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Fire chemistry — Generation and measurement of aerosols

Chimie de la combustion — Production et mesurage des aérosols

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Foreword

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

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Introduction

Aerosols generated in fires are complex, non-homogeneous mixtures of liquid droplets of tar or water, solid-phase carbonaceous agglomerated soot with adsorbed organic compounds, or mineral particles. After formation through complex chemical and physical processes, fire aerosols continuously undergo changes in physical size, structure, and chemical composition as the particles may coalesce, agglomerate, absorb gases, evaporate or deposit on surfaces. The aerosol concentration, particle size, temperature, and gas-phase composition also play a role in the rate of change.[1][2][3]

There are multiple mechanisms by which fire-generated aerosols affect the fire threat to people and the environment. First, small particles are respirable and can penetrate deep into the lung structure. Inhaled particles themselves can be irritating, reducing the ability of people to escape from a fire.[4][5] Next, these particles can adsorb and/or absorb toxic and irritant gases and vapours, providing a means for transport past the respiratory tract natural defences and deep into the lungs.[5][6] Third, even less or non-respirable particles may effectively reduce the concentration of toxic gases and vapours in the fire effluent and can deposit them on surfaces. Fourth, aerosols may obscure vision, potentially reducing the ability of people to move effectively toward safety (see ISO 13571). Finally, the aerosol fraction in fire effluents also has significant potential to adversely affect the environment, particularly where the fires are large and of long duration.[7][4]

Therefore, it is important, within the context of the mechanisms of generation and evolution of aerosols, to be able to measure aerosol concentrations and size distributions accurately; to appreciate the scope and limitations of the apparatus and methodologies available for these measurements; and to interpret such measurements effectively, consistent with the hazards and risks being evaluated. This International Standard provides details of a range of sampling and measurement methods and guidance on which ones to use for particular applications, together with an interpretation scheme based on current knowledge. This document also includes informative annexes that summarize the physical aspects of fire aerosol generation, aerosol movement and modification with and away from the fire plume, the aerosol contribution to fire growth through flame radiation, and the roles of particulates in threat to life and the environment.

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Fire chemistry — Generation and measurement of aerosols

1 Scope

This International Standard provides a guide to the generation of aerosol particles in fires, defines apparatus and procedures for the sampling and measurement of aerosols, and provides procedures for the interpretation and reporting of the data. It is intended to assist fire test designers and those making measurements at unwanted fires to choose and use appropriate methods for aerosol measurement for differing hazards to people and the environment.

This International Standard identifies the scope, applicability, and limitations of each method. The interpretation of the data from these measurements is strongly dependent on the end use of the data.

Fire-generated aerosols may present a direct risk of restricting escape from fire by obscuring an exit route, or they may produce chronic health and environmental hazards from chemical compounds contained in the aerosol (for example, toxic chemicals like polycyclic aromatic hydrocarbons in soot or radionuclides form nuclear plant fires.) Aerosol particles may be inhaled to various depths in the lungs, depending on their size and density, or may be released into the environment and deposited on land and in watercourses.

In particular, this International Standard addresses the following aspects of aerosol generation and measurement in fires:

— Adsorbed/dissolved gas or vapour phase species;

— Physical mechanisms involved in the transport of aerosols, dispersal in the fire plume, coagulation/agglomeration leading to variation in particle sizes and fractions, "thermophoresis" (main cause of soot deposition), "diffusiophoresis" and, sedimentation.

— The interactions between gases and vapours and aerosol: adsorption and removal of species from gas phase, transportation of adsorbed gases into the lungs;

— Sampling and measurement methods, including their principles of operation, method description, the data provided, and in each case their scope, field of application, advantages and disadvantages;

— Metrology of the measurement methods, and in the generation of "standard aerosols", and the related uncertainties;

— Physiological and environmental effects of aerosols insofar as these effects can be used to define the measurement method for specific applications; and

— Hazards of carbon particles present in the fire effluent as visible "smoke" through their size, morphology, chemical nature, and the nature of the effluent in which they are (or were) suspended.

