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Method Development Study for APR Cartridge Evaluation in Fire Overhaul Exposures

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In the US, firefighters do not typically wear respiratory protection during overhaul activities, although fitting multi-gas or chemical, biological, radiological and nuclear cartridges to supplied air respirator facepieces has been proposed to reduce exposures. This work developed a method to evaluate the effectiveness of respirator cartridges in smoke that represents overhaul exposures to residential fires. Chamber and penetration concentrations were measured for 91 contaminants, including aldehydes, polynuclear aromatic hydrocarbons, hydrocarbons and methyl isothiocyanate, along with total and respirable particulates. These laboratory tests generated concentrations in the range of field-reported exposures from overhaul activities. With limited tests, no styrene, benzene, acrolein or particulates were detected in air filtered by the respirator cartridge, yet other compounds were detected penetrating the respirator. Because of the complexity of smoke, an exposure index was determined for challenge and filtered air to determine the relative risk of the aggregate exposure to respiratory irritants. The primary contributors to the irritant exposure index in air filtered by the respirator were formaldehyde and acetaldehyde, with total hydrocarbons contributing only 1% to the irritant index. Respirator cartridges were adequate to minimize firefighter exposures to aggregate respiratory irritants if the American Conference of Governmental Industrial Hygienists ceiling limit for formaldehyde is used (0.3 ppm) but not if National Institute for Occupational Safety and Health Recommended Exposure Limit (NIOSH REL) (0.1 ppm) is used, where three of five concentrations in filtered air exceeded the NIOSH REL. Respirator certification allows 1 ppm of formaldehyde to pass through it when challenged at 100 ppm, which may not adequately protect workers to current short-term exposure/ceiling limits. The method developed here recommends specific contaminants to measure in future work (formaldehyde, acrolein, acetaldehyde, naphthalene, benzene, total hydrocarbons as toluene and particulate mass) along with inclusion of additional irritant gases and hydrogen cyanide to fully evaluate whether air-purifying respirators reduce exposures to the aggregate gases/vapors present in overhaul activities.

Keywords: firefighter; penetration; respirator testing

BACKGROUND

Toxic chemicals associated with fire smoke have been examined for decades. Work in 1977 focused on carbon monoxide (CO) and oxygen (Burgess *et al.*, 1977) and progressed in 1978 to include nitrogen dioxide, hydrochloric acid and hydrogen cyanide (Gold *et al.*, 1978) then acrolein and benzene (Treitman *et al.*, 1980). The preponderance of detectable hydrogen cyanide concentrations were attributed to room fires with upholstered furniture. Half of the samples had concentrations of acrolein exceeding the 1978 American Conference of Governmental Industrial Hygienists (ACGIH) short-term exposure limit (STEL) of 0.3 ppm; 70% of these exposures exceed the 2006 ACGIH ceiling limit for acrolein (0.1 ppm) (ACGIH, 2006). Benzene was detected in nearly all samples at levels below the 1978 immediately dangerous to life and health of 1000 ppm, but 20% of samples exceeded the 2006 ACGIH benzene STEL (2.5 ppm), with 5% exceeding this

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limit by at least one order of magnitude. Because of these data, fire departments adopted mandatory self-contained breathing apparatus (SCBA) use rules in the late 1970s (Treitman, 1980).

One decade later, in 1991, Jankovic *et al.* (1991) measured firefighter exposures while evaluating the performance of SCBAs during structural firefighting, measuring the above contaminants as well as hydrogen sulfide, hydrogen fluoride, carbon tetrachloride, formaldehyde and polynuclear aromatic hydrocarbons (PAHs) during knockdown (initial stages of fire suppression) and overhaul (searching for and extinguishing hidden fire sources) activities. Contaminants were present in both activities, although at lower concentrations during overhaul activities. For overhaul activities, 5% of acrolein measurements exceeded 0.2 ppm and 10% of formaldehyde measurements exceeded the current ACGIH ceiling limit (0.3 ppm). Although elevated for structural firefighting activities, PAH concentrations were in the range of ambient air during overhaul activities.

The use of SCBA respirators is the norm for structural fire responders, but there are many smaller firefighting events for which respiratory protection may not be worn. During overhaul activities, where firefighters search for hidden fires or embers after major fire suppression is complete, respiratory protection is seldom worn. Bolstad-Johnson *et al.* (2000) investigated exposure levels to PAHs, aldehydes, benzene, hydrochloric acid and other contaminants during these 30-min overhaul events. These studies identified exposures exceeding ceiling limits for acrolein, formaldehyde and glutaraldehyde in at least one of 25 structural fires; they also identified benzene, NO_2 and SO_2 levels in excess of STELs in at least two of these fires. Based on these results, the authors recommended respiratory protection use during overhaul activities.

A study to relate health effects with overhaul firefighter exposures was presented by Burgess *et al.* (2001). They measured serum pneumoproteins and lung function before and 1 h after overhaul activities for two groups of firefighters: those using air-purifying respirators (APRs) and those not using respiratory protection. These authors identified acute reductions in spirometry measures in the firefighters [e.g. forced expiratory volume in 1 s (FEV_1) decline of 130 ml ($P < 0.01$) in those wearing respirators and 160 ml ($P > 0.05$) for those without] and increased lung permeability following 30-min overhaul activities in both groups. The study indicated that some protection was afforded to respirator users, as this group worked in environments with larger contaminant concentrations (e.g. formaldehyde of 0.257 ± 0.249 ppm for those wearing respirators versus 0.109 ± 0.182 ppm for those without) but had similar magnitude in changes in FEV_1, forced vital capacity and serum Clara cell protein. The authors postulated that the effects detected in firefighters using respiratory protection could have occurred because the air-purifying respirator cartridge was not effective for all constituents within the smoke.

Because of the complexity of smoke, researchers have looked for a surrogate indicator of exposure to quantify risk. In wildland firefighting, Reinhardt and Ottmar (2004) identified strong interpollutant correlations for CO, acrolein, benzene, formaldehyde and respirable particulates ($R^2 = 0.63$–0.86), allowing for the measurement of one toxin, CO, to predict the overall exposure to irritant contaminants. In structural overhaul activities, however, neither CO nor NO_2 were correlated with other products of combustion (Bolstad-Johnson *et al.*, 2000). Owing to this inability to use a single monitor to understand the aggregate exposure to smoke, additional metrics are being explored. Jankovic *et al.* (1993) reported on a method to measure short-lived and carbon-centered free radical exposures associated with firefighting, as many have postulated that free radicals are a source of both acute and chronic toxicity to those exposed to fire smoke. That work identified that both short- and long-lived radicals could be detected during overhaul activities and their presence was not directly related to visible smoke. Leonard *et al.* (2000) used these same methods to identify that wood smoke air samples can be collected on filter media and analyzed to quantify carbon-centered radicals and the generation of reactive oxygen species on wood smoke.

In the US, respirators must be tested in accordance with 42 CFR 84 to be approved by National Institute for Occupational Safety and Health (NIOSH) (Federal Register, 1995). These tests specify the challenge concentrations, which are at least two orders of magnitude larger than current exposure limits, and flow rates representing moderate to heavy breathing rates. For example, while passing 32 and 64 lpm of test air through the respirator, acid gas cartridges are challenged with 50 000 ppm SO_2 and 5000 ppm Cl_2 and organic vapor cartridges are tested with 5000 ppm CCl_4. These single-gas test mixtures are not as complex as the smoke to which firefighters are exposed, where wood smoke alone contains hundreds of organic compounds (Simoneit *et al.*, 1993; Oras and Simoneit, 2001; Fine *et al.*, 2002, 2004; Hays *et al.*, 2002).

