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Table of Contents

Table of Contents (continued)

List of Figures

List of Figures (continued)

List of Tables

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Barbara C. Levin, Vytenis Babrauskas, Emil Braun,
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Abstract

Some limitations and potential limitations of the NBS toxicity screening test method had been identified in earlier work. These limitations have now been explored in greater detail. Also investigated was an alternative combustion system, consisting of a radiant cone heater, identical to the one in the recently developed Cone Calorimeter, an enclosed combustion chamber, and a slightly revised variant of the animal chamber. The new animal chamber was so constructed that, prior to the insertion of the animals, it could be evacuated and then back-filled with a desired sampling of the combustion products. The radiant combustion system showed a different mix of capabilities and limitations compared to the cup furnace combustor in the existing test method. In the present project, the more detailed assessment of the cup furnace operation leads to the recommendation that there is no single, universally preferable combustion environment, but that the cup furnace is adequate for the intended purpose of providing toxicity screening.

Key words: combustion products; combustion toxicity; NBS toxicity test method; plastics combustion; radiant combustion.

1. INTRODUCTION

The NBS Toxicity Test Method [1] is a bench-scale bioassay test method which was developed as a screening tool to identify materials which may produce unusual or extremely toxic combustion products. The detailed behavior of any material so identified could then be explored by other, more detailed investigations. Work with the NBS test method has shown that most materials behave

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relatively similarly, but that a few, unusual materials exist with substantially different toxicity behavior [1].

The current test method comprises a cup furnace for heating and combusting material specimens connected to a 200 ℓ animal exposure chamber where six rats are exposed to the products generated. The cup furnace used as the combustion system consists of a removable quartz beaker surrounded by a heating element which is encased in insulation (Figure 1). The advantages of this type of combustion furnace were considered to be: (1) a low amount of heat is generated in the animal exposure chamber, compared to other alternative furnaces considered for use in this apparatus; (2) the autoignition temperatures of materials are easily determined and are reproducible; (3) thermal decomposition conditions, both flaming and non-flaming, and experimental results are reproducible; and (4) the quartz beaker is easily removable, easy to clean, and easy to replace, allowing the use of multiple beakers so that experiments can be run without stopping to cool or clean the beaker. In this system, the total mass loss of material during an exposure is determined by weighing the beaker and material before and after the test.

The NBS test method was evaluated by Anderson et al. [2], who prepared a report for the State of New York in which they examined the currently available test methods for evaluating the toxic potency of smoke. For this report, they selected a set of criteria which they considered minimal technical standards for such a test method and then proceeded to review 14 published methods using these criteria (Appendix A). Only two methods (NBS and University of Pittsburgh) were found to comply with all these criteria. In addition to meeting these basic standards, they noted that both these methods were designed as screening tools and had good publicly-available data bases. These two methods were then intensively studied under a number of diverse circumstances and for a variety of commercially available materials. After performing over 600 separate experiments, Anderson et al. found that "both test methods are scientifically sound". "The reproducibility is good between laboratories and the test results can be replicated." The two test methods were "in substantial agreement on the ranking and potency of smoke released by non-char-forming materials." "Char-forming materials showed substantial differences but generally appeared more toxic in the NBS test." Therefore, it can be considered that the NBS test method has been examined and validated by an outside study, found to be of sound design and, if in error, on the more conservative and safe side.

The documentation of the test method [1], published in 1982, stated that there were a number of issues, which were seen as limitations and which deserved further exploration. These items, which centered around the combustion system, were listed as follows:

(1) the size of the quartz beaker which fits into the furnace limits the quantity of low density materials that can be tested,

(2) no means are provided for continuously measuring the mass loss of material during the experiment,

(3) the effect of sample orientation cannot be assessed,

(4) assemblages of non-uniform structure cannot be evaluated, and

(5) the thermal exposure conditions employed do not represent all possible fire conditions.

To this list, in subsequent discussions, was added one more concern:

(6) the sample exposure conditions may represent a substantially oxygen- limited exposure.

Since 1982, considerably more experience has been gained with the test method during normal testing, special tests have been made to determine the effects of some of the variables listed above, and an alternative combustion system coupled to a new, although similar, animal exposure box was built and placed into use. Thus, we intend in this report to (1) investigate the actual performance of the cup furnace combustion system for its intended purpose, (2) consider the advantages and disadvantages of the alternative combustion system, (3) review the expected properties of an "ideal" combustion system, and (4) make recommendations on whether changes are needed to the cup furnace test apparatus. The additional materials assayed in these studies were selected as severe tests of the devices, as well as for their similarity to commercial products used for upholstered furniture, a major presence in fatal fires.

2. CHARACTERISTICS OF THE "IDEAL" COMBUSTION AND EXPOSURE SYSTEM

There are a number of standard technical traits which a good combustor and the animal exposure system should possess, i.e., ruggedness, good reproducibility, safety in operation, etc. Beyond these, however, there are a number of characteristics which should be considered for a combustor in a biotest procedure and for the means that combustion products are delivered to the animals. Some of these characteristics were considered by the National Academy of Sciences and by Huggett [3,4]. Many of these were explored in the original report [1]. In our work, further issues have also emerged as important, and we believe they should be explicitly considered as well.

- Square-wave exposure to the animals

  This is desirable because Haber's rule (which postulates that the product of exposure time and concentration is a constant which is characteristic of a toxicant) cannot be *a priori* assumed to be obeyed for a given gas or a combination of gases.

- Apparatus suitability for a fixed-time exposure

  It has become accepted in the community to do toxicity screening for fixed exposure time, generally 30 minutes. Thus, combined with the previous characteristic, it is considered desirable to be able to provide a square-wave exposure for a prescribed (i.e., not dependent on what is being tested) time, most preferably 30 minutes. In cases where shorter duration testing may be desired, an apparatus capable of a 30 minute exposure will also be adequate.

- ☐ Minimum loss of gases and particulates

  It is generally agreed that toxicity can be caused by particulates and liquid aerosols, not solely by vapors. Some of these aerosols will be lost if they are condensable at a temperature higher than the prevailing animal chamber temperature. It is logically impossible to test for these species without simultaneously subjecting the animals to some heat stress. Particulates will also be lost to some extent because of sedimentation and wall losses. This should be kept to a minimum. Also to be minimized are losses of small, polar molecules (e.g., $HC\ell$), which can be readily adsorbed onto certain wall materials.

- ☐ Representation of full-scale conditions

  Although desirable, this is extremely difficult to determine for two reasons: (1) there are negligibly few full-scale measurements of fire toxicity to animals; and (2) there are very few studies of flow, distribution, and losses of fire gases and aerosols under full-scale conditions.

Our discussions below will thus attempt to address the issues raised not only by the initial concerns, but also take into account these additional characteristics considered desirable.

3. ALTERNATIVE COMBUSTORS

Some of the questions raised can be seen to be difficult to answer without substantially modifying the existing test apparatus. Given that realization, the chosen approach was to use a different apparatus, one whose strong points would be precisely in those areas where limitations were seen with the existing apparatus (which will be here referred to as the cup furnace apparatus). The performance from that system could then be compared to the results obtainable with the cup furnace to see if and where improvements might actually be needed.

Initially, the possibility of using the Weyerhaeuser radiant heating system [5,6] was considered for use as such an alternate apparatus. This scheme involves replacing the cup furnace with a radiant heater which is placed below the animal chamber floor. As shown in Figure 2, the radiant energy is supplied by two tungsten-filament quartz lamps located below the exposure chamber and is focused on the sample. The sample is suspended on a balance pan attached to a load cell which monitors mass loss. The whole system is enclosed in a Vycor glass enclosure. NBS staff ran some tests with this system in 1980. The advantages of this apparatus, relative to the cup furnace, were seen to be: (1) it can accommodate larger samples, (2) composite materials can be placed in the sample holder such that the side normally exposed to the radiant heat of a fire is exposed to the heat flux of the lamps, and (3) the system continuously measures the mass loss of the material during the thermal degradation.

This system also has some relative limitations:

1. The position of the quartz lamps results in a higher average temperature in the animal exposure chamber. (Testing for combustion product toxicity is predicated to only exposing animals to toxic stress, and not to heat stress. Elevated chamber temperatures are undesirable and may lead to erroneous data and conclusions.)

2. The weighing assembly has a lack of precision at low mass, and it is important to distinguish those materials which are toxic in small quantities.

3. To vary the mass loadings, it is necessary to vary proportionately the specimen area, drastically reducing the area for high toxicity specimens. Thus, edge burning and rear surface losses are highly variable and it is not possible to represent the burning on a per-unit-face-area basis.

4. The local oxygen concentration in the combustion system is not monitored and probably drops rapidly in this closed combustion system.

5. There is no means of evaluating sample orientation (vertical vs. horizontal) effects on toxicity.

6. Soot deposits on the glass barrier between the heater and the specimen, with a consequent change in actual irradiance during test, and with the practical difficulty of requiring disassembly, cleaning, and reassembly prior to the next test.

From these experiences, we concluded that some of the shortcomings were operational and could possibly be minimized with sufficiently innovative design. However, one of them--the size reduction requirement--was fundamental enough to negate most of the benefits of radiant heating. Thus, we did not pursue use of the Weyerhaeuser device.

Another system of substantial promise is the German DIN test [7]. In this test a long, narrow specimen, sufficient to produce enough pyrolysate for a full 30 minute exposure is located horizontally inside a quartz tube. The tube is placed on a lathe bed and surrounded by a travelling tube furnace, propelled by the lathe drive. This system has the strong advantage that enough material can be generated to have a true dynamic, or flow-through test. The limitations, however, were seen to be several:

1. The DIN apparatus is dimensioned only for very narrow, non-composite materials, scarcely wider than wires. Even in this small scale, it is a very expensive apparatus. The cost of scaling up to a size sufficient that a composite specimen of adequate width might be burnt was considered prohibitive.

2. The scheme is not well suited to represent the total process of combustion. That is, it cannot be readily made to gather products from the burning of the top layers at the start of test, the middle layers later, and the bottom layers at the end. This issue does not arise if one is testing homogeneous, single-step kinetics substances, but in the case of composites it is a major limitation.

3. The apparatus involves a quartz glass tube between the heater and the specimen, with consequent problems of soot deposition.

4. Adequate mass loss measurements do not appear to be possible with this geometry.

Based on these observations, the travelling furnace type test geometry was also not pursued.

We then considered the fact that the ideal heater, from the point of view of efficiency and uniformity, is a conical heater. Of all the possible heater types known to us, this delivers the highest fraction of its input power to the specimen, with the highest surface radiant flux uniformity. We had used such an arrangement in developing the Cone Calorimeter [8], and achieved good results. With the addition of an animal exposure capability to the Cone Calorimeter, it was considered that the system could meet the requirements set forth for a good combustor, which would not have the limitations outlined for the cup furnace method. The details of design of the new features of the cone radiant heater (as distinct from the Cone Calorimeter, which is the similar, existing device without bioassay capabilities) are shown in Figures 3 and 4 and described in Appendix B. The operation of this alternate test system is described in Appendix C.

4. EVALUATION OF LIMITATIONS

4.1 Amount of material to be tested

4.1.1 Experiments in the cup furnace

Most of the initial data prior to the 1982 report had been obtained with a 300 mℓ beaker. Since that report, all work has been done with the 1000 mℓ beaker. The materials for which beaker capacity is in question are, specifically, foam plastics, which are the lightest density materials that have had their fire performance data evaluated. With the 1000 mℓ beaker, we have been able to test mass loadings of polyurethane foams of 8 g [9]; this amount of material decomposed in a 200 ℓ chamber equates to a concentration of 40 mg/ℓ. In some cases, the materials have been found to have LC_{50} values greater than 40 mg/ℓ. Values of LC_{50} greater than this number would generally be classified as representing materials of low toxicity potential. Since the whole development focus of the test method has been to characterize materials and products likely to be identified as fire concerns, further precision is not needed for an item which proves to be less toxic than the majority of investigated materials.

4.1.2 Experiments in the cone radiant heater

The maximum concentrations (equivalent numerically to mass loadings) that can be introduced with the cone radiant heater can be computed as follows. The specimen maximum size is 0.1 × 0.1 × 0.05 m, giving a volume of 0.0005 m^3. For a specimen density of ρ (kg/m^3), the specimen mass is 0.0005ρ. The animal chamber volume is 200 ℓ. Let the maximum fraction of combustion or pyrolysate product conveyable from the combustion chamber to the animal chamber be β. This maximum value of β is realized at minimum combustion chamber air supply and exhaust rates. Then the maximum loading achievable in the animal exposure chamber is represented by $2.5\rho\beta$ (mg/ℓ). Tests conducted with minimum practical maintainable air flow rates (approximately 25 ℓ/min) going through the combustion chamber suggest that $\beta \approx 0.6$. Rigid plastics can have a density on the order of 10^3 kg/m^3; for them, a large concentration can be generated. Flexible foams, on the other hand, may have a $\rho \approx 16$ kg/m^3. This then will result in a maximum measurable LC_{50} of 24 mg/ℓ. This is acceptable since it is similar to the LC_{50} determined for flexible polyurethane foam in the cup furnace [1,9]. A special operational uncertainty arises in the cone radiant heater method because of the large volume of the combustion chamber, compared to the small air flow rates that are necessary when burning lightweight materials. At the start of the test the combustion chamber represents a large reservoir which the combustion products must gradually fill, before an equilibrium concentration is established. (This limitation does not arise in the Cone Calorimeter, since there the air flow rates are large and the equilibration time is very fast.) If the burn time is not long, then the initial products are somewhat more dilute than calculated on the basis of a steady flow concentration.

4.1.3 Conclusions on amount of material to be tested

On this particular point, the cup furnace method and the cone radiant heater alternative are adequate, and are about equal in performance. Materials of very low toxicity cannot be quantified in either system, but since the purpose of the screening method is to identify materials of high toxicity, this is not considered a real limitation. Furthermore, consideration of more novel, yet practical achievable systems suggests that it would be very difficult to make an improvement here.

4.2 Means of continuous mass monitoring

4.2.1 Experiments in the cup furnace

The normal procedure with the cup furnace has been to obtain the tare mass of the beaker, the initial mass of the specimen, and the final mass of beaker and residue. This is sufficient data to determine the specimen mass lost. The only additional purpose for which a time-dependent mass loss record might be necessary is to assure that the sample combustion time is short compared to the exposure time and, thus, that a square-wave exposure has been achieved. Decomposing materials within 25°C of their autoignition temperatures in the cup furnace system presupposes the maximum pyrolysis rate and that the animals will be exposed to all of the fire gases for close to 30 minutes.

In principle, it might be possible to envision some material which decomposes at a rapid rate only during the last few minutes of the 30 minutes of heating, but, in practice, such materials are usually not found.

That such a problem does not exist can be shown without a real-time mass measurement capability, by deducing the time-behavior of the burning process by using combustion product (CO, CO_2, and HCN) generation data. Figures 5-8 show these results from a diverse group of materials that we have tested. Under flaming conditions, the generation rates of CO and CO_2 indicate that for all of the tested materials the effective burning is completed in 2 to 10 minutes (Figures 6 and 8). This constitutes a reasonable conformance to the desire that the gas generation period be much shorter than the 30 minute total exposure time and that a square-wave exposure is approximated. Under non-flaming conditions (with the exceptions of Douglas fir, red oak and polyester) most of the effective thermal degradation, as indicated by the generation of CO and HCN, is also completed within 10 minutes (Figures 5 to 7).

The error resulting from an imperfect square-wave exposure can be bounded for those materials where Haber's rule is obeyed. In that case, the error is simply the difference between the actual area under the concentration-time curve, and the area of the circumscribed bounding rectangle. Figures 5 through 8 clearly show these differences to be less than a factor of two. It must be emphasized that it cannot be presumed that the test material being screened obeys Haber's rule, and thus that, in general, no *a posteriori* correction could be made to the results to adjust for non-square-wave exposure by the use of load cell data.

Nonetheless, to more fully address the issue of availability of this diagnostic tool, we have installed a load cell in a modified version of the cup furnace (Figure 9). The load cell has a tare capacity of 3500 g, a weighing capacity of 500 g, and a resolution of ±0.01 g. Figure 10 shows an extreme-case result for a flexible polyurethane foam specimen at 25 °C below its autoignition temperature which unpredictably ignited approximately 5 minutes after the start of the test. In experiments where animals are exposed, the results from such a test would be discarded, since in flaming tests, according to the current test protocol [1], the material must ignite within 10 seconds, and in non-flaming tests, the material should not ignite at all. Nonetheless, the results show that close to 90% of the material was consumed at 6 minutes after the start of the test, and, thus, that a reasonable approximation to a square wave exposure holds.

4.2.2 Experiments in the cone radiant heater

The cone radiant heater is equipped with a load cell, whose output is regularly recorded during a test (Figure 3). Mass loss rate data are very important in the normal use of the Cone Calorimeter for obtaining effective heats of combustion, and also for quantification of the release rates of gas and smoke on a per-mass basis. In the operating procedure described in Appendix C, we have found it convenient to use the load cell for determining the mass loss rate over a given period. Since, unlike with the cup furnace, in the cone radiant heater method the combustion products of the complete specimen degradation period are not necessarily introduced into the animal exposure chamber, the specimen load cell is a very convenient feature.

4.2.3 Conclusions on means of continuous mass monitoring

For the cone radiant heater apparatus, the adopted operating procedures serve to assure that a square-wave exposure is being generated. The load cell is useful in that apparatus, nonetheless, for easy determination of the fraction of the specimen pyrolysate which is being introduced into the animal exposure chamber. In the cup furnace apparatus, while it has been demonstrated that a load cell can be successfully implemented, it is not proposed to modify the screening test procedures to add this measurement for the following reasons: (1) the data generated cannot be quantitatively used in assisting the process of screening materials; (2) its use would increase the screening test complexity and cost; and (3) the maximum errors are estimated to be less than a factor of two, which is considered within the validity bounds of the toxicity screening test.

