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The assessment of fire hazards, tenability and human evacuation behaviour for fire safety engineering design
Erasmus Mundus Programme

Yields of toxic products and smoke in fires – use and misuse of small-scale tests

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Toxicity tests and toxic hazard

Is it realistic to classify reaction-to-fire properties of a material or product (such as ignitability, heat release and flame spread) using small-scale tests?

Up to a point YES because these small-scale tests measure relatively fundamental properties of materials and products operating at any scale that can be used to predict full-scale fire behaviour

Is it realistic to represent "toxicity" or toxic hazard of a material or product in terms of a single number generated using a small-scale combustion toxicity test?

NO because:

- Toxic hazard is a property of a full-scale system depending upon the time-varying dynamics of fire growth and effluent spread in specific fire scenarios
- Toxicity involves a time varying set of different physiological effects
- Yields of toxic species and hence toxicity from any material or products are variables which depend upon the combustion conditions.
  (decomposition conditions in existing toxicity test methods give a poor representation of those in any full-scale fire)

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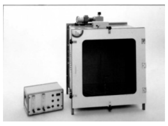
Bench-scale "toxicity" tests



NES 713

ISO Smoke chamber

NFX 70-100 tube furnace – decomposes 1g and collect gases

None of these produce combustion conditions relevant to actual defined fire conditions

Cannot measure yields as a function of equivalence ratio

Do not measure decomposition mode (flaming or non-flaming)

Do not measure "upper layer" temperature

All use simplistic toxicity index

Static boxes result in losses to walls

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Simplistic toxicity test index

Table B.1 BS 6853-1 — IDLH values

Gases IDLH values: "Immediately dangerous to life or health" after 30 minutes

	p.p.m.	mgm–3
Carbon dioxide	40 000	73 000
Carbon monoxide	1 200	1 400
Hydrogen fluoride	30	25
Hydrogen chloride	50	76
Hydrogen bromide	30	101
Hydrogen cyanide	50	56
Nitrogen dioxide + Nitric oxide	20	38
Sulfur dioxide	100	270

Individual gases expressed as fractions of limit concentration then summed to find overall index

- Does relate to effects in humans
- Does not take into account development time of effects – not time-based
- Does not take into account realistic interactions between gases
- No relationship between test decomposition conditions and specific fire conditions

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Toxic fire hazards

Toxic hazard evaluation for buildings or products:

1. Time-concentration curves for major products in full-scale scenario which depends on:

- **Fire growth curve (mass loss rate of fuel [kg/s])**
  Cone calorimeter, SBI, large-scale test, heat of gasification, heat of combustion
- **Yields of toxic products under a range of combustion conditions (e.g. kg CO/kg material burned)**
  ISO TS19700 tube furnace, ASTM E2058 flammability apparatus

Input data into CFAST or FDS to calculate time concentration curves for different specific fire scenarios with specified boundary conditions

2. Physiological effects of the products

exposure concentrations [$kg.m^{-3}$] or exposure doses [$kg.m^{-3}.min$] required to cause toxic effects in terms of :

- **concentrations or doses likely to impair escape efficiency**
- **incapacitating exposure concentrations or doses**
- **lethal exposure concentrations or doses**

Physiological FED methods in ISO 13571, Purser SFPE Handbook, BS7899-2
Combine 1 and 2 to calculate time to incapacitation.
Compare with specified acceptable tenability time for the end use scenario

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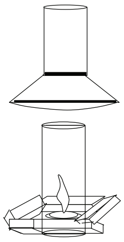
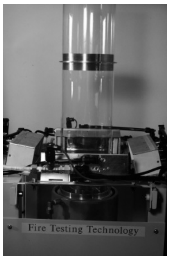
For evaluating building design scenarios or testing products