Even though exposures to overhaul activities typically have lower exposures than fire suppression activities, exposures can still exceed ceiling and STELs. Most overhaul activities, however, do not require SCBA use. Some fire departments have considered the use of air-purifying respirators during these activities. However, the effectiveness of multi-gas respirator cartridges for reducing smoke exposures has not been studied. More importantly, because Burgess *et al.* (2001) identified health effects associated with overhaul firefighting exposures when using air-purifying respirators in overhaul activities, the investigation of fire contaminants' penetration through the respirator cartridges is warranted. This study developed and evaluated a benchtop method to generate smoke representative of overhaul activity smoke and investigated penetration through the respirator cartridges. Although NIOSH respirator certification tests require challenge concentrations in excess of exposure limits, necessary to evaluate efficiencies in the range of 99%, our current study was conducted to test respirator cartridges at concentrations representative of actual worker exposures to a complex mixture of vapors and particles. Running tests at these representative exposure concentrations would allow us to evaluate whether contaminants at field concentrations penetrated respirator cartridges that are currently under consideration for use by local firefighting units. Because of these lower challenge concentrations, it was understood that the sensitivity of these tests may not allow efficiency determinations in this same range as NIOSH certification methods; however, it would determine what, if any, smoke components could penetrate the respirator cartridge if used during overhaul activities. Findings will provide guidance to health-effect studies for firefighters and provide recommendations for future selection and testing of air-purifying respirator equipment by firefighters. This work focused on developing combustion procedures to obtain representative challenge concentrations and evaluating the sensitivity of standard test methods for use in these 30-min tests representing typical overhaul exposure durations and provides recommendations to focus sampling and analysis efforts in future studies. The long-term objective of this work is to determine whether respirator cartridges available for use during overhaul activities offer sufficient protection to firefighters.

METHODS

To complete this work, methods were developed to (i) generate smoke that represents reported field exposures during overhaul operations, (ii) deliver smoke to a test chamber, (iii) quantify challenge concentrations to the respirator cartridges, and (iv) measure concentrations of contaminants passing through the respirator cartridge. Test durations were designed to match the same 30-min periods these cartridges are reported to be used in the field. A general description of the test system is given, followed by the process used to generate smoke for this study. Sampling and analytical methods are briefly detailed, followed by an explanation of methods used to analyze data from these tests.

Test system

The test system included a combustion grill for smoke generation, ductwork and fan to transport the smoke to and exhaust smoke from the test chamber, a smoke chamber, and a manifold to draw air through a respirator cartridge and sample this filtered air. Figure 1 provides an overhead schematic of the chamber with the attached air handling system. The flow rate through the system was 6650 lpm (235 cfm), as measured with horizontal and vertical six-point pitot traverse in the 10.2-cm (4-inch) duct at the position indicated, 11 duct diameters downstream of the elbow and 6.5 duct diameters before the expansion into the fan. A Plexiglas smoke chamber (2.44 by 0.91 by 1.22 m) was used to deliver smoke to the respirator cartridge. The chamber itself was located inside the laboratory, and the smoke generation system was located outside the building, with the duct passing through a wall.

The respirator cartridge was positioned on a manifold extended 15 inches in front of the exhaust duct venting the chamber. Samples were collected inside of the smoke chamber by positioning samplers immediately in front of the respirator cartridge. Measured concentrations from these samples are referred throughout this text as 'chamber concentrations'. The actual position of a given media type was varied

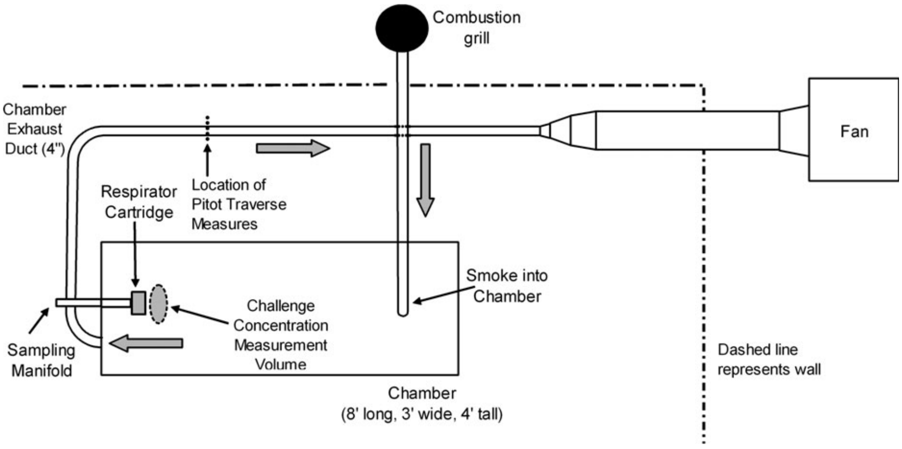

Fig. 1. Chamber schematic (overhead view).

for each run to avoid bias. Prior to each test, a fresh respirator cartridge was placed on the sampling manifold, illustrated schematically in Fig. 2. Respirator cartridges were taken directly from the manufacturer's packaging and were not pre-conditioned, representing field use conditions by firefighters. Prior to installing the new respirator cartridge, the chamber and manifold were purged with fresh outside air for ~30 min to minimize contamination from the previous test run. Air intake during the purging cycle was moved from the combustion chamber, and negligible residual smoke was confirmed with direct-reading CO and particle monitors. Outside of the chamber, ports were connected to the sampling manifold and sealed. Sample media and pumps were connected to these ports to sample air filtered by the respirator cartridge. Measured concentrations from these samples are referred throughout this text as 'filtered-air concentrations'.

For each test, the total flow through the respirator cartridge was targeted to represent the heavy breathing associated with overhaul activities. Using the US EPA (1997) exposure factor data for heavy breathing during short-term activities, a range of 72–82 lpm was used as representative of firefighting breathing rates during overhaul operations. This rate is larger than the NIOSH respirator testing methods for testing acid gas and organic vapor respirator cartridges (64 lpm) but is in the range of the 84 lpm for particulate testing. A flow rate was selected for this study that was between these two NIOSH criteria and was in the range of heavy breathing for short-duration activities to represent firefighter breathing rates. A rate of 78.15 lpm through the respirator cartridge was used throughout this study. Three high-volume pumps achieved a total of 65.3 lpm, monitored with rotameters that were calibrated using primary standards. In addition, airflow through each of the sample pumps contributed to the overall flow through the respirator, totaling 12.85 lpm.

Smoke generation

The goal of the smoke generation procedure was to ensure that (i) concentrations represented firefighter exposure levels and (ii) smoke concentrations delivered to the respirator cartridges were sufficiently large to measure challenge concentrations above the analytical method detection limit within the 30-min period. An additional target in developing this method was to attempt to limit CO levels in the chamber to 150 ppm, a procedural limit established by Phoenix Fire Department to restrict firefighters from working in overhaul areas when CO exceeds 150 ppm.

