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The Evaluation of CBRN Canisters for Use by Firefighters during Overhaul

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Air-purifying respirators (APRs) have been proposed to provide an additional respiratory protection option for structural firefighters involved in overhaul operations and wildland firefighters, where particulate and aldehyde exposures have been documented. Previous studies (Anthony *et al.*, 2007) developed test methods to evaluate APR cartridges and canisters for use in overhaul activities, where initial findings indicated that multi-gas cartridges may not be effective. This study evaluated the performance of three chemical, biological, radiological, and nuclear (CBRN) canisters (MSA, 3M, and Scott) and one multi-gas canister similar in appearance to CBRN canisters but without CBRN certification (3M FR-64040). Challenge concentrations typical of overhaul exposures were generated by combusting common household materials. Twelve tests were conducted, using random canister selection, where challenge air and air filtered by the canisters were tested. All tests examined penetration of CO; NO_2; SO_2; respirable dust; aldehydes, including formaldehyde, acrolein, and glutaraldehyde; and hydrogen cyanide. Six of the tests also investigated naphthalene, benzene, and hydrogen chloride, but challenge concentrations from the simulated overhaul smoke were near the limit of detection (LOD) and were two orders of magnitude below short-term or ceiling concentrations of concern and were eliminated from further study with the combustion materials used in this study. In all tests, an irritant index was computed to evaluate the aggregate penetration of contaminants in the smoke mixture, using 15- and 30-min occupational exposure limits as well as assessing individual penetrations. In all cases, the challenge concentration irritant index exceeded unity, ranging from 2.3 to 21. For all 12 tests, the APR canister reduced the overall irritant index to levels below unity, indicating that these canisters would provide protection for firefighters working in overhaul environments. However, in some tests, levels of carbon monoxide were higher than recommended for persons wearing APRs. Since these canisters do not protect against carbon monoxide, firefighters must still rely on direct reading warning to indicate high CO levels, indicating the need to leave the area if wearing an APR, as these APR canisters would be inappropriate.

Keywords: CBRN; firefighter; penetration; respirator testing

BACKGROUND

Fire overhaul activities occur after a structural fire has been extinguished. It is during this time that firefighters search for small fires or hot embers hidden within the debris of a structural fire. During a fire, firefighters wear a self-contained breathing apparatus (SCBA); however, during overhaul when there is less smoke and carbon monoxide (CO) levels have decreased, firefighters will often remove their respiratory protection. It is during these overhaul events that firefighters can be exposed to harmful levels of combustion products. Bolstad-Johnson *et al.* (2000) conducted a study examining the chemicals firefighters were exposed to during 25 overhaul events. Their results showed concentrations that were above ceiling and short-term exposure limits (STELs) for acrolein, CO, glutaraldehyde, benzene, nitrogen dioxide (NO_2), sulfur dioxide (SO_2), and polynuclear aromatic hydrocarbons. These results demonstrated that overexposure to irritants, chemical asphyxiants, and carcinogens do occur and that respiratory protection is necessary during overhaul events.

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Austin *et al.* (2001) also examined contaminants in smoke. They wanted to characterize volatile organic compounds (VOCs) found at municipal structural fires that may contribute to an increased risk of cancer in firefighters. Firefighters were instructed to collect air samples at nine fires when they believed that conditions had improved such that some firefighters might remove their SCBA masks. In total, 123 VOCs were found with toxicologically important compounds, benzene, toluene, 1,3-butadiene, naphthalene, and styrene, accounting for 31.1% of the total mean, 22.8 p.p.m. (Austin *et al.*, 2001). The maximum benzene concentration was 11 p.p.m., well above the STEL. A stipulation of sampling in this study was that some firefighters would remove their SCBAs; based on results from this study, these firefighters would have been exposed to potentially harmful contaminant levels. Appropriate respiratory protection could prevent these exposures.

De Vos *et al.* (2008) as well as Reisen and Brown (2008) determined the toxic components and their concentrations in Western Australian bushfire smoke. The study conducted by de Vos *et al.* (2008) took static and personal samples in a smoke chamber and during prescribed burns. The study by Reisen and Brown (2008) took personal exposure measurements for toxic compounds at prescribed and experimental burns. The smoke chamber used was a modified sea container. The sea container was used by the Fire and Emergency Services Authority of Western Australia for education and training purposes (de Vos *et al.*, 2008). The prescribed burns were low-intensity fires used to decrease the amount of small vegetative debris on Australian forest floors. The experimental burns were conducted by fire agencies to examine fire behavior as well as ecological assessments (Reisen and Brown, 2008).

Particulate matter, formaldehyde, acrolein, VOCs, and CO were sampled during three trials for 15 min in the smoke chamber; however, only formaldehyde was measured in the single 2-h field trial (de Vos *et al.*, 2008). During the 10 prescribed and two experimental burns, CO, respirable particulates (50% cut point of 4 μm), aldehydes, and VOCs were measured (Reisen and Brown, 2008). Reisen and Brown (2008) conducted personal sampling on firefighters that were actively fighting fires and the majority of samples were collected over a time period of $<$4 h but were considered representative of typical work shifts.

Formaldehyde levels in the smoke chamber were three times as high as measured during field trials (de Vos *et al.*, 2008). de Vos *et al.* (2008) hypothesized that this may be the result of limited airflow through the smoke chamber. In one of the smoke chamber tests, acrolein concentrations reached the STEL of 0.69 mg m^{-3}. CO levels exceeded the STEL (200 p.p.m.) in one of the smoke chamber tests. The mean concentration of particles in the smoke chamber exceeded the time weighted average listed of 10 mg m^{-3}. The mean concentration of VOCs measured by a multi-gas monitor was 2.1 p.p.m. Individual levels of VOCs were not quantified. Clip-on VOC monitors measured VOC concentrations in the breathing zone of eight participants; all levels were low compared with occupational standards (de Vos *et al.*, 2008). The authors noted that these results did not directly replicate field conditions but did identify toxic contaminants in Australian bushfire smoke that could have concerning health effects on firefighters.

Reisen and Brown (2008) found high variability in CO levels; also, one firefighter exceeded the occupational exposure standard of 30 p.p.m. and four firefighters exceeded the excursion limit of 400 p.p.m. The exposure limit of respirable particulates (3 mg m^{-3}) was exceeded in three samples. The major aldehyde identified during sampling was formaldehyde. Average exposures never exceeded the occupational exposure standard of 1 p.p.m. but the ceiling limit of 0.3 p.p.m. was exceeded for 14% of the firefighters (Reisen and Brown, 2008). The VOCs sampled were below their respective standards. The authors also computed an irritancy index examining additive effects of the compounds measured that are known respiratory irritants. Their irritancy index exceeded 1 in 28% of samples which indicated that symptoms of respiratory irritation would be seen (occupational exposure standards: 1 p.p.m. for formaldehyde, 0.1 p.p.m. for acrolein, and 3 mg m^{-3} for respirable particulates) (Reisen and Brown, 2008).

Burgess *et al.* (2001) conducted a study examining the adverse respiratory effects of firefighters involved in overhaul activities. They examined firefighters who wore multipurpose cartridge air-purifying respirators (APRs) during overhaul and those who did not. Acute changes in lung function and increased concentrations of serum pneumoproteins in blood were seen in both groups of firefighters. Inflammation deep in the lungs results in higher concentrations of serum pneumoproteins which was a good indication of lower respiratory tract injury (Burgess *et al.*, 2001). Based on these findings, Burgess *et al.* (2001) hypothesized that APRs with multipurpose cartridges may not provide complete protection against the mixture of chemical contaminants in smoke.

Two studies were conducted by de Vos *et al.* (2006, 2009) that evaluated the effectiveness of the respirator filters for firefighters. The first study's tests were performed in a simulated Australian bushfire environment and utilized the respirator filters available for use by Australian bushfire fighters. Three types of filters were tested, a particulate filter, a particulate–organic vapor filter, and a particulate–organic vapor–formaldehyde filter. The authors produced a controlled environment for conducting their testing by performing controlled standardized combustion of native vegetation in a modified sea container and controlling for temperature and wind as much as possible (de Vos, 2006). Participants were exposed to smoke in the chamber for ∼15 min.

Baseline measurements of respiratory health were taken prior to the test. Air inside the firefighter's masks was sampled during testing. Posttesting, a respiratory system questionnaire and pulmonary function testing was conducted. de Vos *et al.* (2006) results indicated acute changes in pulmonary function and the presence of adverse respiratory symptoms after a 15-min exposure regardless of the type of filter worn. However, the particulate–organic vapor–formaldehyde filter provided the best protection of all three filters under the study's testing conditions. The authors acknowledged that the adverse respiratory effects seen in the bushfire fighters may have been affected by CO, which was not filterable by any of the respirator filters tested, or a synergistic effect due to the complex mixture of contaminants in smoke, inadequate fit, and self-reporting.

