23 June 1978, Volume 200, Number 4348 SCIENCE

Toxic Gases from Fires

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Summary. The major lethal factors in uncontrolled fires are toxic gases, heat, and oxygen deficiency. The predominant toxic gas is carbon monoxide, which is readily generated from the combustion of wood and other cellulosic materials. Increasing use of a variety of synthetic polymers has stimulated interest in screening tests to evaluate the toxicity of polymeric materials when thermally decomposed. As yet, this country lacks a standardized fire toxicity test protocol.

According to ancient Greek mythology, Prometheus suffered extreme torture for giving men heavenly fire. However, without fire it is difficult to envision how humans could have advanced beyond the caves. As people crowded together in cities, the occasional, unwanted fire problem escalated drastically. Some dramatic examples include the Great Fire of London in 1666, the Chicago Fire in 1871, and the destructions of Tokyo, Dresden, and Hamburg during World War II.

Frequent fires in American cities stimulated efforts to test the fire performance of materials to minimize potential fire damage. The American Society for Testing and Materials (ASTM) accordingly devised the first scaled test procedures: door fire resistance [ASTM E-152 (1940)] and wall fire resistance [ASTM E-119 (1917)], ignition resistance [ASTM D-1692 (1959)], and flame spread [ASTM E-84 (1950); E-162 (1960)] (*1*). These procedures were devised through the concerted efforts of materials suppliers, firefighting officials, fire code groups, and the insurance industry.

In the United States today, fire exacts an annual toll of some 8000 to 9000 deaths and property losses amounting to some \$3 billion to \$4 billion (*2*). The survivors may also experience severe anguish. Approximately 70 percent of the 1976 fire deaths occurred in residential fires. To reduce this fire fatality rate, it will be necessary to assess the potential life hazard from dwelling fires or fires in general. The factors leading to fire toxicity must be examined. This knowledge must then be applied toward developing reliable test procedures that will make it possible to evaluate the potential of a combustible material to create an extraordinary toxic gas hazard in a fire.

The total life hazard in fires results from a composite of at least four interlocking and variable sets of conditions, as shown in Fig. 1 (*3*). A few decades ago, the main lethal factors were frequently identified as burns, hot gases, and smoke poisoning. Disastrous fires such as the Cleveland Clinic fire in 1929 (*4*), the Cocoanut Grove fire in 1942 (*5*), the Hartford Circus fire in 1944 (*6*), and the S.S. *Noronic* fire in 1949 (*7*) raised serious questions about how people die in fires. These and other fires resulted in more detailed fire investigations that, together with laboratory experiments with animals, made it possible to begin to identify the lethal factors in fires.

Epidemiologic Study

The first major epidemiologic study was retrospective. The Columbia Presbyterian Hospital team led by Zikria (*8*) conducted an extensive analysis of autopsy records of New York City fire victims during 1966 and 1967. Carbon monoxide (CO) poisoning was noted in 70 percent of all victims with a primary diagnosis of smoke poisoning or asphyxia. Among victims who died in less than 12 hours, 59 percent of the 70 percent who were tested had lethal or significant exposure to CO as determined by the blood carboxyhemoglobin (COHb) concentration (COHb is stable in postmortem tissue); CO poisoning was found almost equally in the presence or absence of surface burns (in 50 percent of the victims with burns and 39 percent of the victims without burns).

An ongoing epidemiologic study was started in September 1971 under the joint auspices of the Johns Hopkins University Applied Physics Laboratory and the Maryland State Medical Examiner's Office (*9, 10*). This study was limited to autopsied victims who died within 6 hours after a particular fire. Data obtained from more than 200 victims through the end of 1974 (*9*) indicate that 50 percent died from CO poisoning (COHb $>$ 50 percent); 30 percent died from CO poisoning plus contributory factors such as heart disease, alcohol, or burns; 10 percent died from causes other than CO poisoning (probable laryngeal spasm, burns, or heart failure); and 10 percent died from undefined causes.

Hydrogen cyanide (HCN), hydrogen chloride (HCl), and other gases associated with the thermal decomposition of synthetic materials did not appear significant in the deaths of the Maryland fire victims. Synthetic materials likely to produce such gases were "the primary articles burning in only 5% of the fires reported" (*9*).

