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Generation and analysis of toxic gases in fire — Calculation of species yields, equivalence ratios and combustion efficiency in experimental fires

Production et analyse des gaz toxiques dans le feu — Calcul des taux de production des espèces, des rapports d'équivalence et de l'efficacité de combustion dans les feux expérimentaux

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Foreword

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

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For an explanation on the 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 the following URL: www.iso.org/iso/foreword.html.

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

This third edition cancels and replaces the second edition (ISO 19703:2010), which has been technically revised.

The main changes compared to the previous edition are as follows:

— redundant symbols have been deleted;

— missing symbols have been added;

— units of some symbols in formulae and tables have been corrected to conform with the ISO/IEC Directives, Part 2;

— unnecessary formulae have been deleted;

— mistakes in formulae have been corrected.

Introduction

It is the view of committees ISO TC 92/SC 3, ISO TC 92/SC 4, and IEC TC 89 that commercial products should not be regulated solely on the basis of the toxic potency of the effluent produced when the product is combusted in a bench-scale test apparatus (physical fire model). Rather, the information that characterizes the toxic potency of the effluent should be used in a fire risk or hazard assessment that includes the other factors that contribute to determining the magnitude and impact of the effluent. It is intended that the characterization of

a) the apparatus used to generate the effluent, and

b) the effluent itself

be in a form usable in such a fire safety assessment.

As described in ISO 13571, the time to incapacitation in a fire is determined by the integrated exposure of a person to the fire effluent components. The toxic species concentrations depend on both the yields originally generated and the successive dilution in air. The former are commonly obtained using a bench-scale apparatus (in which a specimen from a commercial product is burned) or a real-scale fire test of the commercial product. These yields, expressed as the mass of effluent component per mass of fuel consumed, are then inserted into a fluid mechanical model which estimates the rate of fuel consumption, transport and dilution of the effluent throughout the building as the fire evolves.

For the engineering analysis to produce accurate results, it is preferred that the yield data come from an apparatus that has been demonstrated to produce yields comparable to those produced when the full product is burned. In addition to depending on the chemical composition, conformation and physical properties of the test specimen, toxic-product yields are sensitive to the combustion conditions in the apparatus. Thus, one means of increasing the likelihood that the yields from a bench-scale apparatus are accurate is to operate it under combustion conditions similar to those expected when the real product burns. As described in ISO 19706, the important conditions include whether the fuel is flaming or non-flaming, the degree of flame extension, the fuel/air equivalence ratio and the thermal environment. Similarly, these parameters should be known for a real-scale fire test.

The yields of toxic gases, the combustion efficiency and the equivalence ratio are likely to be sensitive to the manner in which the test specimen is sampled from the whole commercial product. There can be difficulty or alternative ways of obtaining a proper test specimen. That is not the subject of this document, which presumes that a specimen has been selected for study and characterizes the combustion conditions and the yields of effluent species for that specimen.

For those experimental fires in which time-resolved data are available, the methods in this document should be used to produce either instantaneous or averaged values. The application can be influenced by changes in the chemistry of the test specimen during combustion. For those fire tests limited to producing time-averaged gas concentrations, the calculated values produced by the methods in this document are limited to being averages as well. In real fires, combustion conditions, the fuel chemistry and the composition of fire effluent from many common materials and products vary continuously during the course of the fire. Thus, how well the average yields obtained using these methods correspond to the yields in a given real fire has much to do with the stage of the fire, the pace of fire development and the chemical nature of the materials and products exposed.

This document provides definitions and equations for the calculation of toxic product yields and the fire conditions under which they have been derived in terms of equivalence ratio and combustion efficiency. Sample calculations for practical cases are provided.

Generation and analysis of toxic gases in fire — Calculation of species yields, equivalence ratios and combustion efficiency in experimental fires

1 Scope

This document provides definitions and equations for the calculation of toxic product yields and the fire conditions under which they have been derived in terms of equivalence ratio and combustion efficiency. Sample calculations for practical cases are provided. The methods are intended to be used to produce either instantaneous or averaged values for those experimental fires in which time-resolved data are available.