In the second study by de Vos *et al.* (2009), the same filters were used for testing. However, the tests in this study were field validation tests conducted during prescribed burns rather than in a simulated environment. Firefighter's baseline lung function was determined via pulmonary function testing. There were two 60-min exposures periods; however, the firefighters did not actively fight the fire but were dressed in their turnout gear. The authors used a questionnaire, pulmonary function testing, oxygen saturation measurements, and active sampling for formaldehyde inside the respirator to determine the effectiveness of the respirator filters tested.

Firefighters in the group wearing the particulate filters experienced more respiratory symptoms than the other groups (de Vos *et al.*, 2009). The authors hypothesized that this could have been due to the increased levels of formaldehyde measured inside the respirators fitted with the particulate filters. A decline in lung function as well as blood oxygen saturation was observed in all firefighters tested after both exposure periods (de Vos *et al.*, 2009). The authors hypothesized that the decline in oxygen saturation could have been due to high levels of CO in the bushfire smoke.

Based on results from the two studies, de Vos *et al.* (2006, 2009) recommended the use of the particulate–organic vapor filters or the particulate–organic vapor–formaldehyde filters by Australian bushfire fighters. However, the authors noted that more research evaluating the efficacy of respiratory protection in a more realistic environment and for longer exposure periods was needed. The authors also pointed out an important fact that these filters did not protect against CO exposures and hypothesized that firefighters wearing respirators may expose themselves to higher levels of smoke, and thus, possibly higher levels of CO, than they normally would (de Vos *et al.*, 2009).

In the USA, APRs must be approved for use by the National Institute of Occupational Safety and Health (NIOSH) under federal regulation 42 CFR 84 (Federal Register, 2004). NIOSH approves APRs based on physical characteristics such as their durability, size, connection to face pieces, breathing resistance, field of view, and lens durability. APRs are also tested for particulate filtering and fit, and, for approval for use in atmospheres with hazardous chemicals, APRs must also undergo tests that certify the length of time the respirator can be challenged with a known concentration of a single gas without experiencing breakthrough (APR service life) (Federal Register, 2004).

NIOSH P100 APRs must be certified as having 99.97% efficient particulate filtering (Federal Register, 2004). An aerosol concentration of 100 ± 10 mg m^{-3} of dioctyl phthalate having a median diameter of 0.185 ± 0.020 μm and a geometric standard deviation of <1.6 is used to challenge the filters' particulate filtering ability (Federal Register, 2004). APRs using only one filtering cartridge or canister are challenged with a flow rate of 115 ± 5 liters per minute (l.p.m.), while APRs with dual-filtering cartridges or canisters are challenged with 57 ± 3 l.p.m. Particulate filter penetration tests are conducted at 25 ± 5°C (Federal Register, 2004). Respirator fit is determined with the laboratory respiratory protection level test. It is a modified test of respirator fit in an atmosphere containing 20–40 mg m^{-3} of corn oil aerosol (Federal Register, 2004).

Chemical, biological, radiological, and nuclear (CBRN) APRs were developed for use by first responders in terrorism events; however, NIOSH considers them to be an appropriate dual-purpose APR for use in non-terrorist involved hazardous incidents (NIOSH Interim Guidance, 2005). Service life testing of CBRN APRs differs from other APRs by the testing agents used and testing procedures required.

NIOSH developed a list of test chemicals by examining known toxic industrial chemicals, toxic industrial materials, and chemical warfare agents. Ten test chemicals are used to challenge CBRN APRs for certification: ammonia, cyanogen chloride, cyclohexane, formaldehyde, hydrogen cyanide, hydrogen sulfide, nitrogen dioxide, phosgene, phosphine, and sulfur dioxide (Federal Register, 2004). Tests certify that CBRN APRs' capacity meets a minimum of 15 min (CAP 1), 30 min (CAP 2), 45 min (CAP 3), or 60 min (CAP 4). Service life tests are conducted at room temperature, 25 ± 5°C, and at two levels of relative humidity, 25 ± 5 and 80 ± 5%. Challenge air is drawn through the CBRN APR canister at a continuous flow rate of 64 l.p.m. at both humidity levels.

Single-contaminant challenge tests may not be sufficient to evaluate respirator effectiveness when users are exposed to multiple contaminants simultaneously, as occurs with smoke. Single-contaminant challenge tests also do not take into account the affinity of some chemicals over others in a mixture to a sorbent in the APR canister. Some contaminants within a mixture may have a stronger affinity for the sorbent in APRs, creating competition (Wood, 2002). Adsorbed contaminants could also be displaced by another contaminant within the mixture flowing through the respirator canister (Wood, 2002). These displaced contaminants could then break through the APR resulting in exposures to a person wearing the equipment. Challenging APRs with one contaminant at a time does not represent field use when multi-contaminant exposures are present. Furthermore, this type of testing would not demonstrate the possibility of contaminant breakthrough, an important differentiation made in the study conducted by Anthony *et al.* (2007). While the NIOSH APR testing process evaluates the respirator cartridge or canister as well as the face piece, Anthony *et al.* (2007) tested only the respirator cartridge. Their study focused on evaluating the filtering ability of the cartridge alone, which provided information about the maximum amount of protection offered by the respirator. That study involved the development of a test system that could generate and deliver complex contaminant concentrations, namely 'overhaul' smoke, to the APR cartridge being studied. To simulate real-world use, their method for challenging respirators with a mixture of contaminants, by necessity, differed from the single challenge contaminant CBRN approval process by NIOSH. The significant contribution of that work was the identification of limitations of multi-gas cartridges at reducing all components of smoke, most importantly formaldehyde. The US National Institute of Standards and Technology held workshops in 2007 to discuss and prioritize respiratory threats to firefighters from particulate and gases (Bryant *et al.*, 2007), where recommendations were made to continue the investigation of protective equipment for firefighters conducting overhaul activities.

Based on the findings by Burgess *et al.* (2001), de Vos *et al.* (2004, 2009), and Anthony *et al.* (2007), additional APR testing was warranted. CBRN APRs are readily available to first responders and prevent inhalation exposure to a wide variety of hazards (CBRN agents). Because of the limitations identified in multi-gas cartridges, CBRN respirator canisters have been proposed for use by firefighters; with the use of adapter kits, the canisters can be fitted into existing SCBA face pieces currently used by firefighters.

The major objective of this study was to apply the method developed by Anthony *et al.* (2007) to evaluate whether CBRN canister respirators are effective at reducing firefighter exposures during overhaul activities. Evaluating these canisters in an environment containing a mixture of contaminants provides a more accurate representation of possible exposure to the penetrating contaminants in smoke. The penetration of both individual smoke components and an aggregated exposure index was investigated.

METHODS

To determine whether CBRN APR canisters were effective at reducing exposures to harmful components of smoke, smoke was generated and then transported to challenge the test canisters. The method and test system are described by Anthony *et al.* (2007) for smoke generation and delivery and were used for all 12 tests in this study. The test system used is depicted in Fig. 1, modified from Anthony *et al.* (2007). It included a combustion box to generate

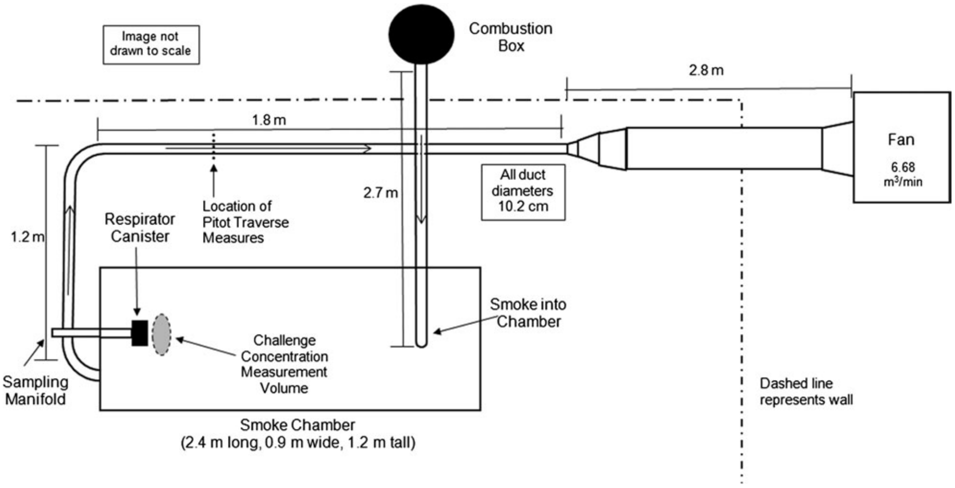

Fig. 1. Overhead schematic of combustion box, smoke chamber, and ventilation system. Flow indicated by arrows through ductwork.

smoke, a ventilation system to transport the smoke to and from a Plexiglas smoke chamber, and sampling manifolds.

