TECHNICAL SPECIFICATION

ISO/TS 19700

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Controlled equivalence ratio method for the determination of hazardous components of fire effluents — Steady-state tube furnace

Méthode du rapport d'équivalence contrôlée pour la détermination des substances dangereuses des effluents du feu — Four tubulaire à conditions stables

Reference number
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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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Any trade name used in this document is information given for the convenience of users and does not constitute an endorsement.

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

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

This second edition cancels and replaces the first edition (ISO/TS 19700:2007), which has been technically revised.

The changes in this document are as follows.

- The interlaboratory reproducibility has been assessed with homogenous thermoplastic materials.
- A verification procedure of the test apparatus with PMMA has been introduced.
- A new section on trueness and uncertainties with respect to steady-state tube furnace concentration and yields has been added.
- A new section on repeatability and reproducibility has been added.
- New informative annexes have been added (see Annexes F and G).
- The list of references has been updated.

Introduction

Fire safety engineering using performance-based design requires engineering methods for specific performance aspects of fire safety, but applicable to all types of structural systems, products and processes. This includes standard test methods for obtaining data on specific fire-related phenomena including the generation of harmful fire effluents. These have been designed to provide the input data necessary for engineering calculation methods for physical, chemical and biological properties. The exposure conditions and performance need to be adequately quantified to allow extrapolation from test conditions to different fire situations occurring in the real world.

The toxic hazard to an occupant of a building or transport enclosure during a fire depends on exposure to the time-varying concentrations of toxic products (gases and smoke particulates) in each occupant's breathing zone, the effect of each toxicant and the interactions between them. The concentrations of toxic gases and particles depend primarily on the mass-loss rate of the fuel, the yields of each toxicant and the dynamics of air entrainment and effluent dispersal within the occupied enclosure(s). Other factors, such as losses from deposition on the walls of the enclosure, may also need to be considered.

For fire safety calculations, such as those described in ISO 16732-1[1], the yields of toxic products from the burning fuel are necessary inputs. Since combustion conditions vary during a fire and between different fires, it is also necessary to measure the toxic product yields under a range of defined combustion conditions. In order to make a performance-based assessment of the toxic hazard in a fire, yield data of toxic products under different specified fire conditions comprise one category of the required inputs.

For any specific material, the effluent yields in fires depend upon the thermal decomposition conditions. The most important variables are whether the decomposition is non-flaming or flaming, and for flaming decomposition, the fuel/oxygen ratio. Based upon these variables, it is possible to classify fires into a number of types, as detailed in ISO 19706:2011, Table 1.

This method has been developed to measure toxic product yields from materials over a range of defined decomposition conditions in fires. At this stage, the interlaboratory reproducibility has been assessed with homogenous thermoplastic materials, and this document is therefore limited in applicability to such materials. The decomposition conditions are defined in terms of fuel/air equivalence ratio, temperature and flaming behaviour.

The method has been shown to replicate the production yields of toxic fire effluents in a number of studies for a range of polymers, described in 14.4 and Annex F.

The use of this document provides data on the range of toxic product yields likely to occur in different types and stages of full-scale fires. More comprehensive data on the relationships between decomposition conditions and product yields can be obtained by using a wider range of apparatus settings. Guidance on the choice of additional decomposition conditions is given in Annex A. The estimation of lethal toxic potency data according to ISO 13344 is described in Annex B. The use of data to assess toxic hazard according to ISO 13571 is described in Annex C. Guidance on the application of data for bioassay purposes is described in Annex D.

The test method has been developed to fulfil the requirements of ISO 16312-1 and ISO 19706, for data on the yields of toxic products in fire effluents evolved under different fire conditions as part of the data required for input to the toxic-hazard-assessment calculation methods described in ISO 13571. The data may also be used as input for the toxic-potency calculation methods described in ISO 13344 and ISO 13571.

Controlled equivalence ratio method for the determination of hazardous components of fire effluents — Steady-state tube furnace

1 Scope

This document describes a steady-state tube furnace (SSTF) method for the generation of fire effluent for the identification and measurement of its constituent combustion products, in particular, the yields of toxicants under a range of fire decomposition conditions.

It uses a moving test specimen and a tube furnace at different temperatures and airflow rates as the fire model. The interlaboratory reproducibility has been assessed with selected homogenous thermoplastic materials and this document is therefore limited in applicability to such materials. The method is validated for testing homogeneous thermoplastic materials that produce yields of a defined consistency. See limitations in Clause 12.

This method has been designed as a performance-based engineering method to provide data for input to hazard assessments and fire safety engineering design calculations. The method can be used to model a wide range of combustion conditions by using different combinations of temperature, non-flaming and flaming decomposition conditions and different fuel/oxygen ratios in the tube furnace. These include the combustion conditions for the following types of fires, as detailed in ISO 19706:2011, Table 1:

- Stage 1: Non-flaming:
  - Stage 1b) Oxidative pyrolysis from externally applied radiation;
- Stage 2: Well-ventilated flaming (representing a flaming developing fire);
- Stage 3: Under-ventilated flaming:
  - Stage 3a) Small localized fires in closed or poorly ventilated compartments;
  - Stage 3b) Post-flashover fires.

For each flaming fire type, the minimum conditions of test are specified in terms of the equivalence ratio, ϕ, as follows:

Stage 2	$\phi \leq 0{,}75$;
Stages 3a) and 3b)	$\phi = 2 \pm 0{,}2$.

Guidance on the choice of additional decomposition conditions is given in Annex A.

The data on toxic product concentrations and yields obtained using this document can be used as part of the estimation of toxic potencies, in conjunction with toxic potency calculation methods in ISO 13344, and as an input to the toxic hazard assessment from fires in conjunction with fire growth and effluent dispersal modelling, and fractional effective dose (FED) calculation methods in ISO 13571.

Application of data from the steady-state tube furnace to the estimation of lethal toxic potency and to the assessment of toxic hazards in fires is considered in Annex B and Annex C, respectively. Guidance on application of data from the steady-state tube furnace to the use of the steady-state tube furnace method for bioassay purposes is given in Annex D.

The test method described in this document can be used solely to measure and describe the production of toxic effluent from homogeneous thermoplastic materials, in response to heat or flame under controlled laboratory conditions. It is not suitable to be used, by itself, for describing or appraising the fire hazard of materials under actual fire conditions, or as the sole source on which regulations pertaining to toxicity can be based.

The yields of combustion products determined using this document pertain to the time interval during which steady-state burning is observed. To the extent that this interval is not a large fraction of the total burning time (i.e. if less than 5 min), the steady-state yield values are applicable with caution to fire safety analyses.

2 Normative references

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

ISO 291, *Plastics — Standard atmospheres for conditioning and testing*

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

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

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

ISO 19702, *Guidance for sampling and analysis of toxic gases and vapours in fire effluents using Fourier Transform Infrared (FTIR) spectroscopy*

ISO 29903, *Guidance for comparison of toxic gas data between different physical fire models and scales*

ISO/IEC Guide 98-3, *Uncertainty of measurement — Part 3: Guide to the expression of uncertainty in measurement (GUM:1995)*

3 Terms and definitions

For the purposes of this document, the terms and definitions given in ISO 13344, ISO 13571, ISO 13943, and the following apply.

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

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

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

3.1
accuracy
extent to which the measured value represents the true value, including the variability and uncertainties of the measured value

Note 1 to entry: The extent to which yields measured in the tube furnace for a specimen are predictive of the yields occurring when specimens are decomposed under the same combustion condition in large-scale compartment fire tests describes accuracy in this case.

Note 2 to entry: Definition of the accuracy of a measured value of a product concentration or yield from a tube furnace test run, see also Clause 14.

3.2
sample
gas-phase fire effluent removed for analysis

3.3
specimen
representative piece of the homogeneous material to be tested

3.4
steady-state burning conditions
combustion of fuel at a constant rate under constant ventilation, providing constant combustion conditions

Note 1 to entry: The steady-state tube furnace is designed to combust test specimens under steady-state conditions, by introducing fuel into the furnace at a constant rate under a constant flow of air. During a test run, steady-state conditions can be confirmed by continuous measurement of the carbon dioxide and oxygen concentrations. The criteria of steady-state combustion conditions using this method are defined in 10.3.

4 Principle

The yields of combustion products from fires depend upon the decomposition conditions.[2][3][4][5][6] The specified test conditions have been chosen to replicate oxidative pyrolysis under non-flaming conditions, well-ventilated flaming conditions at an equivalence ratio of less than 0,75, under-ventilated pre-flashover flaming conditions and post-flashover under-ventilated flaming conditions, both at an equivalence ratio of around 2 as defined in ISO 19706. The test is designed to combust materials under a range of conditions, different fuel/air equivalence ratios and temperatures. This test combusts materials under defined conditions with respect to non-flaming and flaming combustion, different fuel/air equivalence ratios and temperatures experienced in real fires as defined in ISO 19706. It is essential that proper observations are made during testing to ensure that the specified conditions are being met.

Specimens of a material are combusted under one or more steady-state conditions whose temperature and equivalence ratio are representative of a particular stage of a fire. A test specimen (in the form of granules or pellets, or as a continuous material) is uniformly distributed along an 800 mm quartz combustion boat. This is introduced at a constant rate into a quartz furnace tube which passes through a fixed tubular furnace. A stream of primary air is passed through the quartz furnace tube and over the test specimen at constant flow. The test specimen is driven into the hot zone of the tubular furnace. Under flaming conditions, ignition occurs, then the flame stabilizes, burning the test specimen at a fixed rate, in the presence of a controlled flow of primary air. The fire effluent moves through the quartz furnace tube into a mixing and measurement chamber where it is diluted with secondary air, giving a total flow of (50 ± 1) $dm^3 \cdot min^{-1}$ through the chamber, and is then exhausted to the fume extraction system.

In oxidative pyrolysis conditions, the furnace temperature is set below the auto-ignition temperature. The three flaming conditions are accomplished by using furnace temperatures above the auto-ignition temperature. For flaming decomposition conditions, different, constant primary airflows are used at a constant rate of introduction of the test specimen to obtain different fuel-to-oxygen ratios, and hence different equivalence ratios.

The secondary, dilution air generates a greater sample flow and cooler effluent which permits a large number of gas and smoke sampling procedures to be used without the need for additional replicate tests.

The requirement in each test run is to obtain stable, steady-state decomposition conditions, for at least 5 min, or longer if possible, during which the concentrations of effluent gases and particles shall be measured. The time taken for steady-state conditions to be established varies, depending upon the nature of the test specimen and the test conditions.

The concentrations of carbon dioxide and oxygen are recorded continuously to identify the period in which steady-state burning conditions occur and samples of the effluent mixture are taken from the chamber during the steady-state period for analysis. A sample of smoke shall be drawn through a filter and the mass of particles is determined.

5 Apparatus

5.1 General apparatus

The apparatus consists of a tubular furnace and a quartz furnace tube which passes through the furnace and into a mixing and measurement chamber. A drive mechanism pushes the combustion boat into the quartz furnace tube at a pre-set, controlled rate. A constant, known flow of primary air moves through the quartz furnace tube, over the moving test specimen, to the mixing and measurement chamber. A controlled secondary supply goes directly into the mixing and measurement chamber. Gaseous samples are taken from the mixing and measurement chamber.

The arrangement of the apparatus is shown in Figure 1. Unless otherwise stated, all tolerances are ±5 mm.

NOTE A light/photo cell system can be used to determine smoke density across the mixing and measurement chamber (see Annex E).

5.2 Tubular furnace

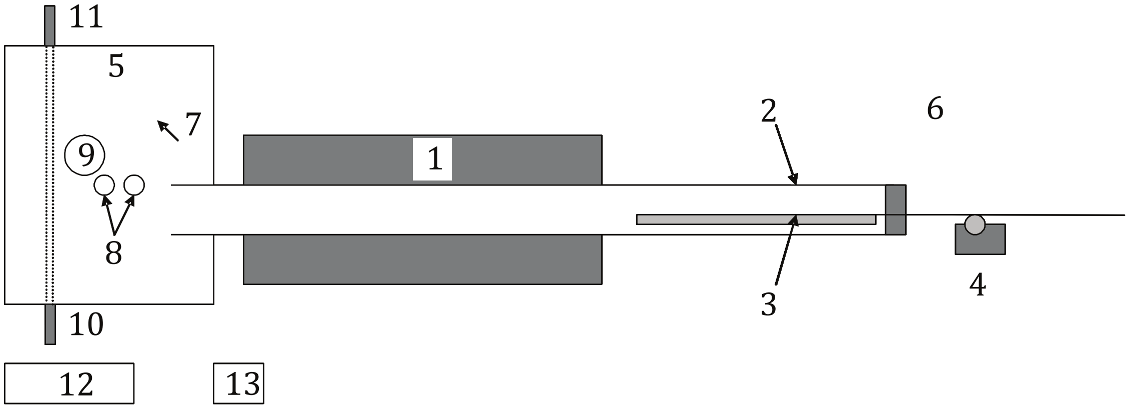
The tubular furnace shall have a heating zone length of 500 mm to 800 mm and an inside diameter of 50 mm to 65 mm. The furnace shall be equipped with an adjustable electric heating system capable of reaching 1 000 °C and maintaining the furnace temperature to within ±2 % of the set temperature with an empty quartz furnace tube in place under static conditions.

The heating element should preferably be rated at 1 300 °C. The furnace is similar to that used in IEC 60754–2.

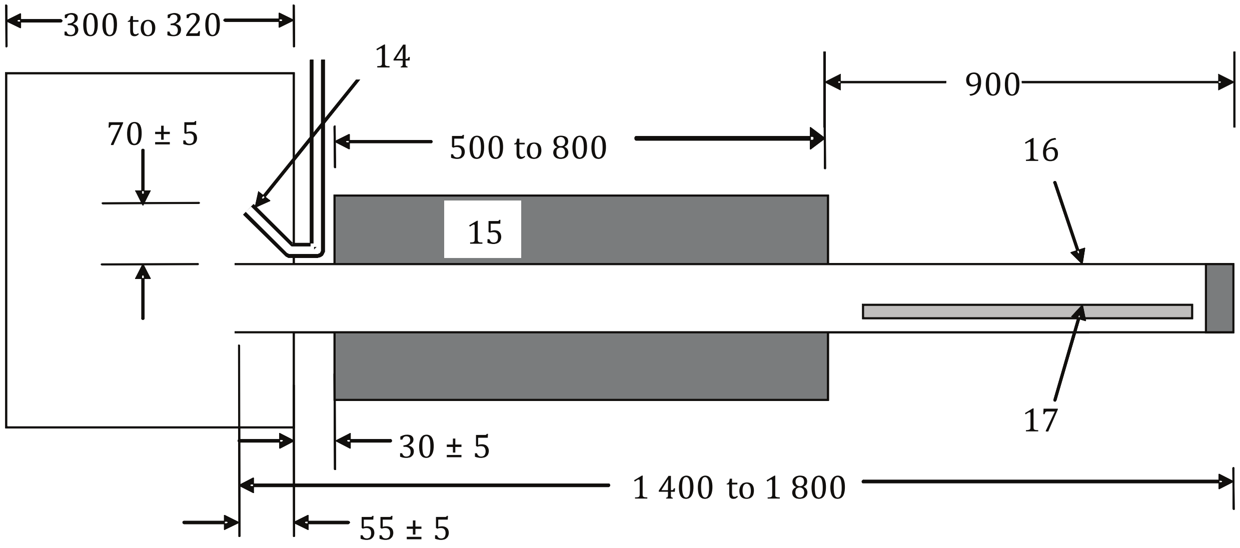
With the peak furnace temperature set at (650 ± 10) °C, the temperature shall not decrease by more than 100 °C over a length of at least ±125 mm from the point of peak temperature measurement. The method used to determine this temperature profile is given in 7.2.

NOTE This will also reduce the likelihood of a hot spot in the furnace, to which the pyrolysis rate will be sensitive.

Dimensions in millimetres



a) General arrangement of apparatus



b) Critical dimensions of assembly

Key

1	tube furnace
2	quartz furnace tube
3	combustion boat
4	combustion boat drive mechanism
5	mixing and measurement chamber
6	primary air inlet
7	secondary air inlet
8	ports for sampling lines
9	smoke-particle filter
10	light source (see Annex E)
11	photodetector (see Annex E)
12	gas bubblers (optional gas sampling method)
13	pump with flow meter (optional, for gas bubblers)
14	secondary air inlet 45° to vertical
15	tube furnace
16	furnace tube
17	combustion boat 800 mm long

Figure 1 — Tube-furnace decomposition and sampling apparatus

5.3 Calibrated thermocouples

Calibrated stainless-steel sheathed thermocouples, (1,5 ± 0,1) mm in diameter, shall be used for measuring the temperature in the furnace tube, the temperature in the mixing and measurement chamber and for calibrating the furnace.