This International Standard is not oriented toward the aerosols generated from controlled combustion. (e.g. incineration). However, much of the material in this document is common to such aerosols.

2 Normative references

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

ISO 13943, *Fire safety — Vocabulary*

3 Terms, definitions, symbols and abbreviated terms

3.1 Terms and definitions

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

3.1.1
aerosol
suspension of liquid droplets, or solid particles in a gas phase matrix which are generated by fires and range in particle size from under 10 nm to over 10 μm

3.1.2
particles
solid-phase products present in aerosols

Note 1 to entry: There are two categories of fire aerosol particles: unburned or partially burned particles containing a high proportion of carbon (i.e. "soot"), and relatively completely combusted, small particle sized "ashes". Soot particles of small diameter, (i.e. about 1 μm), typically consist of small elementary spheres of between 10 nm and 50 nm in diameter. Formation of soot particles is dependent on many parameters including nucleation, agglomeration and surface growth. Oxidation of soot particles (i.e. further combustion) is also possible.

3.1.3
droplets
liquid-phase products present in aerosols, typically generated through pyrolysis (reduced oxygen combustion conditions) from both flaming and smouldering fires and which may condense into tarry-like, spherically-shaped droplets

Note 1 to entry: Water produced from combustion may also condense around particles forming aerosol droplets.

3.1.4
inhalable fraction
mass fraction of the total particles suspended in air, which can be inhaled into the nose and the mouth and depends on particle diameters, the velocity and direction of gas containing the particles, and on the respiratory frequency

3.1.5
extrathoracic fraction
mass fraction of the inhaled particles which cannot penetrate beyond the larynx

3.1.6
thoracic fraction
mass fraction of the inhaled particles penetrating beyond the larynx

3.1.7
tracheobronchic fraction
mass fraction of the inhaled particles penetrating beyond the larynx but not penetrating into the non-ciliated respiratory system

3.1.8
alveolar fraction
mass fraction of the inhaled particles which penetrates into the non-ciliated respiratory system

3.2 Symbols and abbreviated terms

D_p	Physical diameter of a particle
D_a	Aerodynamic diameter of a particle
D_m	Electrical mobility equivalent diameter of a particle

D_{ev}	Volume equivalent diameter of a particle
D_g	Diameter of a spherical shell with the same mass and inertial component as the considered combustion particle
D_{50}	Mass median diameter of a set of particles
D_{pp}	Diameter of primary particles of an agglomerate
N_{pp}	Number of primary particles constituting an agglomerate
R_g	Gyration Radius of a particle
D_f	Fractal Dimension of a particle
k_f	Logarithm of the prefactor for fractal dimension of a particle
χ	Dynamic shape factor
ρ:	Mass density of the particle
μ	Viscosity of the surrounding gas
L	Optical path followed by light through the aerosol (m)
K_{ext}	Extinction coefficient of light by the aerosol (m^{-1})

4 Aerosol properties

4.1 General

Fire effluents consist of combustion gases and vapours, water droplets and aerosols (solids and liquids formed during and after combustion) combustion. The aerosol component of fire effluents forms the visible portion of smoke and is made up of particles and droplets of small size. Aerosols are organic and inorganic particles and droplets produced during the incomplete combustion of fuels.

The liquid droplets present in aerosols are mainly spherical. Solid carbon particles have quasi-fractal morphology, and can be present over a relatively large range of sizes. Inorganic mineral particles can have various forms, depending on their initial form in the fuel and on the fire "history".

The nature of fire products are less dependent on the fuel type at high fire temperatures (i.e. around 1000 °C) than at lower temperatures and at high temperatures appear to depend on the local conditions during formation. It has been demonstrated that combustion of cellulose, tobacco, various polymers can generate approximately the same yield[8] of soot at an imposed high temperature of 1000 °C.

