and the transfer line. Another filter may be used between the line and the gas cell to protect the FTIR analyser gas cell from contamination from fine soot particles.

— The flowmeter is placed after the pump and it is recommended that a moisture trap is included between the pump and flowmeter, to prevent condensed water entering the flowmeter.

— An open-flow rotameter can be placed upstream of the filter before and after each test to check the actual sampling flow. This flow is compared to the flow measured at the outlet of the pump.

— The temperatures of the filter, sampling line and gas cell should be as similar as possible and high enough to prevent condensation.



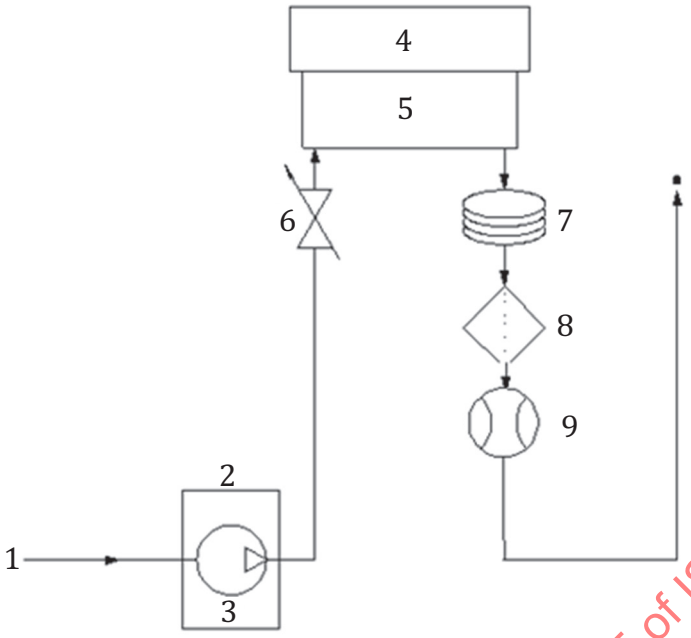
Key

1 probe
2 exhaust duct (fire model)
3 filter 1
4 transfer line
5 filter 2
6 FTIR gas cell
7 pump
8 flowmeter
a Flow rate, (3,5 l/min).
b Part of the sampling system heated to >150 °C.
c Water trap.

Figure B.1 — Schematic diagram for a "pulling" sampling system

B.2 Example of a "pushing" sampling system

The sampling system illustrated in Figure B.2 has been used with the objective of maintaining a constant FTIR gas cell pressure. With the gas cell at the end of the sample train, with no restrictions to flow at the cell's output will result in the gas cell operating close to atmospheric pressure, regardless of any increasing restriction from the build-up of particles within the filtration system.[13] A needle valve is positioned upstream of the heated cell. The pump must be placed upstream of the sample cell to push the sample through the cell. The pump head should be mounted in a thermostatted oven to maintain the desired temperature. A coil of 0,6 cm (1/4 in) outside diameter (OD) tubing [internal diameter (ID) is more important] downstream of the heated cell cools the sample gas to ambient temperature prior to entering a large high capacity filter which protects the downstream flowmeter from the build-up of tarry condensates. This high capacity 0,3 µm filter has a gas filtration area of 625 cm^2. The high surface area of the filter media provides a long filter life, and minimal flow restriction. The cell pressure is very slightly above atmospheric pressure due to the downstream filter.

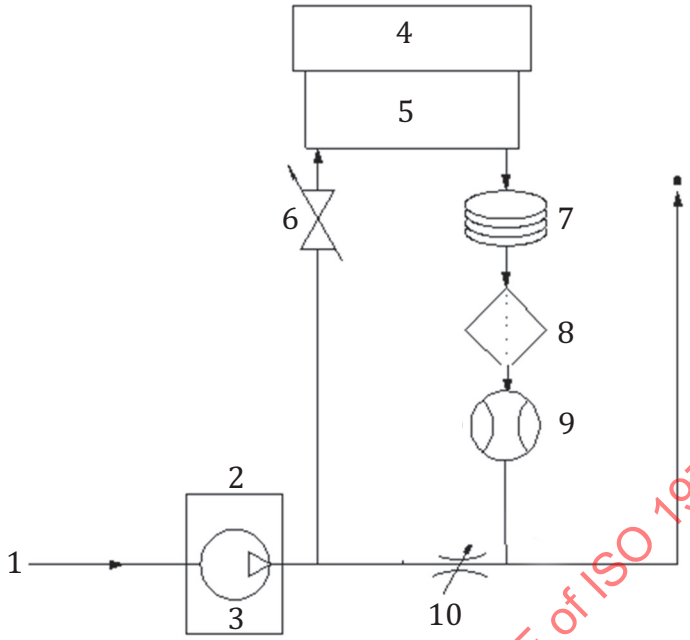


Key

1 heated sample line
2 oven (filters in oven)
3 pump head
4 FTIR
5 heated cell
6 needle valve
7 cooling coil
8 high-capacity filter to protect flowmeter
9 flowmeter
a Flow out.

Figure B.2 — Schematic diagram for a "pushing" sampling system

The sampling system in Figure B.3 is similar to that in Figure B.2, but in addition has a bypass loop and bypass regulator at the cell inlet to ensure a constant flow rate through the sample cell, regardless of gradual blocking of the filter. This configuration is effective in maintaining a constant cell response time profile and constant cell pressure. The desired pressure is set on the bypass regulator and excess flow bypasses the gas cell. The bypass flow decreases as the filter blocking increases. The constant feed pressure into the gas cell results in a constant gas flow rate through the cell.[3][25]

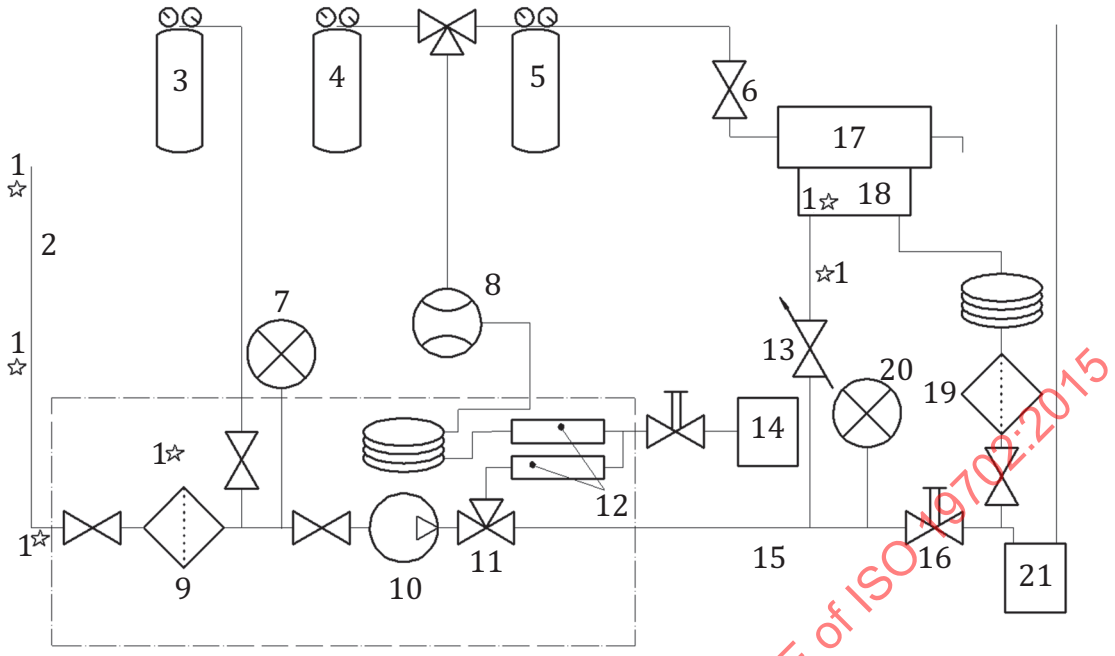


Key

1 heated sample line
2 oven (filters in oven)
3 pump head
4 FTIR
5 heated cell
6 needle valve
7 cooling coil
8 high-capacity filter to protect flowmeter
9 flowmeter
10 back-pressure regulator
a Flow out.