The combustion box was located outside the laboratory and connected to the smoke chamber via round, 10-cm diameter ductwork. The smoke chamber was ~2.4 m long, 0.9 m, wide, and 1.2 m tall. Ductwork was connected to the smoke chamber to allow contaminated air that was drawn through the smoke chamber to be vented outside. On top of the smoke chamber, there was a 48 × 66-cm opening to allow for entry to the interior of the smoke chamber and two small, round 4-cm openings for sampler equipment tubing. These openings were sealed during all tests. The CBRN was positioned within the smoke chamber and was mounted to a sampling manifold, which extended 38 cm into the smoke chamber (Fig. 2). The manifold also allowed for sampling air that had been filtered by the respirator (filtered air concentrations).

Challenge concentration samples were collected upstream of the APR canister within the smoke chamber. In front of the canister (7.6 cm), a wire mesh was used to position sampling media that determined contaminant concentrations in smoke chamber air (chamber concentrations). Sampling media (integrated samplers) or sampler inlets (direct reading instruments) (Table 1) were positioned on the wire mesh 7.6 cm in front of and within 13 cm laterally or vertically of the APR canister. The media or inlets were at least 2.5 cm apart, with random positions assigned for each test to avoid sampling bias. A CBRN respirator canister was removed from the packaging immediately before the test to represent how firefighters would use these filters in the field. It was then secured to the manifold with a rubber seal, hose clamp, and a final layer of tape. A new CBRN canister was used in all but one test where the same respirator canister as in the test directly preceding it was used, which resulted in an evaluation of a 60-min overhaul challenge.

Concentrations of gases and particulates were measured with both integrated samplers and direct reading instruments. Samples were collected for 30 min to mimic reported field tasks of firefighters during overhaul (Bolstad-Johnson *et al.*, 2000). Concentrations of contaminants generated in the challenge smoke needed to represent firefighter exposure levels and needed to be large enough to exceed the analytical method limit of detection (LOD) for these short-term samples. Because fire departments have set a procedural maximum of 150 p.p.m. CO when firefighters work in overhaul environments (Bolstad-Johnson

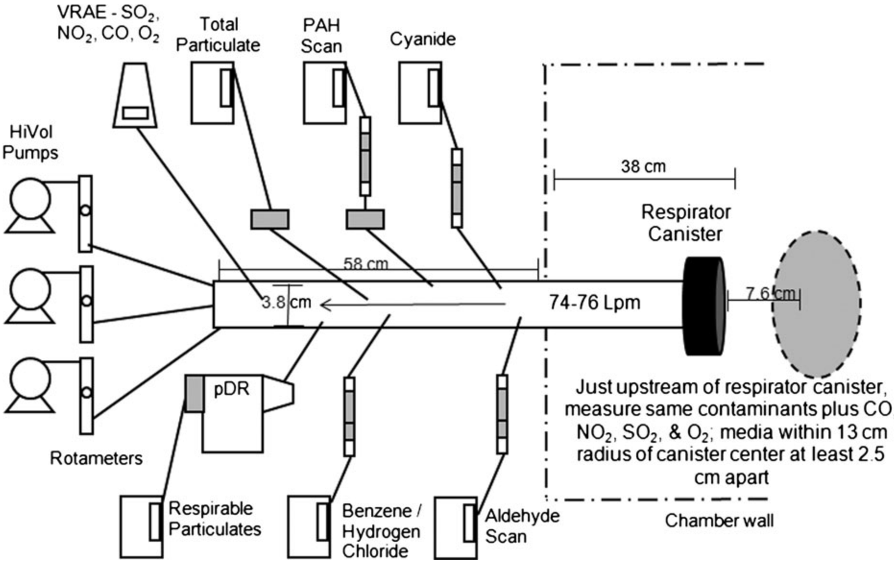

Fig. 2. Schematic of sampling system.

Table 1. Contaminants measured, analysis method used, and sampling flow rate

Contaminant	Method	Flow rate (l.p.m.)	Media
Aldehyde scan (seven compounds)	HPLC, EPA TO11	0.89	Silica gel/2,4-dinitrophenylhydrazine (DNPH) sorbent tube
Benzene	Gas chromatography, OSHA 7	0.2	Charcoal sorbent tube
Cyanides	NIOSH 6010	0.2	Soda lime sorbent tube
Naphthalene	NIOSH 5506	2.0	Polytetrafluoroethylene (PTFE) sorbent tube and 37-mm filter
Hydrochloric acid	NIOSH 7903	0.5	Washed silica gel sorbent tube

et al., 2000), the concentration of CO within the smoke chamber was also assessed.

There were two groups of combustion items. Group 1 consisted of a mixture of pine furring strips, plain white paper, sofa cushion foam, and nylon or olefin/nylon blend Berber carpet. Group 2 consisted of burning the items listed in Group 1 together with polyvinyl chloride (PVC) plastic, laminated medium-density fiberboard flooring, and polymer styrene with laminate face trim. Tests 1 through 6 burned items in Group 1 and Tests 7 through 12 consisted of burning the components listed in Group 2. These additional components in Group 2 were added to the mixture with the aim of enhancing the cyanide concentrations missing from the first six tests. Each component was measured and weighed to standardize the items to be burned. The quantity and weights of the burn components for Tests 1 through 12 consisted of 5–10 sheets of paper, 216.8–229.4 g of wood, 8.7–8.8 g of foam, and 21.5–25.4 g of carpet. The weights of the burn components added to Tests 7 through 12 were 7.6–7.7 g of trim, 1.9–2.1 g of PVC plastic, and 59.2–65.3 g of flooring.

The sequence used to generate the test concentrations consisted of three steps. First, paper and wood were ignited and allowed to burn for ~6 min. Then, household items were added and combustion continued for another 4 min. At ~10 min, the fire was extinguished; ductwork was connected to the combustion box to transport the smoke from the smoldering embers to the smoke chamber. Sampling of challenge air and air filtered by the CBRN canister was started with the connection of ductwork and continued for 30 min. After each test, the smoke chamber was purged with fresh air (6.68 m^3 min^{-1}) for ~2 min prior to entering the chamber to retrieve samples (five air exchanges) and for an additional 10–20 min prior to setting up the next run. All direct reading instruments confirmed zero background concentrations in the chamber during setup for subsequent tests. The smoke was drawn through the respirator canister within the range of 74–76 l.p.m., which represented heavy breathing during short-term activities (US Environmental Protection Agency (US EPA), 1997). Three high-volume pumps drew contaminated air through the respirator canister and manifold at 65.3 l.p.m., as monitored with in-line rotameters that were calibrated using primary standards. Six sample pumps (Tests 1–6) or five sample pumps (Tests 7–12), one for each contaminant or family of contaminants, drew an additional 10.89 l.p.m. (Tests 1–6) or 8.69 l.p.m. (Tests 7–12) of air through the canister. The number of sampling pumps used and the flow rate of air through the sampling pumps depended on what contaminants were being sampled. The decrease in flow rate from Tests 1–6 to Tests 7–12 was due to a reduction in the number of sampling pumps used because naphthalene was removed from the list of contaminants being sampled.

Four different APR canisters were used during testing. Three of the canisters were approved as 15-min negative pressure air-purifying CBRN respirators by NIOSH (2008). The three approved respirator canisters were MSA's Millennium CBRN (Pittsburgh, PA, USA), Scott's CBRN Cap-1 (Monroe, NC, USA), and 3M's FR-15 CBRN Cap-1 (St Paul, MN, USA). The fourth respirator tested was 3M's FR-64, a CBRN-like canister respirator. This respirator did not have CBRN approval but was NIOSH approved for use with certain organic vapors, sulfur dioxide, chlorine, hydrogen chloride, chlorine dioxide, hydrogen fluoride, ammonia, methylamine, formaldehyde, escape from hydrogen sulfide, phosphine, chloroaceteophenone ,or *o*-chlorobenzylidene malononitrile, and particulates (P100). Each canister was tested in 2–4 of the 12 tests, where the order of canister selection was random. Canister identifiers are included with test results to provide useful information to hygienists prescribing firefighter protection.

CO, nitrogen dioxide (NO_2), sulfur dioxide (SO_2), and oxygen levels were monitored inside the smoke chamber and in air filtered by the respirator with two real-time, direct-reading, and data-logging monitors at 0.4 l.p.m. (VRAE, Model PGM-7800, RAE Systems, San Jose, CA, USA). Both VRAE monitors were zeroed in clean air before each test and calibrated with canisters of NO_2 (concentration 5 p.p.m.) and SO_2 (concentration 5 p.p.m.) as well as a mixed challenge gas of CO (concentration 50 p.p.m.), methane (50% LEL), and air. The VRAE's range of quantification for SO_2 and NO_2 was 0–20 p.p.m.

