# Characterization and Toxicity of SMOKE

Harry K. Hasegawa

**EDITOR** 



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The quality of the papers in this publication reflects not only the obvious efforts of the authors and the technical editor(s), but also the work of these peer reviewers. The ASTM Committee on Publications acknowledges with appreciation their dedication and contribution of time and effort on behalf of ASTM.

# **Foreword**

This publication, Characterization and Toxicity of Smoke, contains papers presented at the symposium of the same name held in Phoenix, Arizona on 5 Dec. 1988. The symposium was sponsored by ASTM Committee E-5 on Fire Standards. Harry K. Hasegawa, Lawrence Livermore National Laboratory, presided as symposium chairman and was editor of this publication.

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# Overview

Statistics have consistently shown that a large proportion of fatalities from fires are caused by the inhalation of smoke<sup>2</sup> rather than exposure to the thermal effects of fire. Similarly, extensive damage to property can be attributed to the physical and chemical properties of smoke even when the actual fire has been relatively small. Although, historically, much of the blame has been placed on man-made synthetic polymers, all burning organic materials will generate smoke with the potential to threaten life and property. In terms of life safety, physical properties of smoke such as particulate concentration hamper or prevent the safe exiting of buildings. Toxic effects in the form of asphyxiation and irritation incapacitate and kill in fire situations. The severity of damage to property is dependent on the chemical composition of the smoke and/or the physical properties. Corrosive effects on building structures and contents have become an area of great concern and have prompted a number of regulating bodies to restrict or prohibit the use of materials identified as generating corrosive smokes, e.g., halogenated cable and wire insulations. These regulations raise many questions as to the appropriateness of certain tests in what they measure and how the results are obtained. Until recently, the major thrust of fire research, fire modelling, and standard fire tests dealt with the thermal aspects of fire with smoke as a secondary component. A significant reason for this emphasis was the extreme complexity and magnitude of the many aspects of smoke. However, the following collection of papers will demonstrate that there is a great deal of leading edge research underway in the characterization and toxicity of smoke.

This special technical publication (STP) has been published as a result of the 1988 symposium on Characterization and Toxicity of Smoke held in Phoenix, Arizona in an effort to provide regulators, producers, users, and researchers with an overview of the most current studies in the many facets of smoke. The symposium was conceived within ASTM Subcommittee E 5.32 on Research. The intent was to solicit papers dealing with as many different aspects of smoke as possible. The reader will find a variety of studies which address topics such as smoke hazard assessment, smoke spread modeling, appropriateness of toxicity tests, appropriateness of animal species as human substitutes, effect of materials on "nuclear winter," etc.

A collection of twelve papers published in this volume has been separated into three broad categories. These categories are smoke toxicity, smoke chemistry, and smoke characterization.

# Smoke Toxicity

The papers in this section are divided between quantitative research on smoke toxicity and methodologies to use test results as part of an overall methodology to assess the toxic hazard

<sup>&</sup>lt;sup>1</sup> Fire and Smoke: Understanding the Hazards. Committee on Fire Toxicology, Board of Environmental Studies and Toxicology Commission on Life Sciences, National Research Council, National Academy Press, Washington, DC, 1986.

<sup>&</sup>lt;sup>2</sup> Smoke is defined by ASTM E 176 as "the airborne solid and liquid particulates and gases evolved when a material undergoes pyrolysis or combustion."

of materials. Hinderer and Hirschler present an extensive work which presents an update of information regarding the toxicity of polyvinyl chloride (PVC) smoke and of hydrogen chloride (HCL). Because animals are being used as models for humans in toxicity tests, special attention is given to the sensitivity and appropriateness of certain animal species for specific small-scale tests. The paper also discusses the fate of HCL in realistic fire atmospheres. The authors provide a nice overview on the toxicity of PVC smoke, studies on HCL toxicity, and test methods to measure the toxic potency of smoke produced from burning materials. Some of their conclusions include:

- 1. There is no single toxicity for the products in PVC smoke; it can vary widely.
- 2. The toxic potency of the smoke from most PVC products is similar to that of most ordinary products in use in society.
  - 3. HCL decays rapidly in a fire atmosphere while CO does not.
- 4. Toxicity tests based solely on LC<sub>50</sub>s cannot predict toxic hazard, and the UPITT test is less satisfactory than other tests.

Tewarson presents data to analyze the relationship between the combustion behavior of materials and the toxicity of the resultant environment. The author uses a toxicity relationship suggested by researchers at the National Institute of Standards Technology on the synergism between CO and CO<sub>2</sub> and data measured in the Factory Mutual Small-Scale Flammability Apparatus. He uses the relationship to examine the effects of chemical structure, fire ventilation, and dilution of fire products on the toxicity, created by CO and CO<sub>2</sub>, of the environment. In closing, Tewarson applies his findings to small-scale toxicity tests.