4.3 Specimen orientation effects

4.3.1 Experiments in the cup furnace

Specimen orientation effects are considered important when the modeling of surfaces exposed to fire is done, i.e., in radiant heating environments. In the cup furnace a small mass of specimen is used, not intended to represent the same surface boundary conditions as in actual fires. Thus, it was not appropriate to vary specimen orientation in the cup furnace apparatus. It was possible, nonetheless, to make appropriate experiments in the cone radiant heater, as shown below, which characterize the magnitude of this effect.

4.3.2 Experiments in the cone radiant heater

A detailed investigation was made in the cone radiant heater geometry to assess the effects of material orientation on the generation of the toxic gases CO and CO_2. (Specifically, since only gas generation data were needed, the experiments were done in the Cone Calorimeter). As an example of a typical end use item, a flexible polyurethane foam, with a density of 21.8 kg/m^3, was used. Table 1 shows the results for both this foam alone and as a composite with a cotton fabric covering. The fabric weight was 0.61 kg/m^2. In only one case (non-flaming, no fabric) was there a significant difference in the generation of CO between horizontal and vertical specimen orientation. In that one case, about a 3:1 ratio for CO was observed. This difference could be due to specimen variations, since only small samples were tested, and it is well-known that for some polyurethane foam manufacturing processes substantial variations may occur over the width of a full-scale specimen. Also, the number of specimens tested was small, i.e., 3 for the vertical orientation and 4 for the horizontal orientation. (The data from two of the non-flaming horizontal tests had discarded since flaming occurred. This also happpens occasionally in the standard cup furnace test method. Some materials show sufficient intrinsic variability that in a given test which is at 25 °C below the autoignition temperature and is intended to represent non-flaming conditions, flaming can erupt, in which case these data are to be discarded.)

Additional corroborative data had been gathered earlier with the Cone Calorimeter. For instance, the original report [8] illustrates the rates of heat release for polymethylmethacrylate (PMMA) and red oak. The rates of heat release for PMMA are typically 10% lower in the vertical orientation as compared to the horizontal; for red oak, the comparable figure is 30%. Neither of these would be significant in the context of fire toxicity screening. The difference in ignition times is, again, slight, being longer in the vertical orientation by about one standard deviation. In general, observations of combustion in the Cone Calorimeter point out that there are often slight, but statistically significant differences in ignition times for different orientations; some marginally igniting specimens may ignite in one orientation but not the other; melting/dripping specimens can show anomalous behavior in the vertical orientation; and most specimens show slightly higher rates of heat release in the horizontal orientation. Taken together, these general observations, combined with the specific tests conducted above, suggest that the effects of orientation are minor. There is one caveat to this, namely, that radiant testing in the vertical orientation should not be conducted on specimens prone to melt and drip.

4.3.3 Conclusions on specimen orientation effects

Based on the work with the Cone Calorimeter, it is concluded that specimen orientation effects are small, and that it is sufficient to conduct toxicity screening test using any one orientation of specimen.

4.4 Non-uniform specimens

It is undoubtedly important to be able to evaluate non-uniform (i.e., composite or laminated) specimens, and thus it may be desirable, but not necessarily mandatory to test non-uniform specimens. A lot has to do with the scale of the non-uniformity. A specimen whose only non-uniformity is that it consists of two different bonded layers of fabrics or films could obviously be readily tested. Contrariwise, a wall construction system which is non-uniform on a 16 inch modularity (as has been common for innovative housing) could not be tested by a truly representative specimen in any bench-scale test.

4.4.1 Experiments in the cup furnace

In the cup furnace, we have studied a flexible polyurethane foam and a polyester fabric, two common components of commercially available upholstered chairs. The fabric and foam were heated individually and then together; in the latter case, the fabric was dropped into the cup followed by the foam. These experiments indicated that: (1) Both materials contributed to the toxicity of the combined materials, (2) The gases generated from the mixture in the non-flaming mode could be predicted from a summation of the gases produced by the separate materials, and (3) The amounts of CO and HCN generated by the mixture in the flaming mode were greater than the sum of the concentrations from the individual materials. The results of these experiments were sent to the CPSC in September, 1984 and have been presented at the Eighth Joint Meeting of the U.S.-Japan Panel on Fire Research and Safety in Tsukuba, Japan in May, 1985 [10] and at the First International Meeting on Fire Science

Safety, National Bureau of Standards, Gaithersburg, MD in October, 1985. A copy of the presented paper containing the detailed results is included as Appendix D.

4.4.2 Experiments in the cone radiant heater

One of the primary design considerations with the Cone Calorimeter was the capability to test non-uniform materials under conditions typifying end use. A large number of furniture composites, wall material composites, and composite reinforced plastics have so far been satisfactorily tested in the Cone Calorimeter [11]. This capability is clearly an operational advantage of the cone radiant heater over the cup furnace.

Difficulties, however, were encountered in the determination of LC_{50} values when the above flexible polyurethane foam and polyester fabric were tested singly in the cone under conditions designed to generate the maximum combustion products, i.e., low air flow rates, flux levels close to the materials' autoignition energy levels, maximum amounts of materials, etc. No animal deaths were observed following exposures to either the flaming (F) or non-flaming (NF) combustion products from either materials. The estimated LC_{50} values for the polyurethane would be >20 mg/ℓ, NF and >25 mg/ℓ, F (Table 2). For the polyester, the estimated values would be >5 mg/ℓ, NF and >52 mg/ℓ, F (Table 3). (No animals were exposed to the non-flaming polyester since the concentrations were so low.) However, when the composite, consisting of the fabric covered foam, was decomposed, some animal deaths occurred (Table 4). In these experiments, the results were similar to those of the cup furnace in that post-exposure deaths occurred in the non-flaming mode and with-in exposure deaths occurred in the flaming mode. Estimated LC_{50} values (~30 mg/ℓ, NF and between 34 and 48 mg/ℓ, F) were not greatly different from those achieved with the cup (48 mg/ℓ, NF and 39 mg/ℓ, F) (See Appendix D).

4.4.3 Conclusions on non-uniform specimens

Satisfactory toxicity screening results can be achieved with the use of the cup furnace method. Composites for which it is known that the surface materials do not offer a substantial fire barrier protection to the underneath layers can be tested simply as an agglomeration, instead of a layered composite. (At the other extreme, interstitial materials which are very adequately protected from fire involvement by the surface layer may not need to be tested at all.) There is an intermediate regime, where the surface layers act to slow down, but not to wholly eliminate, the burning of the underneath layers. If a detailed characterization of such construction is required, it is possible, in principle, to determine in the Cone Calorimeter the relative involvement of the layers, and then to conduct several cup furnace tests using individual materials or agglomerations.

We do not believe that the present state of the art of fire hazard modeling warrants such detailed testing plans. That is, the prediction of actual fire involvement in a system where composite materials are involved has not been systematically undertaken. Thus, while it is possible to use the toxicity screening test to evaluate the individual layers and any desired agglomerations (to test for synergisms or antagonisms), it is not at all evident that there would be an application for the data so obtained.

From this, we conclude that the cup furnace method is adequate for testing practical materials, that limitations on testing of non-uniform assemblies can be addressed using a supplementary technique for screening composites, if and when such testing becomes a necessity, but that substantial progress will have to be made with fire hazard modeling before such experimental capabilities will be required.

4.5 Thermal exposure conditions

4.5.1 Experiments in the cup furnace

There can be a very large number of thermal exposure conditions possible in real fires, depending on the fire scenario, article type, location, etc. A screening test cannot possibly take into account this multiplicity of environments. What can be done, however, is to select a set of conditions which tend towards a worst case characterization. The results of NBS work, the findings from the laboratories that participated in the interlaboratory evaluation of the toxicity test method [12], and the literature all indicate that the most toxic conditions are probably generated at temperatures close to each material's autoignition point. In the non-flaming mode, as the temperature rises and approaches the autoignition temperature, more and more of the material is degraded and more toxic products are produced. And, of course, in the flaming mode, the higher the temperature, the more complete the combustion, the ultimate results of which is the production of only carbon dioxide and water. Thus, in the cup furnace, each material is tested at 25 °C above and below that material's autoignition point, i.e., a flaming and non-flaming exposure. The autoignition temperature in this test is defined as the lowest furnace temperature which causes a material sample to ignite spontaneously within 30 minutes. That such an approach is reasonable has been demonstrated in the original report [1]. For example, a modacrylic material was decomposed at different temperatures in both the flaming and non-flaming mode (Table 5). The results clearly showed that as the temperature increases in the non-flaming mode, the LC_{50} decreases, i.e., less material is needed to cause the animals to die. A systematic study on this point with a large number of varied materials has not been done, however, a large number of investigators have studied temperature effects [11]; in most cases, their observations were consonant with our approach to minimize the flaming condition temperatures and maximize the non-flaming temperatures.

4.5.2 Experiments in the cone radiant heater

From several points of view, the cone heater arrangement is extremely versatile: heating fluxes of zero to 110 kW/m^2 can be imposed; air flow rates from negligible to 50 ℓ/s can be set; and combustion air supply O_2/N_2 ratios can be varied across the whole range from pure oxygen to pure nitrogen. The details of thermal exposure conditions and their effects on sample materials have been published for the Cone Calorimeter [8]; the thermal exposure conditions applicable to the cone radiant heater are essentially identical. Nonetheless, even in this highly flexible apparatus, certain scale-associated parameters cannot be independently adjusted. Specifically, a radiant source exposure, over a small sample, still may fail to simulate full-scale phenomena such as turbulence (specifically, large-scale turbulent structures), optically thick plumes or wall layers, and other actual conditions. Thus, while any adequate test method should be capable of heating the specimen to an agreed-upon level, the details of how that heating is accomplished may never be fully under the experimenter's control.

4.5.3 Conclusions on thermal exposure conditions

In the context of a toxicity screening method, great flexibility in varying combustion conditions over wide extremes is not a suitable objective. Some day, fire hazard models may become available which treat finer details of localized combustion phenomena. It is important to realize that, at the moment, there is not even a model to determine what fraction of a building's fire gases may be due to flaming versus non-flaming exposure condition elements.

For the present, the cup furnace, operating in the flaming and non-flaming modes, is clearly capable of identifying highly toxic materials. No other method has detected any such materials that this method has missed. Thus, we conclude that the cup furnace method successfully provides the information which is required for toxicity screening purposes.

4.6 Oxygen limitations

4.6.1 Experiments in the cup furnace

The cup furnace geometry presents a very complex system from a fluid mechanical point of view. Similar combustion systems studied in the past which involved a partly enclosed volume communicating to the environment have on occasion shown "gulping" instabilities and similar patterns. To our knowledge there has not been a study, however, of a combustion geometry which is sufficiently close to the present one, so that quantitative judgments could be made. Indeed, the problem of studying the flows in detail is very difficult and was not considered rewarding enough to make such a large effort.

Instead, we decided to determine the magnitude of the effect of varying the available oxygen. For this investigation, an aerator was constructed (Figure 11). It consisted of a 6 mm diameter glass tubing insert, lowered down into the beaker to sit next to the beaker wall (clear spacing = 3 mm) and to provide a flow of gas to the immediate vicinity of the specimen. This flow was made approximately axisymmetric by providing the aerator with 29 holes, each 1 mm in diameter, equi-spaced along the bottom perimeter. In principle, the aerator could be used to deliver any desired choice of gas. We concluded for these exploratory tests that recirculated chamber air was the best choice. The use of pure oxygen or some other O_2/N_2 mixture would have been tantamount to changing the overall animal chamber environment, and we would have lacked a control.

A series of experiments was conducted under both flaming and non-flaming combustion conditions to determine what effect, if any, ventilating the cup furnace with this aerator would have on the overall composition of the thermal degradation products as indicated by CO and CO_2 generation. A flexible polyurethane foam (code PUF #32) was thermally degraded at 375°C (non-flaming conditions) and 450°C (flaming conditions) with ventilation flows through the aerator of 250, 500, 2000, and 4000 mℓ/min. At the highest flow rate in the 1000 mℓ cup furnace, the air volume in the cup would be exchanged every 15 seconds. During each 30 minute test, CO and CO_2 levels inside the chamber were recorded every 15 seconds.

The CO and CO_2 levels produced under flaming and non-flaming conditions were compared for the various air flow conditions (Figures 12-15). While some differences in the concentrations or generation rates of CO and CO_2 under the different ventilation conditions were observed, it was concluded that they were not consistent enough to indicate a unique trend. Under the flaming conditions, the absolute amounts of CO and CO_2 appear to be greater with the aeration than with no aeration (Figures 12,13). However, this probably indicates only a slightly enhanced combustion rate and not a changed toxicity. A more meaningful evaluation would be based on the CO/CO_2 ratio which is an indication of both the completeness of combustion and of the total ultimate proportioning of the products. Final, 30-minute CO/CO_2 ratios under the different flow conditions were: naturally buoyant = 0.018; 250 mℓ/min = 0.023; 500 mℓ/min = 0.024; 2000 mℓ/min = 0.021; and 4000 mℓ/min = 0.017. Based on these CO/CO_2 ratios, the combustion completeness obtained under the naturally buoyant condition is concluded to be as good as that for the aerated tests.

Under the non-flaming conditions, the average CO concentration was somewhat greater without aeration than with aeration (Figure 14). However, the ultimate CO levels reached in the tests with flow rates of 250 and 4000 mℓ/min were essentially identical to that obtained with no air flow. The CO_2 concentrations also similar to those obtained under the various air flow conditions (Figure 11). The average CO/CO_2 ratios were: naturally buoyant conditions = 0.77; 250 mℓ/min = 0.81; 500 mℓ/min = 0.54; 2000 mℓ/min = 0.55; and 4000 mℓ/min = 0.66. These CO/CO_2 data indicate that ventilating the cup does not necessarily reduce the CO generation tendencies under non-flaming conditions. In fact, since the oxygen level in the total exposure system did not drop below 20% during these tests, it is unlikely that the cup was in a vitiated state. A possible cause for the slightly different overall CO and CO_2 levels in the non-flaming aerated tests may be the shortened residence time volatilized components might spend in the heated zone. Thus, we conclude that even though some slight differences were observed in the CO and CO_2 levels under the static and aerated test conditions, these differences did not indicate a consistent trend.

4.6.2 Experiments in the cone radiant heater

There are no significant shortcomings to the apparatus in this area. In normal operation free access to 21% oxygen supply air is available at all times. If desired, up to 100% pure oxygen can be introduced as the combustion air supply. While the apparatus provides for such a possible operation, we have not operated under conditions of oxygen different from 21%. No specific experiments were considered needed in this area.

4.6.3 Conclusions on oxygen limitations

Based on our aerator experiments, oxygen supply does not appear to be a limitation in the normal operation of the cup furnace test method. Thus, it is not recommended to require the normal use of the aerator, nor to make any other changes for enhanced oxygen delivery.

4.7 Other constraints of the cone radiant heater apparatus

The following limitations, not present in the cup furnace apparatus, were found for the cone heater apparatus:

- ☐ Transfer line clogging. The transfer line clogged badly due to soot deposition. It was not considered desirable to filter or otherwise eliminate the soot since this can have a potential effect on the total effluent toxicity. The amount of deposition required that the line be disassembled after every test, cleaned out, and reassembled. It also meant that toxic products might not be reaching the animals. This deposition might have been lessened by heating the line, since a portion of such wall losses are due to thermophoretic effects, which would be eliminated if the line temperature were kept above the gas temperature. However, since part of the line is located inside the combustion chamber, since a control valve is involved, and since the animal chamber temperatures could be adversely affected, the design of a proper line heater could be quite difficult and was not undertaken. The decomposition of soot in the stack between the combustion chamber and the sampling line also posed the problem of potential carry-over of toxicants from one test to another, especially if the testing mode changed from non-flaming to flaming.

- Difficulties in filling rate control. The filling rate was controlled by monitoring the differential pressure across a length of transfer line, and using the manual control valve to maintain this pressure at a level corresponding to a uniform filling rate. The relationship between the pressure readings and the filling rate was pre-determined from flow calibrations (see Appendix B). In some cases, good control was difficult to achieve under all conditions, i.e., both with the animal chamber evacuated and with the chamber nearly back-filled. A mass flow controller was considered but was not implemented because significant difficulties were expected from sooting.

- Large reservoir volume in the combustion chamber. The Pyrex-enclosed combustion chamber represents a substantial volume of approximately 100 ℓ if the exhaust piping up the stack control valve is included. The mixing and dilution of the combustion products with this volume of initially ambient air is not a problem if combustion rates and flow rates of the air are rapid. In the case of low density foam, however, only a small amount of specimen mass is available. Therefore, very small combustion chamber air flow rates must be set. Under these conditions, there is a substantial error in determining the concentration of combustion products in the combustion chamber, and, consequently, in the equivalent mass loading needed to calculate the LC_{50}. Also, any effects of secondary combustion from heater hot surfaces can likewise be dependent on the combustion chamber air flow rate.

☐ Test running time. It takes about 30 minutes to evacuate the animal test chamber. Another half hour or more may be spent disassembling and cleaning the transfer line. General calibration and setup for the system is also substantially longer than for the cup furnace. Consequently, there is at least a doubling of the time required to conduct tests.