Two smoke sources were generated: burning wood/paper (Tests 1 and 2) and burning wood/paper/foam/carpet (Tests 3 through 6). Preliminary tests were conducted to identify an appropriate burn sequence. This required igniting the fire while diverting smoke away from the test chamber, extinguishing the fire and then redirecting the smoke to the test chamber. The procedure used throughout this study followed the sequence: igniting wood and paper and allowing 6 min of burn time; adding sofa cushions/carpet and allow to burn for additional 2 min (for Tests 3–6 only); extinguishing the fire and waiting 2 min; connecting the chamber duct to the combustion grill to transport smoke from smoldering

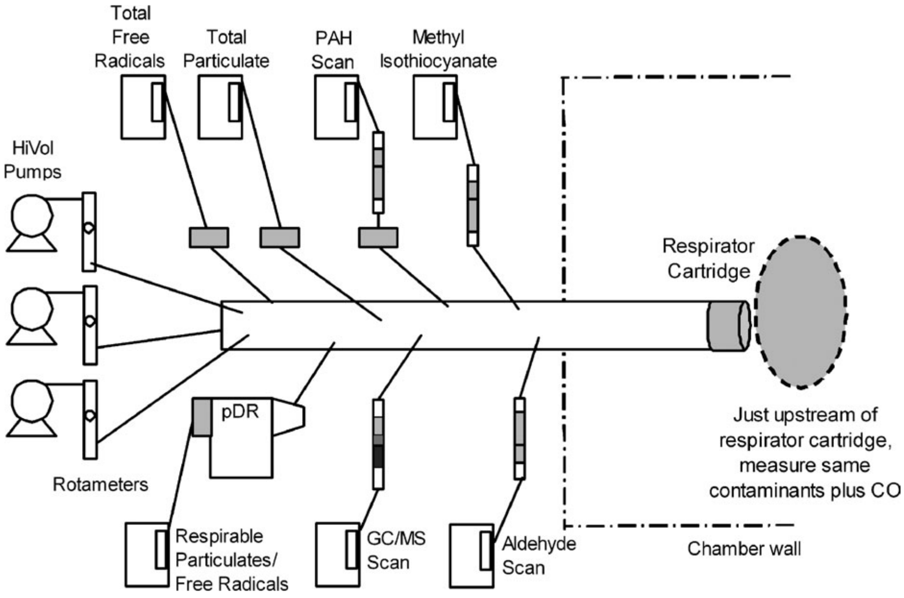

Fig. 2. Respirator and sampling manifold.

embers into the chamber to begin the 30-min test. At this time, all sampling equipment in the chamber and on the filtered-air manifold was turned on for the 30-min test.

The combustion grill was 0.34 m tall and 0.5 by 0.5 m wide. The top half was hinged to allow air to enter through a two-inch gap during the ignition and smoldering phases. The duct connecting the grill to the chamber was removed and blocked during combustion and only connected to the combustion chamber during the 30-min test period. A fire-watch remained by the combustion chamber to extinguish any flare-ups (with water) during the testing period.

Materials were standardized for all burns. Ten sheets of paper were used to ignite the wood, using a common lighter. The burn materials were weighed for each test, with the ranges provided: wood (177–225 g), sofa cushion foam (8.7–8.8 g) and nylon berber carpet (22.0–26.8 g). Although the burn material weights were standardized, wind conditions and completeness of combustion during these test cycles resulted in varied contaminant loading within the chamber, typical of smoke combustion component studies (McDonald *et al.*, 2006). Observations indicated that continued smoldering of the carpet after suppression of the fire was likely the contributor to high particulate levels inside the chamber during these overhaul simulations, and the amount of this smoldering varied in each test.

Chamber temperature and humidity were monitored throughout the tests. The mean temperature was 79.8 °F (SD = 4.9 °F), and the mean relative humidity was 25% (SD = 6.8%), over all tests. Chamber humidity peaked during the initial 3 min of the test burn, as moisture released from combustion was sent to the chamber, with an average decrease of 6.6% over the test duration. The relative humidity of these tests was less than the 95% required by NIOSH certification, to be discussed later.

Sampling and analytical methods

After building and evaluating the smoke chamber and sampling manifold system, respirator cartridge effectiveness testing was evaluated using two respirator cartridges: a multi-gas (Tests 1–4) and a chemical, biological, radiological and nuclear (CBRN) (Tests 5 and 6). The multi-gas cartridges were proposed for use by the Phoenix Fire Department. This APR cartridge was an approved multi-purpose cartridge for atmospheres containing ammonia, chlorine, chlorine dioxide, formaldehyde, hydrogen chloride, hydrogen fluoride, methylamine, organic vapors and sulfur dioxide, with a P100 designation that requires 99.97% protection against particulates. The CBRN respirator was approved for military and industrial chemical agents, including the same agents as the above cartridge as well as nitrogen dioxide and specific other warfare and nerve agents.

CO readings were recorded inside the chamber using a Passport Five-Star personal alarm monitor (MSA, Pittsburgh, PA, USA). The MSA Passport was calibrated before use and zeroed in clean air prior to each burn test. Standard methods were used to collect and analyze 91 chemical compounds: aldehdyes (EPA T011, 0.7 lpm, 15 compounds), methyl isothiocyanate (MITC) (Occupational Safety and Health Administration 2, 0.2 lpm), PAHs (NIOSH 5506, 2.0 lpm, 16 compounds) and hydrocarbons in gas chromatography–mass spectroscopy (GC–MS) scans [Environmental Protection Agency (EPA) T01/T02, 0.05 lpm, 59 compounds]. Samples for these components of smoke were analyzed by ESIS/Environmental Health Lab in Cromwell, CT, USA, Industrial Hygiene Laboratory Accreditation Program (IHLAP) accredited.

These respirator cartridges are certified to meet P100 (99.97% efficiency) NIOSH criteria. Thus, we did not anticipate particle penetration with these respirator cartridges. Particle concentrations in the chamber and in air filtered by the cartridge were monitored to evaluate the tightness of our seals. Two personal DataRAMs (*p*DR, Thermo Electron, Waltham, MA, USA) were used to measure real-time respirable dust concentrations inside the smoke chamber and downstream of the respirator cartridge. Using the manufacturer's directions, the *p*DR was calibrated prior to the study and zeroed in filtered air prior to each test. Gravimetric samples were also collected, with total dust using a closed-face 37-mm cassette with a 3.5-lpm sampling rate (NIOSH 0500) and respirable dust using SKC aluminum cyclones operated at 2.5 Lpm inside the chamber and a BGI cyclone in line with the *p*DR, operated at 2.6 lpm, in filtered air. All gravimetric dust samples were analyzed by Aerotech Laboratory in Phoenix, AZ, USA, IHLAP accredited.

Free radical samples were analyzed by the NIOSH in Morgantown, WV, USA, to determine their capacity to generate carbon and hydroxyl radicals in the samples we collected. We prepared 37-mm cassettes using PVC filters and cellulose backup pad to collect total and respirable dust samples in conformance to NIOSH 0500/0600 gravimetric methods. Total radicals were collected using traditional closed-face 37-mm cassettes; respirable radicals used cyclones (SKC and BGI) to sample respirable particles. Immediately after sampling, these filters were removed from the 37-mm cassettes, transferred to Petri dishes and stored in the freezer at −20°C. When all samples were accumulated, they were transported on dry ice to NIOSH in Morgantown, WV, USA, for analysis. Electron spin resonance techniques (Leonard *et al.*, 2000) were used to investigate the reactivity of the materials trapped by the PVC filter. Spin trapping is the method of choice for detection and identification of free radical generation due to its specificity and sensitivity. Because the method is relatively new to industrial hygienists, a brief description of the analytical method is provided.

Two types of radicals were evaluated: carbon and hydroxyl. The carbon radical is fairly stable and does not provide an indication of how reactive or toxic the material is but rather provides an idea of how much total ‘smoke product’ was on the sample filter. The hydroxyl radical identifies how much hydroxide radical is generated by the compounds collected on the sample filter following the addition of peroxide to the sample, yielding an indication of the radical potential of the smoke once it is inhaled. Data were reported as peak heights (mm) from the electronic spin resonance (ESR) spectra per liter of sampled air (mm l^{-1}).

