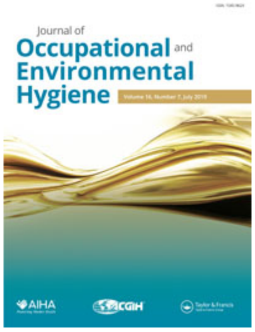

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REPORT

Breakthrough analysis for filtering facepiece respirators impregnated with activated carbon

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ABSTRACT
Several manufacturers are producing disposable dual-use dust masks that are primarily designed to protect against airborne particulate exposures but that also contain a layer of activated carbon to provide protection against organic vapors (OVs) at levels below permissible exposure levels, referred to as "nuisance level" by the FFR manufacturers. Industries identified in the literature as commonly having employees exposed to nuisance-level OVs include beautician salons, dry cleaning operations, and pesticide applications. This study investigated the adsorption capabilities of three different dual-use dust masks that contain both filter media to remove particles and activated carbon to capture OVs. The three dual-use dust masks were tested and compared relative to the 50% breakthrough time for two OVs (acetone and perchloroethylene) and one non-carbon-based contaminant gas (ammonia) often found in agricultural settings at nuisance-level amounts. The dual-use dust masks were exposed to 15 ppm and 50 ppm for all 3 compounds, which represented the range of nuisance-level exposure documented in literature. Most tests were conducted at 21 °C and 50% relative humidity. A relative humidity level of 95% was also created to compare results under that condition. The non-approved dual-use dust masks were ineffective for all vapors and offered less than 10 min of protection before 50% breakthrough occurred. All dual-use dust masks performed poorly when exposed to ammonia, with breakthrough time less than 7 min at 50 ppm and 10 min at 15 ppm. The approved dual-use dust mask had 50% breakthrough times, for example, of 121 min and 233 min for acetone at 15 ppm and 50 ppm, respectively. The less volatile perchloroethylene took over 400 min to achieve 50% breakthrough at 50 ppm. High relative humidity reduced breakthrough times by up to 70%. These results indicate high variability in performance among dual-use dust masks. Performance is also dependent on gas/vapor volatility and levels of water vapor. However, one model tested, the 3M model 8514, did show promise as an acceptable method for greatly reducing nuisance-level OV exposures.

KEYWORDS
Breakthrough time; dust mask; semivolatile organic compounds

Introduction

Respirator manufacturers use the term "nuisance-level" to refer to exposures that do not exceed Occupational Exposure Limits (OELs) and therefore are less likely to be controlled using engineering methods. Since nuisance-level exposures often go uncontrolled, employees may develop minor health symptoms. Nuisance-level organic vapor (OV) sources typically originate from the volatilization of compounds used during an industrial process such as glues, paints, adhesives, pesticides, petroleum, and solvents.[1] For example, studies conducted in nail salons have found nuisance-level concentrations of acetone.[2–6] Employees in that industry can suffer from minor symptoms such as dizziness, cough, headache, and respiratory irritation.[4] Likewise, nuisance levels of perchloroethylene (CAS No. 127-18-4) have been measured in the air of businesses in the dry-cleaning industry.[7,8] Short-term, high levels of perchloroethylene exposures can cause dizziness, drowsiness, and headaches.[9] However, chronic, low-level exposures did not result in clinical health symptoms in a study among dry cleaning workers compared to controls.[7] In livestock production, ammonia is generated as an off-gas from liquid animal waste. Ammonia is a common byproduct of metabolism and is typically excreted in urine, allowing ammonia vapor to occupy working environments inside animal and poultry rearing buildings.[10–12] Long-term exposure to ammonia below its permissible exposure limit has been found to cause a decrement in pulmonary function.[11]

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Controlling workplace exposures will reduce the risk of negative health outcomes among employees. In situations where engineering controls are not feasible, respirators can protect employees from inhalation exposures. Disposable dust masks have been implemented in a wide variety of workplaces where employees are exposed to particulates. Throughout this article, we use the term "dust mask" in accordance with the definition provided in 29 CFR 1910.134(b) to describe any "negative pressure particulate respirator with a filter as an integral part of the facepiece or with the entire facepiece composed of the filtering medium." The particle-capture efficiency of a brand of dust mask can be evaluated and approved by the National Institute for Occupational Safety and Health (NIOSH) using techniques described in 40 CFR 84. However, there are dust mask brands available for purchase that have not been approved by NIOSH for their ability to capture particles. Likewise, there is no established method for determining, and approving, the ability of a dust mask to capture OVs.