- Fire effluent toxicity: a set of physiological effects occurring over different time-scales: concentration-related (smoke and irritants) or dose-related (asphyxiants and heat)
- Toxic hazard is a property of a full-scale system depending upon the time-varying dynamics of fire growth and effluent spread in specific fire scenarios
- Toxic product yields vary considerably with combustion conditions
- "Toxicity" cannot be represented by a single number from a small-scale toxicity test.
- Rather, toxic hazards should be expressed in terms to tenability times in end-use scenarios, measured or calculated using full-scale tests, or fire dynamics modelling and test data, combined with physiological tenability algorithms
- This approach is used for performance-based building design and could be developed to test products against standard end-use performance criteria

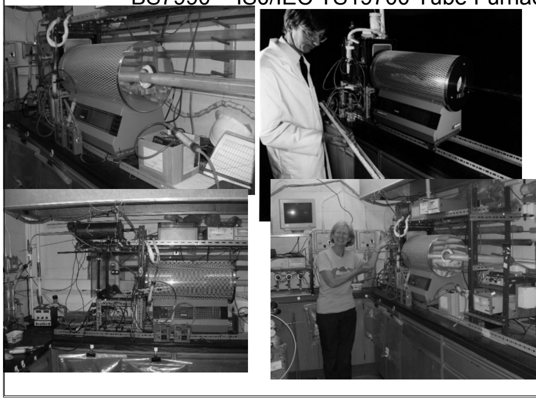
David Purser Factory Mutual ASTM E2058 fire propation apparatus

Bench-scale methods enabling toxic product yields to be measured as a function of equivalence ratio





David Purser BS7990 – IS0/IEC TS19700 Tube Furnace



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Toxic product yields in fires

There are thus three basic ways of using yield data for hazard calculations:

- Use a simple generic constant for smoke and each toxic product
- Use different generic constants for different basic types of fire condition:
  - Non-flaming
  - Early well-ventilated
  - Pre-flashover vitiated
  - Post-flashover
- Use different generic constants for different classes of materials under different fire conditions
- Use an expression to calculate yields for different material classes (or individual materials) as a function of equivalence ratio with time during the fire. For this it is necessary to obtain the calculation expressions derived from experimental data and to calculate global equivalence ration (phi) with time during the fire.
- A more complex method used in conjunction with CFD modelling is to use chemical kinetics equations to calculate product formation.

The method of choice depends upon the sensitivity of the results to the approximations used, and the accuracy of the other stages in the calculation – such as the fire growth rate.

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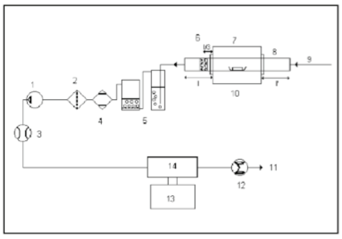
French NFX tube furnace



1 Pump
2 Particle filter
3 Flow meter
4 Drying filter
5 Impingers
6 Silica wool
7 Furnace
8 Tube
9 Dry air inlet
10 Boat + sample
11 Outlet
12 gas counter
13 Data collection
14 Gas analyzer

Figure 7 — Schematic of the French tube furnace.

- Full apparatus
- Of limited use as combustion conditions poorly defined

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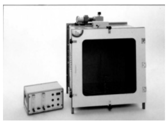
Bench-scale "toxicity" tests



NES 713

NES 713 – simple box with sample placed above a Bunsen burner

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Bench-scale "toxicity" tests

ISO Smoke chamber

Originally a smoke density test now Used by IMO and Airbus as a toxicity test – and being developed by ISO/SC1 for use as a "toxicity" test using FTIR gas measurements,

Sample is heated with Cone heater and products dispersed in static box

- no control or definition of combustion conditions
- no mixing of gases so measured concentrations cannot be used to assess yields
- Poor representation of full-scale fire conditions
- Static chamber so serious losses of gases to walls

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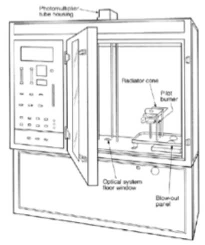
ISO smoke box



This physical fire model is used in ISO 5659-2 [20] and NFPA 270 [21]. It was designed to generate smoke optical density and toxic gas concentration data for qualification of materials.

