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FTIR analysis of fire effluents in cone calorimeter tests

Analyse par FTIR des effluents du feu dans les essais au calorimètre à cône

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Foreword

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The procedures used to develop this document and those intended for its further maintenance are described in the ISO/IEC Directives, Part 1. In particular, the different approval criteria needed for the different types of ISO documents should be noted. This document was drafted in accordance with the editorial rules of the ISO/IEC Directives, Part 2 (see www.iso.org/directives).

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

This document was prepared by Technical Committee ISO/TC 92, *Fire safety*, Subcommittee SC 1, *Fire initiation and growth*.

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

Introduction

The composition of the effluent from an enclosure fire is determined by the combustible items in the enclosure, such as interior furnishings and wall linings, and the fire conditions within the enclosure. To represent any product involved in any fire scenario, the ideal fire test specimen is the complete item, and the ideal test is one conducted in an enclosure of appropriate size. Unfortunately, real-scale testing of commercial products is not generally economically feasible. This document describes an indicative approach for obtaining gas yields under specific fire conditions. It involves the use of a small-scale combustor in which a small test specimen is exposed to a pre-defined radiative heat flux. The test specimen should be representative of the finished product

This document provides a method for continuous quantification of gases (i.e. time-resolved gas analysis) emitted from a test specimen exposed to irradiance in a cone calorimeter, after extraction of effluent gas to a FTIR gas analyser. It produces data as the gas volume fraction (μL/L) or gas yield (mg/kg) during the test period. Data generated allow a better understanding of gas emissions during cone calorimeter tests, which can be useful for Fire Safety Engineering and for material development. Some examples of FTIR analysers used with cone calorimeters are presented in Table A.1.

The cone calorimeter uses a well-ventilated physical fire model, so results are only relevant for this scenario. Toxicity assessment for materials or products are not covered in this document and interpretation of data is covered separately in ISO 13571 or ISO 13344.

TECHNICAL SPECIFICATION ISO/TS 21397:2021(E)

FTIR analysis of fire effluents in cone calorimeter tests

1 Scope

This document specifies a method for determining the kinetics and yields of gaseous emissions from a specimen exposed to radiant heat in a cone calorimeter. Gas yields are determined by exposing small representative specimens to an external heat flux with or without spark ignition. The concentrations of specific gases in the effluent (smoke) are measured. In combination with calculated masses of gases, their yields from the specimen mass, mass loss or mass loss rate can be determined. This document uses Fourier-Transform Infrared (FTIR) spectroscopy as described in ISO 19702, with additional information on the test apparatus and gas analyser suitable for this specific application.

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 13943, *Fire safety — Vocabulary*

ISO 5660-1:2015, *Reaction-to-fire tests — Heat release, smoke production and mass loss rate — Part 1: Heat release rate (cone calorimeter method) and smoke production rate (dynamic measurement)*

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

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*

3 Terms and definitions

For the purposes of this document, the terms and definitions given in ISO 13943, ISO 5660-1, ISO 19702, ISO 12828-1 and ISO 12828-2 apply.

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

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

4 Symbols

Symbol	Designations	Unit
Δm	total mass loss of the test specimen	g
$\dot{m}_g$	mass flow rate of sampled gas species of interest	g s^{-1}
m_g	total mass produced of sampled gas species of interest	g
m_{te}	mass at test end	g
M_g	molecular weight of gas of interest	g mol^{-1}
t	is the time from ignition(t_i) to extinction(t_e)	s

Symbol	Designations	Unit
t_i	time to ignition (onset of sustained flaming)	s
t_e	time of extinction	s
$\dot{V}_{298}$	volume flow rate in exhaust duct at 0,1 MPa and 25 °C	m^3 s^{-1}
$\dot{V}_g$	volume flow rate of sampled gas species at 0,1 MPa and 25 °C	m^3 s^{-1}
V_g	total volume of sampled gas species at 0,1 MPa and 25 °C	m^3
y_g	species yield of gas	g g^{-1}
Æ_g	volume fraction of gas	dimensionless
ρ	gas density	kg m^{-3}

5 Principle

This document specifies a method for measurement of gas yields from small test specimens by exposing them to an incident heat flux in a cone calorimeter. The concentrations (µL/L) of specific gases presented in the effluents are determined via FTIR gas analysis, and their yields are determined in combination with the specimen mass loss.