To protect workers in areas containing particulate and/or OVs, respirator cartridges are available for use with full- and half-face respirators that contain filter media to capture particles and/or activated carbon (AC) to protect against OV exposures. Currently, manufacturers are also producing dust masks impregnated with AC to provide protection against particulate exposures and nuisance-level concentrations of OVs. However, the performance characteristics of these dual-use dust masks for capturing OVs have not been studied extensively. According to the only study found on the performance of dual-use FFRs, Rozzi et al.[13] demonstrated that three models provided protection up to 10% breakthrough for benzene, toluene, and xylene between 64 and 150 min. They explained that the thin bed of carbon found in some dual-use dust masks, a few millimeters thick and a few grams of carbon, may lead to fast or immediate breakthrough times. In addition to the mass of AC in a dual-use dust mask, breakthrough times may change when humidity increases because water vapor molecules competes with OV molecules for AC adsorption sites, and may change for OVs of differing vapor pressures where OV adsorption reduces as vapor pressure increases.

The objectives of this research were to determine: (1) if OV breakthrough times differ between selected dual-use dust masks; (2) if ambient relative humidity decreases breakthrough time; (3) and if dual-use dust masks offer protection from ammonia gas inhalation. Although the mask types chosen for this study were designed to capture both particulates and OVs, this study focused specifically on their abilities to capture OVs and the contaminant gas, ammonia.

Table 1. Vapor pressures and occupational exposure limits of two selected organic compounds and a gas.

Compound	Vapor Pressure, mm Hg[A]	ACGIH TLV®[B], ppm	OSHA PEL[C], ppm
Acetone	180	250	1000
Perchloroethylene	14	25	100
Ammonia	6460	25	50

[A] Vapor pressures at 20 °C
[B] American Conference of Governmental Industrial Hygienists Threshold Limit Value
[C] Occupational Safety and Health Administration Permissible Exposure Level

Methods

Contaminant and dust mask selection

Perchloroethylene, acetone, and ammonia were the selected airborne contaminants given their presence in nuisance-level concentrations in a wide range of workplaces representing the general industry, the service sector, and agriculture, respectively. Table 1 provides the vapor pressure and OELs for each compound. In general, compounds with lower vapor pressures are more readily adsorbed onto activated carbon. Perchloroethylene and acetone represent compounds that produce an organic vapor of the type typically captured by activated carbon. Ammonia is a gas and represents a worst-case for capture by activated carbon because of its high volatility.

Three styles of dual-use dust masks were chosen to encompass most of the available style options for dual-use dust masks on the market (Figure 1). These included a "surgical mask" referred to as "Mask A" (Part # 1330737, Nice Systems, Ra'anana, Israel), a dual-use dust mask that has not been approved by NIOSH for particulate removal, referred to as "Mask B" (Model M1, RZ Mask, Burnsville, MN), and a dual-use dust mask that has been approved by NIOSH for particulate removal, referred to as "Mask C" (Model 8514, 3M Company, Maplewood, MN). Mask A did not have rigid edges, no nose cone, and no facial contouring. Mask B consisted of a neoprene mask with a nose cone and soft edges containing a reusable filter with disposable carbon inserts. Mask C had a nose cone, rigid edges, and an exhalation valve. All masks contained a filter media and activated carbon deposited in a layer throughout the mask, but of unknown, and unmeasurable, quantity.