5. RECOMMENDATIONS

5.1 Modifications to the NBS toxicity test using a cup furnace

We recommend no changes to the NBS toxicity apparatus or procedures at present. Our explorations based on a cone radiant heater alternative apparatus confirmed some limitations of the cup furnace combustor, but also pointed out a number of equally serious limitations in the alternative apparatus. With the acceptance of a new methodology as proposed above, the bulk of the toxicity testing effort will be shifted to the Cone Calorimeter heat release rate apparatus, along with its necessary gas analysis instrumentation. The needs for a final bioassay check can be adequately met by the cup furnace apparatus. Since fire modeling needs will be primarily met by the results from the Cone Calorimeter, it will not be necessary to seek the elusive goal of the "perfect" bioassay tool. It will merely be necessary to be confident that the bioassay tool used is the one best suited for the task. Based on our initial work [1], the studies of the National Academy of Sciences [3], Anderson et al., [2] and Huggett [4], and on our review of the world-wide study of combustion toxicity test methods prepared by Kaplan et al.[17], we do not see any indications at the present that there either is a significantly better tool than the cup furnace, or that one could be feasibly and affordably developed.

5.2 Increased emphasis on achieving full-scale/bench-scale correlation

While great strides have been made over the last few years in quantifying toxic agent effects, essentially no progress has been made on an issue which is every bit as important--the validation of bench-scale techniques against full-scale measurements. Very few such attempts have even been made [13]. In every case, the test programs were very limited and the results subject to enough uncertainty that it could not be fairly concluded that progress was being made. This is not for the lack of good intentions, however. Full-scale testing is at least one, and generally two, orders of magnitude more costly than bench-scale work.

A second impediment to progress has been the lack of an integrated measurement tool. Little progress was made in room fire testing as a science, until it was realized that what had to be measured were not point measurements, such as temperatures, but integrated measurements, especially the heat release rate. Once this was realized, the Furniture Calorimeter and other full-scale heat release rate measuring tools could be constructed, and rapid progress resulted.

In toxicity evaluations, however, such an integrated measure is still somewhat elusive. In a very simple approach, only the total mass outflow rate for specific gases could be monitored. These could be measured in the exhaust system where room and corridor flow products are collected. This may not be adequate, since wall losses are involved, an issue which does not arise in conjunction with measuring oxygen consumption to describe the heat release rate. An even more serious complication is the modeling of local conditions. For heat modeling, it is sufficient to know the heat release rates since models exist for calculating the desired local variables (e.g., temperature) once these rates and basic geometric properties are known. Toxic hazard modeling requires not only all of the necessary heat modeling, but also modeling of local mixing, diffusion, losses, and, potentially, reactions. This is a task, some features of which are starting to be worked, but, which is, nonetheless, unsolved and very difficult.

Thus, it is recommended that greater effort be placed into modeling of full-scale fire toxic hazard conditions, and that close coordination be kept between the development of bench-scale tests and their validation in full scale. This, especially, suggests that excessive fine-tuning of bench-scale methods is not prudent, pending any needed redirection from full-scale findings.

6. ACKNOWLEDGEMENTS

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TABLE 1

Effect of Orientation of Flexible Polyurethane Foam With and Without a Fabric Cover on the Generation of CO and CO_2 in the Cone Calorimeter Tests

Mode	Cover	Orientation	CO (ppm)	CO_2 (ppm)	CO_2/CO ratio
flaming	+	horizontal	970 ± 126	60400 ± 1100	62
	+	vertical	1330 ± 129	50900 ± 4100	38
	-	horizontal	400 ± 28	72900 ± 3000	183
	-	vertical	400 ± 34	77800 ± 3600	230
Non-flaming	+	horizontal	2810 ± 50	42700 ± 9500	15
	+	vertical	2550 ± 473	39500 ± 11800	15
	-	horizontal	1210 ± 104	56800 ± 3600	47
	-	vertical	430 ± 27	62300 ± 7200	145

Values of CO and CO_2 are in ppm ± standard deviations from 2-4 tests. These values were computed on the basis of all the combustion products from an 8 g specimen filling a 200 ℓ box.

TABLE 2

Toxicity Results for Flexible Polyurethane #13 Using the Cone Radiant Heater

	Combustion Chamber Conditions				Exposure Chamber Conditions							Animal Results # died/# tested	
			Mass		Gas Sampling Time		Gas Concentrations						
Mode	Expt. flux[b] (W/cm²)	Air flow (ℓ/min)	loaded (g)	consumed (g)	Initial (min:sec)	End (min:sec)	CO Init./final (ppm)	CO_2 Init./final (ppm)	O_2 Avg. (%)	HCN Avg. (ppm)	Conc[a] (mg/ℓ)	Within Exposure	Within plus post
NF	2.0	25	13.0	7.0	4:00	11:00	630/630	1700/4870	20.6	ND	19	0/6	0/6
		25	14.0	6.3	4:00	11:15	500/440	1600/5680	20.5	ND	17	0/6	0/6
		15	12.8	5.3	5:00	14:50	520/470	1670/5340	20.6	6	13	0/6	0/6
		5	11.9	11.8	5:00	18:40	470/390	970/3130	20.9	6	20	0/6	0/6
F	2.0	60	13.3	7.5	1:00	5:40	1120/1040	36700/41380	16.1	ND	17	0/6	0/6
		40	13.1	ND	2:00	7:40	1690/1583	42080/44870	15.6	ND	-	0/6	0/6
		25	13.9	7.9	2:00	10:10	1140/1010	41000/44840	15.7	20	25	0/6	0/6

---

a. $$C_e = \frac{1}{V_e} \int_{t_1}^{t_2} \frac{f(t)}{V_b} \left(\int_o^{\tau} \frac{dm\,(t)}{dt}\, dt \;\; (1-\exp(-v_{out}\; /V_b)t) \right) dt$$

C_e = mass loading in the exposure chamber
V_e = volume of the exposure chamber
V_b = volume of the combustion chamber
$f(t)$ = sampling flow rate into the exposure chamber
$dm(t)/dt$ = mass loss rate
v_{out} = flow rate out of the combustion chamber
t = time
t_1 = start of sampling into the exposure chamber
t_2 = end of sampling into the exposure chamber
τ = end of test

b. Flux at which experiments were conducted. Flaming was initiated by an electrical spark. Autoignition flux was 2.08 W/cm².

ND. Not determined

NF. Non-flaming

F. Flaming

TABLE 3

Toxicity Results for the Polyester Fabric Using the Cone Radiant Heater

	Combustion Chamber Conditions				Exposure Chamber Conditions							Animal Results	
							Gas Concentrations					# died/# tested	
			Mass		Gas Sampling Time								
Mode	Expt. flux[b] (W/cm^2)	Air flow (ℓ/min)	loaded (g)	consumed (g)	Initial (min:sec)	End (min:sec)	CO Init./final (ppm)	CO_2 Init./final (ppm)	O_2 Avg. (%)	HCN Avg. (ppm)	Conc[a] (mg/ℓ)	Within Exposure	Within plus post
NF	2.0	25	23.9	2.5	2:00	8:00	~100/~100	~650/~650	20.9	ND	<5	NA[c]	NA[c]
F	3.5	25	23.8	18.2	2:00	12:00	1900/1840	49780/53740	15.9	ND	52	0/6	0/6

---

a. same as on Table 2
b. flux at which experiments were conducted. Flaming was initiated by an electrical spark. Autoignition flux was 4.0 W/cm^2.
c. no animals were exposed in this experiment due to low concentrations of combustion products.
ND. not determined
NF. non-flaming
F. flaming

TABLE 4

Toxicity Results for Flexible Polyurethane #13 plus Polyester Using the Cone Radiant Heater

	Combustion Chamber Conditions				Exposure Chamber Conditions							Animal Results # died/# tested	
			Mass		Gas Sampling Time		Gas Concentrations						
Mode	Expt. flux[b] (W/cm^2)	Air flow (ℓ/min)	loaded (g)	consumed (g)	Initial (min:sec)	End (min:sec)	CO Init./final (ppm)	CO_2 Init./final (ppm)	O_2 Avg. (%)	HCN Avg. (ppm)	Conc[a] (mg/ℓ)	Within Exposure	Within plus post
NF	2.0	25	24.0	12.6	5:00	12:15	790/600	800/3290	20.7	ND	30	0/6	3/6[c]
		15	23.7	12.3	5:00	14:20	580/470	1290/3160	20.7	ND	31	0/6	0/6
F	2.0	25	24.7	14.9	2:00	9:20	3650/3420	55600/55950	16.4[d]	28	48	5/6	5/6
		25	25.5	15.1	2:00	10:10	2130/1980	51840/53740	15.8[e]	22	34	0/6	0/6

---

a. same as on Table 2.
b. flux at which experiments were conducted. Flaming was initiated by an electrical spark.
c. 2/6 animals died within 14 days; one died on day 25.
d. O_2 added to exposure chamber.
e. O_2 added to exposure chamber which was then backfilled with air.
ND. not determined
NF. non-flaming
F. flaming

TABLE 5

Toxicity of Modacrylic Decomposed at Different Temperatures [1]

Mode	Temperature (°C)	LC_{50} (30 minutes + 14 days) (mg/ℓ)
Flaming	760 - 775	7.1 (6.4- 7.9)[a]
Non-flaming	710 - 720	7.8 (6.3- 9.7)
	445 - 460	10.0 (6.9-14.4)
	390 - 400	13.6 (10.7-17.3)
	295 - 305	21.8 (18.4-25.8)
	250 - 260	∿23.8[b] (17.0[c]-28.3[d])
	200	>22.6[e]

---

a: 95% confidence limits
b: Approximate value determined from values in brackets
c: 0/6 animals died at this mass loading/chamber volume
d: 5/6 animals died at this mass loading/chamber volume
e: No animals died at this mass loading/chamber volume

