

Observations on the Generation of Toxic Products in the NFPA/ISO Smoke Density Chamber

Nathan D. Marsh, Richard G. Gann, & Marc R. Nyden
Building and Fire Research Laboratory
National Institute of Standards and Technology
Gaithersburg MD 20899 USA

ABSTRACT

Efforts are underway in several research groups to adapt existing flammability test methods for the determination of yields of toxic compounds such as CO, HCN, and HCl. These include the NFPA 269 / ASTM E 1678 radiant apparatus, the ISO/TS 19700 tube furnace, the NFPA 271 / ASTM E 1354 cone calorimeter, and the NFPA 270 / ISO 5659-2 smoke density chamber. In each case a small (on the order of cm) specimen, cut from an item of furnishing or other building content, is burned and the evolved gases measured, in order to calculate the yields of toxic gases, ideally for different fire stages such as well-ventilated flaming or post-flashover flaming.

The goal of these efforts is to facilitate obtaining the yields of toxic gases from principal combustibles for use in fire safety engineering. This will enable managing the exposure of building occupants to fire effluent and, in turn, providing realistic time for their escape.

In our own work, tested specimens representative of finished goods were: a particleboard with a polyvinyl chloride (PVC) veneer, a polyurethane foam with a cotton/polyester cover fabric, or PVC clad, nylon insulated 3-conductor electrical cable. Gas volume fractions were monitored by a non-dispersive infrared gas analyzer (CO, CO₂), a paramagnetic gas analyzer (O₂), and a Fourier transform infrared spectrometer (HCN, HCl, and other gases not detected in this study).

These techniques were most recently applied to the NFPA 270 / ISO 5659-2 smoke density chamber. In addition to the monitoring of optical density, gas samples were drawn continuously from fittings located in the top center of the chamber, and after passing through the gas analyzers, were returned via another fitting nearby. Flows were maintained at a few L/min to avoid “stirring” of the chamber contents; however, we did observe some buoyancy-induced circulation. For the purpose of determining gas yields (in g/g of material burned) the thickness of the hot upper layer is an important factor but is difficult to determine, resulting in an uncertainty in gas yields of a factor of 2.

Among our observations, we found that in addition to the three burning modes found in the standard (50 kW/m² unpiloted, 25 kW/m² piloted and 25 kW/m² unpiloted), in some cases a 50 kW/m² piloted mode can be useful when the specimen is not particularly flammable. We also found that the current practice of reporting gas concentrations only from the moment of peak optical density can give erroneous and unpredictable results—in the experiments with electrical cables composed partly of PVC, HCl was sometimes not observed until after the optical density had peaked. Finally, we found that when we burned the polyurethane foam, we did not observe any HCN, although we have found HCN, using the same instruments and procedures coupled to other physical fire models and in room-scale fire tests of identical products.

INTRODUCTION

Estimation of the time people will have to escape or find a place of refuge in the event of a fire is a principal component of fire hazard or risk assessment. The ability of occupants to move promptly and constructively is partly determined by their exposure to the fire effluent, i.e., the gases, smoke, and heat generated by the fire and transported into the egress paths. The composition of the fire effluent, and therefore its toxic potency, is determined by a complex interaction of the chemical composition and burning mode of the materials and finished goods involved in the fire. It is therefore desirable to have a way to determine the effluent from the burning of these various finished goods, in a manner that reproduces as much as possible the conditions of a real fire.

As frequent testing of materials and finished goods at full scale is impractical, numerous reduced-scale test apparatus and methods have been devised so that representative specimens, usually on the order of grams in mass or centimeters in dimension, can be burned and the gaseous products sampled and analyzed. Some of these test methods have provisions so that different fire stages can be simulated. Details on a variety of devices can be found in ISO/TR 16312-2 ¹. Until recently, however, little has been done to verify the degree to which the effluent from the small-scale test specimens reflects the effluent from the full-scale combustible object. The current work is part of a larger study to address this question, by comparing results from several different bench-scale test methods to those from full-scale tests.

Previously, we have reported observations regarding the NFPA 269/ASTM E 1678 toxicity test ², as well as with the ISO TS/1700 tube furnace ³. In each case, we conducted tests using three canonical materials—a vinyl veneer particleboard, a polyurethane foam with a cotton/polyester fabric cover, and a polyvinyl chloride (PVC) clad 3-conductor electrical cable. The test specimens were cut from the same lot of finished goods that were also burned in previous full-scale tests ⁴ (sofa mock ups, particleboard bookcases, and trays of PVC clad electrical cables), so that the results of the bench-scale and full-scale tests could be compared.