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0036-8075/78/0623-1343\$01.25/0

Other investigators have raised the specter of a significant contribution by HCN (*11*) or HCl (*12*) to fire deaths. Unequivocal data on the effects of HCN in fire victims are meager and open to question because HCN can be either generated or consumed in postmortem blood (*13*). The determination that death is due to HCl in fire smoke is difficult, but for different reasons; HCl cannot be measured directly in the blood. In the few cases where deaths due to HCl have been reported, the conclusions appeared to have been reached on the basis of the course of pulmonary injuries sustained, low COHb concentrations, and the limited number and type of materials involved in the fire. Further studies to assess the relative importance and specific action of these and other toxicants have been recommended (*3*).

Perhaps the continued epidemiologic evidence pointing to CO as a cause of death in fires results from the large use of cellulosics (wood, paper, and cotton) in today's existing buildings. Will other toxicants, such as those listed in Table 1 (*14*), become significant problems in the fires of the future?

Basic Fire Physiology

Laboratory experiments with simulated fires involving animals (*15*) began during World War II. Goats were tethered in a mock bunker that was sprayed with flamethrowers; fuel fires were also statically ignited inside a mock bunker. This program was established to study the mechanisms of the deaths in victims without burns that had occurred in poorly ventilated bunkers neutralized by flamethrowers. Zapp (*15*) found that the basic lethal factors were heat, oxygen (O_2) deficiency, CO, and combinations thereof in the order of importance: CO > heat > O_2 deficiency.

Generally accepted 5-minute lethal values for the individual factors are 200°C, 0.5 to 1.0 percent CO, or 6 percent O_2. Exposures for 15 minutes to 125°C, 0.3 percent CO, or 17 percent O_2 are usually not fatal but are associated with physiologic impairment.

Kinetic studies for human exposure to CO show a rapid uptake and also a rapid elimination (*16*). In healthy sedentary adults the biologic half-life is in the range of 5 hours at sea level. Vigorous treatment with O_2 will accelerate clearance of CO from the blood. The half-life may then be approximately 2 hours even in patients with smoke poisoning (*17*). The relationship between the presence of CO and the depletion of O_2 from the blood is additive. Hemoglobin (Hb) has a greater affinity for CO than O_2, and CO can displace O_2 from Hb: $HbO_2 + CO \rightleftharpoons HbCO + O_2$.

Work by other investigators in the 1950's and 1960's showed that a variety of toxic gases (*3, 18*) could be produced by the burning of various building products. The physiologic action of typical toxic gases and the sources capable of producing the respective gases are listed in Table 1. Many scientists believe that the state of the art is now sufficiently advanced to permit toxicologic evaluation of these fire gases in a variety of full-scale test situations.

Test Conditions

The fire phenomenon is commonly illustrated as the fire triangle (Fig. 2a). The combination of varying amounts of

Table 1. Sources and physiologic effects of selected thermodecomposition gases other than CO and CO_2 [see (*14*)]; ppm, parts per million.

