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The use of face masks to reduce inhalation exposure to reactive disinfectants

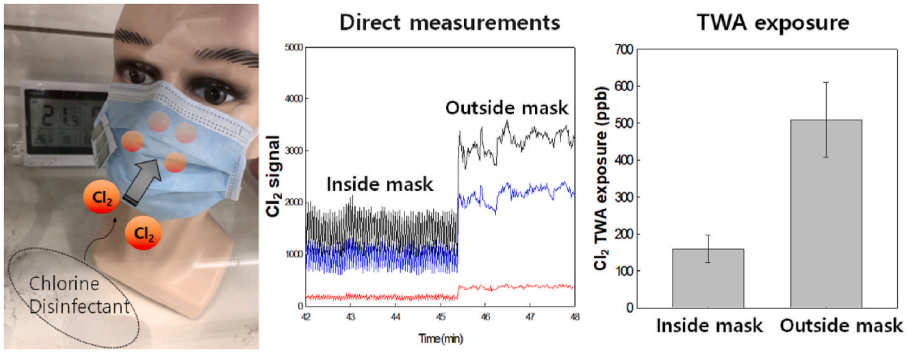
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HIGHLIGHTS

- Wearing face masks reduces inhalation exposure to reactive disinfectants.
- The preventive effect of the mask on VOC inhalation was not significant.
- Exposure reduction of chlorinated gases by masks was confirmed by a panel study.
- Face masks cannot prevent inhalation exposure to trichloramine as much as chlorine.
- Wearing face masks can be a universal means to reduce inhalation of reactive gases.

GRAPHICAL ABSTRACT



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ABSTRACT

Following the COVID-19 pandemic, the use of face masks has become a "new norm" to avoid contagion. Although masks are effective in reducing aerosol transmission, including that of virus particles, studies on the effect of face masks on inhalation exposure to toxic substances are scarce. This study first reports that wearing fabric face masks reduces the inhalation of reactive chlorine gas generated from chlorine disinfectants. Effective chlorine concentrations both inside and outside masks while using a consumer product were compared quantitatively by two methods: real-time measurement using proton transfer reaction time-of-flight mass spectrometry and time-weighted average exposure concentration measured by passive air sampling. Chlorine gas levels within masks were significantly lower than those outside masks; this reduction was not as apparent for the two representative volatile organic compounds, ethylbenzene and trichloroethylene. Notable exposure reduction by wearing face masks was confirmed by a consumer panel of ten people carrying out routine bathroom clean-up. This result suggests that face masks may be a universal and cost-effective tool to reduce respiratory exposure to reactive harmful chemicals.

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1. Introduction

During the ongoing COVID-19 pandemic, the use of face masks has become an unexpected part of daily life to prevent the transmission of the severe acute respiratory syndrome coronavirus 2 (SARS-CoV-2). Several studies have reported that face masks and social distancing effectively reduce the transmission of SARS-CoV-2 (Mitze et al., 2020; Cheng et al., 2021) as well as other circulating infections such as the influenza and respiratory syncytial viruses (Baker et al., 2020). Recent studies have also focused on the effectiveness of face masks on preventing exposure to particulate matters (Singh et al., 2010; Shen et al., 2021). As face masks are based on fabric filters, protection against particulate matter is expected. However, few studies have investigated whether wearing face masks reduces inhalation exposure to other indoor toxic substances, including volatile organic compounds (VOCs) and reactive disinfectant gases. Even after COVID-19 pandemic ends, it is likely that many people will continue to wear face masks indoors (e.g., workplace and public places) and outdoors; particularly after learning that they are a cheap and highly efficient means to protect respiratory health.

Many indoor VOCs and reactive gases are associated with human health impacts such as cancer, asthma, and respiratory irritation (Nazaroff and Weschler, 2004; Gligorovski and Abbatt, 2018; Qin et al., 2021), and even the maternal exposure to air pollution can induce abortion or birth defects (Ha et al., 2018; Zhang et al., 2019). Frequent cleaning of surfaces in households and workplaces using disinfectants is highly effective in preventing viral infections and is highly recommended by the World Health Organization (WHO, 2020). With these current guidelines, the demand for disinfectants has increased; the most popular active ingredient among disinfectants is sodium hypochlorite (NaOCl) (EPA, 2022). Improper usage of chlorine disinfectants is known to increase the concentration of toxic chlorinated gases, such as chlorine (Cl_2) and hypochlorous acid (HOCl), causing severe injuries to the lungs when inhaled (Gorguner et al., 2004; White and Martin, 2010; Kim et al., 2014). Therefore, it is important to evaluate the protective effects of face masks in terms of inhalation exposure to indoor chemicals according to the increasing use of face masks and disinfectants after the COVID-19 pandemic.

To address this requirement, we previously developed a passive air sampler (PAS) for estimating time-weighted average (TWA) concentrations of chlorinated gases generated from chlorine disinfectants (Ha et al., 2021a). It has been considered that the PAS is a powerful tool for monitoring the individual exposure to various compounds, ranged from high exposure levels to low exposure levels, both indoors and outdoors. The PAS has been developed mainly for estimating volatile organic compounds (VOCs), which are non-reactive, while PAS for reactive gases are still rare. The PAS developed in our previous study (Ha et al., 2021a) is consisted with polydimethylsiloxane (PDMS) as a gas permeable medium and *o*-dianisidine doped inside the PDMS. Table S1 in Supplementary Material summarizes molecular structures and characteristics of the PAS components used in this study. Since *o*-dianisidine is a redox dye, the PAS changes its color from transparent to green after the oxidation reaction with chlorine and hypochlorous acid gases. Thus, exposure concentrations can be estimated with the color development. In the previous study (Ha et al., 2021a), the sampling rate of PAS was successfully obtained with aid of direct measurement of chlorine concentration with proton transfer reaction mass spectrometer (PTR-MS) and PAS extraction. Thus, in addition to color change, extraction of PAS provides a more accurate estimate of exposure concentrations. The PAS successfully applied to determine chlorine equivalent concentration generated from different type of disinfectants (e.g., spray, liquid, and gel type) via chamber studies (Ha et al., 2021b).

The objective of this study is to investigate the effects of face masks on inhalation exposure to chlorinated gases generated from chlorine disinfectants. Exposure to effective chlorine was quantified using two methods: (i) real-time measurement using a proton transfer reaction time-of-flight mass spectrometer (PTR-TOF-MS); and (ii) time-weighted average (TWA) exposure using a PAS for reactive chlorine gases. Previous studies (Wu et al., 2021; Ha et al., 2021a) successfully conducted real-time measurements of chlorinated gases, such as chlorine and chloramines, using PTR-TOF-MS. In addition, a panel study was conducted recruiting ten consumers to compare the effects of face masks on inhalation exposure of chlorine gas in household and in a laboratory chamber. Furthermore, other chlorinated byproducts generated from chlorinated disinfectant were analyzed and compare the mask effects on the inhalation exposure to chlorine gas and one major chlorinated byproduct, nitrogen trichloride (NCl_3).

