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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

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

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

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

Attention is drawn to the possibility that some of the elements of this document may be the subject of patent rights. ISO shall not be held responsible for identifying any or all such patent rights.

ISO 19703 was prepared by Technical Committee ISO/TC 92, *Fire safety*, Subcommittee SC 3, *Fire threat to people and environment*.

This corrected version of ISO 19703:2005 incorporates the following corrections:

a) Clause 2:

- ISO/TR 9122-1:1989 has been cancelled and replaced by ISO/TS 19706.
- ISO/TR 19701:—¹) has been modified to ISO/TR 19701:2005 and the associated footnote deleted.
- These two references, plus ISO 5725-1:1994, ISO 5725-2:1994, ISO/TR 9122-4:1993, ISO/TS 13571 and the *International vocabulary of basic and general terms in metrology*, have been moved to the Bibliography as references [21] to [27].

b) 3.6: The definition of mass concentration of gas, has been modified.

c) Clause 4:

- The semi-colon (;) has been replaced by a comma in the subscripts of some of the symbols, such as $m_{m,loss}$ and some of the quantities modified.
- σ_{α} has been amended to $\sigma_{m\alpha}$.

d) 5.3: The second subclause numbered 5.3.1 has been renumbered to 5.3.2.

e) Table 4:

- In row 1, column 2, $m_{A,E}$ has been modified to $m_{A,X}$.
- Footnote a has been modified to read: " $m_{A,X}$ is the atomic mass, expressed in grams, of element X."

f) 7.1, Equation (45): The units for the factor 1 331 have been modified to read: "..., expressed in cubic metres,"

- g) 8.3.2 (twice): The symbol $\chi_{\text{ox,dep}}$ has been modified to χ_{ox} .
- h) 8.3.3.1 (twice) and 8.3.3.3, Equation (58): The symbol $\chi_{\text{ox,prod}}$ has been modified to χ_{prod} .
- i) Equation (57): The reference associated with the definition of χ_{cox} has been changed to “(see 8.4)”.
- j) Table 10:
- Symbols in subtitles 1 and 2 have been modified to $\omega_{\text{O},2,\text{cons}}$ and $\omega_{\text{O},2,\text{der}}$, respectively.
 - The symbol associated with “Combustion efficiency” (fourth row, second column under Oxygen consumption method) has been modified to χ_{ox} .
 - In Footnote a, $m_{\text{A,E}}$ has been modified to $m_{\text{A,X}}$.
 - A footnote indicator has been added to the fourth column of the first and third rows under “Oxygen in products method”, e.g. (microlitres per litre)^p.
- k) Table 11:
- Symbol in subtitle 1 has been modified to $\omega_{\text{O},2,\text{cons}}$.
 - The symbol associated with “Combustion efficiency” (fourteenth row, second column under Oxygen consumption method) has been modified to χ_{ox} .
- l) Bibliography: ISO 5660 has been revised to ISO 5660-1 with the new title: *Reaction-to-fire tests — Heat release, smoke production and mass loss rate — Part 1: Heat release rate (cone calorimeter method)*.
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<http://standards.jteha.com/catalog/standards/cist/16924e0a-cd46-4d7e-a5ff-4ebb738159f8/iso-19703-2005>
- m) Other minor editorial changes to layout, punctuation, etc.

Introduction

It is the view of committees ISO TC92/SC3 (Fire threat to people and the environment), ISO TC92/SC4 (Fire safety engineering), and IEC TC89 (Fire hazard testing) 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. The characterization of (a) the apparatus used to generate the effluent and (b) the effluent itself must thus be in a form usable in such a fire safety assessment.

As described in ISO/TS 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 that estimates the transport and dilution of the effluent throughout the building as the fire evolves.

For the engineering analysis to produce accurate results, the yield data must 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 will be accurate is to operate it under combustion conditions similar to those expected when the real product burns. 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 may be difficulty or alternative ways of obtaining of 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 International Standard can be used to produce either instantaneous or averaged values. The application may 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 International Standard 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 International Standard 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 International Standard 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 can be used to produce either instantaneous or averaged values for those experimental fires in which time-resolved data are available.

This International Standard is intended to provide guidance to fire researchers for

- appropriate experimental fire data to be recorded,
- 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 International Standard 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 referenced documents are indispensable for the application of this document. For dated references, only the edition cited applies. For undated references, the latest edition of the referenced document (including any amendments) applies.

ISO/IEC 13943:2000, *Fire safety — Vocabulary*

3 Terms and definitions

For the purposes of this document, the terms and definitions given in ISO 13943:2000 and the following apply.