Sources of thermodecomposition gases*	Highlights of physiologic effects	Estimate of short-term (10-minute) lethal concentration (ppm)
Hydrogen cyanide (HCN)		
From combustion of various products such as wool, silk, polyacrylonitrile, nylon, polyurethane, and paper, in varying amounts; flammable; difficult to analyze accurately	A rapidly fatal asphyxiant poison; toxicity suspected in some recent fires involving upholstery and fabrics but no definitive data	350
Nitrogen dioxide (NO_2) and other oxides of nitrogen		
Produced in small quantities from fabrics and in larger quantities from cellulose nitrate and celluloid (prepared from cellulose nitrate and camphor, in decreased use today)	Strong pulmonary irritant capable of causing immediate death as well as delayed injury; notorious from the 123 deaths in the 1929 Cleveland Clinic fire caused by burning "nitrocellulose" x-ray films	>200
Ammonia (NH_3)		
Produced in combustion of wool, silk, nylon, and melamine; concentrations generally low in ordinary building fires; inorganic combustion product	Pungent, unbearable odor; irritant to eyes and nose	>1000
Hydrogen chloride (HCl)		
From pyrolysis of some wire insulation materials such as polyvinyl chloride (PVC), also chlorinated acrylics and retardant-treated materials.	Respiratory irritant; potential toxicity of HCl coated on particulate greater than that for an equivalent amount of gaseous HCl	>500, if particulate is absent
Other halogen acid gases		
From combustion of fluorinated resins or films and some fire-retardant materials containing bromine	Respiratory irritants	HF ~ 400 COF_2 ~ 100 HBr > 500
Sulfur dioxide (SO_2)		
From compounds containing sulfur; the common oxidation product of such components in fires	A strong irritant, intolerable well below lethal concentrations	>500
Isocyanates		
From urethane isocyanate polymers; these pyrolysis products, such as toluene-2,4-diisocyanate (TDI), have been reported in small-scale laboratory studies; their significance in actual fires is undefined	Potent respiratory irritants; believed the major irritants in smoke of isocyanate-based urethanes	~ 100 (TDI)
Acrolein		
From pyrolysis of polyolefins and cellulosics at lower temperatures (~ 400°C); significance, if any, in actual fires is undefined	Potent respiratory irritant	30 to 100

*All these gases can be lethal in sufficient concentration. In most common fire situations, these combustion gases would be expected to act as contributory to death rather than as primary causes of death.

O_2, fuel, and heat results in fire, and fire will not occur when there is a substantial deficiency of any of the three ingredients. Both in small-scale tests and in full-size fires, this combination varies widely. Dramatically different combustion product profiles may result, as shown in Table 2 (*19*). In a screening test procedure, only a few points may be selected within the triangle model, as shown in Fig. 2b (*20*). We list below some pertinent variables (*20*).

Selection of animals. Species, sex, number, weight, age, and strain are basic variables in any toxicologic experiment.

Duration of exposure. This is one of the most critical of all test variables. Heat stands out as the unavoidable limiting factor in real fires, and the interval until such heat is generated becomes an absolute maximum for exposure. In small-scale tests an arbitrary, generalized exposure time is selected.

Chamber temperature. The animal chamber must be maintained below the temperature that will produce lethal or appreciable contributory stress from heat.

Oxygen. If the chamber atmosphere is overwhelmed by fire effluents, the O_2 concentration will dip suddenly and critically in experimental tests.

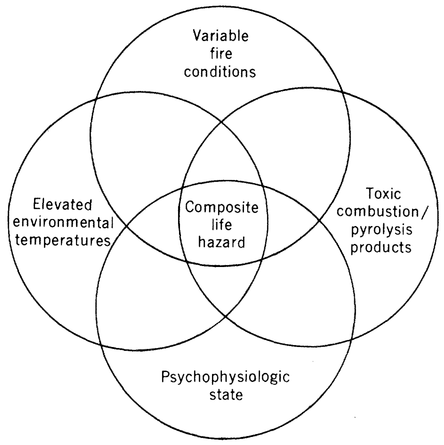

Fig. 1. Composite hazard to fire victims (*3*).

Exercise. Voluntary or forced exercise is an arbitrary selection in animal tests. In real fires, exposed individuals may engage in sudden vigorous activity that can add significant stress, particularly in the case of persons with coronary disease. Activity can also increase the respiration rate, which will increase the rate at which gaseous toxicants enter the blood.

Animal observations. These may include clinical data, neurologic examination to assess incapacitation, blood tests to monitor concentrations of COHb and cyanide (CN), and pathological examination, depending on the scope of the test. (Incapacitation is here understood as the lack of capacity to escape from a fire).

Mode of sample decomposition. This is perhaps the most complicated test variable. The combustion/pyrolysis conditions specify the particular mechanics selected to generate a fire toxicity atmosphere and will directly influence the temperature and fire gas atmosphere.

Configuration of test material. Shape, form, and density can affect heat and O_2 supply.

System configurations. These are the arrangement and use of the test apparatus other than that used for actual combustion/pyrolysis. Specifically, these include the lengths of connecting tubes in the apparatus other than that used for actual combustion/pyrolysis; the lining of the chamber and connecting tubes; and the venting, recycling, heating, dilution, or flow rate of gases given off during combustion.