5.4 Quartz furnace tube

The quartz furnace tube, as shown in Figure 2, is made of clear heat-resistant quartz, resistant to the effects of fire effluent. The tube shall be long enough to accommodate the combustion boat outside the furnace, to pass through the furnace and protrude into the mixing and measurement chamber at the far end of the furnace. The tube shall therefore be at least (furnace length + 895 mm) in length. It has an external, approximately concentric diameter of (47,5 ± 1) mm and a wall thickness of (2 ± 0,5) mm. The outside diameter shall permit a smooth fit within the tube furnace (5.2) and allow expansion at operating temperatures.

The input end of the furnace tube shall have a closure with openings in it to allow the primary air inlet and the combustion boat drive to pass through while maintaining a leak-proof seal.

NOTE 1 A polytetrafluoroethylene (PTFE) gland seal has been found to be suitable.

The downstream end of the furnace tube shall pass through a heat-resisting sealed gland and shall protrude 55 ± 5 mm into the mixing and measurement chamber (5.7).

NOTE 2 A gland made from glass wool or from glass rope inside a metal collar has been found to be suitable.

The end of the furnace tube should be able to accommodate an airflow restrictor reducing the outlet diameter of the quartz furnace tube to the mixing and measurement chamber to a maximum area of 100 mm^2. This prevents air from the mixing chamber diffusing back to the furnace tube at low primary airflows.

NOTE 3 A suitable flow restrictor has been made using a 100 cm^3 borosilicate glass laboratory beaker which fits snugly inside the furnace tube, with a 35 mm diameter circular hole cut into the base. The hole was cut with the beaker under water, using a low voltage “Dremel” drill and grinding bit.

The distance between the exit of the tubular furnace and the mixing and measurement chamber shall be (30 ± 5) mm.

The quartz furnace tube shall be horizontal (within ±1 mm in the vertical direction per metre along the furnace axis) to ensure that molten fuels cannot flow up or down the combustion boat during a run.

5.5 Combustion boat

The combustion boat, as shown in Figure 2, is made from quartz tubing of diameter (41 ± 1) mm, with a length of 800 mm and a wall thickness of (2 ± 0,5) mm. The boat should be cleaned after each test.

NOTE 1 A suitable combustion boat has been made from quartz tubing with a nominal diameter of 41 mm. This was sliced in half along its axis to provide a semi-circular cross-section, nominally of 41 mm width, 18 mm depth and 800 mm length. Flat semi-circular quartz plates were fused onto each end.

NOTE 2 A boat diameter (41 mm) provides the maximum test specimen capacity.

A boat length of 800 mm has been found suitable for testing most materials. Where materials take a long time to reach steady-state burning, or where a steady-state period of longer that 5 min is required, longer boats may be used.

NOTE 3 A convenient method of cleaning both the boat and tube is to remove obvious residues mechanically, then heat in a furnace at 1 000 °C, followed by washing in water to remove any inorganic residues.

5.6 Combustion boat drive

5.6.1 Mechanism

The combustion boat is connected to a notched drive bar, which passes through the gland seal (5.4) at the upstream end of the furnace tube, and connects to a drive mechanism. The drive mechanism advances the boat at a typical rate of (40 ± 1) mm·min^{-1}. The drive mechanism shall allow different advance rates to be selected.

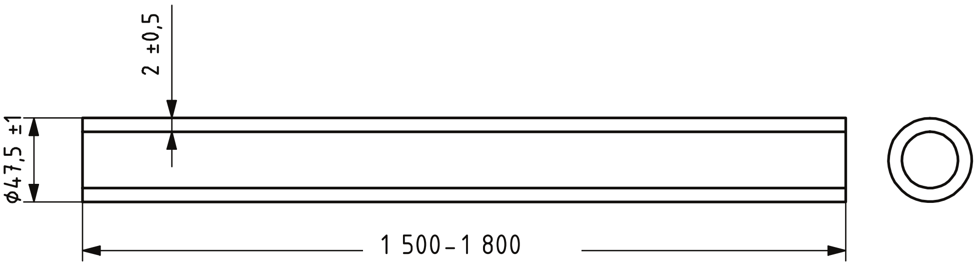
The capacity of the drive mechanism shall be sufficient to move the combustion boat at least 800 mm. This will move the front of the boat from the near end of the furnace all the way to the far end of the furnace, just allowing the rear end of the 800 mm boat to enter the furnace. The mechanism shall enable the boat to be rapidly retracted into the upstream, external part of the furnace tube at the end of the test run. This may be achieved manually after detaching the push rod from the drive mechanism.

A drive advance rate of 40 mm·min^{-1} has been found suitable for most materials under most decomposition conditions. For some fast-burning or low-density materials, it has been found necessary to use advance rates of up to 60 mm·min^{-1}. For tests involving specimens of uniform linear density, such as rods of material, the drive advance rate should be adjusted to give a fuel feed rate of 1 g·min^{-1}.

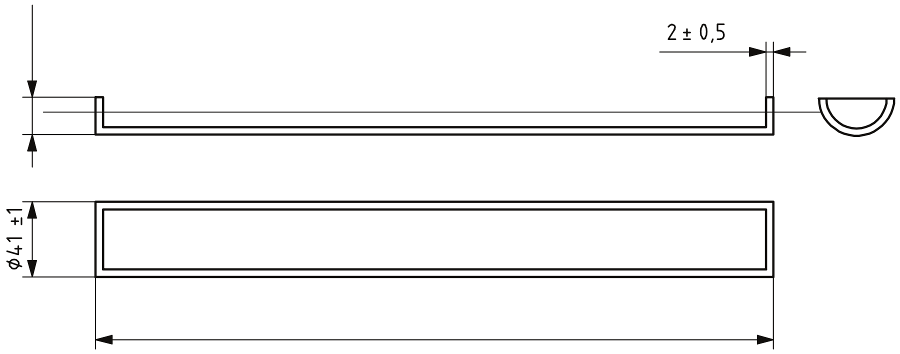
5.6.2 Rate of specimen introduction

The rate of introduction of the combustion boat (in mm·min^{-1}) shall be determined by advancing the boat over a distance of (800 ± 1) mm and measuring the time taken. This is (1 200 ± 12) s at an advance rate of (40 ± 1) mm·min^{-1}. The most important criterion for this parameter is repeatability, which should be within ±1 %. The actual advance rate may be up to 10 % higher or lower than the specified rate. The actual advance rate shall be measured to 1 % accuracy and the specimen mass loading is adjusted to provide a mass feed rate equivalent to that specified (see 9.2 and 9.3).

Dimensions in millimetres



a) Quartz furnace tube



b) Combustion boat

Figure 2 — Dimensions of a suitable quartz furnace tube and combustion boat

5.7 Mixing and measurement chamber

The mixing and measurement chamber shall be an approximately cubic box with a side length of (31 ± 2) cm (see Figure 3), although the exact dimensions are not critical. The front of the chamber has a door, providing a seal when shut, but enabling cleaning of the chamber when open.

NOTE 1 The walls of the box can be made of any suitable material which has a low affinity for the analytes being quantified. Stainless steel coated with PTFE film, PMMA and polycarbonate have been found to be suitable materials. A suitable chamber can be made from a commercially available desiccator cabinet with nominal dimensions of 310 mm × 310 mm × 340 mm (see Figure 3). This would have an internal volume of 33 dm^3 compared with the airflow volume of 50 dm^3 in 1 min. For non-heat resistant wall materials (e.g. PMMA), the back wall of the chamber and the rear portion of the roof are protected by a stainless steel plate fitted to the inner surface, the top of the plate extending 140 mm across the chamber roof, so as to be resistant to heat and any flames emanating from the end of the furnace tube.

The volume of the mixing and measurement chamber needs to be large enough to accommodate the sampling points but smaller than the total volume of air flowing through the chamber in 1 min.

The roof of the chamber shall be fitted with a safety blow-out panel 75 mm in diameter, which will burst in the event of an explosion.

NOTE 2 This is important for safety reasons.

A port approximately 35 mm in diameter is provided at the base of the rear face of the chamber for the test atmosphere to be exhausted to waste.

The chamber shall include all the necessary sampling and measurement points (gas sampling probes to bubblers, etc., and particulate filters). Measurement points are located away from the rising plume and the chamber walls; these may be sited in any convenient location. The open end of each sample probe shall be (30 ± 5) mm from the wall of the mixing and measurement chamber.

NOTE 3 The sampling points are positioned away from the furnace-tube exit plume and chamber walls but can be sited in any convenient location. Suitable locations are shown in Figure 3.

NOTE 4 A thermocouple (5.3), extending approximately 50 mm into the mixing and measurement chamber, can be located as shown in Figure 3, for monitoring of the temperature in the chamber during the tests.

5.8 Analysis of gases

This document requires the determination of certain combustion gases to characterize the fire condition. The means of gas sampling and analysis shall be those given in ISO 19701 and ISO 19702. The mixing chamber thermocouple shall be located in close proximity to the sampling port to ensure isothermal sampling conditions.

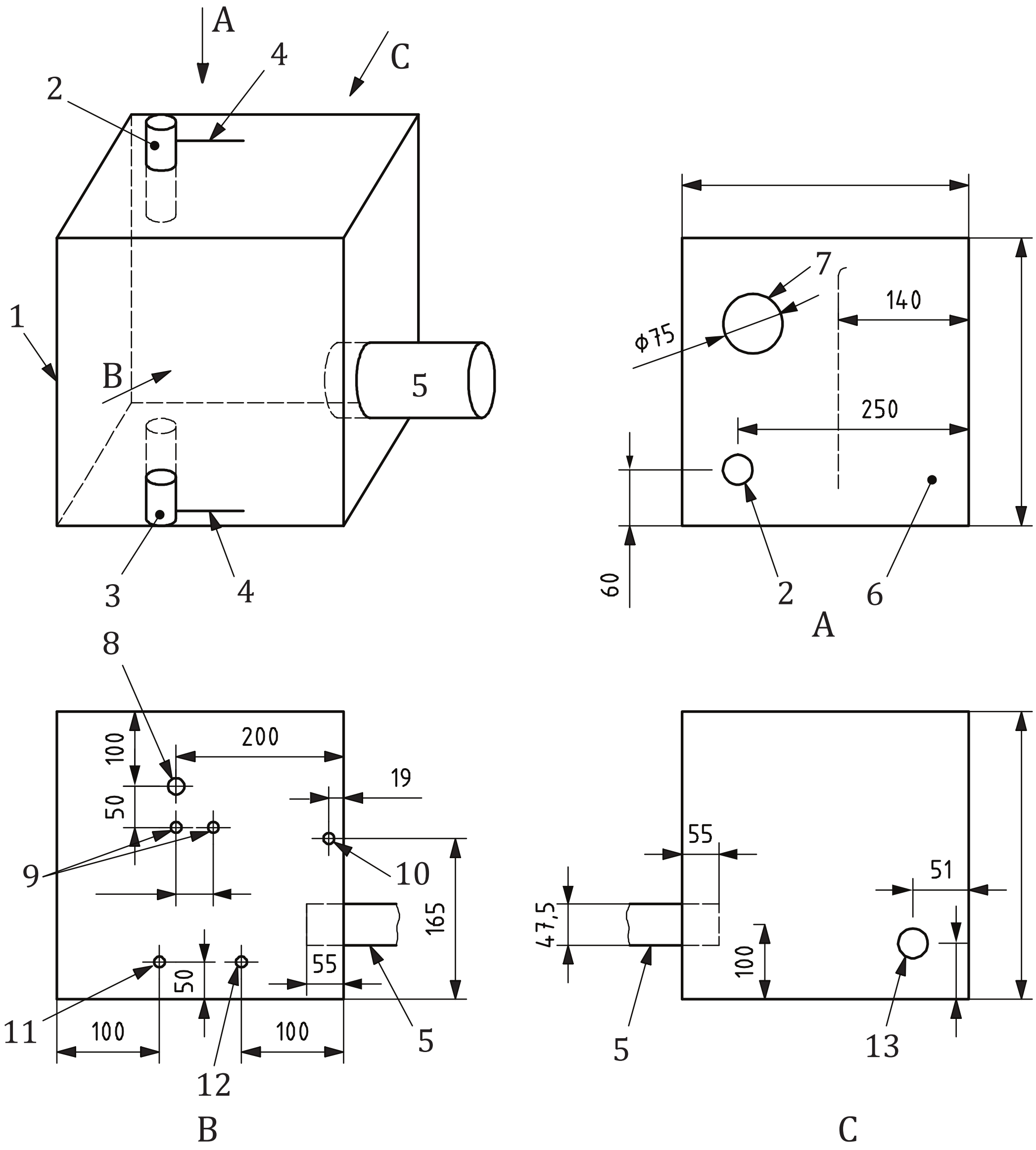
Carbon dioxide and oxygen concentrations shall be determined by continuous sampling throughout the test. These data are used to identify and monitor the steady-state burning period and also to characterize the fire condition. The concentration of carbon monoxide shall also be determined continuously.

The oxygen meter shall be capable of an accuracy of a volume fraction of 0,01 %.

The selection of toxic components of the fire effluent shall follow the appropriate hazard assessment, such as those set out in ISO 13344 or ISO 13571.

Further guidance is given in 10.4.

Dimensions in millimetres



Key

1 door

2 tube containing photodetector (see Annex E)

3 tube containing light source (see Annex E)

4 purge tubes for photodetector and light source (see Annex E)

5 quartz furnace tube

6 stainless-steel plate

7 safety blow-out panel

8 smoke particle filter

9 ports for sampling lines

10 secondary air inlet

11 port for thermocouple

12 port for tube to sample atmosphere in furnace tube for measurement of oxygen concentration

13 exhaust port

A top

B side-view

C side-view

Figure 3 — Dimensions of mixing and measurement chamber

5.9 Determination of smoke aerosols

Smoke aerosols (solid particles and liquid droplets) shall be batch sampled from the mixing and measurement chamber through a particulate filter during the steady-state period, or part thereof. Further guidance is given in 10.4.

NOTE Annex E describes optional measurement of the optical density of smoke.

5.10 Exhaust system

The system shall be connected to an effective exhaust system, to ensure the safety of operators and other personnel, particularly from the toxic fire effluents being generated. However, the exhaust system shall not be connected in such a way that it draws air through the apparatus. When the primary air inlet is removed, with the exhaust system at normal operating speed, and secondary air is not flowing, observable quantities of air shall not be drawn into the furnace tube.

NOTE Airflow direction can easily be observed using a joss-stick. Joss-sticks can be used to verify that smoke is not drawn into the mouth of the furnace, that there is no leakage at the gland on the mixing chamber and to ensure that any extraneous effluents will be drawn into the hood.

6 Air supplies

6.1 Primary and secondary air supplies

The primary and secondary air supplies to the apparatus shall be clean and free from excessive moisture. The water content and/or the relative humidity of the air shall be reported. The flows refer to a pressure of 101 325 Pa and a temperature of 20 °C.

NOTE 1 Compressed air from a cylinder, or compressed air free from water and oil, and passed through a carbon trap and silica gel, has been found to be suitable.

The primary air shall be introduced through the closure at the input end of the furnace tube.

The secondary air shall be introduced into the mixing and measurement chamber using piping of internal diameter (3,5 ± 1) mm, passing through the wall of the mixing and measurement chamber and ending (70 ± 5) mm above, and in line with, the end of the furnace tube, and pointing upwards at an angle of approximately 45°. The secondary air supply intercepts the rising plume to facilitate the efficient mixing of the test atmosphere.

NOTE 2 This system will give good mixing of the furnace effluent and the secondary air and eliminates the need for a mechanical stirring device.

Both the primary and secondary airflows shall be delivered at a constant, predetermined rate, at positive pressure and monitored using in-line flow meters or mass flow controllers. Airflows shall be calibrated at the point of entry to the chamber.

A correction for back pressure at the in-line flow meters may be necessary.

The primary airflow is set to provide the desired combustion conditions and the secondary airflow shall be adjusted to provide a total airflow through the mixing and measurement chamber of (50 ± 1) $\mathrm{dm^3 \cdot min^{-1}}$.

6.2 Primary airflow calibration

Before testing commences, the in-line flow setting device (flow meter or mass flow controller) shall be calibrated for airflows from 2 $\mathrm{dm^3 \cdot min^{-1}}$ to 12 $\mathrm{dm^3 \cdot min^{-1}}$ to an accuracy of 1 % using a bubble meter, or suitable supplementary flow meter with no entry or exit restrictions, with a maximum range of

(5 ± 1) $dm^3 \cdot min^{-1}$ for flows of up to 5 $dm^3 \cdot min^{-1}$ and (12 ± 2) $dm^3 \cdot min^{-1}$ for higher flows, to ensure the correct flow of primary airflow through the furnace tube.

NOTE When needle valves have been fitted in-line to flow meters, these have been found to exert a significant influence on the airflow, even when fully open.

A bored rubber bung inserted into the furnace tube at the mixing chamber end, fitted with a tube of internal diameter at least a factor of 1,5 larger than the internal diameter of the primary air inlet tube, and of length no more than 1 m, shall be used to determine the primary airflow using this calibration procedure, with the drive mechanism in operation.

