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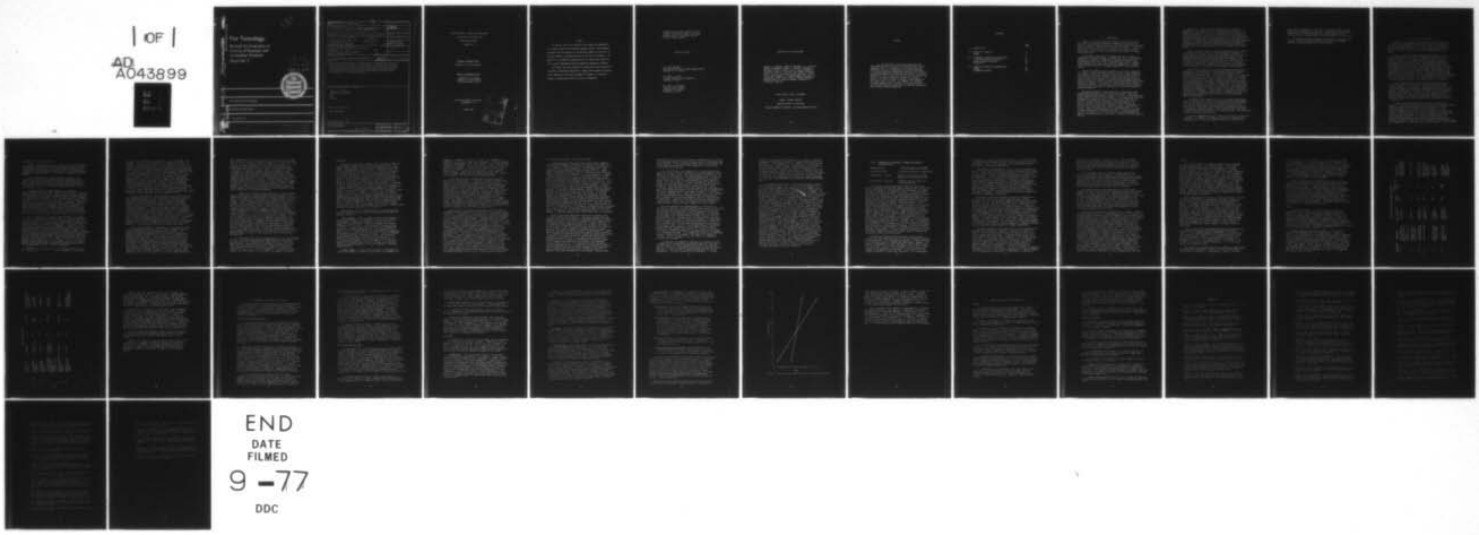

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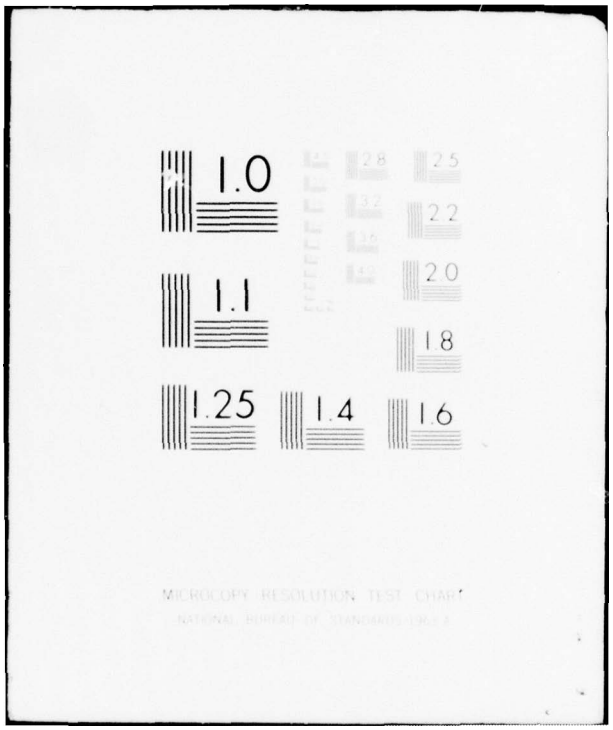
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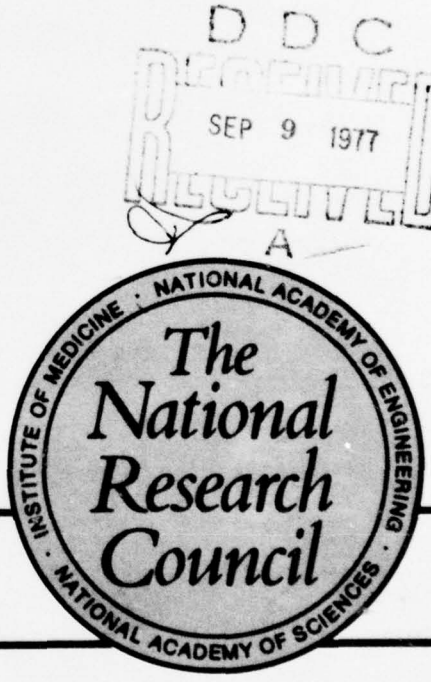
Fire Toxicology:

Methods for Evaluation of Toxicity of Pyrolysis and Combustion Products

Report No. 2



Committee on Fire Toxicology

Assembly of Life Sciences

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16. Abstracts

After reviewing methods currently being used for evaluating the toxicity of pyrolysis/combustion products, the Committee has concluded that acceptable screening tests for evaluating these toxicities are not currently available, as all present methods have one or more shortcomings. The Committee has prepared guidelines for developing the needed methodology and has made recommendations for additional research.

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FIRE TOXICOLOGY: METHODS FOR EVALUATION OF TOXICITY OF PYROLYSIS AND COMBUSTION PRODUCTS

Report No. 2

A Report Prepared by the

Committee on Fire Toxicology

Under the Auspices of the

Committee on Toxicology
Assembly of Life Sciences
National Research Council

National Academy of Sciences
Washington, D.C.

August 1977

NOTICE

The project that is the subject of this report was approved by the Governing Board of the National Research Council, whose members are drawn from the Councils of the National Academy of Sciences, the National Academy of Engineering, and the Institute of Medicine. The members of the Committee responsible for the report were chosen for their special competences and with regard for appropriate balance.

This report has been reviewed by a group other than the authors according to procedures approved by a Report Review Committee consisting of members of the National Academy of Sciences, the National Academy of Engineering, and the Institute of Medicine.

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Preface

At the request of the National Aeronautics and Space Administration (NASA) and the Consumer Product Safety Commission (CPSC), the Committee on Fire Toxicology has undertaken the tasks of evaluating the state-of-knowledge in fire toxicology and recommending guidelines for establishing standard approaches for testing the toxicity of polymeric materials in fires. Both NASA and CPSC have concerns for the toxicity of pyrolysis/combustion products of polymers; however, the type of polymer of concern to each agency may vary greatly due to its use. For example, the thermally resistant polymer used to insulate the electrical system in an aircraft and the polymer used in household furnishings may be vastly different materials.

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I. INTRODUCTION

Fires in the United States have become a very serious concern. They cause an estimated 12,000 deaths, 300,000 injuries, and $11.4 billion in property damage annually in the United States.[34] This nation leads the industrialized world in fire deaths per capita. The rate is nearly twice that of second-ranking Canada. The majority of fire victims die by inhaling smoke or toxic gases well before the flames have reached them.

One approach to decreasing fire damage has been to reduce the flammability of materials used to construct and furnish buildings and transportation systems. Flammability standards have already been established for many items such as carpets and mattresses. Because flame retardants are often used to meet the flammability standards, their production rates have increased dramatically during the past decade.

Because this approach does not address the problem of smoke and toxic gases, it may not decrease deaths or injury. Flame retardants can undergo pyrolysis when exposed to heat and may produce products that are more toxic than those that would result from flaming of the untreated combustible material.[40] Untreated wool produces primarily carbon dioxide, water, carbon monoxide and nitrogen oxides under flaming conditions; however, during pyrolysis, hydrogen cyanide and organic cyanides are produced. The deaths of some aircraft crash victims have been attributed to poisoning by combinations of carbon monoxide and hydrogen cyanide.[30]

The state-of-the-art in fire toxicology is considerably underdeveloped when compared to other areas of toxicology. Relatively standard approaches are used to evaluate the toxicity of food additives, drugs, cosmetics, and pesticides; however, no such approaches have been developed to evaluate the toxicity of products resulting from the pyrolysis and combustion of materials. The rapid growth of the synthetic polymer industry has significantly increased both the quantity and types of materials involved in fires. Investigations on the toxicities of pyrolysis and combustion products began in the fifties. Many of the publications that resulted deal with the types of gases produced from the different polymers. Standard approaches need to be developed to assist engineers in selecting materials for specific uses based partly on the toxicity of their pyrolysis/combustion products.