2. Materials and methods

2.1. Materials

To prepare the PAS, polydimethylsiloxane (PDMS) sheets (product number: SSP-M823-024, thickness: 0.61 mm) were purchased from Specialty Silicon Products Inc. (Ballston Spa, NY, USA) and *o*-dianisidine was obtained from Sigma-Aldrich (St. Louis, MO, USA).

Three different types of disposable face masks were used for the mask test: KF94 white, KF94 black, and surgical masks. KF94 refers to a Korean standard of 94% filtering efficiency, which is near equivalent to the United States N95. A KF94 white mask (model: Tamssa daily mask) and a surgical mask (model: Kleenex dental mask) were selected because these models are the best-selling products for Coupang, a Korean e-commerce company. Additionally, a KF94 black mask from the same model (Tamssa daily mask) was used to test whether the black dye in the face mask affected chlorinated gas filtration through the mask. A polyethylene mask guard (Chaeum Company, Paju, Republic of Korea) was also used to deploy a PAS inside the face masks. Morphology and structure of mask filter were observed with field emission scanning electron microscope (FE-SEM, JEOL Ltd., Tokyo, Japan) after platinum-coating (Each layer of masks was cut into approximately 0.5 cm × 0.5 cm pieces). The details of face masks and SEM images of three layers of face masks used in this study are summarized in Table 1 and Fig. S1 (Supplementary Material), respectively, while Fig. S2 (Supplementary Material) illustrates the mask guard and the PAS deployment inside and outside the face mask.

Spray-type bleach containing 1.7% sodium hypochlorite (LG Household & Health Care, Ltd., Seoul, Republic of Korea) was used as the representative chlorine disinfectant (bleach); this product is commercially available online and offline. All solvents used in this study were of analytical grade. Reagent grade ethylbenzene and trichloroethylene (TCE) were purchased from Sigma-Aldrich (St. Louis, MO, USA).

Table 1
Three types of facemasks used in this study.

Face mask type	KF94 (White)	KF94 (Black)	Surgical
Model	Tamssa daily mask	Tamsaa daily mask	Kleenex dental mask
Level	KF94[a]	KF94	None (Surgical mask)
Layer	Three layers	Three layers	Three layers
Filter	Polypropylene filter (nonwoven fabric)	Polypropylene filter (nonwoven fabric)	Super electrostatic filter
Valve	No	No	No
Nose wire	Yes	Yes	Yes
Picture			

[a] KF94 refers to a Korean filter with a filter efficiency of 94% which is almost equivalent to U.S. N95.

2.2. Passive air sampler (PAS) preparation

The method for preparing the PAS has been previously described (Ha et al., 2021a, 2021b). In brief, a PDMS sheet (thickness: 0.61 mm) was cut into 1.5 × 1.5 cm pieces and cleaned by immersing in *n*-hexane and methanol. Then, *o*-dianisidine was doped inside clean PDMS pieces by soaking the PDMS overnight in a toluene solution with an *o*-dianisidine concentration of 0.5 g L^{-1}. The resultant PDMS pieces were taken from the solution and air-dried for 2 h. Finally, the *o*-dianisidine remaining on the PDMS surface (not doped inside the PDMS), was cleaned with methanol.

For one PAS patch, three individual *o*-dianisidine-doped PDMS pieces were attached to white paper using a stapler. To prevent possible reaction of *o*-dianisidine with other contacting materials, doped PDMS were fixed physically using a stapler (Ha et al., 2021a). All PAS patches were stored in vacuum packaging prior to use to prevent unknown reactions with ambient air.

2.3. Chamber study

To investigate the effects of face masks on inhalation exposure to chlorinated gases, a mask test was set up in a 125 L acrylic chamber; Fig. 1(a) presents an image of the experimental set-up and a schematic diagram representing the human respiratory system. A vacuum pump (Korea Ace Scientific, Seoul, Republic of Korea) and an air generation pump (SK TECH, Namyangju, Republic of Korea) were connected to cycling timers (ELECTEL, Seoul, Republic of Korea, 1.5 s per cycle was used (Shen et al., 2021)), to mimic inhalation and exhalation, respectively. Each pump was connected to an airflow meter (Sungho Sigma, Suwon, Republic of Korea) to adjust the respiratory rate. A representative respiratory rate of 15 L min^{-1} was used, assuming light intensity activities based on the Exposure Factors Handbook by the United States Environmental Protection Agency (EPA, 2011).

A face mask and a mask guard with PAS patches were mounted on the 540 mm-sized mannequin head, and the respiratory-mimicking system was connected to the mannequin. To maximize the fit of the masks on the mannequin head, a mask joint as shown in Fig. S3 (Supplementary Material), was used for all experiments. One PAS patch was attached to the mask guard and placed inside the face mask and the other PAS patch was attached to the outside of the face mask. PAS patches affixed inside and outside the mask are shown in Fig. S2. The bleach was sprayed on the bottom of the chamber approximately 15 times (Fig. 1(b)), then the respiratory system was switched on. The proton transfer reaction time-of-flight mass spectrometry (PTR-TOF-MS) was connected to the top of the chamber for the first 40 min to monitor the generation of chlorinated gases. After 40 min, the PTR-TOF-MS port was moved inside the face mask for 5 min, then moved outside the face mask (the PTR-TOF-MS port was manually fixed approximately 10 mm away from the mannequin nose), for 5 min to measure gas concentrations inside and outside the mask (Fig. 1(c)). Then, the port was connected to the top of the chamber for 10 min (results are shown in Section 3.1). The face mask and the mask guard were carefully removed 60 min into the experiment, and color changes in the samplers were evaluated. For PAS extraction, each individual PAS was removed from the patch and placed into a glass vial containing 10 mL isopropyl alcohol; this was left overnight for spectrophotometric analysis.

To monitor chlorine and other chlorinated gases inside the face mask (results are shown in Section 3.4), the sampling port of the PTR-TOF-MS was first placed inside the face mask for 60 min after spraying bleach on the bottom of the chamber. The port was then moved outside the mask for 10 min, and connected to the top of the chamber for 10 min. The respiratory-mimicking system was established using the method