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NBS toxicity test

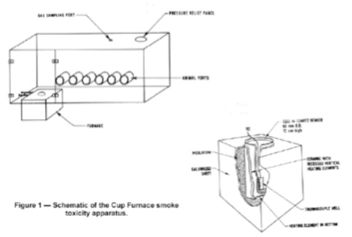

Figure 1 — Schematic of the Cup Furnace smoke toxicity apparatus.

- Sample dropped into crucible under non-flaming and flaming decomposition conditions
- Products evolved into static box so losses on walls
- Combustion conditions not well defined but more or less well-ventilated flaming
- No longer used but extensive database of rat lethality data coupled with gas measurements so useful for development of toxic gas interaction models

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Development of improved model

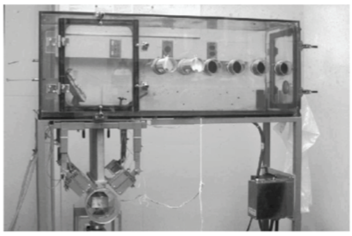

Figure 2 — Photograph of the NFPA 269 apparatus.

- Sample as small strip irradiated from above. Gases rise through slit into closed chamber.
- Non-flaming and flaming decomposition conditions
- Products evolved into static box so losses on walls
- Combustion conditions not well defined but more or less well-ventilated flaming
- Not currently used but extensive database of rat lethality data coupled with gas measurements so useful for development of toxic gas interaction models

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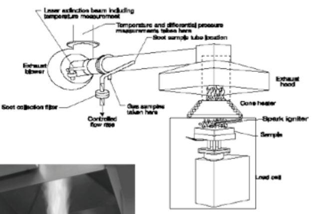
Cone calorimeter and vitiated cone



natic of the Cone Calorimeter.

- Sample as small disc irradiated from above. Gases rise through cone heater and drawn through duct.
- Non-flaming and flaming decomposition conditions
- Products carried through steel duct so losses on walls and heavily diluted
- Main combustion condition is extremely well-ventilated fire case
- Vitiated Cone version has Cone heater mounted above a box through which Air-N_2 mixture is passed.

For vitiated case a chimney is placed above the cone so during early stages combustion conditions can be defined in terms of phi. As heat release rate increases flames pass from top of chimney so that secondary combustion results in well-ventilated flaming

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University of Pittsburgh test

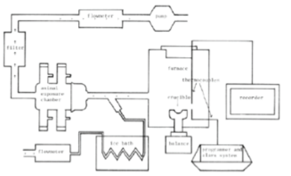

Figure 5 — Schematic of the University of Pittsburgh furnace.

- Another crucible method widely used in the 1970's with mice
- Data of very little value since combustion conditions are not defined and change throughout the test and there are few analytical data for gases available

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German DIN 53436 method

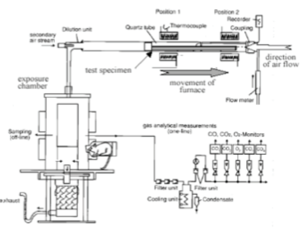

Figure 6 — Schematic of the DIN furnace.

- Moving tube furnace method early pre-cursor to ISO 19700 method.
- Some limited rat lethality and analytical data available
- Combustion conditions poorly defined so of limited use for yield estimated in relation to full-scale fires
- Method still used sometimes in Europe

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Japanese toxicity apparatus

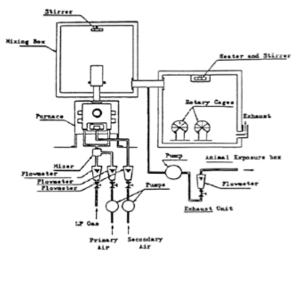

Figure 12 — Schematic of the Japanese smoke toxicity apparatus.

- Another static box method of limited relevance to fire conditions
- Exposes mice on a treadmill

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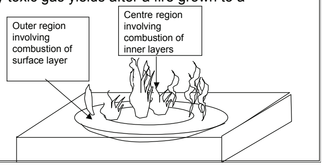
Surface irradiation of total combustion?