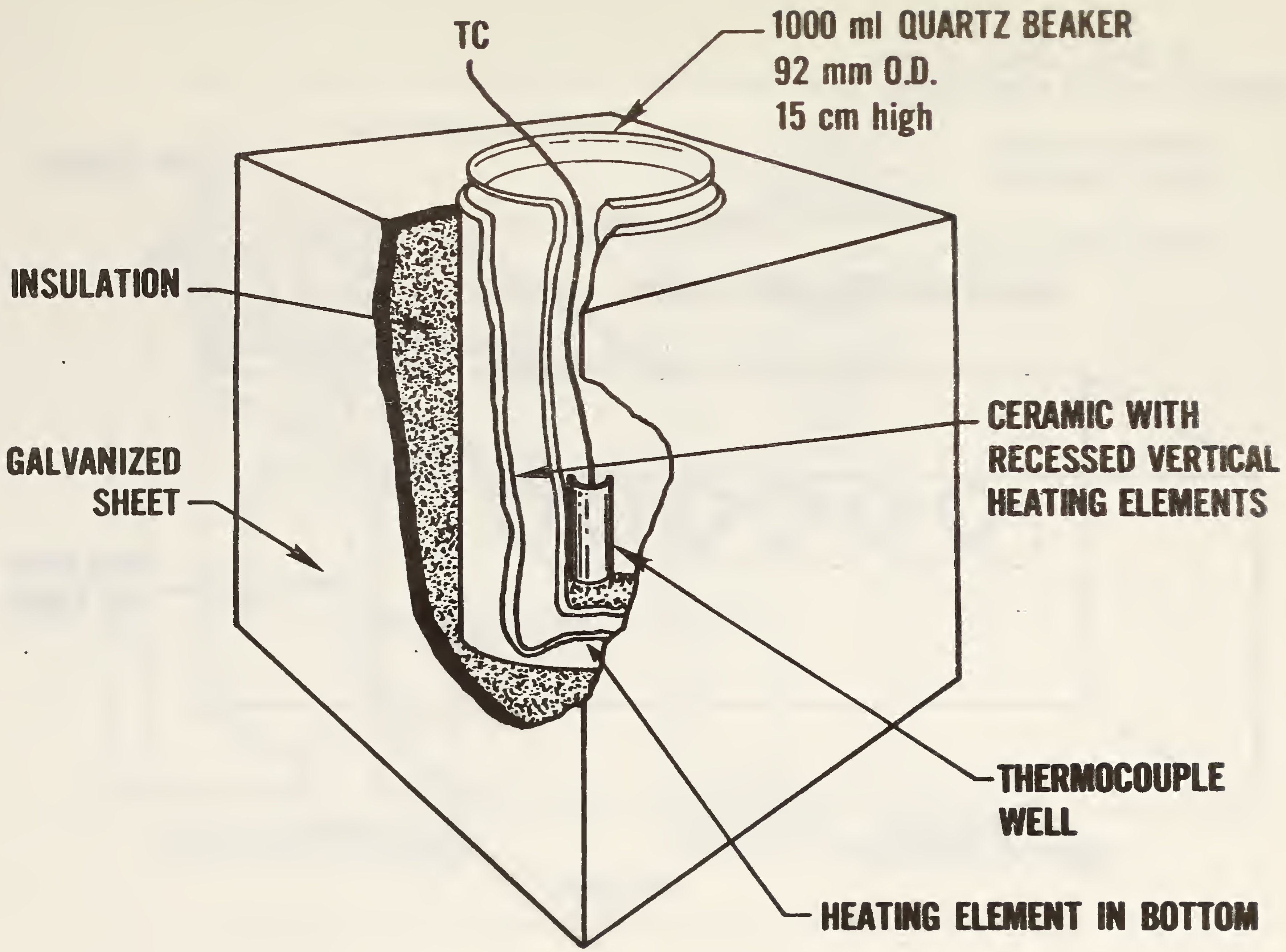

Figure 1. Cup Furnace

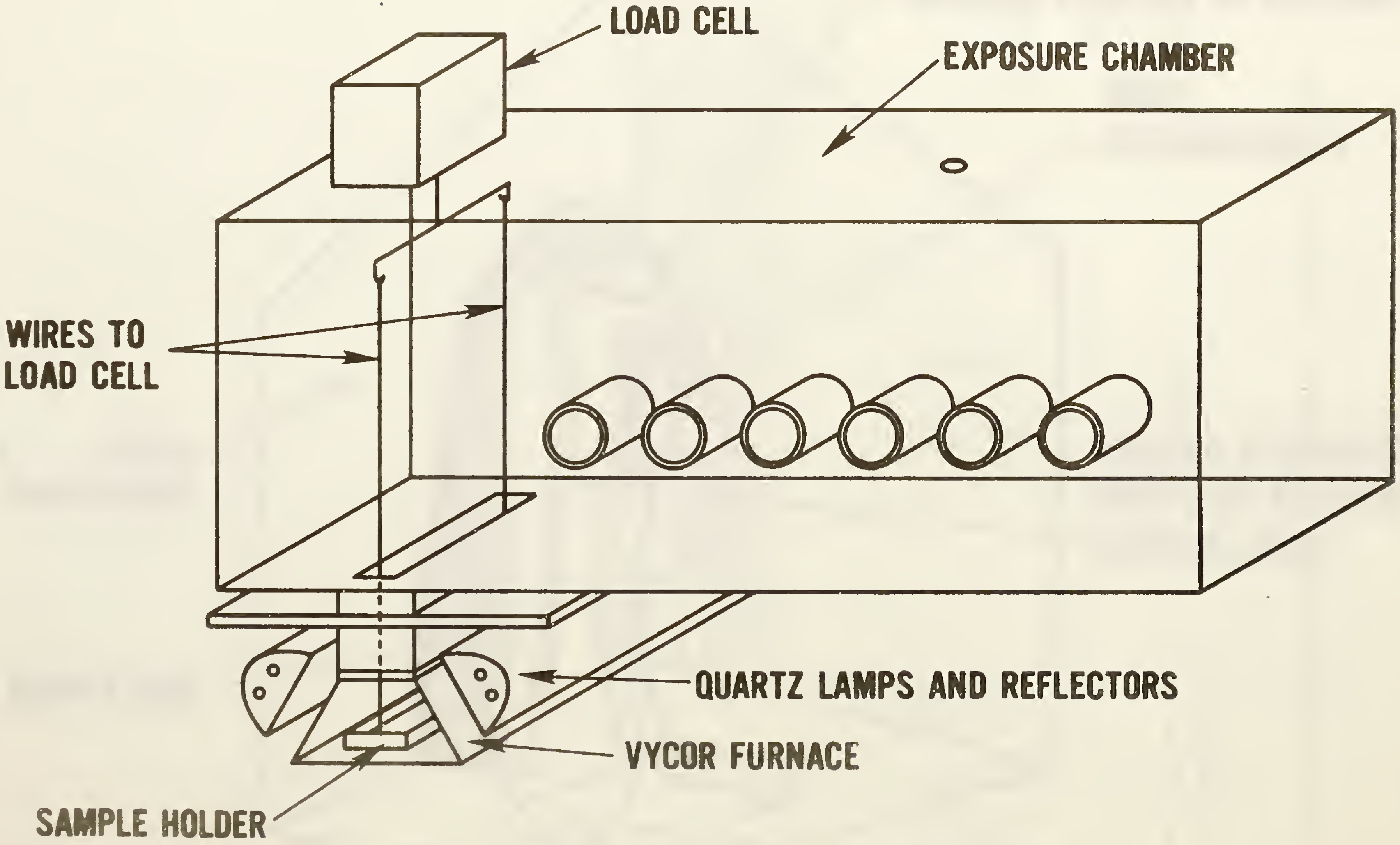

Figure 2. Design of the Weyerhaeuser radiant heat toxicity test apparatus

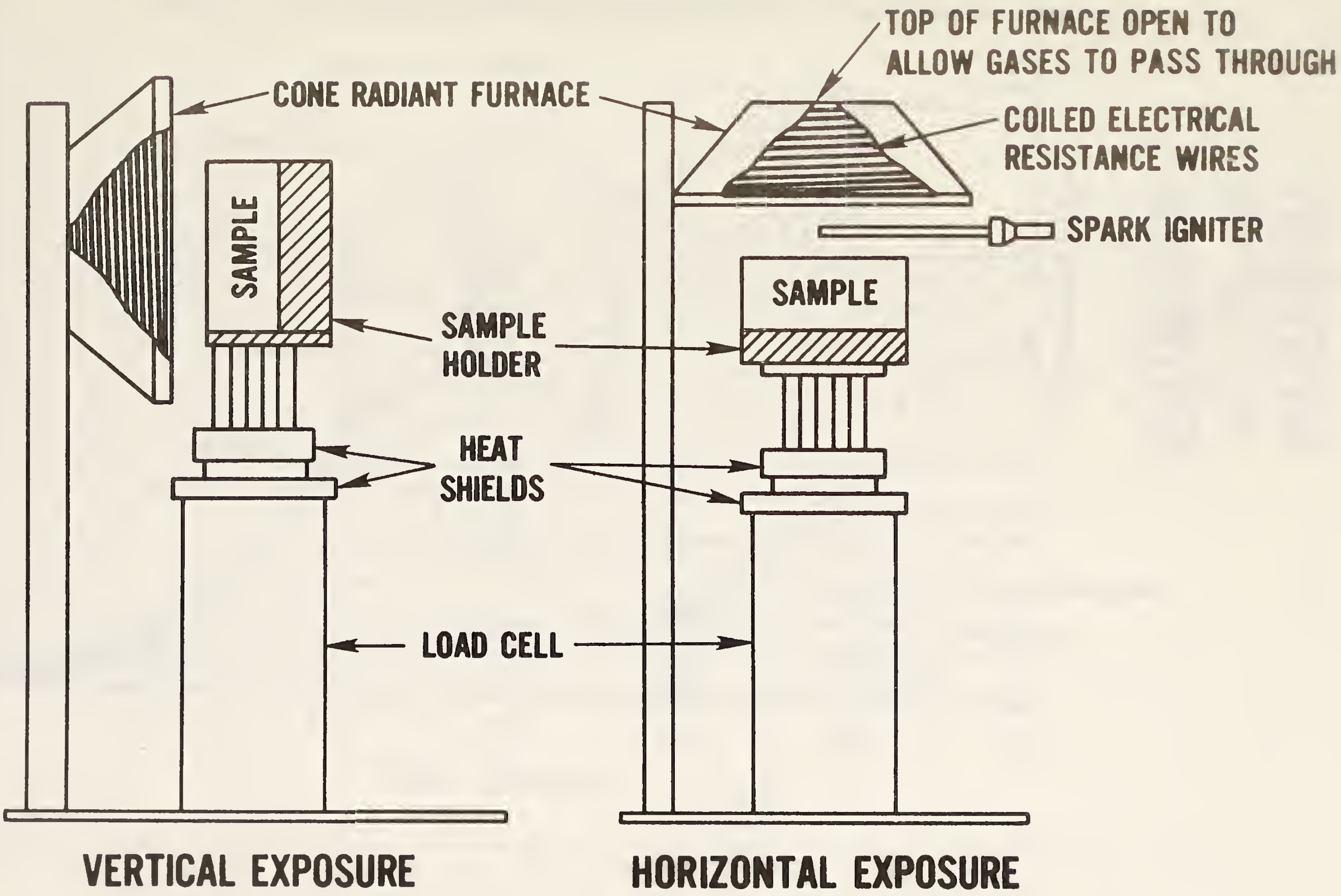

Figure 3. The cone radiant furnace in vertical and horizontal modes

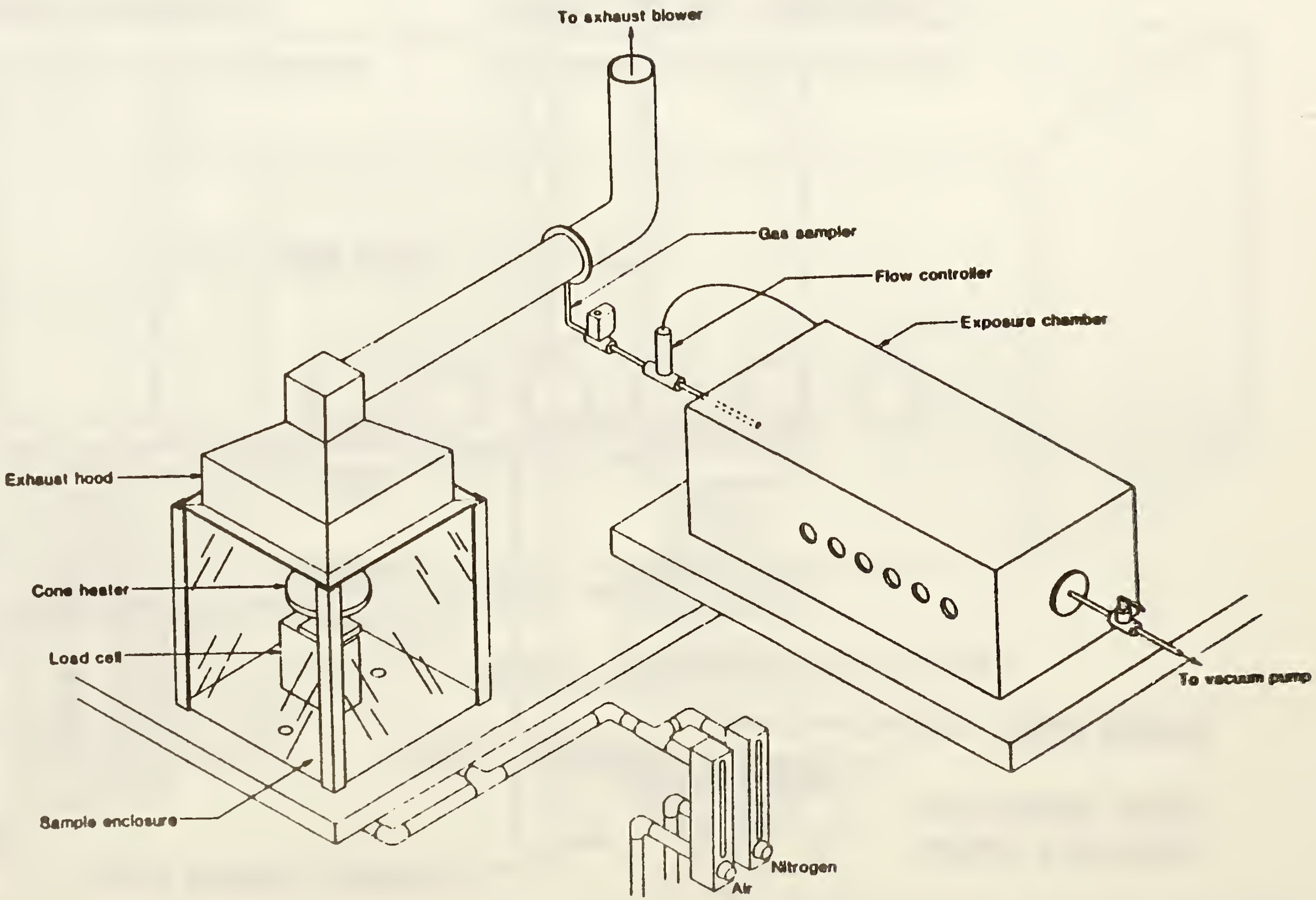

Figure 4. Cone radiant furnace in combination with animal exposure chamber.

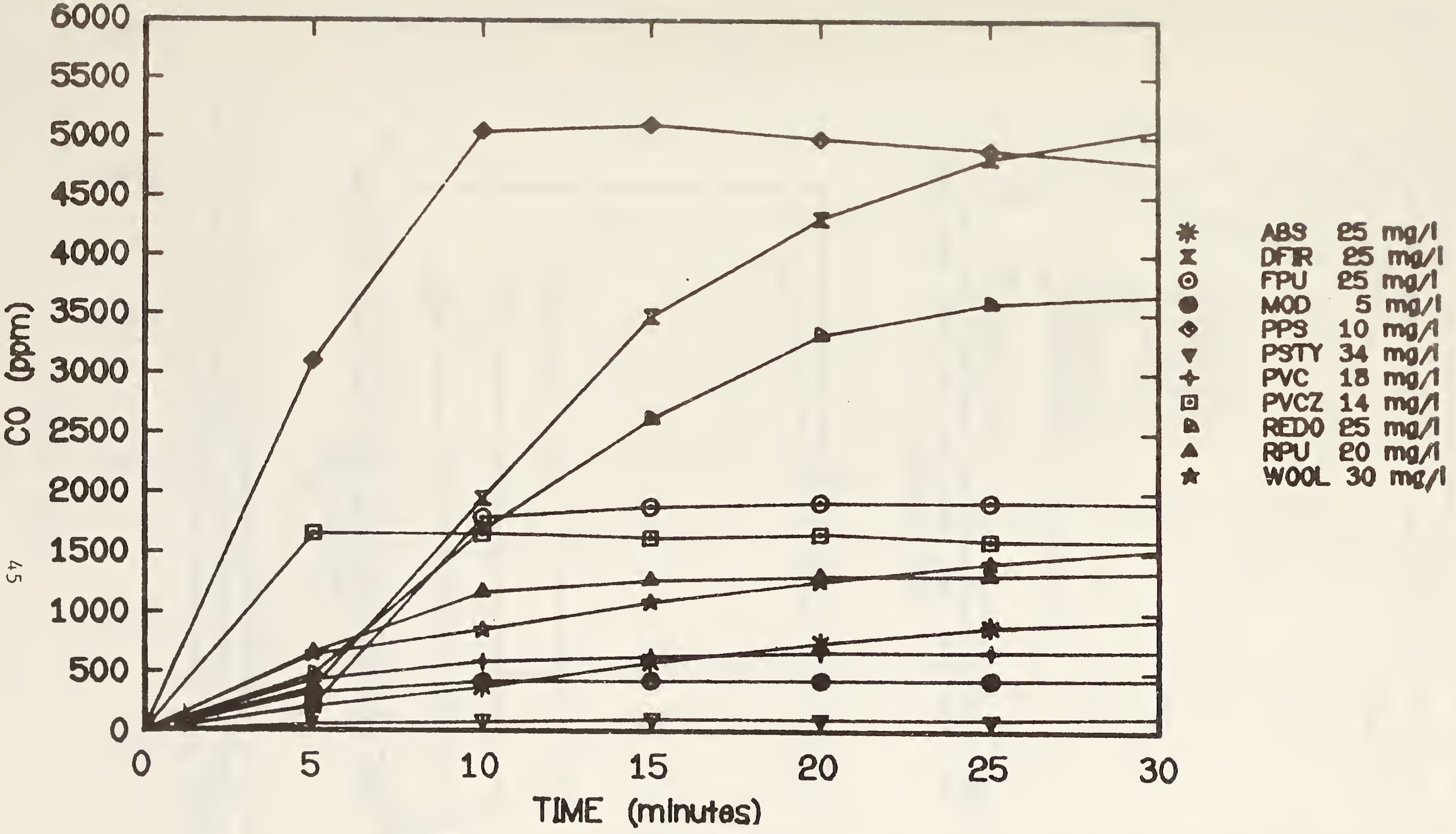

Figure 5. Carbon monoxide generation from materials decomposed in the non-flaming mode at various mass loadings. ABS: acrylonitrile-butadiene-styrene; DFIR: Douglas fir; FPU: flexible polyurethane foam; MOD: modacrylic; PPS: polyphenylsulfone; PSTY: polystyrene; PVC: poly(vinyl chloride); PVCZ: poly(vinyl chloride) with zinc ferrocyanide; REDO: red oak; RPU: rigid polyurethane [1]

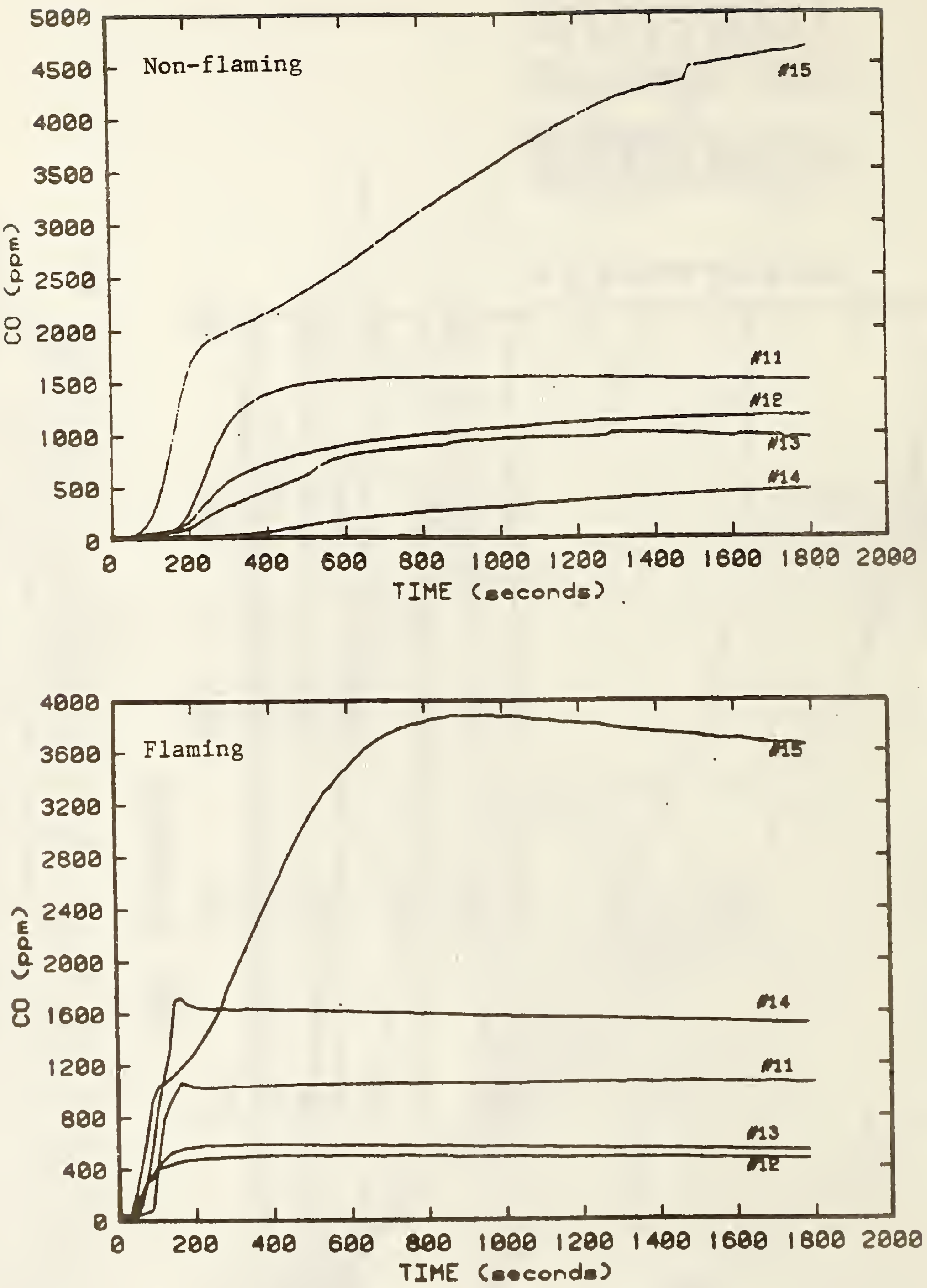

Figure 6. Rate of carbon monoxide generation (ppm) during decomposition of flexible polyurethane foams (Samples 11,12,13 and 14) and polyester (Sample 15) at a concentration of 30 mg/l [9]

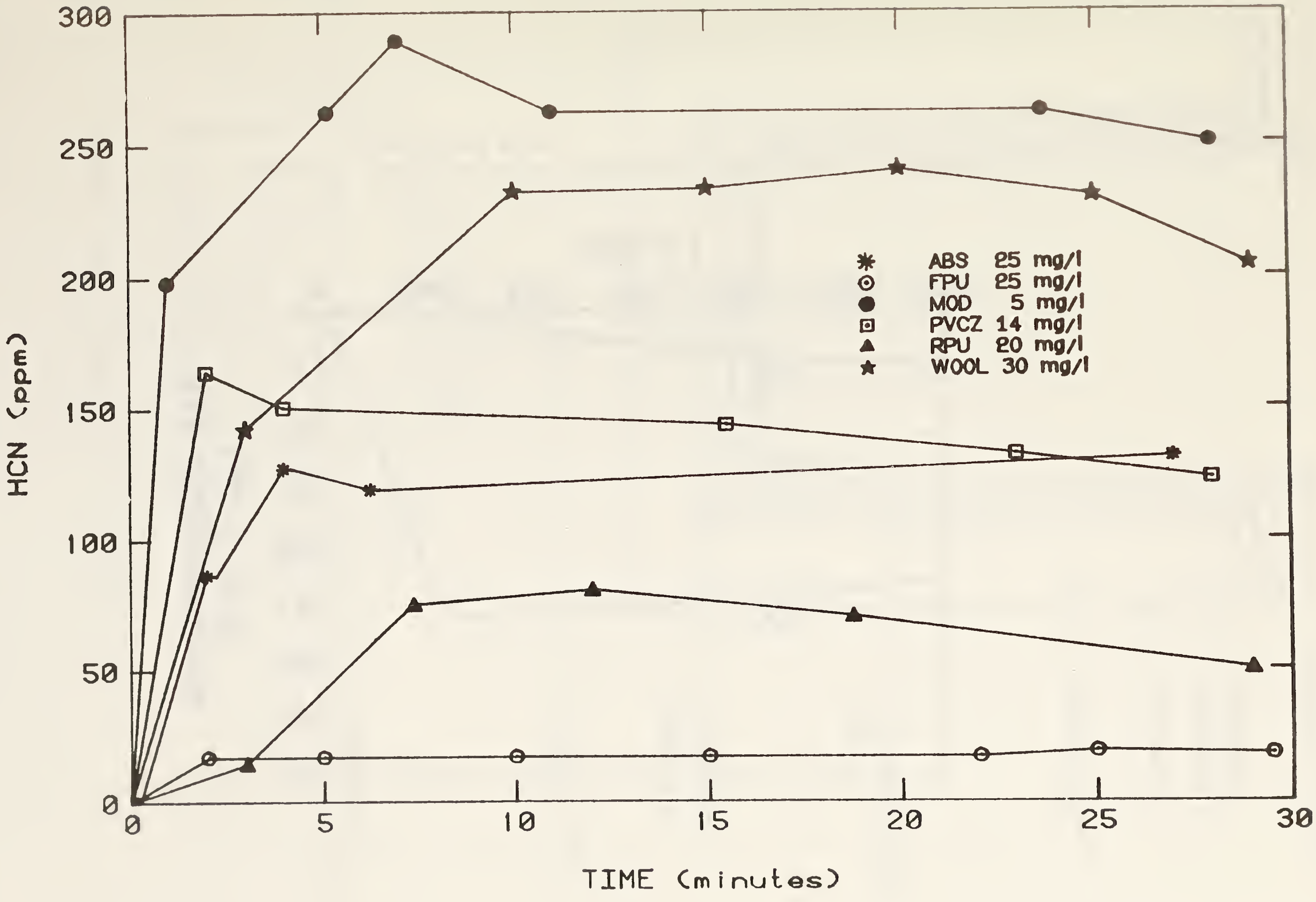

Figure 7. Hydrogen cyanide generation from nitrogen-containing materials decomposed in the non-flaming mode at various mass loadings (for abbreviations, see Figure 5) [1]