Figure B.3 — Schematic diagram for maintaining constant pressure and constant flow to the sample cell using a back pressure regulator[3][25]

Note that the same oven can be used to house many of the required valves required for FTIR sampling and analysis of fire gases as shown in Figure B.4. These are valves required to select calibration gases or fire gas samples (see Figure B.4, item 11) and valves required to pressure test the filter housing seal after changing filters. The same oven can also be used to dynamically dispense calibration gases that are liquid at room temperature by placing a Teflon-lined stainless steel coil in the oven, connected by "T" joints to PTFE-lined stainless steel expansion bottles. A liquid-filled syringe driven by a syringe pump directs the liquid through a 1/100 in ID, 1/16 in OD, PEEK (polyether ether ketone) tubing which extends 2 cm into the expansion bottle which is fed by a metered hot nitrogen stream. The outflow of the expansion bottles leads to the FTIR cell. This sampling system is described in References [3] and [25].



Key

1 thermocouples
2 heated sampling line
3 nitrogen for pressure testing
4 calibration gas
5 liquid nitrogen
6 FTIR purge gas
7 pressure/vacuum gauge
8 flowmeter
9 filters
10 pump head
11 selection valve
12 PTFE-lined stainless steel bottles
13 needle valve
14 syringe pump
15 heated line
16 back-pressure regulator
17 FTIR
18 sample cell
19 high-capacity filter
20 flowmeter
21 water trap

Figure B.4 — Schematic diagram of an FTIR sampling system with a back-pressure regulator

Annex C
(informative)

Analysis of filter(s), the sampling line and probe for effluent retention

C.1 Washing procedures for filters

Acid gases, amongst others can be adsorbed on particulates retained by the filter. When the total amount of one specific acid gas has to be measured, the quantity retained on the filter should be added to the total amount of acid gases analysed by the FTIR. However it must be appreciated that where "continuous" time/concentration measurements are required, it is not possible to correct the data from a single measurement of the species retained on filters.

The washing procedures for filters are as follows:

a) Procedure for planar (i.e. flat surface) and for cylindrical filters:

   — After each test, the filter is removed and placed in a minimum volume of analytical grade water to completely cover the filter.

   — The solution with the filter is placed in an ultrasonic bath for at least 10 min.

   — The solution is made up to a known volume before analysis of the required species. Analytical methods presented in ISO 19701:2013 can be used.

   NOTE The filter can be rinsed and removed from the washing solution before making up to a known volume. Alternatively, the filter can remain in the washing vessel (beaker) if the volume of the washing water is known.

b) Alternative procedure for cylindrical filters:

   — Wash the filter with hot water in a "Soxhlet" apparatus for approximately 20 min. The solution is made up to a known volume before analysis. Analytical methods presented in ISO 19701:2013 can be used.

   — The same protocol (with a Soxhlet extractor) can be used to wash new filters prior to first use. The filters should be dried before use (250 °C in an oven is acceptable).

C.2 Washing procedures for transfer line and probe

The transfer line and the probe should be rinsed with analytical grade water. Before rinsing the systems, their temperatures must be allowed to cool to approximately 70 °C to avoid significant vaporization of water. For each part of the sampling system, the washing solutions are collected in volumetric flasks and the solutions are made up to a known volume before analysis by appropriate analytical methods (see C.1).

Annex D
(normative)

Response time determination of the complete FTIR sampling system

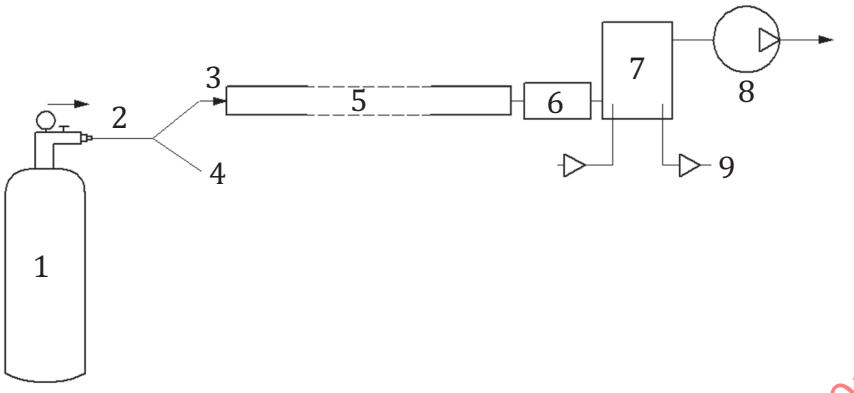
D.1 General

For many applications it is necessary to show the change in concentration of toxic species as a function of time. **Line delay time (t_l)** is the time that it takes for a sample to travel from the sampling point to the detector. Because of mixing and diffusion effects a short pulse of input gas will become broadened as it passes along the sampling line. The **response time (t_r)** measures the effect of the line delay plus the effect of signal broadening, as measured by the detector when gas is switched at a sampling probe from one pure gas to another. The example below in D.2 shows a procedure to determine the response time of the sampling system.

D.2 Principle of determination

The sampling pump and sample flow rate, and sampling system temperatures shall be set for their normal use. The sampling configuration shall also be the same as for normal use. For the measurement procedure a gas cylinder/bottle containing any IR-absorbing gas in nitrogen (e.g. CO_2, C_2H_4) can be used. A 3-way "T" valve at the gas bottle is used to select between the diluted gas and room air (see Figure D.1). Set the flow rate lower than the normal sampling system flow rate. It will be diluted by air entering the "T" to make up the flow rate in normal use. Both line A (from the bottle to the "T") and line B (from the "T" to the heated sampling line's entry) shall be as short as practicable. The use of a "T" allows the dilution of the gas and ensures that the input pressure to the sample line is maintained at atmospheric pressure when switching between that gas and room air.

An example of a plot for a response time determination is shown in Figure D.1.



Key

1 bottle containing analyte gas
2 line A — from the bottle to the "T"
3 line B — from the "T" to the entry to the heated sampling line
4 ambient air
5 heated sampling line
6 filter
7 FTIR gas cell
8 pump; normal flow rate (l/min)
9 IR beam

Figure D.1 — System set-up to measure sampling response time

NOTE 1 Select an appropriate type and concentration for the IR-absorbing gas. It is best using a gas and concentration with a linear response over the measured concentration range. If using a linear concentration range, an accurate calibration is not necessary. If the gas used does not have a linear response in the concentration range to be measured, the FTIR shall be calibrated for the full measured gas concentration range to obtain an accurate response time.

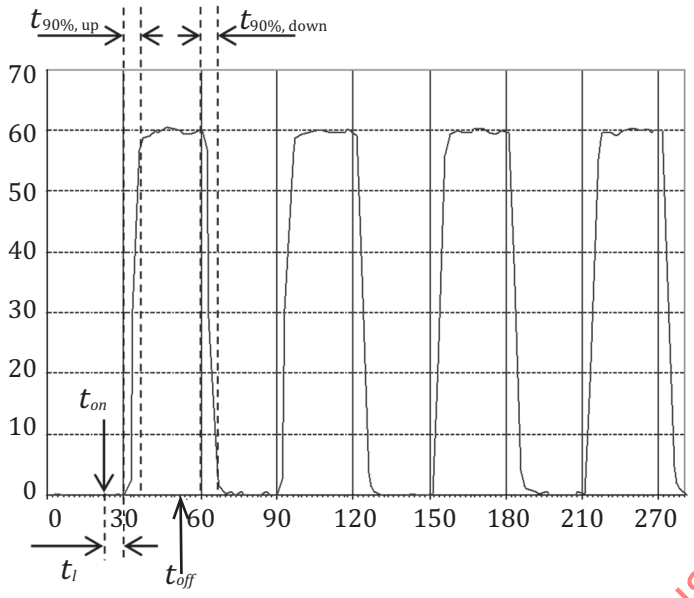
Once the FTIR and sampling system are equilibrated in terms of temperature, pressure and flow rate, start the acquisition of spectra. After a stable baseline is attained, introduce the analyte gas into the heated sampling line (see Figure D.1) by switching the 3-way "T" valve from air to bottled gas. Note the time (t_{on}) at which the analyte gas is introduced. After obtaining a stable concentration as shown by a flat response from the FTIR detector, switch back to air, allowing the analyte concentration to return to a stable baseline. Note the time (t_{off}) at which the input of analyte gas ceases. This process can be repeated to check accuracy.

NOTE 2 Use an acquisition rate as high as possible when collecting the spectra in order to be able to determine the most accurate response time possible.

Plot the concentration as a function of time. Determine the average concentration of the "plateau" of the curve, i.e. the concentration value of the flat detector response. Calculate the 90 % rise time ($t_{90\ \%,\ up}$) and the 90 % fall time ($t_{90\ \%,\ down}$). The 90 % rise time is the time from the onset of the rise in gas concentration to the time of attaining 90 % of the "plateau" concentration. The 90 % fall time is the time from the onset of the fall of concentration to the time of attaining a 90 % decrease in concentration. See an example in Figure D.2.