Calibration of hyperfine couplings were measured (to 0.1 G) directly from magnetic field separation using potassium tetraperoxochromate (K_3CrO_8) and 1,1-diphenyl-2-picrylhydrazyl (DPPH) as reference standards (Buettner, 1987). Carbon radicals were measured directly by placing the filter into a 5-mm quartz sample tube and placing it in the ESR cavity. Hydroxyl radicals were measured using the addition-type reaction of a short-lived radical with a paramagnetic compound (spin trap) to form a relatively long-lived free radical product (spin adduct), which can then be studied using conventional ESR. Reactants were mixed in test tubes in a final volume of 1.0 ml. The reaction mixture was then transferred to a flat cell for ESR measurement. The intensity of the signal indicates the amount of short-lived radicals trapped, and the hyperfine couplings of the spin adduct are characteristic of the original trapped radicals. Relative radical intensity was calculated using peak-to-peak measurement. All ESR measurements were conducted using a Bruker EMX spectrometer (Bruker Instruments Inc., Billerica, MA, USA) and a flat cell assembly. Acquisit software provided by Bruker Instruments Inc., was used for data acquisitions and analyses. Analyses were performed at room temperature and under ambient air.

Even though there are currently no exposure limits to determine what measure of free radicals are ‘safe’, the free radical results can provide an indication of relative toxicity of the sampled smoke. A comparison of the amount of free radicals in the chamber and those that passed through the respirator provides an indication of the ability of air-purifying respirators to remove smoke-generated free radicals from the breathing air.

With the exception of CO, all samples for this study were collected simultaneously both inside the chamber and in air filtered by the respirator cartridge. Data for six test burns were paired, by test, to evaluate contaminant penetration. CO measures were taken only within the smoke chamber, as these respirators do not protect against this gas.

Data analysis

Penetration of each contaminant through the respirator cartridge during each test was determined by using equation (1):

$$\text{Penetration}_i = (\text{Conc.}_{\text{Filtered}}/\text{Conc.}_{\text{Chamber}}) \times 100\%, \quad (1)$$

where i refers to the test identification (1 through 6), $\text{Conc.}_{\text{Filtered}}$ is the contaminant concentration in air filtered by the respirator cartridge and $\text{Conc.}_{\text{Chamber}}$ is the concentration of the same contaminant measured in the chamber.

Standard investigations of respirator performance require testing the cartridge with the respirator facepiece rather than solely the respirator cartridge. Owing to our goal of evaluating the performance of the cartridge itself in environments with smoldering embers, the performance of the cartridge-only was tested. As such, the inverse of the penetration calculated here does not directly relate to the workplace protection factor. However, the values of penetration determined here could be inverted to determine the ‘maximum’ workplace protection factor for firefighters using these respirator cartridges for overhaul exposures.

By using lower challenge concentrations than in NIOSH methods, evaluations of penetration became difficult when both the challenge and filtered concentrations were in the range of the analytical limit of quantitation (LOQ). Penetration of <5% could only be quantified when the challenge concentration was at least 20 times greater than the detection limit.

In addition to penetration calculations, aggregate challenge and filtered concentrations were evaluated to determine an exposure index as an aggregate exposure metric. The use of an exposure index requires that only contaminants with similar health end points be aggregated. For wildland firefighting studies, Reinhardt and Ottmar (2004) determined an irritant exposure index, generated for full-shift exposures to formaldehyde, acrolein and respirable dust:

$$\text{Irritant exposure index} = \sum_i \frac{\text{concentration}_i}{\text{OEL}_i}, \quad (2)$$

where i indicates the ith compound in the challenge concentration and OEL indicates the occupational exposure limit.

Owing to the short-term (30-min) exposures of these tasks, the OEL in the denominator should reflect short-term exposure limits (STELs) or ceiling limits. Where STELs and ceiling limits were available, they were used in these calculations. When contaminants had no STEL, the ACGIH excursion limit of three times the full-shift threshold limit value was used to assign a short-term OEL (ACGIH, 2006). The following OELs were used to compute this index: 0.3 ppm formaldehyde (ACGIH ceiling), 0.1 ppm acrolein (ACGIH ceiling), 25 ppm acetaldehyde (ACGIH ceiling) and 9 mg m^{-3} respirable dust (3 mg m^{-3} ACGIH Time-weighted Average (TWA) converted to 30-min STEL). Additional upper respiratory tract irritants were evaluated to determine their contribution to an irritant index, including naphthalene (15 ppm ACGIH STEL), toluene (50 ppm ACGIH TWA, yielding STEL of 150 ppm) and total hydrocarbons, reported as toluene (150 ppm = 186 mg m^{-3} STEL).

RESULTS

Comparison to field exposures

The mass and composition of burn material used to generate the smoke for these tests were selected to standardize the burn cycle procedure rather than to represent the true proportion of materials consumed in structural fires. That being said, the smoke contaminant concentrations compared well with the range of values reported by Bolstad-Johnson *et al.* (2000) who monitored firefighter exposures during overhaul activities. From the 91 contaminants examined in this study, eight compounds common to the field study are presented in Table 1 to compare their field exposures to our chamber concentrations. Exposure measures identified concentrations of acrolein and formaldehyde exceeding the ACGIH ceiling limits (0.1 and 0.3 ppm, respectively), similar to our chamber test results. Formaldehyde and respirable particulates were the only contaminants with larger mean chamber concentrations. With the exception of particulate concentrations, our chamber tests operated below the maximum concentrations reported in exposure studies. Hence, the smoke used to perform respirator cartridge breakthrough studies was a reasonable surrogate for the overhaul phase of firefighting exposure. Knowing the aggregate concentrations after the completion of these tests, future work could look at the addition of more smoldering materials (e.g. carpet) or not restricting the tests to the 150-ppm CO ceiling in attempts to increase the challenge concentration.

The mean chamber CO level over all six tests was 145 ppm, with half of the tests yielding CO concentrations greater than the 150 ppm criterion used by fire departments. This trade-off was needed to improve detection of hydrocarbon and PAH compounds.

Respirator cartridge penetration

Neither total nor respirable particulate mass was detected in air filtered by the respirator cartridge. Owing to the 100-μg LOQ in gravimetric samples, we can only report penetration as <2% for these 30-min tests. However, the direct-reading equipment proved more sensitive, allowing quantification of 0.03% penetration (99.97% efficient) for both the cartridge types tested. This demonstrates acceptable performance given the P100 certification for these respirators.

Table 1. Comparison of firefighter exposure data (Bolstad-Johnson *et al.*, 2000) to chamber concentrations

Contaminant	Field	Chamber
Acetaldehyde	0.34 ppm mean	0.335 ppm mean
	1.75 ppm max	0.59 ppm max
	74% > LOQ	100% > LOQ
Acrolein	0.12 ppm mean	0.073 ppm mean
	0.3 ppm max	0.16 ppm max
	7% > LOQ	60% > LOQ
Formaldehyde	0.25 ppm mean	0.70 ppm mean
	1.18 ppm max	1.2 ppm max
	90% > LOQ	100% > LOQ
Benzene	0.38 ppm mean	0.157 ppm mean
	1.99 ppm max	0.31 ppm max
	55% > LOQ	100% > LOQ
Acenaphthylene	415 μg m^{-3} mean	59 μg m^{-3} mean
	2400 μg m^{-3} max	72 μg m^{-3} max
	38% > LOQ	100% > LOQ
Naphthalene	223 μg m^{-3} mean	97 μg m^{-3} mean
	540 μg m^{-3} max	130 μg m^{-3} max
	31% > LOQ	100% > LOQ
Benzo(a)pyrene	33.2 μg m^{-3} mean	6 μg m^{-3} mean
	50 μg m^{-3} max	8.5 μg m^{-3} max
	6% > LOQ	50% > LOQ
Respirable particulates—gravimetric	8 mg m^{-3} mean	17.2 mg m^{-3} mean
	25.7 mg m^{-3} max	30.1 mg m^{-3} max
	30% > LOQ	100% > LOQ

Table 2 contains a summary of the compounds detected in these six tests. Data in bold exceeded exposure limits. Of the 91 compounds assessed per smoke test, this table reports only those that were detected in the chamber at concentrations greater than twice the detection limit, namely, 32 compounds. PAH data were limited to two in-chamber and three filtered-air samples, where media loading was problematic: the range of sampled mass between the LOQ and exceeding the capacity of the sampling media was narrow. Table 2 indicates which PAH compounds were detected, but quantification was problematic for the laboratory and the data are unsuitable to calculate respirator cartridge penetration.