3.1

atomic mass

(of an element) value proportional to the mass of its atom relative to carbon (isotope ^{12}C) that is assigned the value of 12,00 containing 1 mole of carbon atoms

3.2

combustion efficiency

ratio of the heat released in a combustion reaction to the theoretical heat of complete combustion

NOTE 1 Combustion efficiency can be calculated only for cases where complete combustion can be defined.

NOTE 2 Combustion efficiency can also be expressed as a percentage.

3.3
empirical formula

chemical formula of a substance in which the relative numbers of atoms of each type are given

NOTE Typically, the number for one type of atom is chosen, to be an integer (usually C or O), e.g. a particular sample might be represented as $C_6H_{8,9}O_{4,1}N_{0,3}Cl_{0,01}$.

3.4
equivalence ratio

ϕ
actual fuel-to-air mass ratio divided by the stoichiometric fuel-to-air mass ratio for that fuel

NOTE 1 For $\phi < 1$, as in small or well-ventilated fires, the fuel/air mixture is said to be fuel lean and complete combustion (i.e., to CO_2 and H_2O) will dominate. For $\phi = 1$, the mixture is stoichiometric. For $\phi > 1$, as in ventilation-controlled fires, the mixture is fuel rich and relatively high concentrations of pyrolysis and incomplete combustion gases will result.

NOTE 2 Standard, dry air contains 20,95 % oxygen by volume. In practice, the oxygen concentration in entrained air can vary, requiring correction in the calculation of ϕ to a standard, dry air basis. In this International Standard, fuel-to-oxygen ratios, rather than fuel/air ratios, are used for the equivalence ratio calculations.

NOTE 3 For gaseous fuels, an alternative expression of the equivalence ratio can be based on the fuel-to-air volume ratio.

3.5
mass loss concentration

mass of a test specimen consumed during combustion per unit chamber volume (closed system) or per total volume of air passing through an open system

NOTE 1 Mass loss concentration is typically expressed in units of grams per cubic metre.

NOTE 2 For an open system, the definition assumes that the mass is dispersed in the air flow uniformly over time.

3.6
mass concentration of gas

mass of gas per unit volume

NOTE 1 The mass concentration of a gas can be derived directly from the measured volume fraction and its molar mass, or measured directly.

NOTE 2 Mass concentration is typically expressed in units of grams per cubic metre.

3.7
mass concentration of particles

mass of solid and liquid aerosol particles per unit volume

NOTE Mass concentration of particles is typically expressed in units of grams per cubic metre.

3.8
molar mass

mass of 1 mole

NOTE Molar mass is normally expressed in units of grams per mole.

3.9
net heat of combustion

enthalpy, per unit mass of fuel consumed, generated in complete combustion with the water produced being in the gaseous state

NOTE Net heat of combustion is typically expressed in units of kilojoules per gram or megajoules per kilogram.

3.10**notional yield
stoichiometric yield**

maximum possible mass of a combustion product generated during combustion, per unit mass of test specimen consumed

NOTE Notional yield is typically expressed in units of grams per gram or kilograms per kilogram.

3.11**recovery of element**

(in a specified combustion product) degree of conversion of an element in the test specimen to a corresponding gas, i.e. a ratio of the actual yield to notional yield of the gas containing that element

3.12**stoichiometric mixture**

mixture of fuel and oxidizer which has the correct composition to produce only the products of complete combustion

3.13**stoichiometric oxygen demand
stoichiometric oxygen-to-fuel mass ratio**

amount of oxygen needed by a material for complete combustion

NOTE Stoichiometric oxygen demand is typically expressed in units of grams per gram or kilograms per kilogram.

3.14**uncertainty of measurement**

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

NOTE The description and propagation of uncertainty in measurements is described in GUM^[20].

3.15**yield**

mass of a combustion product generated during combustion per unit mass of test specimen consumed

NOTE Yield is typically expressed in units of grams per gram or kilograms per kilogram.

4 Symbols and abbreviated terms

Symbol	Quantity	Typical units
A	extinction area of smoke	square metre
A_{of} 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})	cubic metres per gram or cubic metres per kilogram
$F_{\text{R,E}}$	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 or enthalpy generated in complete combustion	kilojoules per gram
I / I_0	fraction of light transmitted through smoke	dimensionless
L	is the light path through the smoke	metre
$m_{\text{A,E}}$	atomic mass of the element E	gram
m_{E}	mass of element E per unit mass of material	dimensionless