In the current work, we tested the same specimens using the ISO 5659-2 smoke density chamber (also ASTM E 1995 and NFPA 270). This test apparatus is identical to the more widely-used ASTM E 662 test method, with the exception that the specimen is mounted horizontally rather than vertically, and the heating element is a truncated cone rather than a cup furnace. The configuration of the pilot flame is somewhat different as well. This apparatus has been adapted for the measurement of smoke toxicity: BSS 7239 Test Method for Toxic Gas Generation by Materials on Combustion uses the ASTM E 662 vertical specimen orientation and IMO Resolution MSC 61(67): Annex 1, AKA Fire Test Procedures (FTP) Code, Part 2 for the horizontal specimen orientation. However, the literature is extremely limited on the use of this adaptation. The vertical orientation was considered by Curry ⁵, while the horizontal orientation was considered by Nazaré *et al.* ⁶. A single study by Willson *et al.* ⁷ compared both orientations.

EXPERIMENTAL EQUIPMENT AND PROCEDURES

The ISO 5659-2 smoke density chamber, depicted in Figure 1, is an enclosed chamber test method with a (truncated) conical radiant heater, air/propane pilot flame, load cell, and an optical attenuation measuring system for measuring smoke density. The three standard test configurations

are 50 kW/m² unpiloted, 25 kW/m² piloted, and 25 kW/m² unpiloted. In this study, a fourth configuration of 50 kW/m² piloted was also investigated.

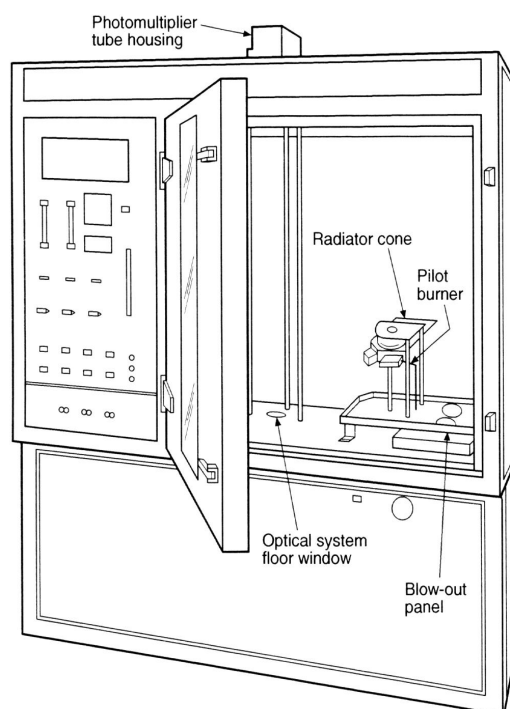


Figure 1. Smoke Density Chamber.

Test specimens from the three finished goods were burned as intact specimens. The particleboard and foam were cut into squares of 7.5 cm on a side, with the particleboard being 1.0 cm thick and the polyurethane foam being 2.5 cm thick. The cable specimens consisted of 5 lengths of 7.5 cm each arranged side-by-side. All of the specimens were wrapped on the bottom and sides in aluminum foil as specified in the test method. In the standard procedure, test specimens are placed in the sample holder on the load cell and the chamber is then closed. If the pilot flame is to be used, the gas supplies are turned on and a spark igniter automatically ignites the flame. (If the flame goes out, the spark igniter will reestablish it.) From the control panel, a shutter is opened to expose the specimen to the heating element. The specimen pyrolyzes or burns, emitting smoke, which attenuates a beam of light spanning the chamber vertically. In the standard procedure, the maximum optical density is recorded, although in our apparatus the value is continuously recorded. The maximum usually occurs around the time that the flame goes out, although these events do not always occur simultaneously. Once the specimen has extinguished and no longer produces smoke, the measured optical density decreases due to smoke particle agglomeration, wall deposits, and sedimentation. All of our tests were run for over 30 min after ignition, in order to model the 30-minute exposure scenario used in the NFPA 269 / ASTM E 1678 toxicity test.

In addition to measuring optical density as in the standard test, we also measured gas composition continuously. CO and CO₂ were quantified using a non-dispersive infrared (NDIR) gas analyzer; oxygen was quantified by a paramagnetic analyzer in the same instrument. Gas was continuously circulated from the top of the chamber by a small pump and passed through a series of traps and filters, first a coiled tube immersed in a water ice bath, then an impinger bottle immersed in dry ice, with its upper half filled with glass wool, and finally a glass fiber disk filter. The intent was to remove particulates and condensable species, including water, that would otherwise interfere with and possibly harm the analyzer. Once analyzed, the gas was returned to the chamber. While sampling,

the flow was maintained at 1 L/min for the CO and CO₂ detectors and 0.2 L/min for the O₂ detector. The analyzer itself was calibrated daily with zero and span gases (a mixture of 5000 µL/L CO and 0.08 L/L of CO₂ in nitrogen, and ambient air (0.2095 L/L oxygen on a dry basis)).

HCN and HCl were quantified using a Fourier transform infrared (FTIR) spectrometer, equipped with a stainless steel flow cell with 2 mm KBr windows and a 0.1 m pathlength, maintained at 170 °C. Samples were circulated through heated 0.6 cm (¼ in.) copper tubes from the top of the chamber. The sample was pulled through the sampling lines and flow cell by a small pump located downstream from the flow cell, and then returned to the chamber in order to minimize the effect of gas removal on the contents of the chamber. The pump flow was measured at 3 L/min maximum, but was at times lower due to fouling of the sampling lines with smoke deposits.