Table 2 also presents total mass estimates of families of contaminants. The total hydrocarbon as toluene concentrations were reported by the laboratory. Total aldehydes and total PAHs were computed from individual compounds and are reported as 'less than' due to summation of constituents reported at less than their detection limits. The values of 'totals' presented for each chemical grouping were computed from each sample collected and do not reflect the

Table 2. Range of concentrations studied

Chemicals	Chamber concentrations (ppm)		Filtered concentrations (ppm)		ACGIH TLV ppm	Effect[a]
	Min	Max	Min	Max		
Aldehyde scan (9 of 15 in scan)						
Formaldehyde	0.22	**1.2**	<0.0038	0.12	**0.3 C**	I, C
Acetaldehyde	0.16	0.59	0.019	0.67	25 C	I, CNS
Acrolein	<0.0021	**0.16**	<0.0017	<0.0021	**0.1 C**	I, P, C*
Acetone	<0.031	0.17	<0.031	<0.039	750 STEL	I, CNS
Propionaldehyde	0.028	0.2	<0.0078	<0.0098	—	I, C*
Crotonaldehyde	0.0023	0.019	<0.0014	<0.0017	0.3 C	I, C*
Butyraldehyde	0.012	0.033	0.0068	<0.0079	—	I, C*
Benzaldehyde	0.0018	0.012	0.0017	<0.0021	—	I
Valeraldehyde	<0.0052	0.02	<0.0053	<0.0066	50 TWA	I, C*
Total aldehydes (mg m^{-3})	1.39	4.8	0.51	1.82	—	I, C*
GC–MS scan (17 of 59 in scan)						
Dichlorodifluoromethane	0.00068	0.0062	<0.00078	0.0011	1000 TWA	L
Methyl chloride	0.0016	0.022	0.0013	0.0028	100 STEL	L, CNS
Methyl bromide	0.00055	0.0085	<0.00067	<0.0009	1 TWA	I
Methylene chloride	0.0029	0.021	0.0034	0.012	100 STEL	CNS
Benzene	0.086	0.31	<0.00081	<0.0011	2.5 STEL	I, CNS, C
Toluene	0.046	0.25	<0.00083	0.0013	50 TWA	I, CNS
Ethyl benzene	0.0052	0.073	<0.00060	<0.00081	125 STEL	I, CNS
m, *p*-Xylene	0.013	0.068	0.0012	0.0016	150 STEL	I, CNS
Styrene	0.008	0.44	<0.00061	<0.00082	40 STEL	I, CNS
o-Xylene	0.003	0.021	<0.00061	<0.00081	150 STEL	I, CNS
Cumene	0.00094	0.0036	<0.00053	<0.00071	50 TWA	I, CNS
Propylbenzene	0.00063	0.012	<0.00053	<0.00071	—	—
1,3,5-Trimethyl benzene	0.0014	0.023	<0.00053	<0.00071	—	—
1,2,4-Trimethyl benzene	0.0016	0.015	<0.00053	<0.00071	25 TWA	CNS, H
p-Isopropyltoluene	0.00095	0.0099	<0.00047	<0.00057	25 TWA	CNS, H
Butyl benzene	0.00041	0.0041	<0.00047	<0.00064	—	—
Naphthalene	0.01	0.078	0.00058	0.00058	15 STEL	I, H
Total HC (mg m^{-3}, as toluene)	10	**90**	0.29	1.4	—	—
PAH scan (4 of 16 in scan)						
Acenaphthylene	0.012	>0.0074	0.0018	<0.0022	—	I, H
Acenaphthene	<0.0023	>0.0065	<0.0030	>0.0037	—	I
Fluorene	0.0023	0.0044	<0.0011	0.0014	—	I
Phenanthrene	0.0003	0.00048	<0.00021	>0.00047	—	I
Total PAH estimates (mg m^{-3})	<0.21	**<0.30**	<0.10	<0.13	0.2 mg m^{-3} as CTPV	I, C
Methyl isothiocyanate	<0.081	**2.1**	<0.079	<0.11	—	I

Table includes only those compounds for which chamber concentrations were at least twice the detection limit on at least one test. Data in bold exceeded exposure limits. TLV = threshold limit value.

[a] Key to effect codes: I = upper respiratory track irritation; C = carcinogen; C* = low molecular weight aldehydes that are potential carcinogens, per NIOSH (NIOSH, 1991); CNS = central nervous system effects, H = hematologic effects; L = liver effects; P = severe pulmonary effects.

sum of the values immediately above them within this table.

Formaldehyde (CAS 50-00-0) and acrolein (107-02-8) were the only aldehyde components of smoke that exceeded ceiling limits within the chamber. Figure 3 presents penetration data for the four aldehyde components with (i) chamber concentrations exceeding ceiling limits or (ii) detectable mass in the air filtered by the respirator cartridge. Computed penetration percentages were incorporated into these graphs, along with the ceiling limits to provide relative hazard information for each constituent. The 11 other compounds in the aldehyde scans were present in the chamber at concentrations near the detection limits and well below any exposure limit: these were not considered in further analyses.

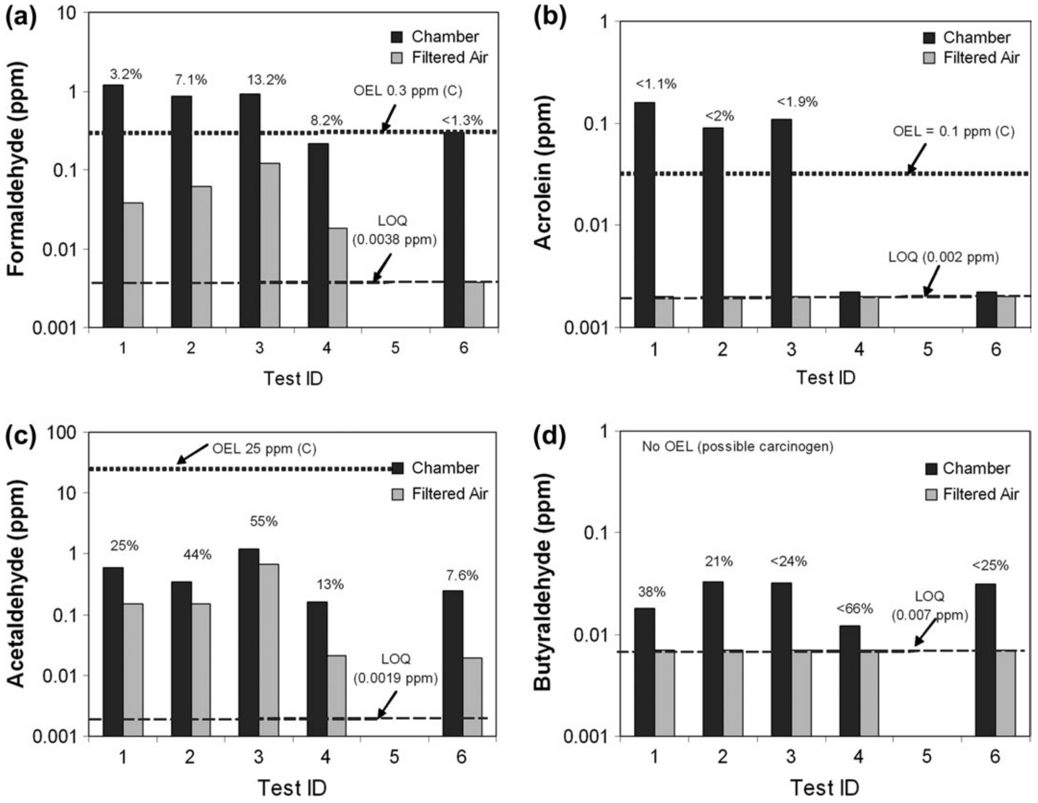

Fig. 3. Aldehyde penetration data for (a) formaldehyde, (b) acrolein, (c) acetaldehyde and (d) butyraldehyde. Percentages indicate percent penetration for each test. Ceiling limit OELs and LOQs are indicated.