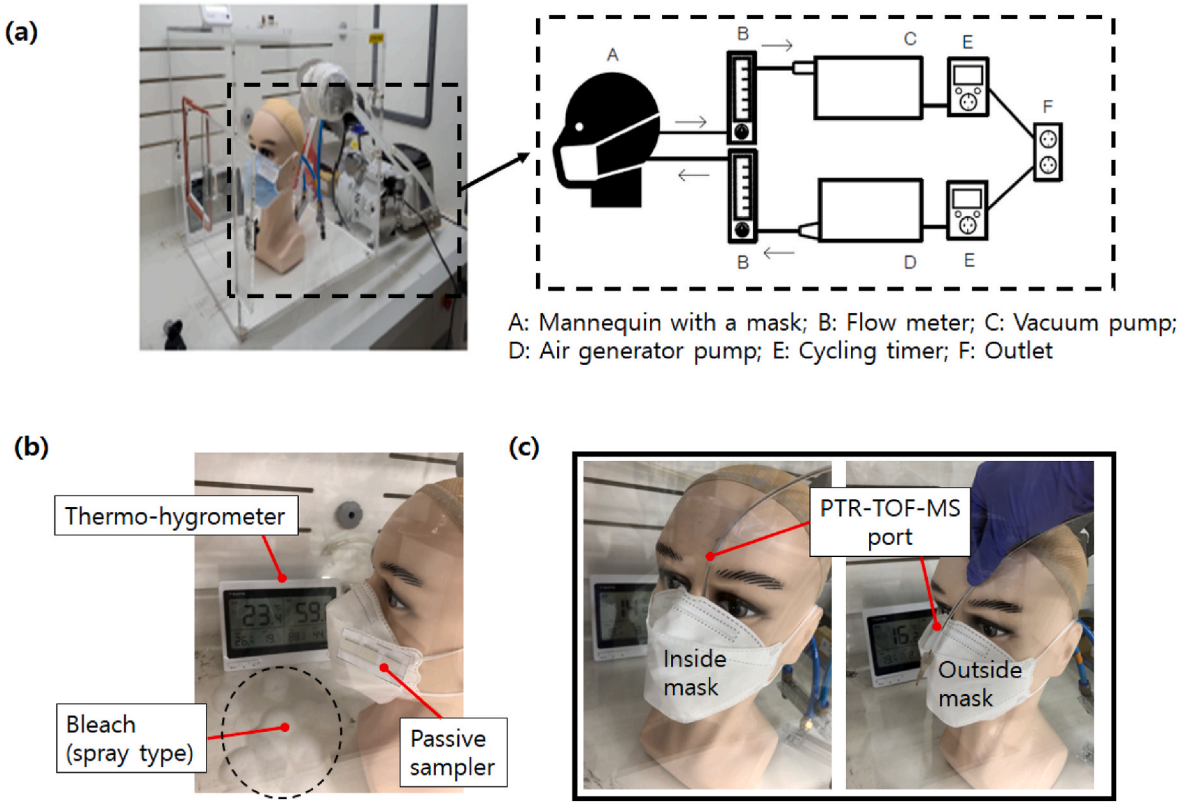


Fig. 1. Experimental set-up for the chamber study. (a) Schematic of the mask test set up in a 125 L acrylic chamber utilized. To mimic the human respiratory system, a vacuum pump (for inhalation) and an air generator pump (for exhalation) were used, and a cycling timer was used to control respiratory rates; (b) images of the thermo-hygrometer, mannequin with a mask deploying a passive air sampler patch, and bleach spraying on the bottom of the chamber; (c) location of the PTR-TOF-MS port used to measure gas concentrations inside and outside masks.

described above. Finally, the respiratory system was switched off, and the PTR-TOF-MS was transferred inside the face mask for 1 min, and then outside mask for 1 min. This was carried out rapidly to check for signal differences inside and outside masks via gas diffusion through the masks.

The amount of bleach was calculated by measuring the mass before and after treatment. The temperature and humidity inside the chamber were monitored throughout the experiment using a thermo-hygrometer (DAIHAN Scientific, Wonju, Republic of Korea) (Fig. 1(b)). The mass of bleach used in each chamber ranged from 12.3 to 14.0 g. The temperature and relative humidity ranges in the chamber at the beginning of the experiment were 12.0–16.5 °C and 26–59%, respectively. Although temperature in the chamber did not change significantly during the experiment, the relative humidity increased by 20% due to the evaporation of the bleach.

Two volatile organic compound (VOC) gases (i.e., ethylbenzene and trichloroethylene (TCE)) were selected to compare the mask effects on inhalation exposure to VOCs and reactive chlorine gases. The 10 μL of 866 ppm (ethylbenzene) or 1460 ppm (TCE) of each standard solution in ethanol was placed on the bottom of the 125 L acrylic chamber containing a face mask-mounted mannequin and the respiratory system. After switching the respiratory system on, the gas signal was monitored by connecting a PTR-TOF-MS port on the top of the chamber (~17–18 min). This port was placed inside a face mask (5 min), outside the face mask (5 min), top of the chamber (5 min), and inside the mask by turning off the respiratory system to confirm that VOC gases freely diffused inside face masks.

2.4. Estimation of the time-weighted average (TWA) of chlorine equivalent gas using a PAS

In our previous study (Ha et al., 2021a), the sampling rate of the PAS was obtained using two methods: (i) measuring the chlorine gas concentration using proton transfer reaction/selective reagent ionization-mass spectrometry (PTR/SRI-MS); and (ii) measuring the mass of chlorine gas reacted with *o*-dianisidine doped inside the PDMS after extracting PAS. The steps used to determine the sampling rate of the PAS are described in a previous study (Ha et al., 2021a), and the resultant sampling rate is 0.00253 $m^3\ h^{-1}$.

To estimate the time-weighted average of chlorine equivalent gas by deploying PASs, the extraction solution of each PAS was analyzed using a UV/Vis spectrophotometer (OPTIZEN, Daejeon, Republic of Korea). The mass of chlorine gas reacting with *o*-dianisidine ($M_{sampled}$) was first calculated based on the increased mass of the oxidized form of *o*-dianisidine in the PAS; this is due to the oxidation reaction with chlorinated gases after sampler extraction (Equation (1)):

$$M_{sampled}(mol) = \left(C_f - C_i\right) \times V_E \times \frac{1}{2} \quad (1)$$

where C_f and C_i are the final and initial oxidized *o*-dianisidine concentrations in the extraction solvents, respectively (mol L^{-1}); and V_E is the volume of the extraction solvent (0.01 L). C_f and C_i were calculated based on absorbance at 429 nm via UV/Vis analysis and the ratio of reduced mass of *o*-dianisidine to 429 nm absorbance obtained in the chamber test when performed for the determination of the sampling rate. It was assumed that the mass of oxidized *o*-dianisidine was proportional to the decreasing *o*-dianisidine after exposure to chlorinated gas. C_i was obtained after extracting control PASs that were not exposed to chlorinated gases, and the 429 nm absorbance of the control PASs was approximately 0 for every experiment ($C_i = 0$). A factor, ½, is the stoichiometric ratio of oxidized *o*-dianisidine to Cl_2.

The time-weighted average of chlorine gas (C_{TWA}) was obtained from Equation (2):

$$C_{TWA}\left(mol\ Cl_2 m^{-3}\right) = \frac{M_{sampled}}{R_s t} \quad (2)$$

where R_s is the sampling rate of the PAS (0.00253 $m^3\ h^{-1}$); and t is the deployment time (h). The ideal gas equation was applied for the unit conversion of C_{TWA} from mol $Cl_2\ m^{-3}$ to ppb.

A previous study (Ha et al., 2021a) calculated C_{TWA} values based on the reduction in the *o*-dianisidine mass; however, we found that the decrease in *o*-dianisidine in the mask test in the chamber and panel studies using respiration was not proportional to the color change in the PAS. This is potentially due to other gas components in the exhalation, whereas the increase in the oxidized *o*-dianisidine mass was approximately proportional to color change. Thus, this study estimated the C_{TWA} based on the increased amount of oxidized *o*-dianisidine.