This document is intended to provide guidance to fire researchers for

— recording appropriate experimental fire data,

— calculating average yields of gases and smoke in fire effluents in fire tests and fire-like combustion in reduced scale apparatus,

— characterizing burning behaviour in experimental fires in terms of equivalence ratio and combustion efficiency using oxygen consumption and product generation data.

This document does not provide guidance on the operating procedure of any particular piece of apparatus or interpretation of data obtained therein (e.g. toxicological significance of results).

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*

3 Terms and definitions

For the purposes of this document, the terms and definitions given in 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
mass concentration of gas
mass of gas per unit volume

Note 1 to entry: The mass concentration of a gas shall be derived directly from the measured volume fraction and its molar mass or measured directly.

Note 2 to entry: Mass concentration is typically expressed in units of grams per cubic metre.

3.2
mass concentration of particles
mass of solid and liquid aerosol particles per unit volume

Note 1 to entry: Mass concentration of particles is typically expressed in units of grams per cubic metre.

3.3
molar mass
mass of 1 mole

Note 1 to entry: Molar mass is normally expressed in units of grams per mole.

3.4
recovery of element
⟨in a specified combustion product⟩ degree of conversion of an element in the test specimen to a corresponding gas

Note 1 to entry: It is the ratio of the actual yield to notional yield of the gas containing that element.

3.5
relative atomic mass
average mass of one atom of an element divided by one twelfth of the mass of one atom of carbon (isotope ^{12}C)

3.6
stoichiometric oxygen-to-fuel mass ratio
amount of oxygen needed by a material for complete combustion

Note 1 to entry: Stoichiometric oxygen-to-fuel mass ratio is typically expressed in units of grams of oxygen per gram or kilogram of burnt material.

3.7
uncertainty
uncertainty of measurement
parameter, associated with the result of a measurement, that characterizes the dispersion of the values that could reasonably be attributed to the measurement

Note 1 to entry: The description and propagation of uncertainty in measurements are described in ISO/IEC Guide 98-3[24].

[SOURCE: ISO/IEC Guide 98-3:2008, 2.2.3, modified—The term has been changed from "uncertainty (of measurement)" to "uncertainty"; "uncertainty of measurement" has been added as an admitted term; the original Notes 1, 2 and 3 to entry have been deleted and a new Note 1 to entry has been added.]

3.8
expanded uncertainty
quantity defining an interval about the result of a measurement that may be expected to encompass a large fraction of the distribution of values that could reasonably be attributed to the measurement

Note 1 to entry: Adapted from ISO/IEC Guide 98-3:2008, 2.3.5.

