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Development of a personal passive air sampler for estimating exposure to effective chlorine while using chlorine-based disinfectants

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Abstract

With an increasing use of indoor disinfectants such as chlorine (Cl_2) and hypochlorous acid, a convenient sampler for estimating exposure to oxidants, such as effective chlorine, is necessary. Here, we developed a personal passive air sampler (PPAS) composed of a redox dye, *o*-dianisidine, in a polydimethylsiloxane (PDMS) sheet. *o*-Dianisidine readily reacts with gaseous oxidants generated by bleach usage, and its color changes as the reaction progresses; hence, personal exposure to effective chlorine could be easily detected by the naked eye, while cumulative exposure could be determined by measuring concentrations of *o*-dianisidine reacting with it. The PPAS was calibrated, and a sampling rate of $0.00253 \text{ m}^3/\text{h}$ was obtained using a small test chamber. The PPAS was tested with the help of ten volunteers whose personal exposure to Cl_2 -equivalent gas was estimated after bathrooms were cleaned using spray and liquid-type household disinfection products, and the accumulated exposure-gas concentrations ranged from 69 to 408 ppbv and 148 to 435 ppbv, respectively. These PPAS-derived exposure concentrations were approximately two orders lower than those estimated using ConsExpo, suggesting a significant overestimation by prevailing screening models, possibly due to the ignorance of transformation reactions.

KEYWORDS

bleach, chlorine, disinfection, inhalation exposure, *o*-dianisidine, personal passive air sampler

1 | INTRODUCTION

Bleach, a hypochlorite (OCl^-) solution, is the most common chlorinated disinfectant used in homes and workplaces globally. As the hypochlorite solution (hereafter termed bleach) is a good oxidizing agent and effectively inactivates a broad spectrum of microorganisms,¹ it has been extensively used as an antimicrobial agent for cleaning surfaces, bleaching laundry, disinfecting food, and sanitizing drinking-water and swimming pools. However, its use has raised

concerns associated with adverse respiratory health effects due to the generation of reactive chlorine and their gaseous by-products (eg, chloroform and carbon tetrachloride) in indoor air.²⁻⁵

Two important effective chlorine species from bleach are chlorine (Cl_2) and hypochlorous acid (HOCl); recent studies have reported that concentrations of both these gases in indoor air significantly increased while using commercial bleach, with concentrations of Cl_2 and HOCl reaching 20-25 and 50-250 of ppbv, respectively.^{6,7} Acute inhalation of these gases generally causes

health problems such as reactive airways dysfunction syndrome (RADS) owing to Cl_2 gas generation from bleach use, especially when bleach mixes with acidic solutions such as hydrochloric acid (HCl) and vinegar.⁸⁻¹⁰ Even at low exposures (1-15 ppmv), Cl_2 gas could cause mucous membrane irritation. At 30 ppmv of Cl_2 exposure, cough, substernal chest pain, and shortness of breath could occur.¹¹ Inhalation toxicity of HOCl gas has not yet been reported; however, being a good oxidant, it could damage mammalian cells by oxidizing glutathione (GSH) and protein thiols.¹² In addition, once Cl_2 and HOCl gas are liberated, OH and Cl radicals could be generated by photolysis, thus increasing the oxidizing capacity of indoor air.⁶

The coronavirus disease (COVID-19) is an ongoing global pandemic, caused by the severe acute respiratory syndrome coronavirus 2 (SARS-CoV-2).¹³ On 19 March 2020, the World Health Organization (WHO) published a document offering guidance on control measures and quarantining of individuals for prevention of infection.¹⁴ They recommended cleaning and disinfecting frequently touched surfaces, bathrooms, and toilets with a diluted bleach solution daily. Thereby, the demand for bleach rapidly increased while concerns arose associated with accidental poisoning caused by disinfection and cleaning with bleach. On 20 April 2020, the Centers for Disease Control and Prevention (CDC) of the US Department of Health and Human Services reported that poison control centers received a spike in calls (45 550) related to cleaners and disinfectants during January-March, 2020.¹⁵ Bleaches indicated the largest percentage increase (62.1%) among all disinfectants from 2019 to 2020, while inhalation accounted for the largest percentage increase (108.8%) for all disinfectants among all exposure routes.¹⁵ Disinfection could become increasingly important for preventing infections caused by various viruses and bacteria, while bleach has been reported as the most likely cause of accidental inhalation poisoning; hence, estimating personal exposure to oxidant gases generated from bleaches is an urgent requirement.