Selection and sensitivity of analytic methods. These are governed by the scope of the tests as well as by the methods available. Analytic data should be

Table 2. Effects of oxygen supply, temperature, and heating rate on varying combustion products of polyvinyl chloride (homopolymer; molecular weight, 109,000; mesh size, 80) [see (*19*)]. Combustion products are expressed in milligrams per gram of product.

Compound	Variation with O_2 supply			Variation with temperature					Variation with heating rate	
	Air (30 cm³/min)	Air (60 cm³/min)	Air (25 cm³/min) + O_2 (21 cm³/min)	25° to 280°C	280° to 350°C	350° to 430°C	430° to 510°C	510° to 580°C	(3°C/min)	(50°C/min)
CO_2	861	619	814		9.7	181	244	237	619	397
CO	357	429	401		20	46	151	181	429	269
Methane	6.7	4.7	3.8		0.20	1.3	1.8	0.31	4.7	8.7
Ethylene	0.76	0.53	0.28	0.04	0.33	0.39			0.53	2.3
Ethane	2.6	2.1	1.7		0.12	0.94	0.41		2.1	3.5
Propylene	0.80	0.53	0.28	0.06	0.11	0.31			0.53	1.5
Propane	1.3	1.0	0.66		0.08	0.44	0.11		1.0	1.3
Vinyl chloride	0.51	0.59	0.66	0.04	0.25	0.17	0.02		0.59	0.64
1-Butene	0.25	0.18	0.06	0.02	0.04	0.08			0.18	0.67
Butane	0.53	0.31	0.15		0.03	0.20	0.02		0.31	0.69
Isopentane	0.02	0.02	0.01			0.005	0.001		0.02	0.02
1-Pentene	0.10	0.08	0.04		0.01	0.03			0.08	0.18
Pentane	0.26	0.20	0.11		0.01	0.08	0.01		0.20	0.29
Cyclopentene	0.07	0.05	0.03		0.02	0.01			0.05	0.19
Cyclopentane	0.08	0.07	0.03		0.01	0.02			0.07	0.11
1-Hexene	0.07	0.06	0.03		0.01	0.02			0.06	0.13
Hexane	0.16	0.14	0.09		0.01	0.05	0.01		0.14	0.20
Methylcyclopentane	0.06	0.05	0.03			0.02			0.05	0.08
Benzene	35	31	32	24	6.6	0.35	0.16		31	43
Toluene	1.5	1.1	0.68	0.12	0.18	0.55	0.03	0.01	1.1	3.5
HCl	580 ± 5, "independent of air conditions and accounts for nearly all the chlorine atoms of the polymer" (*19*, p. 388)			"Production of HCl . . . roughly parallels that of benzene" (*19*, p. 388)					"The heating rate has no significant effect on the amount of HCl produced" (*19*, p. 389)	

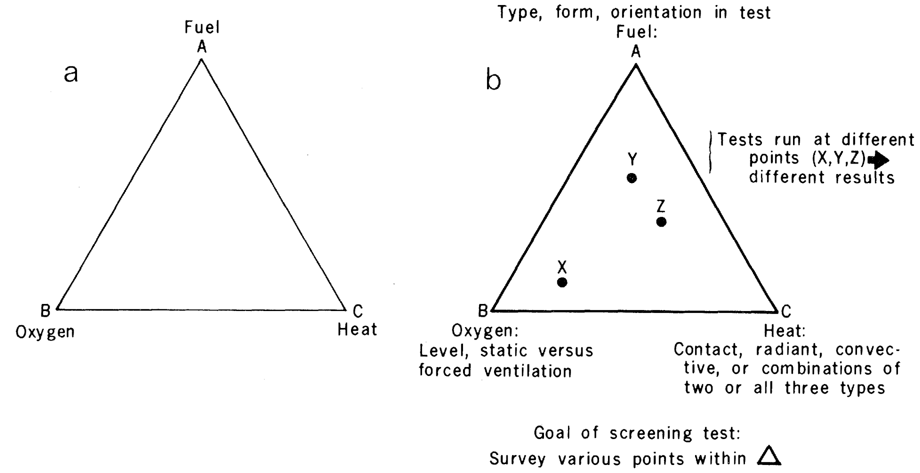

Fig. 2. Traditional fire triangle (a) and fire triangle as a test model (b) (*20*).

correlated with biologic data rather than used independently in an attempt to "determine" the composite toxicity of a polymer from thermal degradation.