4 Symbols and units

Table 1 — Symbols

Symbol	Quantity	Typical unit
A	extinction area of smoke	square metre
$A_{\sigma f}$ or A_{SEA}	specific extinction area of smoke per unit mass of material burned	square metres per gram or square metres per kilogram
D_{MO}	mass optical density ($\log_{10}$ analogue of A_{SEA})	square metres per gram or square metres per kilogram
$F_{R,E}$	recovery fraction of element E in gas containing E	dimensionless
ΔH_{act}	measured heat release in a combustion	kilojoules per gram
ΔH_c	net heat of combustion or enthalpy generated in complete combustion	kilojoules per gram
I/I_o	fraction of light transmitted through smoke	dimensionless
L	is the length of the light path through the smoke	metre
$m_{A,E}$	relative atomic mass of the element E	dimensionless
m_E	mass fraction of element E in the material	dimensionless
m_{fuel}	mass of fuel	gram
m_{gas}	total mass of the gas of interest	gram
$m_{m,loss}$	total mass loss of material	gram
$\dot{m}_{m,loss}$	material mass loss rate	grams per minute
$m_{O,act}$	actual mass of oxygen available for combustion	gram
$\dot{m}_{O,act}$	actual mass flow of oxygen available for combustion	grams per minute
$m_{O,stoich}$	stoichiometric mass of oxygen required for complete combustion	gram
m_{part}	total mass of particles	gram
M_{gas}	molar mass of the gas of interest	grams per mole
M_{poly}	molar mass of the polymer unit	grams per mole
n_E	number of atoms of element E in one molecule of gas	dimensionless
$n_{E,poly}$	number of atoms of element E in the polymer unit	dimensionless
P_{amb}	ambient pressure	kilopascal
P_{std}	standard pressure	101,3 kPa
T_C	thermodynamic temperature of the gas of interest at the point of measurement	kelvin
V	volume of chamber	cubic meter
V_{eff}	total volume of fire effluent	cubic metre
$\dot{V}_{air}$	volume air flow	cubic metres per minute
$w_{O,cons}$	measured mass fraction of oxygen consumed per unit mass of fuel	dimensionless
$w_{O,der}$	derived mass fraction of oxygen consumed per unit mass of fuel	dimensionless
$w_{Oex,poly}$	mass fraction of oxygen in polymer that contributes to the formation of oxygen-containing products	dimensionless
$w_{O,gases}$	mass fraction of oxygen consumed in the form of the major oxygen-containing products ($w_{O,CO2} + w_{O,CO} + w_{O,H2O}$)	dimensionless
$w_{O,poly}$	mass fraction of oxygen in the polymer	dimensionless
Y_{gas}	measured mass yield of gas of interest	dimensionless
Y_{part}	measured mass yield of smoke particles	dimensionless
α	linear decadic absorption coefficient (or optical density)	inverse metre

Table 1 *(continued)*

Symbol	Quantity	Typical unit
α_k	light extinction coefficient	inverse metre
χ	combustion efficiency	dimensionless
χ_{cox}	combustion efficiency calculated from the generation efficiency of carbon in the fuel to oxides of carbon	dimensionless
χ_0	combustion efficiency calculated from oxygen depletion	dimensionless
χ_{prod}	combustion efficiency calculated from the oxygen in the major combustion products	dimensionless
ϕ	equivalence ratio	dimensionless
η	generation efficiency for oxides of carbon	dimensionless
φ_{gas}	volume fraction of the gas of interest	dimensionless
φ_0	volume fraction oxygen in the air supply (0,209 5 for dry air)	dimensionless
ρ_{gas}	mass concentration of the gas of interest	grams per cubic metre
$\rho_{m,loss}$	mass loss concentration of the material	grams per cubic metre
$\rho_{0,act}$	actual mass concentration of oxygen available for combustion	grams per cubic metre
ρ_{part}	mass concentration of the smoke particles	grams per cubic metre
$\sigma_{m,\alpha}$	mass specific extinction coefficient	square metres per gram or square metres per kilogram
Ψ_{gas}	notional yield (mass fraction) of gas of interest	dimensionless
Ψ_0	stoichiometric oxygen-to-fuel mass ratio	dimensionless

5 Appropriate input data required for calculations

5.1 Data handling

5.1.1 Uncertainty

In calculating the fire parameters described in this document, the uncertainty or error associated with each component shall be taken into account and they shall be combined in the correct manner[1]. Uncertainty is derived from accuracy (how close the measured value is to the true value) and precision (how well the values agree with each other). There are uncertainties relating to physically measured parameters (e.g. mass loss and gas concentrations).

Assuming all errors to be independent, the total error, δq, is obtained by summing the squares of the errors in accordance with the general Formula (1):

$$\delta q = \sqrt{\left(\frac{\delta q}{\delta a}\delta a\right)^2 + \dots + \left(\frac{\delta q}{\delta z}\delta z\right)^2} \tag{1}$$

In other words, evaluate the error caused by each of the individual measurements, then combine them by taking the root of the sum of the squares.