6.3 Secondary airflow calibration

The secondary air inlet tube shall be disconnected from the chamber. Using a tube of greater diameter than that at the chamber entry, for all connections, measure the secondary airflow over a range from 35 $dm^3 \cdot min^{-1}$ to 50 $dm^3 \cdot min^{-1}$ to an accuracy of 1 % using an appropriate method.

NOTE A simple method is to use a large bore, calibrated, 50 $dm^3 \cdot min^{-1}$ range flow meter with no entry or exit restrictions (i.e. no upper or lower valves) and check measured against indicated flows on the in-line flow meter or mass flow controller.

6.4 Overall confirmation

The apparatus shall be set up with the furnace off, and the primary air supply connected to a nitrogen supply. Using a primary nitrogen flow of 10 $dm^3 \cdot min^{-1}$, and a secondary airflow of 40 $dm^3 \cdot min^{-1}$, the oxygen volume fraction in the mixing chamber shall be measured until stable, and then recorded over a period of 5 min. The measured average oxygen depletion should be (0,041 9 ± 0,000 5).

For example, if the oxygen meter reads (16,75 ± 0,05) %-O_2 then this conformation criterion has been met because the volume fraction of oxygen depletion is 0,209 5 − (0,167 5 ± 0,000 5) = (0,042 ± 0,000 5).

In order to confirm other secondary airflows, carry out the following measurements:

- The secondary airflow shall then be increased to 45 $dm^3 \cdot min^{-1}$. The measured average oxygen depletion should be (0,038 1 ± 0,000 5).
- The secondary airflow shall then be increased to 47 $dm^3 \cdot min^{-1}$. The measured average oxygen depletion should be (0,036 8 ± 0,000 5).
- The secondary airflow shall then be increased to 48 $dm^3 \cdot min^{-1}$. The measured average oxygen depletion should be (0,036 1 ± 0,000 5).

In order to confirm a lower primary airflow, carry out the following measurement:

- The primary nitrogen flow shall be set to 3,0 $dm^3 \cdot min^{-1}$ and the secondary airflow to 47,0 $dm^3 \cdot min^{-1}$. The measured average oxygen depletion should be (0,012 6 ± 0,000 5).

If the result is outside these limits, the primary and secondary flow meters shall be recalibrated and the procedure is repeated until confirmation is obtained.

7 Establishment of furnace temperature and setting of furnace temperature

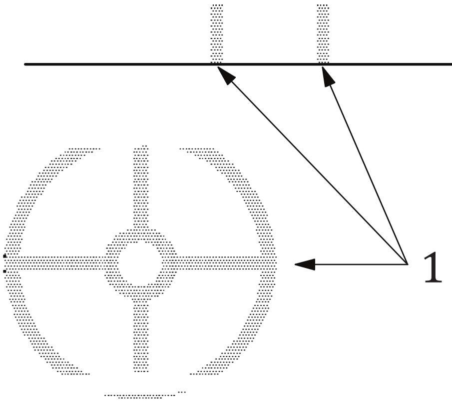
7.1 General

There are two stages included in the temperature standardization. The first stage is to establish that the temperature profile (change of temperature with distance through the furnace tube) of the particular furnace to be used is suitable; the second stage is to determine the temperature setting needed for the particular test run condition to be carried out.

7.2 Establishing furnace temperature profile to determine furnace suitability

Set up the furnace, with an empty quartz furnace tube in place, under static conditions (i.e. with no airflow through the furnace tube). Close the furnace tube at one end with a bung to prevent airflow through the furnace and set the furnace temperature controller to 680 °C. Introduce the calibrated thermocouple (5.3) into the centre of the quartz furnace tube, with the tip of the thermocouple within a 10 mm radius of the centre of the quartz furnace tube.

NOTE A suitable support for the thermocouple is shown in Figure 4.



Key

1 position of thermocouple supports inside furnace tube to position thermocouple in centre of tube

Figure 4 — Wire thermocouple support rings allowing thermocouple to move along in required position

Allow the furnace to reach equilibrium. Then measure the temperature profile along the furnace tube by recording the temperature at intervals of 25 mm to find the point of maximum temperature. This should be near the centre of the furnace and the maximum temperature should be (650 ± 10) °C. If the maximum temperature is outside this range, adjust the furnace temperature controller to bring the maximum temperature into this range.

In many cases, it may be preferable to use the boat drive mechanism at normal advance rate to also drive the thermocouple into the furnace to record the temperature profile, as a function of position in the furnace.

From the results obtained, determine the location of the point of maximum temperature and record the temperature at that point. Make further measurements at intervals of 25 mm on each side of the point of maximum temperature, until points are reached at which the temperature decrease relative to the maximum temperature exceeds 100 °C. For the furnace to be acceptable, these points shall lie between 125 mm and 250 mm from the location of the point of maximum temperature.

7.3 Setting the temperature for an individual test run condition

The maximum temperature for an individual test run condition shall be determined under airflow conditions (T_{run}), with the quartz furnace tube in place in the tubular furnace and primary air flowing through the quartz furnace tube. The calibrated thermocouple shall be placed (5.3) in the quartz furnace tube as described in 7.2 and allowed to equilibrate. Once a primary airflow has been established, the point of maximum temperature moves downstream relative to its location under static conditions. In order to compensate for this shift, position the thermocouple tip (75 ± 10) mm downstream of the point of maximum temperature established under static conditions (determined in 7.2). This position minimizes the temperature deviation for flow rates of up to 20 $\text{dm}^3 \cdot \text{min}^{-1}$. When the position has been established, the furnace temperature controller shall be adjusted until a temperature within ±5 °C of the desired value for T_{run} is obtained.

NOTE It is necessary to specify the furnace conditions for the test. The conditions given above are based on experimental work using typical commercially available furnaces 500 mm to 600 mm long. If the furnace hot zone is too short then the test specimen and decomposition products might not be heated for a sufficient time. Hot zones longer than 600 mm are less likely to present problems, but it is possible that the longer period for which the test specimen and decomposition products are heated could result in small differences in the combustion product yields. The above has been found to be satisfactory in use.

8 Test specimen preparation

8.1 Test specimen form

The test specimen shall be in the form of either

a) granules or pellets, or

b) a rod or other continuous material provided steady-state conditions can be achieved (10.3).

Details of the test specimen and its form shall be included in the test report (see Clause 12).

8.2 Combustible loading

The test specimen shall be uniformly distributed along the length of the combustion boat, so that a constant flow of decomposition products is produced as the test specimen passes through the furnace. The specimen combustible loading shall be approximately 25 $\mathrm{mg{\cdot}mm^{-1}}$ (this corresponds to 20 g spread over 800 mm).

Materials having densities below approximately 0,05 $\mathrm{g{\cdot}cm^{-3}}$ can be so bulky that they restrict the flow of air through the furnace tube at a specimen loading of 25 $\mathrm{mg{\cdot}mm^{-1}}$. To overcome this problem, it is acceptable to reduce the specimen loading and increase the combustion boat advance rate to compensate (5.6).

For materials which contain an inert matrix or fillers which do not form part of the combustible mass, the mass loading of material in the test specimen may need to be increased to compensate, according to Clause 9.

8.3 Specimen conditioning

Before the test, specimens shall be conditioned to constant mass at a temperature of (23 ± 2) °C and a relative humidity of (50 ± 5) %.

Constant mass is considered to be reached when two successive weighing operations, carried out at an interval of 24 h, do not differ by more than 0,1 % of the mass of the test specimen or 0,1 g, whichever is the greater.

Materials such as polyamides, which require more than 1 week in a conditioning atmosphere to reach constant mass, may be tested after conditioning in accordance with ISO 291. This period shall be not less than 1 week and shall be described in the test report.

9 Selection of test decomposition conditions

9.1 Selection of decomposition conditions for fire hazard analysis or fire safety engineering

Test specimens shall be decomposed or combusted under one or more of the test conditions specified in 9.2 to 9.5 for the required fire stages.

The various fire stages are defined in ISO 19706:2011, Table 1 [1b), 2, 3a) and 3b)]. For stage 2, the procedure provides an equivalence ratio, Φ, of ≤0,75. For stages 3a) and 3b), the procedure provides a Φ of 2,0 ± 0,2.

For materials of unknown decomposition behaviour, preliminary test runs shall be carried out to determine the test conditions according to the procedures of Clause 10. Carbon dioxide and oxygen concentrations, and the average mass loss, shall be measured in order to establish the combustible component of the test material and determine the appropriate specimen mass loading as specified in 9.2 to 9.5. Guidance on the selection of additional decomposition conditions is presented in Annex A.

NOTE 1 A well-ventilated test with a T_{run} of 900 °C according to c) in Annex A can be used to determine the combustible content of a material with unknown composition.

A test run is only valid if the selected steady-state conditions (10.3) are maintained for a period of at least 5 min during the test. If ignition occurs during a non-flaming run, or fails to occur during a flaming run, then the furnace temperature shall be raised or lowered in 25 °C steps until the required behaviour is obtained. A new test run shall then be carried out with a fresh test specimen. For flaming behaviour, it is also necessary to ensure that the correct primary airflows are used, as specified in 9.3, 9.4 and 9.5.

NOTE 2 The equivalence ratio, ϕ, can be calculated from the average mass loss of combustible effluent from the test specimen, in milligrams per minute (mg·min^{-1}), divided by the mass flow rate of oxygen in the primary air, in milligrams per minute (mg·min^{-1}), divided by the stoichiometric fuel mass to oxygen mass ratio for the material under test. See worked example in Annex A.

9.2 Stage 1b): oxidative pyrolysis from externally applied radiation

Place a test-specimen combustible loading in the combustion boat to provide a mass feed rate of 1 000 mg·min^{-1} (nominally 25 mg·mm^{-1} at an advance rate of 40 mm·min^{-1}).

Set the furnace temperature to obtain a T_{run} of 350 °C.

Set the primary airflow rate to 2 dm^{3}·min^{-1} and the secondary airflow rate to 48 dm^{3}·min^{-1}.

Complete a test run as described in the procedure in 10.2.

If flaming decomposition occurs during the run, repeat at temperatures progressively 25 °C lower until continuous, non-flaming decomposition is obtained throughout the steady-state period.

9.3 Stage 2: well-ventilated flaming

Place a test-specimen combustible loading in the combustion boat to provide a mass feed rate of 1 000 mg·min^{-1} (nominally 25 mg·mm^{-1} at an advance rate of 40 mm·min^{-1}).

Set the furnace temperature to obtain a T_{run} of 650 °C. Set the primary airflow rate to 10 dm^{3}·min^{-1} and the secondary airflow rate to 40 dm^{3}·min^{-1}.

Complete a test run as described in the procedure in 10.2.

From the average volume fraction of oxygen in the mixing and measurement chamber, $\left(M_{\text{O}_2}\right)$, calculated to four decimal places, calculate the oxygen depletion, $\left(D_{\text{O}_2}\right)$, as follows:

$$D_{\text{O}_2} = 0{,}2095 - M_{\text{O}_2} \tag{1}$$

When ϕ = 1,00, the oxygen depletion in the primary air stream will approach 0,209 5 (i.e. 20,95 % O_2) and the measured oxygen depletion, D_{O_2}, will be 10/50 × 0,209 5 = 0,041 9.

When $\phi = 0{,}75$, $D_{\text{O}_2} = 0{,}031\,4\left(0{,}75 \times 0{,}041\,9\right)$.

When $\phi = 0{,}50$, $D_{O_2} = 0{,}021\,0\left(0{,}50 \times 0{,}041\,9\right)$.

When $\phi = 0{,}36$, $D_{O_2} = 0{,}015\,0\left(0{,}36 \times 0{,}041\,9\right)$.

If $D_{O_2} \leq 0{,}031\,4$ and $\geq 0{,}021\,0$, then ϕ will be $\leq 0{,}75$ and $\geq 0{,}50$. The run therefore meets the criteria for well-ventilated flaming ($\phi \leq 0{,}75$). A lower limit of $\phi = 0{,}50$ is also specified because, below this, the combustible fuel content is too low to obtain reliable data.

If $D_{O_2} > 0{,}031\,4$, then $\phi > 0{,}75$ and the run is unacceptable. Repeat with a reduced specimen feed rate by a factor of $\frac{2{,}50}{D_{O_2}}$, either by reducing the combustible loading, or by reducing the boat advance rate.

If $D_{O_2} < 0{,}021\,0$ and $\geq 0{,}015\,0$, then $\phi < 0{,}50$ and $\geq 0{,}36$ and the combustible fuel content is too low to obtain reliable data. Repeat the run, increasing the specimen mass loading by a factor of 1,5.

If $D_{O_2} < 0{,}015\,0$, then $\phi < 0{,}36$ and the combustible fuel content is too low to obtain reliable data. Repeat the run increasing the specimen mass loading by a factor of 2.

If flaming decomposition does not occur or is intermittent during the run, repeat at temperatures progressively 25 °C higher, until continuous flaming decomposition is obtained throughout the steady-state period. If continuous flaming cannot be obtained, this shall be reported, together with the maximum furnace temperature investigated.

In each case, only data calculated from the acceptable run shall be described as representing well-ventilated flaming.

NOTE A suitable value of D_{O2} can also be obtained by setting the furnace temperature to obtain a T_{run} of 900 °C (see Annex A).

9.4 Stage 3a): small vitiated fires in closed or poorly ventilated compartments

Use the same test specimen material, loading and boat advance rate as in 9.3 in order to obtain the same specimen feed rate.

Set the furnace temperature to obtain a T_{run} of 650 °C. Set the primary airflow rate to P $dm^3 \cdot min^{-1}$ (see below for the calculation of P) and the secondary airflow rate to (50-P) $dm^3 \cdot min^{-1}$. Complete a test run as described in the procedure in 10.2.

Calculate the primary airflow rate (P) for the 3a) test as follows:

$$P = D_{O_2} \times 125\,\mathrm{dm}^3 \cdot \mathrm{min}^{-1} \tag{2}$$

For example, if $D_{O_2} = 0{,}029\,5$, then $P = 0{,}029\,5 \times 125\ dm^3 \cdot min^{-1} = 3{,}69\ dm^3 \cdot min^{-1}$

This will create conditions where $\phi = 2{,}0$.

If $P < 3{,}2\ dm^3 \cdot min^{-1}$, set the primary airflow to $3{,}2\ dm^3 \cdot min^{-1}$.

NOTE 1 The factor of 125 $dm^3 \cdot min^{-1}$ is derived from the total airflow, the volume fraction of oxygen in the air supply and the target value of ϕ, as follows, taking into account an average combustion efficiency fraction of 0,95.

$$\begin{aligned} P &= D_{O_2} \times \left(\text{total air flow}\right) / \left(0{,}209\,5 \times \text{target}\,\phi \times 0{,}95\right) \\ &= D_{O_2} \times \left(50\,\mathrm{dm}^3 \cdot \mathrm{min}^{-1}\right) / \left(0{,}209\,5 \times 2{,}0 \times 0{,}95\right) \\ &= D_{O_2} \times 125\,\mathrm{dm}^3 \cdot \mathrm{min}^{-1} \end{aligned} \tag{3}$$

NOTE 2 The factor of 0,95 has been shown to compensate for less than complete mixing of fuel and oxidizer in the furnace tube.

The factor of 125 $dm^3 \cdot min^{-1}$ relates only to a total specified airflow of 50 $dm^3 \cdot min^{-1}$. Total airflows different from this should be taken into account and the factor recalculated.

NOTE 3 The minimum primary airflow of 3,2 $dm^3 \cdot min^{-1}$ is to ensure that the target condition of $\phi = 2{,}0 \pm 0{,}2$ is met, even when well-ventilated combustion is incomplete. For example, flame inhibition by halogens can reduce the combustion efficiency in well-ventilated conditions leading to an incorrectly low calculated primary airflow.

If flaming decomposition does not occur or is intermittent during the run, the run shall be repeated at temperatures progressively 25 °C higher, until continuous flaming decomposition is obtained throughout the steady-state period. If continuous flaming cannot be obtained, this shall be reported, together with the maximum temperature investigated.

In each case, only data calculated from the acceptable run shall be described as representing under-ventilated flaming.

9.5 Stage 3b): post-flashover fires in open compartments

The procedure is the same as that specified in 9.4, except that the furnace temperature is set at a T_{run} of 825 °C.

10 Procedure

10.1 Safety considerations

WARNING — So that suitable precautions are taken to safeguard health, the attention of all concerned in fire tests is drawn to the possibility that toxic or harmful gases can be evolved during exposure of test specimens.

The test procedures involve high temperatures and combustion processes. Therefore, hazards can exist such as burns or the ignition of flammable gases, extraneous objects or clothing. The operator shall use protective gloves for insertion and removal of test specimens. Neither the furnace nor the associated fixtures shall be touched while hot except with the use of protective gloves. The exhaust system of the apparatus shall be checked for proper operation and shall discharge into a building exhaust system with adequate capacity. The possibility of the accumulation of flammable fire effluent in the mixing chamber which then ignites causing an explosion cannot totally be discounted, and it is therefore essential that eye protection be worn.