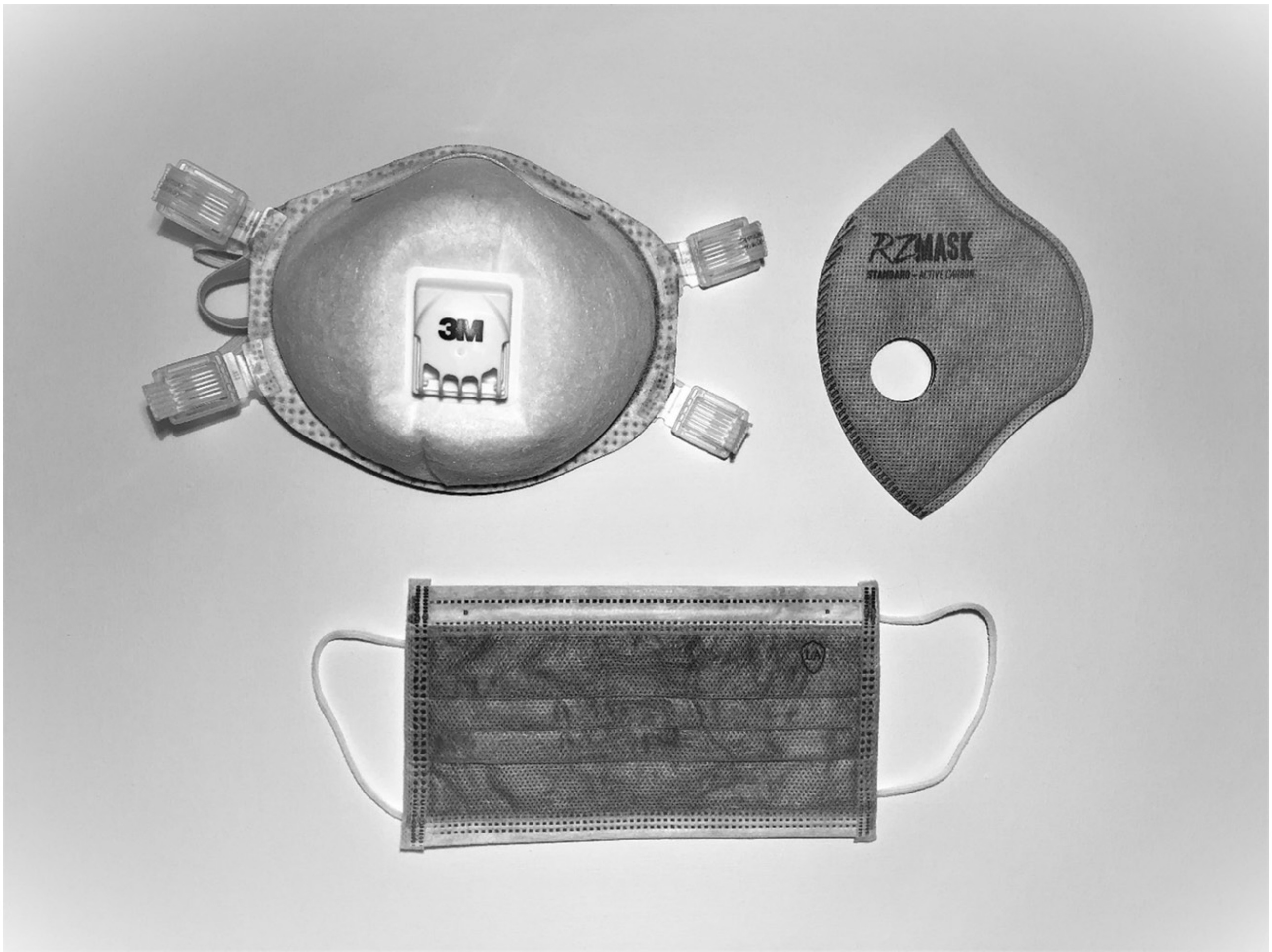

Figure 1. Photograph of the three dual-use dust masks evaluated in this study: Mask C (upper-left), Mask B (upper-right), Mask A (lower-center). Mask B, as shown, is the filter media insert of a larger neoprene mask worn by the user.

Equipment set-up

The testing system included a vapor mixing chamber and an exposure chamber (Figure 2). To generate OVs, solvent liquid was placed in a test tube (9 mL) inside a small chamber (11.7 L). Filtered, compressed air flowed through the mixing area and into a containment chamber (57.7 L) at 0.1 liter per minute (LPM) to 5 LPM, adjusted to maintain desired steady-state OV concentrations. The containment chamber had two ventilation holes in the sides to allow dilution ventilation to enter the chamber, drawn in through a fixed connection on one side of the chamber connected to a vacuum pump.

To ensure accurate evaluation of filter media despite different mask structures, a representative section of each respirator was placed in a pass-through column placed within the containment chamber next to a mixing fan (Figure 2). The section was cut from a portion of a dual-use dust mask free from seams or edges. The pass-through column was designed with two 5-cm diameter hollow cylinders with an inner diameter of 2.7 cm, placed end-to-end. The filter section with shortest side length >2.7 cm was placed between the two cylinders. The bottom of the top cylinder contained an “O” ring to create a seal between the filter material and the two cylinders. Metal plates on the top and bottom of the two cylinders were hand-tightened together with the use of bolts and wing nuts to provide sufficient compression to form a tight seal around the filter section. Air exiting the column was drawn through tubing connected to the OV sampling device and another pump in order to achieve the desired air flow through the entire column.