In empirically derived equations, uncertainties in "constant" values shall be treated similarly to measurement uncertainties. If a constant is truly constant, i.e. has negligible uncertainty, it can be neglected.

5.1.2 Significant figures and rounding off

When recording and reporting data, significant figures shall be handled properly. The general approach is to carry one digit beyond the last certain one. When rounding off, the typical rule is to round up when the figure to be dropped is 5 or more and round down when it is less than 5.

5.2 Test specimen information

5.2.1 Composition

Information shall be given where possible on the combustible fraction, organic and inorganic combustible components, inert components, elemental composition, empirical formula and molecular or formula weight.

Where the combustible in a fire experiment is a single, homogenous material, perhaps with dispersed additives, the molecular formula of the material shall be provided. Commercial products, however, are generally non-homogeneous combinations of materials, with each component containing one or more polymers and possibly multiple additives. For complex materials representative of commercial products, the yields, effective heats of combustion, etc. vary with time as the various components become involved. For some of the following (global) calculations, a simplification is the use of an empirical formula for the composite.

5.2.2 Net heat of combustion

The net heat of combustion for combustible components shall be required for some of the calculations (e.g. combustion efficiency).

5.3 Fire conditions

5.3.1 Apparatus

Give the name of the apparatus with a brief description of mode of operation (e.g. flow-through steady state, calorimeter and closed chamber system). Refer to the appropriate standard or other reference relating to the procedure.

5.3.2 Set-up procedure

The fire conditions are generally apparatus-dependent and largely dictated by the set-up procedure for the particular apparatus. The following information shall be required:

a) test specimen details, its mass, dimensions and orientation of the combustible;

b) thermal environment, in terms of the temperature (expressed in degrees Celsius) and irradiance (expressed in kilowatts per square metre) to which test specimen is subjected;

NOTE   The temperature distribution and the radiation field in a test are frequently not uniform and, as a result, are rarely well documented. Sufficient information about the thermal and radiative conditions is intended to allow another person to reproduce the results using the same apparatus, compare the results with results for the same specimen tested in another apparatus, etc.

c) oxygen concentration in the air supply (volume percent or volume fraction);

d) volume of chamber or air flow. For a closed system, give the air volume (expressed in litres or cubic metres) and for an open system, give the air flow (expressed in litres per minute or in cubic metres per minute) and the dynamics of the flow. In both cases, give information on the atmospheric mixing conditions and the degree of homogeneity of the fire effluent.

5.4 Data collection

5.4.1 Data acquisition

Time-resolved data or time-integrated data may be acquired. The method of data acquisition shall be specified in the test protocol.

5.4.2 Measured data and observations

Most of the following data parameters shall be used to calculate yields, equivalence ratios and combustion efficiencies in experimental fires. Usually, the units applied to data should be dictated by the operational procedure associated with a particular piece of apparatus. The following are a number of suggested typical units:

a) mass loss of the test specimen, derived by measuring the test specimen mass before and after test to give overall mass loss (expressed in milligrams, grams or kilograms) or mass loss fraction (expressed in mass percent, grams per gram or kilograms per kilogram), or by measuring the specimen mass throughout a test to give mass loss rate (expressed in milligrams per second, grams per minute or kilograms per minute);

b) gas and vapour concentrations and oxygen depletion (expressed in volume percent, volume fraction, microlitres per litre, milligrams per litre or milligrams per cubic metre);

c) smoke particulate concentration (expressed in milligrams per litre or milligrams per cubic metre) and smoke obscuration (expressed in optical density per metre or square metres per kilogram);

d) heat release (expressed in kilojoules per gram), used to calculate combustion efficiency, forms part of the protocol for some apparatuses;

e) combustion mode, time to ignition (expressed in minutes or seconds) and whether the specimen flames or not throughout the test.