With open, well-ventilated fires, production of soot is therefore highly dependent on the temperatures in the flame (or smouldering) zone, the oxidation conditions (e.g. degree of air access to the fire), and the extent of aerosol agglomeration or re-oxidation.

The similarity of aerosol types during the combustion of different fuels can be partly explained by the fact that many fuels are based on hydrocarbons or hydrocarbon polymers which have relatively similar "cracking" patterns during thermal decomposition, generating common products such as methane, ethane and ethylene, propane.

Depending on the end use of data from the measurement of the various properties of the aerosol portion of fire effluents, these properties will have a varying prominence. For example:

a)   For studying escape from fire, the aerosol opacity will affect human visibility (see ISO 13571). In many fire scenarios, the impact of aerosols on visibility is one of the most important parameters in determining the ability to escape. Pre-movement actions and movement speed are strongly dependent

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on the visibility in smoke-filled spaces. It has been suggested that above a certain opacity of smoke, many would consider that escape would be seriously impeded. See Annex D for further details.

b) In fire modelling, soot yield is an important input parameter. It has a very significant effect on the heat radiation properties of flames (often a sub-model of the main model), and therefore on the general heat transfer by radiation, which can affect escape from a fire (see ISO 13571) and can significantly influence fire growth and the occurrence of "flashover". See Annex D for further details.

c) The direct physiological effect of aerosols on people is related to the size fractions within the aerosol and the morphology of the particles and droplets. It is therefore often more important to know the particle and aerosol distribution by size rather than the total aerosol mass for the determination of physiological effects. Unfortunately, size distribution is a parameter, which is often difficult to measure, principally due to the processes of agglomeration over short time intervals. Agglomeration can greatly affect the structure of the particles and droplets, as well as their density and optical (i.e. obscuration) properties. In addition, volatile species that may evaporate to a varying degree while being sampled and measured will influence the data recorded. Furthermore, measuring instruments operating on different principles will give different effective size fractions, and the methods cannot be assumed to be equivalent. The main parameter to consider for physiological effect of aerosols is their deposition in the respiratory tract. Different classes of particle size, based on their relation to physiological effects, have been defined: "PM10", "PM2.5", "inhalable" (D_p < 100 μm), "thoracic" (D_p < 10 μm), "respirable" (D_p < 4 μm), "ultrafine" (D_p < 0,1 μm), and "nanoparticulates" (D_p < 0,050 μm). See Annex C for further details.

Mass concentration and particle and droplet size fraction can also be valuable parameters for computational fluid dynamics (CFD) computer modelling of fire processes. This is especially true as models become capable of simulating the evolution of the aerosols and the effects of the evolution on flame radiation.

4.2   Movement and evolution of fire aerosol

Knowing how and where to sample the fire effluent is critical to obtaining an accurate and useful aerosol distribution. Thus, it is important to take into account the local transport processes that can result in non-uniform particle distributions.

The generation of particles begins within the flame or combustion zone in smouldering. Upon release into the fire atmosphere, agglomeration can occur to varying degrees. In the fire plume, because of thermophoresis (movement of particles due to a temperature gradient) and due to the upward, buoyancy-driven movement of the fire plume, particles will be entrained and carried initially upwards above the fire. Glowing carbon particles are the most important contributor to heat radiation from the fire plume, especially because these particles are typically present in a relatively high concentration, have an emissivity close to blackbody (i.e. radiate over a very large spectral range), and are present at high temperature.

Thermophoresis is a very important parameter governing the movement of aerosols in a hot fire and their deposition on any relatively cool surfaces. Thermophoretic movement may be considered as the mechanism by which the aerosols are repelled by a hot body and attracted to a cooler body resulting in a movement of particles and droplets from hot to cold areas. This results in the observed deposition of particles and droplets onto cool surfaces such as windows and walls in the structure containing the fire. Hot zones can be relatively free of particles, but are potentially capable of generating them if temperature conditions change. This is because, as the temperature drops, gaseous organic molecules can condense to form aerosols. In fact, the very act of sampling from these areas of apparently low or zero particles can give rise to measured particles through the intrusive (particularly cooling) effect of the measuring apparatus.