The value of $t_{90\ \%,\ up}$ shall equal $t_{90\ \%,\ down}$. If it does not, the analyser is not properly calibrated for the concentration range of the analyte, and the response time value will be erroneous.

The response time for the measurement system is the line delay time (t_l) plus the 90 % rise time (or alternatively, 90 % fall time). The line delay is the time between t_{on} and the first rise in gas concentration (or alternatively the time between t_{off} and the first drop in gas concentration). That is: Response time (t_r) = line delay time (t_l) + $t_{90\ \%,\ up}$.



Key

X-axis time, in seconds

Y-axis volume fraction, in µl/l

NOTE Plotted data are from Reference [25].

Figure D.2 — Schematic plot for measurement of response times

Annex E
(informative)

Considerations for FTIR optical cell selection

E.1 Uniformity of gas concentrations within the FTIR cell

Typically the interpretation of an absorption spectrum assumes that the concentrations of the measured gases are uniform across the entire optical path. It is important to know that this is true for the combination of cell volume, sample flow, and flow mixing characteristics within the cell. Corrections for non-uniformity are difficult and will compromise the accuracy of the gas concentrations.

E.2 Mixing within the FTIR cell

The ideal cell geometry is one in which the sample flows directly from the inlet port to the outlet port with no axial or radial mixing. Such mixing, if it occurs will result in measured gas concentration/time profiles which will differ from those actually occurring in the sampled atmosphere. Mixing can be reduced by reducing the cell volume and increasing the sample flow.

E.3 Time resolution

The cell volume should be selected such that the passage of the sample flow through it provides sufficient time resolution for requirements of the particular test being monitored. Where the test produces a steady-state period, the rise time (see Annex D) of the measured gas concentrations shall be short enough that they reach plateau values and remain at those values long enough to obtain quantitative concentration measurements with the needed precision. Where the test produces rapidly changing gas concentrations, the rise time needs to be sufficiently short in order to follow the changing concentration profiles in a manner consistent with the objectives of the test. See Annex D, for a detailed discussion on determination of 90 % rise time and system response time.

NOTE Many FTIR cells are designed for monitoring slowly varying concentrations, such as in ambient air quality assessments or incinerator exhaust monitoring. Cells with 500 ml volume and larger cells designed for these applications are generally inappropriate for sampling from fire experiments where accurate concentration histories over much shorter time periods are important.

E.4 Optical paths in FTIR cells

E.4.1 Folded optical path cells

Long optical paths enable increased sensitivity, i.e. lower limits of detection and quantification. Since these cells contain internal mirrors, the entrance flow must be filtered to remove aerosols that will deposit on and foul the reflective surfaces. Temperature conditions in the cell must also be such that condensation of vapours within the sampled gas stream is not possible.

NOTE 1 Historically, cells with folded optical paths had large volumes, of the order of 1 l. At present, cells are available with 2 m path lengths and volumes below 100 ml. An optical path length between 2 m and 10 m has been found suitable for detecting concentrations at the low end of values needed for toxicity assessment.[18] Adjustable path length cells are also available.

NOTE 2 The absorbance of infrared radiation is theoretically proportional to the path length of the optical cell.

E.4.2 Single path optical cells

The optical path through this type of cell is determined by the length of the cell, typically a fraction of a metre. There are no internal mirrors, and thus the inlet flow filtration is not as important. The cell may be cleaned with common solvents. The shorter optical paths result in reduced sensitivity although the smaller cell volume enables a higher time resolution.

Annex F
(normative)

Verification of FTIR optical cell performance

F.1 Calibration of gas cell temperature

Annually and whenever the gas cell is opened or the sampling train modified, the temperature set-point and homogeneity in gas cell should be verified. The critical temperature is the temperature of the sample gas itself rather than the set-point temperature. Verification of cell gas temperature can be carried out follows:

— Preheat the sample stream entering the gas cell using a representative length of sample line with an appropriate number of separately thermostatted heated segments (see 5.5).

— Insert a thermocouple in the gas cell (with an appropriate leak-tight connection) at a given depth.

— Start the sampling pump at the normal flow rate and wait until the temperature stabilises.

— Note the temperature at a number of points within the cell. Adjust the temperature set-point of the gas cell to the mean value obtained at these points and note the correction needed between the real (mean) temperature and the set point temperature.

— The standard deviation between temperatures measured along the cell shall not exceed 5 % of the mean value.

NOTE It is important that the sampling line used during temperature calibration of the cell preheats the gas to the same temperature as that normally used for sampling from the test apparatus. This temperature should match the sample cell temperature.

F.2 Pressure control and measurement

A pressure transducer should be permanently mounted in the gas cell. It should be calibrated and have an accuracy better than 0,5 %. The cell pressure, as well as temperature, should be logged with each spectrum.

The cell pressure shall match the pressure at which the calibration spectra were obtained otherwise corrections must be applied to the quantified data. Such corrections are made using the universal gas law.

The effectiveness of the pressure correction over a selected pressure range shall be quantified for the FTIR analyser to determine the allowable deviation in cell pressure (from the pressure at calibration) during a measurement. The allowable deviation in cell pressure should give a minimal influence on the quantitative results and shall not induce an error that exceeds 5 %.

NOTE 1 The effectiveness of the pressure correction can be quantified by measurements on a calibration gas of carbon monoxide (CO) over a typical range of concentrations encountered in tests. The cell pressure is regulated by the inlet valve of the gas cell and the cell pressure registered for each pressure level for each concentration. The predicted gas concentration corrected by using the universal gas law is plotted versus the cell pressure and the allowable pressure deviation can be extracted from the plot.

NOTE 2 The effectiveness of cell pressure correction has been studied by Guillaume et al.[17] The recommendation from their work is to not allow cell pressure variations greater than 10 Torr compared to calibration cell pressure.

Sampling systems can be designed to maintain a constant cell pressure that is not affected by changes in filter loading through progressive blocking of the filter. This technique requires a loop

that bypasses the analyser and a back pressure regulator in that loop. (See the discussion of sampling system design in Annex B).

NOTE In spectroscopy, pressure is usually expressed in Torr, which is a non-SI unit corresponding to 1 mm Hg. The conversion between atmospheres, Torrs, and pascals is: 1 atm = 760 Torr = 101 325 Pa.

F.3 Verification of gas cell leak-tightness

Annually, and at each time the gas cell is opened or windows changed, the leak- tightness of the cell should be verified. The verification may be carried out as follows:

— Install two stop valves, the first at the cell input and the second at the cell output.

— Close the input valve, and start the sampling pump. When the pressure measured in the cell is around 300 Torr, close the output valve and turn the pump off.

— Wait 10 seconds until the system stabilizes.

— Note the initial pressure value P_0, then wait 30 seconds and note the value P_1.

— The deviation between P_0 and P_1 should not exceed 3 Torr.

F.4 Cell mirrors cleaning

Cell mirrors are subject to condensation during contact with some vapours producing a film on the mirror surface. The mirrors may also attract solid deposits which will affect their reflectivity. When the FTIR detector signal decreases (see 8.2), the mirrors must be cleaned. However, great care is needed to clean them as they are very sensitive. This is particularly important if a gold coating is present; this should not be touched with bare fingers, as oil/grease from fingers will be deposited on the surface of the mirror. The following procedure is suitable:

— The procedure should be carried out in a clean room (i.e. with low levels of airborne or surface dust or grime).

— Wait until the gas cell is at ambient temperature; then disassemble it.

— As cell mirrors are concave, place acetone of chromatographic quality in them.

— Wait 5 min, then change the solvent to a non-polar one (e.g. n-hexane), also of chromatographic quality.

— Rinse with acetone; then wait until no solids or surface film (or acetone) are present on the mirror.

— Do not wipe the mirror with a cloth (not even a tissue wipe), as this may scratch it.

— Reassemble the gas cell, heat it to operating temperature and check for leak-tightness.

— Carry out a quantitative analysis control procedure as set out in 8.2.2.

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

Annex G
(informative)

Spectrophotometer

G.1 Detectors

Various types of detectors are available, mainly distinguished by their different sensitivities. In the mid-infrared region, the detectors frequently used are Deuterated Triglycine Sulfate (DTGS), which operate satisfactorily at ambient temperature, and Mercury Cadmium Telluride (MCT), which need to be cooled. The MCT detector can be cooled using either thermoelectric coolers, liquid nitrogen Dewar flasks or Sterling engine coolers. Liquid nitrogen and Sterling cooling provide the best cooling.