Based on its literature review, presentations by selected researchers to the committee, and the experience of its members, the committee concluded that there are no acceptable screening tests to evaluate relative toxicities of pyrolysis and combustion products of polymeric materials. All present methods have one or more shortcomings. It further concluded that the state-of-knowledge in fire toxicology precludes the establishment of a standard protocol for screening materials. However, the committee has developed some guidelines that would limit the variables so that the data obtained could serve as a basis for devising screening systems and results could be compared among laboratories.

There is an urgent need for reliable screening methods to identify materials which evolve highly toxic products when subjected to either pyrolysis or flaming conditions. An adequate screening method should provide a basis for ranking materials into toxicity groups; however, relevance to the real fire situation would depend on the intended use of the materials and other factors. Since incapacitation is related to the ability to escape the fire scene, this end point should be stressed in any screening method as well as the measurement of acute toxicity. Toxicity data must be used to evaluate hazard.

Shortcomings and limitations of all screening procedures must be emphasized. To be practical, a screening method must be economical and relatively easy to conduct. This probably eliminates tests simulating a large-scale "real fire" situation; however, it is important that the toxic pyrolysis/combustion products produced in a screening system be representative of those occurring in a "real fire". Since the screening system is designed to identify highly toxic materials and to rank materials, the primary toxic agent might not be identified nor would the mechanism of toxicity be determined. The results from screening systems for determining the toxicity of pyrolysis/combustion products are comparable to "range-finding" studies used to determine the toxicity of chemicals. In many cases, a screening system will not provide all the information required about the material; however, the results should certainly provide a sound basis for planning more definitive experiments.

This report briefly describes most of the current methodologies used to investigate the toxicity of pyrolysis and combustion products. Although many gaps in the scientific knowledge must be filled before protocols for standardized screening methods can be written on a scientifically sound basis, the committee has recommended guidelines for developing screening systems. These guidelines limit the number of variables in a screening method in three major areas: burn conditions, exposure conditions, and end points.

Detailed recommendations cannot always be made due to the state-of-knowledge. For example, the committee considers the measurement of incapacitation to be the most important end point; however, no one

method can be recommended at this time. This report points out these areas in which research is needed. They are important for developing the basis for fire toxicology screening systems, and are not an inclusive list of research needs in the general area of fire toxicology.

This document is directed toward those persons in government and industry who are primarily concerned with reproducible standard methods for screening materials for fire toxicity.

II. REVIEW OF METHODOLOGY

The report by Zapp[49] marked the beginning of fire toxicology. It contained the assessment of toxic factors created by fire as well as protective measures against injury due to fire. He reported that excessive concentrations of carbon monoxide and deficiencies of oxygen - not direct thermal effects - were the predominant lethal factors.

In 1954, Coleman and Thomas[12] emphasized the necessity of determining whether any special fire hazards could result from new polymeric materials. They stressed the need to investigate the possible formation of toxic gaseous products during the combustion or decomposition of these materials. They degraded chlorinated plastics and determined their thermal decomposition products, which were primarily hydrogen chloride, carbon monoxide, and carbon dioxide. Considerable quantities of hydrogen chloride, corresponding to 30% of the chlorine content of the original materials, were evolved at the comparatively low temperature of 300°C. Traces of carbonyl chloride were evolved in some instances, but the quantities were small compared with those of the other gases. Materials decomposed included chlorinated polymethyl methacrylate, polyvinyl chloride, vinyl chloride and vinylidene chloride copolymer, and stabilized polyvinyl chlorides.

In 1962 MacFarland and Leong[29] reported the hazards from the thermal decomposition of polyurethane, polyurethane-coated nylon, and epoxy resins. In the same year, Zapp[50] discussed the toxicity of the thermal decomposition products. He compared the mortality of rats exposed to the decomposition products of different plastics produced under the same conditions. He concluded, "In judging the safety of a synthetic resin for a proposed use, the hazard from combustion or thermal decomposition should be compared under equivalent conditions with that of alternative materials which have, if possible, a history of similar use."

In 1968, MacFarland[28] discussed the problems of defining the toxicity of the pyrolysis products of plastics. These problems included dosage and variable decomposition products depending on the burn conditions as well as the composition of the plastic. In 1970, Autian[5] reviewed the toxicity of a number of combustion products. He discussed the needs for testing and for the development of standardized toxicity testing procedures. This need still exists and will be discussed later. A similar, less intensive review from Autian's laboratory[36] emphasized the urgent need to develop standard testing systems for rating the toxicity of burning materials. Two separate tests were recommended on the same material, one heating without the introduction

of flame and the other with flame.

Recently, numerous reports on the toxicity of pyrolysis/combustion products and on various evaluative methodologies have been published. In this report the committee has reviewed those methodologies that have been or are being used for polymers. Many of these methods were designed for research and were not intended to be applied as screening methods.

It was recognized in the Federal Republic of Germany that a standard method should be developed and that an appropriate way to assess the hazards of the pyrolysis products of a synthetic material was to compare their toxic effects with those of products formed by a conventional material.[25] The proposed standard method was limited to smoldering conditions.

In agreement with the German Commission of Standards, an apparatus was developed (DIN Draft 53 436 of August 1966)[25] to administer the toxic product to test animals. Essentially, the apparatus consists of a fused silica tube at least 1,000 mm long with an outside diameter of 40 mm and a wall thickness of 2 mm. An annular electric oven tightly enclosing the tube is moved around the tube. The oven is moved over the sample at the rate of 10 mm/min against the airstream. Kimmerle's[25] conditions for testing are as follows: Temperature of pyrolysis varies from 200°C-600°C in increments of 50°; air is supplied to the combustion chamber at a rate of 100 liters/hr, and air is mixed with the pyrolysis products at 100 or 300 liters/hr. The exposure chamber is a 50-liter box connected to the combustion chamber by a glass tube which has two angles, one, approximately 45° and the other about 150°.

With this apparatus, the heads of twenty male rats are exposed for 30 min. The observation period is normally 7 days but is extended to 14, if necessary. Concentrations of the most important gases are analyzed during the test; carboxyhemoglobin determinations and swimming tests are conducted at the end of the exposure. For comparing the toxicities of the pyrolysis products, emphasis is placed on the temperature range between those where no deaths occurred and those where deaths did occur with a given weight or given volume of sample. Based on equal volumes, polystyrene was the safest material tested; polyethylene, cork, pine wood and spruce plywood were in an intermediate group; and polyvinyl chloride, wood-chipboard, insulating board, hard board, and nitrocellulose were the most toxic. Based on equal weights, pine wood drops to a lower temperature toxicity group. A number of building materials were compared based on equal volumes. None of the synthetic polymers tested produced deaths below 400°C; however, spruce wood and cork produced deaths at 350°C and 300°C, respectively.

Hoffmann and Oettel[22] developed a test apparatus that complies with the temperature specified in the draft standard DIN 53436 except

the value of the temperature is read without the 1.5 min delay in the standard. Again the oven is passed over the sample at a velocity of 10 mm/min. Air at a rate of 100 liters/hr is forced through the tube counter to the motion of the oven. At the other end of the oven, this current of air and pyrolysis products are mixed with fresh air admitted at 100 liters/hr. The combined mixture is led through a glass distributor to rats which are kept in six small glass respiration chambers. The decomposition temperatures are 300°C, 400°C, 500°C, and 600°C. As a rule, the exposure period is 30 min and the experiments are repeated once or twice for a total of 12 to 18 animals at each temperature. Immediately in front of the respiration chambers the carbon monoxide content of the fumes is measured. Immediately after the exposure, the carboxyhemoglobin content of the animals' blood is determined. Death is the other end point. With sample weights of 5 g, a number of expanded polystyrenes were found to produce no deaths when pyrolyzed at 400°C or below. Expanded cork and rubber produced deaths when pyrolyzed at 400°C; wool, pine wood, felt and leather produced deaths when pyrolyzed at 300°C, which was the lowest temperature used.