2.5. PTR-TOF-MS analysis

Analysis of chlorinated gases in the chamber test was conducted using PTR-TOF-MS (IONICON, Innsbruck, Austria), in which O_2^+ as the selective reagent ion. Essentially, O_2^+ ion has a higher ionization energy (12.1 eV) compared with the equivalent for Cl_2 (11.5 eV). Thus, chlorine gas is analyzed through an electron transfer reaction ($O_2^+ + Cl_2 \rightarrow O_2 + Cl_2^+$) and confirmed by mass spectra along with the natural expected isotopic ratios of ^{35}Cl to ^{37}Cl. For the ion signals of Cl_2, mass to charge ratios (m/z) at 69.9378, 71.9348, and 73.9318 with a ratio of 9:6:1 were analyzed.

Under the O_2^+ mode, the O_2^+ ion was provided through a connection with O_2 gas of ultrahigh purity (99.995%, Hankook Special Gases, Iksan, Republic of Korea) at a gas flow rate of 6.00 $cm^3\ min^{-1}$. The inlet temperature, E/N ratio, and pressure of the drift tube were set as 80.0 °C, 137 Td, and 2.3 mbar, respectively. For m/z analysis, two-point mass axis calibration ($m/z = 19.0178$ and 329.8308) was conducted every 30 s according to manufacturer's instructions. To confirm that the PTR-TOF-MS responses linearly increased with chlorine gas concentration, 1 mL of NaOCl standard solution (available chlorine 10–15%, Sigma Aldrich, St. Louis, MO, USA) was sequentially added to the 0.4 M hydrochloric acid solution (500 mL). Fig. S4(a) (Supplementary Material) shows that 1 mL NaOCl solution led to a dramatic and immediate increase in the PTR-TOF-MS signal, and this signal decreased to a certain level and remained constant for 10 min. The observed ratios of $^{70}Cl_2$, $^{72}Cl_2$, and $^{74}Cl_2$ were approximately 9:6:1 throughout the experiment. The average PTR-TOF-MS signal summation of $^{70}Cl_2$, $^{72}Cl_2$, and $^{74}Cl_2$ linearly increased with the volume of the NaOCl solution; the R^2 of the linear regression was 0.9943 (Fig. S4(b)).

Among the various chlorinated gases generated from chlorine disinfectants, NCl_3 was the major gas because the PTR-TOF-MS signals representing NCl_3 were highest compared with other signals. The PTR-TOF-MS signals of NCl_3 (m/z = 118.9096, 120.9067, 122.9037, 124.9001), and NCl_2^+ (m/z = 83.9408, 85.9378, 87.9349) were considered signals for NCl_3. This was because a previous study recognized NCl_2^+ as a fragment of NCl_3 when O_2^+ was used as the reagent ion (Wu et al., 2021).

For the PTR-TOF-MS measurement of two representative VOCs (i.e., ethylbenzene and TCE), the H_3O^+ mode was applied; the gas flow rate, inlet temperature, E/N ratio, and the pressure of the drift tube were set as 6.00 $cm^3\ min^{-1}$, 80.0 °C, 140 Td, and 2.3 mbar, respectively. The m/z values of 107.0855 ($(C_8H_{10})H^+$) and 132.9187 ($(C_2HCl_3)H^+$) were used to analyze ethylbenzene and TCE, respectively.

2.6. Consumer panel study

To investigate the effect of face masks on inhalation exposure during the cleaning of household bathrooms using a spray-type bleach, a consumer panel study was conducted. This involved recruiting a panel of ten volunteers (five from Cheongju, Republic of Korea, and five from Gimhae, Republic of Korea) for December 26–29, 2021. Two types of masks, a KF94 (white) and surgical mask (described in Table 1), were used for five volunteers each. The package for each volunteer included

two PAS patches (for deploying outside mask and inside the mask), a mask (KF94 (white) or surgical), a mask guard, a spray-type chlorine disinfectant (LG Household & Health Care, Ltd., Seoul, Republic of Korea), six 10 mL isopropyl alcohol containing glass vials, tweezers for detaching PASs from the patch, and laboratory gloves; it was delivered to the residence of each participant. PAS patches were sealed with vacuum packing to prevent any reactions between *o*-dianisidine and the gas components in ambient air. Each panel was first asked to wear a face mask by deploying PAS patches inside and outside the face mask. Then, they cleaned their bathrooms (all panels possessed one or two bathrooms in their residence) using a bleach product. Upon the completion of cleaning, participants were asked to record the cleaning time, whether they turned on the ventilation system, and the type of cleaning work (e.g., cleaning a toilet, bath tub, washstand, floor/wall tiles, and mold removal). With an exception of one participant (Surgical mask panel #1), all participants turned on the ventilation system during cleaning and they carried out similar types of cleaning. Then, an image of each PAS patch was captured to check color changes on the patch; subsequently, each PAS was placed in a glass vial containing isopropyl alcohol. All glass vials and disinfectants were transported back to the laboratory for UV/Vis analysis to measure the amount of disinfectant used during cleaning. This panel study was approved by the Institutional Review Board (IRB) of Korea University (approval number: KUIRB-2021-0423-01).

3. Results and discussion

3.1. Effects of face masks on the inhalation exposure to the chlorine gas generated from a consumer disinfectant

The mask test was set up within a custom-made 125 L acrylic chamber with a mannequin that mounted a face mask. Fig. 2(a) and (b) show a continuous increase in the PTR-TOF-MS signals for chlorine isotopes in the 125 L chamber, confirming the generation of chlorine gas from the chlorine disinfectant. Once the PTR-TOF-MS sampling port was moved inside the mask, the chlorine gas signals significantly decreased, then increased again once the port was moved outside the mask (approximately 1 cm away from the mannequin nose). These results indicate that the KF94 (white) and surgical masks effectively reduce the exposure to chlorine gas generated from the consumer disinfectant despite the difference in pore size in the outer layers of KF94 (white) and surgical masks shown in SEM images (Fig. S1). Reduced chlorine gas exposure from wearing face masks was also confirmed through the deployment of PASs inside and outside the face masks. The PASs