Likely end-use conditions. Whether proposed use of the test material is minimal or extensive, industrial or consumer, in the furnishings or structurally concealed in many buildings, can, in many cases, govern the type of testing warranted. As a particular example, compare the use of textile fibers in draperies to their use in carpets.

End-use conditions are included as a factor because a screening test should simulate a real fire and should, if aimed at comparing various materials, evaluate them all under similar constraints. Specific uses may require consideration of additional factors, such as (i) the amounts of test material, compared to the amounts of other materials that may also be present; (ii) the rate of combustion of the test material in a fire; (iii) the nature of the actual combustion, nonflaming or flaming; (iv) the rate of ventilation; and (v) the ease of egress.

Coordination of research results has not yet generated a combustion gas toxicity test that would be useful in screening programs for identifying materials with an extraordinarily toxic potential. More than a dozen different laboratory test methods were described in the National Academy of Sciences' recent review (*18*) of small-scale combustion/pyrolysis methodologies. Moreover, some procedures appear to have been adopted solely on the basis of the reproducibility of results (precision) or the equipment currently available in the investigator's laboratory, not the parameters of the actual fire.

The importance of test design is strongly underscored by the study of Cornish *et al.* at the University of Michigan (*21*), in which the ranking order, based on the toxicity of gases given off in a test with ten common materials, literally depended on the test procedure. Subsequently, Hilado at the University of San Francisco and Crane at the Federal Aviation Administration in Oklahoma City—both using a tube furnace for sample decomposition—reported a distinct variation in their comparative ranking "best-to-worst" for seven materials (*22*). Each used slightly different conditions, such as different airflows and different amounts of sample, but the pyrolysis temperature and heating mode were the same.

The dependence of the off-gas profile on the pyrolysis temperature is further illustrated by specific studies of polyvinyl chloride (PVC), polyurethane, and polyolefins. With PVC, HCl is released between 200° to 400°C as well as at higher temperatures (Table 2). The yield per gram of polymer is independent of heating rate and ventilation. However, these two parameters, as well as temperature, strongly affect the production of CO from PVC (*19*). In the case of the polyolefins, Fig. 3 (*23*) shows that production of acrolein, which is highly toxic, occurs only over a fairly narrow temperature range.

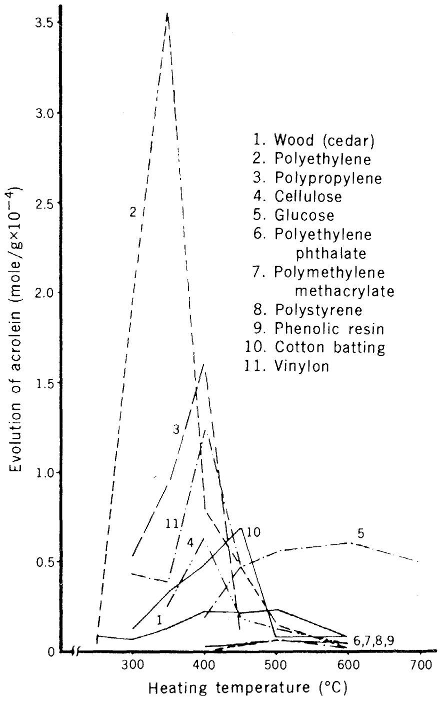

Fig. 3. Evolution of acrolein from various materials, based on a sample weight of 500 milligrams (*23*).

Polyurethane products contain both carbon and nitrogen. Woolley and Fardell (*24*) report that peak yields of HCN are typically observed at 800°C. Toxicologically important isocyanates were found in low-temperature (300°C) pyrolysis but are destroyed at 800°C (*24*). Combustion/pyrolysis data obtained with other nitrogenous polymers at > 650°C (*25, 26*) also show the strong dependence of HCN production on temperature.