- In all these tests there are two main ways to heat the sample – either by irradiation from above or all round heating of whole sample
- For a homogeneous material it doesn't matter but for a layered composite such as a kitchen worktop or an armchair the initial decomposition (approximately the first 1-2 minutes or a flaming fires) both in surface irradiation tests such as the Cone Calorimeter and full-scale fires is of the upper layer.
- Once the fire has grown and is spreading sufficiently to be serious the burning object is more totally involved, so that in the middle of the fire the inner layers are exposed while at the edges new surface material is burning. Later on the whole item is likely to be fully involved.
- For this reason it is proposed that a method combusting the whole sample provides the best indication of likely toxic gas yields after a fire grown to a sufficient size to be hazardous.



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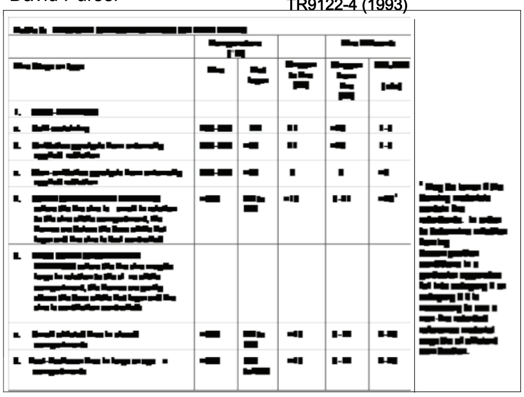
Fire Classification-BS7899-2(1999) and ISO TR9122-4 (1993)



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Applications of tube furnace data

- Fire model - A small scale combustion apparatus which decomposes materials and products so that the yields of toxic products can be measured
- Yield data can be used as input data for full-scale fire model
- FED model used to calculate time to incapacitation of exposed human subjects.
- Alternatively: Rodent Lethal FED Toxic potency calculation model can be used to calculate LC_{50} concentration of gas mixtures for rats. If rats are exposed to the atmosphere from the fire model at the same time it is possible to determine the extent to which the observed toxic effects from different materials can be explained in terms of the measured gases.
- This is useful to determine if different materials produce any toxic gases other than the small number of common gases considered important.

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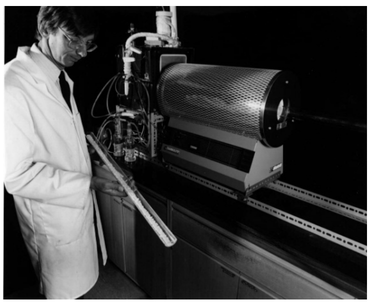
ISO 19700 tube furnace



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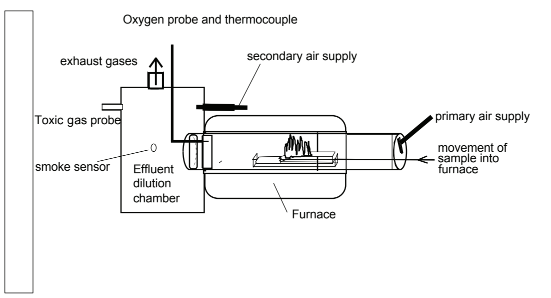
Data:Oxygen and temperature in furnace;CO_2, CO, other gases and smoke in chamber

The ISO 19700 Tube Furnace



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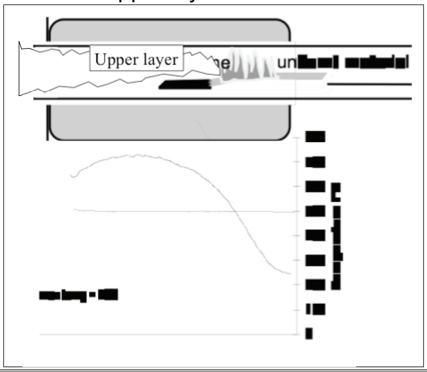
Formation of an upper layer in the ISO Furnace