Calibration spectra were obtained from a quantitative spectral library assembled by Midac ^{*, 8} and from a collection of spectra provided by the Federal Aviation Administration, which performed bench-scale fire tests on similar materials ⁹. In this analysis, the least squares fits were restricted to characteristic frequency regions or windows for each compound that were selected in such a way as to maximize the discrimination of the compounds of interest from other components present in fire gases. Table 1 lists the species included in this analysis and the frequency windows used for their quantification. Other species including HBr, acetylene, and acrolein were initially included in the analysis, but after the careful examination of the spectra recorded in the experiments, it was determined that they were not present in measurable quantities. Although CO and CO₂ were not quantified by this method, they were included in the analysis so that their presence did not produce “false positives” in other species that absorb in the same frequency regions. All reference spectra were recorded at 170 °C and ambient pressure.

Table 1. Species and Frequency Windows for FTIR Analysis.

Compound	Reference Volume Fraction (µL/L)	Frequency Window (cm ⁻¹)	Minimum Detection Limit (µL/L)
CH ₄	483	2800 to 3215	NA ^a
CO	2410	2050 to 2225	50
H ₂ O	100,000	1225 to 2150, 3400 to 4000	NA ^a
HCl	9870	2600 to 3100	50
HCN	507	710 to 722, 3200 to 3310	50
CO ₂	47,850	660 to 725, 2230 to 2300, 3500 to 3760	50

^aBecause these compounds do not contribute to toxicity, their minimum detection limits were not quantified.

RESULTS AND DISCUSSION

Figure 2 shows the overlay of 3 separate runs testing polyurethane foam irradiated at 50 kW/m² without a pilot flame. In all three cases, ignition took place at around 100 s. In one of the

* Certain commercial equipment, instruments, or materials are identified in this paper in order to specify the experimental procedure adequately. Such identification is not intended to imply recommendation or endorsement by the National Institute of Standards and Technology, nor is it intended to imply that the materials or equipment identified are necessarily the best available for the purpose.

runs, a small disturbance around 70 s after ignition retarded the fire for 20 s before it resumed burning with the same intensity as in the other two tests. Peak optical density occurred at the same time as the first peak in CO₂ volume fraction. Under the normal rules of the test method, this is the time for which the gas volume fractions or yields are to be reported, in which case we would have a CO₂ volume fraction of 0.93 % $\pm$ 0.02 %[†]. However, using the same procedure, we would report that the CO volume fraction was below the detection limit.

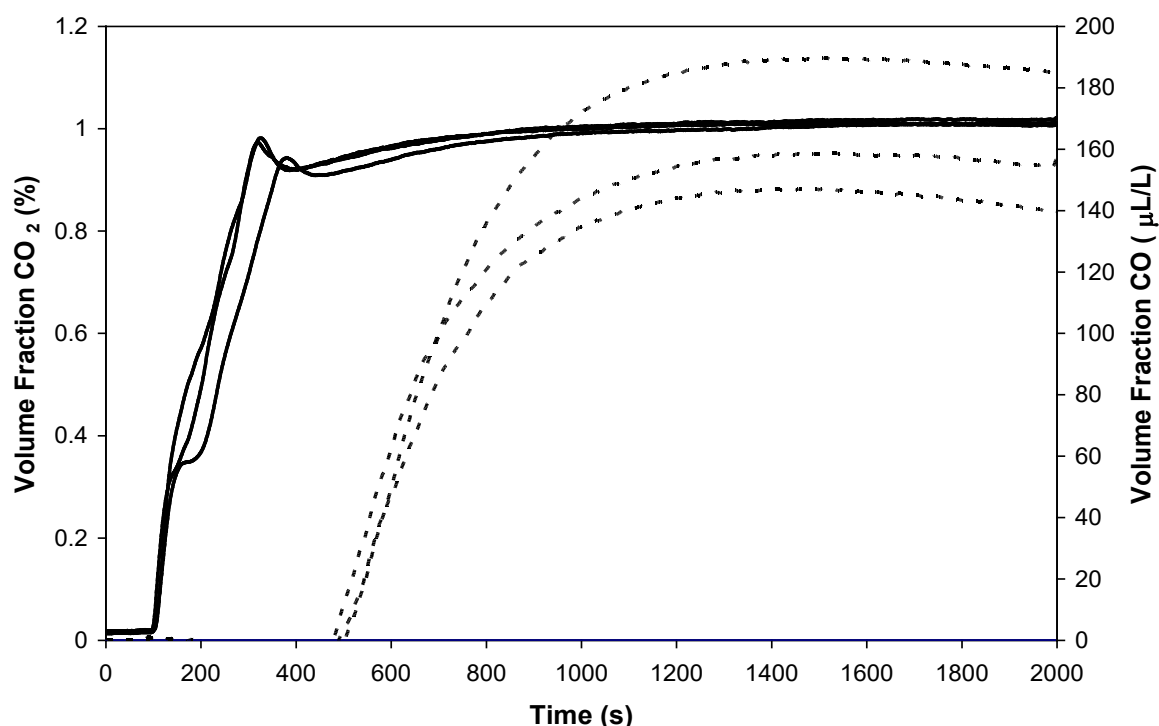


Figure 2. Polyurethane foam 50 kW/m² unpiloted. CO (dashed line) and CO₂ (solid line).
CO uncertainty is $\pm$ 20 µL/L