When the furnace is hot, the chamber walls shall only be cleaned with water-based fluids. Cleaning the chamber walls with flammable solvent-based fluids should only be carried out when the furnace is cold.

10.2 Decomposition of the test specimen

The furnace tube and combustion boat shall be clean before each test (5.5, Note 4). The mixing chamber shall be free of any loose material before each test. A blank test run carried out before each series of tests can be used to confirm the cleanliness of the apparatus.

Set up the tubular furnace at the specified temperature and primary airflow rate in accordance with 9.2 to 9.5, as applicable.

Set the secondary airflow to provide a total airflow through the mixing chamber of (50 ± 1) $dm^3 \cdot min^{-1}$.

The sampling and measurement equipment shall be calibrated daily.

Introduce the combustion boat containing a test specimen of known mass, prepared in accordance with Clause 8, into the quartz furnace tube with the front end of the boat just outside the air inlet end of the tubular furnace entrance. Connect the drive mechanism and quartz furnace tube closure, with the primary air flowing.

Begin continuous sampling from the chamber through the gas analysers (carbon dioxide, carbon monoxide and oxygen). Start recording the data from these and from the smoke density monitor if fitted (see Annex E).

Start the test run by switching on the boat drive mechanism to introduce the combustion boat containing the test specimen into the furnace at an advance rate of 40 $mm \cdot min^{-1}$.

For some fast-burning and low-density materials, it is permissible to use boat advance rates of up to 60 $mm \cdot min^{-1}$. In this case, it may be necessary to change the specimen mass and airflow rates to maintain a constant fuel-mass/airflow ratio (5.6 and 8.2).

Regular visual observation of the specimen inside the furnace tube shall be made to determine when ignition occurs, that flaming is continuous during flaming decomposition tests and that flaming does not occur during non-flaming decomposition tests.

NOTE 1 A convex mirror at the primary air inlet end of the furnace tube has been found useful for this.

The fire condition can also be verified from the gas analysis where flaming will be indicated by relatively high CO_2 concentrations and yields.

The signals from the gas analysers (carbon dioxide, carbon monoxide, oxygen and the smoke density monitor if fitted) shall be recorded throughout the run and the signals observed during the early stages of the run. When these have reached approximately constant levels, then dynamic steady-state conditions have been achieved. Record the time and begin any batch sampling from the chamber after this point. The data logging interval shall be no longer than 15 s.

Development of steady-state conditions: During the first few minutes of a 20-min run, the leading edge of the specimen become progressively hotter until a stable flame is established from approximately 4 min. After a further 2 min, during which equilibrium conditions are established in the mixing chamber, steady-state conditions are established for non-char forming materials and maintained for the remainder of the run. For char-forming materials, a further few minutes are required for the char decomposition rate to reach equilibrium. For all materials, including char formers, steady-state conditions have been found to exist from approximately 13 min after the start of the test run. Batch sampling can then be started at any time between 13 min and 15 min to provide a sampling period of at least 5 min. For results calculations after a run, a default steady-state period from 13 min to 20 min may be used, but increased accuracy can be obtained by retrospective examination of the data which can extend the period used for calculation of steady-state gas concentrations to earlier times and lengthen the steady-state period when possible.

NOTE 2 For many materials, initial peaks in CO_2 and CO are observed near the start of the run as the flame stabilizes, after which a period of steady burning is generally observed for the remainder of the run up to 20 min. If the run is prolonged beyond the specified period, or a shorter than specified test specimen is used, so that fuel is consumed over the entire length of the combustion boat, then irregularities can occur towards the end of the run, so that the period of steady burning is then between these two regions.

Continue to observe the test specimen and signals from the gas monitors. The decomposition conditions shall remain approximately steady for a minimum of 5 min, but longer if possible, to enable the specimen decomposition behaviour and toxic product yields to be characterized. All measured parameter data shall be used to obtain average values over this steady-state period.

When the up-stream end of the combustion boat enters the tubular furnace, the run is completed. Switch off the boat drive mechanism and gas sampling systems, pumps and bubblers. Immediately withdraw the boat to its starting position in the furnace tube and extinguish any flame by temporarily interrupting the primary airflow.

When the test specimen residue and combustion boat have cooled, remove them from the quartz furnace tube, store in a cool, stable atmosphere and reweigh when the boat and contents have reached constant mass, according to 10.4.3.

10.3 Steady-state period

The steady-state period shall be used as the basis for calculating results. If flaming combustion cannot be obtained, or where only intermittent flaming occurs, this shall be reported. The results of the tests are not valid in terms of the specified fire stages 1b), 2, 3a) or 3b) if steady-state conditions as defined below are not obtained for a minimum of 5 min. If flaming occurs in the mixing chamber during the steady-state period, this invalidates the quantification of the equivalence ratio and the run should be repeated; if necessary, the primary airflow shall be increased, generating data corresponding to a slightly lower equivalence ratio.

During dynamic steady-state conditions, the volume fractions of carbon dioxide and oxygen depletion in the mixing and measurement chamber shall remain approximately constant, such that both

a) for any long-term trend, the average rate of change of volume fraction divided by the average value of the volume fraction over the 5-min period shall be less than ±0,020 min^{-1};

b) for any short-term fluctuations, the standard deviation of the volume fraction divided by the average value of the volume fraction, over the 5-min period shall be less than 0,20.

Carbon monoxide (CO) and smoke concentrations may be somewhat more variable in some cases. If larger fluctuations occur, then this shall be reported. If steady-state conditions cannot be maintained for at least 5 min, then it is necessary to use a longer furnace combustion boat or reduce the rate of introduction of the combustion boat to increase the duration of the run. A 20-min run has been found to provide a steady-state period of at least 10 min duration for most materials. If this is not achievable in replicate runs, the observed variation shall be included in the report.

Where difficulties are encountered in obtaining steady flaming conditions, these can often be overcome by varying the fuel load or decomposition temperature. If ignition occurs during a non-flaming run, or fails to occur during a flaming run, then the furnace temperature shall be raised or lowered in 25 °C steps until the required behaviour is obtained. A new test run shall then be carried out with a fresh test specimen. For flaming behaviour, it is also necessary to ensure that the primary airflow rates are correct for one of the three states: well-ventilated flaming, small under-ventilated or post-flashover under-ventilated. There shall be excess oxygen during well-ventilated flaming and fuel-rich conditions for under-ventilated flaming. This is achieved by following the procedure described in Clause 9. The burning behaviour of certain materials is so dependent on the ventilation condition that the results from the well-ventilated test do not allow accurate prediction of the degree of combustion in under-ventilated conditions (see 9.3). In these circumstances, it is necessary to repeat an under-ventilated test with a smaller primary airflow in order to satisfy the equivalence ratio criterion (i.e. $\phi = 2{,}0 \pm 0{,}2$). If this procedure fails to satisfy the equivalence ratio criterion, this shall be reported.

10.4 Sampling and analysis of fire effluent

10.4.1 General

The concentrations of all effluent components (gases and respirable aerosols) that contribute significantly to the computation of the toxic hazard shall be measured during the steady-state test period. The methods of analysis shall conform to the specifications in ISO 19701 and ISO 19702, and as defined below. The individual components are identified in the appropriate hazard assessments (such as ISO 13571 and ISO 13344).

NOTE ISO 19706:2011, Clause 7 provides guidance regarding the potential importance of unmeasured components.

10.4.2 Sampling of fire effluent

10.4.2.1 Sampling guidelines

The fire effluent shall be sampled continuously from the mixing and measurement chamber throughout the run for key gases O_2, CO and CO_2, and any batch samples shall be taken during the steady-state period. The total extracted flow shall not exceed 5 $dm^3 \cdot min^{-1}$. If additional effluent is required, it shall be taken from the exhaust port of the mixing chamber, close to the chamber. ISO 19701 and ISO 19702 provide information on the sampling of fire effluent.

10.4.2.2 Sampling and analysis of O_2, CO and CO_2

A continuous flow of approximately 2 $dm^3 \cdot min^{-1}$ for the analysis of O_2, CO and CO_2 shall pass through a suitable drying agent and a smoke filtration system *en route* to the appropriate analysers. The concentrations of these gases shall be determined continuously.

NOTE 1 Details of a suitable filtration and drying system and analysers for these are given in ISO 5660-1.[7]

NOTE 2 The results for oxygen, carbon monoxide and carbon dioxide concentrations are relative to dry gas, after water vapour has been removed.

10.4.2.3 Sampling and analysis of acid gases

The following acid gases shall be determined, unless measurement has been deemed unnecessary by elemental analysis or citable knowledge.

HCN, HCl, HBr, HF, NO_x and SO_2 may be determined either by sampling through bubblers as described below, followed by analytical procedures described in ISO 19701, or by gas phase Fourier transform infrared analysis (FTIR) described in ISO 19702.

Pass a continuous sample of the fire effluent at an appropriate flow rate through two gas bubblers placed in series, each containing an appropriate volume of the appropriate absorbent. The sampling shall be carried out at a constant rate for a minimum of 5 min during the period for which dynamic steady-state conditions are maintained.

NOTE 1 Calibrate the sampling flow rate using a bubble meter (described in ISO 19701).

NOTE 2 A flow rate of 1 $dm^3 \cdot min^{-1}$ passing through two 250 ml Dreschel bottles fitted with sintered glass of porosity zero, each containing 150 ml of absorbing solution, has been found to be effective.

0,1 M aqueous sodium hydroxide solution has been found suitable for the acid gases listed above, except for SO_2, which should be passed through 3 % aqueous hydrogen peroxide solution, and NO_x which needs to be determined by a dedicated method. Details are given in ISO 19701.

10.4.2.4 Sampling and analysis of organic gases

The organic fraction of the effluent contains many irritant species. A number of methods are suitable for quantifying the organic fraction of the effluent and, if appropriate, the concentrations and yields of individual organic compounds. The procedures are described in ISO 19701 and ISO 19702.

The minimum requirement is for an estimate of the total organic content of the effluent.

One of the following methods shall be used to measure the organic content of the effluent.

a) A total hydrocarbon analyser shall be used to obtain an approximate estimate of the total hydrocarbon content of the effluent.

   NOTE 1 A total hydrocarbon analysis does not enable an accurate measure of the potency of the organics because the organic fraction of the smoke contains many irritant species. The irritant potency of non-oxidized organics is relatively low compared with that of the partially oxidized compounds, but the sum of the latter concentrations is generally much smaller than the sum of the former concentrations. Overall, a high organic content is associated with higher levels of irritancy. Crucially, this determination provides the data to quantify the fraction of unburnt and partially burnt carbon and therefore allows carbon balances to be established.

   NOTE 2 A limitation of this method is that, since the identities of the organic compounds in the effluent are unknown, the appropriate response factors are also unknown.

b) The fraction of carbon in the effluent in the form of organic carbon shall be determined by oxidizing a sample of the effluent from the mixing and measurement chamber and measuring the CO_2 concentration. The organic fraction shall then be determined by comparing the CO_2 concentration in the oxidized sample with the concentrations of CO_2, CO and soot particulates in the mixing and measurement chamber in accordance with 11.4.

c) For test specimens with a known composition, the organic fraction shall be estimated approximately from the CO_2, CO and soot particulates in the mixing and measurement chamber, and the estimated carbon-mass-loss concentration from the test specimen.

d) Direct measurements shall be made of a range of individual organic species. This may include irritants (e.g. acrolein and formaldehyde) and other toxic organic species (e.g. benzene, polycyclic aromatic hydrocarbons).

10.4.2.5 Sampling of aerosols and particulates

Smoke aerosols (solid particles and liquid droplets) are batch sampled from the mixing and measurement chamber through a particulate filter during the steady-state period, or part thereof. The fire effluent in the mixing and measurement chamber shall be sampled continuously through a particulate filter at an appropriate flow rate using the same procedure as in 10.4.2.3.

A sampling period of 5 min at a flow of 1,0 $dm^3 \cdot min^{-1}$ is recommended.

The filter shall be weighed before sampling and within 10 min after sampling, and also after conditioning to constant mass in a desiccator charged with a drying agent (to isolate the effects of condensed moisture), in order to calculate the mass of particulates deposited.

NOTE 1 A glass microfibre filter 0,26 mm thick with a 1,6 µm particle retention characteristic and a diameter of 37 mm has been found to be suitable.

NOTE 2 For excessively sooty samples, a shorter sampling period or lower flow can be used to ensure consistent flow through the filter.

NOTE 3 It is not possible to design true isokinetic sampling for the mixing and measurement chamber without characterization of the flow environment at the sample point. However, as the content in chamber is well mixed and the flow is rather slow, anisokinetic, sampling is expected to have very little impact on the total soot yield measured. Guidance on sampling for aerosol measurements, to ensure negligible anisokinetic sampling errors is provided in ISO 29904:2013, 5.6.1).[8]

10.4.3 Determination of the mass of the specimen residue

At the end of the run, when the combustion boat has cooled sufficiently, it shall be removed from the entrance of the furnace tube and stored in a cool, stable atmosphere to achieve constant mass.

Inspect the boat for the presence of residue in the first 400 mm. If residue is present in this region (which may be inert material or char), mark the boat at 400 mm from the front end, carefully remove the portion of residue contained therein, weigh it and record its mass. Record the length as 400 mm and calculate the mass of residue per millimetre ($mg \cdot mm^{-1}$). If there is no visible residue in this region, record the length of residue as 400 mm and the mass of residue per millimetre as zero. Do not include other residue or unaffected material beyond 400 mm. Do not include soot deposits at the front end of the boat, as these will have been quantified according to 10.4.2.5

NOTE This represents the mass of residue per millimetre obtained under steady-state conditions (m_{res}) and is required in 11.2.2 to calculate the average mass-loss concentration in the mixing and measurement chamber during the steady-state period.

10.4.4 Ambient conditions

The temperature and pressure of the surroundings shall be recorded so that they can be used to apply corrections to the calculations.

10.5 Validity of test run

A test run is only valid if the selected steady-state burning conditions (see Clause 9 and 10.3) are maintained for a period of at least 5 min during the test. If ignition occurs during a non-flaming run, or fails to occur during a flaming run, then the furnace temperature shall be raised or lowered in 25 °C steps until the required behaviour is obtained. A new test run shall then be carried out with a fresh test specimen. For flaming behaviour, it is also necessary to ensure that the primary airflow rates are correct as specified in 9.3, 9.4 and 9.5.

11 Calculations

11.1 General

The calculated values are averages over the duration of the steady-state part of the test. This period is defined in terms of the concentrations of carbon dioxide, carbon monoxide and oxygen (10.3). Steady consumption of O_2 and production of CO_2 is taken to be indicative of steady production of all volatile combustion products. For continuously monitored parameters, the mean, standard deviation and standard error shall be calculated from the data logged at progressive intervals throughout the steady-state period.

The results shall be calculated to two significant figures.

11.2 Mass-charge concentration and mass-loss concentration

11.2.1 Mass-charge concentration

Calculate the mass-charge concentration, $C_{\text{m.charge}}$, in grams per cubic metre (g·m^{-3}), using Formula (4):

$$C_{\text{m.charge}} = \frac{\dot{m}}{\dot{a}} \tag{4}$$

where

$\dot{m}$ is the rate of introduction of the test specimen mass into the furnace, in milligrams per minute (mg·min^{-1});

$\dot{a}$ is the total airflow rate through the mixing and measurement chamber, in litres per minute ($\text{dm}^3\text{·min}^{-1}$).

For example, if $\dot{m}$ = 1 000 mg·min^{-1} and $\dot{a}$ = 50 $\text{dm}^3\text{·min}^{-1}$, then $C_{\text{m.charge}}$ = 20 g·m^{-3}.

11.2.2 Mass-loss concentration

Calculate the mass-loss concentration as follows.

a) Calculate the mass loss per unit length, m_{loss}, in milligrams per millimetre (mg·mm^{-1}), using Formula (5):

$$m_{\text{loss}} = m_{\text{load}} - m_{\text{res}} \tag{5}$$

where

m_{load} is the test-specimen mass loading, in milligrams per millimetre (mg·mm^{-1});

m_{res} is the test-specimen residue mass loading, in milligrams per millimetre (mg·mm^{-1}).

b) Calculate the mass-loss rate, $\dot{m}_{\text{loss}}$, in milligrams per minute (mg·min^{-1}), using Formula (6):

$$\dot{m}_{\text{loss}} = m_{\text{loss}} \times \dot{b} \tag{6}$$

where

$\dot{b}$ is the combustion boat advance rate, in millimetres per minute (mm·min^{-1}).

c) Calculate the mass-loss concentration, $C_{\text{m.loss}}$, in grams per cubic metre (g·m^{-3}), using Formula (7):

$$C_{\text{m.loss}} = \frac{\dot{m}_{\text{loss}}}{\dot{a}} \tag{7}$$

where

$\dot{a}$ is as given in 11.2.1.

NOTE Mass-loss concentration calculated in this way from the mass loading and the residue mass loading has been shown to be in agreement with mass-loss concentration during the steady-state period calculated from the continuously measured products for both non-charring and char forming materials.