The choice of the detector depends on the requirements for sensitivity and the limit of detection. MCT detectors can provide a sensitivity of up to 10 times that of a DTGS detector. However, MCT detectors are less linear than DTGS detectors.

NOTE 1 The MCT detector must be cooled by one of the above methods and has a superior signal-to-noise ratio to the DTGS detector. The signal to noise ratio is dependent on the cooling method. Also, more time is needed to stabilize the MCT detector.

NOTE 2 A limitation of the Liquid Nitrogen-cooled MCT detector is that extra-equipment is needed to supply the FTIR apparatus with liquid nitrogen. Another drawback is the concern of suffocation hazards of liquid nitrogen when used in confined spaces such as small instrumentation trailers.

NOTE 3 A limitation of the Sterling-cooled MCT detector is high cost.

G.2 IR-source

The source of IR radiation used in an FTIR spectrophotometer is an approximation to a blackbody radiator. The intensity of the radiation increases with wavenumber, to a maximum, and then it decreases. Overall sensitivity of the FTIR instrument will be highest at the maximum of the IR wavenumber distribution.

Two types of source are frequently used:

— The Nernst source, which consists of zirconium, yttrium and thorium oxides coated on an electrically heated filament maintained at 1 827 °C.

— The "Globar" source, which is a silicon carbide element electrically heated to 1 227 °C.

G.3 Wavenumber region

It is important to acknowledge that FTIR determines the infrared absorption of a gas or mixture of gases over a wide range of wavenumbers (typically 400 cm^{-1} to 4 500 cm^{-1} for KBr windows) and 650 cm^{-1} to 4 500 cm^{-1} (for ZnSe windows). The infrared absorption bands for the main fire gases are given in Annex I. It should be noted that many other gases found in fire atmospheres, e.g. hydrocarbons, also absorb infrared radiation over this region. It is therefore rare for a fire gas to absorb infrared within a given wavenumber region without interference from other fire gases in the same region. However using a spectrophotometer resolution of 0,5 cm^{-1} or higher, provides an acceptable solution

for avoiding overlap of absorbances for fire gases such as hydrogen cyanide (HCN), acetylene (C_2H_2), nitric oxide (NO) and water, that would not be possible at lower resolutions.

NOTE 1 Measurements using spectrophotometer resolutions as low as 4 cm^{-1} have proved acceptable for measurements of fire gases, as long as spectrally interfering (overlapping) compounds can be addressed in the mathematical evaluation of the spectra.[18]

Fire gases are identified by the characteristic wavenumbers where they absorb the infrared beam and are quantified by the degree of infrared absorption. The reliability and accuracy of the identification and quantification depend directly on the ability of the spectrometer to identify and separate the spectrum of the required fire gas from that of the spectra of other gases in the mixture.

When the spectra of all species of interest and interfering species are available, a matrix of quantification should be defined. Annex I indicates wavenumbers to be used for identification and quantification (and those which can cause interference) of many compounds of interest in fire toxicology. Band selection (i.e. the range or ranges of contiguous wavenumbers chosen for a specific compound) should be made by selecting regions or groups of narrow bands common to the required compound, in order to maximize the signal for a given compound and to minimize the influence of its interfering species.

G.4 Resolution

G.4.1 General

The resolution (in wavelengths or wavenumbers), sample gas temperature, flow rate and cell temperature and pressure must be the same for both the calibration spectra and for the spectra obtained during use in fire tests.

G.4.2 Resolution over the spectral range

The resolution "r" of the spectrometer is function of the difference in path length "Δ" between the two beams of the interferometer. As a first approximation, resolution is defined as:

$$r = \frac{1}{\Delta}$$

The resolution is ideally constant over the entire spectral range. This is not the case with conventional dispersive spectrometry. Nevertheless, resolution can be modified in FTIR instruments due to angular deviations of the beam in the interferometer. Such deviations will increase with infrared frequency.

A resolution of at least 0,5 cm^{-1} is recommended for the practical elimination of interferences in fire gas analysis; although a lower resolution is allowable if spectral interference from overlapping compounds can be corrected by the software.

G.5 Additional spectrometer parameters important for calibration

G.5.1 Background noise

Excessive background noise could be produced from a number of sources such as the IR source, detector or a poor optical path alignment. It can also be caused by electronic problems in the FTIR instrument circuitry. It is also a function of resolution, apodisation function, zero filling used as well as mobile mirror speed.

The background noise should be determined in various positions in the spectrum to be used. In general, three regions are considered sufficient.

Determination of the background noise is recommended to be performed at least every six months, and/or when the interferometer is subject to any maintenance operation (e.g. beam splitter change, interferometer mirrors cleaning or change of any parts). The following procedure has been found suitable:

— Measure the resolution and set up a suitable number of scans, note the iris aperture, the detector amplifier gain and mirror speed used.

— Set the spectrophotometer to "single beam" transmission mode (i.e. an absorption spectrum where a background spectrum not has been subtracted).

— Acquire transmission spectra, then note the maximum and the minimum transmission values found in the following regions:

  — From 3 950 cm^{-1} to 4 050 cm^{-1}.

  — From 1 950 cm^{-1} to 2 050 cm^{-1}.

  — From 450 cm^{-1} to 550 cm^{-1} for KBr windows.

  — From 600 cm^{-1} to 4 500 cm^{-1} for ZnSe windows.

G.5.2 Stray radiation

Stray radiation is radiation originating from extraneous sources. Stray radiation could be determined by comparing a zero transmission spectra with the transmission obtained when a sample absorbing 100 %, in a given range, is placed across the beam. References frequently used are:

— Silica sample with a thickness more than 1 mm, for wavenumbers <2 000 cm^{-1}.

— Sodium chloride with a thickness more than 6 mm, for wavenumbers <450 cm^{-1}.

— Polystyrene film with a thickness of 50 µm, at 2 924 cm^{-1} and 698,9 cm^{-1}.

— Indene in a KBr test tube with a path of 0,4 mm, at 392 cm^{-1}, 420 cm^{-1} and 551 cm^{-1}.

Deviation from zero should not exceed 2 % (in transmission) for wavenumbers >600 cm^{-1}.

G.5.3 Limits of detection and of quantification (L_D and L_Q)

The cell path length and signal-to-noise ratio of the output from the FTIR instrument, determine the limit of detection (L_D) and the limit of quantification (L_Q) of the method. The ISO 12828-1 standard describes different methods to estimate these limits. The method adapted for this FTIR standard is the determination from a data matrix of blank samples. This procedure is fully described in ISO 12828-1.

In summary, this method is based on the noise level present over a region of the IR spectrum to be used for quantification. It assumes that a wanted spectral absorbance can be detected when it is just above the noise level. It should be appreciated that greater the number of scans, the greater the signal-to-noise ratio. It is also assumed that a linear relationship exists between the IR absorbance and the concentration of the required species at low concentrations. Because the method is applied only in the wavenumber region used for quantification, and because sensitivity is different for each gas, the values obtained for L_D and L_Q could be significantly different for each component measured in the fire effluent.

Table G.1 shows some examples of how the combination of resolution and number of scans that are being averaged, affects the minimum detection limit of carbon monoxide (CO).

Table G.1 — The effect of resolution and number of scans on the L_D of CO

Resolution cm^{-1}	Number of scans	L_D µl/l
1	1	16
	4	8
4	1	15
	4	7

NOTE For some gases, it has been found that low concentrations can become partially trapped by the sampling line. This problem has been especially identified for hydrogen bromide (HBr) at a volume fraction of below 10 µl/l and for hydrogen chloride (HCl). For such species, the limits of detection and quantification are affected by the whole sampling train and not just by the spectrometer and its calibration. Confirmation of the limit of detection may be carried out by introducing a reference gas with a concentration equivalent to the expected limit of quantification, then using the method based on blank samples presented ISO 12828-1.

Annex H
(normative)

Verification of spectrometer performance

H.1 Verification of wavenumber accuracy

Trueness of wavenumbers is mainly governed by the spectrometer design, but it is also dependent on experimental conditions, especially resolution. Sources of wavenumber errors include aging lasers (timing errors), corrosive environments and misalignment of optics. Quantitative errors due to post-calibration wavenumber shifts are most pronounced at the highest IR frequencies where narrow absorbance peaks are used for quantification. For example, a small post-calibration wavenumber shift can result in a large quantification error in Hydrogen Fluoride (HF), particularly when high resolutions are used. Overlaying recently collected spectra containing HF with the HF calibration spectra in the region of quantification indicates the magnitude of the post-calibration shift. Verification of trueness is achieved by comparing absorption maximums to the expected values using standard reference substances.