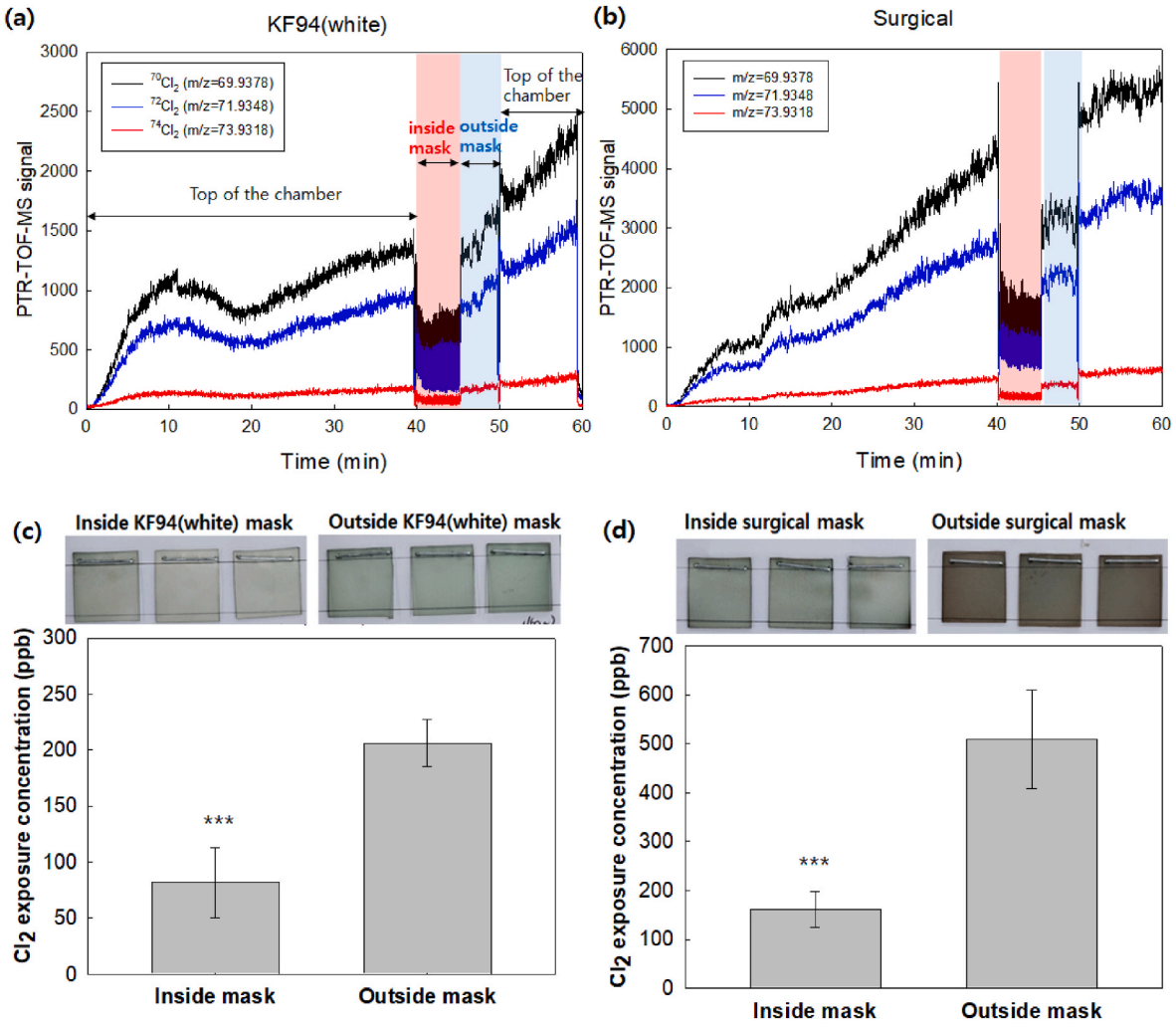


Fig. 2. Effects of face masks on the inhalation exposure of chlorine gas generated from bleach. Instantaneous chlorine signals inside and outside (a) KF94 (white); and (b) surgical face masks measured by PTR-TOF-MS signals. Passive air samplers were deployed inside and outside face masks: color development of passive air samplers; and mean values of chlorine gas equivalent exposure concentrations obtained from samplers using (c) a KF94 (white); and (d) a surgical face mask, respectively. Chlorine gas equivalent concentrations inside masks significantly differed from concentrations outside masks. ***$p < 0.005$ obtained from the Student's *t*-test. Error bars indicate the standard deviation of triplicate analyses.

attached inside the masks had less color development than those outside the masks (Fig. 2(c) and (d)). Specifically, the TWA chlorine equivalent exposure inside masks was significantly lower than that outside masks based on the extraction of samplers; for example, the Cl_2 equivalent TWA through the KF94 (white) mask was 81.8 ± 31.5 ppb, while that outside this mask was 206 ± 21 ppb (Fig. 2(c) from triplicate analyses each). The Cl_2 equivalent exposure concentration through the surgical mask was 161 ± 37 ppb, while that outside the mask was 509 ± 101 ppb (Fig. 2(d) from triplicate analyses each). The KF94 (black) face mask was also applied to investigate whether potential reactions between the chlorine gas and black dyes within the mask affects inhalation exposure to chlorine gas (Fig. S5). The PTR-TOF-MS signals for chlorine gas and chlorine equivalent exposure concentrations inside the KF94 (black) mask were significantly lower than those outside the mask (the Cl_2 equivalent TWA inside the KF94 (black) mask was 63.7 ± 32.8 ppb, while that outside the mask was 136 ± 18 ppb, $p < 0.05$ obtained by