To address this requirement, a personal passive air sampler (PPAS) was developed for estimating personal exposure levels to reactive chlorine gases resulting from disinfection using bleaches. The PPAS has been considered as a powerful tool for sensitive personal monitoring and estimating time-weighted average concentrations of individual chemical exposure to various gaseous compounds.¹⁶⁻¹⁹ The PPAS developed in this study consists of two components: (a) polydimethylsiloxane (PDMS) as a permeable medium and (b) a redox dye, *o*-dianisidine, contained within it. PDMS has been successfully used as a main component of passive air samplers in numerous studies as gas molecules easily permeate through their pores.²⁰⁻²⁴ Previous studies have assessed the exposure to volatile organic compounds (VOCs) or semi-volatile organic compounds (SVOCs) such as *n*-alkanes, aromatic hydrocarbons, and phthalates; however, studies related to passive air samplers that could estimate exposure levels of reactive gases, especially chlorine gases generated by bleach use, have not been reported. *o*-Dianisidine was chosen as a dye that changes color rapidly and stably on oxidation. The objectives of this study are (a) to develop and calibrate a PPAS for estimating personal

Practical Implications

- With the ongoing coronavirus disease pandemic, concerns have been raised regarding accidental poisoning caused by inhalation of exposure gases generated from chlorinated disinfectants.
- A simple, user-friendly, and cost-effective personal passive air sampler (PPAS) designed here can help estimate personal exposure levels to oxidant gases such as chlorine and hypochlorous acid.
- Since the PPAS changes color on exposure to chlorinated gases, it could also be used as an individual sensor in preventing acute inhalation poisoning caused by disinfection.

Cl_2 -equivalent gas exposure from bleach use and (b) to conduct a panel study to estimate the personal exposure levels of chlorinated gases when consumers clean residential bathrooms using chlorinated disinfectants. In addition, we compared the exposure levels estimated by the PPAS to that calculated using a screening model, ConExpo.²⁵