11.3 Yield

Calculate the mass charge and mass loss yields, $Y_{\text{m.charge}}$ and $Y_{\text{m.loss}}$ (these are both dimensionless, but are often expressed as g·g^{-1} or kg·kg^{-1} for clarity), of each effluent component (and for continuously measured parameters their standard deviations and standard errors) using Formulae (8) to (13):

$$Y_{\text{m.charge}} = (M/V_{\text{m}}) \times (F_{\text{v}}/C_{\text{m.charge}}) \tag{8}$$

$$Y_{\text{m.chargeSD}} = Y_{\text{m.charge}} \times (F_{\text{vSD}}/F_{\text{v}}) \tag{9}$$

$$Y_{\text{m.chargeSE}} = Y_{\text{m.charge}} \times (F_{\text{vSE}}/F_{\text{v}}) \tag{10}$$

and

$$Y_{\text{m.loss}} = (M/V_{\text{m}}) \times (F_{\text{v}}/C_{\text{m.loss}}) \tag{11}$$

$$Y_{\text{m.lossSD}} = Y_{\text{m.charge}} \times (F_{\text{vSD}}/F_{\text{v}}) \tag{12}$$

$$Y_{\text{m.lossSE}} = Y_{\text{m.charge}} \times (F_{\text{vSE}}/F_{\text{v}}) \tag{13}$$

where

M	is the molar mass of the component;
V_{m}	is the molar volume of the component at 20 °C temperature and 101,325 kPa pressure, assuming that it behaves as an ideal gas (=0,024 055 $\text{m}^3\text{·mol}^{-1}$);
F_{v}	is the measured volume fraction of the component in the mixing and measurement chamber;
$C_{\text{m.charge}}$	is the mass-charge concentration, calculated in accordance with 11.2.1;

$C_{m.loss}$	is the mass-loss concentration, calculated in accordance with 11.2.2;
$Y_{m.chargeSD}$	is the mass charge yield standard deviation of the component;
$Y_{m.chargeSE}$	is the mass charge yield standard error of the component;
$Y_{m.lossSD}$	is the mass loss yield standard deviation of the component;
$Y_{m.lossSE}$	is the mass loss yield standard error of the component.

Where there is no measurable residue (10.4.3), the mass loss yield will equal the mass charge yield.

EXAMPLE

CO_2 is measured continuously in a test on a specimen of PMMA.

F_v is found to be 2,40 % (=0,024), standard deviation = 0,001 41, standard error = 0,000 182 (for 60 logged measurements throughout the steady-state period).

M for CO_2 is 44,01 g·mol^{-1}.

$C_{m.loss}$ is 20 g·m^{-3}.

Therefore, $Y_{m.loss}(CO_2) = [44{,}01\ \text{g·mol}^{-1}/0{,}024\ 055\ \text{m}^3\text{·mol}^{-1}] \times [0{,}024\ 0/20\ \text{g·m}^{-3}]$

$= 1830\ \text{g·m}^{-3} \times 0{,}0012\ \text{m}^3\text{·g}^{-1}$

$= 2{,}20$

The standard deviation and standard error of the yield are then:

$$Y_{m.loss}(CO_2)_{SD} = Y_{m.loss}(CO_2) \times F_{vSD}(CO_2)/F_v(CO_2) = 2{,}2 \times [0{,}001\ 41/0{,}024] = 0{,}129$$

$$Y_{m.loss}(CO_2)_{SE} = Y_{m.loss}(CO_2) \times F_{vSE}(CO_2)/F_v(CO_2) = 2{,}2 \times [0{,}000\ 182/0{,}024] = 0{,}017$$

where

$F_v(CO_2)$	is the mean CO_2 concentration;
$F_{vSD}(CO_2)$	is the standard deviation of the CO_2 concentration;
$F_{vSE}(CO_2)$	is the standard error of the CO_2 concentration;
$Y_{m.loss}(CO_2)_{SD}$	is the standard deviation of the CO_2 yield;
$Y_{m.loss}(CO_2)_{SE}$	is the standard error of the CO_2 yield.

To aid calculations, values of the molar mass factor (M/V_m) are given in Table 1 for a number of effluent components.

Table 1 — Values of (M/V_m)

Component	**Molar mass** g·mol^{-1}	(M/V_m) g·dm^{-3}
CO_2	44,01	1,830
CO	28,01	1,164
HCN	27,03	1,124
NO_2	46,01	1,913
NO	30,01	1,248
HCl	36,46	1,516

Table 1 *(continued)*

Component	Molar mass $g\cdot mol^{-1}$	(M/V_m) $g\cdot dm^{-3}$
HBr	80,91	3,364
HF	20,01	0,832
SO_2	64,06	2,663
Acrolein (C_3H_4O)	56,06	2,331
Formaldehyde (CH_2O)	30,03	1,248

11.4 Organic fraction

The fraction of carbon in the effluent in the form of organic carbon, $F_{C.org}$ (see 10.4.2.4), shall be calculated using Formula (14):

$$F_{C.org} = \frac{\left[CO_2\right]_{oxidized} - \left(\left[CO_2\right]_{chamber} + \left[CO\right]_{chamber} + \left[soot\right]_{chamber}\right)}{\left[CO_2\right]_{oxidized}} \qquad (14)$$

where

$F_{C.org}$	is the fraction of the effluent carbon in the form of organic carbon;
$[CO_2]_{oxidized}$	is the volume fraction of CO_2, in the oxidized sample;
$[CO_2]_{chamber}$	is the volume fraction of CO_2, in the mixing and measurement chamber;
$[CO]_{chamber}$	is the volume fraction of CO, in the mixing and measurement chamber;
$[soot]_{chamber}$	is the soot concentration [measured in grams per cubic metre ($g\cdot m^{-3}$)] expressed as an equivalent volume fraction of CO_2, in the mixing and measurement chamber (assuming that soot is 100 % carbon). For example, assume that the “soot” concentration is 0,20 $g\cdot m^{-3}$. This equates to 0,20 × (44/12) = 0,733 $g\cdot m^{-3}$ CO_2 which in turn equates to 0,733 $g\cdot m^{-3}$/1 830 $g\cdot m^{-3}$ = 0,000 40 volume fraction at 101,325 kPa and 20 °C.

NOTE Where the carbon content of the mass loss can be estimated from the known composition of the test specimen, it is possible to make an approximation of the fraction of effluent carbon in the form of organic carbon by calculating the theoretical CO_2 concentration that would be formed in the mixing and measurement chamber, if all the specimen mass loss was oxidized to CO_2. This can then be substituted for $[CO_2]_{oxidized}$ in Formula (14).

12 Test report

12.1 Contents of test report

The test report shall include any observations made during the test and comments on any difficulties experienced during testing. The units for all measurements shall be clearly stated in the test report. The numerical data specified in 12.4 g), h), i) and j) shall include an estimation of the uncertainty in accordance with the ISO/IEC Guide 98-3 and validation of the quantitative methods according to ISO 12828-2. For continuously measured parameters, the standard deviation and standard error of the means values shall be reported. The limit of detection (LoD) and limit of quantification (LoQ) should be specified in accordance with ISO 12828-1 for the concentrations reported in 12.4 h).

The test report shall additionally contain the information given in 12.2 to 12.4.

Tests conducted that do not meet the requirements of this document shall be reported. The information shall include burning behaviour; gas analysis data are not necessary to report.

If the yields calculated from the full burning period (minus the initial ignition period and chamber equilibration period) differ from the yields calculated during the steady-state period by more than 50 %, the report shall mention that the yields shall not be used for fire safety engineering.

12.2 Test laboratory details

Record the name and address of the testing laboratory, names of responsible persons at the testing laboratory, test identification and date, laboratory ambient conditions (temperature and humidity).

12.3 Specimen details

Give a description of the test specimen, including details of any preparation and conditioning (if relevant), its configuration and condition relative to the end use of the material being examined.

12.4 Test conditions and procedures

The test report shall include the following information for data obtained during the steady-state decomposition period:

a) the decomposition conditions [fire stage 1b), 2, 3a) or 3b)];

b) the run temperature (T_{run}), in degrees Celsius (°C);

c) the primary airflow rate, in litres per minute ($\text{dm}^3 \cdot \text{min}^{-1}$);

d) the burning behaviour (flaming/non-flaming) and stability (10.2);

e) the duration and the start time in the test of the steady-state period and the total burning time of the test specimen;

f) information on the existence of multiple steady-state periods and the rationale for selecting one of them;

g) the mass-charge concentration and mass-loss concentration of the test specimen;

h) the mean concentration of each component of the effluent (including standard deviation and standard error of the mean for continuously measured parameters);

i) the mean mass charge yield of each component of the effluent, calculated in accordance with 11.3 (including standard deviation and standard error of the mean for continuously measured parameters);

j) the mean mass loss yield of each component of the effluent, calculated in accordance with 11.3 (including standard deviation and standard error of the mean for continuously measured parameters) (unless there was no measurable residue, in which case this should be reported instead);

k) the methods used to determine the effluent yields;

l) observations and comments on the test procedure;

m) the report shall contain the following statement:

> "The following test results relate only to the toxic effluents generated from the test specimen under the particular test conditions stated: They are intended for use as an input for calculations of toxic potency using, for example, ISO 13344 and as an input to fire hazard assessment of toxic potency using, for example ISO 13571. They are not intended as a means of assessing the full potential fire hazards of the material in its end use, and the interpretation and application of these test data require care."

13 Verification of test apparatus with PMMA

13.1 Procedure

The establishment of the tube furnace apparatus and procedure shall be verified by conducting a well-ventilated flaming run at 650 °C with standard PMMA pellets in each laboratory, prior to any testing in accordance with this document. Carbon dioxide yield and oxygen consumption shall be recorded and compared with target values representing the stoichiometric maxima for PMMA minus corrections for experimentally determined values for the formation of traces of soot, CO and hydrocarbons.

The procedure shall be carried out following this document, with the settings below:

- primary air = 10 $dm^3 \cdot min^{-1}$;
- secondary air = 40 $dm^3 \cdot min^{-1}$;
- furnace temperature = 650 °C (in accordance with 9.3);
- specimen feed = 1 000 $mg \cdot min^{-1}$ (i.e. 25 $mg \cdot mm^{-1}$ at 40 $mm \cdot min^{-1}$).

13.2 Verification criteria

There should be no measurable residue, according to the criteria of 10.4.3. The CO_2 yield shall be (2,06 ± 0,13) $g \cdot g^{-1}$ and the O_2 consumption shall be (1,83 ± 0,11) $g \cdot g^{-1}$, representing between 94 % and 106 % of target values.

If the results are outside these ranges, the cause shall be identified and corrected, and the PMMA test shall be repeated to demonstrate that compliance has been achieved.

NOTE 1 The verification criteria are calculated from the stoichiometric maxima of 2,20 $g \cdot g^{-1}$ (for CO_2 yield) and 1,92 $g \cdot g^{-1}$ (for O_2 consumption) minus the experimentally determined corrections for traces of unburnt species, equivalent to 0,14 $g \cdot g^{-1}$ and 0,09 $g \cdot g^{-1}$ for CO_2 yield and O_2 consumption, respectively. The corrected target values become (2,20 $g \cdot g^{-1}$ – 0,14 $g \cdot g^{-1}$ = 2,06 $g \cdot g^{-1}$) for CO_2 yield and (1,92 $g \cdot g^{-1}$ – 0,09 $g \cdot g^{-1}$ = 1,83 $g \cdot g^{-1}$) for O_2 consumption.

NOTE 2 After the gas analysers have been calibrated and leaks in the system have been eliminated, the most frequent cause of non-compliance is incorrect calibration of primary and secondary airflows.

14 Trueness and uncertainties with respect to steady-state tube furnace concentration and yields

14.1 Accuracy, trueness and uncertainty

Accuracy of a measured value of a product concentration or yield from a tube furnace run represents the extent to which the measured value represents the true value, the variability and uncertainties of the measured value and the extent to which yields measured in the tube furnace for a specimen are predictive of the yields occurring when specimens are decomposed under the same combustion condition in large-scale compartment fire tests.

14.2 Accuracy and trueness of concentration and yield measurements in the steady-state tube furnace (SSTF)

When a specimen is burned in the tube furnace in a test run, it produces specific concentrations of products in the mixing chamber at specific yields in relation to the true mass-charge and mass-loss concentrations of the test specimen combustion products. The accuracy of the measured concentration and yield for each component of the effluent depends upon the accuracy and stability of the test conditions in terms of the specified primary and secondary airflow rates, the rate of introduction of the test specimen and the calibrations of the gas analysers and other analytical methods. Details for the required calibrations and limits for all test parameters have been specified in the appropriate paragraphs. For any test specimen of known elemental composition, it is possible to measure the accuracy of the performance of an SSTF test run by comparing the recovery of fuel elements in the effluents with those calculated from the specimen content.

14.3 Extent of variability of concentration and yield measurements from test specimens in the steady-state tube furnace

When a specimen is tested in the SSTF, the primary parameters reported are the mean concentrations and yields of each effluent component during the steady-state period under the specified test conditions. The true yields of effluent components from specimens are subject to some degree of variability and therefore uncertainty due to variations in burning behaviour of the specimen. For continuously measured parameters, the concentrations are required to be logged at least every 15 s (10.2) so that a minimum of 20 independent concentration measurements are made as successive segments of the test specimen are combusted. The standard deviation and standard error of the mean concentration and yield is calculated. These then provide a measure of the uncertainty of the concentration and yield and the deviation of the sample mean from the population mean.

EXAMPLE

11.3 shows a worked example for the CO_2 concentration and yield from a test run with PMMA. From 60 measurements of CO_2 logged at 10 s intervals throughout the steady-state period of this run, the results were as follows:

Mean CO_2 volume fraction: 0,024 0; standard deviation: 0,001 41; standard error of mean: 0,000 182.

Mean CO_2 yield: 2,20; standard deviation: 0,129; standard error of mean: 0,017.

Because PMMA is an ideal fuel, the standard errors here are best values that might not be typical for other materials.

Another basis for comparison of the variability of concentrations and yields is to compare the mean values of all effluent parameters between repeat test runs with specimens from the same sample. Examples of this are provided on interlaboratory repeatability and reproducibility trial results described in Clause 15.

14.4 Correlation of effluent yields from the steady-state tube furnace with those obtained from large-scale compartment fire tests under the same combustion conditions

The SSTF has been designed to provide the combustion conditions for the four main fire stages specified in ISO 19706[6][9] within ranges of uncertainty which are quantifiable as described in 14.2 and 14.3.

For flaming compartment fire tests on a range of fuels, it has been established that the yields of combustion products are heavily dependent on the equivalence ratio.[3][4][5] The SSTF reproduces specified decomposition conditions in terms of temperature range, flaming behaviour and equivalence ratio known to occur in real-scale fires and yields of effluents generically similar to those obtained from flaming compartment fires under similar combustion conditions.[10] Well-ventilated fires involving non-flame-retarded fuels show efficient combustion with high CO_2 yields and conversion efficiencies (efficiency closely approaching 1) and low yields of CO and other products of inefficient combustion. Under-ventilated (fuel-rich) combustion reduces CO_2 yield in proportion to the equivalence ratio and produces much higher yields of CO and other products. CO yields in the SSTF for under-ventilated combustion are typically in the 0.2 $g \cdot g^{-1}$ to 0.25 $g \cdot g^{-1}$ range. These are similar to the yields those produced by ISO 12136[11] as a function of equivalence ratio and very similar to the average and range cited for post-flashover fires in ISO 16312-1 of (0.24 ± 0.09) $g \cdot g^{-1}$. For flame-retarded materials, especially halogenated materials, the yields of CO and other products of incomplete combustion are higher than for non-flame retarded materials under well-ventilated combustion conditions, approximately in relation to the halogen content, but similar to those from non-halogenated materials for under-ventilated combustion conditions. These general findings for CO_2 and CO are well-replicated in the SSTF and a strong correlation has been demonstrated between the yields/recoveries of CO and other products of inefficient combustion.

Direct comparison of yields between the SSTF and large-scale compartments fire results for the same materials requires data from multiple measurements during steady-state burning from repeat compartment fire tests under ranges of the same, closely defined, combustion conditions. Accurate measurements of compartment fire parameters can be challenging and results for compartment fires are subject to inherent variability for fire parameters, including product yields, even when test conditions are tightly specified. “Trueness” comparisons between SSTF and compartment fire results depend on the extent to which the averages are similar and ranges of data overlap. A number of studies exist for which materials tested in the SSTF have also been tested in sets of real-scale, large-scale and intermediate scale compartment fires carried out so as to provide periods of several minutes steady burning over a range of specific (measured) equivalence ratios. For these experiments, it is possible to make direct comparisons between combustion product yields in the SSTF and compartment fires. It is also possible to obtain and compare estimates of the range of variation (uncertainty) in both the SSTF and compartment fires.