6 Apparatus

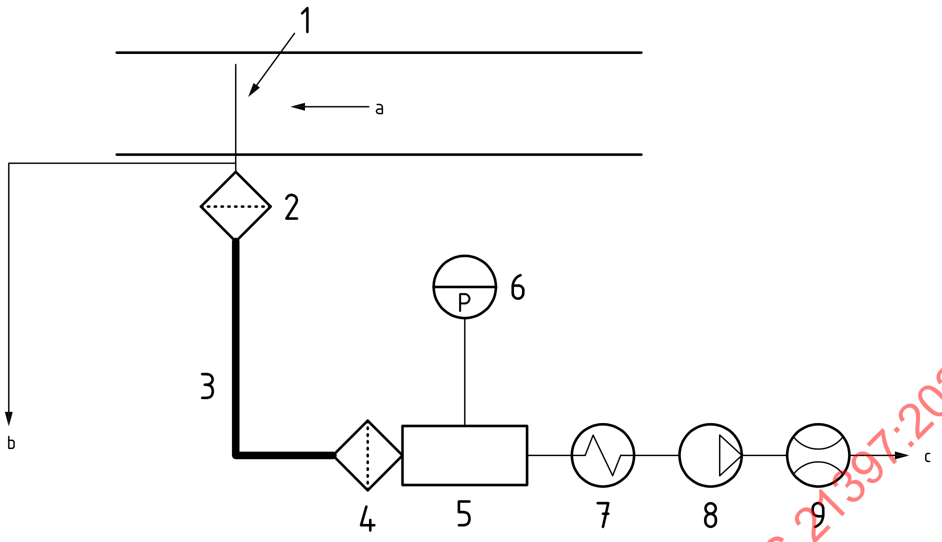
The test apparatus is specified in ISO 5660-1 and the gas measurement system described in Clause 7 shall be used.

7 Gas measurement system

7.1 General arrangement

The gas sampling system shall consist of a sampling probe, a heated primary filter, a heated gas sampling line, a heated gas cell fitted with a gas pressure transducer, a pump and flow meter. An optional heated secondary filter and an optional gas cooler may also be fitted. The sampling system shall be heated to an even temperature which shall not be greater than the gas cell temperature in order to avoid condensation in the cell. Other conditions not described in this document shall be in accordance with ISO 19702. Examples of alternative sampling system schematics are provided in Figure 1 and Figure 2 respectively.

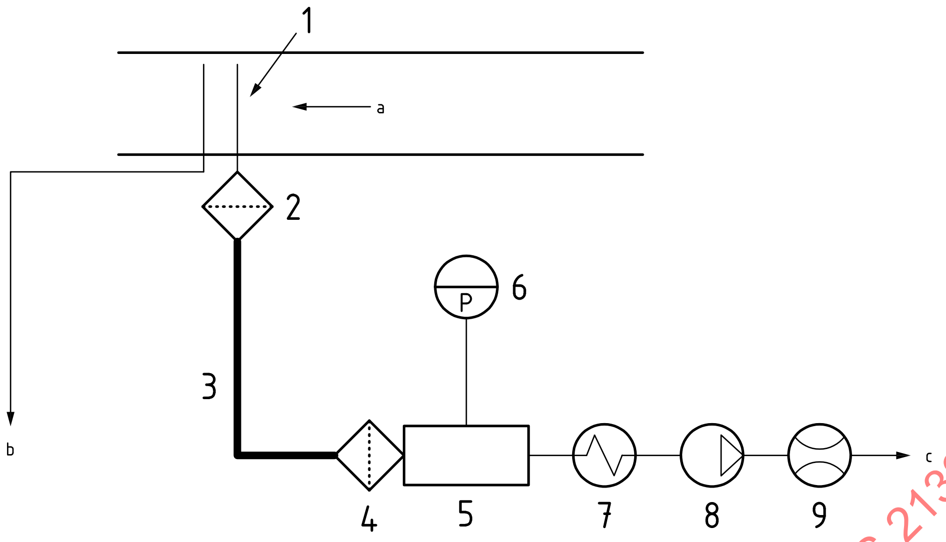
A procedure to determine the response time for the complete FTIR gas measurement system is given in ISO 19702:2015, Annex D.