The phenomenon of particle deposition can, for example, damage property at considerable distances from the fire. The pattern of smoke deposits after a fire, typically as an inverted "V" from the source can provide valuable evidence on the origin of the fire when arson is suspected. The same pattern can also be used to determine areas of the fire scenario which are likely to be free from contamination by

smoke – an important economic consideration for example with respect to restoration requirements following a fire.

There are three other transport processes that can affect the distribution of aerosols within the airflow away from a fire:

— Diffusiophoresis is the process by which suspended particles in a hot medium with a concentration gradient move from areas of high concentration to areas of low concentration.

— Photophoresis characterizes reaction of the particle with light. In photophoresis, a particle absorbs light and is heated by this absorbed energy in the highlighted direction. In reaction, the particle then moves away from the light (toward a cooler region).

— Sedimentation is the downward movement of the particles due to gravity and to the properties of the surrounding matrix (especially viscosity). The rate of sedimentation is dependent on the viscous properties of the overall flow, the temperature, and the aerosol size and mass. Large, heavy particles settle quickly, whereas fine, low mass particles can remain suspended indefinitely.

In the presence of an electrical field, movement of the particles (especially carbon particles) will be modified. The effects of this phenomenon are largely influenced by gravity and thermophoresis. This phenomenon is the principle of measurement of some instruments described in this Standard.

The agglomeration and coagulation processes, present during the formation of the aerosol may continue at considerable distances from the fire source, although the effects decrease as the aerosols become diluted in increasing volumes of air. Thus, at relatively great distances from the fire, large-mass clusters of particles may be formed and may sediment rapidly. As an illustration of the importance of time in decreasing the concentration of particles through coagulation effects, Table 1, [see Reference (2)], shows the relationship between an initially monodispersed aerosol over a range of initial concentrations and the corresponding times needed to double the diameter and halve the concentration of the particles. This shows that if such particles are to be sampled for meaningful measurement, rapid dilution is necessary to preserve as much as possible the original particle size distribution and total aerosol mass.

Table 1 — Measured change of the size and mass concentration of an initially monodispersed aerosol due to coagulation, according to Reference [2]

Initial concentration (particles/mL)	Time to double the mean diameter of aerosol	Time to halve the mass concentration
10^{14}	140 µs	20 µs
10^{12}	0,014 s	0,002 s
10^{10}	1,4 s	0,2 s
10^{8}	140 s	20 s
10^{6}	4 h	33 min
10^{4}	16 days	55 h
10^{2}	4 years	231 days

Under conditions of fixed temperature, the aerosol size distribution tends towards a state known as "self preserving", i.e. equilibrium tends to exist between the rate of agglomeration and the rate of separation.[2]

4.3   Measurable properties of aerosols

4.3.1   Size and shape

Aerosol droplets are spherical at the time of their formation and typically remain spherical as they grow by aggregation or condensation. The droplet diameters range from under 1 nm to more than 100 µm.

Carboneous particles formed initially are spherical, with diameters D_p, are homogenous, and have a size range varying between 10 nm and 50 nm. The frequency distribution of such particles is normally

Gaussian.[2][3] However, as these small particles stick together to form larger particles, aged and agglomerated carbon particles in fire effluents are rarely spherical, their fractal structure being a result of the growth process. Therefore, they need to be characterized using parameters other than those used to describe a sphere. The main parameters used are the aerodynamic diameter and the electric mobility diameter. These and some additional parameters are defined below.