It is recommended that the verification of the trueness of wavenumbers is carried out at least every 6 months, and/or whenever the spectrometer is subject to any maintenance operation (e.g. beam splitter change, interferometer mirrors cleaning or change of any parts). The following procedure has been found suitable:

— Establish the resolution, note iris aperture, gain and mirror speed used.

— Record a background reference spectrum using a suitably large number of scans (usually >50).

— Place a calibrated reference of polystyrene film in the beam, or place an appropriate calibration gas in the gas cell, and scan the absorption spectrum.

— Compare values found to the nominal values shown in Table H.1, which includes acceptable tolerances for spectra collected using a resolution of 2 cm^{-1}. Tolerances shown in the table should be adapted to the resolution obtained in practice, and be less than or equal to the resolution used.

Table H.1 — Wavenumbers for trueness verification using a resolution of 2 cm^{-1}

Wavenumbers in cm^{-1}	
Band	**Tolerance**
3 060,1	±0,4
2 849,7	±0,4
1 942,8	±0,6
1 601,3	±0,5
1 583,1	±0,5
1 154,7	±0,4
1 028,5	±0,4

NOTE 1 Calibrated reference polystyrene films (PS) can be obtained by NIST (USA) or NPL (UK). The film should be protected from light and excessive temperature, in clean conditions and discarded if stripes are present on the surface.

An alternative procedure could be conducted using gases/ vapours. Suitable bands for verification are:

— For CO_2: 667,4 cm^{-1}, 2 339,3 cm^{-1} and 2 361,4 cm^{-1}

— For H_2O: 1 616,7 cm^{-1} and 3 701,9 cm^{-1}

— For HCl: 2 980,9 cm^{-1} and 2 997,8 cm^{-1}

The tolerances for the procedure using gases should be adapted to the measured resolution, as previously stated for PS film. Reference [29] recommends 0,5 % for trueness.

H.2 Verification of resolution

Direct verification

It is recommended that the verification of resolution is carried out at least every six months, and/or when the spectrometer is subject to any maintenance operation: beam splitter change, interferometer mirrors cleaning or change of any parts.

For resolutions <2 cm^{-1}, the determination of resolution is performed according to the analysis of specific couples (i.e. double absorption peaks for standard compounds). Standards commonly used for resolution verification are the gases/vapours of CO_2, H_2O and HCl. The following procedure has been found suitable:

— Establish the resolution expected, note iris aperture, gain and mirror speed used.

— Choose the number of scans per spectrum; then acquire spectra in "absorption" mode.

— For each pair of absorption peaks for each standard compound calculate the difference in wavenumbers between the peaks. Using Table H.2, compare the minimum acceptable value between the two peaks of each pair.[30]

— Treat only pairs where the minimum absorbance at the wavenumber position between both peaks is lower than 50 % of the absorbance of the less intense of the two peaks (absorbances of the two peaks are denoted by noted v_1 and v_2). The difference of wavenumber between both peaks (for the pair i) is noted Δv_i.

— The value used in the calculation is the minimum of Δv_i, expressed as $\Delta v_{\min}$ and corresponding to the pair $\bar{v}_1$ and $\bar{v}_2$. The resolution is: In wavenumber: $\boldsymbol{r} \leq \Delta v_{\min}$, In relative value: $\boldsymbol{r} \geq \frac{(\bar{v}_1 + \bar{v}_2)}{2\Delta v_{\min}}$.

Table H.2 — Wavenumbers of the pairs (couples) used for determination of the resolution of the spectrophotometer, for resolutions under 2 cm^{-1}

Gas	Wavenumbers in cm^{-1}		
	$\bar{\nu}_1$	$\bar{\nu}_2$	$\Delta\nu$ expected
CO_2	2 377,80	2 376,80	1,00
	2 354,40	2 352,90	1,50
	656,60	655,10	1,50
	2 321,10	2 319,10	2,00
H_2O	1 700,60	1 700,10	0,50
	3 651,20	3 650,65	0,55
	1 653,30	1 652,50	0,80
	3 821,70	3 820,70	1,00
	3 675,90	3 675,90	1,00
	1 490,90	1 489,90	1,00
	3 629,50	3 628,30	1,20
	1 734,60	1 733,40	1,20
	1 507,10	1 505,60	1,50
	1 690,10	1 688,40	1,70
	3 546,90	3 545,15	1,75
	3 588,60	3 586,60	2,00
	1 319,00	1 317,00	2,00
HCl[a]	3 014,41	3012,12	2,29
	2 981,00	2 978,75	2,25
	2 963,29	2 961,07	2,22
	2 944,90	2 942,72	2,18
	2 925,90	2 923,72	2,18
	2 906,24	2 904,11	2,13
	2 865,10	2 863,02	2,08
	2 843,62	2 841,56	2,06
	2 821,54	2 819,56	1,98
	2 798,94	2 796,97	1,97
	2 775,76	2 773,82	1,94

[a] The ratio of the absorbances of both HCl peaks is in proportion (3/1), which corresponds to relative natural proportions between the relative abundance of the isotopes of chlorine ^{35}Cl and ^{37}Cl.

Indirect verification

Indirect verification can be made according to Reference [10] at the same time as measuring the trueness and reproducibility of wavenumbers. It is not suitable for low resolutions and is not recommended under 2 cm^{-1}. The following procedure has been found suitable.

— Establish the number of scans per spectra, note iris aperture, gain and mirror speed used.

— Place a polystyrene film across the IR-beam (nominal thickness recommended is 0,05 mm).

— Measure X as the difference between transmission values (in %) measured at 2 870 cm^{-1} and at 2 851 cm^{-1}.

— Measure Y as the difference between transmission values (in %) measured at 1 589 cm^{-1} and at 1 583 cm^{-1}.

— Performances of the spectrometer are considered as compliant with the verification if X >18 and Y >10.

Annex I
(informative)

Reference gases

I.1 Producing known concentrations of reference gases

When collecting the spectra of reference gases, the FTIR settings need to be identical to the settings during a test (as far as practically possible). Generally, it is sufficient to obtain one or two pressurized gas bottles (cylinders) of different concentrations of each reference gases in nitrogen and dilute these further to obtain a number of reference gas concentrations. In some cases, it can be necessary to create reference gases in the testing laboratory as they can be difficult to obtain commercially. In such cases, a variety of methods can be used depending on the gas to be generated. Some FTIR manufacturers will generate calibration spectra for a specific instrument for specific temperatures, pressures, and gases. In all cases, of key importance, is that the reference gas be free from contaminants that have absorbances in the infrared region of the spectrum and that the concentration and accuracy of the reference gas concentration is known It is also considered good practice to periodically check the reference gas concentration using an independent method, especially where the gases may be stored for long periods.

Accurate reference spectra for the calibration of each gas to be analysed have to be generated over a range of concentrations which cover the concentrations likely to be encountered in the fire effluents to be measured The calibration spectra of each gas should be obtained with as little interference from other gases as possible. The FTIR gas cell, sample lines, filters and filter boxes must be heated before the calibration, to ensure that all the system has stabilized. It is also necessary for the pressure in the cell to be the same during sampling from fire effluents and during calibration. A reference spectrum of nitrogen or purge air (free of H_2O and CO_2) is recorded before each calibration under the same conditions as for the calibration gas. The system sampling lines should be purged with preheated dry non-IR absorbing diluent gas such as nitrogen to remove adsorbed water from the components such the tubing, as valves and regulators prior to calibration. Calibration gases in pressurized gas bottles/cylinders containing water soluble gases such as HF in nitrogen should have specialized regulators that allow the regulator and the line to be purged with nitrogen prior to dispensing the calibration gas. During this purging stage, the nitrogen gas stream should be continuously monitored for water content with the FTIR spectrometer until the water absorbance is minimized. Additional filters may be inserted into the calibration gas system to further minimize carbon dioxide and water absorbances if these prove significant. The background nitrogen spectra can then be obtained. The background spectra and calibration gas spectra should not be acquired until all unwanted absorbances are minimized.

Calibration gases may be prepared in a number of ways:

a) Calibration gases in nitrogen or any other non-absorbing diluent gas may be purchased ready made in pressurized cylinders. These calibration gases may be diluted further using suitable equipment to extend the calibration range.