Key

1	ISO 5660-1 gas sampling ring probe
2	heated primary filter
3	heated line for gas sample transport
4	heated secondary filter
5	heated FTIR gas cell
6	pressure transducer
7	optional gas cooler
8	sampling pump (here located downstream of the gas cell; upstream location is also allowed but requires a heated pump head)
9	flow meter
a	Direction of Combustion gas flow.
b	To O_2, CO_2 and CO analyser.
c	To exhaust.

Figure 1 — Example schematic diagram of sampling system when using the ISO 5660-1 ring probe fitted with a T-connection for sampling to FTIR analysis



Key

1	linear multi-hole sampling probe fitted in the cone calorimeter exhaust duct
2	heated primary filter
3	heated line for gas sample transport
4	heated secondary filter
5	heated FTIR gas cell
6	pressure transducer
7	optional gas cooler
8	sampling pump (here located downstream of the gas cell; upstream location is also allowed but requires a heated pump head)
9	flow meter
a	Direction of Combustion gas flow.
b	To O_2, CO_2 and CO analyser.
c	To exhaust.

Figure 2 — Example of schematic diagram of sampling system when using a linear multi-hole probe for sampling to FTIR

7.2 Sampling probe

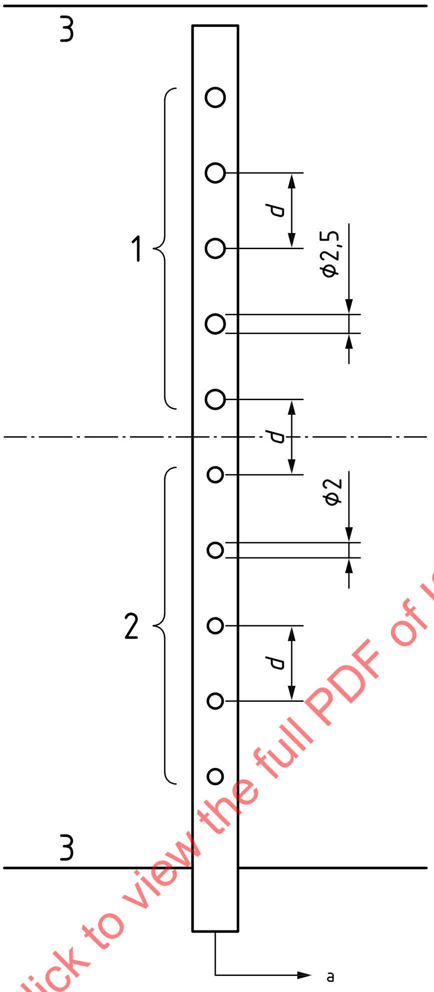
The ISO 5660-1 gas sampling ring probe can be used. A heated tee-connection/heated gas line is required to sample from the main gas sampling line from the ring probe (connecting the sampling ring to the cone calorimeter oxygen analyser) for transfer to the FTIR analyser. The tee-connection shall be located as close as possible to the sampling ring and shall as a minimum be efficiently insulated in order not to cool the sampled gases.

NOTE When using the ring probe for sampling to the FTIR it can be necessary to adjust the sampling flow rate to the oxygen analyser.

Alternatively, a separate linear multi-hole probe may be used for gas sampling. This is positioned vertically in the duct either 100 mm upstream[3],[4] or at 50 mm downstream of the ISO 5660-1 gas sampling ring probe. The probe shall be made from 6 mm (OD) stainless steel tubing, closed at the sampling end, and shall have 10 holes evenly distributed along the length of the tube. The 10 holes on the probe shall face downstream to prevent clogging due to the soot deposition.

The five holes furthest from the pump shall have a diameter of 2,5 mm, while the five holes closest to the pump shall have a diameter of 2,0 mm. The probe shall be long enough to sample over the whole inner diameter of the duct. A Schematic diagram of the linear multi-hole probe is provided in Figure 3.