During trials, temperature and humidity resulted from lab conditions near 25 °C and 50% RH that were recorded during each trial with a digital temperature/humidity sensor (Model HM70, Vaisala Oyj, Helsinki, Finland). High humidity (near 95% RH) was also produced for some trials during which the system remained the same except that another tube was

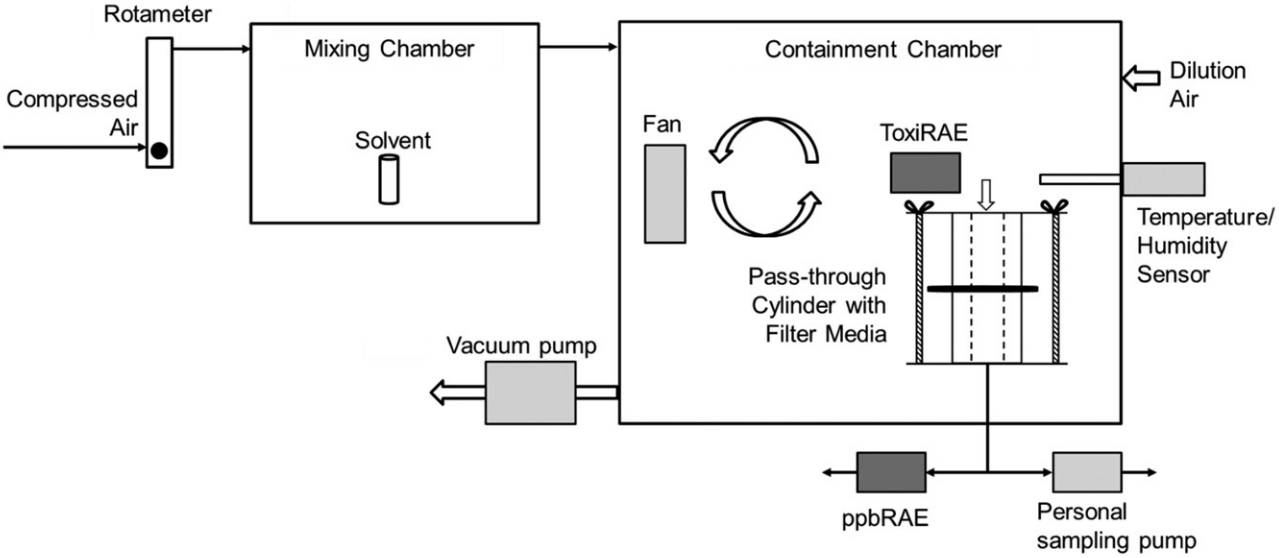

Figure 2. Schematic of breakthrough measurement apparatus.

connected to a previously sealed inlet in the top of the exposure chamber. Humidity was generated by placing a submersible aerator in a heated, sealed beaker of deionized water. Water vapor flowed out of the beaker, through a tube with heat wrap and into the exposure chamber to develop the desired relative humidity. Air flow into the system, dilution flow, and humidity flow were all measured with a rotameter and adjusted as needed to achieve the desired challenge conditions.

Trial flow rates

Trial flow rates were based on breathing rates for occupations with an assumed worst case metabolic rate of "moderate intensity" as defined by the American Conference of Governmental Industrial Hygienists (ACGIH®).[14] Most work conducted at nail salons, dry cleaners, and animal production operations should fall under this definition or a lower metabolic rate. Janssen et al.[15] established moderate respiratory flow rates (40% work rate) to be near 30 LPM. The U.S. EPA also compiled data from a number of sources and found moderate inhalation rates of 22–29 LPM for people age 16- to 81-years-old.[16]

Given an intended flow rate through a dual-use dust mask of 30 LPM, the flow rate through the column was adjusted to provide the same superficial face velocity (SFV) across the filter portion within the column as across the entire dual-use dust mask. Under the assumption that AC is uniformly distributed and having the same thickness throughout a dual-use dust mask, this adjustment in flow rate allows a direct comparison between the breakthrough time of an OC associated with the filter portion to that of the entire dual-use dust mask. To make that adjustment the surface area of each dual-use dust mask was measured using a photocopied image of the flattened mask and software capable of determining the area of an image (ImageJ, National Institutes of Health). Then the ratio of the areas of the 2.7-cm cylinder hole ($5.72\,\text{cm}^2$) and the measured total surface area for each mask (varying from $157–174\,\text{cm}^2$) was determined. Flowrates through the column of 0.99 and 1.09 LPM were then determined by multiplying the area ratio by 30 LPM to provide the same SFVs as for 30 LPM through the entire dual-use dust masks.