   NOTE Experience has shown that particularly for reactive gases, the stated certificated concentrations given by the supplier are sometimes not realized especially after a protracted period. It is considered good practice to periodically check the reference gas concentration using an independent method, especially where the gases may be stored for long periods.

b) Calibration gases may be made in a dynamic system using permeation or diffusion tubes to produce a range of concentrations (Figure I.1). Gas concentrations are calculated from the mass loss of the diffusion or permeation tube. Subsequent independent analyses for verification may be carried out if needed.

c) A calibration gas stream for a gas or vapour that is liquid at room temperature (e.g. water) can be generated by metering the liquid via a motor driven syringe pump into a preheated metered nitrogen stream with PTFE-lined expansion bottles using a technique described in Reference [25].

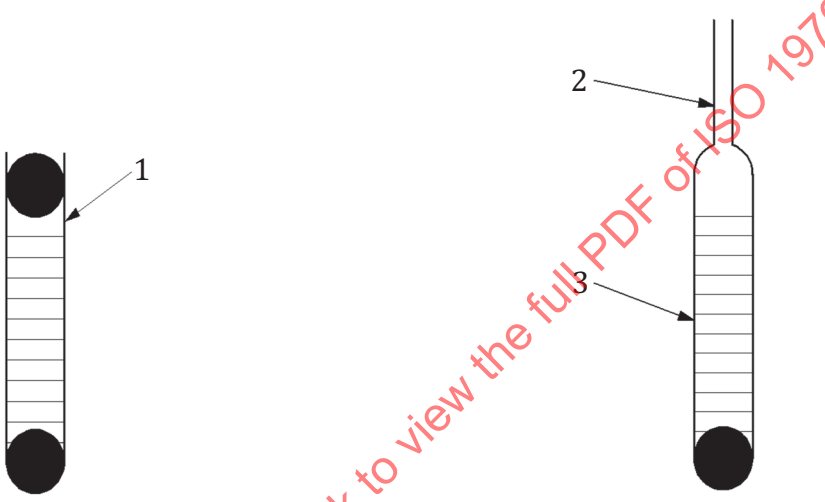
d) Calibration of various gases by pressure regulation.

e) Calibration by using concentrated acids.

f) Recirculation system.

See below for methods of preparing calibration gases for water and other gases that are liquid at room temperature.

Schematics of prepared permeation and diffusion tubes are shown in Figure I.1 (where the black filled circles schematically represent solid stoppers)



a) Permeation tube **b) Diffusion tube**

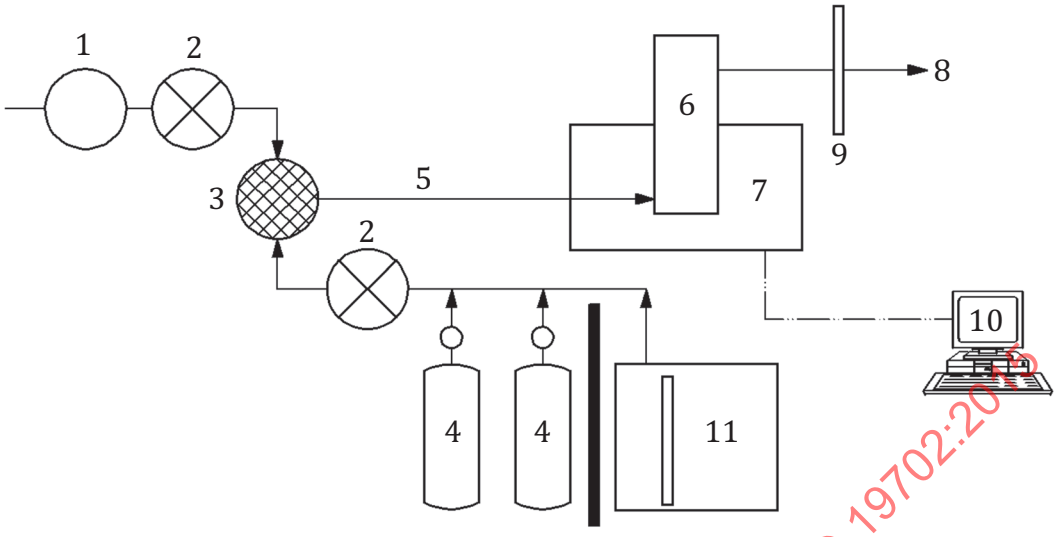
Key

1 PFTE tube
2 capillary tube
3 glass

Figure I.1 — Schematic diagram of prepared tubes with solid stoppers

A schematic of the calibration set-up when using gas cylinders or permeation tubes is shown in Figure I.2.

Move items 1 and 2 and 3 (in Figure I.2) as close to the output of the permeation (alternatively diffusion) tubes as possible, and upstream of the permeation tube output and all other calibration gas sources for which line losses are to be expected (e.g. water soluble gases such as acid gases and gases with low boiling points. The diluent gas should also be preheated such that the gas itself is equilibrated to at least 150 °C to drive off adsorbed water from the line. Each heated line should be appropriately thermostatted to match the detector cell temperature. The entire line and all valves from the permeation tubes to the FTIR cell must be heated to prevent wall losses. A heated 4-way selector valve is used to select calibration gas sources, such that there is no dead volume in the lines leading to the other calibration gas sources.



Key

1	diluent in	7	FTIR
2	flowmeter	8	flow out
3	mixer	9	total flow
4	reference cylinder gases	10	date system
5	heated line	11	diffusion or permeation tubes
6	heated cell		

Figure I.2 — Schematic flow diagram for calibration by gas cylinder and permeation tubes

Calibration of gases by pressure regulation is based on passing the gases to the FTIR gas cell through the pump to the exhaust line (Figure I.3). This is achieved by first flushing the entire system with nitrogen and then the required calibration gas for the time required to obtain a steady-state concentration reading. The valves into and out of the gas cell are opened and closed until the cell is completely filled. After recording the spectrum the gas is flushed away and the pressure is decreased to a set value. The gas cell is filled with nitrogen to the original pressure. This procedure is repeated several times to obtain a range of concentrations. It is necessary after each calibration series to clean the gas cell and lines with nitrogen or purge air, and to record a reference spectrum. Additional precautions need to be made to dry the sampling system lines for calibrations of water soluble gases.

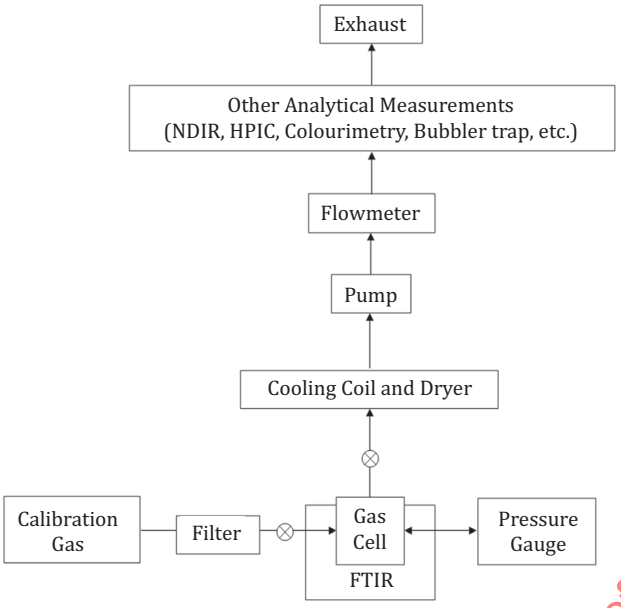
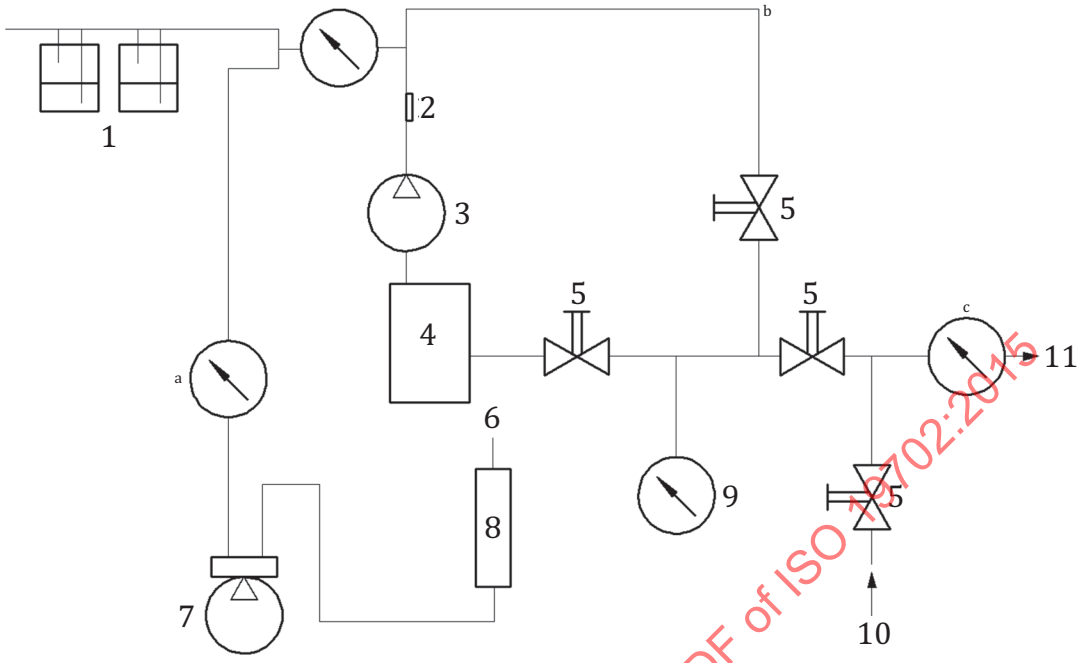