The paper by *P. J. Briggs* presents a potential methodology for smoke hazard assessment that considers fire test, product design, and room scenarios in a way that would reflect the dangers of a product in a realistic fire situation. This proposed methodology would prevent misinterpretation of test data which can occur when smoke test data is compared in isolation without reference to other fire parameters. The author reviews and evaluates the current status of selected small-scale smoke tests as well as large-scale room tests. A standard protocol for smoke hazard analysis is presented with the following components:

- 1. Fire scenario definition and probability of occurrence.
- 2. Consideration of ignitability.
- 3. Consideration of fire growth.
- 4. Consideration of smoke test data.
- 5. Consideration of rate of smoke hazard development.

Clarke, van Kuijk, and Steele also present a global toxic hazard assessment tool which is specifically oriented to burning electrical cables. This tool for fire hazard assessment utilizes small-scale fire property tests, computer modeling, and full-scale tests to estimate cable smoke hazard in a fire environment. The paper provides an update on predicting cable toxic hazard using a modified Harvard V mathematical model and how laboratory-based hazard prediction methods, i.e., toxic potency and the newly established NIBS test, compare with toxic hazard assessment in their ability to distinguish between the performance of several different kinds of cable. Material input data for the model were obtained from lab scale tests such as the Cone Calorimeter and Lateral Ignition and Flammability Tester (LIFT). Model-based predictions were compared to two-full-scale fire test series of various cable insulating materials. One of the authors' conclusions is that no laboratory test by itself can make allowances for the conditions of use in more than one fire scenario. Therefore, hazard assessment, whether by mathematical modelling and small-scale testing or by full-scale fire test, will remain the most reliable method of determining relative cable performance.

Norris presents an investigation of dual LC<sub>50</sub> values for red oak from combustion toxicity testing using the University of Pittsburgh Combustion Toxicity (UPITT) apparatus. No report of any material displaying a dual LC<sub>50</sub> value had been made to this point in time. Since red oak was the first reported to have this dual value, white oak, southern pine, and Douglas fir were also selected for testing. The study also attempts to correlate the maximum concentrations and concentration  $\times$  time (Ct) products of carbon monoxide (CO), the ratio of carbon dioxide (CO<sub>2</sub>) to carbon monoxide, and Maximum  $\partial$  Temperature Area with LC<sub>50</sub> values. As a result of the study, three LC<sub>50</sub> values were found for red oak and southern pine, while one was found for white oak and Douglas fir. Maximum CO concentrations offered no correlation with the LC<sub>50</sub> values. The Ct products of CO did not clearly correlate with the LC<sub>50</sub> values. The Maximum  $\partial$  Temperature Area indicated there was a continuous change in burning characteristics as the specimen weight increased, but it did not correlate with the LC<sub>50</sub> values.

# Smoke Chemistry

Two of the papers in this section address corrosive aspects of smoke while the third relates to animal toxicity studies. Ryan, Babrauskas, O'Neill, and Hirschler propose a series of criteria and a specific test method to measure the corrosive effects of combustion products. The paper addresses the emergence of the corrosion issue and attempts to formulate an appropriate response to it. One of the authors' contentions is that laboratory tests proposed to date to measure the corrosive effects of combustion products all have significant deficiencies; some methods are not performance-based at all and are merely tests for pH. In others, unrealistic specimen heating or unrealistic exposure targets are used. These shortcomings are addressed by sections on fire hazard assessment, damage from corrosion-related effects, and test development. Ten criteria for an acceptable test for corrosion and related damage listed by the ASTM E5.21 TG70 Task Group are used to evaluate a number of laboratory tests. The authors' conclusions call for a systematic and rational means for assessing actual corrosivity performance of materials and to develop an acceptable test.

The paper by *Grand* describes a laboratory method for the combustion of PVC and other polymeric materials in such a manner as to produce a constantly flowing, steady-state atmosphere for animal toxicity studies. Although the method is based on the principles of the German Standard DIN 53 436, the method described has a much larger combustion tube and specimen, greater versatility in specimen size and air dilution rates, utilizes radiant heating, and has achieved continuous flaming as well as nonflaming. Because hydrogen chloride gas has a tendency to "decay" from smoke atmospheres, this flow-through combustion system was developed to provide a constant level of HCL in PVC smoke for between 15 and 30 min. Other materials (besides PVC) used to evaluate this methodology included: Douglas fir, flexible polyurethane foam, and two rigid polyurethane/polyisocyanurate foams. Primary conclusions from this study were:

- 1. The apparatus performed very well for its intended design—combustion of PVC. Steady-state combustion of PVC was maintained for 20 to 25 min flaming, and for approximately 60 min nonflaming.
- 2. From the three other materials tested, it appears from the experiments conducted so far that the device is more suited to materials that burn relatively slowly.