Temperatures in full-scale fires vary widely, and therefore some full-scale fire tests, such as with these three products, appear needed in order to assess the significance of quantitative small-scale combustion gas toxicity data. Nevertheless, several standard combustion/pyrolysis toxicity test methods have now been formulated or are being currently explored. Germany specifies a pyrolysis method based on an annular, revolving combustion furnace for all construction materials (*27*). Samples are rated on the basis of the lowest temperature (typically 300° to 600°C) causing death in exposed rats. The French test (*28*) that became effective on 10 January 1977 applies only to synthetic polymers that are used in the furnishing or construction of public buildings and contain nitrogen or chlorine atoms. Materials are scored on their chlorine or nitrogen content and relative flammability; no animal exposure is required. In this country the National Bureau of Standards is currently engaged in a cooperative effort with some 20 organizations from government, academia, and industry to develop a screening test based primarily on the combustion system of Potts and Lederer (*29*).

Further variations in test methodology and experimental sophistication are evident in methods used to determine incapacitation—the lack of capacity to escape from a fire—as a test end point. Considerable attention has recently been given to neuromuscular dysfunction, which in fire situations is primarily due to various forms of tissue anoxia. One or more physiologic mechanisms may be involved, but the net result is the same—loss of the individual's own capacity to escape from a fire before being burned or otherwise killed. Nonfatal but elevated blood concentrations of CO and HCN have been correlated with neuromuscular dysfunction determined by failure in tests with mechanically rotated activity wheels (*30*), with rotating rods (*31*), and in conditioned avoidance as leg-flexion response (*32*). Data obtained with rats exposed to the pyrolysis/combustion offgases of 75 materials used in aircraft shows that the time to loss of function was roughly two-thirds of the time to death (*30*).

Another approach for determining incapacitation of the fire victim is to study overwhelming irritation of the eyes and nose. Although the physiologic effect of irritants as riot control agents is well understood, the contribution of these irritants to incapacitation in humans exposed to smoke remains undefined. Mice exposed to upper-respiratory irritants exhibit a characteristic pause in respiratory expiration and an overall decrease in the respiratory rate. Alarie and his coworkers (*33*) have used this technique to predict the potential irritation to humans of smoke from various polymers. However, subsequent work by Potts and Lederer (*34*) indicates that the concentration of red oak smoke predicted on the basis of tests with mice as "intolerable" to human volunteers was only irritating; they were clearly *not* incapacitated. Thus, further understanding of this mouse-to-human extrapolation appears necessary before this technique can be used in a quantitative manner to evaluate a variety of materials.

Conclusion

Overall, the most concise statement on screening tests comes from the National Academy of Sciences' subcommittee (*18*, p. 28): "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." This committee went on to give detailed recommendations on testing for methodologies. In their recommendations for research, particular emphasis was placed on developing a simple reproducible technique for assessing incapacitation.

Future Trends

We appear to be at a crossroads in the development and acceptance of a meaningful small-scale screening test that would identify combustible materials having great potential to yield large amounts of toxic agents. Three pathways can be followed. One way would be to abandon consideration of such a test because the variability of actual fires prohibits the selection of fixed testing conditions. A second way would be to adopt an available test, simply to have a test, immediately. The third way would be to continue additional research and to refine existing methodology toward a useful preliminary screening test. The third is the only viable choice. Real protection of the public is essential, but no generally acceptable test protocol exists at the present time.

A clear blueprint for development of such a first-tier screening test is contained in the report from the National Academy of Sciences (*18*). These guidelines are an integral part of a national commitment to reduce this country's fire death toll. In conjunction with the safe use of the many new exotic types of materials in our built environment, "men of good intent" must work together to construct a first-tier toxicity screening test. Such a test (used in conjunction with other fire performance tests) would denote materials that generate significant quantities of highly toxic gases when pyrolyzed or burned. Some material suppliers may forego the expense of testing, unless some minimal testing regulations come into effect. Furthermore, we need to obtain significant scientific advancement within a finite time period, preferably the next decade. It is therefore imperative to have nationally funded, well-managed test projects with clear objectives, technically qualified personnel, and realistic goals.

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