Currently, comparisons between SSTF and compartment fire data sets have been made for four polymers: polyamide, polypropylene, polyisocyanurate foam and polymethyl-methacrylate (PMMA). For three of these materials, both SSTF and large-scale tests were carried out on specimens from the same samples and also from separately sourced samples of the same and chemically similar materials with the same elemental compositions.[12][13][14] Examples are described in Annex F. For PMMA, the SSTF data have been compared with published compartment fire data from separately sourced PMMA samples.[24] The results for the four polymers show similar averages and ranges of variation and overlap for the compartment fire and SSTF results.

NOTE Additionally, comparisons between SSTF and compartment fire data sets for wood and medium density fibreboard have been made.[15] For wood, comparisons have been made between SSTF data for samples of Scots pine and compartment fire data from the same sample of Scots pine, from published data on Spruce and on Ponderosa pine. These also showed similar average yields, ranges of variation and overlap for the compartment fire and SSTF results.

15 Repeatability and reproducibility

An interlaboratory trial[16] has been conducted using four polymeric materials in pellet form. The materials tested were polymethylmethacrylate (PMMA), low-density polyethylene (LDPE), polyamide 6,6 (PA 6,6) and polyvinyl chloride (PVC). Three replicates of each material were tested by three laboratories under well-ventilated fire conditions at 650 °C, and post-flashover, under-ventilated fire conditions at 825 °C in accordance with this document.

Values for the relative repeatability and reproducibility parameters (s_r/m and s_R/m, respectively) were calculated for the data set in accordance with the principles of ISO 5725-2.[17] The quantities evaluated were O_2 consumption and yields of CO_2, CO, HCl and HCN. The results are presented in Table 2.

Table 2 — Relative repeatability (s_r/m) and reproducibility (s_R/m) parameters for measured quantities from four materials under two fire conditions

Fire condition:		**Well-ventilated**			**Post-flashover**		
Measured quantity	**Material**	**Quantity** mean – m^a (g·g^{-1})	s_r/m (%)	s_R/m (%)	**Quantity** mean – m^a (g·g^{-1})	s_r/m (%)	s_R/m (%)
O_2 consumption	PMMA	1,78	3,2	4,2	0,97	1,5	5,0
	LDPE	2,80	4,2	9,3	1,48	3,0	9,8
	PA 6,6	2,11	9,1	12,4	1,06	3,0	13,6
	PVC	0,91	4,1	13,4	0,63	3,0	4,2
CO_2 yield	PMMA	2,07	3,3	3,9	0,97	3,7	4,1
	LDPE	2,68	6,5	10,8	1,17	5,0	21,6
	PA 6,6	2,04	3,4	5,2	0,87	3,2	21,1
	PVC	0,75	2,1	11,0	0,46	1,3	10,3
CO yield	PMMA	0,005	42,0	71,8	0,228	4,4	5,9
	LDPE	0,021	36,2	68,0	0,111	7,0	19,5
	PA 6,6	0,003	11,7	9,7	0,161	7,5	9,6
	PVC	0,147	5,9	9,2	0,115	2,0	16,3
HCN yield	PA 6,6	0,000 4	23,8	39,1	0,0625	8,1	9,2
HCl yield	PVC	0,449	5,7	13,9	0,451	3,4	11,2

[a] Quantity means have been rounded in relation to the accuracy of the analytical method and to the significance of the toxicity of the quantity. This was to two decimal places for O_2 consumption and CO_2 yield, three decimal places for CO and HCl yields and four decimal places for HCN yield.

Annex A
(informative)

Guidance on the choice of additional decomposition conditions

Since the yields of combustion products in fires depend upon the decomposition conditions,[2][3][4][5][6] it is possible to examine the relationships between combustion product yield and a range of variables affecting the decomposition conditions using this apparatus and the methodology described.[18][19] This could be valuable for research purposes. The specified test conditions stipulated in the main body of this document represent a minimum set designed to obtain data for oxidative pyrolysis under non-flaming conditions, for well-ventilated flaming conditions at an equivalence ratio of less than 0,75 and for vitiated flaming conditions at an equivalence ratio of 2. The latter includes small vitiated fires in closed or poorly ventilated compartments for which the furnace temperature is set to 650 °C and post-flashover fires in open compartments for which the furnace temperature is set to 825 °C.

Although not included as a normative requirement of the document, for a more comprehensive analysis of yields under non-flaming conditions, it is possible to vary the furnace temperature in separate runs over a range from low temperatures, at which little or no thermal decomposition occurs, to a temperature at which flaming ignition occurs. By this means, combustion product yields can be measured throughout the temperature range over which non-flaming oxidative decomposition is possible for a particular material.

For flaming decomposition conditions, combustion product yields for any specific material are affected by the fuel/oxygen ratio under which the test is carried out [from which the equivalence ratio is calculated; see Formula (A.1)] and from the furnace temperature. For any material, it is therefore possible to map the relationship between equivalence ratio and combustion product yields. This then enables comparison of the behaviour of materials over the entire range of equivalence ratios over which flaming decomposition can be obtained. By varying the furnace temperature, it is also possible to investigate the effects on flaming decomposition of the temperature.

In full-scale fires, the equivalence ratios, and hence the combustion product yields and concentrations in the fire compartment, change as the fire develops. Data on the effects of equivalence ratio on combustion product yields for materials can therefore be useful in calculations of time-concentration curves for combustion products from those materials involved in full-scale fires.

For any tube-furnace test run, the equivalence ratio, ϕ, is given by the mass-loss rate of combustible effluent from the material under test, in milligrams per minute ($\text{mg}\cdot\text{min}^{-1}$), divided by the mass flow rate of oxygen in the primary air introduced into the furnace, in milligrams per minute ($\text{mg}\cdot\text{min}^{-1}$), relative to the stoichiometric fuel mass to oxygen mass ratio for the material under test, i.e.

$$\phi = \frac{\dot{m}_{\text{loss}} \times \Psi_0}{O} \tag{A.1}$$

where

$\dot{m}_{\text{loss}}$ is the mass-loss rate of the test specimen, calculated in accordance with 11.2.2 b);

Ψ_0 is the stoichiometric oxygen mass to fuel mass ratio;

O is the oxygen supply rate, given by Formula (A.2):

$$O = P \times 0{,}209\,5 \times 1\,330\ \text{g}\cdot\text{m}^{-3} \tag{A.2}$$

where

P is the primary airflow rate;

$1\,330\ \text{g}\cdot\text{m}^{-3}$ is the density of oxygen at 20 °C and 101 325 Pa.

EXAMPLE

If P is $10\ \text{dm}^3\cdot\text{min}^{-1}$ (i.e. $0{,}01\ \text{m}^3\cdot\text{min}^{-1}$),

then $O = 0{,}01\ \text{m}^3\cdot\text{min}^{-1} \times 0{,}209\,5 \times 1\,330\ \text{g}\cdot\text{m}^{-3} = 2{,}786\ \text{g}\cdot\text{min}^{-1} = 2\,786\ \text{mg}\cdot\text{min}^{-1}$.

If $\dot{m}_{\text{loss}}$ is $843\ \text{mg}\cdot\text{min}^{-1}$ and ψ_0 is 1,72,

then $\phi = [843\ \text{mg}\cdot\text{min}^{-1} \times 1{,}72]/2\,786\ \text{mg}\cdot\text{min}^{-1} = 0{,}52$.

The stoichiometric oxygen mass to fuel mass ratio, Ψ_0 (also known as the stoichiometric oxygen demand of the material), can be obtained in one of three ways, depending upon the information available on the test material, as follows:

a) from the elemental composition or empirical formula for the test material;

b) from the net heat of complete combustion for the test material (ΔH_T);

It has been empirically determined that when a material burns, for every gram of oxygen consumed, the heat released is approximately 13,1 kJ. Thus, if the net heat of complete combustion for the test material (ΔH_T) is known (e.g. as measured by bomb calorimetry), the stoichiometric oxygen mass to fuel mass ratio, Ψ_0, for the particular test material can be calculated using Formula (A.3):

$$\Psi_0 = (\Delta H_T)/13{,}1\ \text{kJ}\cdot\text{g}^{-1} \tag{A.3}$$

c) from the oxygen depletion in the mixing and measurement chamber and the mass-loss concentration of the test specimen during a well-ventilated tube-furnace test run obtained by setting the furnace temperature to obtain a T_{run} of 900 °C. The stoichiometric oxygen mass to fuel mass ratio, Ψ_0, can be calculated using Formula (A.4):

$$\Psi_0 = \frac{D_{O_2} \times 1330\ \text{g}\cdot\text{m}^{-3}}{C_{\text{m.loss}}} \tag{A.4}$$

where

Ψ_0 is the oxygen depletion in the mixing and measurement chamber, as a volume or mole fraction (see 9.3);

$C_{\text{m.loss}}$ is the mass-loss concentration of the test specimen, calculated in accordance with 11.2.2 c).

EXAMPLE

If D_{O_2} is 0, 021 8 and $C_{\text{m.loss}}$ is $16{,}86\ \text{g}\cdot\text{m}^{-3}$.

then $\Psi_0 = [0{,}021\,8 \times 1\,330\ \text{g}\cdot\text{m}^{-3}]/16{,}86\ \text{g}\cdot\text{m}^{-3} = 1{,}72$.

Annex B
(informative)

Estimation of lethal toxic potency for combustion products according to ISO 13344 using tube-furnace data

The following procedure can be used in conjunction with ISO 13344 to calculate estimated LC_{50} concentration and LCt_{50} exposure dose for a material tested in the tube furnace under a specified thermal-decomposition condition.

a) Measure toxic gas concentrations and material mass-loss concentrations during a furnace run as described in this document.

b) Calculate the fractional effective dose (FED) according to ISO 13344. This then represents the FED for the mass-loss concentration of the material specimen tested.

c) If the calculated FED is less than (or greater than) 1, calculate toxic gas concentrations for a greater (or smaller) material mass-loss concentration (for example, the gas concentrations for a mass-loss concentration double that used for the test would be twice the original).

d) Recalculate the FED for the new toxic gas mixture.

e) Iterate the calculation until FED = 1 then the mass-loss concentration represents the estimated LC_{50} concentration for the material under test. The estimated LCt_{50} concentration is given by Formula (B.1):

$$LCt_{50} = LC_{50} \times 30\ \text{min} \tag{B.1}$$

NOTE This document is intended for materials and not for products. Further, the extent of burning of the different layers of a layered material or the different phases of a char forming material in a real fire scenario is variably and cannot be evaluated from the test results of the SSTF method.

Annex C
(informative)

Application of data from the tube-furnace test to estimation and assessment of toxic hazard in fires according to ISO 13571

The data from the tube-furnace test may be used as part of the information needed for toxic hazard assessment in a fire. Note, however, that this document is intended for materials and not for products. Further, the extent of burning of the different layers of a layered material or the different phases of a char forming material in a real fire scenario is variably and cannot be evaluated from the test results of the SSTF method.

Toxic hazard assessments include the following considerations:

a) the point in time during a fire by which a person will have been exposed to a concentration of smoke and irritants capable of impairing the efficiency of escape or causing incapacitation;

b) the point in time during a fire by which a person will have been exposed to a dose of asphyxiants capable of causing incapacitation and/or significant post-exposure health effects;

c) the point in time during a fire by which a person will have been exposed to a dose of lung irritants capable of causing post-exposure lung inflammation capable of causing long-term health effects or death.

There are a number of ways in which such assessments can be made as described in a) and b) can be made as specified in ISO 13571. Part of the data required for these assessments include either

a) the lethal toxic potencies [mass loss LCt_{50} values (see Annex B)] for materials involved in the fire (mass-loss model in ISO 13571), or

b) the yields of individual toxic gases from materials involved in the fire (toxic gas model in ISO 13571).

For the first method, mass-loss and gas concentration data obtained from the tube-furnace test can be combined with mass-loss curves for the materials in the fire to calculate the time at which an exposed subject is predicted to have received an incapacitating exposure dose.

For the second method, the yield of toxic gases measured using the tube-furnace test can be combined with mass-loss time-concentration curves for the fire to provide estimates of the time-concentration curves for individual toxic gases in the fire. These data can then be used with the fractional effective concentration (FEC) and fractional effective dose (FED) methods described in ISO 13571 to estimate times to different incapacitation and lethal end points for exposed persons.

Where more than one material is burning simultaneously, it may be necessary to consider the extent to which the effluents from each material are generated independently and mixed, so that the effluent gases from each material can be summed, or where chemical interactions between combustion products might affect overall effluent yields.

NOTE The correlation between SSTF data and large-scale fire test data on gas component yields have currently only been demonstrated for the combustion of homogeneous materials (see Annex F).

The combustion conditions varies and changes spatially and transiently in a real fire scenario and information of the prevailing combustion conditions shall thus always be taken into account when using bench-scale data as input to an assessments of toxic gases in a real fire scenario. ISO 29903 gives requirements for the scaling of toxic gas data.

Annex D
(informative)

Use of the tube-furnace method for bioassay purposes

The tube-furnace method was originally used for bioassay work to examine the mechanisms whereby combustion products cause incapacitation during fires. Work with combustion product atmospheres generated from a range of materials and with individual gases (CO, HCN, low O_2 and CO_2) established that incapacitation (asphyxiation) was caused by these gases and models were developed to enable these effects to be predicted from the chemical composition of the effluent atmospheres.[20][21] A further important effect of exposure to fire effluent was found to be sensory irritation and work was done to measure sensory irritancy for a range of effluent atmospheres.[22][23]

It is possible that bioassay methods may still be required for the evaluation of toxic combustion product evolution for certain special cases. The procedures described in this document can be used for this purpose but minor modifications of the apparatus are required. Rodents can be exposed nose-only by placing them in rodent restrain tubes which can be inserted in ports in the mixing and measurement chamber. In order to obtain a 30-min exposure period, the specimen advance rate can be slowed or a longer boat is used. It is advantageous to obtain a “square wave” exposure profile for bioassay exposure, particularly when evaluating sensory irritancy. Two methods have been used to achieve this previously for the tube furnace. For one method, a small chamber was fitted on the side of a rectangular chamber similar to that described. Nose-only exposure tubes were fitted to the side chamber. The side chamber was flushed with air during a pre-exposure monitoring period. In order to start an exposure, a flap between the main and side chamber was lifted so that exposure to the steady-state atmosphere commenced.

Another chamber used for most biosassays consisted of a horizontally placed, low volume, cylindrical chamber with a door in the middle. The steady-state atmosphere was established in one-half of the chamber (the mixing chamber part). The bioassay pre-exposure conditions were set up in the other end. Nose-only exposure tubes were attached to the chamber which was flushed with air. To begin the exposure, the extract line was moved from the mixing chamber end to the bioassay end, so that the steady-state atmosphere was established in the bioassay end within a few seconds. The method is described in Reference [22].

The concept of lethal toxic potency was derived originally from experiments on rats, on the assumption that an exposure dose of effluent lethal to rats is likely to be equally lethal to humans. The lethal toxic potency is expressed in terms of the exposure dose of effluent lethal to 50 % of exposed rats (LCt_{50}), which depends upon the concentration of toxic fire effluent to which the animals are exposed, multiplied by the exposure time (including a 14-day post-exposure period during which any additional deaths are scored). The concentration of toxic fire effluent can be expressed in a number of ways, but the most commonly used parameters are related to the material under test in terms of the mass-charge or mass-loss concentrations and the yields of individual toxic combustion products.

Although estimates of toxic potency have been made primarily using animal exposures, it is now considered that, for most test specimens, reasonable estimates of toxic potency can be made, based upon chemical analytical measurements of the composition of fire effluent atmospheres. Therefore, the method described in this document is intended principally for use with chemical analysis measurements.

Annex E
(informative)

Measurement of optical density from the steady-state tube furnace

E.1 General

The normative part of this document specifies measurement of toxic combustion product yields. This apparatus is also capable of measuring smoke obscuration although this was not specifically included in the interlaboratory reproducibility exercise. Smoke yield may be calculated from measurement of the attenuation of a light beam by the combustion effluent stream in the mixing chamber.

NOTE The measurement of smoke obscuration has not been validated and there is thus no information available on repeatability or reproducibility.

E.1.1 Optical density of smoke

The smoke optical density is calculated from measurement of the attenuation of a light beam by the combustion product atmosphere in the mixing chamber. This is shown in vertical orientation in Figure 1 a), for clarity, but may also be oriented horizontally, near the centre of the chamber. Smoke obscuration is recorded continuously for the steady-state burn period of the test.

A suitable smoke-determining system is given in ISO 5660-1.[7]

Two glass neutral-density dispersion filters, accurately calibrated at the laser wavelength of 632,8 nm, are required to calibrate the smoke-determining system. The filters used should not be of the coated type because these filters can give rise to interference effects with laser light and can deteriorate with time. The filters should have nominal optical densities (D) of 0,3 and 0,8. Values of extinction coefficient, k, in reciprocal metres (m^{-1}), measured through smoke, are obtained from Formula (E.1):

$$k = (2{,}303D)L^{-1} \tag{E.1}$$

where

L is the distance in metres through the smoke;

D is the measured optical density.