Formaldehyde challenge concentrations exceeded the 0.3-ppm ceiling limit on four of five tests (mean 0.7 ppm) and were found to penetrate the respirator cartridges in four of five tests (mean 0.048 ppm). In Test 3 (multi-gas cartridge), the penetrating concentration also exceeded the National Institute for Occupational Safety and Health Recommended Exposure Limit (NIOSH REL) ceiling limit of 0.1 ppm but not the ACGIH ceiling limit (13% penetration). In three of the five chamber tests, acrolein was measured in concentrations exceeding the ceiling limit, but none was detected after passing through the respirator cartridges, with penetrations $<2\%$. Acetaldehyde (CAS 75-07-0) challenge concentrations were an order of magnitude below the 25-ppm ceiling limit, but still penetrated all but one cartridge at $\geq 10\%$. Butyraldehyde (CAS 78-84-2) challenge concentrations were detectable in all samples but were identified in air filtered by the respirator cartridge near the LOQ. This graph illustrates the difficulty computing penetration with challenge concentrations in the range of two to five times the detection limit. This trend became more problematic in PAH and GC–MS scans where the majority of challenge concentrations in the chamber were near the detection limit.

Only 17 of the 59 hydrocarbon compounds analyzed were identified within the smoke chamber using the GC–MS scan. Of these 17, only five compounds were identified in the air filtered by the respirator cartridge. Breakthrough fractions of the five compounds detected behind the respirator cartridge are indicated in Fig. 4. Chamber concentrations for individual compounds were well below exposure limits, as were the concentrations in air filtered by the respirator cartridge. Similar to butyraldehyde results, chamber concentrations of chlorodifluroethane (CAS 75-71-8) and methyl chloride (CAS 74-87-3) were close to the LOQ. Where filtered-air concentrations were above the LOQ, penetrations of 16% and 13% were determined for these contaminants, respectively. Challenge concentrations of naphthalene were at least two orders of magnitude below exposure limits, and penetrations of 1.7% were identified. Benzene (CAS 71-43-2) was another constituent consistently identified in the contaminant smoke, albeit at concentrations one-tenth the 2.5-ppm STEL. No benzene was detected in air filtered by the respirator (0.001 ppm LOQ), resulting in penetrations $<0.8\%$ for all tests. Toluene (CAS 108-88-3) chamber concentrations were two to three orders of magnitude below STELs but were also orders of

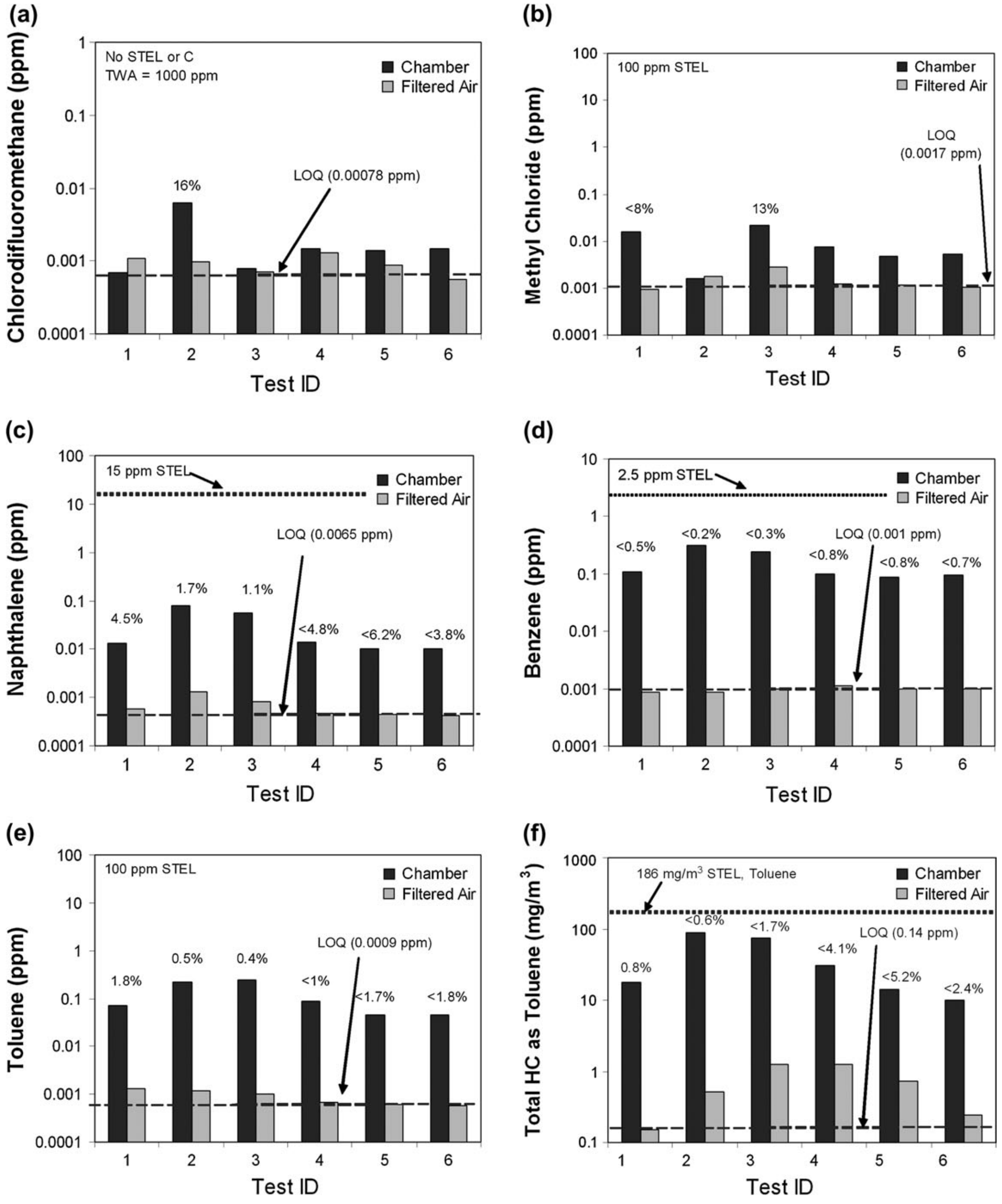

Fig. 4. Hydrocarbon penetration data for (a) chlorofluoromethane, (b) methyl chloride, (c) naphthalene, (d) benzene, (e) toluene and (f) total hydrocarbon as toluene. Percentages indicate percent penetration for each test. STELs and LOQ are indicated.

magnitude greater than the LOQ. Where toluene was measured in the filtered air, the worst-case penetration was quantified at 1.8%. Methylene chloride (CAS 75-09-2) chamber concentrations were also low (0.01 ppm), but quantification was not reliable: the measured concentration downstream was higher than that found inside the chamber and proper quantification of methylene chloride should be examined using NIOSH method 1005. For all compounds, a firefighter would not need respiratory protection to protect against hydrocarbons, hence both respirator cartridge types were suitable for the 59 hydrocarbons assessed.