Kishitani and Nakamura[26] have described two test methods, one for basic research and the other as a new method for judging the safety of a building material during a fire. The research test apparatus is composed of a combustion furnace, exposure chamber, and movement-detecting device. The combustion furnace has a gas burner and a quartz tube system with which the interior of the tube can be kept at a constant temperature. The combustion products generated are led by a natural draft into a 56-liter exposure chamber made of transparent glass which contains the movement detection device. The natural draft is created during the test by an exhaust at a rate of 4 liters/min from the exposure chamber through a smoke concentration meter. The three levels of heating temperatures are 350°C, 500°C and 750°C. The testing time is 15 min. The smoke and carbon monoxide concentrations are measured continuously and a sample of gas is collected from the exposure chamber every 1 to 3 min. to analyze for hydrogen cyanide or hydrogen chloride. Mice that survive the test are observed for 1 week.

The second test apparatus, developed for the screening of toxicity of building materials, consists of a combustion furnace,[26] dilution chamber, exposure chamber, and movement detection device. The specimen is heated by radiation from a 1.5 kw electric heater and a propane gas flame (contacting the bottom part of the surface of the specimen) from a gas burner. Three liters of air and 0.35 liter of propane gas are mixed every minute and delivered to the gas burner; 25 liters of air are delivered further into the combustion furnace each minute. The combustion products generated from the specimen as a result of the heating enter a 0.5 m^3 dilution chamber where they are adjusted to a suitable temperature and concentration. They are then led to the exposure chamber through a connecting tube with an inner diameter of 5 cm. The exposure chamber is a 0.5 m^3 stainless steel cube with a vent hole on one side. In the exposure chamber there are

eight movement-detecting devices, both "revolving" and "strain" types, each containing one mouse. Samples are heated with the gas burner for the first 3 min; then radiation heat is added for the next 3 min. After heating is stopped, exposures continue for 9 min more, making the exposure period a total of 15 min. A part of the gases produced is vented from the connecting tube at a rate of 10 liters/min to reduce the quantity of combustion products entering the exposure chamber. The temperature inside the exposure chamber is maintained at 30°C. Throughout the testing period, the concentrations of carbon monoxide, carbon dioxide, and oxygen within the exposure chamber and the exhaust temperature are measured continuously. Analyses are also made for hydrogen cyanide and hydrogen chloride. Toxicity evaluation is based on the state of activity of the mice. The combustion products impeded activity of the mice even when concentrations were fairly low. This suggests that humans in a burning building could become incapable of freely performing evacuation activities at the early stages of a fire due to toxicities of the combustion products.

Carter et al.[10] have described a modified 142-liter Bethlehem exposure chamber with Plexiglas® replacing the glass viewport. One viewport was removed and replaced with an airlock constructed so that the door on the chamber end of the airlock can be opened remotely from the outside. A stainless steel wire partition confines the rats to the forward third of the chamber where the pyrolysate is introduced. The pyrolysis chamber consists of a 1-in diameter stainless steel tube which delivers the pyrolysate directly into the exposure chamber. A Lindberg furnace equipped with a temperature controller produces the thermal decomposition. After the sample is placed in the pyrolysis tube, the pressure in the system is reduced to 600 torr. The preheated furnace is placed around the pyrolysis tube below the sample. The tube is then heated for 10 min prior to introduction of the sample. With the furnace and the pyrolysis tube at temperature equilibrium, air flow is initiated through the sample tube from a compressed air source at a rate of 100 cm^3/min. The sample is then moved into the hot zone where pyrolysis is initiated while the air flow moves the pyrolysate into the exposure chamber. After 30 min, when complete pyrolysis is assured, the furnace is removed. The air flow is then increased to bring the internal system to ambient pressure, simultaneously sweeping any residual pyrolysis products out of the combustion tube and into the exposure chamber. After the 30-min exposures, the rats are removed and observed.

In this method, acute toxicity studies are based on 48-hr postexposure survival. Gross and histopathological examinations are performed on all rats that survive this period and, where possible, on those that expire earlier. Carboxyhemoglobin is measured to determine if lethal levels are reached during the exposures. Samples for quantitating carbon monoxide and carbon dioxide concentrations in the chamber are obtained 0, 19, and 30 min during the exposures. Pyrolysis tests are conducted at 550°C and 800°C, and the amount of polymer for an LC50 is

determined.

Dressler[15] has designed an apparatus that includes a combustion chamber, animal chamber, various valves, and sampling ports. The animal chamber provides for the simultaneous exposure of 16 animals (rats), unrestrained and unanesthetized, in individual cages. One port provides for an environmental analysis; the other for ongoing physiological monitoring. All parts of the apparatus are Pyrex® with Teflon® gaskets, except for the modified self-cleaning oven. This facilitates cleaning, a prerequisite for obtaining reproducible results. The fuel load is placed in the combustion chamber on a weight or volume basis. A radiant heat source is used to either smolder or ignite the load at a predesignated temperature. The smoke is cooled by being drawn by in-line fans through a length of pipe. If increased temperature is desired, a heating element of Nichrome® wire is placed in-line; otherwise, the smoke proceeds either through a bypass or into the animal chamber. Following this, the smoke is either vented or returned on a closed circuit to the combustion chamber. Periodic samples are monitored by gas chromatography, and both the temperature of the combustion chamber and animal chamber are monitored. Selected animals are also monitored for temperature, respiratory rate, heart rate, electrocardiogram, carboxyhemoglobin, blood pH, and blood gases. Animals are exposed for 15 min to smoke produced from the burning of acrylic carpet, nylon carpet, vinyl flooring, urethane and rayon upholstery, and vinyl and paper wall covering. Aircraft carpet materials have also been tested by this method.[16]

Cornish et al.[13,14] have reported results from two drastically different exposure systems. Only male rats were studied under both exposure conditions.

Static Chamber: Groups of animals (usually 15) are exposed to the combustion products of the sample in a 1,500-liter stainless steel chamber. Polymers are combusted in a Vycor tube that is wrapped with resistance wire. Combustion temperature is usually reached within 1 to 2 min. A 700°C temperature is maintained for 6 to 10 min. Fifteen animals are kept in the static chamber and exposed to the combustion products, both vapors and particulate matter, for 4 hr. Animals are serially sacrificed, five immediately after exposure, five at 24-36 hrs, and five at 7 days for blood and tissue analyses and for histological studies. Carboxyhemoglobin determinations are made at the end of the exposure period. To determine the approximate LC50 for a particular polymer, groups of 15 animals are exposed in the static chamber to the combustion products of increasing quantities of the polymer being evaluated. These animals are observed for 7 days after exposure to determine delayed mortality.

Dynamic Chamber: In this system the sample is decomposed in a ceramic boat placed in a combustion furnace that is programmed for

temperature increases at the rate of 5°C/min. The temperature is measured in the combustion boat by a thermocouple. It usually reaches a maximum of approximately 700°C after 140 min, at which time pyrolysis is essentially complete. During the pyrolysis, 1 liter of air/min is passed over the sample. This airstream is cooled by dilution with an additional 2 liters of air/min prior to its entry into the animal exposure chamber. The animals are exposed in a Pyrex® glass tube containing small chambers that are constructed so that only the rat's nose is exposed to a flow of diluted pyrolysis materials.

The two exposure conditions described by Cornish et al.[13,14] are obviously very different. In the static chamber the animals are exposed to the total products of combustion for a 4-hr period. In the dynamic system the animals are exposed to the thermal degradation products only during the time that they are actually being released from the polymer, since the airstream carries the gases past the animal and out into the exhaust system. Thus, in the dynamic chamber, the animals may be exposed to a specific decomposition product for a relatively short time as products vary at different temperatures. Another difference is that volatile organics produced from the decomposing polymer are likely to be burned because of the flaming in the static chamber in contrast to the pyrolysis in the dynamic system. Concentrations of carbon monoxide, hydrogen chloride, hydrogen cyanide, and oxides of nitrogen are monitored in both exposure chambers. The natural product, wool, was among the least toxic when rapidly combusted, but among the most toxic after slow pyrolysis.