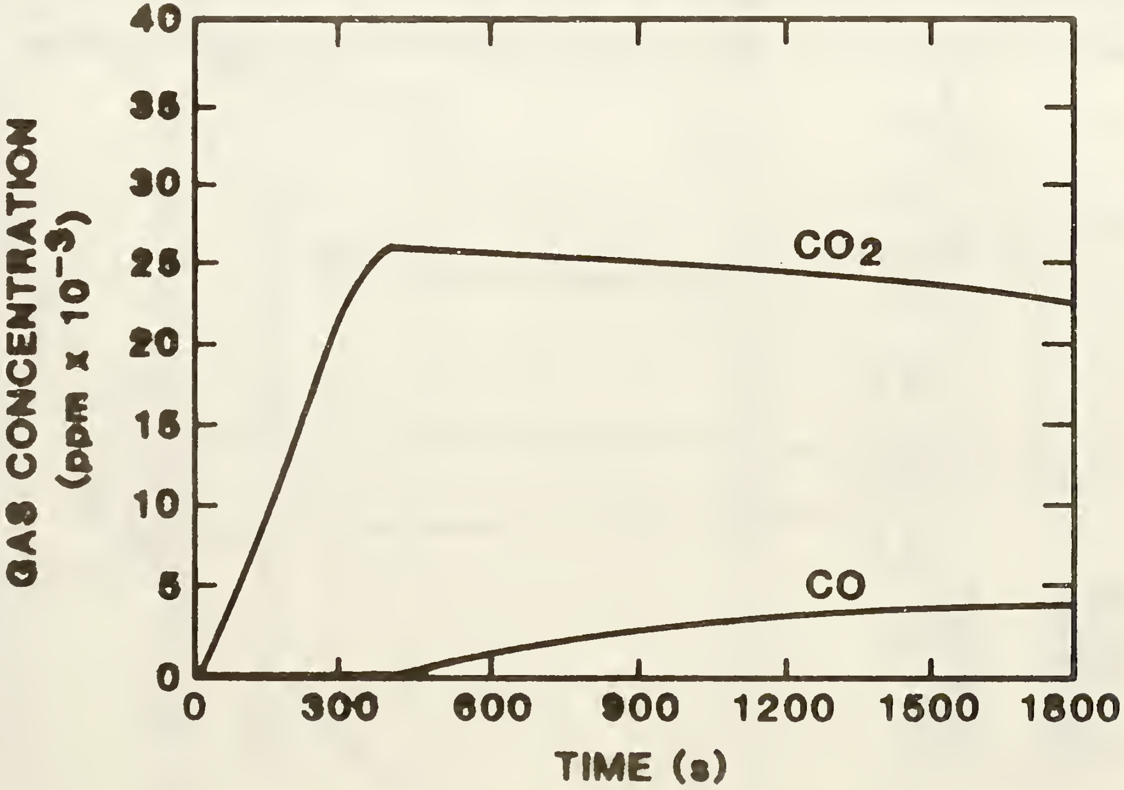

Figure 8. Rate of CO and CO_2 generation from Douglas fir decomposed in the flaming mode.

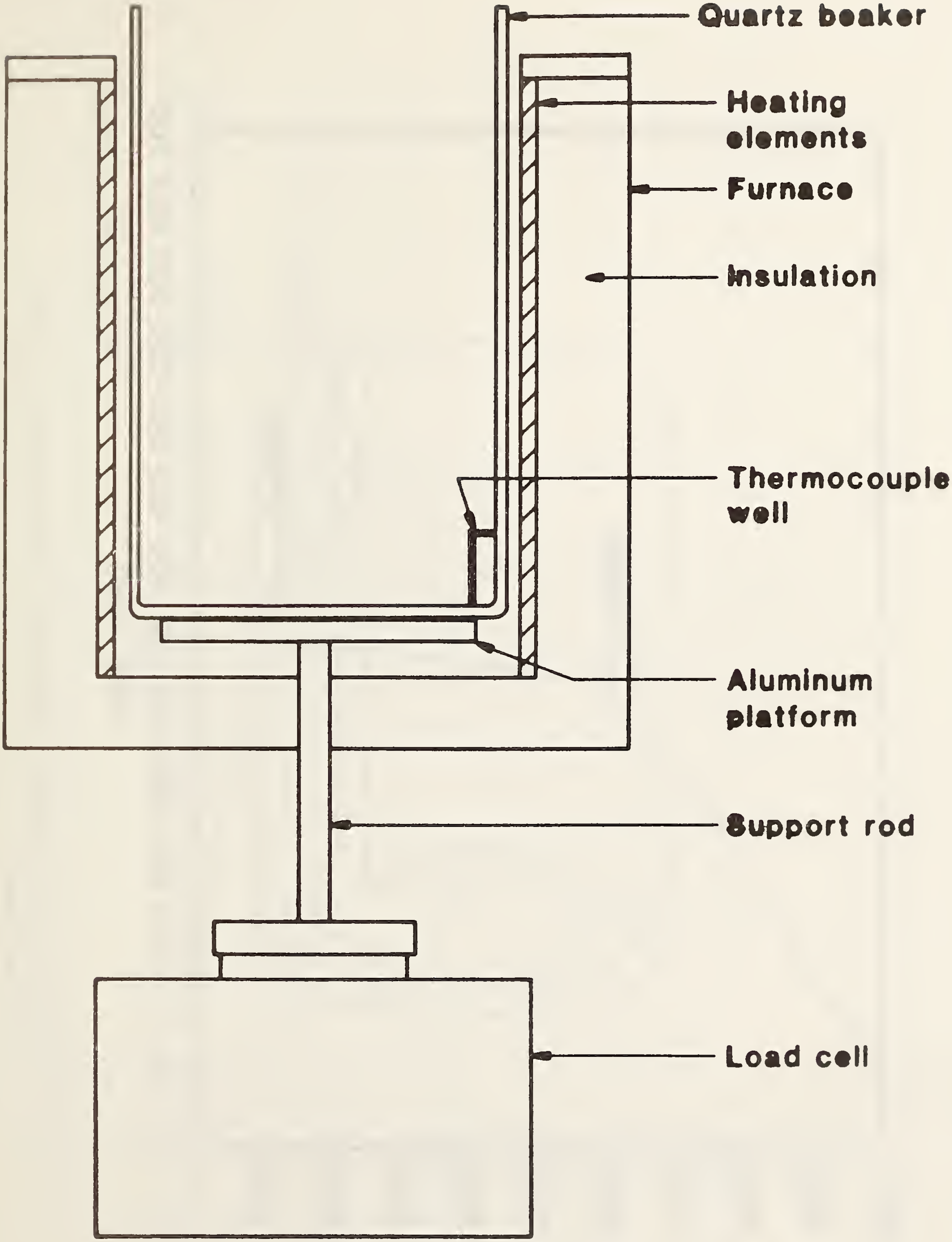

Figure 9. Load cell attached to cup furnace

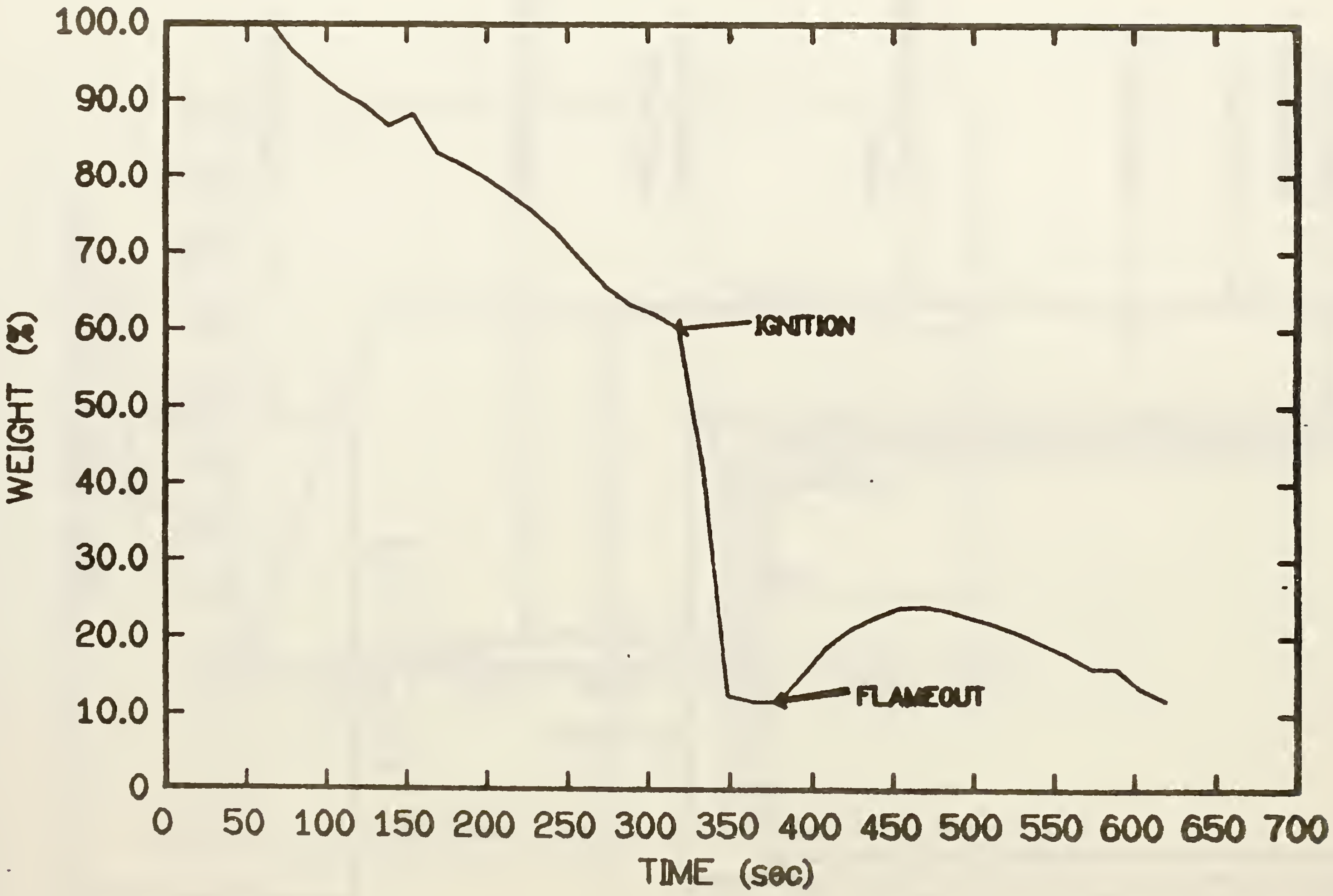

Figure 10. Weight loss of flexible polyurethane foam decomposed at 375°C in the cup furnace

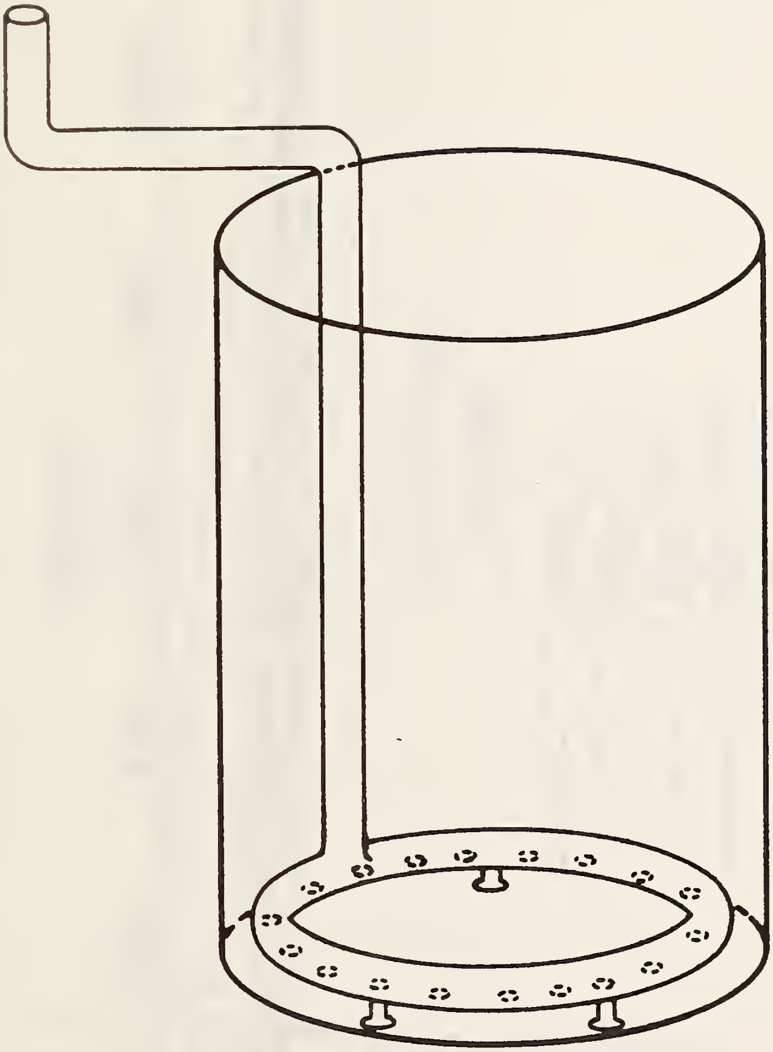

Figure 11. Aerator inside quartz beaker that fits into cup furnace. Aeration holes are on bottom of ring.

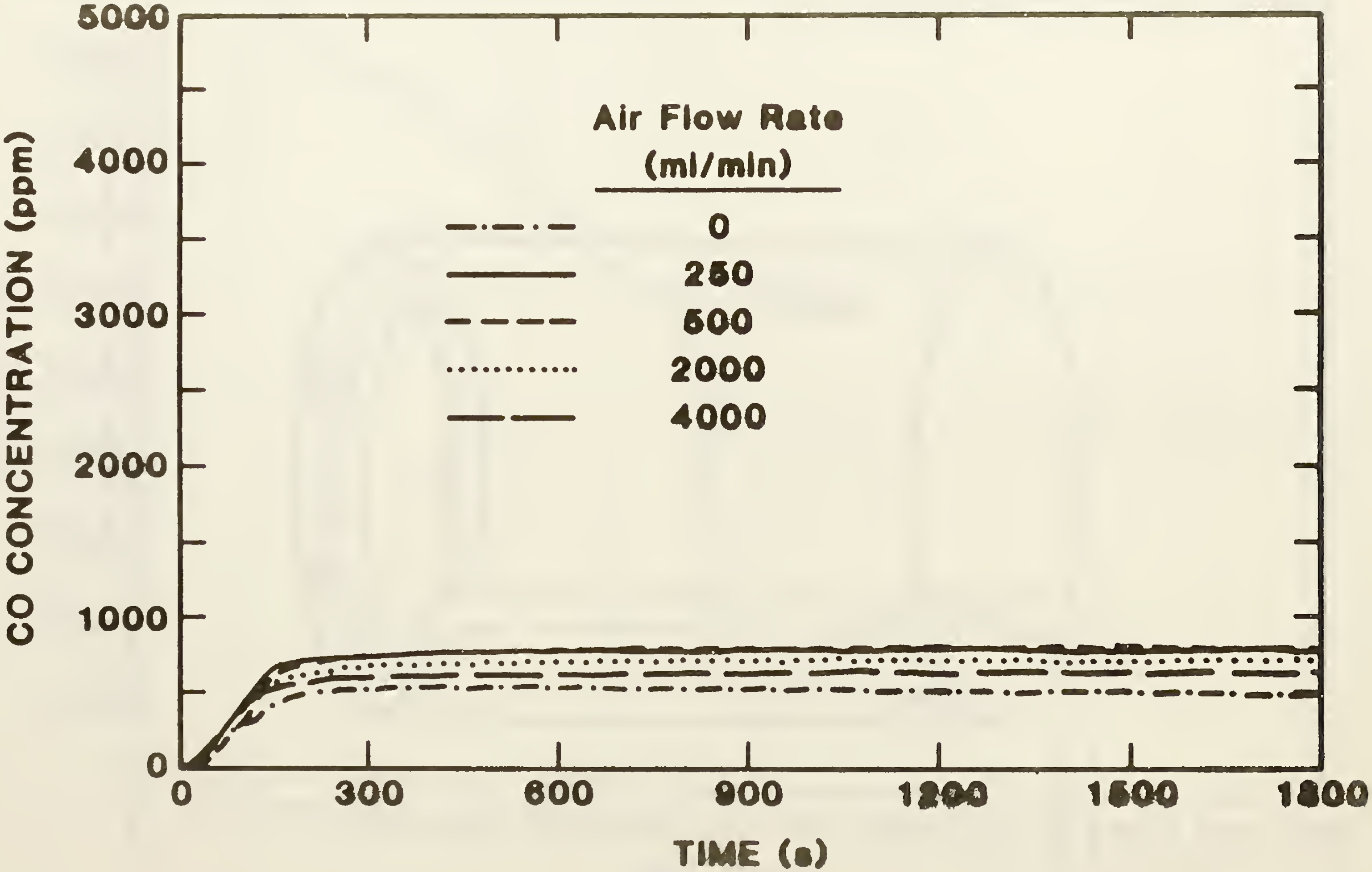

Figure 12. Generation of CO from the flaming combustion of flexible polyurethane foam in the presence of various air flow rates through the cup furnace.