However, it is worth considering the cause of this discrepancy, and why CO is not detectable at the time of peak optical density, but does appear later. After the peak optical density is reached, there continues to be a slow increase in CO₂ volume fraction and the flame dies down and eventually goes out. Visually, the chamber is full of smoke that continues to circulate, driven by the buoyant plume created by the cone heater heating the sample char, sample holder, and therefore surrounding gas. We hypothesize that the source of the CO in this case is the cone heater pyrolysing the char and / or the smoke particles. Observing that CO is not produced in detectable quantities until the flame completely extinguishes, we further hypothesize that at least for the polyurethane foam, and the smoke it produces, the flame is sufficiently hot to complete conversion to CO₂. In other words, there are really three fire stages being modeled in these tests: well ventilated flaming up to the time of peak optical density, under-ventilated flaming from this point until the flame extinguishes, and oxidative pyrolysis for the remainder of the test. This raises the important question of how well the smoke density chamber, horizontal orientation models a real fire. In other words, is it reasonable to suppose that in a real fire, some smoke would pass over relatively hot surfaces, without being exposed to open flames, and convert into a significant quantity of CO?

[†] Uncertainties are the standard deviations across multiple tests, representing run-to-run variation. In the figures, the uncertainty is twice the instrument resolution, and except where indicated, is smaller than the line thickness.

Next, we compare the response of polyurethane foam to the different thermal exposures. Figure 3 shows the measured CO and CO₂ volume fractions for 3 of the 4 combinations of flux and piloting described previously. (At 25 kW/m² unpiloted (25 U), the specimen smoldered but did not ignite. The resulting fumes and residue were sufficiently odorous that we did not attempt any additional runs.) At 25 kW/m² piloted (25 P), there was no detectable CO, while at 50 kW/m² piloted (50 P), the yield of CO was extremely low, on the order of twice the instrument resolution. This supports the previous hypothesis that the presence of a flame, either from the pilot or the specimen itself, enhances carbon oxidation, promoting the complete combustion to CO₂.

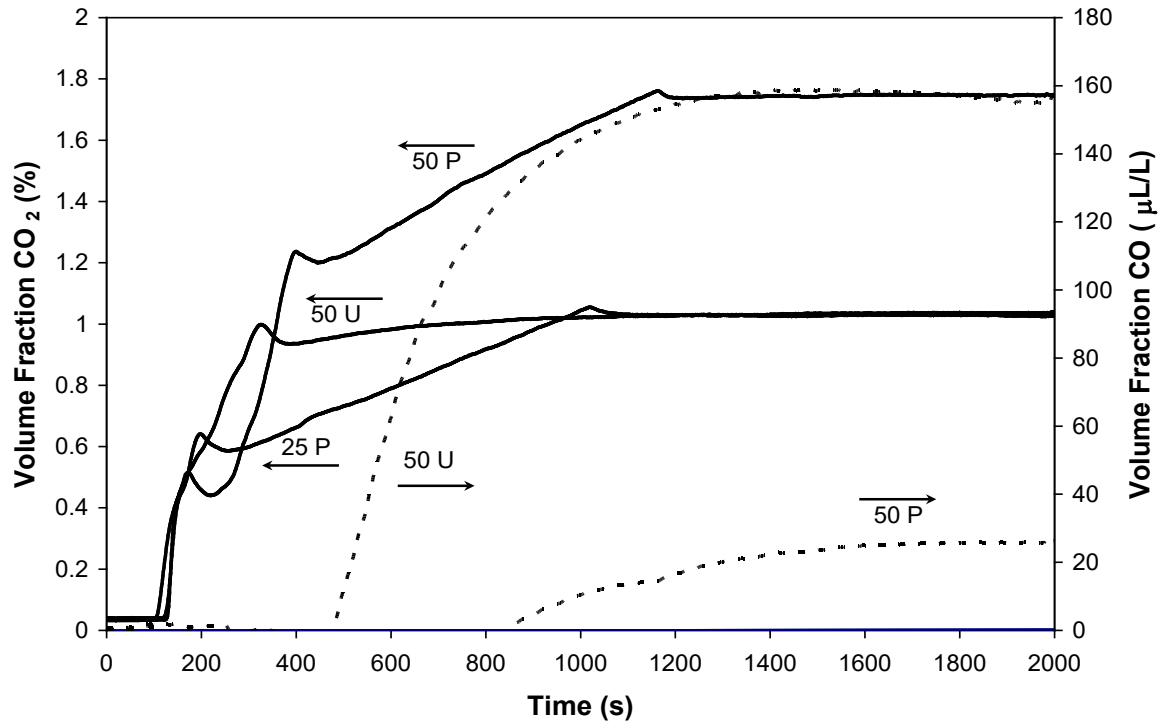


Figure 3. CO (dashed line) and CO₂ (solid line) volume fractions for polyurethane foam at different thermal exposures. CO uncertainty is $\pm 20 \mu\text{L/L}$