The probe shall be connected directly to the primary heated filter without any cold-trap between.



Key

1	five evenly-distributed sampling holes with 2,5 mm dimeter
2	five evenly-distributed sampling holes with 2,0 mm dimeter
3	cone calorimeter exhaust duct wall
d	hole spacing, (10,0 ± 0,2) mm
a	To gas sampling system.

Figure 3 — Schematic diagram of the linear multi-hole probe

7.3 Primary filter

A primary filter unit shall be connected directly to the tee-connection (or multi-hole probe) to protect the FTIR gas cell from soot and other solid particles, and its temperature shall be maintained at (180 ± 10) °C. The filter element shall be easy to change and inert to fire effluents. The dimensions and materials of the filter are described in ISO 19702. The replacement interval shall be determined from considerations of the sampling rate, test duration and soot production in the specific test. The filter shall normally be replaced before tests.

NOTE Cylindrical filters with high particle capture capacity have been found to be most effective[6]. A cylindrical filter with a porosity of 2 µm is recommended in ISO 19702.

7.4 Sampling line

The sampling line prior to the gas cell shall be made of a material that is inert to the combustion gases. The line shall be heated to the temperature of (180 ± 10) °C. It shall have an inner diameter of (4,0 ± 0,2) mm and a maximum length of 3 m.

7.5 Gas cell

The gas cell shall be made of an inert material resistant to corrosion and shall have a sufficient optical path length for the specific application. It shall be maintained at (180 ± 10) °C. The gas cell shall be fitted with both a pressure transmitter and temperature measurement sensor. The associated data acquisition system shall be able to continuously collect pressure and temperature data with the same or shorter scan time than FTIR spectra collection. The pressure and temperature data shall be used with the measured gas concentrations to calculate the corrected concentrations. This calculation can either be done manually or automatically by the instrument software. The deviation in cell pressure should give a minimal influence on the quantitative results and shall not induce an error that exceeds 5 relative-% after correction. Detailed information is available in ISO 19702:2015, F.2.

The optical path length and the type of detector determine the sensitivity of the FTIR system. Limits of detection and quantification shall be determined according to ISO 12828-1.

The inner volume of the gas cell together with the sampling flow rate (see 7.6) set restrictions on the temporal resolution of the measurement. The content of the gas cell shall be renewed at least 4 times a minute, resulting in an interval between spectra of less or equal to 15 s. The minimum sampling flow rate can be calculated so that the renewal of the gases in the gas cell is not less than 4 times per minute. Advice on how to determine the response time for the complete FTIR sampling system is given in ISO 19702:2015, Annex D.

A secondary filter can be positioned in front of the cell and be heated to the same temperature as the sampling line and gas cell.

NOTE A small circular planar filter using a 1 µm porosity PTFE membrane has been found suitable as secondary filter.

7.6 Pump and sampling flow rate

The pump can be placed either downstream or upstream from gas cell, as specified in ISO 19702. If it is placed upstream of the gas cell, the pump head shall be heated in order to avoid condensation and losses of condensable gas species. The pump shall operate at a constant rate during the test period and be capable of pumping soot- and tar-laden gas from the sampling point. A gas cooling system can be positioned between the gas cell and the flow meter to protect the flow meter and provide a normalized reading. The minimum sampling flow rate shall be calculated in order for the renewal of the gases in the gas cell to be not less than 4 times per minute.

NOTE A diaphragm pump has been found to be suitable.

The sampling flow rate shall be small compared to the flow rate in the cone calorimeter duct, a requirement which in practice is always met, considering that the standard duct flow is 1 440 L/min and the sampling flow to the FTIR cell is normally less than 10 L/min. Too low a sampling flow rate shall be avoided in order to maintain a high temporal resolution of the measurement. The maximum allowable flow rate is selected considering both the degree of turbulence within the cell and the effect on other measurements being made concurrently in the experiment.

7.7 FTIR spectrometer

The spectrometer shall have a range from 600 cm^{-1} to 4 400 cm^{-1}, and a resolution of 4,0 cm^{-1} or finer. The collection rate shall be at least 4 spectra per minute. Spectra shall be recorded for subsequent analysis.