4.3.1.1 Aerodynamic diameter

This diameter D_a represents the diameter of a sphere of density 1 g/cm^3 having the same settling velocity in calm air as the aerosol particle being considered. For an unspecified particle, the following relation links this diameter to the mass median diameter of the distribution:

$$D_a = \sqrt{\frac{\rho}{\chi}} \cdot d_{50}$$

4.3.1.2 Electrical mobility equivalent diameter

This diameter represents the diameter of a sphere, having the same electric mobility Zp as the considered particle, following the relation:

$$D_m = \frac{Cc}{3\pi\mu B}$$

where

 Cc is the Cunningham correction factor

 B is the dynamic mobility, which characterizes forces produced by surrounding gas on the particle.

4.3.1.3 Volume equivalent diameter

This diameter represents the diameter of a sphere with the same mass as the considered particle and the same density.

$$D_{ev} = \left[\frac{m}{(\pi/6)\rho}\right]^{1/3}$$

4.3.1.4 Gyration diameter

This diameter, D_g, represents the diameter of a spherical shell with the same mass and inertial moment as the considered combustion particle. This diameter is particularly useful in order to describe the fractal morphology of combustion aerosol and will be described in 5.2.3.

4.3.1.5 Additional diameters

Other diameters can be used to define particles, see References [2] and [3] They include diameter of primary particles D_{pp}, aggregate diameter D_{agr} (diameter of a sphere, which includes totally the particle), Martin diameter, Feret diameter or Stokes diameter. Figure 1 presents these different diameters for a carbon particle.
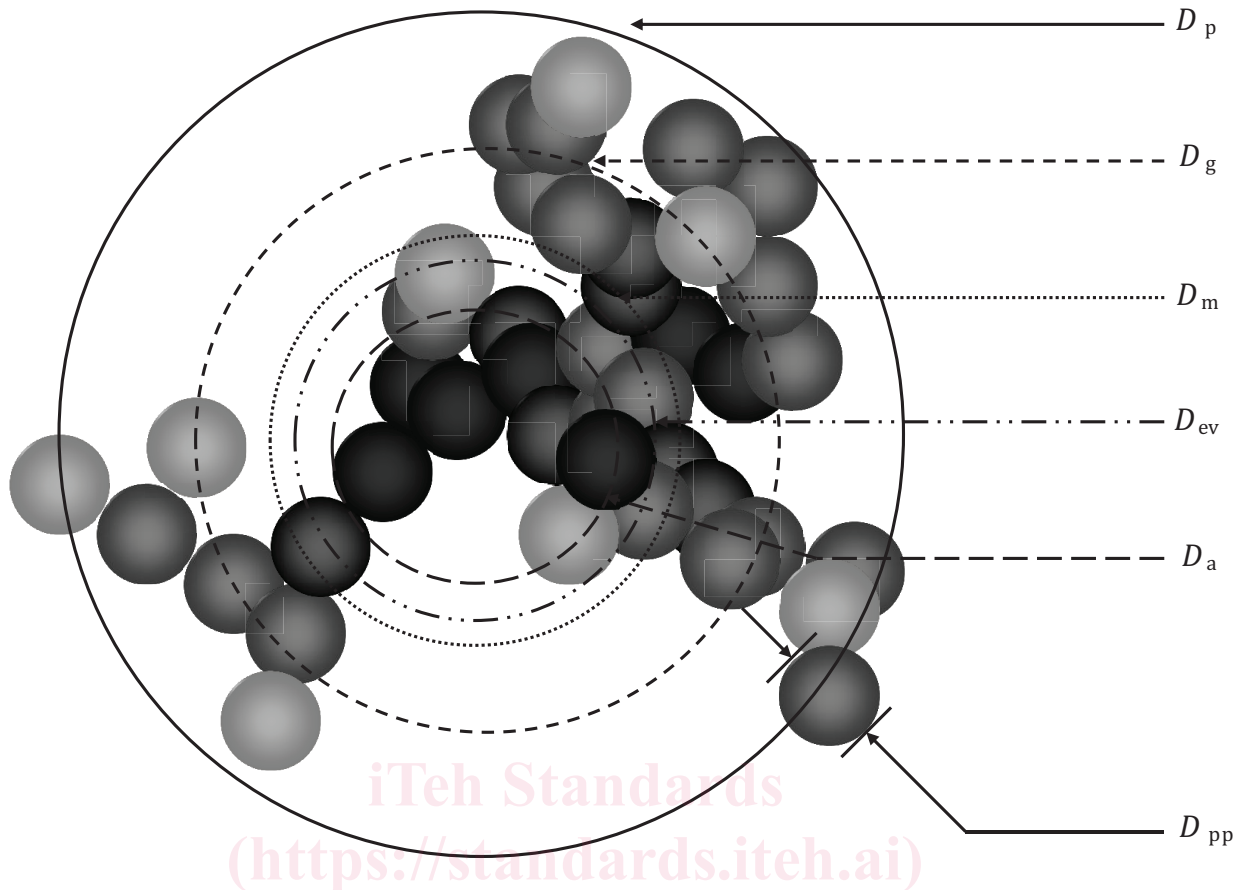
Figure 1 — Different characteristic diameters of a carbon particle