Experimental work has been performed with ISO 5660-1 with systems using a white light source with collimating optics. Such systems have been shown to yield generally similar results, but not under all conditions. White light systems may be used if they are shown to have an equivalent accuracy.

E.1.2 Measurement of smoke density

The reduction, expressed as a percentage, in the intensity of light due to its passage through smoke, as determined by the output from the photodetector, may be recorded continuously.

Figure 3 shows a vertically mounted light source and photodiode, although a horizontally mounted arrangement is also acceptable. Ports may be provided in the mixing and measurement chamber for the insertion of a light source and detector for the measurement of smoke density.

NOTE 1 A suitable smoke-measurement path length has been found to be approximately 300 mm.

Suitable methods for the prevention of the deposition of particles on the surfaces of both the light source and detector should be used.

NOTE 2 A suitable method has been to mount the light source and the photodectector in hollow, airtight vessels and pass a small portion of the chamber diluent air through the vessels into the mixing and measurement chamber.

E.1.3 Calculation of smoke density

The smoke density is reported as the smoke extinction coefficient, k, and the smoke-specific extinction area, σ_f, which are calculated as follows.

Calculate the smoke extinction coefficient, k, in reciprocal metres (m^{-1}) using Formula (E.2):

$$k = \frac{1}{L} \ln \left(\frac{I_o}{I} \right) \tag{E.2}$$

where

I_o is the intensity of a beam of parallel light rays, measured in a smoke-free environment with a photodetector having the same spectral sensitivity as the human eye;

I is the intensity of the same beam of parallel light rays, measured after traversing the environment containing the smoke;

L is the length of the beam of light that has traversed the environment containing the smoke, in metres (m).

Calculate the smoke-specific extinction area, σ_f, in metres squared per gram ($m^2 \cdot g^{-1}$), using Formula (E.3):

$$\sigma_f = \frac{k}{C_{m.loss}} \tag{E.3}$$

where

k is the smoke extinction coefficient, in reciprocal metres (m^{-1});

$C_{m.loss}$ is the mass-loss concentration of the test specimen calculated in accordance with 11.2.2, in grams per cubic metre ($g \cdot m^{-3}$).

Annex F
(informative)

Comparison of data from the steady-state tube furnace, the ISO 9705 room and other compartment fire experiments

Comparison of the yields of carbon monoxide, hydrogen cyanide and total hydrocarbons from a range of polymers generated in the steady-state tube furnace (SSTF), ISO 9705 room and other compartment fire experiments have shown a strong dependence on equivalence ratio.[3][4][5][10][12][15][16][24][25][26][27][28][29][30][31][32][33][34]

A good agreement was found between CO yields from a polymethylmethacrylate in the SSTF and compartment fire experiments[24], across a range of equivalence ratios and also between the SSTF and the ISO 9705 room for a burning polypropylene (see Figure F.1).[27]

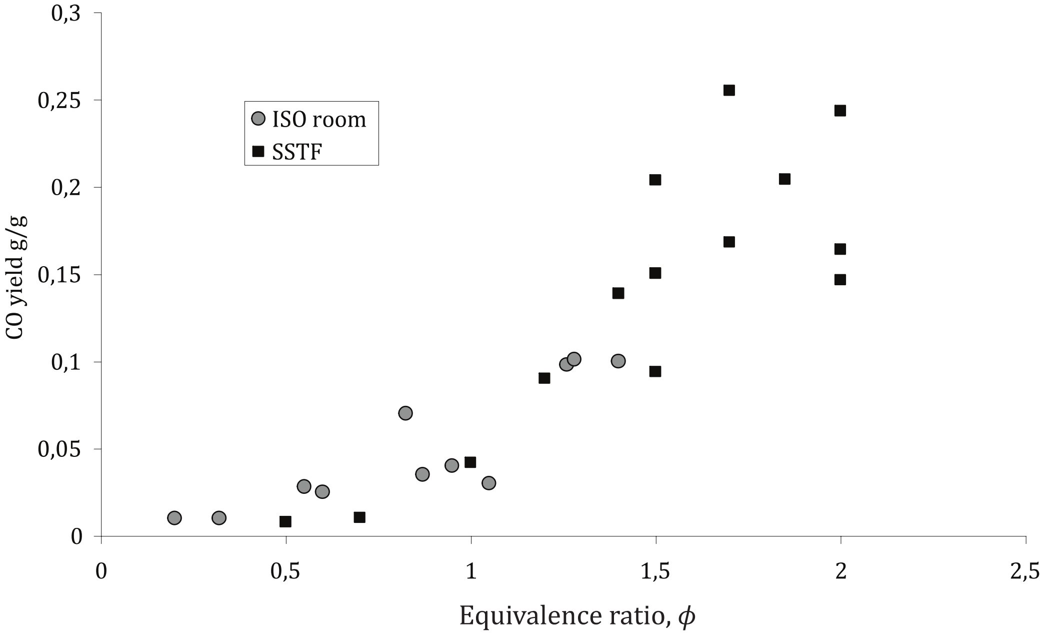
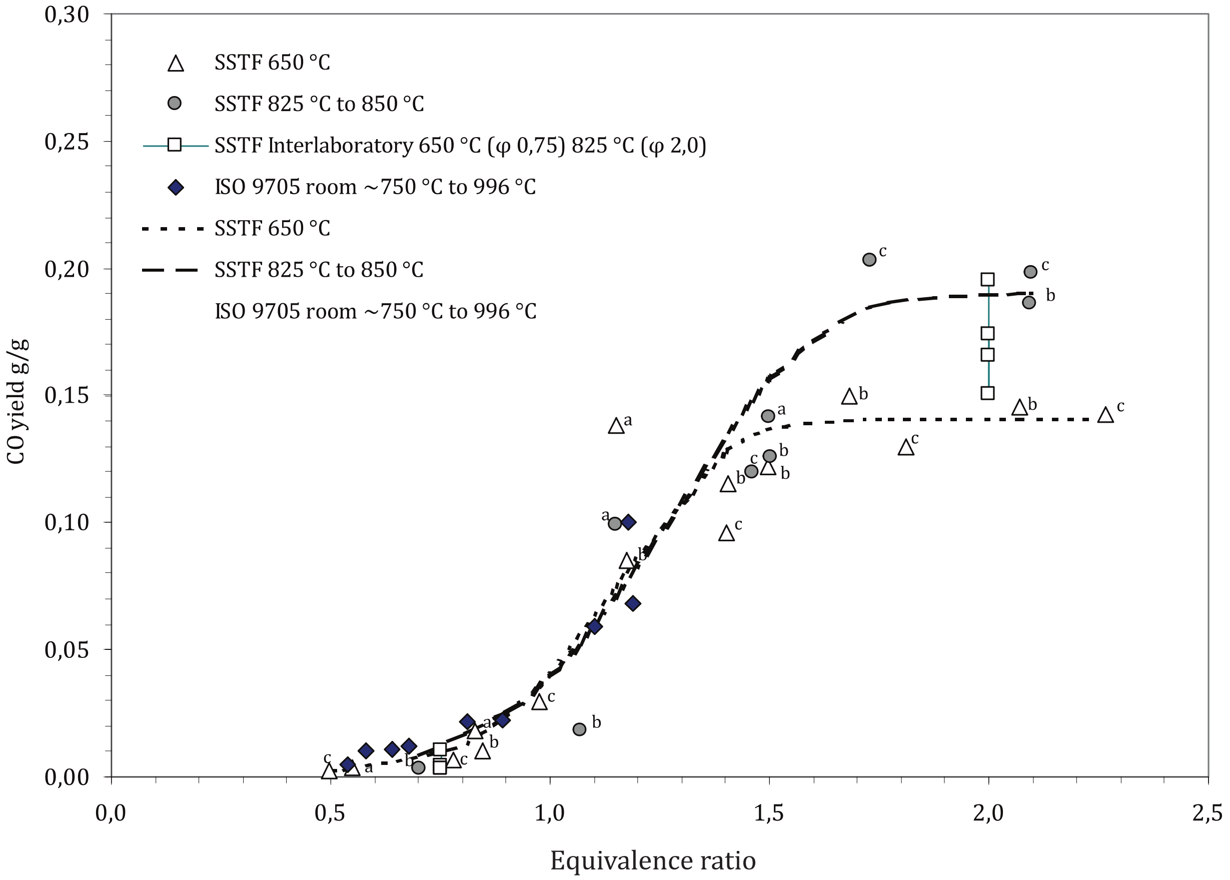


Figure F.1 — Comparison of tube furnace CO yields with large scale for polypropylene

Figure F.1 shows a comparison of CO yield from a polypropylene (PP) obtained in the steady-state tube furnace[27] with that obtained by Blomqvist in the TOXFIRE project.[28][29] In well-ventilated conditions ($\phi < 0{,}75$), both the tube furnace and the large-scale fire gave low CO yields of below 0,03.

For under-ventilated flaming, as the equivalence ratio rises to 1,5, the CO yields at both scales rise steadily to about 0,1. Although the polypropylene samples were from different sources, there is a good agreement between the SSTF data and the large-scale data in this case.

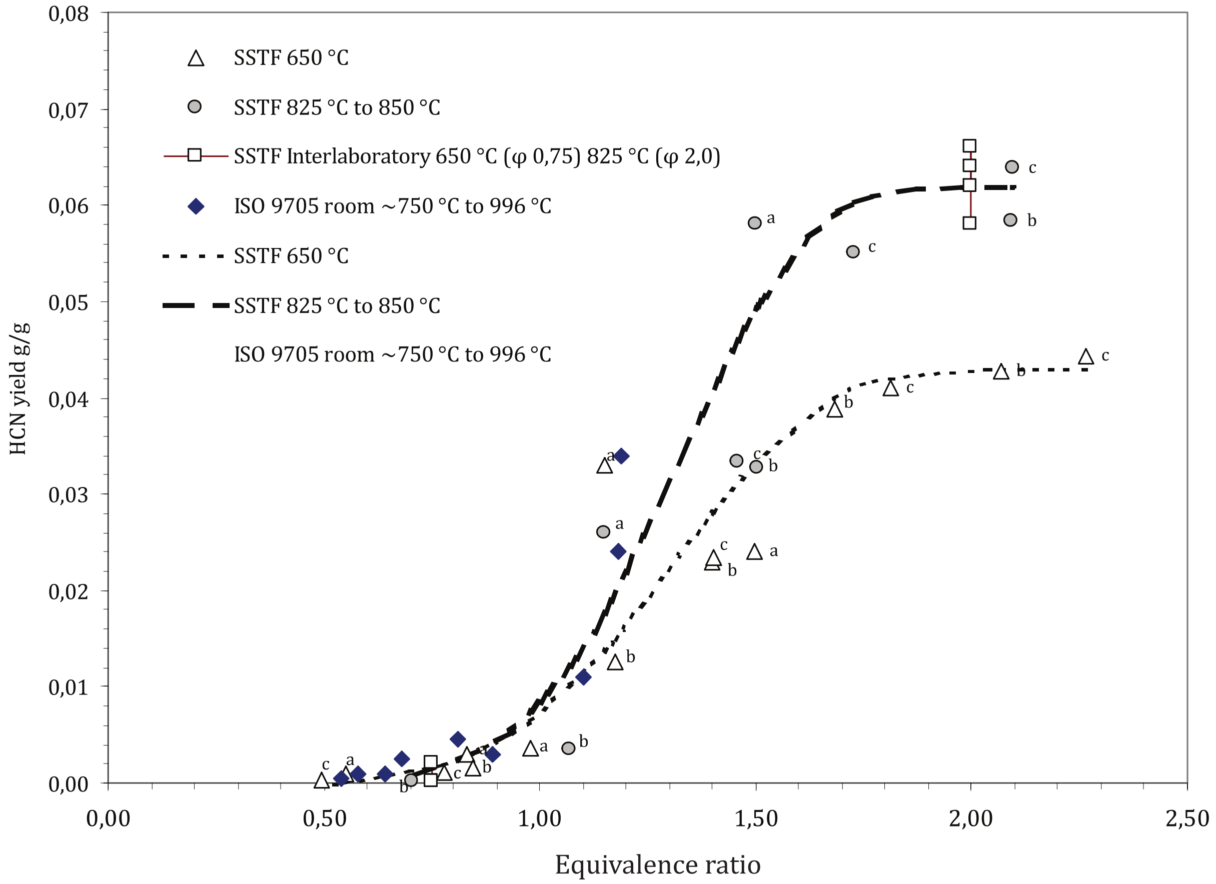


NOTE Letters indicate data source and material: a) polyamide 6,6[34], b) polyamide 6,6[31], c) polyamide 6.[12]

Figure F.2 — Comparison of CO yield for aliphatic polyamide from steady-state tube furnace with ISO room as a function of equivalence ratio, ϕ

Figure F.2 shows a comparison of the CO yield for a polyamide as a function of equivalence ratio for the steady-state tube furnace. The SSTF data include results from four data sets (from References [34], [31], [12] and the SSTF interlaboratory study[16]). They include tests carried out at 650 °C and higher temperatures (825 °C and 850 °C). The SSTF data are compared with data for the ISO 9705 room reported in References [29] and [30], from the TOXFIRE project. Of the four SSTF data sets, set a) was obtained using the same polyamide 6,6 as was used for the ISO 9705 TOXFIRE project. Set b) was also polyamide 6,6, but obtained from a different source, and was also used for the interlaboratory study, while set c) was for polyamide 6.

As with polypropylene, there is a strong dependence of CO yield on equivalence ratio and a generally good agreement between the SSTF and ISO room data. At low equivalence ratios ($\phi < 0,75$), CO yields from both methods are very low, but generally slightly lower in the SSTF than the ISO room. At equivalence ratios close to stoichiometry (ϕ approximately 0,9 to 1,2), CO yield changes considerably over the transition from well-ventilated to under-ventilated combustion conditions, and for both methods is very sensitive to small changes in equivalence ratio. At higher equivalence ratios ($\phi >$ approximately 1,5), CO yields in the SSTF were found to be more stable, but temperature sensitive, with somewhat higher yields at 825 °C to 850 °C than at 650 °C. During the ISO room tests at the higher equivalence ratios, the upper layer temperatures were 750 °C to 996 °C, corresponding more with the higher temperature SSTF results. The SSTF results are very similar from all three aliphatic polyamide samples (i.e. two polyamide 6,6 and one polyamide 6).



NOTE Letters indicate data source and material: a) polyamide 6,6[34], b) polyamide 6,6[31], c) polyamide 6.[12]

Figure F.3 — Comparison of HCN yield for aliphatic polyamide from steady-state tube furnace with ISO Room as a function of equivalence ratio, ϕ

Figure F.3 shows a comparison of the hydrogen cyanide (HCN) yields from the same steady-state tube furnace experiments[34][31][16][12] with those from the same ISO room experiments.[29][30] Again, HCN yields are very low at low equivalence ratios, but show a dramatic increase associated with under-ventilation as the equivalence ratio rises above unity, in both the SSTF and the ISO room. At higher equivalence ratios, there is also an effect of temperature on HCN yields, and a closer agreement between the SSTF and ISO room data. Similar relationships between HCN yields and equivalence ratios in the SSTF, ISO room and other compartment fire experiments have been reported for other nitrogen-containing polymers.[12] The SSTF yields for HCN are very similar for all three polyamide samples, showing corresponding behaviour to the CO yields for aliphatic polyamides.

In summary, the data demonstrate that SSTF measurements enable some predications to be made of combustion product yields in larger-scale compartment fires. However, in the examples given above, there are only data available for limited under-ventilated conditions (phi 0,5 to 1,2); the prediction at higher equivalence ratios is unknown. Although SSTF data are available for a range of polymers, more data are needed, especially for large- and real-scale compartment fire experiments. The combustion conditions in large-scale compartment fires are inherently variable so that making accurate measurements of equivalence ratios and yields can be challenging. A particular issue with equivalence ratio measurements in compartment fires is that secondary air entrainment occurs in the effluent plume as it flows away from the combustion zone. When fire gases are sampled in these regions, this secondary mixing can result in an underestimates of the true equivalence ratio in the combustion zone, resulting in a left shift of the apparent curve for the relationship between equivalence ratio and product yields.[12]

NOTE Another study[15] using a larger data set, for which no equivalence ratio data were available, demonstrated a correlation between product yields in the steady-state tube furnace and the ISO room as a function of CO_2/CO ratio, and included NO_x, hydrocarbons and soot, as well as CO_2, CO and HCN, for polyethylene, polypropylene, nylon 6,6, medium-density fibreboard (MDF), polystyrene and fire retarded MDF.