Moreci et al.[32] have extensively modified a National Bureau of Standards (NBS) Smoke Chamber[19] to expose mice to the gaseous products of pyrolysis. The apparatus consists essentially of a metallic chamber to which is attached a Plexiglas® ductwork for observation and exposure of test animals to circulating gases. A radiant heater with a power output of 2.5 W/cm^2 is used to heat the materials being evaluated. The ductwork contains an animal test chamber in which a group of four mice can move freely. A cylindrical holder restrains one animal. Monitoring usually includes electrocardiograms and recording of respiratory movements. Oxygen, carbon monoxide, and temperature are monitored in the exposure chamber. Periodic gas samples are collected from the chamber for later analysis by gas/liquid chromatography and mass spectrometry. The duration of the pyrolysis varies with each experiment. It usually ranges from 20 to 36 minutes. The experiments are terminated when the animals die or appear to be at the point of death. In the latter situation, the animals are immediately transported from the exposure chamber to fresh air to see if they will recover. Survivors are held for 1 week after exposure. Temperature in the animal exposure chamber does not exceed 34°C and oxygen never falls below 17.5%. Results of investigations using this system indicate that unique thermodecomposition products of the polymeric materials (chlorinated aromatic polyamide and a copolymer of vinylidene fluoride and hexafluoropropene) are more toxic to mice than are the products

from cotton under similar, controlled conditions.

Montgomery et al.[31] have described a static exposure apparatus consisting of two separate stainless steel chambers, each measuring 1' x 1' base x 2' height and coated on the inside with polytetrafluoroethylene (PTFE) to minimize adsorption of polar molecules. These chambers are placed about a foot apart and connected by 2" diameter pipes. Observation portholes of Lucite® abrasion-resistant sheet are located in the front of the chambers. A 10-g polymer sheet is placed on a glass hanger in the right of the combustion chamber. The lower edge of the test polymer is placed 3/4 inch above the flame source which is a horizontal torch regulated to give six 3-inch jets of flame. The 30-sec burn time is counted from contact of the polymer with the flame to torch shut-off. No attempt is made to extinguish the polymer if it continues to burn after the torch is extinguished. A blower in the top of the right chamber circulates gaseous combustion products and soot. In the left or animal chamber, six albino rats are exposed from ignition through the 30-sec burn time and for 1 hr thereafter at which time the rats are removed from the chamber. During the exposure, the concentrations of oxygen, carbon monoxide, nitrogen oxides, carbon dioxide, hydrogen cyanide, and ammonia are determined. Depending on the composition of the product being tested, analysis may be made for hydrogen chloride, hydrogen bromide, or sulfur dioxide. Exposure chamber temperatures are less than 33°C. Analytical data on the chamber atmosphere and the mortality ratio are correlated with the weight of the burned portion of the sample. Montgomery et al.[31] suggested that LD50 and ED50 data for principal combustion gases be established. ED50 is that dose that will produce a specified effect in 50% of the animals. It was also suggested that ED50 criteria need to be generated.

Jouany et al.[23] have described a system for the evaluation of the toxicity of combustion products. The annular furnace technique produces combustion or pyrolysis with a maximum temperature of 1,000°C. Combustion in which the air and the furnace move in the same direction is irregular and best represents a real fire. Flaming combustion is at 840°C with excess oxygen (airflow at 120 liters/hr); pyrolysis occurs at 400°C to 500°C with limited oxygen (airflow at 20 liters/hr.) After pyrolysis, oxygen is added to the products prior to animal exposure. The gases are mixed and cooled to room temperature. Oxygen, carbon dioxide, carbon monoxide, and other important toxic substances (e.g., hydrogen chloride and hydrogen cyanide) are measured continuously by aliquots. The various weights of the materials are recorded in grams per cubic meter of air. The animals (rats or rabbits) are exposed for 30 min, the maximum time generally accepted by firemen that is needed to give assistance with efficacy; the immediate recovery period lasts 4 hr. The combustion or pyrolysis products reach the pulmonary alveoli by tracheotomy and controlled ventilation. Arterial blood is monitored for carbon monoxide, carbon hemoglobin, partial pressures of oxygen and carbon dioxide and blood pH. In addition, free breathing experiments are conducted. Cardiovascular

and central nervous system activities are recorded continuously by electrocardiograms, readings of arterial pressure, and electroencephalograms. Using these data, a three-coordinate diagram called a "physiogram," can be developed for comparisons of effects among major toxicants alone and with associated toxicants.

Smith et al.[43] place their samples into a 2-inch diameter Vycor combustion tube which is then inserted into a closed preheated furnace. Samples are burned at 600°C. The system insures an oxidative burn by recirculating the gases within the closed system through the burn zone at a flow rate of 4 liters/min. Oxygen concentration is monitored and maintained within 90% of normal atmosphere by manual addition of oxygen. The total volume of 12.6 liters includes the recirculation pathway and the animal chamber of 10" x 10" x 10" constructed of 1/4" Plexiglas®. White rats are exposed in groups of three in three cylindrical cages rotating at 6 rpm, which enables the investigator to make a very precise determination of the time to physical incapacitation. The average temperature within the chamber is kept at or below 32°C; typically it averages 28°C. Sample size is adjusted so that a response can be observed within 30 min. Hydrogen cyanide, carbon monoxide, carbon dioxide, and oxygen are monitored at various intervals during the experiments. Survivors of the 30-min exposure are observed for 7 days or more. Results from the burning of the test materials are compared based on times to physical incapacitation and to death.

Potts and Lederer[41] have exposed animals to the products of combustion or pyrolysis in a cubic chamber having a volume of 160 liters. The sides and front are constructed of glass; the top, bottom, and back are made of stainless steel. Heat is supplied by an electric furnace containing a stainless steel cylindrical cup. A cylindrical quartz beaker, 6 cm in diameter and 12 cm high, slip-fits into the stainless steel cup. The upper lip of the beaker slightly protrudes above the top of the steel box encasing the furnace. A thermocouple, which is placed at the junction of the bottom and side, controls the electrical heat input via a pyrometer and maintains the temperature at the preset level to $\pm$ 15°C. Initial experiments with no animals present determine the temperature that readily sustains complete combustion of the sample, after ignition. To initiate an exposure, a few drops of ethanol are placed on the sample which is then dropped into the preheated furnace. It is immediately ignited with a spark-gap located in the mouth of the beaker. The combustion is carefully observed. Should the flame go out at any time, it is immediately reignited with the spark.

For pyrolysis, the temperature selected is the maximum to which the sample can be heated without causing self-ignition. Rats are observed throughout the 30-min exposure and for 30 min postexposure. Rats that die during the exposure are subjected to gross pathological examination. The survivors are observed periodically for 14 days postexposure. They are then sacrificed by anesthesia. A few are

subjected to gross pathological examination. The amount of material decomposed is determined by weighing the sample before and after the pyrolysis. The air temperature in the chamber is monitored and does not exceed 35°C. Carbon monoxide, carbon dioxide, nitrogen, oxygen, nitrogen oxides, hydrogen cyanide, formaldehyde, acrolein, and certain other possible products generated by the sample are monitored at regular intervals. Fatalities and body weight changes, which are the most objective end points, are the basis for the conclusions drawn in this study. The following materials have been combusted in this technique: red oak, yellow pine, fire plywood, corrugated cardboard, cotton linters, three formulations of polystyrene, and rigid urethane foam.

The method of Alarie et al.[3] consists of an exposure chamber which is a glass cylinder 25 cm long with a 10.5 cm diameter. It is fitted with a groundglass cover containing a 1.5 cm diameter entry port and a glass diffusion plate for dispersion of the decomposition products. A 2 cm diameter exit is used to exhaust the chamber. Four albino male mice are exposed simultaneously to each concentration of the decomposition products. The mice are positioned in small, cylindrical restraining tubes so that their heads protrude into the exposure chamber. Respiratory rate is monitored by a pressure transducer that is connected to a port on the sealed tube. The decomposition furnace has a linear temperature programmer that insures uniform heating of the sample. The temperature is monitored with a recording pyrometer and a heating rate of 25°C/min is used. Airflow through the furnace is 2 liters/min; however, the concentration of the decomposition products is changed by varying the airflow through the exposure chamber (up to 100 liter/min): this keeps the amount of sample decomposed constant. In the case of highly irritating products, the concentration is changed by burning less material and holding the exposure airflow constant (100 liters/min). After the mice have been been secured in the exposure chamber, the respiratory rate is recorded for 2 min before the decomposition is started, thus giving the control value. Monitoring of the respiratory rate continues during the appearance of visible smoke and terminates 5 min after the smoke disappears. The percentage decrease in respiration rate during the exposure period is calculated. Dose-response curves are determined for each material. The RD50 values (the concentration required to decrease the respiratory rate by 50%) is determined. Thermal gravimetric analysis (TGA) curves are recorded to indicate when the decomposition occurs. To characterize the decomposition products of some polyurethane foams, gases are analyzed by chromatography and mass spectrometry. Based on investigations of sensory irritation of the upper respiratory tracts in mice and humans by various chemicals,[1] Alarie et al.[3] offer the following speculations, as listed in Table I.