Sampling equipment

Two photoionization detectors (PIDs) were used in this study to quantify airborne concentrations. A PPB Rae 3000 (Rae Systems, San Jose, CA) sampling at 0.5 LPM was used to quantify the downstream concentrations for all contaminants. A ToxiRae Pro PID (Rae Systems, San Jose, CA) was used to measure the containment chamber concentration to ensure steady-state conditions were met (upstream). A second ToxiRae Pro PID, configured with an electrochemical NH_3 sensor (P/N C03-0950-000), capable of measuring from 0–100 ppm, was used to measure the ammonia concentration inside the chamber (upstream). Instruments were calibrated each day following the manufacturers recommendations which included a zero and span gas calibrations. To accurately compare between different instruments, regression analyses were completed by exposing instruments to the same range of contaminant concentrations without filter

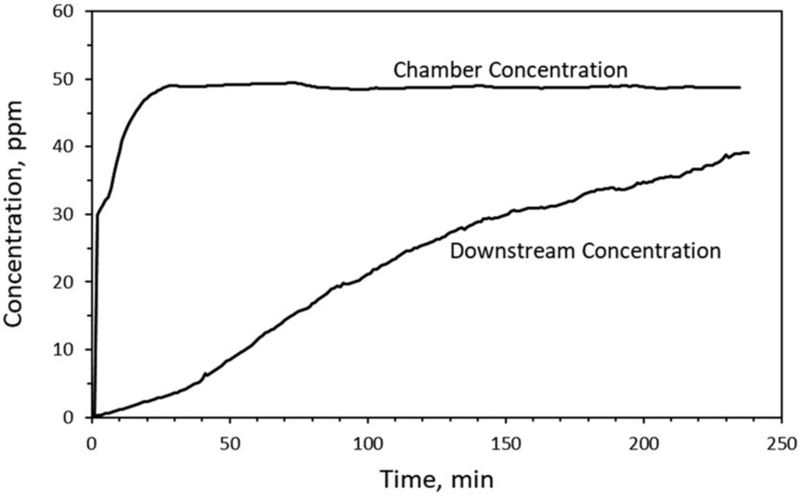

Figure 3. Example of trial output. Chamber concentration and breakthrough curve for Mask C media challenged with 50 ppm of perchloroethylene at lab air conditions (25 °C, 50% RH).

media in place. During trials, the test contaminant was chosen from the PID chemical library. Changing the measurement gas on the PID allowed the instrument to apply contaminant specific correction factors for each contaminant. A personal sampling pump (Model 4140, Sensidyne, St. Petersburg, FL) was used to provide the additional 0.5 LPM needed to maintain a flowrate near 1 LPM through the column.

Data collection

Steady-state concentrations of 15 ppm and 50 ppm were generated in the exposure chamber for each of the three contaminants. These levels were chosen to be consistent among the three compound types to enable inter-mask comparisons and to provide a range relative to the OELS of each compound analyzed. This range necessarily differed by compound given the wide variation in OELs between the three compounds. Three trials were completed for each vapor at each concentration with Mask C. Two trials were completed for each vapor at each concentration for Masks A and B. However, additional trials were conducted while creating a 95% RH atmosphere using Mask C with acetone and perchloroethylene at 50 ppm to test the influence of humidity on capture performance. Each trial was conducted with an unused portion of a mask applied to the pass-through cylinder.

Carrier air and dilution air into the containment chamber were adjusted to achieve the desired concentrations. Trials were terminated if 100% breakthrough was achieved in less than 4 hr. Otherwise, trials were conducted up to a maximum of 8 hr to achieve 50% breakthrough. Given a nuisance-level exposure environment in which these masks would be used, 50% breakthrough was deemed to be an appropriate level at which a dual-use dust mask should be replaced with a new mask.