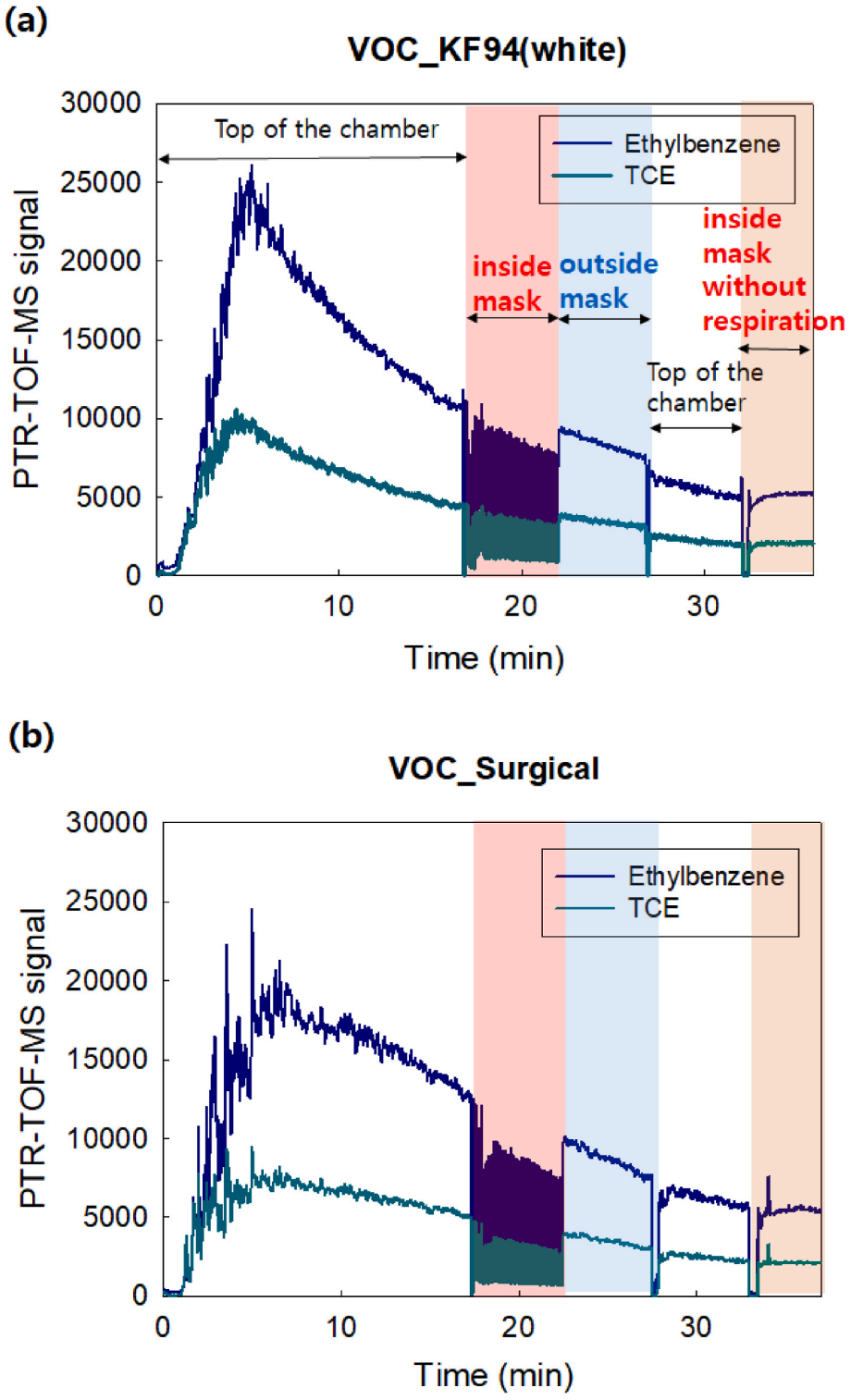


Fig. 3. Effects of face masks on the inhalation exposure of two representative volatile organic compounds (VOCs): ethylbenzene and trichloroethylene (TCE). Instantaneous PTR-TOF-MS signals for ethylbenzene and TCE inside and outside (a) KF94 (white); and (b) surgical face masks.

Student's *t*-test); however, the black mask did not show any unique effects on inhalation exposure to chlorine gas compared to the KF94 (white) and surgical masks. The use of the PAS in chamber studies, we can confirm that the PAS effectively assesses the impact of face masks on chlorine gas respiratory exposure while excluding other confounding factors generated during bathroom cleaning such as other contaminants and chemical reagents (e.g., diffusers).

Due to the high reactivity of chlorine, chlorine generated from bleach exists both in the aerosol and gas phases. Indeed, Wong et al. (2017) have reported that aerosol particulate signals of chlorine increased during mopping a floor with a bleach solution possibly due to the partitioning to the indoor particulate matter and uptake of vapor chlorinated species. Since there is increasing evidence that face masks effectively prevent the penetration of virus laden aerosols and droplets (Tang et al., 2020; Liao et al., 2021) and particulate matters (Langrish et al., 2009; Faridi et al., 2020), face masks can also prevent the transport of aerosol particulate phases of chlorine. In addition, chlorine can rapidly react with chemicals on the surface and inside face masks synthesizing other gas species. For example, it is generally acknowledged that chlorine reacts with reactive dyes forming chlorinated organic compounds which have plausible eco/genotoxicity (Rajkumar and Kim, 2006; Vacchi et al., 2013). In this study, we tried to analyze other gas species near the mask surface and inside mask especially for face masks which have color (e.g., surgical mask and KF94 (black) mask) via PTR-TOF-MS, however, no significant evidence was found. For further studies, face mask extractions or head space analysis of face masks after exposing to chlorinated gases can be conducted to identify unknown disinfection byproducts. The chamber experiments were conducted at a broad range of humidity (17–90%), temperature (10–25 °C), and chlorine concentrations. However, no consistent differences in the reaction of gas transmission through the facemasks were observed based on these factors.

3.2. Effects of face masks on the inhalation exposure to volatile organic compounds (VOCs)

To evaluate exposure reduction by wearing masks, two representative VOCs, ethylbenzene and trichloroethylene (TCE), were selected based on their relatively high octanol-air partition constants (K_{oa}) (log K_{oa} of ethylbenzene and TCE are 3.74 and 2.99, respectively (Meylan and Howard, 2005)). The mask test set up was exactly same as the test for chlorine gas, and PTR-TOF-MS signals were monitored after dropping the standard solution of ethylbenzene and TCE on the bottom of chamber. Fig. 3 shows that the signals for ethylbenzene and TCE initially increased sharply due to the evaporation of the standard solution; however, after reaching a maximum, the signals continuously decreased because of the respiratory system with the inhalation rate of 15 L min^{-1}. When the sampling port of the PTR-TOF-MS was moved inside the mask, the mass signals of ethylbenzene and TCE were slightly lower compared to their outside mask equivalents for both KF94 (white) (Fig. 3(a)) and surgical masks (Fig. 3(b)). However, the signal differences of VOCs inside and outside masks were much smaller than those of reactive chlorine gas, shown in Fig. 2. It was also confirmed that VOCs freely diffused within the KF94 (white) and surgical face masks because these VOCs signals did not differ from signals outside the mask after turning off the respiratory outflow (Fig. 3). The sorptive removal of hydrophobic VOCs was negligible because the time scale of their diffusive penetration through masks was shorter than the sorption time scale (Singer et al., 2007).

Very recent studies have concerned that wearing face masks might increase inhalation exposure to volatile chemicals vaporized from the petroleum-derived polymer layer of face masks themselves (Jin et al., 2021; Liu et al., 2022), however, studies on effects of face masks on inhaled exposure to VOCs present indoors/outdoors are still scarce. To the best of our knowledge, one study (Chen et al., 2012) investigated effects of face masks on the inhalation exposure to polycyclic aromatic hydrocarbons (PAHs) in workplaces, demonstrating that face masks can reduce the exposure to particulate phase PAHs, but has no significant effect on vapor phase PAHs in a foundry and plastic industries. In addition, it was reported that fabric face masks have less preventive effects of naphthalene compared to three-ring or larger PAHs possibly due to the higher vapor pressure of naphthalene (Chang et al., 2020). Thus, it can be concluded that face masks are more preventive to chemicals bound to aerosols or particulate phases compared to vapor phase chemicals having low reactivity.

3.3. Protective effects of face masks on the chlorine gas exposure during bathroom clean-up

Table S2 summarizes results of the panel study including usage amount of disinfectants, cleaning time, pictures of PAS inside and outside masks, and chlorine equivalent TWA exposure inside and outside masks determined by the PAS extraction. As shown in Table S2, the color development of PASs attached to the outside of masks was significantly greater than that inside masks for all consumers, regardless of mask type, usage amount of disinfectants, and cleaning time. The mean values of the estimated chlorine equivalent exposure concentration outside of masks were higher than those inside masks (Fig. 4); for six panels, the chlorine gas concentration inside the mask was significantly lower than those outside the mask ($p < 0.05$ obtained by Student's *t*-test). Chlorine gas generation from chlorine based disinfectants is known to be dependent on various factors such as environmental (e.g., light, temperature, and humidity), pollution in the workplace, and working patterns (Wong et al., 2017; Mattila et al., 2020). This panel study demonstrated that KF94 and surgical face masks adequately reduce chlorine inhalation exposure during home disinfection activities regardless of those various factors.