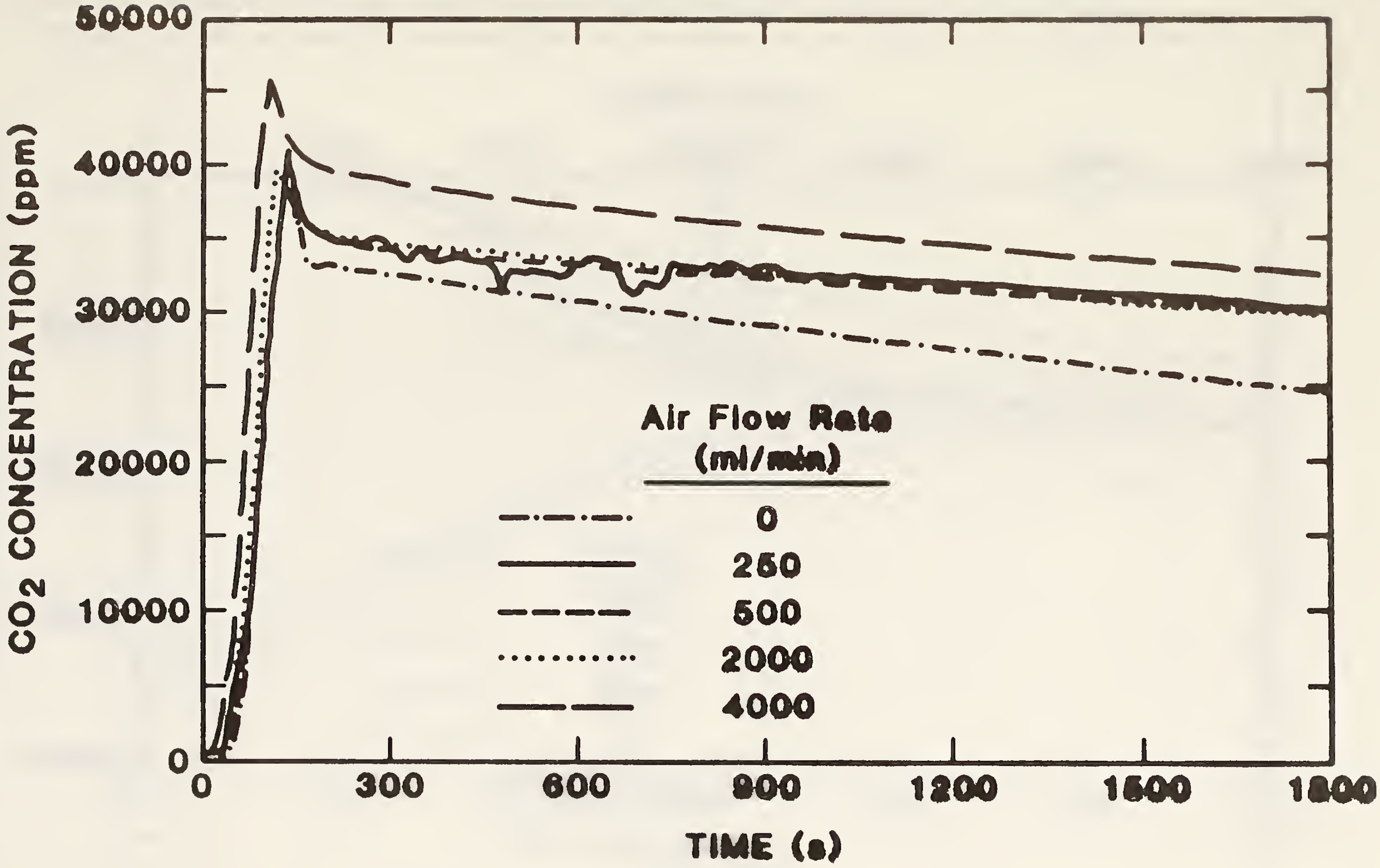

Figure 13. Generation of CO_2 from the flaming combustion of flexible polyurethane foam in the presence of various air flow rates through the cup furnace

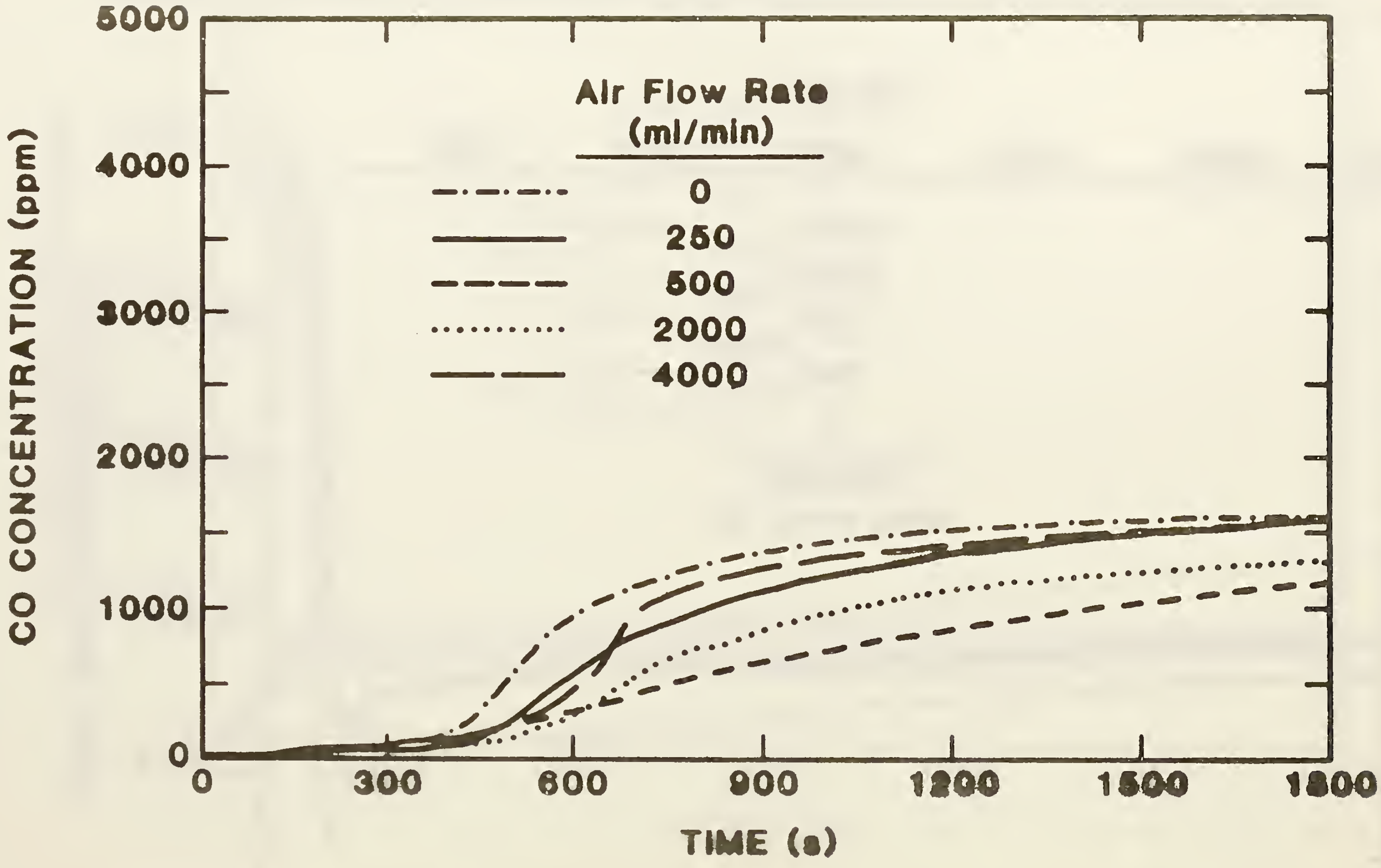

Figure 14. Generation of CO from the non-flaming thermal decomposition of flexible polyurethane foam in the presence of various air flow rates through the cup furnace

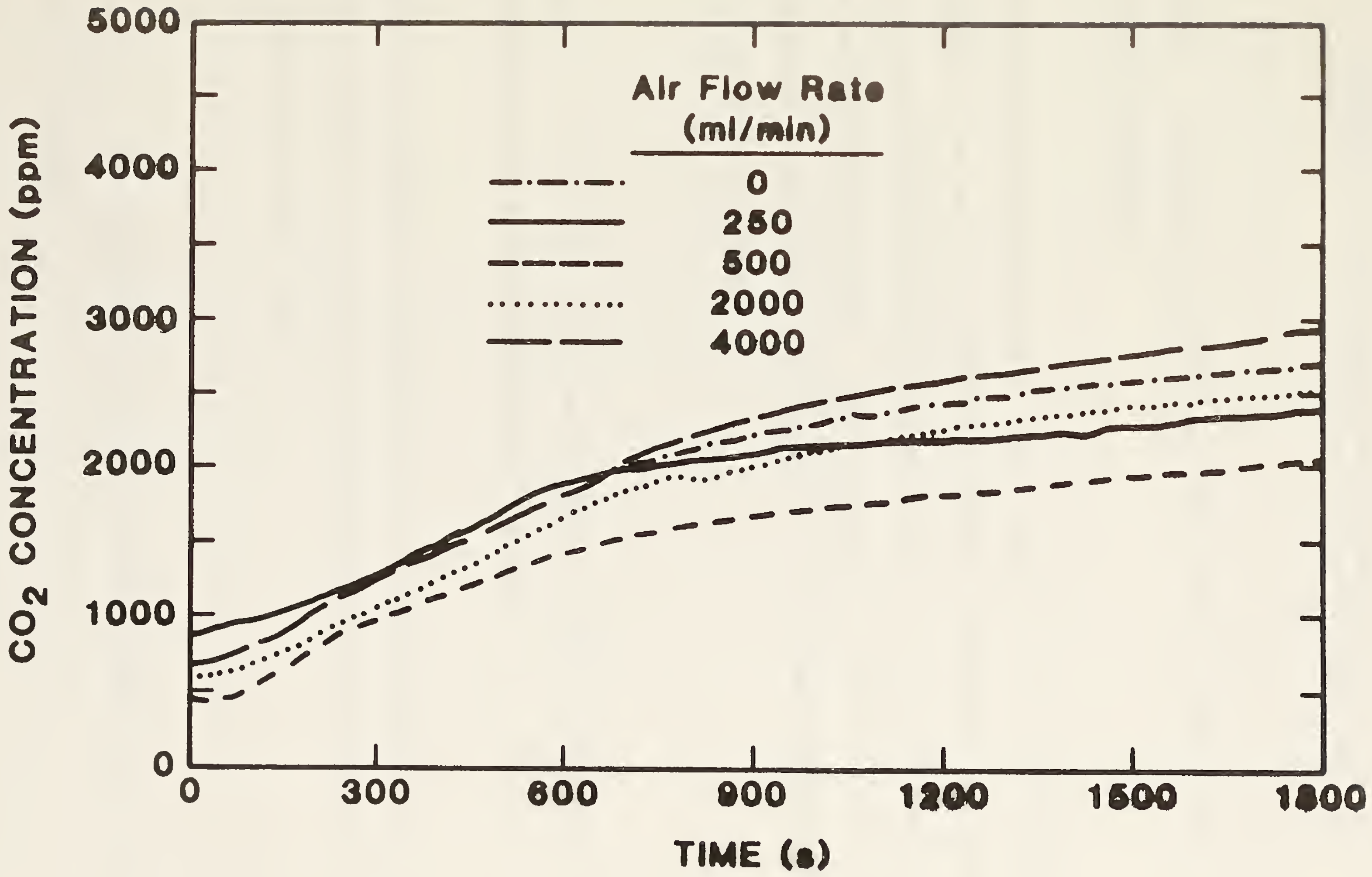

Figure 15. Generation of CO_2 from the non-flaming thermal decomposition of flexible polyurethane foam in the presence of various air flow rates through the cup furnace.

Appendix A. Criteria Developed by Anderson et al., [2] for a Satisfactory Fire Toxicity Test Method

Criterion 1 - temperature range or more than one fixed temperature will be used for sample decomposition.

The reason for criterion one is that toxicity is clearly dependent on temperature. The use of a single predetermined temperature will compare materials under identical conditions but will not explore the range of behavior of the material being studied. Since one aim of a toxicity study is to determine the worst behavior of the material, the single fixed temperature is not a successful approach.

Criterion 2 - The sample should be tested as a single piece unless in actual use the product is used in multiple small pieces.

This is in response to observations that burning behavior of materials is geometry dependent, and subdivided samples may not yield toxicity data consistent with single piece samples.

Criterion 3 - The combustible portion of the test sample must fully decompose in the test process.

Criterion three provides for evaluation of the entire combustible portion of the test product as opposed to the rapidly released toxicants.

Criterion 4 - Test animals must be exposed to the full range of decomposition products.

Criterion four follows directly from criterion three.

Criterion 5 - The exposure chamber must be adequate in size.

Criterion five requires that the oxygen and carbon dioxide in the test chamber remain within physiological limits during control conditions.

Criterion 6 - Timed endpoints must be clearly determined.

Criterion six requires that if a time event is used as an endpoint it must be possible to determine that endpoint accurately. The respiration of a rodent is frequently very shallow and difficult to detect near the point of death. A monitoring system for measuring heart or respiration rate would be a satisfactory alternative.

Criterion 7 - Physical contact between animals should be prevented during exposure.

Criterion seven is directed toward avoiding uneven exposure conditions which result when animals huddle together, breathing through each others fur during the exposure period.

Appendix B. Design Features of the Cone Radiant Heater Apparatus

Size and scale

It was decided at the start that any major scaling-up of the apparatus, compared to the existing Cone Calorimeter, would not be economically feasible, and any minor variations to the specimen size would not have a practical effect. Thus, we were committed to a specimen face size of 100 mm by 100 mm. In the Cone Calorimeter [5], the specimen depth is not standardized unless a specific application category is identified. It is considered reasonable to test specimens from 6 mm to 50 mm deep. The lower limit arises because of the desire not to be overwhelmed by the heat loss effects to the backing substrate. The upper limit comes from the objective of maintaining planar burning, which would not be viable if the ratio of width to depth dropped below about 2:1.

Means of achieving a square-wave exposure

Plastic foam materials, when tested at the maximum size of 100 x 100 x 50 mm, can burn for as short a time as 3 minutes. Conversely, a slab of solid, high density plastic may burn for a half hour or more. The fact that some test materials can be consumed in as short a time as 3 minutes was seen to preclude any straightforward type of "dynamic" or flow-through geometry, if Haber's Rule is not to be unwittingly invoked. This is because the standard methodology for toxicity testing requires that the animal be exposed for a fixed, specified amount of time. If, however, the concentration during that period is not nearly constant, it is not possible to conclude that the animals were exposed to a given concentration for that fixed time. Instead, all that can be concluded is that a concentration × time product was delivered. It was then observed that a time scale mismatch could be accommodated if the combustion and the animal exposure processes were separated. Thus, the following scheme was evolved:

-- The animal chamber is built so that it can be evacuated. After each test, the chamber is flushed out with clean air and then evacuated to a low-grade vacuum.

-- The animal chamber is filled with combustion products from the combustion chamber at a controlled rate. This rate can be so chosen as to backfill the animal chamber with either a uniform representation of the products of the complete burning sequence, or, for longer burning specimens, only the initial products, or only the late products, etc.

-- Once the animal chamber is backfilled to ambient pressure, the animal ports can be opened, animals exposed, and the actual animal testing started.

This operational description is highly simplified; details of construction are illustrated in Figures 3 and 4 of main text; the operational procedures are described in Appendix C.

Appendix C. Operational Description of the Cone Radiant Heater Toxicity Apparatus

The Cone Radiant Heater Toxicity Test Apparatus is composed of two independent enclosures that are connected by a 9 mm I.D. stainless steel pipe. The pipe is connected to a ball valve which manually controls the gas flow rate between the combustion chamber and exposure chamber. A differential pressure transducer is connected to two points along a straight section of the tube to allow for the actual measurement of flow rate.

The combustion system is a modified Cone Calorimeter. It includes a cone heater, load cell, and Pyrex enclosure connected to a hood discharging to an exhaust duct with a damper control installed. The volume of the combustion chamber is estimated to be about 100 ℓ; if one includes the duct work up to the damper control, the volume is estimated to be 175 ℓ. Sampling of the combustion atmosphere is performed 30 cm upstream of the damper control. Unlike with the Cone Calorimeter, where the normal combustion air comes from the surrounding environment, flow through the combustion chamber in the present apparatus is controlled by metering compressed gases into the bottom of the combustion chamber. The gases flow from below the sample and cone support structure up to the hood and out the exhaust duct. The duct continues beyond the damper control to a blower system that is turned on to vent the various enclosures as needed.