Furthermore, the pilot flame itself is a source of CO₂ as can be seen in Figure 3 for both piloted cases—in each, the pilot flame was extinguished after 1000 s. Thus the plateau after 1000 s is the CO₂ volume fraction resulting from both the specimen and the pilot flame operating for 1000 s, while the rise before 1000 s is the result of the rate of CO₂ generation from the pilot flame alone. This production rate can be subtracted from the plots, resulting in the CO₂ volume fraction resulting from the specimen alone, as depicted in Figure 4.

With this adjustment, we find that the presence of the pilot flame does not significantly affect the yield of CO₂ from the specimen. However, it does illustrate the need to compensate for the additional CO₂ produced by the pilot flame when calculating yields for a given specimen. Making this adjustment or correction also shows that the lower incident heat flux results in roughly half the yield of CO₂ compared to the higher heat flux. However, the mass loss under the lower heat flux was around 70 % of that under the higher heat flux, indicating that the lower yield is not simply a result of lower mass loss, and illustrating the importance of the selection of test conditions in correctly modeling a real fire.

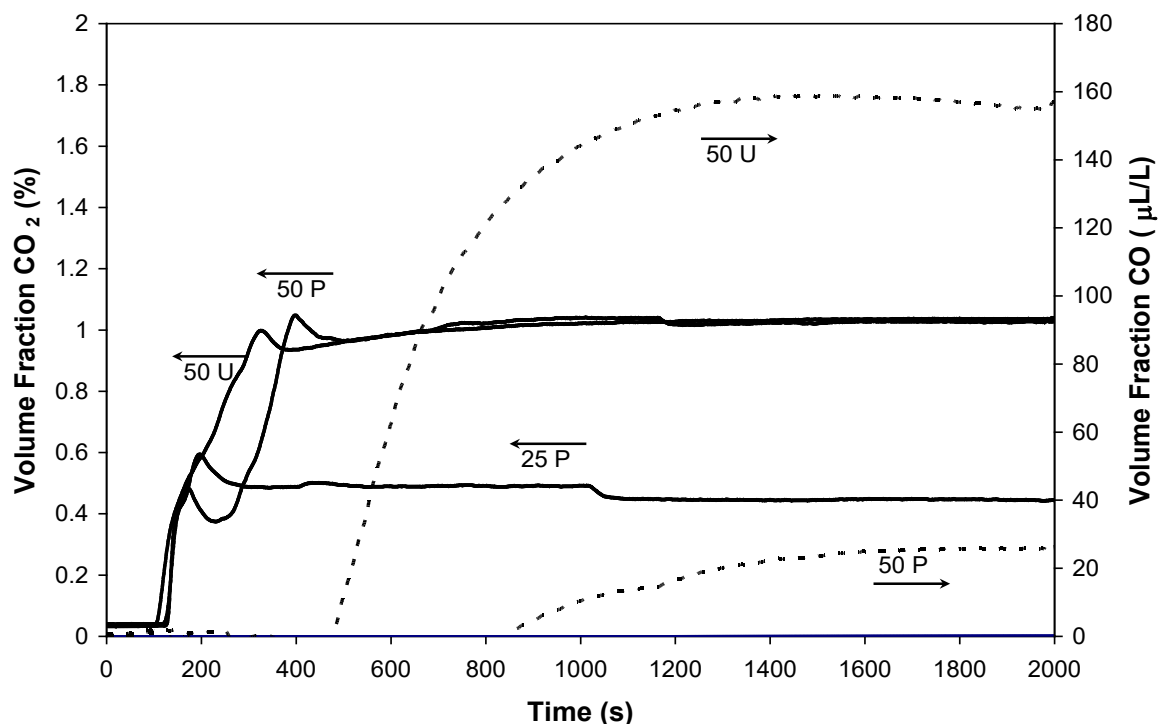


Figure 4. CO (dashed line) and CO₂ (solid line) volume fractions for polyurethane foam at different thermal exposures, with pilot flame contribution removed. CO uncertainty is $\pm 20 \mu\text{L/L}$

Most surprising, there was no HCN detected in any of the polyurethane foam experiments. In our previous work with the same materials²⁻⁴, HCN was found to contribute a significant fraction, in the fractional effective dose model, to the lethality of smoke from this polyurethane foam. That it is not detected in the smoke density chamber is troubling, because it indicates that this test method would significantly underestimate the hazard from at least this material, and possibly others as well. We do not yet have a satisfactory explanation of why HCN was not detected under any of the test conditions in this apparatus.