Two personal DataRAMs (pDR-1000AN: chamber and pDR-1200: filtered air, Thermo Scientific, Waltham, MA, USA) were used to monitor respirable particulates inside the smoke chamber and in air filtered by the respirator set to 2-s averaging intervals. The pDR is able to measure particles with a size range of 0.1–10 μm and concentrations from 0.001 to 400 mg m^{-3}. Preliminary studies used a Marple impactor to determine the size distribution of the smoke particles; no quantifiable particle mass was observed for particles >3.5 μm (aerodynamic diameter) when the impactor was positioned immediately upstream of the APR canister, confirming that the pDR did not exclude large particles from the challenge concentration determination. Both pDRs were calibrated according to the manufacturer's specifications and zeroed in clean air before each test and were compared to gravimetric samples colocated in the smoke chamber (Caseman, 2008). Based on the filtering efficiency of the respirators (certified at 99.97%), any particles detected in filtered air would indicate inadequate sealing of the APR canister or manifold and would suggest that chemical contaminants in filtered air could be attributed to improper sealing and not canister performance. Therefore, the filtered air pDR tests provided additional system quality assurance.

Integrated sampling techniques were used to quantify 11 additional chemical components of smoke. Acetaldehyde, acrolein, benzaldehyde, formaldehyde, glutaraldehyde, butyraldehyde, crontonaldehyde, and cyanide were sampled in all 12 tests; benzene and naphthalene were sampled only in Tests 1–6; and hydrochloric acid was sampled in Tests 7–12. Benzene and naphthalene were not sampled in Tests 7–12 because they were not produced in adequate concentrations to be quantified in Tests 1–6. Hydrochloric acid was added to the list of chemicals to be sampled in Tests 7–12 because it is also a respiratory irritant associated with firefighter exposures (Hartzell, 1989). The chemicals were sampled and analyzed using standard methods (Table 1). ESIS Environmental Health Laboratory in Cromwell, CT, USA (American Industrial Hygiene Association and Environmental Lead Laboratory Accreditation Program Lab #100127) analyzed the 30-min integrated samples. Blanks were taken for each day of testing, and no contamination of these blanks was identified throughout the study.

Twelve canister challenge tests were conducted. Samples were collected from air in the smoke chamber and from air filtered by the respirator. For each test, smoke chamber concentrations (chamber air) and filtered air concentrations (filtered air) were compared to determine the percent penetration using equation (1):

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

where the subscript i references the test identification (1–12). Penetration calculations were performed for individual contaminants (e.g. respirable dust) of each test.

Assessing the penetration of all compounds simultaneously is critical to performance evaluation of the canisters in the field. To do this, compounds within the smoke that had similar health effects were aggregated. In this study, seven of the test compounds were known respiratory irritants. Hence, an irritant exposure index was computed for both the challenge and filtered air to provide an additional indicator of an APR canister's performance. Respirable particulates, acrolein, glutaraldehyde, SO_2, formaldehyde, acetaldehyde, and NO_2 are all respiratory irritants and were included in the hazardous irritant exposure index, given as (OSHA Technical Manual, 2008):

$$\text{Irritant exposure index} = \sum_j \frac{\text{Concentration}_j}{\text{OEL}_j}, \quad (2)$$

where the subscript j indicates the contaminant measured and OEL indicates the occupational exposure limit for contaminant j. The OELs used for the contaminants measured were STELs and ceiling limits, appropriate to account for short-term exposures in overhaul activities, ∼30 min (Bolstad-Johnson *et al.*, 2000). The OELs used are in Table 2. While respirable particulates have no STEL, the American Conference of Governmental Industrial Hygienists (ACGIH) recommends that for any substance for which there is no STEL, excursion limits should apply. The excursion limit is equal to three times the threshold limit value (TLV) and should not occur for >30 min (ACGIH, 2007). Therefore, an excursion three times the full-shift TLV of 3 or 9 mg m^{-3} was utilized as a STEL to respirable dust. For each test, the penetration of the overall smoke mixture was computed using the chamber-air and filtered-air irritant exposure indices in the penetration equation (1).

RESULTS

Contaminant concentrations varied by test because of incomplete combustion but were in the range of field tests previously reported (Bolstad-Johnson *et al.*, 2000). Seven compounds common to both studies are presented in Table 3 to compare contaminant concentrations generated in this study to a range of typical field concentrations. Mean concentrations of acetaldehyde, formaldehyde, and respirable dust were greater than those produced in typical field concentrations. Acrolein and benzaldehyde concentrations were in the range of concentrations produced in the field. Glutaraldehyde and hydrochloric acid concentrations were lower than field concentrations. A larger proportion of the tests conducted in this study were above the limit of quantification (LOQ). LOQs were similar in both studies for acrolein, formaldehyde, and glutaraldehyde. LOQs in field tests for acetaldehyde, benzaldehyde, hydrochloric acid, and respirable dust were larger than in this study. Concentrations of acrolein exceeded the OEL of 0.1 p.p.m. in chamber air in 4 of 12 tests. Concentrations of formaldehyde exceeded the OEL of 0.3 p.p.m. in

Table 2. OELs used as guidelines for calculations and comparisons

Contaminant	OEL
SO_2	5 p.p.m., ACGIH STEL
NO_2	5 p.p.m., ACGIH STEL
Glutaraldehyde	0.05 p.p.m., ACGIH ceiling
Acetaldehyde	25 p.p.m., ACGIH ceiling
Acrolein	0.1 p.p.m., ACGIH ceiling
Formaldehyde	0.3 p.p.m., ACGIH ceiling
Respirable particulates[a]	9 mg m^{-3}

[a] An excursion limit three times the full-shift TLV of 3 mg m^{-3} (3×3 mg m^{-3} = 9 mg m^{-3}) was utilized as an OEL for respirable dust which does not have a STEL.

chamber air in 10 of 12 tests. Respirable dust concentrations in chamber air exceeded the OEL of 9 mg m^{-3} in all 12 tests.

The mean CO level was 40 p.p.m.; however, four tests had peak CO levels that exceeded the 150 p.p.m. procedural limit established by fire stations for firefighters to enter overhaul environments. CO penetrated all respirator canisters (Fig. 3), which was not surprising because none of the canisters tested are approved for use in environments with high CO concentrations. All respirator canisters were able to filter respirable particulates to their certified levels: penetration was <0.03% (99.97% efficiency) for all respirators tested (Fig. 4).

Acrolein and formaldehyde were produced in concentrations that were able to be quantified (Fig. 5) and

Table 3. Comparison of field-generated (Bolstad-Johnson *et al.*, 2000) contaminant concentrations and study concentrations

Contaminant	Field average sample concentration	Chamber concentration
Acetaldehyde ($n = 12$)	0.34 p.p.m. mean	0.58 p.p.m. mean
	1.75 p.p.m. maximum	>1.1 p.p.m. maximum
	74% > LOQ	100% > LOQ
Acrolein ($n = 12$)	0.12 p.p.m. mean	0.066 p.p.m. mean
	0.3 p.p.m. maximum	0.22 p.p.m. maximum
	7% > LOQ	75% > LOQ
Benzaldehyde ($n = 12$)	0.057 p.p.m. mean	0.03 p.p.m. mean
	0.13 p.p.m. maximum	0.052 maximum
	19% > LOQ	92% > LOQ
Formaldehyde ($n = 12$)	0.25 p.p.m. mean	>0.79 p.p.m. mean
	1.18 p.p.m. maximum	>1.6 p.p.m. maximum
	90% > LOQ	100% > LOQ
Glutaraldehyde ($n = 12$)	0.046 p.p.m. mean	0.018 p.p.m. mean
	0.15 p.p.m. maximum	0.043 p.p.m. maximum
	25% > LOQ	100% > LOQ
Hydrochloric acid ($n = 6$)	0.99 mg m^{-3} mean	0.129 mg m^{-3} mean
	3.96 mg m^{-3} maximum	0.33 mg m^{-3} maximum
	36% > LOQ	83% > LOQ
Respirable particulates ($n = 12$)	8 mg m^{-3} mean	43.6 mg m^{-3} mean
	25.7 mg m^{-3} maximum	107 mg m^{-3} maximum
	30% > LOQ	100% > LOQ

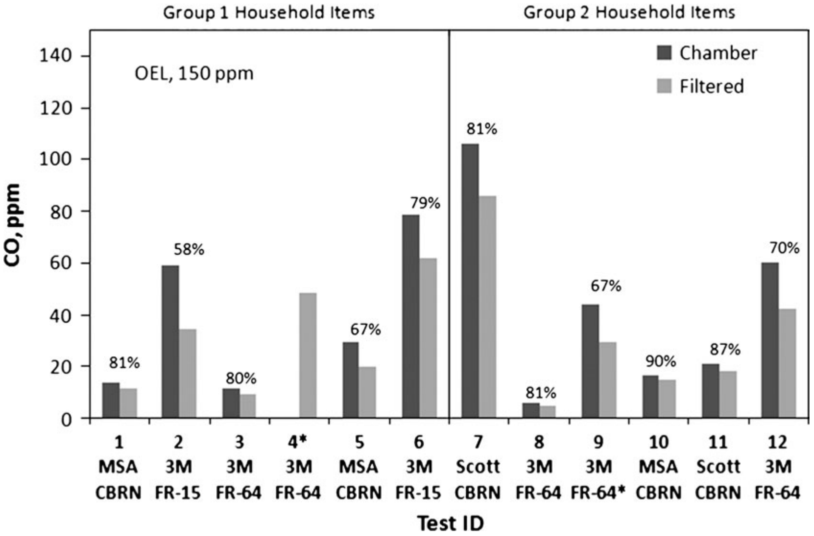

Fig. 3. Chamber and filtered air concentrations of CO. Percentages indicate amount of respirator penetration. Test 4 in the chamber had a pump failure. Tests 8 and 9 same canister.