4.3.1.6 Aerosol morphology

The shape of combustion aerosol particles and droplets has been intensively investigated since the pioneering work of Witten and Sander[9] and Julien and Botet.[10] Due to their mode of formation, particles produced by flames have a shape mainly governed by the "diffusion limited aggregation" phenomenon (DLA). A quasi-fractal relationship has been introduced in order to fully describe the morphology of a combustion aerosol through the aggregation process from a small number of primary particles N_p to a large number in the mature aggregate:

$$N_{pp} = k_f \cdot \left(\frac{D_g}{D_{pp}} \right)^{D_f}$$

This relationship is regarded as a *quasi*-fractal as it is only possible to define the morphology of the smallest primary particles and the highest limit for the agglomerated particles. Some measurements of D_{pp}, N_{pp}, R_g, D_f and k_f are presented in Annex A.

4.3.1.7 Aerosol size distribution

The parameters typically used to characterize the granulometric distribution of the aerosol are the mass median aerodynamic diameter (MMAD), the standard deviation of the diameters, and the distribution function. This distribution is generally assumed to fit a log/normal distribution.

4.3.2   Aerosol global parameters

4.3.2.1   Optical extinction coefficient

The Bouguer-Beer-Lambert relation describes the attenuation of light through a suspension of particles, usually normalized for fire studies for a unit path length. The law is dependent upon the wavelength of the light, although an approximation is normally used and ignores this spectral dependence. The extinction coefficient of light depends on soot concentration and the particles' propensity to absorb light, characterized by their specific extinction surface. The average attenuation of the light beam is stated through the expression:

$$\frac{I}{I_0} = e^{-K_{ext} \cdot L}$$

where

   L   is the optical path (path followed by the light through smoke) (m)

   K_{ext} is the extinction coefficient of the light (m^{-1})

The extinction coefficient of an aerosol depends on the extinction cross section of aggregates stated through the expression:

$$K_{ext}(N,m) = N \int f(d) C^{ext}(d,m) dd$$

where

   N is the particle concentration (m^{-3})

   m is the soot refractive index (/)

   $f(d)$ is the particle diameter distribution function (/)

   d is the particle diameter (m)

   $C^{ext}(d,m)$ is the extinction cross section for the particle diameter d (m^{-2}sr^{-1})

When the size parameter $x_p = \pi \dfrac{d_p}{\lambda}$ is small enough, C^{ext} is given by the Rayleigh approximation:

$$C^{ext} = \frac{-\pi^2}{\lambda} E(m) d^3$$

With $E(m) = Im\left(\dfrac{m^2 - 1}{m^2 + 2} \right)$

The extinction coefficient is the main value used to represent smoke opacity. It provides information on the ability of people to find egress paths, see exit signs, etc, in a smoke-filled building.