Table I. Speculations on Response in Humans from Results Obtained in Mice.

Exposure of Mice	Predicted reactions of humans
Concentration RD50	Intolerable and rapidly incapacitating
Concentration 1/10 RD50	Slightly irritating with burning sensation of the eye-nose-throat
Concentration 1/100 RD50	Tolerable with very slight or no irritating sensation

In the screening method developed by Rider et al.[42] a known amount of material is subjected to radiant heat at a rate of 2.5 W/cm^2. Ten rats are exposed to the emissions of the materials in a chamber connected by a tube to the combustion chamber. They are observed until 50% $\pm$ 10% fatalities occur. Survivors are observed for 14 days after exposure for changes in behavioral responses as well as for mortality. The radiant heat source is housed in all-glass, 20 liter heating chamber, which is used for oxidative pyrolysis of the study materials. The pyrolysis products are ducted through a top port to a glass 40-liter exposure chamber. Sufficient oxygen ($>$ 16%) is maintained by adding air to the system at the rate of 8 liters/min. After a 5-min preheat period, the sample is placed on the heating element and the exposure begins. The following observations are made throughout the exposure period: oxygen content of the exposure chamber, temperature in the exposure chamber, animal behavior, and time of death of each test animal. At the time of death of the fourth and/or fifth test animal, the flow of oxidative pyrolysis products into the exposure chamber is terminated. The survivors are observed for 14 days after exposure. The upper limit for temperature in the exposure chamber is 30°C in this method, and the exposures do not exceed 30 min. Blood samples from two of the dead rats are drawn from the aorta for carboxyhemoglobin analysis. No attempt is made to evaluate relative oxygen depletion or incapacitation as a factor that may lead to fire fatality. Studies using this methodology have been conducted on samples of polyvinyl chloride, styrene, urethane foam, southern white pine, red oak, and wool.

Petajan et al.[40] described the technique in which extreme toxicity from the combustion products of a fire-retarded polyurethane foam was observed. Long-Evans rats are exposed in a chamber designed by the National Bureau of Standards for smoke density research. The chamber is equipped with a heater modified to give a radiant-energy flux of 5 W/cm^2. Four rats are held radially nose-to-nose in slings that permit free movement of legs and head. In this position all animals inhale smoke from the same zone. The blood of one of the animals is removed by intraarterial cannulation. The blood samples

are analyzed for hemoglobin and carboxyhemoglobin. The rate of return to a baseline carboxyhemoglobin level is used to indicate the efficiency of pulmonary function. Clinical signs are recorded and animals are subjected to gross pathology examination.

Petajan[39] described experiments in which one rat is exposed in a "static" chamber, which is a 40-liter acrylic glass-lined box. Fluxes of 1 to 7.5 W/cm^2 are used to combust materials in both the flaming and nonflaming modes. Conditioned avoidance responses are studied. In each experiment, the rat is trained to avoid a shock that is delivered to its left hind foot on contact with a metal plate located a predetermined distance below the foot. Responses to polyquinoxaline foam, trimethylol propane-based polyurethane foam with a phosphate-containing fire retardant, and polyvinyl chloride foam were described. Numerous blood parameters including blood counts, oxyhemoglobin, carboxyhemoglobin, hemoglobin, blood pH, and partial pressures of carbon dioxide and oxygen, are monitored at intervals up to 35 min from start of exposure. The work illustrates the various examples of intoxication syndromes from materials.

Nunez and Autian[35] have described three distinct approaches to fire toxicology studies, all of which have been used in their laboratory. In one, the combustion chamber has an infrared gas burner mounted in the top. Heat is reflected down on the sample, which rests on a metal support grid directly under the burner. The combustion chamber is mounted on one end of the exposure chamber. Ten rats are held individually in stainless steel cages in the exposure chamber, which is equipped with circulating fans and a thermometer. The total capacity of the two chambers is 462 liters. A weighed sample is placed on the support grid and raised to within 5 cm of the ignited burner in the presence of a 10 liters/min airflow through the combustion and exposure chambers. The sample usually bursts into flames. Three minutes after ignition the burner is turned off, the air flow stopped, and the exhaust tube sealed with a diaphragm. The rats remain in the exposure chamber for 2 hr during which time the chamber atmosphere is chemically analyzed. Surviving rats are removed and kept for 2 weeks, postexposure.

The second approach of Nunez and Autian[35] involves pyrolyzing the material slowly in a quartz furnace, by increasing the temperature 10°C/min. The products are transferred via a flexible Teflon® tube into a 63-liter exposure chamber. The quartz furnace tube is 25 mm inside diameter with thermocouples to measure the air temperature in the vicinity of the sample. The airflow rate is 1.0 liter/min before the furnace tube and an additional 0.5 liter/min after it passes through the sample tube. Four rats are individually caged in the exposure chamber which is equipped with the thermocouple and a magnetically driven circulating fan. Folded fabric samples are placed in the center of the furnace. The run is initiated by temperature programming at a rate of 10°C/min and terminated at the maximum temperature (the temperature, determined by thermogravimetric analysis, at

which no further degradation occurs plus 50°C). The airflow and exposure are continued for 1 hour after the termination of heating. The survivors are then removed and maintained for 14 days. As in the previously described combustion experiments, the amount of material required to kill half the animals may be evaluated and a comparison scale constructed.

Their third method used the hyperbaric chamber apparatus as previously described by Carter et al.[10] In all approaches, the exposure chamber atmosphere is sampled periodically for carbon monoxide by gas chromatography. Oxygen is monitored by a paramagnetic analyzer. Bendix gas detector tubes are used to check for hydrogen cyanide, phosphine, etc. Rats that die during the experiment are autopsied, and gross histopathological observations are recorded. The relative carboxyhemoglobin content of the rats' blood is determined.

The literature also contains descriptions of three exposure chambers that can be used either with combustion sources or as portable chambers in a larger fire situation. Hilado[20] described a National Aeronautics and Space Administration (NASA) chamber, which is constructed of clear polymethylmethacrylate. The chamber is composed of two sections - an upper dome and a lower base. The diameter of both is 20.3 cm. For short-exposure acute toxicity tests, the chamber can accommodate up to six mice or two rats. Instrumentation of one test animal provides useful information on responses such as respiration rate and electrocardiograph. The chamber may accommodate two small exercise wheels without external drive.

Hilado et al.[21] have recently developed a test apparatus in which a pyrolysis tube is connected to the exposure chamber. A tare weight is obtained before and after pyrolyzing the sample so that the weight of the pyrolyzed sample can be calculated. The mice are placed in the exposure chamber and given 5 min to adjust to their surroundings. After both the sample and animals are in place, the system is sealed and the furnace is turned on at the predetermined heating rate of 40°C/min. When the upper limit temperature of 500°C or 800°C is reached, it is maintained at that level until the end of the 30-min test period or until all animals die, whichever occurs first. Survivors are observed for 14 days postexposure. Mortality is recorded at 10, 20 and 30 min to provide information for different fire situations. Time to incapacitation is judged as the time to the first observed losses of equilibrium, prostration, collapse, or convulsions. Time to death is judged as the time to cessation of observable movement and respiration. In actual tests conducted with this system the highest temperature in the chamber has been 30.5°C and the lowest oxygen concentration, 15.0%. These measurements are not used in every experiment. They are determined in various experiments at random. A fixed weight of each material is pyrolyzed under a specific set of conditions so that the relative toxicity of materials can be ranked. This ranking is based on such criteria as mortality, time to incapacitation, and time

to death.

Birky et al.[9] have used an exposure chamber in tests of animal exposures to larger fires. A 3" diameter exhaust line is used to transfer combustion products from the fire area to a motorized revolving cage which is enclosed in a Plexiglas® box. The cage contains three male rats. Each rat is placed in a separate compartment within the wheel, which is rotated at 8 rpm. Prior to the experiment the animals are trained to walk in the wheel in two 5-min training sessions a day for 5 days. Two days prior to each test, an abdominal-aorta cannula is surgically placed in one animal so that blood can be rapidly removed for carboxyhemoglobin determinations. This animal is not trained to walk in the wheel prior to exposure. Since a large blood sample is required for hydrogen cyanide determination, one animal is sacrificed for this purpose. Sampling ports are installed just before the interface of the transfer line at the animal exposure chamber. Sampling for continuous analysis of carbon monoxide, carbon dioxide, and hydrogen chloride and intermittent sampling for hydrogen cyanide takes place at these ports.