Figure I.3 — Schematic flow diagram for calibration by pressure regulation

A heated, pumped, closed loop system (see Figure I.4) attached to the inlet and outlet of FTIR cell may also be used to generate known gas concentrations for calibration. If the system is of known volume, then injecting known amounts of materials gives known concentrations. After the calibration spectra have been obtained, the contents of the cell and loop may be swept into an appropriate trapping medium for subsequent analysis to determine concentrations.[27] Alternatively, the concentration in the closed loop can be checked by a separate primary standard method.



Key

1	bubblers	7	pump
2	septum	8	rotameter
3	pump	9	manometer
4	3,6 m path length FTIR cell	10	purge air
5	on/off valve	11	FTIR sampling line
6	exhaust		

a C2: flow and cell pressure control with 6 mm stainless steel bellow valves.

b Calibration loop system.

c C1: flow and cell pressure control with 6 stainless steel bellow valves.

Figure I.4 — Schematic flow diagram for the closed-loop calibration method

I.2 Producing known concentrations of water

Water spectra are necessary in all quantification methods, as water interferes with the absorptions of many of the other gases which need quantification. Water is the main interfering species over a large portion of the mid-IR spectrum, and it is typically present in relatively large quantities in fire effluents. It is essential to correct for this interference. Although the exact concentration of water produced in a fire is generally not required, it is important to quantify this in FTIR measurements in order to correct the spectra of wanted species for the presence of water.

Quantitative spectra can be obtained for water and other gases that are liquid at room temperature by metering the liquid via a motor driven syringe pump into a preheated metered nitrogen stream with Teflon-lined stainless steel expansion/mixing bottles using the technique described in Reference [25]. See Figure B.4 for a sampling system with a built-in water calibration system. The bottles and heating coil are housed in the sampling/calibration system's oven. A short length of microbore 1,6 mm (1/16 in) OD polyimide tubing leads from an external programmable syringe pump through the oven wall and through a stainless steel 6,4 mm (1/4 in) tee connected to the first bottle. The use of predrilled reducing "vespel" ferrules allows the narrow bore tubing to enter a "Swagelok" compression connector

and to seat inside the bottle inboard of the tee. Preheated nitrogen enters the first bottle and propels the liquid spray entering the bottle. This enables preheating the diluant gas stream and assists in the vaporization of the fine water mist.

An alternative method for collecting pure water spectra is to let a flow of nitrogen pass through a semi-permeable tube that is positioned over a closed water-bath and the into the gas cell of the FTIR. By slowly increasing the temperature of the water-bath, a range of concentrations of water are produced. This method is practical for producing a large number of water spectra over many concentrations. The absolute concentration of water is, however, unknown for these spectra. If quantitative information is needed it is necessary to complement this technique with a quantitative calibration method for water.[25]

Annex J
(informative)

Calibration methods

J.1 General principles

The calibration of an FTIR instrument for fire gas analysis is a complex and time-consuming process. The following are the main problems:

— In many cases a reference and certificated standard concentration for a species of interest is not readily available and may need to be generated and verified in the laboratory.

— Most gases do not give a linear correlation between concentration and absorbance and it is not practicable to carry out such calibrations on a daily basis.

— It is not usually readily obvious if there is a problem with the calibration during use.

However, the problems inherent in the analysis of complex mixtures such as fire effluents necessitate independent verification of the FTIR calibration for each species of interest.

Calibration of any FTIR spectrometer used for fire gases analysis, involves the following steps.

a) Define the species of interest and any known interfering species.

b) Acquire spectra for each required species for a range of gas concentrations in nitrogen. Note that some data reduction methods, e.g. CLS (Classical Least Square), need reference spectra of pure gases, whereas other methods can work with spectra containing multiple gases, e.g. PLS (Partial Least Square).

c) Define the spectral bands to be used for quantification and for correction procedures.

d) Define the quantification model to be used. The model may be defined as a univariate or a multivariate type, as available in commercial software packages.

e) Validate the method by comparison with other techniques.

The calibration will be specific to a particular gas cell at a given temperature and operated at a given pressure, with the same spectrometer. If any of these parameters change, a new calibration is needed.

Sensitivity and linearity depend on the detector-type used. The MCT detector is far more sensitive but more nonlinear than the DTGS detector. The overall sensitivity of a MCT detector depends on its method of cooling, which is usually either by a piezoelectric method or by liquid nitrogen.

J.2 Practical methods for obtaining calibration spectra

Calibration spectra should be obtained with as little interference from unknown species as possible. It is therefore important that the calibration gases are dry and free from contaminants. Gas mixtures of known concentrations may be used as reference gases for calibration where the precision of the volume fraction of mixture components is consistent with requirements (e.g. the components of the mixture are in a suitable concentration range and will not produce significant overlapping absorption peaks). Calibration gases are typically a single or dual gas mixture in nitrogen, although in some cases it can be useful to obtain calibration spectra containing fire gases from a well-defined fire scenario. Gas mixtures can also be made using “diffusion tubes” or a “closed loop” calibration system. Where mixtures of several gases are used, more refined data reduction methods must normally be used, (especially in matrix based analysis methods such as PLS). In some cases, gases supplied in pressurized

cylinders (e.g. hydrogen chloride, hydrogen bromide and hydrogen cyanide) can incur significant losses over relatively short time periods and these compounds (and others) may need to be generated in the laboratory just prior to calibration. See References [4], [18], [24], [25] and [27] for more details.

Calibration spectra must be collected using the same FTIR arrangements as required for fire gas analysis. Any difference in cell path length, resolution, temperature, pressure, or spectrophotometer throughput, can significantly reduce the reliability of a quantitative evaluation.

Details concerning the collection of a calibration data set are included in Annex I and Annex K. Once a calibration data set has been obtained, several methods can be used to create a calibration model depending on the analysis method chosen (see J.3).

J.3 Quantification methods

J.3.1 General

FTIR analysis methods are capable of providing an acceptable degree of accuracy for most fire effluent analysis applications especially for a single gas or for a simple mixture of known gases. However it must be acknowledged that as the complexity of the gas mixture increases and the number of known and unknown interferences are increased, then the accuracy of the FTIR analysis can decrease. In practice, it may be desirable to use a combination of quantification techniques (i.e. both univariate and multivariate methods) to analyse fire gas samples which inherently contain a large number of gases, some of which may be unknown or unexpected. It is increasingly common for most spectroscopic software packages to include most of the methods listed below. The calibration procedure will therefore depend on the requirements of the method selected and the software package being used. The main quantification methods are covered in detail in the literature (see Reference [16]) and typically in the software package provided with an FTIR spectrometer. Only an outline of the methods and their scope is provided here.

J.3.2 Univariate analysis

These methods include the use of absorption peak “height” and “area”.

Specific regions of the spectra of the required gas are selected, which are as free as possible from interference from other gases. It may often be necessary to select more than one region. The fire effluent spectra are then compared to that of the specified gas and, where necessary, the spectrum of interfering gases can be subtracted from that of the fire effluent spectrum. The required fire gas is then quantified using either the height or area of a selected absorption peak or peaks and corrected for any nonlinearity of the absorption/concentration characteristics of the gas as determined from prior calibration.