Figure 5 shows the results for triplicate tests of the PVC-clad electrical cables exposed to 50 kW/m^2 without a pilot flame. In addition to CO and CO₂, the electrical cables also produce significant quantities of HCl, as was also observed in our previous work²⁻⁴. The variation in yield of HCl, with one run producing half that of the other two, we attribute to typical run-to-run variations experienced with more complex specimens made up of multiple layers of differing materials. We also observe that, unlike CO and CO₂, HCl exhibits a significant reduction in volume fraction as the test proceeds. This is due to its propensity for depositing on solid surfaces, which include walls and carbon particles. In each case, over the course of 30 min it is reduced to roughly half its peak volume fraction. These losses, which are not normally accounted for in fire modeling, could have a significant positive impact on tenability. HCl is considered an irritant gas, which has a threshold volume fraction above which it becomes incapacitating. Given these losses, the volume fraction far from the fire will be substantially lower than near, resulting in a less hazardous environment than might initially be assumed. This makes such calculations conservative, but also could lead to overdesign of effluent control approaches. Furthermore, a location in a building might be only temporarily untenable—as HCl is lost to the surroundings the volume fraction will ultimately fall below the incapacitating level. Unfortunately there are no data on the effect of lower volume fractions of irritant gases on people who have already been exposed to an incapacitating volume fraction.

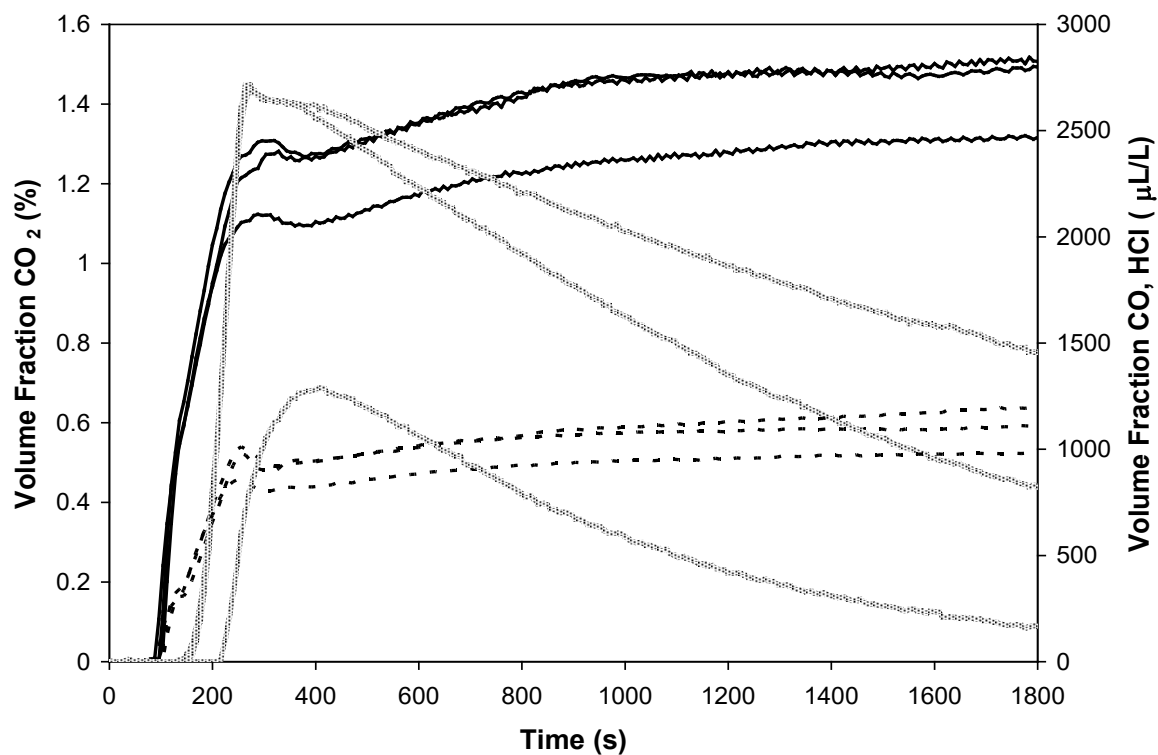


Figure 5. PVC-clad electrical cables 50 kW/m² unpiloted.
CO (dashed line); CO₂ (solid line); HCl (grey line).