NOTE A resolution of 0,5 cm^{-1} has been found suitable for minimizing the interferences in fire gas analysis[14].

7.8 Detector

The choice of detector sets limits on the sensitivity of the FTIR instrument. Two types of detectors are common: DTGS (deuterated triglycide sulphate) and MCT (mercury cadmium telluride) detectors. MCT detectors are normally more sensitive compared to DTGS detectors. These types of detectors are described in more detail in ISO 19702:2015, Annex G.

NOTE When a DTGS detector is not appropriate for achieving the required limits of detection and quantification, a MCT detector or a gas cell with longer optical path length are suitable alternatives[6],[7].

8 Suitability of a product for testing

The requirements are the same as for ISO 5660-1.

9 Specimen preparation

The requirements are the same as for ISO 5660-1.

10 Test environment

The apparatus shall be located in an essentially draught-free environment in an atmosphere of relative humidity of between 20 % and 80 % and a temperature between 15 °C and 30 °C.

11 Calibrations

11.1 Calibration of cone calorimeter

The apparatus shall be calibrated daily following the procedure in ISO 5660-1:2015, 10.2.

11.2 Gas analyser calibration

This calibration aims to collect a series of absorbance spectra for the gas species to be analysed from certified standard bottled gas mixtures. Calibration of the FTIR gas analyser shall be made under similar atmospheric conditions to those experienced during testing (including the temperature and pressure of the gas cell and sampling flow rate). Calibration details can be found in ISO 19702. A background spectrum using high purity nitrogen shall be collected before each test.

12 Test procedure

12.1 General precautions

The test procedures involve high temperatures and combustion processes. Therefore, hazards can exist such as burns or the ignition of extraneous objects or clothing. The operator shall use protective gloves for insertion and removal of test specimens. Neither the cone heater nor the associated fixtures shall be touched while hot. Care shall be taken to avoid touching the spark igniter which carries a substantial potential (10 kV). The outlet from the FTIR sampling system shall be connected to an exhaust to be safely disposed of. The possibility of the violent ejection of molten hot material or sharp fragments from specimens when irradiated can occur and it is therefore essential that eye protection be worn.

12.2 Operation before each test

The filter, sampling line and the FTIR gas cell shall be heated for at least a minimum of 90 minutes with the specified air flow running, before starting the daily series of tests, to allow thermal stabilization. Before starting the test, the following preparation for gas measurement shall be performed.

a) Clean or change the filter element of the main filtering system. The filter shall be changed if analyses are to be made on the filter. See ISO 19702:2015, Annex C for analyses of filters. Note that acid gases, amongst others, can be adsorbed on particulates retained by the filter. When the total amount of one specific gas has to be measured, the quantity retained on the filter should be added to the total amount of acid gases analysed by the FTIR.

b) Clean or change the filter element of the optional secondary filtering system if necessary.

c) Flush the sampling line and FTIR cell with nitrogen for at least 10 minutes.

d) Collect the background reference spectrum with the sampling line and cell flushed with nitrogen gas. The pump is normally used at the working sampling flow rate during this procedure to provide the operative cell pressure.

e) Start the pump (if not started in the previous step) and draw air through the sampling system for at least 10 minutes to flush the line and cell and set the pre-established operative sampling flow rate. During this operation, the pressure in the gas cell shall attain an acceptable constant value (see 7.5 and 11.2).

12.3 Operation during a test

The procedures found in ISO 5660-1:2015, 11.2 and 11.3 shall be followed.

a) At least 1 minute before starting the cone calorimeter tests, start recording the following data at a time interval of at least 15 s or faster. Record all of the following measurements until the end of the cone calorimeter test.

  - Pressure and temperature inside the gas cell;
  - Continuous FTIR spectra.

b) After at least 1 minute of pre-recording, start the cone calorimeter test. Spectral data collection shall be started at least one minute prior to the beginning of the test in order to allow for detection of any significant contaminants. The test shall be aborted if such contaminants are discovered. Ambient CO_2 shall be measured quantitatively (during pre-measurement period) and can be subtracted from reported values if appropriate.

The response time should have been previously determined according to the procedure described in ISO 19702. The gas generation rate curves should be time-shifted taking into consideration this delay time.