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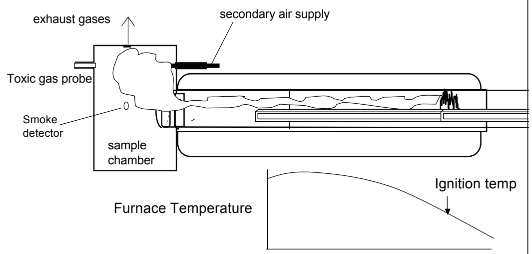
Steady state burning in the Purser Furnace



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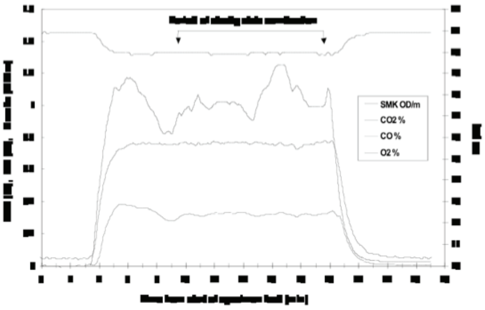
Combustion profile for PMMA - vitiated flaming conditions



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Apparatus variables

- ➔ **Decomposition temperature** **(ambient - 1000^{o}C)**
- ➔ **Primary air flow rate** **(1.0 - 20 l/min)**
- ➔ **Secondary (dilution) air flow rate** **(30 - 50 l/min)**
- ➔ **Specimen feed rate** **(0.5 - 3.0 g/min)**

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Fire decomposition conditions replicated by the Purser Furnace method

- Non-flaming/smouldering decomposition
- Well ventilated flaming decomposition
- Vitiated flaming decomposition
  - Small vitiated fires in enclosed spaces
  - Post-flashover vitiated fires in large or open enclosures

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Derived and measured parameters

- **Mass charge concentration** **(mg/l)**
- **Mass loss concentration** **(mg/l)**
- **CO_2/CO ratio** **(Volume ratio)**
- **Oxygen consumed** **(g/g)**
- **Mass loss / oxygen ratio** **(g/g)**
- **Yields of smoke and gases** **(g/g)**

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Yields of toxic products in full-scale fires and small scale tests: dependency on ϕ the equivalence ratio

- Although flaming fires can be classified into the general types defined by ISO SC3, in practice the yields of toxic products including CO and CO_2 vary continuously depending upon the fuel/air ratio in the fire plume
- For common hydrocarbon fuels and common polymers (non-fire retarded) the relationship between ϕ and yields of products such as CO have been plotted using a range of large scale and small scale fire tests (Pitts, Beyler, Gottuk, Tewarson)
- For the tube furnace test, it is possible to express the results in terms of ϕ
- The advantages are that all polymers can be compared on a common fundamental basis and data from the tube furnace can be compared to the results from large scale fires.

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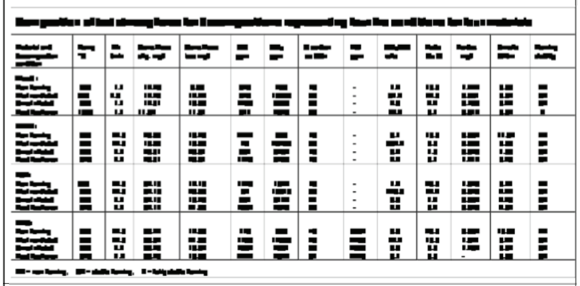
Test results



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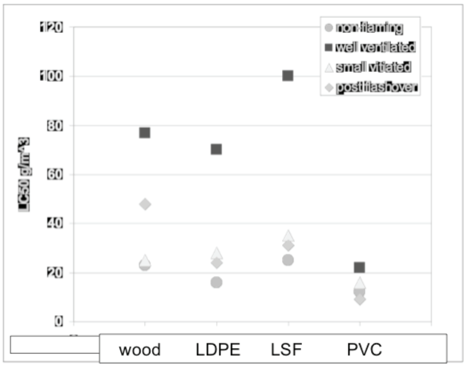
Summary of toxic potency estimations



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Effect of ϕ on LC_{50}