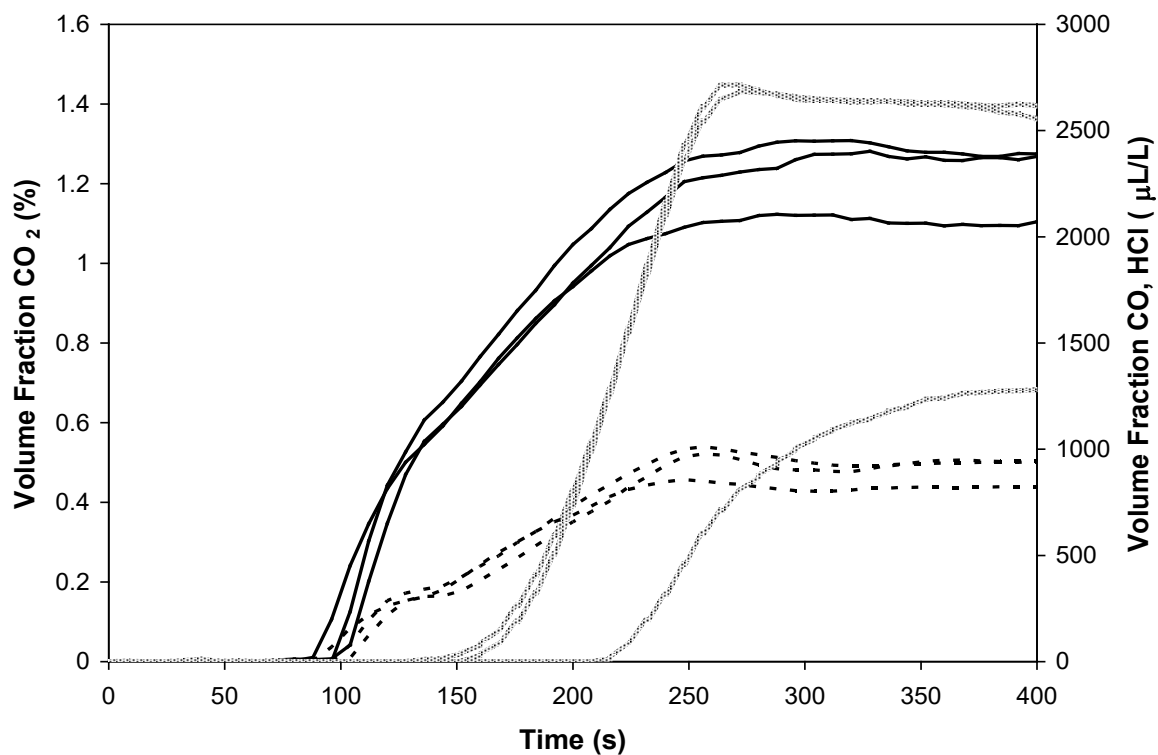


Figure 6. Detail of the initial few minutes of the PVC-clad electrical cables 50 kW/m² unpiloted.
CO (dashed line); CO₂ (solid line); HCl (grey line).

Also of note in Figure 5 is that, unlike the foam which did not produce CO until after the flame had extinguished, the electrical cables produce CO starting at ignition. However, there is a substantial delay of nearly a minute between ignition and the first detection of HCl, which is shown in more detail in Figure 6. This delay is unexpected because HCl is normally thought to be the initial product of decomposition; in fact, this property is essential in the functioning of chlorinated flame retardants. However, it is not clear whether the delay is an effect of the chemical decomposition, an effect of a physical process taking place within the chamber, or a sampling artifact. Possible physical processes include the trapping of Cl or HCl in the smoke particles which is liberated by subsequent heating, or deposition of the majority of the HCl on the upper surface of the chamber, to be released as the fire plume heats the surface above some critical temperature. A sampling artifact could consist of the HCl depositing on a cold spot in the sampling line, although great care was taken to prevent this from happening and has not been observed in our previous work^{2,4}. In any event, this delay is problematic because the optical density peaks around 250 s after ignition—at this point in one of the tests, the HCl had not reached one third of its maximum volume fraction. In other words, the uncertainty across multiple tests is magnified if one only looks at the volume fractions at the point of maximum optical density.