3.4. Generation of volatile disinfection byproducts (DBPs)

Rapid reactions between chlorine disinfectants and surrounding chemicals inevitably generate reaction byproducts, including volatile disinfection byproducts (DBPs) that may be harmful when inhaled (Weaver et al., 2009; Wu et al., 2021). Recent studies have focused on mono-, di-, and trichloramines (NH_2Cl, $NHCl_2$, and NCl_3, respectively), which are well-known compounds formed via reactions between hypochlorous acid (HOCl) and nitrogenated compounds (e.g., NH_3). In particular, trichloride (NCl_3) has been reported as a compound of most concern for two reasons: (i) considerably higher NCl_3 concentrations are generated in the bleach headspace (Wong et al., 2017), bleach cleaning experiments (Wong et al., 2017; Mattila et al., 2020), and indoor swimming centers during a swimming event (Wu et al., 2021) because of its higher Henry's law constant (H) compared to other chloramines (summarized in Table S3); and (ii) NCl_3 is a well-known upper respiratory irritant (Jacobs et al., 2007; Kaydos-Daniels et al., 2008). Indeed, the chamber study results showed that NCl_3 had the highest PTR-TOF-MS signal compared to other potential inorganic chlorinated gases produced from bleach (listed in Table S3) (Fig. 5(a)). The NCl_3 concentration in the face mask was highest immediately after chlorine disinfectant was sprayed, indicating that gaseous NCl_3 may rapidly penetrate the face masks used in this study (Fig. 5(a) and Fig. S6). The scan mode of PTR-TOF-MS (m/z ranging from 60 to 130) was used to confirm that NCl_3 had the highest signals among possible DBPs inside and outside the face masks (Fig. 5(a)). Furthermore, the Cl_2 and NCl_3 signal differences between the inside and outside masks were detected after the respiratory system was turned off, as shown in Fig. 5(b). Notably, NCl_3 signal differences between the inside and outside masks was smaller than that of Cl_2, indicating that face masks cannot prevent inhalation exposure to NCl_3 as much as Cl_2. This was applicable even without respiration, in which the NCl_3 level inside the surgical mask was the same as that outside the mask (Fig. S6(c)); this is likely due to the lower reactivity of NCl_3. NCl_3 mainly exists in the gaseous phase and is

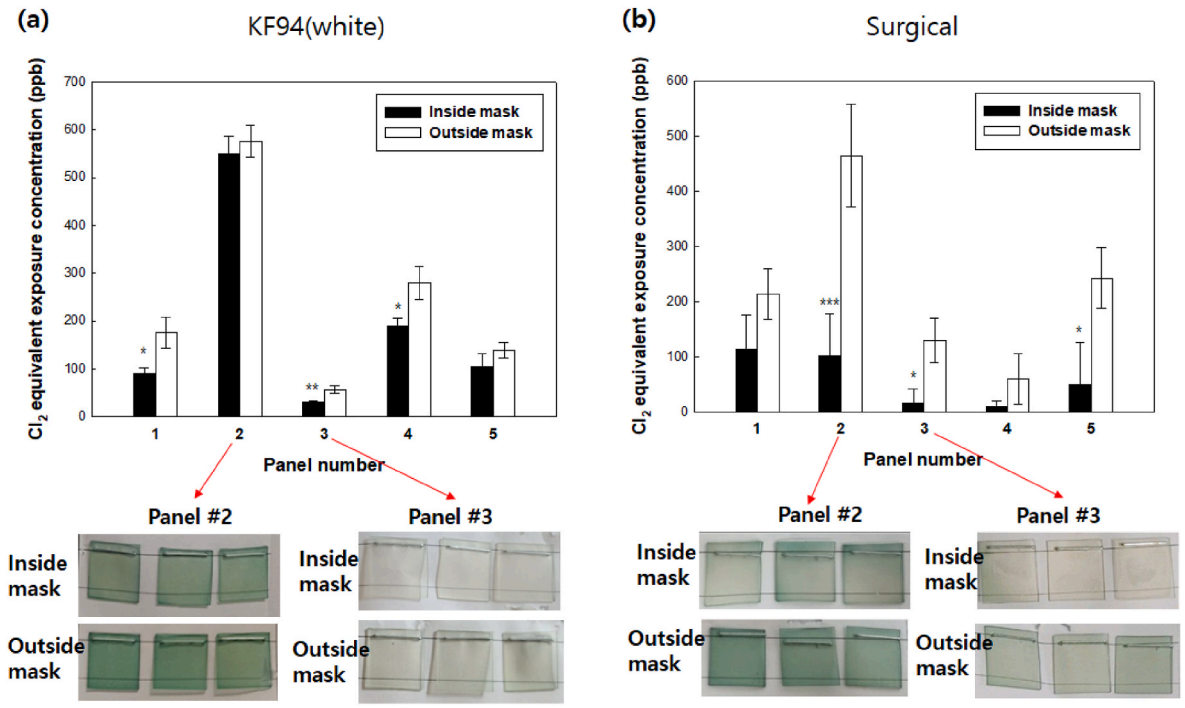


Fig. 4. Accumulative exposure of Cl_2 equivalent concentrations (mean values) inside and outside (a) KF94 (white); and (b) surgical masks while cleaning one or two restroom(s) in household apartments, and pictures of passive air samplers deployed inside and outside face masks. *Denotes that the exposure concentration outside the mask was significantly higher than that inside the mask (*$p < 0.05$, **$p < 0.01$, and ***$p < 0.005$ obtained from the Student's *t*-test). Error bars indicate the standard deviation of triplicate analyses.

less reactive (e.g., the oxidation-reduction potential (ORP) of chloramines is much smaller than the ORP of free chlorine (Devkota et al., 2000)). By contrast, Cl_2 exists as an aerosol chlorine potentially because of the partitioning or uptake of gaseous Cl_2 to indoor particulates (Wong et al., 2017); it then reacts with various chemicals nearby (e.g., various nitrogenated pollutants in the environment, and chemical dye in face masks). Other well-known DBPs synthesized from chlorine-based disinfectants (e.g., trihalamethanes and haloacetic acids) (Benjamin and Lawler, 2013) were also analyzed. However, this analysis rendered no significant evidence regarding the generation of these chemicals from bleach.