The total hydrocarbon mass concentrations for each of the test runs were much higher than the sum of the individual components reported by the laboratory (Fig. 4f). For all but Test 1, the laboratory reported that the total hydrocarbon mass for all chamber samples exceeded the capacity of the mixed-media sampling tube, hence the penetration fraction is reportedly less than the computed value. The total hydrocarbon concentrations in the chamber were below an equivalent toluene STEL (186 mg m^{-3}), and penetrations ranging from $<0.6\%$ to $<5.2\%$ would not overexpose a firefighter to hydrocarbons.

As discussed earlier, the PAH data provide us only with the following qualitative information: over all tests, only acenaphthene, phenanthrene, benzo(a)pyrene and fluorene were identified downstream from the respirator cartridge (Table 2).

The final compound in Table 2 was MITC. MITC is a combustion product of foam that may result in severe respiratory tract irritation and burns upon inhalation. Tests for MITC yielded concentration patterns similar to butyraldehyde in that, for most tests, the chamber concentrations were near the LOQ (0.1 ppm). However, in one wood/foam/carpet test, the chamber 30-min average concentration was 2.1 ppm, allowing a determination that respirator cartridge penetration was $<5\%$ ($>95\%$ efficient). Tests confirmed no MITC was generated in the wood-only burns, as anticipated. Although firefighters were interested in this component of smoke, limited exposure limit guidance is available. Russia recommends short-term exposures be maintained below 0.034 ppm; however, current analytical methods are insufficiently sensitive to evaluate exposures this low.

Free radicals

Figure 5 summarizes the free radical measures, both carbon-centered and hydroxyl-based, and computed penetration fractions for each of the six tests. Over all tests, no carbon radicals were detected behind the respirator cartridge for either total or respirable samples. This confirms that the carbon-based radicals are associated with the non-reactive smoke particles, which we have demonstrated have been removed with a minimum efficiency of 99.7%. However, hydroxyl radical was identified on all samples behind the respirator cartridge. Six blanks and 10 background samples were prepared and analyzed, and no hydroxyl radical was identified on these filters, indicating no systematic contamination of these samples.

Note that the same amount of hydroxyl radical was identified in the chamber and in the respirator cartridge filtered air in Test 2. The ESR peak heights for both the chamber and filtered air were identified as 31 mm, an order of magnitude less than other chamber hydroxyl radicals, and was reanalyzed by the laboratory, confirming the reported peak height. This smoke test had the second highest in-chamber carbon radical and the lowest in-chamber hydroxyl radical over all tests. Excluding this test, an average of 8% (total) and 18% (respirable) of the hydroxyl free radical generating capacity of the smoke penetrated through the respirator cartridge, much higher than the penetration of respirable particulate mass ($<0.07\%$, gravimetric). These results indicate that something other than particulates penetrated through the respirator cartridge and was collected on the PVC filters.

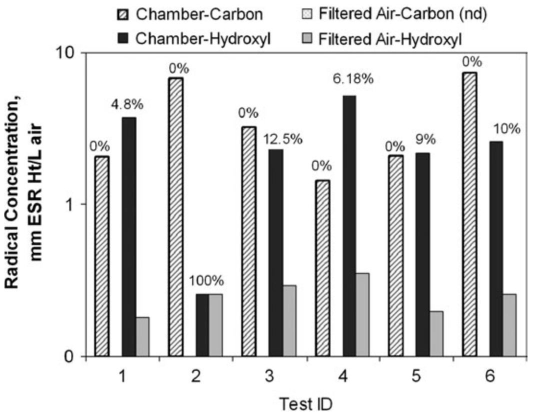

Fig. 5. Total free radical concentrations, in peak ht (mm) per sampled liter of air. No carbon-centered radicals penetrated through the respirator cartridge, as indicated by nd, yielding 0% penetration. Hydroxyl-forming radicals were identified in filtered air. Percent penetration is indicated.

Irritant exposure index

Firefighters are exposed to multiple respiratory hazards simultaneously, many of which are upper respiratory tract irritants. Formaldehyde, acrolein and dust were the only individual components that exceeded the OELs in the challenge air, but additional compounds measured in the smoke were also irritants. To determine an exposure metric for the mixture of contaminants in the chamber and filtered air, irritant exposure indices were calculated for each test run, using equation (2). Figure 6 illustrates the contribution of each component in this calculation to the overall irritant index. For each test, the index exceeded 1 within the chamber, indicating the need for respiratory protection to protect against the multiple irritant gases and particles. In no test did the index exceed 1 in air filtered by the respirator cartridge when using a 0.3-ppm ceiling limit for formaldehyde. Over all tests, the average filtered-air irritant exposure index was 0.2, with a peak 0.46 occurring in Test 3. The primary contributors to the irritant index in the chamber were formaldehyde, acrolein and respirable dust. In air filtered by the respirator cartridge, formaldehyde (mean contribution was 0.16, max 0.46) was the major contributor, and acrolein and respirable dusts were not detected penetrating the respirator cartridge.

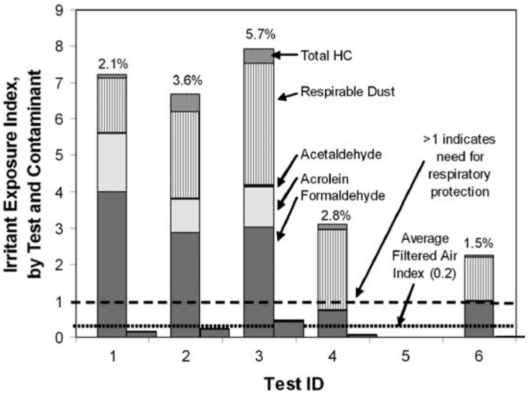

Fig. 6. Irritant exposure indices for chamber tests. An index greater than 1 indicates respiratory protection is required. For each test, the left bar represents the chamber exposure index and the right bar indicates the filtered-air exposure index using 0.3 ppm ceiling for formaldehyde. The computed penetration percentages of the irritant hazard through the respirator cartridges are indicated.

The above calculations were based on the 0.3-ppm ACGIH ceiling limit for formaldehyde and not the NIOSH REL of 0.1 ppm. Computations using the 0.1-ppm REL yield even larger hazard indices (4.2–15 in the chamber and 0.06–1.2 in filtered air), where the 0.12-ppm formaldehyde penetration in Test 3 (multi-gas cartridge) now results in the determination of ineffective respiratory protection for firefighters.

DISCUSSION

Smoke characterization

Although this method development study was limited to only six tests, information on 92 contaminants guides future respirator penetration testing in real-concentration environments. These extensive scans were completed to determine whether additional compounds should be included in exposure considerations beyond those reported in field studies. Aldehyde scans indicated that the primary exposures were formaldehyde, acrolein and acetaldehyde. Only the first two were present in concentrations above their respective exposure limits, while the third was nearly 100 times lower the exposure limit but was identified as penetrating the respirator cartridge and contributed moderately to the irritant exposure indices. The laboratory used to analyze aldehyde samples did not include gularaldehyde in their panel, and field studies indicate exposures to this compound have exceeded the ACGIH STEL by a factor of 3 (Bolstad-Johnson *et al.*, 2000). Future studies should assess glutaraldehyde along with formaldehyde, acrolien and acetaldehyde. No other aldehyde was present in concentrations warranting further investigation.

The 59-component hydrocarbon scan identified only two components with a significant exposure potential: benzene at 8–30 times below the STEL and naphthalene at 200–1500 times below STEL. While the toluene concentrations were consistently detectable, they were on the order of 0.1 ppm, well below the 100-ppm STEL. However, measures of total hydrocarbons, reported as toluene, approached a surrogate STEL (186 mg m^{-3} as toluene). Whether this exposure limit is appropriate is open for debate, but a total hydrocarbon measure may be an effective exposure indicator in health effect and respirator cartridge penetration studies. Because of detection limit restrictions, future chamber studies should focus on benzene, naphthalene and total hydrocarbon as toluene.