Data analysis methods

Breakthrough was calculated by dividing the filter portion downstream concentration (C_{out}) by the chamber concentration (C_{in}) and reported in fraction form. Instrument concentrations in ppm were also converted to mg/m^3 from the molecular weight of each contaminant. Contaminant mass collected when reaching 50% breakthrough was then determined by calculation using the following equation:

$$M_{col,50\%} = \sum_{t=0}^{t=t_{50}\%} (C_{out}Q - C_{in}Q)\Delta t, \qquad (1)$$

where Q is the flowrate through the pass-through column and Δt is the time interval associated with one sample period of the PID sensor (1 min in every case). These values were comparable across dual-use dust mask types because the surface area over which collection occurred was the same for each type and equal to the area of the inner circular area of the pass-through column.

Results

An example of PID sensor concentration measurements from a single trial is provided in Figure 3. Figure 4 provides representative breakthrough curves for each dual-use dust mask for the same contaminant. Dual-use dust mask performance is given in Tables 2–4, which show the average of the trials conducted for each concentration in terms of minutes to

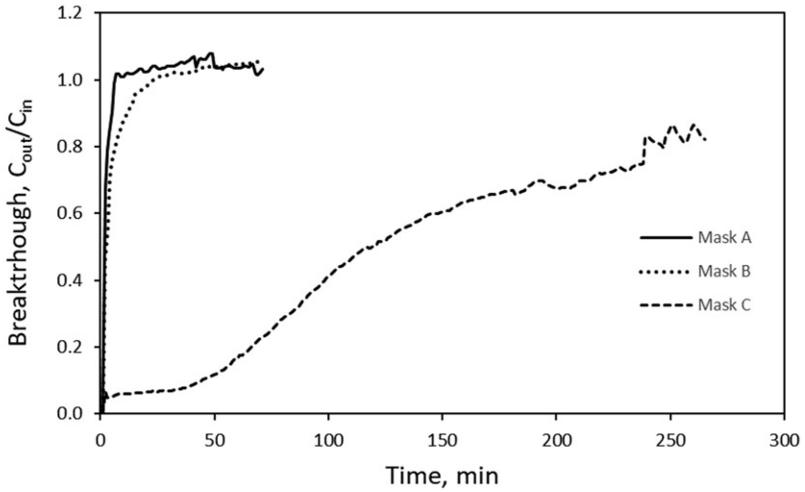

Figure 4. Example of trial output. Breakthrough curves for each mask type when challenged with 50 ppm of acetone at lab air conditions (25 °C, 50% RH).

Table 2. Average (and standard deviation) time (min) and mass (μg) collected at 50% breakthrough for Mask A subjected to two concentration levels of acetone, perchloroethylene, and ammonia at 50% RH and 25 °C.

		Concentration, ppm / RH %	
		15 / 50	50 / 50
Acetone (n = 2)	Time, min	1.0 (0.0)	2.0 (1.4)
	Mass, μg	2.7 (0.0)	7.7 (3.3)
Perchloroethylene (n = 2)	Time, min	2.5 (0.7)	2.0 (0.0)
	Mass, μg	28.1 (11.3)	21.1 (1.9)
Ammonia (n = 2)	Time, min	1.0 (0.0)	1.0 (0.0)
	Mass, μg	0.2 (0.0)	0.05 (0.3)

Table 3. Average (and standard deviation) time (min) and mass (μg) collected at 50% breakthrough for Mask B subjected to two concentration levels of acetone, perchloroethylene and ammonia at 50% RH and 25 °C.

		Concentration, ppm / RH %	
		15 / 50	50 / 50
Acetone (n = 2)	Time, min	4.5 (6.4)	2.0 (1.4)
	Mass, μg	37.6 (31.4)	28.4 (15.3)
Perchloroethylene (n = 2)	Time, min	6.5 (0.7)	5.0 (2.8)
	Mass, μg	100.6 (12.7)	60.7 (63.7)
Ammonia (n = 2)	Time, min	4.0 (4.2)	1.0 (0.0)
	Mass, μg	4.7 (6.0)	15.8 (17.4)

50% breakthrough and mass collected at 50% breakthrough. Masks A and B performed in a similar way with 50% breakthrough times less than seven min. Average 50% breakthrough times for Mask C ranged from 2.5 min to > 480 min depending on trial conditions.

In general, breakthrough time and mass collected decreased in order of perchloroethylene > acetone > ammonia, and 15 ppm > 50 ppm trials for each contaminant type. An atmosphere of 95% humidity reduced the Mask C performance when challenged with 50 ppm of acetone (Figure 5) and perchloroethylene. For both contaminants, the time to breakthrough and mass collected was lowered by more than 50% when in a high humidity environment. However, high relative humidity improved performance when challenged with ammonia, greatly increasing breakthrough time and mass collected (Table 4).