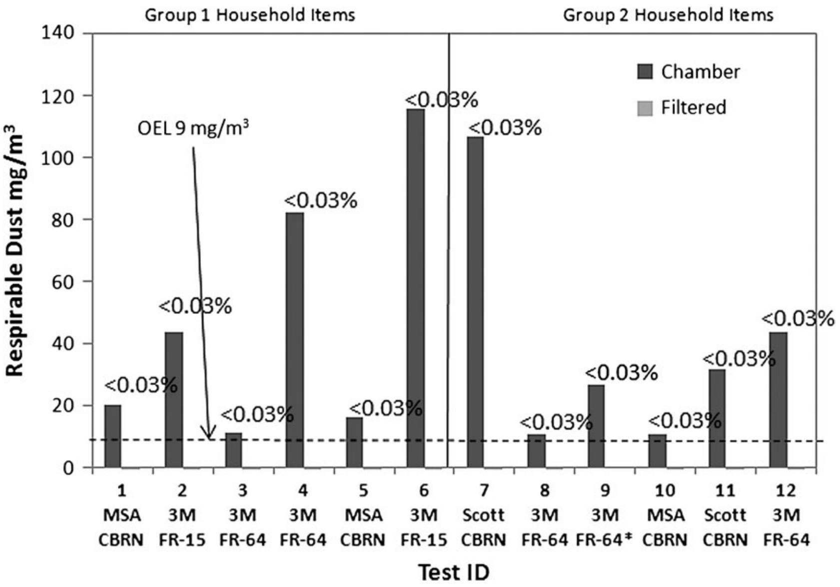

Fig. 4. Chamber and filtered air concentrations of respirable particulates. Percentages indicate amount of respirator penetration. OEL is labeled. Tests 8 and 9 used the same canister.

were present in the challenge air at concentrations that exceeded the OELs. However, in each test conducted, the CBRN canisters were found to reduce these contaminants to concentrations $<1\%$ of the OEL for formaldehyde and nearly that for acrolein.

Acetaldehyde, glutaraldehyde, and crontonaldehyde were produced in sufficient concentrations to be quantified in the chamber air; however, all concentrations in the challenge smoke were below specified OELs (Fig. 6). Acetaldehyde concentrations were reduced in air filtered by the respirator canister but not to below the LOQ in all tests. The highest chamber concentration of acetaldehyde was produced in Test 7, 1.1 p.p.m., and it was reduced to below the LOQ in CBRN-filtered air. However, in Tests 2 and 6, concentrations of acetaldehyde in the filtered air were not below the LOQ although they were below the OEL. Penetration for these two tests was calculated at 28 and 22%. The same type of respirator canister was used for both of these tests, 3M's FR-15 CBRN Cap-1 canister respirator. These results may be an indication of reduced filtering ability of this respirator canister for acetaldehyde. Glutaraldehyde and crontonaldehyde concentrations were reduced to levels that were below the LOQ by the respirator canister, well below any STEL.

Benzaldehyde and butyraldehyde were produced in sufficient concentrations to be quantified in chamber air; however, concentrations were reduced to nearly the LOQ or below in air filtered by the respirator canister in all tests (Fig. 7). Both are upper respiratory tract irritants, and butyraldehyde is also a possible carcinogen (NIOSH Current Intelligence Bulletin 55, 1991). Concentrations in both chamber and filtered air for NO_2 and SO_2 were both low; NO_2 concentrations for 11 tests were $<10\%$ of the STEL (5 p.p.m.) and SO_2 concentrations were $<60\%$ of the STEL (5 p.p.m.) in 11 of the 12 tests (Fig. 8). During Test 4, a pump failure occurred on the VRAE sampling the concentrations of SO_2 and NO_2 in chamber smoke, resulting in incomplete data. Over the course of the study, sensor drift was identified in the data from SO_2 and NO_2 sensors. The sensors did not always return to zero after exposed to fresh air toward the end of the 30-min tests. Even though the monitors were new at the start of the study and were zeroed and fully calibrated with new calibration gases before each test, sensor drift was identified. This may be responsible for the trended increasing NO_2 concentrations over the duration of the study (Fig. 8a), indicating that the lifetime of this sensor in the field may be extremely limited in firefighting investigations. Future research into the response range and lifetime of these sensors in the highly complex mixture of overhaul smoke is needed when relied upon to protect firefighters in the field. The other VRAE sensors (O_2, LEL, and CO) did not show any drifting throughout this study.

Although of interest to firefighter exposures, hydrogen cyanide (HCN), naphthalene, benzene, and hydrochloric acid (HCl) were generally not produced in these tests at chamber concentrations great enough to be quantified. All hydrogen cyanide concentrations within the smoke chamber were below the detection limit (0.038 p.p.m.), nearly two orders of magnitude below the 4.7 p.p.m. STEL. In Tests 1 through 7, Naphthalene and benzene concentrations in the smoke chamber were below their respective

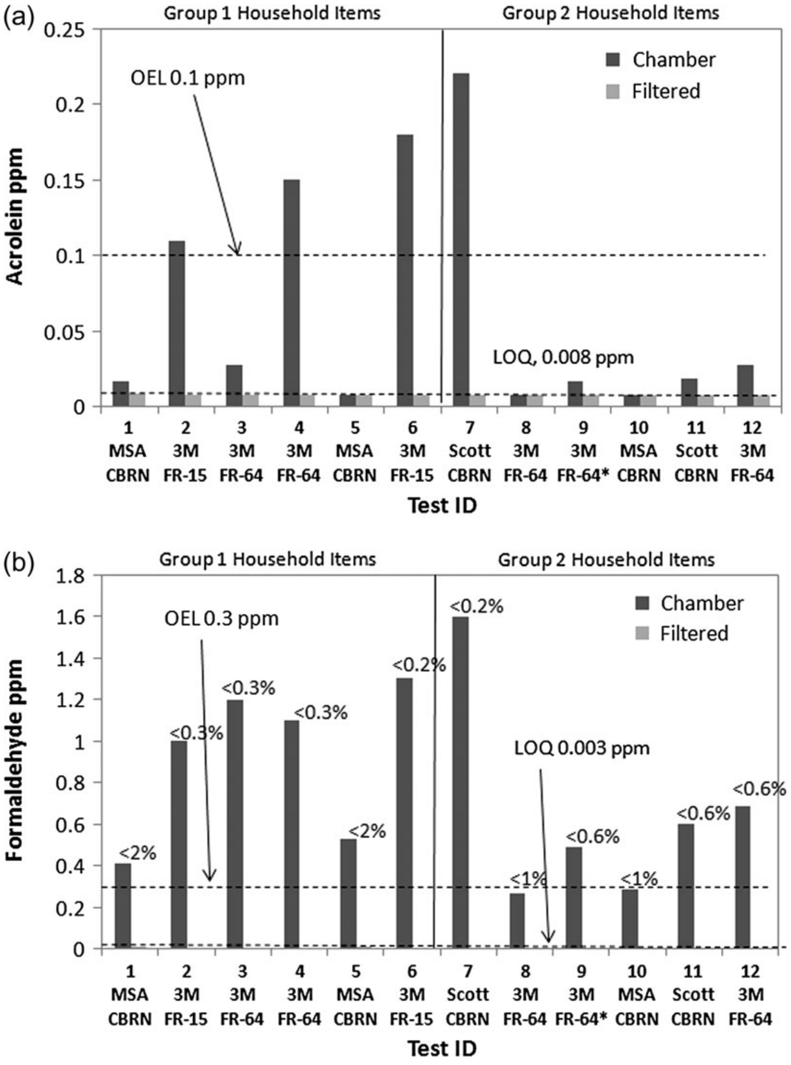

Fig. 5. Chamber and filtered air concentrations of (a) acrolein and (b) formaldehyde. Percentages indicate amount of respirator penetration. OELs and LOQs are labeled. Tests 8 and 9 used the same canister.

limits of detection (0.0032 and 0.088 p.p.m.) which were three and two orders of magnitude below their respective exposure limits. These two compounds were eliminated from Tests 7–12 because concentrations of these two contaminants were below LOQs in Tests 1–6. Finally, chamber concentrations of hydrochloric acid in Tests 7 through 12 were quantifiable in the chamber for only three tests (9, 10, and 11) but at concentrations less than one order of magnitude of the 5 p.p.m. exposure limit; all filtered air concentrations were below the 0.027 p.p.m. LOD. Blanks for all tests showed no field or transportation contamination of samples over the course of this study, as chemicals analyzed were all below detection limits.