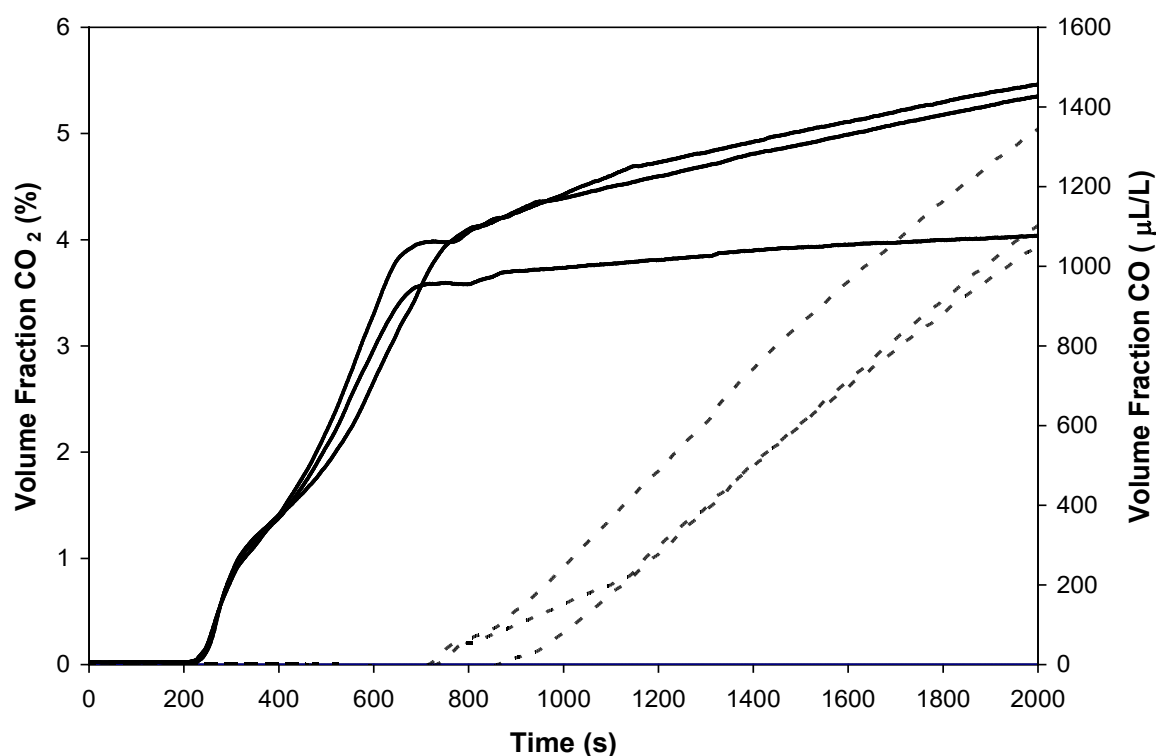


Figure 7. Particleboard 50 kW/m² piloted, with pilot flame contribution removed. CO (dashed line) and CO₂ (solid line).

Finally in Figure 7 we show results from the particleboard with a thermal exposure of 50 kW/m² with a pilot flame. These data have also been corrected to remove the contribution of CO₂ from the pilot flame. Even at the higher heat flux, these specimens did not achieve flaming combustion without the pilot flame. Unlike the polyurethane foam, where we attributed the late production of a small amount of CO to pyrolyzing char and or smoke particles, for the particleboard we attribute the post-flaming generation of CO and additional CO₂ to oxidative pyrolyzing of the char alone, as it still had significant mass at this point. The CO volume fractions are ultimately about 10 times higher than

those produced from the polyurethane foam, and of the same order as those produced by the electrical cables. It is also worth noting that the test with lower CO₂ also had higher CO, indicating some physical variation in the charring process between tests.

CONCLUSIONS

In this work we adapted the ISO 5659-2 smoke density chamber for the measurement of yields of toxic gases. We burned the same 3 specimen types, particleboard, polyurethane foam, and electrical cables, as we have in our previous full-scale and bench-scale ^{2, 3} studies. Among our observations, we found that in addition to the three burning modes found in the standard (50 kW/m² unpiloted, 25 kW/m² piloted and 25 kW/m² unpiloted) in some cases a 50 kW/m² piloted mode can be useful for obtaining well ventilated flaming data when the specimen is not very flammable. We also found that the current practice of reporting gas concentrations only from the moment of peak optical density can give erroneous and unpredictable results—in the experiments with electrical cables composed partly of PVC, HCl was sometimes not observed until after the optical density had peaked. Finally, we found that when we burned the polyurethane foam, we did not observe any HCN above our minimum detection limit of 50 µL/L, although we have in the past using the same instruments, materials, and procedures coupled to other physical fire models. The absence of HCN in the smoke density chamber requires further study.

REFERENCES

- ¹ ISO 16312-2-2007, Guidance for Assessing the Validity of Physical Fire Models for Obtaining Fire Effluent Toxicity Data for Fire Hazard and Risk Assessment – Part 2: Evaluation of Individual Physical Fire Models, International Standards Organization, Geneva.
- ² Marsh, N. D., Gann, R. G., Averill, J. D., and Nyden, M. R., “Sensitivity of a Smoke Toxicity Test Method to Test Conditions,” *Proceedings of the 9th International Symposium on Fire Safety Science* 687-698 (2008).
- ³ Unpublished results, National Institute of Standards and Technology.
- ⁴ Gann, R. G., Averill, J. D., Johnsson, E. L., Nyden, M. R., and Peacock, R. D., “Smoke Component Yields from Room-scale Fire Tests” National Institute of Standards and Technology Report NIST TN 1453, Gaithersburg, MD, 20899, 2003, 139 p.
- ⁵ Curry, B. “Comparison of flame, smoke and toxicity in a halogen-free and a halogenated reinforced composite.” *Journal of Advanced Materials* **37**, 36-39 (2005).
- ⁶ Nazaré S., Kandola, B. K., and Horrocks, A. R., “Smoke, CO, and CO₂ measurements and evaluation using different fire testing techniques for flame retardant unsaturated polyester resin formulations”, *Journal of Fire Sciences* **26**, 215-242 (2008).
- ⁷ Willson, K. R., Janssens, M. L., Griffith, A. L., Carpenter, K. C., AND Huczek, J. P. “Smoke toxicity measurements of automotive materials”, , in *Fire and Polymers IV: Materials and Concepts for Hazard Prevention, ACS Symposium Series* **922** 321-333 (2006)
- ⁸ *Gas Phase Infrared Spectral Standards, Revision B*, Midac Corp.; Irvine, CA (1999).
- ⁹ Speitel, L. C., “Fourier Transform Infrared Analysis of Combustion Gases,” Federal Aviation Administration Report DOT/FAA/AR-01/88, 2001.