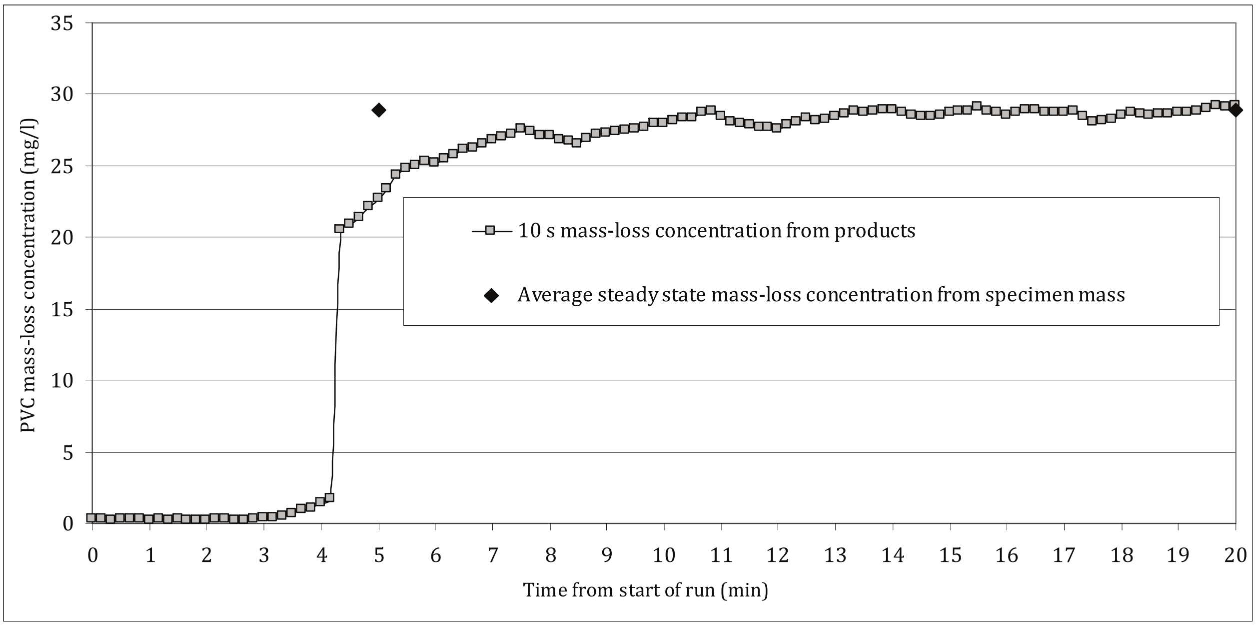
Annex G
(informative)

Assessment of mass-loss rate data

G.1 Validation of mass-loss rate calculations

The method for calculating the mass-loss rate and mass-loss calculation is based on the constant rate of sample introduction into the furnace using the specimen mass charge and residue mass. To validate this procedure, it is possible to perform a calculation of continuous mass-loss rate from the measured total combustion products (using the secondary oxidizing furnace CO_2 data). By this means, it is possible to calculate the mass-loss rate throughout the run including the reduced rate at the beginning of the run before char (e.g. in the case of PVC) has formed any additional specimen mass loss during the steady-state period above the average level. Such calculations have been performed for two well-ventilated PVC runs below.

Figure G.1 shows results for test T203 (well-ventilated flaming PVC 650 °C phi 0,8). The continuous mass-loss concentration calculated is plotted from the products data logged at 10-s intervals throughout the run. The results show that after the start of flaming around 4 min, the initial mass concentration (mass-loss rate/chamber airflow) is lower than the averaged value.



NOTE Mass average 0,75 % greater than 12,5 min to 20 min products average.

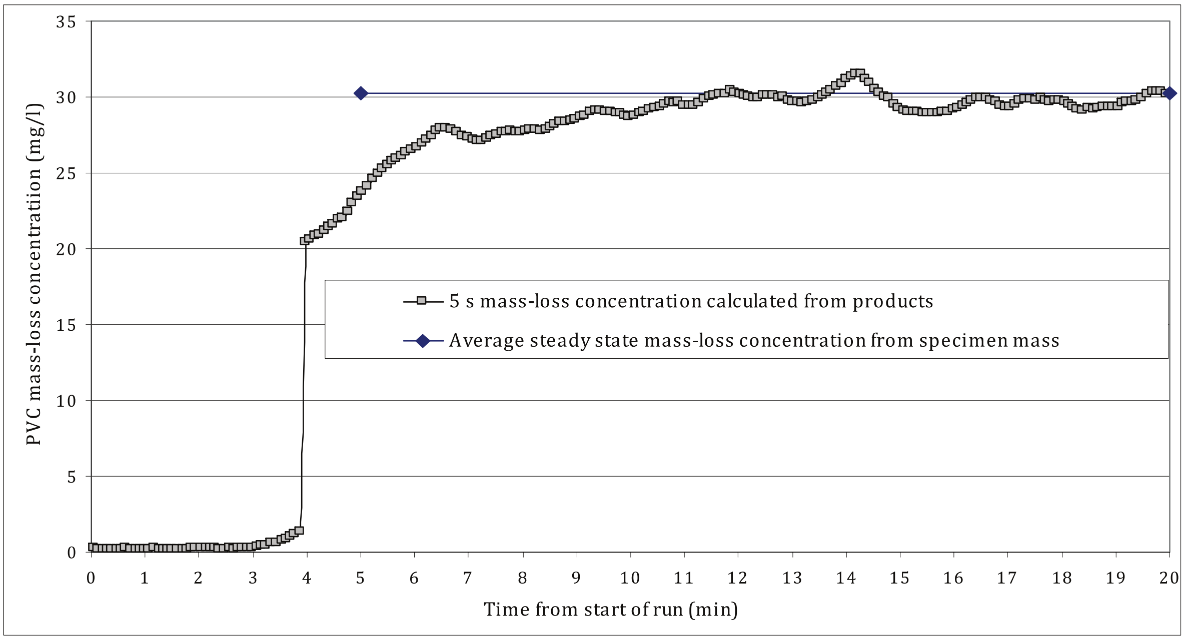
Figure G.1 — Continuous mass-loss concentration calculated from products compared with average mass-loss concentration calculated from specimen mass for Test 203 PVC flaming 650 °C φ 0,8

There is then a rapid increase in mass-loss concentration to 87 % of the steady-state level by 5,5 min as the chamber concentration reaches equilibrium, and then a slow gradual increase up to around 11 min as the char decomposition component increases. The average mass-loss concentration calculated from the products during the steady-state period from 12,5 min to 20 min was 28,652 mg/l (standard deviation, 0,265). This compares with the average value calculated from specimen mass loss of

28,895 mg/l according to the procedure in this document. The difference between the two methods for calculating the steady-state mass-loss rate is therefore very small at 0,75 %.

The results demonstrate that during the first few minutes of the flaming period of the run, the mass-loss rate was somewhat lower than the steady-state level, but that during the steady-state period, the continuous mass-loss rate was essentially constant (coefficient of variation 0,9 %) and very close to the average value calculated from specimen mass according to the procedure in this document.

Figure G.2 shows the same data plotted for Test 385, another well-ventilated flaming run for PVC.



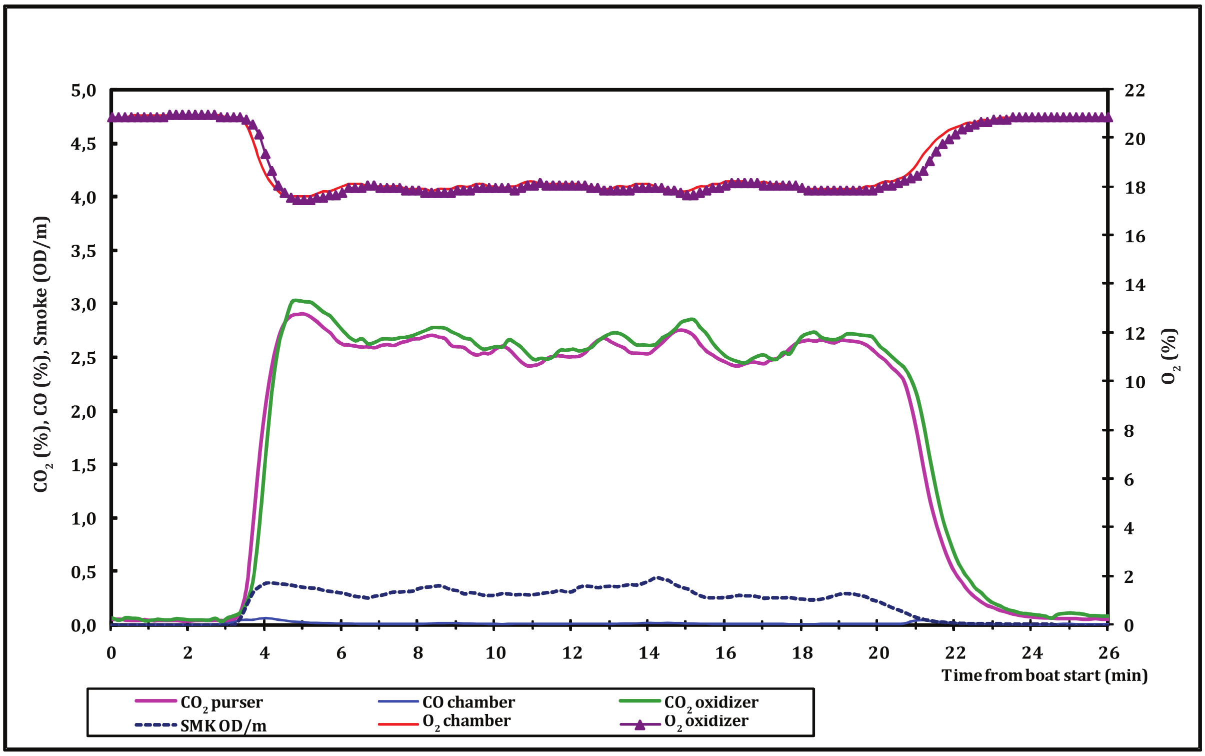
NOTE Mass average 1,46 % greater than 12,5 min to 20 min products average.

Figure G.2 — Continuous mass-loss concentration calculated from products compared with average mass-loss concentration calculated from specimen mass for Test 385 PVC flaming 650 °C φ 0,6

The continuous mass rate increases during the early part of the flaming stage of the run as in the previous case and is then very close to the average value calculated from specimen mass for the remainder of the test run. For this example, the average mass-loss concentration calculated from the products during the steady-state period from 12 min to 20 min was 29,783 mg/l (standard deviation, 0,574), giving a coefficient of variation of 1,9 %. This compares with the average value calculated from specimen mass loss of 28,895 mg/l calculated according to the procedure in this document. The difference between the two methods for calculating the steady-state mass-loss rate is also in this example very small at 1,46 %.

G.2 Effect of char decomposition

The following demonstrates the effect of char decomposition on carbon dioxide and oxygen concentrations using one of the well-ventilated PVC runs as an example and compares with a well-ventilated run with PMMA. This phenomenon occurs only during well-ventilated flaming when there is sufficient downstream oxygen to decompose any char. Figure G.3 shows the case for a run of a non-char forming material PMMA. The test data for PMMA include measurements of O_2 and CO_2 after complete oxidation of the effluents.



NOTE T 192, PMMA, well-ventilated, φ =0,5 includes fully oxidized hydrocarbon data.

Figure G.3 — Well-ventilated flaming combustion of PMMA

As Figure G.3 shows, there is no decomposition during the first 3 min of the run as the leading edge of the specimen moves from the furnace entrance towards the hot zone. Ignition occurs just after 3,5 min and there is a period of approximately 1 min during which the combustion stabilizes and the gas concentrations reach equilibrium in the mixing chamber. After this, steady-state conditions are maintained for the remainder of the run up to 20 min.

Figure G.4 shows one of the runs for well-ventilated PVC. For this run, ignition occurs after 4,5 min and stable flaming is established at the leading edge of the specimen. As for PMMA, the chamber concentration of CO_2 increases rapidly over a period of 1,5 min as the concentrations reach equilibrium in the mixing chamber by 6 min into the run. However, in this case, from around 6 min to 9 min into the run, there is a further small increase in CO_2 concentration (due to char decomposition) until steady-state conditions are established (with no further average upward slope in CO_2 concentration towards the end of the run). There is a brief period of variation at 14 min, but this is within the procedures set limits for short-term variations and does not represent a significant change in combustion conditions.

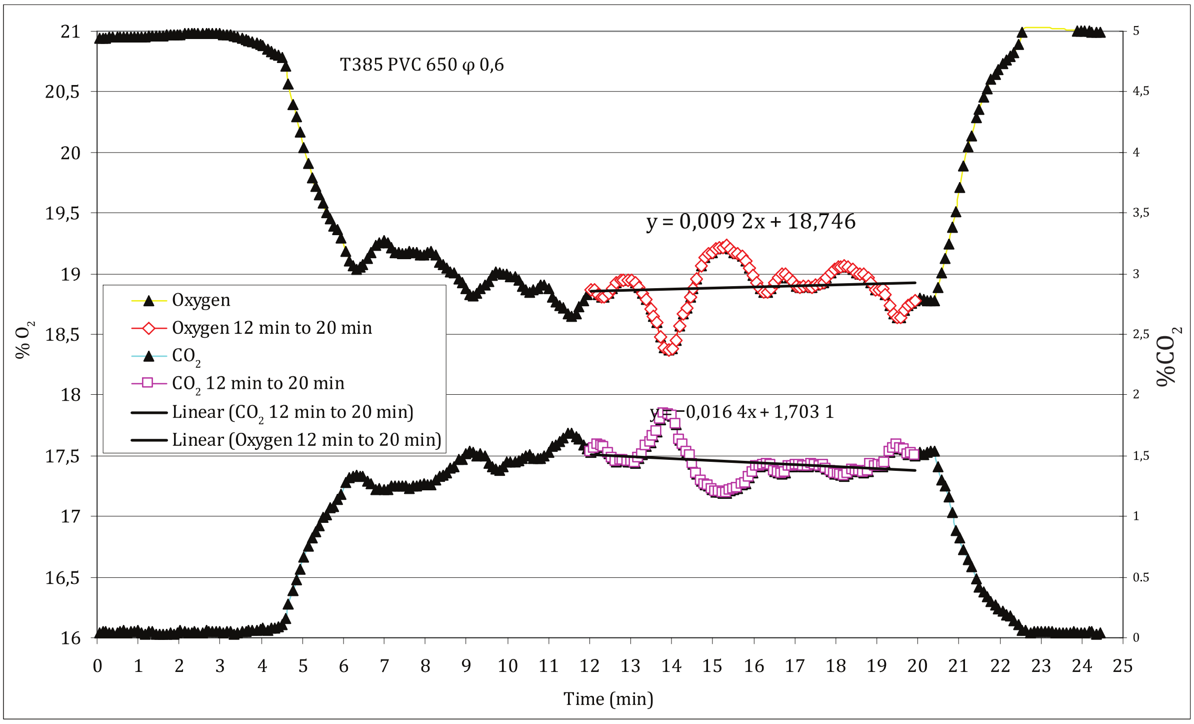


Figure G.4 — Well-ventilated flaming combustion of PVC (T385, 650 °C φ 0,6)

A question is, however, does the low mass loss and CO_2 concentration during the early stage of a flaming run represent a significant difference in overall CO_2 and CO yields calculated for the entire period of flaming compared with the steady-state period. In order to answer this, a comparison have been made of the concentration of carbon in the form of carbon oxides over the entire period of flaming from 6 min to 20 min with that over the steady-state period from 13 min to 20 min recommended in the test procedure. Any difference in carbon mass-loss concentration between these two periods represents the effect of the lack of char combustion during the early stage of the run. Table G.1 shows data for the two well-ventilated runs with PVC presented above. For both cases, there is a small difference in COx concentration between the entire flaming period and the steady-state period, but the differences are both very small representing an actual mass-loss concentration difference of 1,2 % of the average value.

Table G.1 — Calculation of percentage difference in mass-loss concentration for total flaming period compared with steady-state period for PVC flaming combustion φ 0,8 and 0,6 due to reduced char mass loss during the early part of the runs

Test no:	T385	T203
Average CO_2 + CO = COx (%) during:		
Total flaming period 6 min to 20 min (Period A)	1,86 %	1,456 %
Default steady-state period 13 min to 20 min (Period B)	1,94 %	1,526 %
COx (%) difference B – A	0,074 %	0,112 %
Carbon mass-concentration difference (g/m^3)	0,36	0,35
Average mass-loss concentration (by weight before and after) (g/m^3)	30,22	28,89
Percentage difference in mass-loss concentration between whole flaming period and steady-state period	1,19 %	1,21 %

G.3 Conclusions for char formers

For well-ventilated flaming conditions for char-forming materials, a small amount of char is formed ahead of the flame front and then consumed at a constant rate as steady-state conditions develop. The mass-loss rate is then constant for the remainder of the run and close to the mass-charge rate less than any non-combustible ash residue.

The effect of variations in yields taking into account the whole flaming period rather than the steady-state period is very small. These calculations presented above demonstrate that the requirements of steady-state conditions are fulfilled and that the differences in mass-loss rate throughout the run does not vary significantly from the steady-state value.

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[38] IEC 60754-2, *Test on gases evolved during combustion of materials from cables — Part 2: Determination of acidity (by pH measurement) and conductivity*

[39] ISO 9705, *Reaction to fire tests — Room corner test for wall and ceiling lining products*

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