Irritant exposure indices were calculated for each test to develop an index for chamber (Fig. 9) and filtered air (Fig. 10), using equation (2). An irritant exposure index of ≥ 1 indicates an environment that could be detrimental to respiratory health and that respiratory protection is needed. For each test, the chamber air index exceeded unity, indicating a need for respiratory protection within this simulated overhaul environment. In air filtered by the respirator canister, each test had an irritant exposure index below unity. This indicated that each of the respirator canisters tested was successful at reducing exposure to the irritant gas mixture as well as individual compounds tested by this study. Respirable dust, formaldehyde, and acrolein were the major contributors to the irritant exposure index in chamber air, where concentrations of individual components exceeded short-term and ceiling limts. However, SO_2, acrolein, and glutaraldehyde were the major contributors to the filtered-air irritant exposure index, although at concentrations much lower than their associated short-term or ceiling limits.

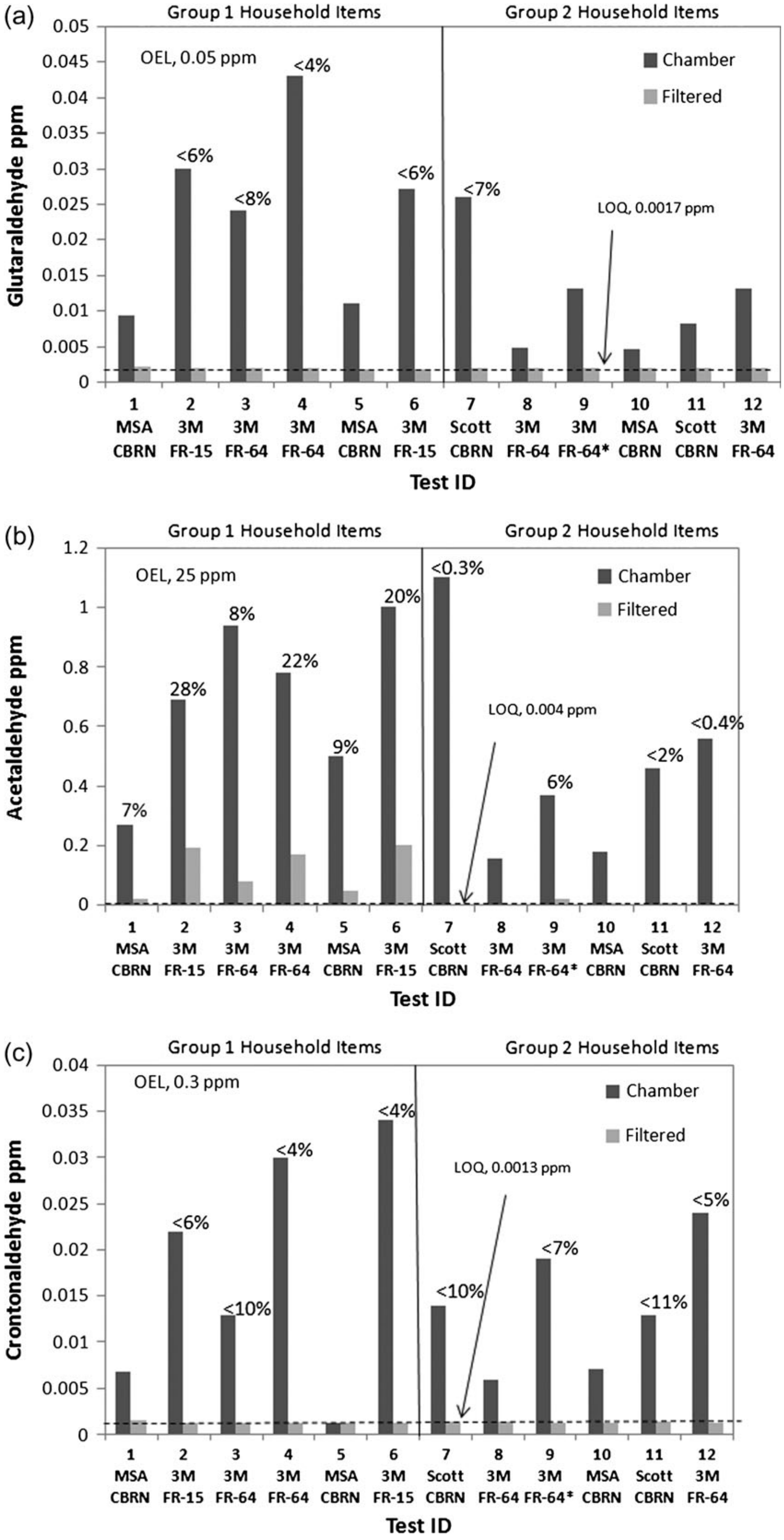

Fig. 6. Chamber and filtered air concentrations of (a) glutaraldehyde, (b) acetaldehyde, and (c) crontonaldehyde. Percentages indicate amount of respirator penetration. OELs and LOQs are labeled. Tests 8 and 9 used the same canister.

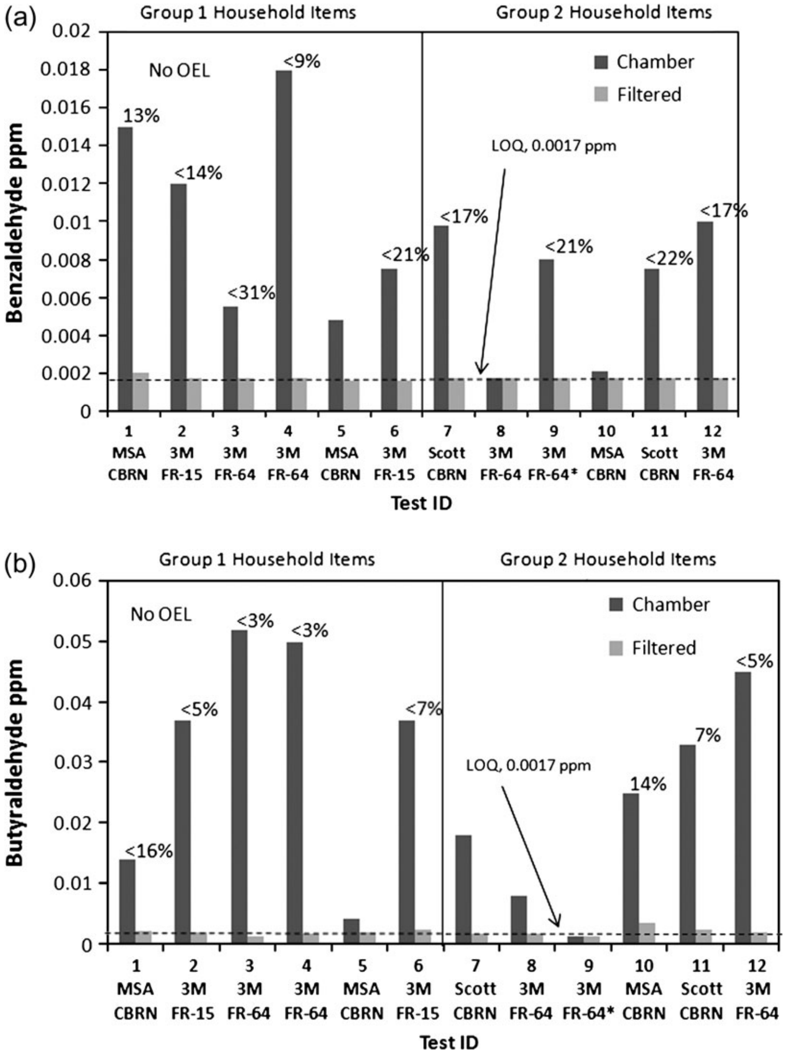

Fig. 7. Chamber and filtered air concentrations of (a) benzaldehyde and (b) butyraldehyde. Percentages indicate amount of respirator penetration. OELs and LOQs are labeled. Tests 8 and 9 used the same canister.

DISCUSSION

Because of the acute adverse respiratory effects reported for firefighters (Burgess *et al.*, 2001; de Vos *et al.*, 2006, 2009), it is important that the respiratory protection worn by firefighters provide adequate protection. This work was completed to assess whether the CBRN canisters provided better protection than was found in initial multi-gas APR cartridge tests.

Each of the respirator canisters tested in this study was effective at reducing respirable particulate concentrations in filtered air. The highest challenge concentration of acrolein (0.22 p.p.m.) was more than twice the OEL (0.1 p.p.m.), and the peak challenge concentrations of formaldehyde (1.6 p.p.m.) were more than five times the OEL (0.3 p.p.m.). These represented real-world concentrations and provided sufficiently large challenge concentrations to evaluate respirator canister performance. Both acrolein and formaldehyde were successfully filtered by the canisters to below the individual component's OELs. Penetrations were calculated at <7% for acrolein and <2% for formaldehyde. All of the respirator canisters tested were also successful at reducing the irritant exposure index to below unity. This data indicated that all of the respirator canisters used in this study are suitable for use in overhaul environments, including the canister not certified as a CBRN canister (3M FR-15). This work identified that no one manufacturer's canister performed better than another, and firefighters could work with their current SCBA suppliers to purchase canister adapters for the face pieces and use the appropriate CBRN canister for overhaul activities.