Discussion

For Masks A and B, breakthrough often occurred even before reaching the intended steady-state levels of 15 ppm and 50 ppm. Measurements made downstream of these masks began with the initiation of air flow containing the contaminant through the containment chamber and therefore the initial measurements included start-up conditions. An alternative procedure would have been to allow compound concentration to reach a desired steady-state level and then begin pulling air through the sample column. However, we wanted to avoid contacting the mask sample with an unknown amount of compound prior to making downstream measurements. Furthermore, we were unable to match the sample times between the chamber and downstream PIDs and so would be unable to know when the downstream PID started sampling relative to the upstream PID samples.

For the reason stated above, the mass collected at breakthrough is a more accurate assessment of dual-use dust mask performance than breakthrough time. Theoretically, the mass of OV collected by activated carbon (AC) is directly related to the mass of AC present, the ambient temperature, the partial pressure of the OV, and the adsorption potential of the AC for a particular OV.[17] Given a constant temperature,

Table 4. Average (and standard deviation) time (min) and mass (μg) collected at 50% breakthrough for Mask C subjected to two concentration levels of acetone, perchloroethylene, and ammonia at 50% RH and 25 °C or 95% RH and 25 °C.

		Concentration, ppm / RH %		
		15 / 50	50 / 50	50 / 95
Acetone (n = 3)	Time, min	232.0 (16.5)	121.3 (10.6)	39.7 (10.2)
	Mass, μg	6,717 (393)	9,230 (2217)	4,776 (3019)
Perchloroethylene (n = 3)	Time, min	>480	404.7 (95.7)	144.7 (38.4)
	Mass, μg	NA*	34,410 (10718)	12,097 (2612)
Ammonia (n = 2)	Time, min	10.5 (4.9)	3.0 (2.8)	21.0 (1.4)
	Mass, μg	54 (37)	50 (66)	481 (106)

*50% breakthrough was not achieved within 480 min, therefore a mass collected comparable to the other trials could not be obtained.

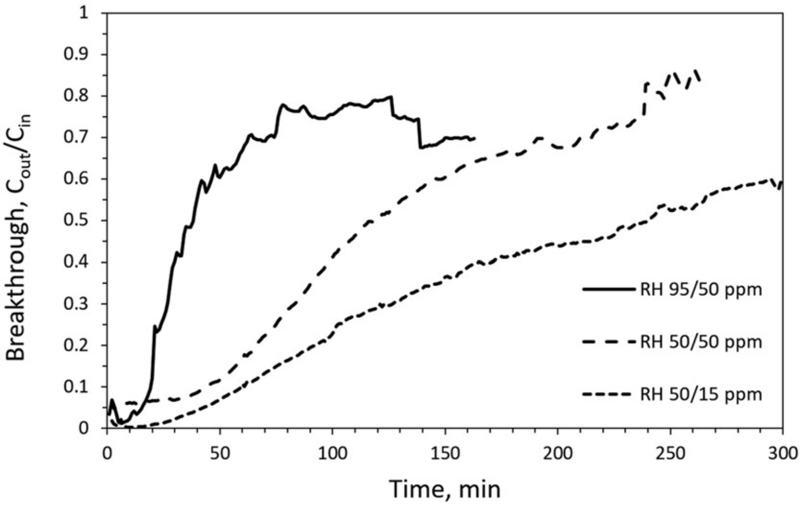

Figure 5. Example breakthrough curves for Mask C with changes in humidity between 50% and 95% RH and and changes in acetone concentration between 15 and 50 ppm.

negligible difference in partial pressure between 15 ppm and 50 ppm, and, very likely, the same type of AC with the same adsorption potential in each mask, then the mass of compound adsorbed was essentially a function of the mass of AC in each dual-use dust mask. Furthermore, the mass of a compound collected by a dual-use dust mask during the time to reach 50% breakthrough is independent of contaminant concentration and therefore should be equivalent for the two compound concentrations tested. The variations in mass collected between the two concentration levels at the same humidity level therefore represent variation in the amount of AC between dual-use dust mask sections applied to the pass-through column.