PAH tests were less useful in this study. Chamber concentrations were predominantly near the limit of detection, precluding penetration calculations for the 30-min tests. To improve quantification of PAHs, respirator penetration tests could sample over three sequential 30-min tests onto the same sample media to improve detection. However, because PAH exposures to firefighters during overhaul have been reported in the range of background, this effort is likely unwarranted given that other components of exposure have been identified in concentrations where health effects are of concern.

Free radical testing identified that carbon-based radicals did not penetrate any respirator cartridge. This is consistent with reports that the carbon radicals are associated with the stable, non-reactive portion of the smoke particles. That is, the respirator cartridge was >99.97% efficient for the particles in these penetration tests. The penetration of hydroxyl-based radicals indicates non-particle phase components penetrated through the respirator cartridge and were collected onto PVC filters. Additional investigation of this phenomenon warrants further investigation. Unfortunately, with our limited data set, comparison of both free radicals to other individual components or to the irritant exposure index yielded low coefficients of determination (e.g. R^2 =0.03 for chamber irritant exposure index and hydroxyl-based free radical).

The average CO and respirable dust concentrations within the chamber were explored to determine whether any predictive relationship existed between these two contaminants, as has been identified in wildland firefighting. The ratio of CO/respirable particulates ranged from 1.2 to 9.0 over the six tests, with no dependency on the test sequence order. Linear regression identified a positive relationship between these two contaminants; however, the R^2 was only 0.21, indicating the variability in respirable dust is not explained solely by CO concentrations. Limited data (n = 6) preclude further analysis, but confirm the lack of predictability in the field study of Bolstad-Johnson *et al.* (2000). While CO monitoring is recommended to protect firefighters in overhaul operations, there is no evidence that it serves as an indicator to any single contaminant or the aggregated irritant index in the challenge gas ($R^2 < 0.01$).

Respirator cartridge performance

Both of these respirators were certified for use with particulates (P100), which were adequately controlled in these tests, and formaldehyde, which were identified as penetrating the respirator cartridge. Cartridges were certified for formaldehyde use by testing at 64 lpm and 50% relative humidity, with challenge concentrations of 100 ppm: the maximum allowed breakthrough of formaldehyde is 1 ppm, tested for at least 50 min. Our formaldehyde penetration tests met the 1-ppm breakthrough criterion. However, this criterion is greater than the current ceiling limits (0.3 ppm ACGIH, 0.1 ppm NIOSH). One of our tests exhibited breakthrough at 0.12 ppm, exceeding the NIOSH ceiling limit.

This study objective was to test respirator cartridges against contaminants in the range of their actual use; hence, our challenge concentrations were lower than those prescribed in respirator certification standards. In addition, our tests differed from certification criteria by pulling air through the cartridge at a flow rate larger than non-particulate certification procedures (78.15 lpm), which was selected to mimic breathing rates during short-term heavy workloads typical of firefighting. The higher flow rate studied could prevent the gases/vapors from adsorbing onto the cartridge media for removal, but reflect conditions that may exist in the field. Coyne *et al.* (2006) recommended testing respirator performance at even higher airflow rates, with a sinusoidal minute ventilation of 135 lpm (peak 424 lpm) to encompass 99% of their study group's heavy breathing rate. Another difference between these protocol and certification criteria was the relative humidity (25%). Lower humidity is typically reported to improve respirator performance, as the sorbent material in the respirator is typically hygroscopic; hence, the low humidity should allow more sorbent to be available for the compounds in the smoke (Wood and Snyder, 2007). Finally, the certification tests typically focus on one contaminant at a time, but firefighters are exposed simultaneously to multiple contaminants. The multiple compounds drawn through a respirator compete for adsorption, but one adsorbed compound may also be displaced by other compounds with greater affinity for the sorbent material (Wood and Snyder, 2007). Compounds other than formaldehyde may have a greater affinity for the sorbent material causing formaldehyde to pass through the respirator cartridge. Additional tests are needed, and a reevaluation of respirator performance criterion for formaldehyde certification is in order.

Study limitations

While we attempted to standardize the burn sequence, it is obvious from the figures in this text that contaminant concentrations varied from burn to burn. While problematic for analyzing the results, it does reflect the variable nature of smoke exposures to firefighters.

As discussed previously, the humidity in these tests reflected the low-humidity environment of Arizona, where the tests were conducted. Contaminant adsorption onto respirator media is known to be affected by humidity, and NIOSH requires respirator cartridge certification at 50–95% humidity (Fed. Reg., 1995). By increasing the moisture in the test chamber, the adsorptive capacity of the respirator cartridge would be reduced, and contaminant penetration through the respirators may be even greater than what was found in these tests.

While our list of contaminants investigated was lengthy, additional compounds of concern were not assessed during these tests. Irritants such as hydrochloric acid, sulfur dioxide and nitrogen dioxide were not assessed during this method development study. Furthermore, hydrogen cyanide had not been assessed but is currently a toxin of concern to firefighters, as residential homes have increasingly more plastic-based products that release hydrogen cyanide during combustion. We did detect methyl isothiocyanate during our tests that included foam and carpet materials in the smoke generation process; hence, we anticipate the ability to measure hydrogen cyanide in the chamber when using the wood/foam/carpet to generate smoke. Thirty-minute samples should provide adequate detection limits using NIOSH 6010 (Schlecht and O'Connor, 1994). Hydrogen cyanide and the above irritant gases should be considered in future work to complete the challenge and filtered-air profiles.

Caution should be taken to apply this study to other firefighting operations where SCBAs are not currently used and air-purifying respirators are being considered. The materials that were combusted do not necessarily reflect what may occur in dumpster fires or automobile fires. Firefighter exposures have not been assessed in these conditions and the challenge concentration may be significantly different than our study tests that matched overhaul concentrations reasonably well.

CONCLUSIONS

Additional work is required to evaluate whether an acceptable air-purifying respirator cartridge is suitable for use in overhaul activities. The method developed here recommends specific contaminants to measure (formaldehyde, acrolein, acetaldehyde, naphthalene, benzene, total hydrocarbons as toluene and particulate mass), although additional irritants should be included in future studies (hydrogen chloride, hydrogen cyanide, nitrogen dioxide and sulfur dioxide) to better quantify the total irritant exposure index for the challenge gas and evaluate the performance of respirator cartridges currently under consideration by firefighters.

To develop a NIOSH method to approve air-purifying respirators for firefighting in overhaul studies, contaminant concentrations much greater than those used in this study would be necessary to quantify breakthrough. Bench testing for NIOSH certification for overhaul smoke would require less dilution of smoke from smoldering wood/household products to increase the challenge concentration. Alternatively, the generation of a synthetic mix of the contaminants in proportion to the concentrations reported here and in field studies, but at higher total concentrations, would be a reasonable surrogate to test respirator cartridge performance for overhaul use.

No respirator cartridge is approved specifically to protect firefighters from smoke, and caution should be taken by current users in the field. With evidence of formaldehyde exposures of 1.2 ppm in the field and our worst-performing test indicating 13.2% penetration with one multi-gas respirator cartridge test, exposures to air filtered by the respirator cartridge, regardless of the fit factor for the facepiece, may result in exposures exceeding the NIOSH REL ceiling limit. Additional tests of the CBRN cartridges with higher challenge concentrations than were generated in Tests 5 and 6 of this study are needed to evaluate their effectiveness for overhaul smoke. Breakthrough of these irritating components of overhaul smoke exposures should be considered when evaluating acute health effects associated with firefighter exposures, and a true control group should include firefighters wearing SCBAs during overhaul.

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