One respirator canister was inadvertently used for two consecutive 30-min tests and still performed well (Test 7, canister: 3M FR-64). This data may indicate

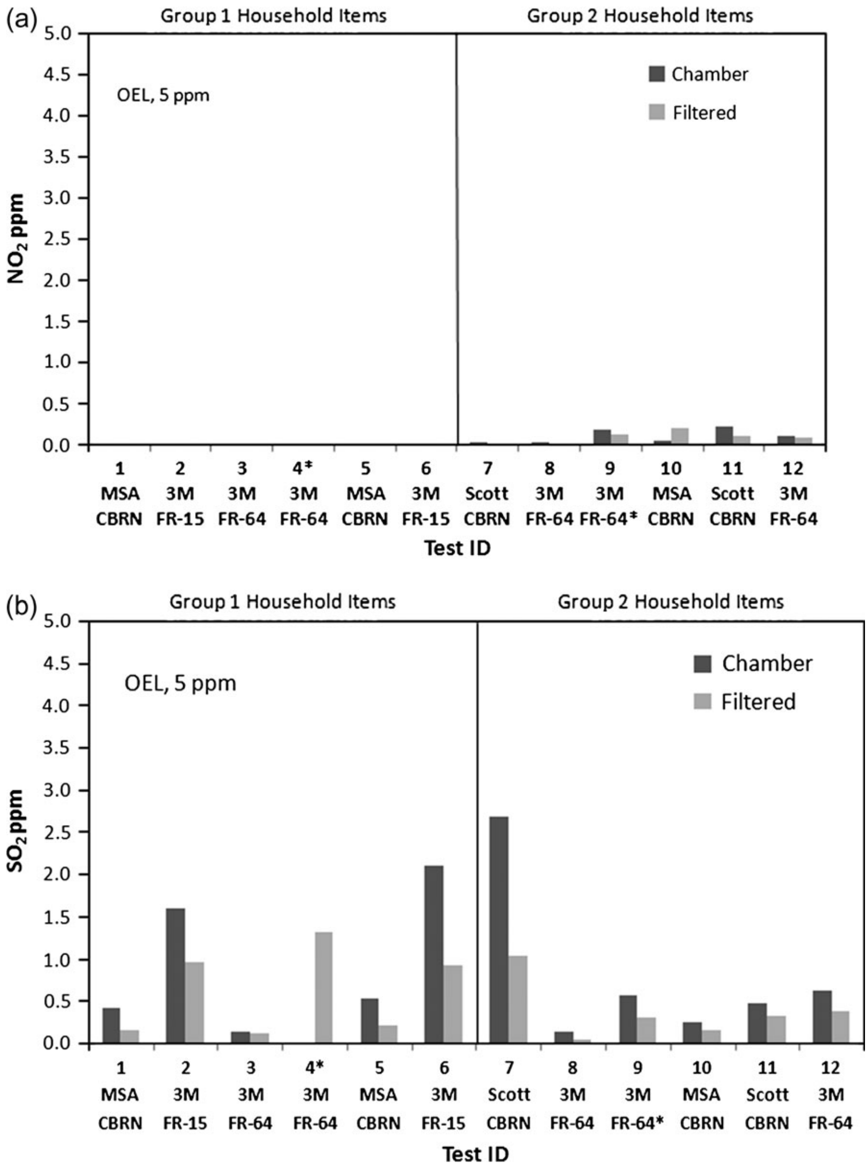

Fig. 8. Chamber and filtered air concentrations of (a) NO2 and (b) SO2. Percentages indicate amount of respirator penetration. OEL is labeled. Test 4 in the chamber had a pump failure. Tests 8 and 9 used the same canister.

that the 3M FR-64 respirator canister could be used for >30 min, although additional work should be conducted with longer challenge periods to determine the suitability of using these respirator canisters in multiple overhaul activities.

Because benzene, naphthalene, and cyanide concentrations were low after the first six tests, other household components were examined for combustion with the aim of producing higher contaminant yields. Gann *et al.* (2003) conducted a study examining the smoke component yields from room-scale fire tests. They burned individual household components, including sofa, particleboard bookcases with laminated vinyl finishes, and rigid PVC sheeting, in separate tests and sampled combustion air. They assumed that all concentrations of hydrogen chloride were from the PVC sheeting and all concentrations of HCN were from the bookcases. Based on their results, the PVC, laminated medium-density fiberboard flooring, and polymer styrene with laminate face trim were added to the burn components in the second phase of this study, although in necessarily small amounts. Size was limited by the dimensions of the combustion box and attempts were made to keep all of the components similar in size. Even with the addition of these burn materials in this study, the concentrations of HCl and HCN were low. Based on these results, future tests may include components that more closely resemble the items used by Gann *et al.* (2003).

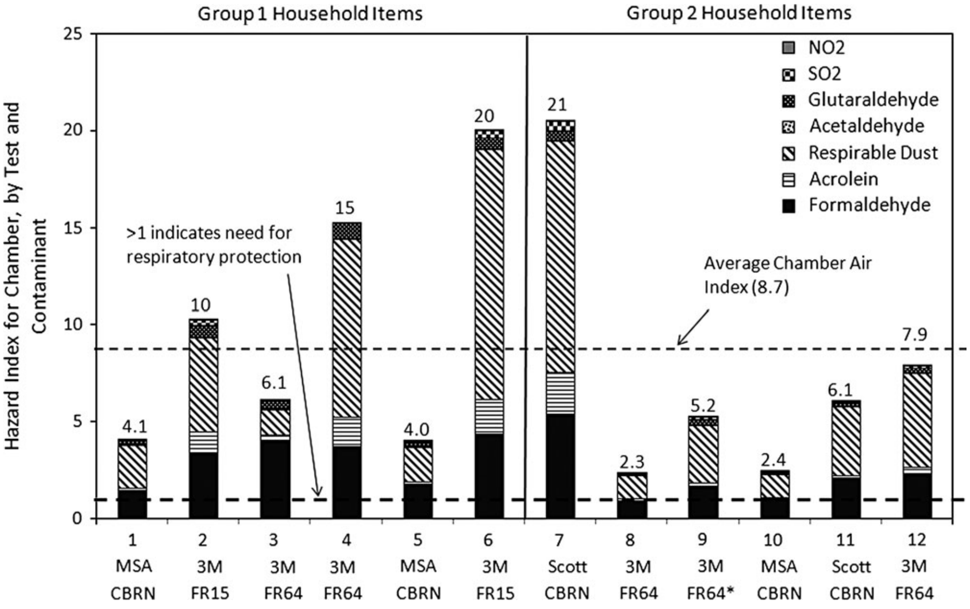

Fig. 9. Hazard index for irritant gas mixture in chamber air. An index >1 indicates the need for respiratory protection. The average chamber index over all tests was 8.7. Tests 8 and 9 used the same canister.

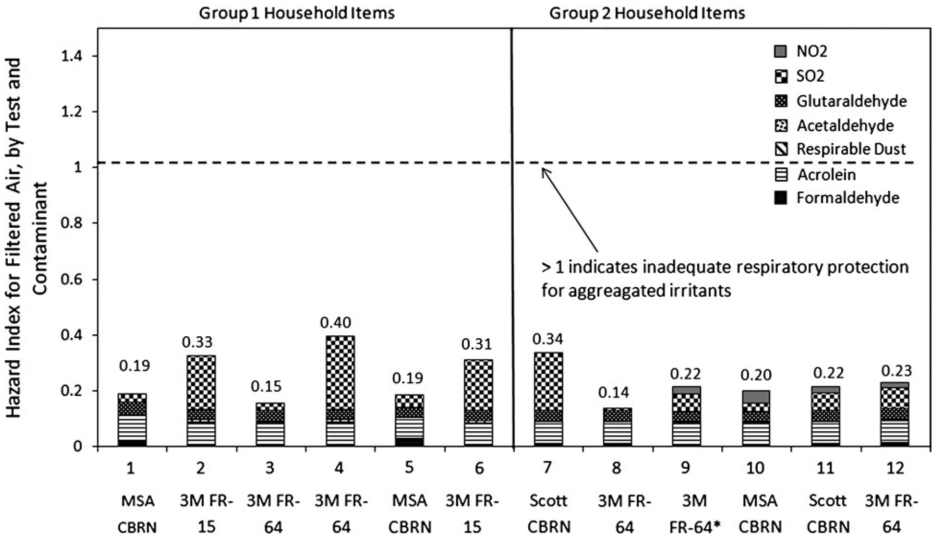

Fig. 10. Hazard index for irritant gas mixture in filtered air. An index >1 indicates that the filter provided inadequate respiratory protection. Tests 8 and 9 used the same canister.