Gaume[17] described a system in which physiological data on rats are collected and analyzed during large-scale burn tests to assess the relative toxicity of burning materials and selected extinguishing agents. Instrumentation for measuring electrocardiogram (ECG), respiration, and cage temperature are used. This system has a simple design and a relatively low cost. It is easy to transport, deploy, and operate. It is also adaptable to a wide variety of fire test facilities. Some very good physiological recordings of heart and respiration rates have been obtained in a wide range of testing, from the automatic discharge of extinguishing agents to prolonged (30 min) full-scale burn tests. The exposure chamber is equipped with rotary wheels for measuring time of useful function (TUF). Gaume observed additional end points that are more sensitive than TUF and are also worthy of consideration in toxicity screening. These include bradycardia, cardiac arrhythmias, changes in respiratory patterns, and hiccups.

Sumi and Tsuchiya[46,47] have suggested a method for evaluating the toxic hazard from experimental data on decomposition products. Toxicity, t, of a gaseous compound is defined as $\underline{t} = c/c_f$ where c is the concentration of the gas and c_f is the concentration of the gas that is fatal to man in 30 min. If an atmosphere contains two or more toxic components, a first approximation of the toxicity is assumed to be $t = \Sigma\, t_i$. If synergistic effect is confirmed, it can be taken into account by using the expression $\underline{t} = t_1 + t_2 + st_1t_2$ where s is a synergistic factor.

The propensity of different materials for generating harmful gases and vapors can be determined by using the "Toxicity Index" concept. When a material of weight, W, is decomposed in volume, V, and the

resulting toxicity of the atmosphere is $\underline{t}$, then the toxicity index, T, is defined as $\underline{T} = tV/W$. If the number of toxic components in a mixture of decomposition products is more than one, $\underline{T} = T_1 + T_2 + \text{etc.}$, where T_1 and T_2 are the toxicity indices due to component 1, component 2, etc. These authors have recently stated that they believe that animal experiments provide the best data from which materials that generate toxic gases can be regulated.[47] Assessment of the fire toxicity of materials does not account for all the harmful components found in a fire atmosphere; therefore, small quantities of some extremely toxic components can be overlooked.

Birky[8] has discussed the philosophy of fire toxicity testing. He concluded, as did MacFarland in an earlier publication,[28] that an assessment of the toxicity of combustion products from various materials is very complex. Chemical analysis of the pyrolysis or combustion products cannot be used as a basis of toxicity assessment. The effects of these products on living organisms must be determined. He outlined three major methods required for the assessment of relative toxicities of pyrolysis/combustion products of materials. These three methods are: the method of product generation, the method of animal exposure, and the method of analysis of toxicants and correlation with toxicological results. Each method specifies the many parameters that must be measured. An important method not listed is determination of toxicological end points.

SUMMARY

The methods reviewed in this report represent a spectrum of approaches currently used to assess the toxicological hazard of materials in fires. Some of the important characteristics of the majority of these methods are tabulated in Table II. The burn conditions vary from pyrolysis conditions to ignition with a flame. A standard method has been adopted in the Federal Republic of Germany; however, it is limited to smoldering conditions. Several other methods use only pyrolyzing conditions; some are at fixed temperatures,[43] while others are pyrolyzed by increasing temperature linear with time.[3,13] Other methods use combustion conditions only.[13,26,31,35]

Exposure conditions are equally variable. In a few cases, combustion and exposure occur in the same chamber; however, the majority of the methods involve the transfer of the pyrolysis/combustion gases into a separate chamber. The large system designed by Dressler[15] uses large samples and the combustion products travel long distances through Pyrex® tubes and are routed around corners. This may remove significant amounts of materials prior to animal exposure. Nunez and Autian[35] use a quartz furnace tube that is connected by a Teflon® tube to the animal chamber. In this method, only pyrolysis products whose lifetimes exceed 16 sec are breathed by the rats. Nunez and Autian also point out that this technique may be too slow to be compatible with a "real fire" situation.

Table II. Summary of Selected Methods

Reference	Apparatus	Burn Conditions	Species	Exposure Time (min)	End Points
22, 25	Tube furnace and exposure chamber for head only exposure (Dynamic system)	Pyrolysis 200 - 600°C	Rats	30	Carboxyhemoglobin (CO-Hb) swimming-test[25] mortality
26	Furnace, dilution chamber, and exposure chamber	Combustion	Mice	15	Activity of mice
10, 35	Tube furnace and Bethlehem chamber	Pyrolysis 550 and 800°C	Rats	30	Acute toxicity, pathology, CO-Hb
15	Combustion chamber	Pyrolysis and combustion	Rats	15	Respiratory and heat rates, EKG, CO-Hb, pH and blood gases
13	Tube furnace and exposure chamber (Dynamic system)	Pyrolysis T increasing 5°C/min	Rats	240	LC50, CO-Hb, histological studies
13, 41	Chamber for both combustion and exposure	Combustion[13] Pyrolysis and combustion[41]	Rats	240[13] 30[41]	LC50, CO-Hb, histological studies[13] mortality and pathology[41]

Table II.(continued)

32	Modified NBS chamber	Pyrolysis 21-36 min	Mice	Variable	Electrocardiogram and respiratory movements
31, 35	Twin chambers combustion; Exposure	Combustion (flame ignition)	Rats	60[31] 120[35]	LC50, ED50[31] mortality[35]
43	Tube furnace and exposure chamber	Pyrolysis	Rats	30	Incapacitation
3	Tube furnace and exposure chamber for head only exposure (Dynamic system)	Pyrolysis T increasing 25°C/min	Mice	Variable	RD50 (sensory irritation)
42	Combustion chamber and exposure chamber	Pyrolysis	Rats	Variable	Mortality and CO-Hb
39	Chamber for both combustion and exposure	Pyrolysis	Rats	$\leq$ 35	Conditioned avoidance response, blood parameters

Exposure times vary from a few minutes to 2 hr; however, the majority range from 15 to 30 min. Cornish et al.[14] have developed two systems and have used them in the same laboratory. When the same polymers are evaluated by the two methods, extremely different results are obtained. This emphasizes the requirement for a "standardized" test system using comparision standards, if materials are to be compared in different laboratories. It also underscores the limited conclusions that can be reached from a single experimental protocol.

A multiplicity of end points is used; however, the most common are mortality, time to incapacitation, and time to death. Mortality includes the death of animals occurring during the test period and those that occur from 2 to 14 days after exposure. A number of investigators consider that time to incapacitation is an important end point. Techniques to measure incapacitation include the swimming test of Kimmerle,[25] performance in a rotary wheel,[9,15,17,43] conditioned avoidance response[39] and simple observations.[21] The time to death has been determined by observation and by physiological measurements such as the plethysmograph used by Alarie et al.[3] Most of these end points have not been evaluated for sensitivity, accuracy, or reproducibility.

The various methodologies used for product generation, exposures, and end points prevent any comparison of data obtained on the same polymeric materials that have been investigated in more than one laboratory.

Based on this review, the committee has concluded that acceptable screening tests to evaluate the relative toxicities of polymeric materials are not available. All present methods have one or more shortcomings. Many of the methods described in this report were designed for research; they were not intended for use as screening methods.

III. RECOMMENDED GUIDELINES ON METHODOLOGY

The committee has developed guidelines for a screening procedure to evaluate the toxicity of the pyrolysis/combustion products of polymeric materials. Its objectives are to suggest a standard method for pyrolyzing or burning samples that will simulate the noxious atmospheres that could be encountered in "real" fires and to specify standardized exposure conditions and end points for first-level screening of materials.

PYROLYSIS/COMBUSTION CONDITIONS

Since pyrolysis and combustion occur under an almost infinite number of actual conditions, the laboratory simulation should bracket likely conditions and should attempt to simulate the worst case that could occur in "real" fires. Fire reaction processes generally involve oxidation and/or decomposition, so that the product molecules are breakdown or oxidation products of the original material. The two major variables are heat transfer to the sample--particularly by radiation, which controls surface temperature--and the availability of oxygen. The two extremes are free burning of the sample with ready access of air and pyrolysis under reducing conditions; therefore, specimens should be tested under both pyrolysis modes and flaming combustion.