These methods are simple, but can usually be applied only in simple cases, i.e. cases with minimal interference between different fire gases. This is often not the case for fire effluents where there are numerous gases present in the fire effluents. For complex mixture of gases, the univariate methods can provide erroneous results. To identify errors from univariate methods, it is important to manually inspect selected spectra to identify possible interfering gases and erroneous concentration calculations.

J.3.3 Multivariate analysis

These methods include the following:

— multilinear regression (MLR);

— classical least squares (CLS);

— piecewise-linear classical least squares (PCLS);

— ridged regression (RR);

— partial least squares (PLS);

— implicit non-linear latent regression;

— target factor analysis (TFA).

It is not proposed to discuss these techniques here. In essence, they use a number of mathematical models and processes to combine the spectra of known or suspected interferences to match the fire gas spectrum. The spectrum of the specified gas is then identified and the gas quantified using correction curves to allow for any nonlinearity in the response of the FTIR. More information can be found in Reference [16].

These methods require the interferences to be identified within the analysis method or selected from a large database of spectra obtained by the analytical method.

Calibrations corrected for interferences, are generally not linear with concentration and depend on the FTIR spectrophotometer characteristics, the chemical and physical nature of the gases of interest and more fundamentally the nature of chemical bond and type vibration studied.

J.3.4 Confirmation of quantification method

When the quantification method has been defined, the calibration should be confirmed with alternative reference analytical techniques. It is recommended that for this procedure, the same calibration sample stream is split between the FTIR method and the alternative method. In some cases it will be appropriate to pass on the outlet sample from the FTIR to the alternative method, i.e. the methods are "in series". The main alternative techniques suitable for fire effluents are defined in ISO 19701.

NOTE Some laboratories consider it necessary to perform continuous analysis of at least 2 gases such as CO and CO_2 analysis simultaneous with the FTIR using independent analysers (such as NDIR) or to provide an alternative method for ensuring the validity of the data.

Where a comprehensive analysis of fire gases is required, the analysis of components which are not suitable for FTIR analysis can be achieved according to ISO 19701.

Annex K
(informative)

Recording reference spectra and building a calibration set

K.1 Spectral properties of reference gases

The gases specifically studied within the SAFIR project[18] [19] were H_2O, CO_2, CO, NO, NO_2, HCN, HBr, HCl, and acrolein. Each gas has a unique FTIR spectrum which exhibits specific absorption peaks. In Table K.1, the spectral regions where these absorption peaks are observed are summarized.

NOTE The absorbance values relate to the specific spectrophotometer set-up used when the spectra were collected and are cited here in order to show the relative absorbance of the various spectral regions for respective gas. The values for individual instruments may vary from those shown as they will be dependent on the choice of spectral resolution, gas cell path length, detector, etc.

Table K.1 — Summary of spectral regions where absorption peaks are observed

Reference gas	Volume fraction µl/l	Spectral region		Maximum absorbance
		Start cm^{-1}	End cm^{-1}	
H_2O	12 000	4 000	3 400	
		2 000	1 170	
		500	—	
CO_2	15 100	3 764	3 480	0,63
		2 400	2 200	>6,0
		800	520	2,46
CO	3 005	2 264	1 975	0,17
Acrolein	322	3 457	3 374	0,01
		3 160	2 600	0,08
		1 783	1 584	0,55
		1 452	1 336	0,04
		1 200	1 100	0,08
		1 054	872	0,12
		670	500	0,02
NO	510	2 000	1 775	0,05
NO_2	470	2 939	2 815	0,08
		1 667	1 518	1,16
SO_2	960	2 525	2 442	0,04
		1 410	1 290	1,5
		1 253	1 029	0,13
		640	437	0,14
HCN	566	3 400	3 200	0,11
		1 550	1 300	0,04
		833	533	>6

Table K.1 *(continued)*

Reference gas	Volume fraction µl/l	Spectral region		Maximum absorbance
		Start cm^{-1}	End cm^{-1}	
HCl	5 420	3 150	2 500	0,28
HBr	1 000	2 744	2 290	0,04
HF	148	4 200	4 000	0,01

K.2 Collecting the reference spectra

The calibration response for a particular gas is usually determined by building a set of reference spectra obtained from pure samples of the gas over a range of concentrations.

NOTE The reference spectra may be composed of known combinations of gases in certain cases.

The number of concentrations which are necessary to obtain a calibration response of sufficient reliability depends on the degree of linearity between absorbance and concentration. When the absorbance-concentration relationship can be shown to be linear, two concentrations are theoretically sufficient, although three are recommended. When deviation from linearity is not strong then three concentrations are sufficient, but four are recommended; and when there is strong nonlinear behaviour, five concentrations are recommended.

For high concentration ranges, it may be necessary to use a second or even third lower absorbing spectral region for the higher concentrations to attain sufficient linearity to maintain concentration accuracy. This is necessary for example, to accurately quantify a wide concentration range of gases such as CO and CO_2 and HCN when using the MCT detector. Some instrument software will automatically generate full concentration/time curves when different spectral regions are uses for the lower, mid and higher concentrations. The concentration ranges normally expected in fire gases for each species (except water) and the recommended number of concentration points used to create the calibration model are summarized in Table K.2. It should be noted that the MCT detector is significantly more nonlinear than the DTGS detector over the same concentration range.

Table K.2 — Recommended ranges of volume fractions and number of points for calibration

Reference gas	Recommended number of concentrations	Minimum volume fraction µl/l	Maximum volume fraction µl/l
CO_2	5	50	40 000
CO	5	50	5 000
SO_2	2 to 3	20	1 000
Acrolein	2 to 3	20	300
NO	3	10	500
NO_2	3	20	500
HCl	5	50	10 000
HCN	4	10	1 000
HBr	4	50	1 000
HF	4	50	1 000

K.3 Overlapping spectra

A major problem with the FTIR technique for fire gas analysis is the presence of water which is a very strong absorber of infrared radiation over a wide range of wavenumbers and is thus capable of

obscuring the absorbance from many of the required species. Table K.3 shows which spectral regions and which species overlap. However, there are many other species not listed, with absorptions of infrared within the same region.

Table K.3 — Analytical limitations and interferences for different gases

Analysed gas	Common range	Analytical limitations	Interferences
CO_2	Few µl/l to 10 thousands µl/l		N_2O, H_2O
CO	Few µl/l to 10 thousands µl/l		N_2O, H_2O, COS
NO	Few µl/l to thousands µl/l		C_2H_4, H_2O
NO_2	Few µl/l to thousands µl/l		SO_2
HCN	Few µl/l to thousands µl/l		C_2H_2
NH_3	Few µl/l to thousands µl/l	Water soluble. Must heat entire sampling system.	C_2H_4
SO_2	Few µl/l to thousands µl/l		H_2O, C_2H_2, HCN, CH_4
HF	Few µl/l to hundreds µl/l	Adsorption by pipes and filters, water soluble. Must heat entire sampling system.	H_2O
HBr	Few µl/l to hundreds µl/l	Adsorption by pipes and filters, water soluble. Must heat entire sampling system.	
HCl	Few µl/l to hundreds µl/l	Adsorption by pipes and filters, water soluble. Must heat entire sampling system.	H_4, C-C, C-H
HCHO	Few µl/l to tenths µl/l	Adsorption by pipes and filters.	HCl, CH_4, C-C, C-H
CH_4	Few µl/l to hundreds µl/l		HCl, HCHO
C_2H_2	Few µl/l to hundreds µl/l		HCN
C_2H_4	Few µl/l to hundreds µl/l		NH_3
C_2H_6	Few µl/l to hundreds µl/l		

Resolutions of ≤0,5 cm^{-1} are needed to resolve these interferences. The species do not need to be resolved to take interferences into account when the interferences are known and are corrected in the quantification method. However, a resolution of ≤0,5 cm^{-1} enables visualization of this interference for combustion gas spectra. In developing a FTIR method for a particular combustion gas mix, it is desirable to select spectral regions with minimal spectral interferences. Interferences can be best minimized by having sufficient resolution over selected regions of the spectrum with minimal spectral overlap. This will assist quantification of a species in the presence of interferences. This is especially critical when only a narrow spectral range is available, as is the case for the analysis of NO in the presence of H_2O, and HCN in the presence of C_2H_2 (C_2H_2 is common fire gas, and is a significant interference for HCN).

This information is presented in Figure K.1, where the spectral absorption regions are plotted against the wave number of absorption. Using this figure, it is possible to verify which spectral regions overlap.