6 Calculation of yields of fire gases and smoke, stoichiometric oxygen-to-fuel mass ratio and recovery of key elements

6.1 Calculation of measured yields from fire gas concentration data

In experimental fires, the mass yield, Y_{gas}, of a gas shall be calculated from the measured mass concentration of the gas of interest and the mass loss concentration of the material in accordance with Formula (2) (see NOTES 1, 2 and 3):

$$Y_{gas} = \frac{\rho_{gas}}{\rho_{m,loss}} \tag{2}$$

where

ρ_{gas} is the mass concentration of the gas;

$\rho_{m,loss}$ is the mass loss concentration of the material.

Alternatively, Y_{gas} shall be calculated from the total mass of gas generated and the total mass loss of material in accordance with Formula (3):

$$Y_{gas} = \frac{m_{gas}}{m_{m,loss}} \tag{3}$$

where

m_{gas} is the total mass of the gas;

$m_{m,loss}$ is the total mass loss of the material.

NOTE 1   These calculations can be derived from instantaneous data or from data which assumes that the gases are uniformly dispersed in a certain volume and that this volume is the same one in which the lost sample mass is (evenly) dispersed. If the dispersion is not uniform, the equations still work if the lost mass and the gas in question are dispersed equivalently. If a combustion gas is prone to surface losses within the apparatus, the apparent yield depends on where the concentration is being measured.

NOTE 2   In flow-through devices, the total effluent is generally well mixed at some distance downstream. For closed-box combustion systems, it is not necessarily so, especially if there are large molecular weight differences and large thermal gradients. If multiple fuels are involved, only some averaged combined yield can be calculated.

NOTE 3   In setting up these calculations, uncertainties relating to lost sample mass, fluctuations in the measured concentration, etc. occur.

The uncertainty shall be monitored. The calculated yield shall take account of and combine these uncertainties, enabling a sound basis for comparing yields under different combustion conditions, comparing yields from different materials and so on.

Whilst concentrations of the specific gas are most often measured in volume fractions, Formulae (4) and (5) show how to convert the volume fraction of a gas to its mass concentration:

$$\rho_{gas} = \varphi_{gas} \times \frac{M_{gas}}{22{,}414 \, \text{dm}^3 \cdot \text{mol}^{-1}} \times \frac{273{,}15 \, \text{K}}{T_C} \times \frac{P_{amb}}{101{,}325 \, \text{kPa}} \tag{4}$$

where

ρ_{gas} is the mass concentration of the gas;

φ_{gas} is the volume fraction of the gas;

M_{gas} is the molar mass of the gas;

T_C is the thermodynamic temperature of the gas at the point of measurement;

P_{amb} is the ambient pressure;

273,15 K   is the standard thermodynamic temperature;

101,325 kPa   is the standard pressure;

22,414 dm^3·mol^{-1} is the molar volume of an ideal gas at standard temperature and pressure.

Thus, for fire effluent at 20 °C and standard pressure, Formula (4) simplifies to Formula (5):

$$\rho_{gas} = \varphi_{gas} \times \frac{M_{gas}}{24{,}055 \, \text{dm}^3 \cdot \text{mol}^{-1}} \tag{5}$$

EXAMPLE   The calculations for a well-ventilated fire atmosphere where mass loss concentration of the material is 25 g·m^{-3} and the volume fraction of carbon monoxide (CO) is 0,125% (or 0,001 25) at 20 °C are shown in Formulae (6) and (7):

$$\rho_{CO} = 0{,}001\,25 \times \frac{28{,}01 \, \text{g} \cdot \text{mol}^{-1}}{24{,}055 \, \text{dm}^3 \cdot \text{mol}^{-1}} = 0{,}001\,456 \, \text{g} \cdot \text{dm}^{-3} = 1{,}456 \, \text{g} \cdot \text{m}^{-3} \tag{6}$$

$$Y_{co} = 1{,}456 \, \text{g} \cdot \text{m}^{-3} / 25 \, \text{g} \cdot \text{m}^{-3} = 0{,}058\,2 \tag{7}$$

where