13 Calculations

13.1 General

Carry out the gas analysis of collected FTIR spectra in accordance with ISO 19702.

NOTE If required, other gases (such as acrolein, formaldehyde and ammonia) can also be determined.

13.2 Total mass loss

This is the initial mass, m_0, minus the mass at t_e. If there is no ignition, m_{te} is the mass at test end as defined by ISO 5660-1:2015, 11.3.5. See Formula (1):

$$\Delta m = m_0 - m_{te} \tag{1}$$

13.3 Mass of gas evolved

For the time of each FTIR data point, calculate the volume flow rate in the exhaust duct, $\dot{V}_{298}$, expressed in cubic metres per second, related to 0,1 MPa and 25 °C, from Formula (2):

$$\dot{V}_{298} = \frac{\dot{m}_e}{\rho_{298}} \tag{2}$$

where

$\dot{m}_e$ is the mass flow rate in the exhaust, expressed in kg s^{-1}, as given by ISO 5660-1:2015, Formula (10);

ρ_{298} is the density of air at 0,1 MPa and 25 °C (=1,168 4 kg m^{-3}).

The gas species flow, $\dot{V}_g$, expressed in cubic metres per second at 0,1 MPa and 25 °C and the total amount of gas species production, V_g, expressed in cubic metres per second at 0,1 MPa and 25 °C can be calculated from the following Formula (3) and Formula (4):

$$\dot{V}_g = \dot{V}_{298} \times \varphi_g \tag{3}$$

$$V_g = \int_{t_i}^{t_e} \dot{V}_g \, dt \tag{4}$$

where

φ_g is the volume fraction of a gas species

t is the time from ignition (t_i) to extinction (t_e), expressed in s.

In order to obtain the mass flow of a gas, Formula (5) can be used:

$$\dot{m}_g = \frac{\dot{V}_{298} \times \varphi_g \times M_g}{0{,}024\ 79} \tag{5}$$

where 0,024 79 m^3 mol^{-1} is the volume occupied by one mole of the gas at 25 °C and 0,1 MPa pressure assuming ideal gas behaviour.

In order to obtain the total mass generated during the test period, in this case the period of flaming combustion, Formula (5) can be integrated.

$$m_\text{g} = \int_{t_\text{i}}^{t_\text{e}} \dot{m}_\text{g} \ dt \tag{6}$$

A trapezoidal numerical integration shall be used; see Formula (7):

$$m_\text{g}\left(t_\text{i}\right) = 0$$

$$m_\text{g} = \sum_{t_\text{i}+\Delta t}^{t_\text{e}} (0{,}5)\left[\dot{m}_\text{g}\left(t-\Delta t\right)+\dot{m}_\text{g}\left(t\right)\right]\Delta t \tag{7}$$

13.4 Yield of gas

The yield of each gas species is the ratio of the mass evolved to the mass lost from the specimen; see Formula (8):

$$y_\text{g} = m_\text{g} / \Delta m \tag{8}$$

13.5 Upper limits

When gases are not present in sufficient concentration to be detected by the gas analyser, their upper limits shall be calculated. This is first done by assessing the limit of detection for each gas, following ISO 12828-1. Then the preceding series of calculations are conducted, substituting the limit of detection for φ in Formula (3).

14 Test report

These test results relate only to the behaviour of the test specimens under the particular conditions of the test.

The test report shall be as comprehensive as possible and 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 report. The essential information given in the test report shall be the same as in ISO 5660-1:2015, Clause 13, with the exception of parts q, r, s, v, w, z, aa, bb, and cc.

In addition, the report will include:

a) The names of the species analysed.

b) The maximum volume fraction of each gas of interest, or in the case of undetected gases, their limits of detection, expressed as "$< \varphi_\text{LOD}$".

c) The total yields of each gas of interest, or in the case of undetected gases, the upper limit yield based on the limit of detection, expressed as "$< y_\text{LOD}$".

d) Average yields of each gas of interest from multiple tests of identical specimens (normally triplicate tests according to ISO 5660-1).

e) Graph of $\dot{m}_\text{g}$ versus time, for each gas of interest.