Acrylic fabric or fibers could also be added to the items to be burned. A study by Bertol *et al.* (1983) found that combustion of 1 g of fibers containing polyacrylonitrile (PAN) in a 15.6 liter combustion chamber produced 1500 p.p.m. of HCN. Their results showed that higher concentrations of HCN were produced from combustion of PAN containing fibers than from foam rubber or wool.

However, the studies conducted by Gann *et al.* (2003) and Bertol and Brown (1983) evaluated combustion smoke and not smoke from smoldering embers of an extinguished fire (overhaul smoke), the focus of this work. The studies by de Vos *et al.* (2006, 2008, 2009) and Reisen and Brown (2008) also examined contaminant concentrations or respirator filter performance in the presence of combustion smoke not overhaul smoke. The differences between the two types of smoke, including high-temperature combustion versus low-temperature smoldering, could possibly contribute to lower contaminant levels (benzene, cyanide, and HCl) in the present study. Austin *et al.* (2001) hypothesized that low-temperature smoldering, which is present at the later stages of a fire such as in overhaul, does not result in higher levels of toxic combustion products, with the exception of particulates. One could hypothesize that the smoldering smoke in this study may not have been sufficiently high to release significant amounts of these compounds.

The method used in the present study to evaluate the effectiveness of CBRN canister respirators intentionally differs from the standard NIOSH approval method. Concentrations of a complex mixture of contaminants were much smaller than those used in the standard method, but this represents typical field conditions of CBRN canister use. The test-average temperature of challenge air (mean = 28°C) was within the range of the test standard, 25 ± 5°C (Federal Register, 2004). Flow rates through the canister (74–76 l.p.m.) were larger than the standard 65 l.p.m. (Federal Register, 2004) to better represent actual use.

The study by Anthony *et al.* (2007) found 13.2% penetration of formaldehyde in one of their tests of the effectiveness of multi-gas respirator cartridges. In the present study, the canister respirators were more effective at filtering formaldehyde as represented by their low penetration percentages ($<2\%$). Activated charcoal is the most common sorbent used in respirators. Cartridge respirators contain a small amount of sorbent, $\sim$50–200 cm^3, whereas canister respirators contain $\sim$250 to 500 cm^3 (NIOSH Technical Guide, 1987). Additional work could examine if the effectiveness of the CBRN canister respirator in reducing formaldehyde concentrations versus the cartridge respirator used in the Anthony *et al.* (2007) study is due in part to the larger sorbent volume of the canister respirator.

Limitations of this study included variability in contaminant generation and difficulty producing concentrations that could be quantified. These challenges were also seen in the study conducted by Anthony *et al.* (2007) and were also due to incomplete combustion of the household items. Household items could be burned for a longer period of time increasing the total amount of each item consumed by the fire and possibly contaminant concentrations. In the study by Gann *et al.* (2003) the mass of the items burned and consumed is monitored and standardized for each test to improve reproducibility. Different methods for burning household components could be investigated such as making smaller pieces, or pellets. Smaller pieces of components may increase the amount of product combusted, which may help with combustion uniformity, but may also affect the ability to smolder after the main fire is extinguished.

CONCLUSIONS

CBRN canister respirators were effective at reducing concentrations of both irritant gases and respirable dust produced in the present study's overhaul environment. The compounds with the largest contribution to exposure risk in the air filtered by these canisters were identified as acetaldehyde, acrolein, glutaraldehyde and possibly SO_2, albeit at concentrations below current STELs. These findings should assist those studying health effects of firefighters wearing CBRN canisters in the field, providing an indication of the compounds of highest exposure risk. Based on these results the CBRN canisters tested are recommended for use by firefighters during overhaul in situations where typical household materials have been combusted. The APR respirators used in this study are not recommended for use in environments with CO concentrations at or above STELs because these respirator canisters do not protect the wearer from CO. In addition, the effectiveness of CBRN canisters in environments where respirable dust concentrations exceed 110 mg m^{-3} has not been assessed. Finally, the use of CBRN canisters for longer exposure durations has not been assessed. The 30-min study duration was selected based on firefighter input; should APRs be needed for events of longer durations, performance analysis of CBRN canisters requires the incorporation of lower full-shift exposure limits and more complete time-activity information.

To examine the service life of CBRN canister respirators in overhaul environments, additional break through tests would be required. This work evaluated 30-min exposure periods; testing performance for longer challenge periods could provide information on a change-out schedule, as represented by the positive results from the single test that used the same canister for two 30-min tests. Determining an actual service life of APRs could assist firefighters in developing an effective and cost efficient respirator program. Although a current exposure concern for firefighters, cyanide and hydrochloric acid were two irritant gases that were not produced in adequate concentrations to be quantified in these smoke chamber studies. Future tests should investigate the inclusion of other household materials in the burn sequence, such as those used in Gann *et al.* (2003) and Bertol *et al.* (1983) studies, with the aim of increasing cyanide and hydrochloric acid concentrations.

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REFERENCES

ACGIH. (2007) TLVs and BEIs based on the documentation of the threshold limit values for chemical substances and physical agents & biological exposure indices. Cincinnati, OH: American Conference of Governmental Industrial Hygienists.

Anthony TR, Joggerst P, James L *et al.* (2007) Method development study for APR cartridge evaluation in fire overhaul exposures. Ann Occup Hyg; 51: 703–16.

Austin CC, Wang D, Ecobichon DJ *et al.* (2001) Characterization of volatile organic compounds in smoke at municipal structural fires. J Toxicol Environ Health; 63: 437–58.

Bertol EA, Mari F, Orzalesi G *et al.* (1983) Combustion products from various kinds of fibers: toxicological hazards from smoke exposure. Forensic Sci Int; 22: 111–6.

Bolstad-Johnson DM, Burgess JL, Crutchfield CD *et al.* (2000) Characterization of firefighter exposures during fire overhaul. Am Ind Hyg Assoc J; 61: 636–41.

Bryant RA, Butler KM, Vettori RL *et al.* (2007) NIST special publication 1051: real-time particulate monitoring—detecting respiratory threats for first responders: Workshop Proceedings. National Institute of Standards and Technology, Technology Administration, US Department of Commerce.

Burgess JL, Nanson CJ, Bolstad-Johnson DM *et al.* (2001) Adverse respiratory effects following overhaul in firefighters. J Occup Environ Med; 43: 467–73.

Caseman DL. (2008) Smoke particulates in a chamber. MPH Technical Report, Mel & Enid Zuckerman College of Public Health, University of Arizona.

de Vos A, Cook A, Devine B *et al.* (2006) Effect of protective filters on fire fighter respiratory health during simulated bushfire smoke exposure. Am J Ind Med; 49: 740–50.

de Vos A, Cook A, Devine B *et al.* (2009) Effect of protective filters on fire fighter respiratory health: field validation during prescribed burns. Am J Ind Med; 52: 76–97.

de Vos A, Reisen F, Cook A *et al.* (2008) Respiratory irritants in Australian bushfire smoke: air toxics sampling in a smoke chamber and during prescribed burns. Arch Environ Contam Toxicol; E-Pub 2008 Aug 20.

Federal Register, 60 Fed. Reg. 110, 30336–30398 (Revised 1 October 2004). 42 CFR part 84.

Gann RG, Averill JD, Johnsson EL *et al.* (2003) Smoke component yields from room-scale fire tests. Gaithersburg, MD: NIST, Building and Fire Research Laboratory. NIST Technical Note 1453.

Hartzell GE. (1989) Prediction of the toxic effects of fire effluents. J Fire Sci; 7: 179.

National Institute for Occupational Safety and Health (NIOSH). (2008) CBRN approved respirators. Available at http://www.cdc.gov/niosh/npptl/topics/respirators/cbrnapproved/apr/default.html. Accessed 28 July 2008.

NIOSH Current Intelligence Bulletin 55. (1991) Carcinogenicity of acetaldehyde and malonaldehyde, and mutagenicity of related low-molecular-weight aldehydes. Cincinnati, OH: NIOSH. DHHS (NIOSH) Publication No. 91–112.

NIOSH Interim Guidance. (2005) Interim guidance on using CBRN canisters for activities other than response to terrorist event. Cincinnati, OH: NIOSH. DHHS (NIOSH) Publication No. 91–505.

NIOSH Technical Guide. (1987) NIOSH guide to industrial respiratory protection. Cincinnati, OH: NIOSH. DHHS (NIOSH) Publication No. 87–116.

OSHA Technical Manual. (2008) SAEs for exposure to chemical mixtures. Washington, DC: OSHA Section II, Chapter 1, Part K. TED 01-00-015 [TED 1-0.15A].

Reisen F, Brown S. (2008) Australian firefighters' exposure to air toxics during bushfire burns of autumn 2005 and 2006. Environ Int; E-Pub 2008 Oct 1.

US Environmental Protection Agency (US EPA). (1997) Exposure factors handbook. Washington, DC: National Center for Environmental Assessment, Office of Research and Development.

Wood GO. (2002) A review of the effects of covapors on adsorption rate coefficients of organic vapors adsorbed onto activated carbon from flowing gases. Carbon; 40: 685–94.