Temperatures in free burning will be high and the molecules relatively simple and usually predictable by thermodynamic methods.[45] The common toxic substances are carbon monoxide, hydrogen cyanide, and, where halogens are present, hydrogen halides and free halogens. The inhalation toxicity of these individual gases is reasonably well understood.[48] Synergisms undoubtedly exist, but they are yet to be clearly demonstrated. Of these gases the most common lethal agent is carbon monoxide.[7] If conditions are rich enough to produce soot, the absorption of gases on particles that are carried into the lungs and subsequently liberated may be a serious problem.[44] By contrast, pyrolysis of material in atmospheres of low oxygen concentration under reducing conditions is poorly understood. Here, depending on the level of heating (radiant or convective), complex species can be volatilized or produced and the prediction of products is difficult.

For the limited goal of a screening test, heat fluxes (temperatures) should be chosen at three levels - one just above that necessary to sustain pyrolysis, one just below that required for flaming combustion with normal oxygen concentration, and one that supports flaming combustion when supplied with a source of ignition. If a furnace is used, the static temperatures prior to introducing

the specimen should be recorded. If a radiant heat source is used, the flux should be calibrated.

The heating mode is not specified in the committee's recommendations since the chemical decomposition is not governed explicitly by the mode of heat transfer. Therefore, the apparatus for burning or pyrolyzing the sample need not operate in a purely radiant or conductive mode; rather, it should be reproducible and relatively simple in construction, characterization, and operation. For this reason, the committee prefers a shallow furnace with a weighable sample cup over elaborate radiant heating devices. The furnace should provide a uniform temperature in the sample region and be designed so that undue condensation and repyrolysis of the sample within the test chamber are avoided. Temperature, radiation flux, or some other characteristic parameter should be monitored to ensure constancy of conditions. The cup should be of resistant material such as quartz or aluminum oxide.

The sample should be prepared in a standard manner and its physical properties reported. Weight, volume, subdivision, porosity and geometry should be recorded. Sample size should be scaled so that it reaches the specified test end point within 30 min. The sample should be introduced rapidly into a preheated furnace or a preset radiant flux. The time of pyrolysis or combustion should be short compared with the animal exposure time. Pyrolysis or combustion time and the weight and character of any residue should be reported. The dose should be expressed as the amount decomposed in the chamber volume in units of mg/m^3.

ANIMAL EXPOSURE CONDITIONS

A single chamber for both pyrolysis/combustion and animal exposure is highly desirable. Both static and dynamic chambers are feasible; however, the committee's opinion is that the single static chamber with integral pyrolysis furnace is a simple approach that provides more realistic information. This not only approximates the real fire situation but prevents large losses of combustion particles and gases on the walls of any transfer apparatus. The sample holder and pyrolysis elements should be enclosed in the exposure chamber as close to the animal area as practical, consistent with providing thermal shielding from heat and hot gases. Adequate mixing of toxic gases and particulates, either by convection or mechanical agitation, is required. Other means of temperature control at the location of the exposed animals may include size of the chamber and the placement of the pyrolysis/combustion unit.

The chamber should be airtight to prevent toxic gases from leaking into the laboratory; however, there should be a safety pressure relief diaphragm vented to a laboratory hood. Construction materials

should be inert and easy to clean between runs. Glass is an excellent choice except for fluoropolymers, which generate molecules that attack the glass surface. Care should be taken to avoid reaching explosive limits during pyrolysis. Safety precautions should be outlined. Compliance by operating and cleaning personnel should be enforced.

A small rodent species, such as the rat or mouse or a combination of both, should be used as the animal models. Enough animals must be used at each exposure condition to give statistically valid results.

The exposure time should range from 15 to 30 min, preferably 30 min. Measurement of exposure time should begin at the time pyrolysis or combustion is initiated.

In addition to temperature, carbon dioxide, carbon monoxide, humidity, and oxygen levels should be monitored in the chamber during exposure. The oxygen should be maintained above 16%. This is usually accomplished by limiting sample size. Other expected toxic degradation products such as hydrochloric acid or hydrogen cyanide should be monitored. The optical density should be recorded as a measure of smoke obscuration. Additional analyses for volatile gases may be desirable as an indication of reproducibility of pyrolysis/combustion and for deducing the mechanism of intoxication.

END POINTS

The end points for toxicity tests in animals should be applicable to the interpretation of effects in humans. Incapacitation is considered to be the most important end point as this is related to the ability to escape from the fire. Next in importance would be the latent impairment of organ function or damage to organ structure. Rats and mice are generally used because of practical considerations. The end points that can be measured in animals are as follows:

Incapacitation. The time of useful function (TUF) has been used to indicate the time available for a person to escape the fire environment before incapacitation by fire gases.[18] Animal end points that can be related to TUF should be measured. Incapacitation of animals has been measured by many techniques including mechanically rotated activity wheels;[43] the conditioned avoidance response, which measures an animal's avoidance of foot placement against a constant electric shock;[39] and failure of a trained animal to respond to a buzzer and to withdraw from one shuttle-box compartment to another compartment to avoid electric shock.[6] Another measurement is the ability of an animal to maintain its position on a rotorod to avoid the shock that would result if it were to fall from the rod onto an electric grid.[24]

Mortality. Death during exposure, or from 24 hr to 2 weeks after, may be related to concentration of the substance and the duration of exposure. From these an LC50 for a specified time of exposure may be derived.

Irritancy. This may be judged subjectively, by a magnitude estimation scale in human exposures, or objectively, by measurements such as the amount of afferent sensory nerve traffic in animals. It also may be estimated by measuring reflex changes affecting visceral functions. These effects may be mediated by the parasympathetic or sympathetic nervous system, or by other mechanisms such as the "Hering-Breuer" response, or components of the J-reflex of Paintal.[38] The amount of irritancy may also be measured from the resultant tissue reaction as reflected in the gross or microscopic appearance of the tissues of the eyes, airways, or lungs. Respiratory frequency (inhibition of rate or depth of breathing) was described by Kratschmer[27] and reviewed by Alarie.[1] During exposure, sensory irritation by decomposition products has been assessed by measuring the respiration rate.[3]

Morbidity. Observation of animal behavior and physical condition during and after exposure by a qualified investigator can detect the presence of convulsions and other signs of morbidity. Carboxyhemoglobin levels at the end of exposure can indicate if the toxic response is due to carbon monoxide concentration or to other toxic components in the combustion products. Gross and microscopic pathological findings at 24 hrs or 2 weeks after exposure can give information on the mechanisms of damage and the target organs.

Pathophysiology. Another main group of criteria for end point of effect would be functional abnormalities of the body that could contribute to incapacitation as described above. First are those functions required for escape, e.g., vision, hearing (if needed to locate exits), and respiratory, circulatory, and central nervous systems; others have to do with latent impairment of function of the kidneys, liver, and central nervous systems. Gaume[17] has measured bradycardia, cardiac arrhythmias, and change in respiratory patterns.

All these criteria would relate to or be translated more to healthy humans than those who have specific diseases (e.g., coronary insufficiency, pulmonary insufficiency, or intoxication by alcohol, drugs, or other soporifics). The mechanism for comparison of animal with human data depends on juxtaposition of dose-response relationships in nonprimates and humans. This is possible in estimates of sensory stimulation as for odors in cranial nerve I (Cr I),[11] for eye or nasal irritation (Cr V),[2] and, to some extent, for the effects of lower airway responses to such irritants as sulfur dioxide or sulfates on airway resistance (afferent Cr IX, efferent Cr X).[4,33]

In the opinion of the committee, the simplest and least costly measurements should be those made most frequently; the more difficult or costly ones should be reserved for understanding of mechanisms and resolution of special problems that arise. The committee specifically recommends that the chosen end points provide a measure of both incapacitation and delayed effects. As a minimum, the end points of a screening test should be as follows:

- Observation--Observations of animal behavior and physical condition during and after exposure are extremely important; thus, these should be done by a qualified investigator. Some type of quantitative test may be required to evaluate observations made by the investigator.

- Incapacitation--Incapacitation should be measured using a rotating wheel or an equivalent test. Measurements should be reproducible, sensitive, and valid. Packham et al.[37] have reported that the activity wheel and a conditioned leg-flexion avoidance response are reproducible paradigms for carbon monoxide toxicity. Measurement of sensory irritation may provide a basis for assessing incapacitation. The rotating wheel or an equivalent test is a tentative recommendation until a more valid measure of incapacitation is determined.

- Mortality--Deaths during exposure and those occurring within 14 days postexposure should be recorded. Postexposure observations and mortality are a simple approach to investigating delayed effects.