Therefore, the primary factor affecting breakthrough performance of these dual-use dust masks is the amount of AC impregnated within the mask material. The thickness of the layer of AC for a given mass of AC will also affect breakthrough time, with thicker layers having longer breakthrough times.[18] Although we could not accurately quantify the amount of AC in each mask type, it was evident from visual inspection that Mask C had the thickest layer of activated carbon with obvious granules of AC and also produced the best performance results. Masks A and B contained a thin layer of fabric with a dusting of AC.

As discussed previously, Rozzi et al.[13] conducted a similar study on three entire dual-use dust masks at 20 ppm and 37 LPM flow rate compared to the dual-use dust mask portions used in this study subjected to a flowrate comparable to 30 LPM if an entire dual-use dust mask had been used. Likewise, we assumed that the total mass of AC, and the thickness of that AC, was uniformly distributed throughout a dual-use dust mask so that breakthrough times associated with a portion of the mask could be compared to an entire mask. Rozzi et al. used benzene, toluene, and xylene. These OVs have vapor pressures ranging from 10–84 mmHg at room temperatures and are therefore comparable to perchloroethylene. They reported 10% breakthrough times ranging from 91–150 min for a dual-use dust mask very similar to Mask C, which suggest that the 50% breakthrough times reported here that approach or exceed 480 min (8 hr) are reasonable.

As expected, results here demonstrate that OVs with a lower molecular weight and higher vapor pressure have decreased breakthrough times. For example, perchloroethylene (vapor pressure = 14 mmHg), adsorbed to the AC much more readily than acetone (vapor pressure = 180 mmHg) resulting in much longer breakthrough times. Ammonia has low molecular weight, polarity, and high volatility, which greatly reduced its adsorption onto AC. Respirator cartridges to protect against ammonia exist although their adsorbent material type is uncertain because it constitutes proprietary information. However, patents for these adsorbents indicate that they consist of AC impregnated with metals such as copper and zinc.[19,20] Regardless, ammonia serves as a worst-case gaseous compound when using dual-use dust masks. It is also notable that acetone breakthrough curves typically stabilized around 80% (Figure 5). Stabilization below 100% may occur because, as the carbon pores become occupied by more acetone, the respirator begins to "off gas" at the same rate that it adsorbs new acetone.[21]

Data showed that OV contaminant breakthrough times at 95% RH were much shorter when compared to ambient room RH at the same concentration. This was expected given the ability of water vapor molecules to compete for adsorption sites on AC.[17,22] However, water vapor may enhance ammonia capture. Ammonia has a high affinity for water and therefore can be readily absorbed into water that has adsorbed onto filter media.[23]

Limitations of this study include the following. Breakthrough trials were conducted without consideration of potential mask leakage and were therefore solely focused on the adsorption capabilities of the dual-use dust mask media. The study was conducted over several months and tested a range of conditions (three dual-use dust masks, three vapor concentrations, and three vapors). The large range of conditions and length of time required to obtain one measurement (up to 4 hr) prevented the opportunity for a large number of trials for each condition. Breakthrough times measured represent those obtained with the test system described, which was unable to instantaneously obtain a desired steady-state concentration level (Figure 3). The breakthrough times reported are therefore longer than if the dual-use dust mask was immediately subject to the steady-state concentration. Likewise, the testing method did not include a cyclic-flow system to mimic human breathing. Such a system would likely result in increased breakthrough times by a factor of two given that the exhalation time, in which no OV went through the media, would be equal to the inhalation time. Although ambient relative humidity was a factor in this study, the effect of humidity exhaled from a user of a dual-use dust mask, was not evaluated.

Conclusion

Organic vapor breakthrough times varied considerably between the three dual-use dust masks evaluated in this study. Breakthrough times were dependent on concentration, humidity, and molecular characteristics of the vapor. As expected, breakthrough times were inversely related to OV concentration. Breakthrough curves were shifted left with higher ambient humidity, when all other conditions were held fixed, indicating decreased breakthrough times for high humid environments. Likewise, breakthrough times lengthened for organic vapors with low vapor pressures. None of the dual-use dust masks could provide extended protection from ammonia vapors although high humidity enhanced its capture by AC. Although not measured directly, visual observation indicated that the dual-use dust mask exhibiting the longest breakthrough times also had the most AC mass per area. This dual-used dust mask, the 3M Model 8514, was capable of 50% breakthrough times that exceeded an 8-hr workshift for a low vapor pressure OV (perchloroethylene) at a concentration level that was 15% of its PEL. These results suggest that testing should be conducted to determine that the OV exposure level is well below an OEL before considering their use in a workplace.

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