The animal exposure chamber is a 25 mm thick PMMA enclosure having a volume of 200 ℓ and which is reinforced with steel supports. The enclosure is fitted with provisions for the insertion of up to six animals in a head-only exposure, and with a series of valves for gas inflow, outflow, and monitoring.

The valves connect the exposure chamber to either a vacuum pump, a series of gas analyzers, and the combustion chamber. A thermocouple is installed through one of the pipe fittings to allow for the measurement of exposure chamber temperature. This is provided so that the animals would not be introduced into the chamber if the temperature exceeds the maximum allowable value of 40 °C. It is the intent of this design to expose the animals to fixed combustion product concentrations previously piped in from the combustion chamber (i.e., square wave exposures).

Setup Procedure

Prior to beginning a test, the combustion and exposure chambers are cleaned. It was found necessary to also clean the sampling pipe and control valve connecting the two chambers after each test. Repeated use of the uncleaned connecting hardware could result in clogging of components.

Because of the variability in sample thickness, the cone heater must be adjusted to the proper height to insure that the upper sample surface is at the proper distance from the cone heater. Power is applied to the cone heater and the heater controller is set to maintain the cone heater at a constant temperature. A water cooled heat flux meter is used to measure the actual heat flux incident on the sample surface. When the cone heater is stabilized at a desired energy level, the heat flux meter is removed.

While the cone heater is reaching equilibrium, the exposure chamber is sealed at all openings. The ball control valve is shut, and the analyzer lines and the animal ports are closed. The line to the vacuum pump is opened and the pump is turned on. The exposure chamber is evacuated to approximately 3 kPa or less of pressure.

The data acquisition system is turned on and the gas analyzers are calibrated with zero and span gases. Continuous gas analysis is performed for three gases: CO, CO_2, O_2. The gas sampling line is equipped with a dead space sampling loop that allows for intermittent gas sampling for gas chromatographic analysis. For example, HCN would be sampled from the dead space sampling loop.

Preliminary Testing

The autoignition heat flux for a given sample is determined by exposing a series of specimens to different incident heat flux levels and noting the minimum heat flux necessary to cause a sample to self-ignite. In general, if a specimen has not self-ignited within ten minutes, the incident heat flux level needs to be increased. Actual testing is conducted with the incident heat flux level set 1 to 2 kW/m^2 below the autoignition heat flux. This results in a non-flaming exposure. The same flux level is used for flaming exposures, however, the decomposition products are induced into flaming by the use of an AC electric spark discharge.

Sample Testing

Following the set-up procedure previously described, an airflow rate through the combustion chamber is selected. It has been found that 25 ℓ/min appears to be a usable value. The data acquisition system is initialized. The sample is inserted into the combustion chamber and the data acquisition is begun. With the damper control opened approximately 40%, the sample is allowed to decompose. Depending on the combustion mode, flaming or non-flaming, sampling of the duct gases into the exposure chamber begins two to four minutes after the start of the sample exposure.

The exposure chamber is filled at a rate that is less than the combustion chamber airflow rate. This sampling rate is maintained throughout the filling process by means of manual control, using the differential pressure gage. This filling process is driven solely by pressure difference between the evacuated animal chamber and the essentially neutral pressure combustion chamber; thus, complete filling with combustion products would take an infinite time. Instead, when the chamber is filled to a pressure of 95 kPa with combustion products, the control valve is shut. The exposure chamber is then filled to neutral pressure by introducing clean air from a supply tank. The combustion chamber is cleared using the blower system with the damper control completely opened.

With the exposure chamber at atmospheric pressure, the gas analyzers are connected to the exposure chamber. Gases are drawn through the dead space sampling loop unless a sample is to be taken for GC analysis. Switching the four-way valve creates the dead space volume without interrupting the flow to the gas analyzers. After this, the animal chamber temperature is noted to determine if it is below the maximum value permitted for the animals. It is possible to wait until the gases have sufficiently cooled before inserting the animals.

The animals are inserted and can be clearly observed throughout the exposure time. Data is collected prior to and during the exposure.

Data Reduction

The mass loading (i.e., pyrolysate concentration) in the animal chamber, in units of mg/ℓ, is computed as follows. The specimen mass loss rate, dm(t)/dt (mg/s), during the period of combustion sampling is determined from the load cell data. The air flow rate in the combustion chamber, V_{out}, is taken to be the value as metered in by the rotameters (ℓ/s). The concentration in the combustion chamber outflow during the sampling period is given by

$$C_b = \frac{1}{V_b} \int^{\tau} \frac{dm(t)}{dt} \, dt \, (1-\exp(-V_{out}/V_b)t)$$

It is assumed that the animal exposure box is being filled at the same concentration. The concentration in the animal exposure box is then

$$C_e = \frac{1}{V_e} \int_{t_1}^{t_2} \frac{f(t)}{V_b} \; C_b \; dt$$

Post Exposure

Following the preselected exposure time, the animals are withdrawn and the exposure chamber is connected to the exhaust blower to clear remaining decomposition products. Animals are treated as in the NBS Toxicity Test Method.

Appendix D

Toxicity of the Combustion Products From a Flexible Polyurethane Foam and a Polyester Fabric Evaluated Separately and Together by the NBS Toxicity Test Method[1]

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ABSTRACT

Representative specimens of two materials, a flexible polyurethane foam and a polyester, were thermally decomposed separately and together in order to compare the toxicological effects of the combustion products from the combined materials with those from the single homogeneous materials. Gas concentrations (CO, CO_2, O_2 and HCN), blood carboxyhemoglobin, and LC_{50} values [the concentration of material necessary to kill 50% of the test animals (Fischer 344 male rats) during a 30 minute exposure and a 14 day post-exposure observation period] were determined for the separate and combined materials under both flaming and non-flaming conditions. The results of the combined experiments indicated that under non-flaming conditions, both materials contributed in an additive manner to the concentration of the combustion products. However, under flaming conditions, the generation of HCN and CO is greater than that predicted from the addition of the maximum amounts produced by the materials separately.

INTRODUCTION

In the industrialized world, the United States is second only to Canada in the number of fire deaths per capita [1]. The fire scenario which produces the most fire deaths in the U.S. begins with an inadvertently dropped cigarette in an upholstered piece of furniture. Since the majority of commercially available upholstered furniture today contains some formulation of flexible polyurethane foam as a filling material and a covering fabric which is either a cellulosic or a thermoplastic such as polyester, these two materials were chosen for this study. Many small-scale laboratory studies have examined the toxicity of the combustion products from flexible polyurethane foams [2] or polyesters [3]. There have also been numerous large-scale room burns of chairs, multiple materials, or composite materials which included these materials. Alarie et al. compared the toxicity of individual materials (determined in small-scale tests) with the toxicity of multiple combined materials (determined in large-scale chair burns) [4]. However, the objective of their study was to compare the toxicity of the major components of the chairs (flexible polyurethane foam, polyester, and

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[1] This paper is a contribution of the National Bureau of Standards and not subject to copyright

cotton fiber) with their individual toxicity in small-scale tests. They did not study the toxicity of the combined components in the small-scale tests.

This study was designed to examine and to compare the toxicological effects from the combustion products of a flexible polyurethane foam and a polyester fabric in order to determine the contribution of the combustion products from each material to the overall toxicity of the mixture. Two separate aspects of this problem were considered: (1) Would the toxicity be affected merely because the increased mass of the combined materials increase the concentrations of the pyrolysis or combustion products or does some unexpected toxicological interaction occur? (2) Would the types or yields of toxicants be affected?

MATERIALS AND METHODS

The materials studied, polyester fabric and a flexible polyurethane foam, were generically classified, i.e., the specific chemical formulations were unknown. Both the polyester upholstery fabric (100% polyester, scoured and dyed dark blue) and the flexible polyurethane foam were obtained from the Consumer Product Safety Commission, Washington, DC 20207. The results of a previous toxicological study on this polyurethane foam, designated CPSC #13, have been published [5].

The acute inhalation toxicity of the combustion products from these materials was evaluated according to the NBS Toxicity Test Method [6]. Each material was examined at 25°C above and below its autoignition temperature (Tables 1 & 2). In addition, polyester was tested at the non-flaming temperature of the polyurethane foam (375°C), and the flexible polyurethane foam was examined at the flaming temperature of the polyester (525°C). Combinations of the two materials were thermally decomposed in the cup furnace at a non-flaming temperature of 375°C (which was the highest possible non-flaming temperature, since the polyurethane foam would flame at higher temperatures) and a flaming temperature of 525°C (the temperature at which both the polyurethane and polyester would undergo flaming combustion, if tested separately). In all cases, the amount of material consumed was determined by weighing the residue.

Carbon monoxide (CO) and carbon dioxide (CO_2) were measured continuously by non-dispersive infrared spectroscopy. Oxygen concentrations were measured continuously by a galvanic cell or a paramagnetic analyzer. The HCN generated from the polyurethane foam was sampled with a gas-tight syringe approximately every three minutes and analyzed with a gas chromatograph equipped with a thermionic detector [7].

Fischer 344 male rats, weighing 200-300 grams, were obtained from the Harlan Sprague-Dawley Company (Walkersville, Maryland) or Taconic Farms (Germantown, New York) and were allowed to acclimate to our laboratory conditions for 10 days prior to experimentation. Animal care and maintenance were performed in accordance with the procedures outlined in the National Institutes of Health's "Guide for the Care and Use of Laboratory Animals" [8].

Six animals were exposed in the head-only mode in each experiment. Exposures were for 30 minutes, during which blood for carboxyhemoglobin (COHb) analysis was taken at 0 time, approximately 15 minutes and just before the end of the experiment from cannulated animals (one or two animals per exposure were surgically prepared with a femoral arterial cannulae 24 hours before experiments [9]). The number of animals that died at each mass loading of material was plotted to produce a concentration-response curve from which an LC_{50} value was calculated [10]. The LC_{50}, in this case, is defined as the mass loading of material per unit chamber volume (mg/ℓ) which caused 50% of the animals to die during the 30 minute exposure plus the 14 day post-exposure observation period. (Animals that were still losing weight on day 14 were kept until they died or recovered as indicated by three days of successive weight gain. All deaths were included in the LC_{50} calculation. Surviving cannulated animals were sacrificed following the test and only counted in the determination of the LC_{50} if they died during the exposure.) If no deaths occurred at the highest concentration tested, the LC_{50} is listed as greater than that concentration.

RESULTS AND DISCUSSION

Flexible Polyurethane Foam

The chemical and toxicological data obtained from the flexible polyurethane foam thermally decomposed under non-flaming (375°C) and flaming (425°C and 525°C) conditions are presented in table 1. Similar to other non-fire retarded flexible polyurethane foams tested in this laboratory, no animal deaths occurred during the 30 minute exposures to concentrations up to 40 mg/ℓ regardless of the mode of decomposition [5,6]. Post-exposure deaths only occurred following the non-flaming experiments. The LC_{50} value for the non-flaming mode was 37.0 mg/ℓ with 95% confidence limits of 29.8-46.0 mg/ℓ, whereas, the LC_{50} value for the flaming mode was greater than 40 mg/ℓ, i.e., no animal deaths were noted from any of the concentrations tested up to 40 mg/ℓ.

Recent results [11] from this laboratory on the toxicity of CO, CO_2 and HCN alone and in various combinations have shown that the 30 minute LC_{50} for CO in air was 4600 ppm. No animals died below 4100 ppm or post-exposure. The 30 minute LC_{50} for CO_2 in air was greater than 18% (1% = 10,000 ppm). However, when CO and CO_2 were combined, the presence of 5% CO_2 increased the toxicity of CO such that animals died from 30 minute exposures to 2500 ppm. Some of these deaths were within 24 hours. The combination of CO and HCN (30 minute HCN LC_{50} = 160 ppm) showed the following additive effect:

If $\frac{[CO]}{LC_{50}\ CO} + \frac{[HCN]}{LC_{50}\ HCN} \geq 1$, the animals died.

When this formula equalled less than 1, the animals lived. Again deaths were observed up to 24 hours post-exposure.

Comparison of the gas concentrations generated from the polyurethane experiments to the pure gas experiments quoted above showed that lethal amounts were not produced in any of the tests (Table 1). Therefore, the deaths, which occurred as late as 14 days in the non-flaming mode, were due to other toxic combustion products or undetermined factor(s).

Polyester

All the chemical and toxicological data collected from the thermal degradation of polyester are shown in table 2. In the non-flaming mode at 475°C, the LC_{50} value of the polyester was 39.0 mg/ℓ with 95% confidence limits of 38.4 - 39.5 mg/ℓ. Animal deaths were noted both during and following the 30 minute exposures. At 375°C, however, no animal deaths were observed up to concentrations of 50 mg/ℓ. However, it is important to note that at the lower temperature (375°C), only 22-55% of the original sample was consumed; whereas, at 475°C, approximately 85% of the sample was consumed. Based upon a comparison of the toxicological effects at the actual masses consumed at 475°C, deaths would not be expected at the masses consumed at the lower temperature.

Table 1

Material	AIT (°C)	Mode	Initial Temp. of Expt. (°C)	Type of Expt.	Mass / Chamber Vol.		Average Gas Concentration[1]				Max. CO (ppm)	Highest % COHb (30 min)	No. died / No. tested		Latest Day of Death	LC_{50} 30 min. + 14 days (mg/ℓ)
					Loaded (mg/ℓ)	Consumed (mg/ℓ)	CO (ppm)	CO_2 (ppm)	O_2 (%)	HCN (ppm)			Within Exp.	Within & Post		
Poly-urethane #13	400	NF	374	A	10.0	9.3	420	470	20.8	8	540	NA	NA	NA	NA	
			375	R	19.8	17.9	620	2370	20.4	ND	800	ND	0/6	1/6	14	
			375	R	30.0	26.6	700	2690	20.4	4	1000	ND	0/6	1/6	11	37.0
			375	R	32.0	27.4	600	2800	20.3	5	1100	26.3	0/6	1/5	7	(29.8-46.0)*
			377	R	35.0	31.1	ND	ND	ND	9	ND	47.0	0/6	4/4	11	
			375	R	40.0	34.3	740	2500	ND	1	1320	ND	0/6	3/5	12	
Poly-urethane #13	400	F	425	A	10.0	9.7	170	8700	19.9	19	210	NA	NA	NA	NA	
			425	R	20.0	19.9	320	21400	18.2	17	370	ND	0/6	0/6	NA	>40
			425	R	30.0	29.8	520	28400	17.4	24	590	ND	0/6	0/6	NA	
			425	R	40.0	39.1	840	33500	16.7	27	940	46.5	0/6	0/4	NA	
			524	A	20.0	19.9	630	10700	19.5	51	720	NA	NA	NA	NA	
			528	A	20.0	19.9	390	19100	18.7	37	430	NA	NA	NA	NA	

Legend:

1. Average gas concentration = $\dfrac{\text{integrated area under instrument response curve for 30 minutes}}{\text{30 minutes}} = \dfrac{\text{ppm-min}}{\text{30 min}}$

A. Analytical experiment
R. Rat experiment
ND. Not determined
NA. Not applicable
F. Flaming
NF. Non-flaming
AIT. Auto-ignition temperature
*. 95% confidence limits
FPU 13. Flexible polyurethane #13
PE. Polyester
Comb. Combined weight of FPU 13 + PE

Table 2

Material	AIT (°C)	Mode	Initial Temp. of Expt. (°C)	Type of Expt.	Mass Chamber Vol.		Average Gas Concentration^1				Max. CO (ppm)	Highest % COHb (30 min)	No. died / No. tested		Latest Day of Death	LC$_{50}$ 30 min. + 14 days (mg/ℓ)
					Loaded (mg/ℓ)	Consumed (mg/ℓ)	CO (ppm)	CO$_2$ (ppm)	O$_2$ (%)	HCN (ppm)			Within Exp.	Within & Post		
Polyester	500	NF	474	A	20.0	16.4	970	1700	20.7	NA	1270	NA	NA	NA	NA	
			474	A	25.0	21.3	1670	2550	20.6	NA	2330	NA	NA	NA	NA	
			473	R	35.0	30.6	2440	4770	20.5	NA	3460	81.6	0/6	0/4	NA	
			473	R	36.5	30.9	2330	4910	20.4	NA	3140	67.8	0/6	0/4	NA	
			476	R	37.1	32.5	2810	5590	20.3	NA	3900	83.7	0/6	0/4	NA	39.0
			475	R	37.5	32.4	2570	5350	20.4	NA	3590	79.3	1/6	5/5	2	(38.4-39.5)*
			475	R	38.5	34.3	2910	5920	20.3	NA	4090	82.7	2/6	3/6	12	
			473	R	39.2	33.2	2650	5300	20.4	NA	3730	75.0	2/6	3/5	2	
			475	R	40.0	34.9	2660	4990	20.4	NA	3830	81.0	4/6	5/6	1	
			377	A	20.0	4.3	50	600	20.9	NA	160	NA	NA	NA	NA	
			376	R	40.0	21.9	370	2980	20.5	NA	770	13.5	0/6	0/4	NA	>50
			375	R	50.0	20.4	410	2710	20.6	NA	840	15.2	0/6	0/5	NA	
Polyester	500	F	524	R	30.0	28.7	2220	25200	18.4	NA	2990	82.0	0/6	0/4	NA	37.5
			525	R	35.0	33.7	2290	27300	18.2	NA	3400	83.0	1/6	2/5	0	(35.3-39.8)*
			523	R	37.5	36.1	2640	28500	18.0	NA	3860	83.2	3/6	3/6	NA	
			524	R	40.0	38.8	2990	30500	17.8	NA	4310	84.6	4/6	4/5	NA	

For Legend, see Table 1

Examination and comparison of the gas concentrations that were generated during these non-flaming experiments with our pure and combined gas toxicity experiments discussed above indicate that the average CO levels are 37-80% lower than that necessary to cause death by CO alone. In many experiments, the CO levels did not plateau but continued to rise throughout the exposures reaching a maximum at 30 minutes. This maximum value, however, was still lower than the 30 minute LC_{50} value for CO in air (4600 ppm) (Table 2). The average CO_2 present is about 10% of that necessary to increase the susceptibility of the rats to lower levels of CO. However, the maximum COHb levels at the end of these 30 minute lethal exposures are relatively high, 75-83%. These results indicate that CO, although low, is contributing to the within-exposure deaths, but other toxic or irritant gas(es) are also acting in conjunction with or to potentiate the effects of the CO. The cause of the late post-exposure deaths are unexplained.