- Carboxyhemoglobin determination--Carboxyhemoglobin levels should be measured at the end of the exposure to determine if the toxic response is due to carbon monoxide concentration or to other toxic components in the combustion products.

The second echelon should be used for more definitive and mechanistic studies, and includes: blood pH, partial pressures of oxygen and carbon dioxide, and blood cyanide; electrocardigram; respiratory record by plethysmograph; organ functions; and gross and microscopic pathology. The animal data obtained by some or all of these methods should be interpreted as well as possible in terms of human ability to see or to hear the direction for escape, to judge a course of action, to move from or remain in the area, and to avoid serious sequelae that affect the heart, lungs, liver and kidney. This would pertain to normal healthy people as well as to those especially 'at risk' from preexisting conditions such as old age, coronary heart disease, or other disabilities.

Relative toxicity of materials should be determined on the basis of dose-response relationships in animals (Fig.I). A steep slope

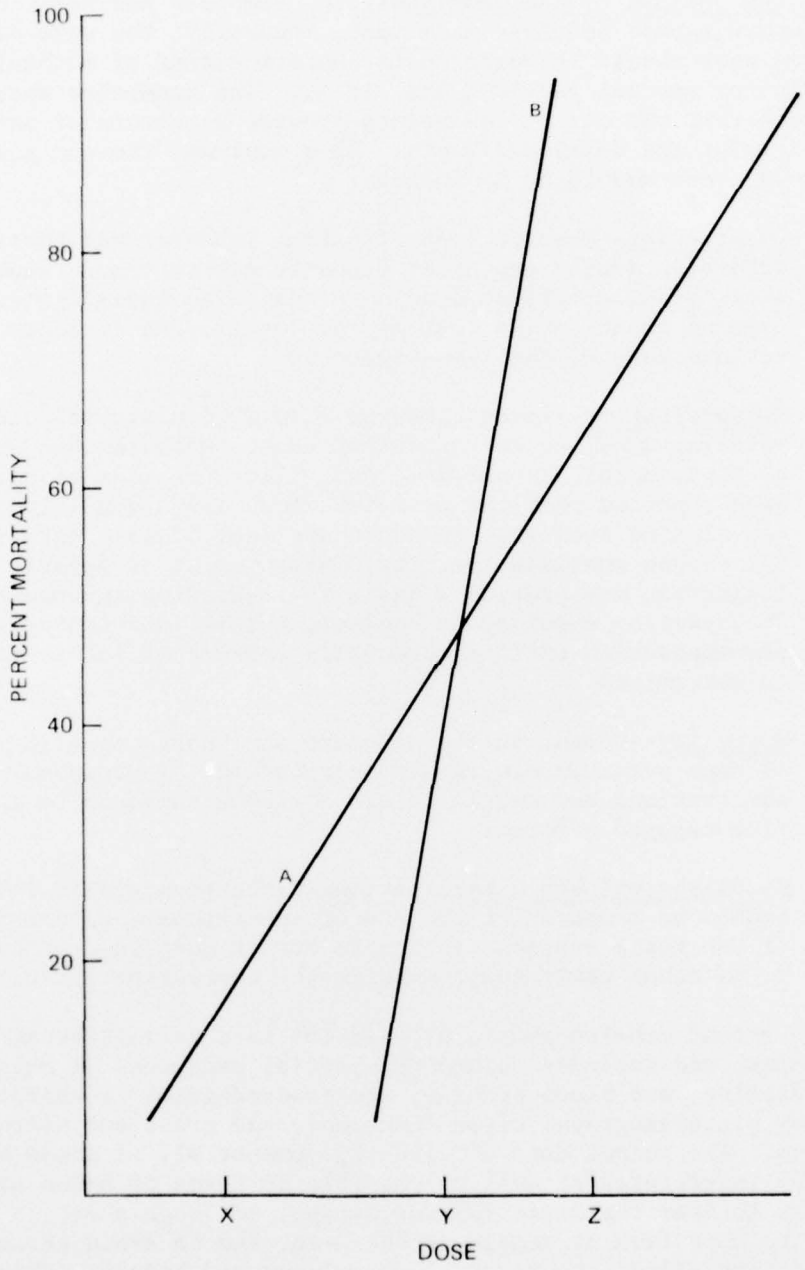

FIGURE 1 Comparison of mortality produced at dose levels X, Y, and Z by substances A and B.

(high exponent) indicates a low margin of safety between the onset of toxic signs and more severe, possibly lethal, effects. A shallow slope (low exponent) indicates a wider margin of safety between the onset of signs and severe effects. A "saturated" response level indicates the maximum response that can be obtained from any level for the duration of the exposure. Sideways displacement to right indicates that more material is required to saturate the receptor sites or that normal enzymes compete for those sites.

Toxicity data should be relatable to human capability for escape and effective survival. This requires the comparison of different test materials with reference materials. The latter may be either a defined material in common use or a reference material, currently used for a particular purpose, that is being considered for replacement by the new material to be tested against it. In addition, the absolute toxicity can sometimes be judged in relation to the fire conditions that might occur, the amount of material that would be used, and the amount of this material evolved or combusted under these circumstances.

IV. SUMMARY AND RESEARCH RECOMMENDATIONS

SUMMARY

The methods currently being used for evaluating the toxicity of pyrolysis/combustion products have been reviewed. These methods include those designed primarily for research and those designed for screening tests. The burn conditions vary from smoldering to flaming, exposure conditions and times are variable, and the majority of methods involve transfer of products to separate exposure chambers.

Because of the variety of burn conditions, exposures, and end points, quantitative comparison of data on the same polymeric materials cannot be made among laboratories.

The Committee on Fire Toxicology has concluded that acceptable screening tests to evaluate the relative toxicities of the pyrolysis/combustion products of materials are not currently available, as all present methods have one or more shortcomings. The state-of-knowledge is not advanced sufficiently for the committee to recommend a standard procedure for evaluating the toxicity of pyrolysis/combustion products. It has, however, prepared the following guidelines for developing the needed methodology.

A. Materials should be evaluated under both pyrolysis and flaming conditions. Both gaseous and particulate combustion products should be mixed uniformly in the chamber atmosphere without being unduly subjected to surface condensation. Therefore, it is highly desirable to use one chamber for both pyrolysis and animal exposure.

B. Small rodent species such as rats or mice should be used as the animal model. Enough animals to give statistically valid results must be used at each exposure condition. The time of exposure should be in the range of 15 to 30 min, preferably 30 min. The temperature in the animal exposure chamber should not exceed 35°C and the oxygen level should be maintained above 16%.

C. Incapacitation is considered to be the most important end point since it should be directly related to escape capability. Laboratory animals should be held for 2 weeks postexposure and observed for behavioral and physical changes as a measure of latent effects.

D. As a minimum set of parameters, temperature, carbon monoxide, carbon dioxide, and humidity should be monitored in the chamber during exposure of animals. Other toxic degradation products such as hydrogen chloride or hydrogen cyanide, which could be anticipated because of the type of polymer under test, should also be monitored. Further, the smoke density in the animal chamber should be measured as a function of time following initiation of pyrolysis/combustion of the material.

E. Relative toxicity of material should be determined by comparing test materials with reference materials, either those currently in use or candidate materials, rather than attempting to make absolute toxicity evaluations.

RECOMMENDED RESEARCH

The review of the fire toxicology literature clearly indicates that additional research is required before a standard procedure for fire toxicity testing can be established. The committee recommends the following areas of research.

1. Exposure chambers equipped with pyrolysis/combustion apparatus should be built according to the committee's recommendation in order to validate the general methodology. More elaborate measures than the ones discussed in this report may be useful to evaluate the suitability of test parameters for characterizing the toxicity of materials.

2. The extent of mixing and effects of stratification should be investigated by temperature and gas mapping during typical runs of the test system. If stratification appears serious, a fan or other mixing device or redesign may be required.

3. The temperature and the flow of the thermal plume above the furnace or radiant heater and the rate at which the thermal wave penetrates the sample should be measured.

4. The effects of subdivision of the sample (powder and foam vs bulk material) should be investigated.

5. Research should be conducted to determine which end points in animal models are most applicable to the evaluation of comparative toxicity of pyrolysis/combustion products and to the extrapolating of these data to both immediate and delayed response in humans. Particular emphasis should be placed on developing simple reproducible techniques for assessing incapacitation.

6. Basic research should continue on fire toxicology methodologies and mechanisms to provide a scientific basis for improved methods in the future.

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