3.5. Environmental implications

The results of this study have important implications in that face masks effectively contribute to reducing inhalation exposure to reactive hazardous chemicals. As this study was limited to chlorinated gases, there is an urgent need for extending to the protective effects of face masks against the aerosol and gas phases of other reactive substances. During the COVID-19 pandemic, the number of calls received by the United States poison control centers indicate that bleaches and accidental inhalation exposures accounted for the largest percentage increases among all disinfectant usages and exposure routes, respectively (Chang et al., 2020). This indicates that people are concerned regarding the inhalation of toxic chlorinated gases during disinfection. The universal face mask mandate has been applied to many geographic regions, increasing its accessibility at lower prices. This study shows that inexpensive and commercially available face masks reduce inhalation exposure to chlorine gas generated from bleach in laboratory experiments and consumer panel studies. The PAS-derived chlorine equivalent concentration outside the masks of ten consumers ranged from 56.8 to 576 ppb. This range is lower than or slightly higher than the 500 ppb, the Acute Exposure Guideline Levels 1 reported by the National Research Council of the National Academics (NRC, 2009), or the permissible exposure limits of chlorine reported by the Occupational Safety and Health Administration (OSHA, 1981). By contrast, the chlorine levels inside masks were lowered by up to eight times. Although face masks may not guarantee a reduction in health damage, the results in this study show that wearing face masks is a universal and cost-effective means to reduce exposure to harmful reactive gases and ultimately reduce health expenses vis-à-vis indoor chemical exposure. At the same time, there have been raised concerns about increasing inhalation risk caused by wearing face masks because masks themselves contain chemicals that may have harmful health effects (Fernández-Arribas et al., 2021; Jin et al., 2021; Li et al., 2021; Liu et al., 2022). Thus, follow-up studies should focus on the mixture effects, including potential DBPs, face masks induced chemicals, and the removal of other harmful reactive gases.

Based on our investigation, we suggest that face mask can be used to reduce chlorinated gas inhalation, particularly in situations where the exposure level is below 500 ppb (e.g., cleaning and sanitizing bathrooms and public places under good ventilation systems). However, for workers who may be exposed to high concentrations of chlorine gas for long periods of time, the mask reduction effects are not proven in this study. In such cases, workers should wear masks specifically designed to protect against chlorine gas exposure.

4. Conclusion

For the first time, preventive effects of face masks were identified on the inhalation exposure to harmful reactive gases especially for chlorinated gases while using chlorine disinfectants. A chamber study with human respiratory mimicking system showed that common face masks against the COVID-19 pandemic reduce the inhalation of chlorine gas generated from a consumer product. On the other hand, the masks did not efficiently lower the exposure to conventional VOCs, diffusing freely through face masks. Trichloramine (NCl_3) was found to be the dominant chlorinated DBP under the experimental condition of this study. However, it is necessary to identify potential harmful byproducts under various use conditions formed via chlorine chemistry with indoor materials, fibers and residual chemicals in diverse face masks. In

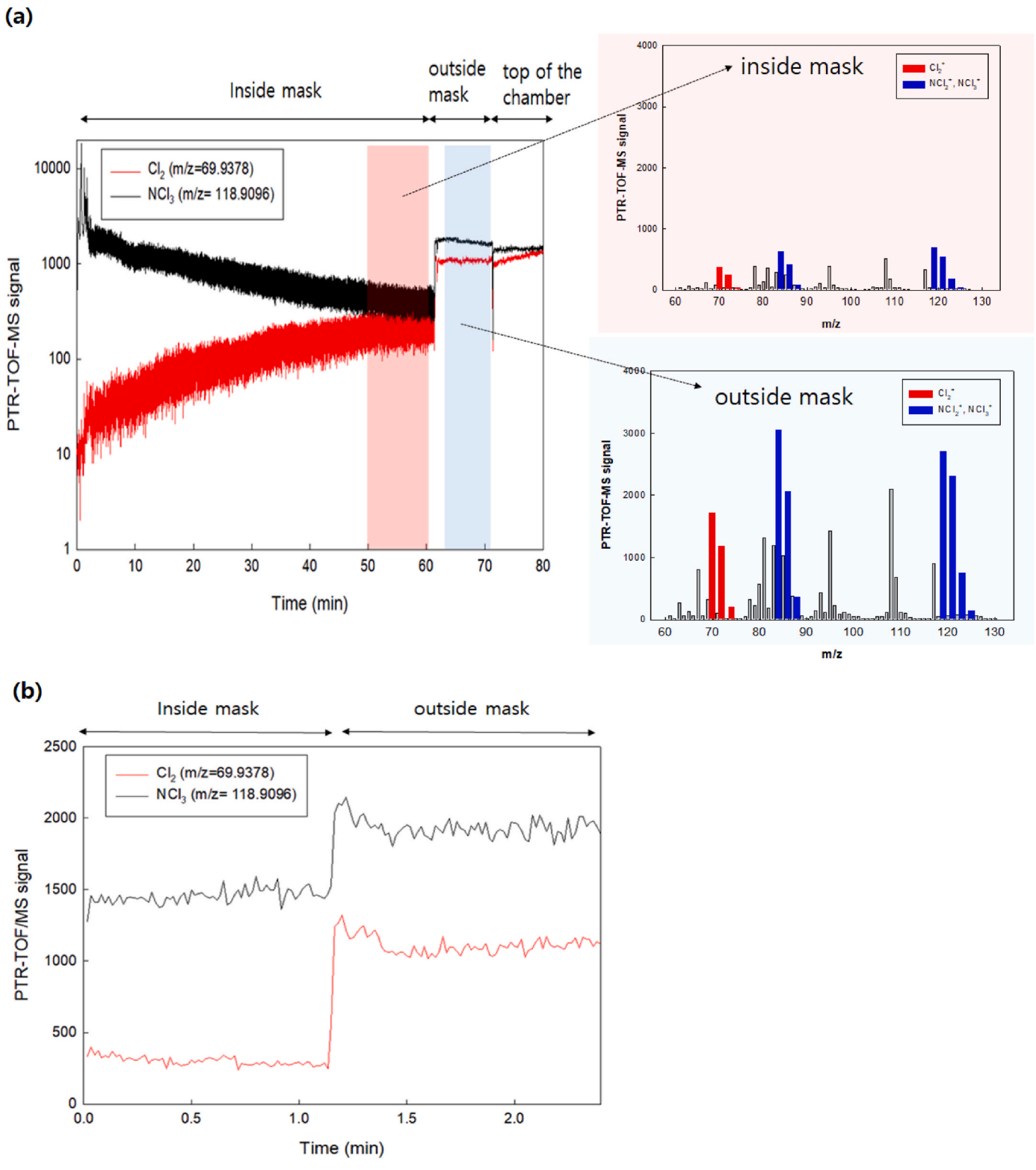


Fig. 5. Chlorine (Cl_2) and trichloramine (NCl_3) PTR-TOF-MS signals inside and outside KF94 (white) face masks: (a) instantaneous Cl_2 and NCl_3 PTR-TOF-MS signals and *m/z* profiles inside and outside masks; (b) comparison of Cl_2 and NCl_3 PTR-TOF-MS signal differences between inside and outside masks, after turning off the respiratory system.

conclusions, wearing face masks can effectively reduce the risk of harmful chlorine and nitrogen trichloride generated from disinfectants and it is urgently needed to evaluate the protective effects of face masks in more comprehensive studies.

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CRediT authorship contribution statement

Yeonjeong Ha: Conceptualization, Data curation, Investigation, Writing – original draft. **Yerim Koo:** Data curation, Investigation. **Dabin Kim:** Data curation, Investigation. **Pil-Gon Kim:** Data curation, Investigation. **Eugene Song:** Investigation, Methodology. **Hyun Jung Yoo:** Funding acquisition, Methodology. **Jung-Hwan Kwon:** Conceptualization, Funding acquisition, Supervision, Writing – review & editing.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data will be made available on request.

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.atmosenv.2023.120023.

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