In the flaming mode, the LC_{50} value for the polyester was 37.5 mg/ℓ with 95% confidence levels of 35.3 - 39.8 mg/ℓ (Table 2). In the lethal experiments, the COHb levels ranged from 83-85% and the rats died within exposure or shortly thereafter. These factors would implicate CO as the main toxicant. However, the average CO is approximately 50-65% of the lethal concentration determined for CO alone. Even considering the effect of CO_2 on CO, the average values of CO and CO_2 from flaming polyester are still too low to account for the deaths that occurred during these 30 minute exposures. Only if one considers the maximum CO levels along with the CO_2 concentrations would the deaths be predictable.

Combined Flexible Polyurethane Foam and Polyester

Non-flaming experiments. The thermal decomposition of both flexible polyurethane foam and polyester in the non-flaming mode was studied at 375°C which was 25°C below the autoignition temperatures of the polyurethane. In these experiments, the polyester fabric was folded and dropped into the cup furnace immediately preceding the polyurethane foam. Upon heating, the samples collapsed in less than one minute and formed a black ball in approximately two minutes.

Since the polyester, by itself, was not toxic at 375°C[2] even at the highest loading tested (50 mg/ℓ), a sublethal amount of polyester (20 mg/ℓ) was chosen to test whether this addition would increase the toxicity (lethality) of the polyurethane foam in the combination experiments. If the polyester component has no effect at this temperatures, then the addition of 20 mg/ℓ of polyester to the LC_{50} value of the polyurethane would increase the LC_{50} value of the mixture by 20 mg/ℓ; that is, the LC_{50} value of the polyurethane, 37 mg/ℓ, would increase to approximately 57 mg/ℓ. The results, however, showed that the LC_{50} value of the combined materials only increased to 47.5 mg/ℓ, an indication that the polyester was not inert but contributed to the toxicity by about 10 mg/ℓ (Table 3). The total amount of polyurethane in the combined LC_{50} is only 27.5 mg/ℓ, which is outside the 95% confidence limits of the LC_{50} for polyurethane alone.

Since a significant proportion of the polyester is not decomposed at 375°C, these data were also analyzed on the basis of mass consumed/chamber volume. The experiments on the polyester alone at 375°C showed that when 3.88 grams (20 mg/ℓ) were loaded into the cup furnace, 78% remained as residue and only 4.3 mg/ℓ

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[2] This lower toxicity is probably due to the large fraction (more than 45% of the initial mass loading) of the polyester which is not consumed at the lower temperature.

were actually consumed. Using the same null hypothesis as before, that is, the polyester at this temperature has no effect on the combined toxicity, then one would expect the LC_{50} of the polyurethane (31.9 mg/ℓ, consumed weight) should increase by 4.3 mg/ℓ producing a combined LC_{50} of 36.2 mg/ℓ. However, the LC_{50} of the combination is only 26.2 mg/ℓ, consumed weight, indicating that the polyester increases the toxicity by about 10 mg/ℓ; this is the same value calculated when the mass loaded, rather than mass consumed, was considered.

In these non-flaming experiments in which 20 mg/ℓ of polyester were added to different loadings of flexible polyurethane foam, all deaths occurred during the post-exposure period. These results are more characteristic of the polyurethane experiments, decomposed by itself, and different from those seen with the polyester alone. The concentrations of measured gases (CO, CO_2, HCN) were not responsible for the post-exposure deaths that occurred.

The average concentration of the primary gases (CO, CO_2, HCN) generated from the thermal decomposition of the mixture of the materials appear to be approximately equal to the sum of the average concentrations generated from the individual materials under non-flaming conditions (Table 4 and Figure 1). Therefore, if the concentrations of the primary gases from the thermal decomposition of the individual components are known, then a reasonable prediction of the gas concentrations from the mixture decomposed under the same conditions can be made.

Flaming experiments. The experiments in which the flexible polyurethane foam and polyester were combined and tested in the flaming mode were conducted at 525°C (25°C above the autoignition temperature of the polyester) to ensure that both materials would flame. In these experiments, the mass concentration of polyurethane was kept constant at 20 mg/ℓ and only that of the polyester was varied (Table 3). The reason for this approach was to see if a non-lethal amount of the less toxic material (in this case, the polyurethane foam) would increase the toxicity of the polyester whose LC_{50} could be measured. The polyurethane foam when tested by itself in the flaming mode at 425°C had produced no deaths either during or post-exposure at concentrations up to 40 mg/ℓ, whereas, the polyester fabric when decomposed by itself in the flaming mode at 525°C had produced both within and post-exposure deaths. The LC_{50} value for the flaming polyester fabric by itself was 37.5 mg/ℓ. Therefore, if the polyurethane was toxicologically inert, the addition of 20 mg/ℓ of polyurethane should have raised the LC_{50} value to 57.5 mg/ℓ. In actuality, the 30 minute and 14 day LC_{50} value calculated for the combined exposures was 39.0 mg/ℓ with 95% confidence limits of 36.0 - 42.2 mg/ℓ. These results, showing that the LC_{50} value for the combined materials was lower than expected by almost the exact amount of polyurethane added to the system, are an indication that the polyurethane and the polyester are both contributing in an additive manner to the toxicity. In other words, the combination of 19 mg/ℓ of polyester and 20 mg/ℓ of polyurethane produced the LC_{50}; whereas, 20 mg/ℓ of the polyurethane foam decomposed by itself in the flaming mode produced no deaths (Table 1) and the polyester decomposed by itself did not produce any deaths below a concentration of 35 mg/ℓ (Table 2). Thus individual sublethal concentrations of this polyurethane foam and polyester fabric are adding up to a concentration which is lethal.

Examination of the average gas concentrations of CO, CO_2, and HCN which were generated during these exposures and comparison of these gas values with our pure gas toxicological studies shows that the concentrations of these gases were sufficient to account for the deaths that occurred. Table 3 also shows HCN levels higher than those seen in the flaming exposures of polyurethane alone at 525°C which, in turn, were greater than at 425°C (Table 1). Figure 2 shows the

Table 3

					Mass				Average Gas Concentration[1]						No. died			
					Chamber Volume										No. tested			
Material	AIT (°C)	Mode	Initial Temp. of Expt. (°C)	Type of Expt.	Loaded (mg/ℓ) FPU 13	PE	Comb.	Consumed (mg/ℓ)	CO (ppm)	CO_2 (ppm)	O_2 (%)	HCN (ppm)	Max. CO (ppm)	Highest % COHb (30 min)	Within Exp.	Within & Post	Latest Day of Death	LC_{50} 30 min. + 14 days (mg/ℓ)
Polyester																		
plus	500	NF	373	R	20.0	20.0	40.0	21.0	690	2600	20.5	ND	890	31.9	0/6	0/4	NA	
poly-	400		375	R	27.5	20.0	47.5	26.2	670	3120	20.5	ND	960	26.4	0/6	2/4	8	
urethane			373	R	30.0	20.0	50.0	31.2	850	3400	20.5	5	1270	35.2	0/6	3/4	7	47.5
#13			373	R	32.5	20.0	52.5	33.4	1130	3920	20.3	ND	1420	43.9	0/6	3/4	2	(43.0-
			374	R	35.0	20.0	55.0	35.4	1300	3810	20.4	ND	1710	35.4	0/6	4/4	16	52.5)*
			376	R	37.5	20.0	57.5	37.3	1390	3850	20.4	ND	1860	54.9	0/6	4/4	2	
			375	R	40.0	20.0	60.0	43.1	1160	4090	20.4	ND	1550	40.9	0/6	4/4	2	
Polyester	500	F	527	R	20.0	15.0	35.0	34.0	1870	30200	17.5	62	2370	76.2	1/6	1/5	NA	
plus			523	R	20.0	20.0	40.0	38.9	2270	33600	17.1	63	3120	80.2	3/6	3/5	NA	39.0
poly-	400		525	R	20.0	22.5	42.5	41.8	2410	31100	17.4	50	3420	78.7	5/6	5/6	NA	(36.0-
urethane			524	R	20.0	25.0	45.0	44.0	2780	34400	16.8	48	3930	ND	6/6	6/6	NA	42.2)*
#13			524	R	20.0	30.0	50.0	49.0	3070	34700	17.1	59	4500	ND	6/6	6/6	NA	
			425	R	20.0	30.0	50.0	43.7	1750	31500	17.4	13	1950	69.1	1/6	1/5	NA	

For legend, see Table 1

generation of HCN from 20 mg/ℓ of the flexible polyurethane when decomposed alone or combined with the polyester under various flaming conditions. Polyurethane decomposed alone at 425°C produced an average HCN concentration of 19 ppm; whereas, at 525°C, it produced an average of 37 ppm in one experiment and 51 ppm in another. The flaming decomposition of various amounts of polyester with 20 mg/ℓ of polyurethane at 525°C produced greater concentrations of HCN than in any of the experiments on the polyurethane alone (Tables 1,3 and Fig. 2). This result was unexpected since polyester contains no nitrogen and should not contribute to the HCN generation. Figure 2 also shows that the HCN generation over time from 20 mg/ℓ of flaming polyurethane foam alone tends to plateau during the 30 minute test, whereas, in the combination studies of this polyurethane (20 mg/ℓ) and polyester, the HCN continues to increase throughout the experiments. The reason for this increased level of HCN is unexplained at this time.

Table 4

Gas Concentrations from the Thermal decomposition of Polyurethane Foam and Polyester Alone and in Combination

			Mass Loaded	Average Gas Concentration[1]		
Mode	Temp. (°C)	Material	Chamber Volume (mg/ℓ)	CO (ppm)	CO_2 (ppm)	HCN (ppm)
Flaming	525	Polyurethane	20[2]	510 (± 120)	14900 (± 4200)	44 (± 47)
		Polyester	30	2220	25200	--
		Total		2730	40100	44
		Polyurethane + Polyester	20 + 30	3070	34700	59
Non-Flaming	375	Polyurethane	30	700	2690	4
		Polyester	20[3]	50	600	--
		Total		750	3290	4
		Polyurethane + Polyester	20 + 30	850	3400	5

---

1 Average gas concentration:

$$\frac{\text{integrated area under instrument response curve for 30 minutes}}{\text{30 minutes}} = \frac{\text{ppm-min}}{\text{30 min}}$$

2 Results are average ± range of two analytical experiments

3 Analytical experiment (no animals)

In the flaming mode, the concentrations of CO from combined materials was also greater than the sum of the CO concentrations from the individual materials (Figure 3). This was more apparent from the graphic representation of the actual generation of CO than from the tabular depiction of the average concentrations (Table 4).

CONCLUSIONS

Individual Materials

- The decomposition products of the flexible polyurethane foam produced no deaths during exposure and only caused post-exposure deaths in the non-flaming mode.

- The polyester when decomposed 25°C above or below its autoignition temperature caused deaths both during and following exposures.

- Comparison of the CO, CO_2, and HCN concentrations generated from the individual materials with pure gas toxicity experiments (performed with single and multiple gases) indicated:

    1. the deaths from flexible polyurethane could not be explained by the concentrations of these gases,

    2. non-flaming polyester produced relatively high COHb (75-83%) levels, but lower than lethal average or maximum CO concentrations. Even when CO was considered with CO_2 (which potentiates the toxicity of CO), the combination was not sufficient to account for the deaths, and

    3. the deaths from exposures to flaming polyester products were probably due to CO since COHb values were 83-85%. In this case, the maximum (not the average) concentrations of CO plus CO_2 were sufficient to predict the deaths.

Combined Materials

- Depending on the amount thermally decomposed, both materials contributed to the combined toxicity. In the flaming mode, the contribution was additive.

- Similar to the polyurethane results, the non-flaming combined experiments only produced post-exposure deaths which were not attributable to the generated CO, CO_2, and HCN concentrations.

- The deaths observed from the flaming combined experiments were explainable based on the concentrations of CO, CO_2, and HCN.

- Comparison of the gas concentrations from the combined materials to those from the individual materials indicated:

    1. The non-flaming generation of CO, CO_2, and HCN appear to be approximately equal to the sum of the concentrations from the single materials.

2. The flaming generations of CO and HCN were greater than the sum of those from the single materials.

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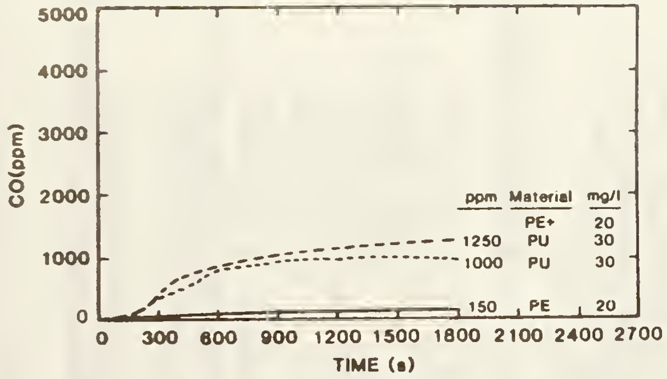

Figure 1. CO Generation from Flexible Polyurethane Foam and Polyester Decomposed Alone and Together. Non-Flaming 375°C.

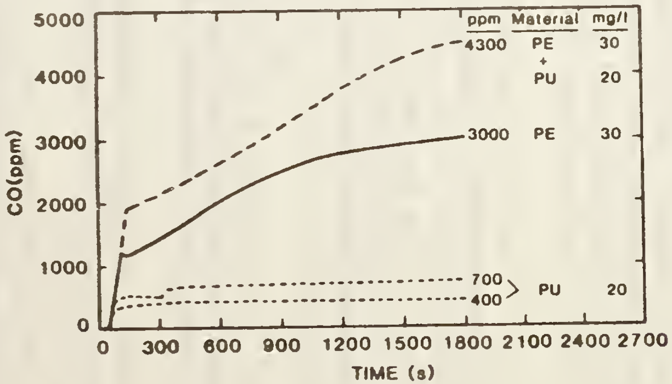

Figure 3. CO Generation from Flexible Polyurethane Foam and Polyester Decomposed Alone and Together. Flaming 525°C.

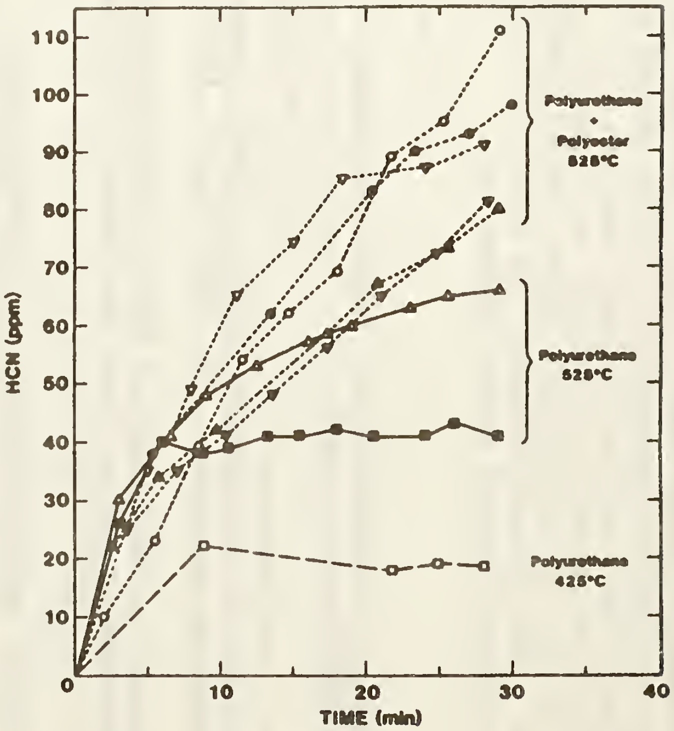

Figure 2. Generation of HCN from 20 mg/ℓ of Polyurethane Decomposed Alone and with Different Amounts of Polyester Under Flaming Conditions.

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Some limitations and potential limitations of the NBS toxicity screening test method had been identified in earlier work. These limitations have now been explored in greater detail. Also investigated was an alternative combustion system, consisting of a radiant cone heater, identical to the one in the recently developed Cone Calorimeter, an enclosed combustion chamber, and a slightly revised variant of the animal chamber. The new animal chamber was so constructed that, prior to the insertion of the animals, it could be evacuated and then back-filled with a desired sampling of the combustion products. The radiant combustion system showed a different mix of capabilities and limitations compared to the cup furnace combustor in the existing test method. In the present project, the more detailed assessment of the cup furnace operation leads to the recommendation that there is no single, universally preferable combustion environment, but that the cup furnace is adequate for the intended purpose of providing toxicity screening.

12. KEY WORDS (*Six to twelve entries; alphabetical order; capitalize only proper names; and separate key words by semicolons*)

Combustion products; combustion toxicity; NBS toxicity test method; plastics; radiant combustion

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