$m_{E,per}$	mass of element E in the material	percent
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
$m_{O_2,act}$	actual mass of oxygen available for combustion	gram
$\dot{m}_{O_2,act}$	actual mass flow rate of oxygen available for combustion	grams per minute
$m_{O_2,stoich}$	stoichiometric mass of oxygen required for complete combustion	gram
m_{part}	total mass of particles	gram
m_s	mass concentration of smoke	grams per cubic metre
M_{gas}	molar mass of the gas of interest	grams per mole
M_{poly}	molar mass of the polymer unit	gram
n_E	number of atoms of element E in the 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	temperature of the gas of interest at the point of measurement	degree Celsius
V_{eff}	total volume of fire effluent	cubic metre
\dot{V}_{air}	volume air flow rate	cubic metres per minute
$w_{O_2,cons}$	measured mass fraction of oxygen consumed	dimensionless
$w_{O_2,der}$	derived mass fraction of oxygen consumed	dimensionless
$w_{Oex,poly}$	mass fraction of oxygen in polymer that contributes to the formation of oxygen-containing products	dimensionless
w_{Ogases}	mass fraction of oxygen consumed in the form of the major oxygen-containing products ($w_{OCO_2} + w_{OCO} + w_{OH_2O}$)	dimensionless
w_{Opoly}	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
α_k	light extinction coefficient	inverse metre
χ	combustion efficiency ratio	dimensionless
χ_{cox}	combustion efficiency ratio calculated from the generation efficiency of carbon in the fuel to oxides of carbon	dimensionless
χ_{ox}	combustion efficiency ratio calculated from oxygen depletion	dimensionless
χ_{prod}	combustion efficiency ratio 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 concentration of the gas of interest	volume per volume, percent, [parts per million (ppm) deprecated]
φ_{O_2}	volume fraction oxygen in the air supply (0,209 5 for dry air)	dimensionless

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ρ_{gas}	mass concentration of the gas of interest	grams per cubic metre
$\rho_{\text{m,loss}}$	mass loss concentration of the material	grams per cubic metre
ρ_{part}	mass concentration of the smoke particles	grams per cubic metre
$\sigma_{\text{m},\alpha}$	mass specific extinction coefficient	square metres per gram or square metres per kilogram
Ψ_{gas}	notional mass yield of gas of interest	dimensionless
Ψ_{O}	stoichiometric mass oxygen-to-fuel ratio (stoichiometric oxygen demand)	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, it is essential to take into account the uncertainty or error associated with each component, and to combine them 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 will be uncertainties relating to physically measured parameters (e.g. mass loss, gas concentrations etc.).

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

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

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

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

5.1.2 Significant figures and rounding off

When recording and reporting data, it is also important to handle significant figures 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 should be given where possible on the combustible fraction, organic and inorganic combustible components, inert components, elemental composition, empirical formula, and molecular or formula weight

The combustible in a fire experiment of any scale is often a single, homogenous material, perhaps with dispersed additives. In this case, the molecular formula of the material should 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. will 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 may 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, closed chamber system, etc.). 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 is 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/or 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 needed that another person can 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 metre), 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 will be specified in the test protocol.

5.4.2 Measured data and observations

Most of the following data parameters will be required in order to calculate yields, equivalence ratios and combustion efficiencies in experimental fires. The units applied to data will be usually dictated by the operational procedure associated with a particular piece of apparatus. A number of typical units are suggested below:

- 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 (parts per million is deprecated)];

- 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 demand, 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 can be calculated from the measured mass concentration of the gas of interest and the mass loss concentration of the material, or from the total mass of gas generated and the total mass loss of material in accordance with Equation (2); see Notes 1, 2, and 3:

$$Y_{\text{gas}} = \frac{\rho_{\text{gas}}}{\rho_{\text{m,loss}}} \quad (2)$$

where

ρ_{gas} is the mass concentration, expressed in grams per cubic metre, of the gas ;

$\rho_{\text{m,loss}}$ is the mass loss concentration, expressed in grams per cubic metre, of the material.

Alternatively, the expression can be written as given in Equation (3):

$$Y_{\text{gas}} = \frac{m_{\text{gas}}}{m_{\text{m,loss}}} \quad (3)$$

where

m_{gas} is the total mass, expressed in grams, of the gas;

$m_{\text{m,loss}}$ is the total material mass loss, expressed in grams.

NOTE 1 These calculations can be derived from instantaneous data or from data which assumes (a) that the gases are uniformly dispersed in a certain volume and (b) 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 will depend 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 could be calculated.

NOTE 3 In setting up these calculations, it is important to keep track of the uncertainty. There will be uncertainties relating to lost sample mass, fluctuations in the measured concentration, etc. The calculated yield needs to take account of and combine these, enabling a sound basis for comparing yields under different combustion conditions, comparing yields from different materials, etc.

Whilst concentrations of the specific gas are most often measured in volume units, the mass loss from a solid will almost always be in mass units, since the molecular weight of the effluent is difficult to determine.