Another paper dealing with the smoke generated from burning electrical cables is presented by *Tewarson* and *Khan*. Their study describes results for the generation of smoke in terms of smoke yield, mass optical density, and specific corrosion constant for electrical cables during fire propagation. The authors use the results of this study to classify cables into

three groups based on the Fire Propagation Index. Small-scale cable fire propagation experiments were performed in the Factory Mutual Small- (50 kW-) and Intermediate- (500 kW-) Scale Flammability Apparatuses. Large-scale cable fire propagation experiments were performed in the Factory Mutual Large- (5000 kW-) Scale Flammability Apparatus. Preliminary conclusions from the study suggest that nonthermal fire damage is not expected if the following conditions are satisfied: (1) fire propagation index is less than 10; (2) yield of smoke is less than 0.03 g/g; (3) mass optical density is less than  $0.11 \text{ m}^2/\text{g}$ ; and (4) the specific corrosion constant of the cable is less than  $0.92 \times 10^{-6} \mu\text{m/h}$  ppm.

## Smoke Characterization

The final section on smoke characterization contains four papers that deal with the physical properties of smoke, from micro to macroscales. *Newman* presents a study on smoke transport and characterization in large enclosure fires to complement detailed laboratory results for smoke particulate properties (e.g., volume fraction, mass concentration, generation efficiency, particulate size, and particulate yield). Fire experiments of fire sources, including heptane, methanol, propylene, PMMA, and various electrical cable types with variable forced ventilation conditions, were performed in a large heavily instrumented enclosure. Results of this study discuss heat release rates, fire product transit times, temperature distributions, distribution of carbon dioxide concentration, distribution of smoke particulate concentration, and ventilation effects.

In contrast, *Tran* reports on a comparative study of smoke generation from red oak and Douglas fir plywood using the National Bureau of Standards (NBS) smoke density chamber and the Ohio State University (OSU) heat release rate calorimeter. In the NBS smoke chamber, three nonpiloted heating fluxes of 2.0, 2.5, and 3.0 W/cm² were used for each material. A total of 90 tests were conducted (two materials, three flux levels, five durations, and three replicates). Comparative data were obtained of smoke release rates (SRR) from red oak and Douglas fir plywood at a nonpiloted heat flux of 2.5 W/cm² in the OSU apparatus. The conditions were analogous to those in the NBS unit at the same heating flux, except that in the OSU apparatus, the smoke was swept out continuously. The unit of particulate mass produced per unit area was found to be an appropriate basis to compare the data from the two apparatuses. Although the reduced data from the two methods were of the same order of magnitude, the data could not be reconciled exactly.

Fleischmann et al. present a study which has global implications as input into predictions for "nuclear winter." The concept of "nuclear winter" has been postulated with a number of assumptions regarding the smoke produced by postnuclear exchange fires. The general premise is that following the use of nuclear weapons, sufficient smoke would be generated from fires and deposited in the atmosphere to cause a decrease in the incident solar energy reaching the earth's surface. The paper describes results from a series of "medium-scale" (200 to 1000-kW) smoke experiments of representative urban fuels such as wood, plywood, asphalt roofing, and liquid hydrocarbons burned in the open with no ventilation restrictions. In addition, some of the fuels were burned in a test room under limited ventilation conditions. Smoke was characterized by the mass of airborne particulates, the size and distribution of the particulates, i.e., "graphitic" or "black" carbon and organic carbon. Mass loss and heat release rate were recorded during each experiment to characterize combustion. Results of the 16 experiments demonstrated the considerable influence of the compartment on smoke production. The smoke emission factors measured for wood cribs burning in the compartment were more than an order of magnitude higher than those burning in the open. Conversely, the fuel oil burned in the compartment produced significantly less smoke than being burned in the open. Results for asphalt shingles demonstrated the significant impact a single material might have on the urban smoke production in a post nuclear war environment. The smoke emission factors found for asphalt roofing shingles, averaged for two experiments, was over 12% with more than 60% being black carbon.

The final article by *Tamura* and *Klote* presents a study to develop a fire-safe elevator for evacuating handicapped people and for aiding firefighters. The paper describes methods for calculating pressure differences caused by wind and stack action and the results of tests conducted in the ten-story experimental fire tower of the National Research Council of Canada National Fire Laboratory. The researchers' conclusions included the following:

- 1. Good agreement was found between experimental results and stack effect theory over a wide range of leakage conditions representative of many commercial buildings.
- 2. For the conditions of these experiments, the adverse pressure differences of stack action and fire can be added to provide a good approximation of the pressure difference resulting from the two acting in combination and, hence, the amount of pressurization required to prevent smoke migration into elevator lobbies under these conditions. A broken window can result in a jump in pressure differential, which is an important design consideration.
- 3. Mechanical pressurization of the elevator shaft or lobbies greatly reduces the possibility of smoke contamination of these spaces due to stack action.
- 4. Although further studies of wind effects are needed, mechanical pressurization of the elevator shaft greatly reduces the possibility of smoke contamination of elevator shafts and lobbies due to wind action.

The papers summarized above should provide the reader with an overview of state-of-theart information pertaining to the very broad and complicated field of smoke research. One conclusion common to all studies is that further work is needed in the understanding and characterization of smoke. The selection of papers reflects the efforts of the symposium committee to provide a program that touched on as many areas of ongoing research in smoke as possible. The symposium committee gratefully acknowledges the efforts of the authors and ASTM personnel who have made this publication possible.

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