2 | EXPERIMENTAL METHODS

2.1 | PPAS

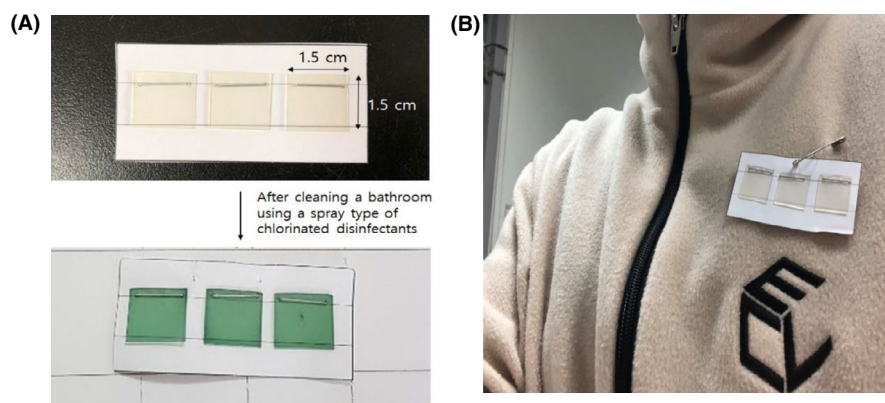
2.1.1 | Preparation

PDMS sheets were obtained from Specialty Silicone Products Inc (Ballston Spa, NY, USA), cut into 1.5×1.5 cm pieces, and then cleaned using *n*-hexane and methanol. The clean sheets were then doped with *o*-dianisidine by soaking them in a toluene solution with 0.5 g/L *o*-dianisidine over 24 hours; the PDMS swelled, causing a significant increase in volume. Then, the sheets were taken from the toluene solution and air-dried in a fume hood for over 2 hours. Thereafter, the swollen PDMS sheets shrunk, returning to their original volume as toluene evaporated. The surfaces of the PDMS sheets were cleaned with methanol to remove any remaining *o*-dianisidine on surfaces. The PPAS was then sealed in vacuum until used.

2.1.2 | Extraction and instrumental analysis

After exposing the PPAS to oxidant gases, its color changed from transparent to green/brown, forming an oxidized form of *o*-dianisidine (dianisidine quinonediimine and bisazobiphenyl), as described further in Section 3.1. *o*-Dianisidine and its oxidized form in the PPAS were extracted using 10 mL isopropyl alcohol for 24-48 hours. All samples were then analyzed by a UV/vis spectrophotometer

FIGURE 1 A, Configuration of a passive air sampler patch used here. Triplicate passive air samplers (1.5×1.5 cm) attached on plain paper by stapler. After cleaning a bathroom, the color of the passive samplers changed to transparent-green (the picture was taken by panel member #1 after using a spray-type of chlorinated disinfectant for 45 min); B, A single patch deployment



(OPTIZEN, Daejeon, Republic of Korea) with a maximum absorbance of 305 nm for *o*-dianisidine and 429 nm for its oxidized form.

2.2 | Calibrating PPAS color changes on exposure to Cl_2 gas

2.2.1 | Proton transfer reaction/selective reagent ionization-mass spectrometer (PTR/SRI-MS) calibration

Chlorine gas concentrations were measured using a PTR/SRI-MS (IONICON, Innsbruck, Austria) with O_2^+ as a selective reagent ion. Since O_2^+ has an ionization energy (IE) of 12.1 eV, which is considerably higher than that of Cl_2 (11.5 eV),¹ concentration measurements of Cl_2 gas were made via an electron transfer reaction: $\text{O}_2^+ + \text{Cl}_2 \rightarrow \text{O}_2 + \text{Cl}_2^+$. Cl_2 was identified by mass spectra and expected isotopic ratios of ^{37}Cl to ^{35}Cl .

Responses of PTR/SRI-MS to Cl_2 gas were calibrated using standard chlorine gas (4.7 ppmv) purchased from RIGAS (Daejeon, Republic of Korea). This standard Cl_2 gas was injected continuously at a flow-rate of 5.0 L min^{-1} into a custom-made 125 L acrylic chamber at $23\text{--}24^\circ\text{C}$. Signals for Cl_2 gas were detected at six intervals (1, 5, 9, 12, 16, and 20 minutes) to cover a Cl_2 concentration range of 0.19–2.6 ppmv in the chamber. An average signal of ± 0.1 minute at each interval was used as a response of PTR/SRI-MS.

2.2.2 | Calibrating the sampling rate of PPAS

To calibrate the sampling rate of the passive sampler, 30 mL of a liquid-bleach (Yuhanrox, Yuhan-clorox Inc, Seoul, Republic of Korea) containing about 4.0% (m/v) NaOCl was spread on the bottom of a clean 125 L chamber. After 40 minutes, six passive sampler patches (each patch having three passive samplers) were hung at the top of the chamber. Then, one passive sampler patch was removed from the chamber at each time interval (10, 15, 20, 25, 35, and 45 minutes) and placed into a glass vial containing 10 mL isopropyl alcohol for extraction. Chlorine gas concentration ($C_{\text{Cl}_2, \text{air}}$) in the chamber was

measured by the PTR/SRI-MS thrice: before hanging the passive samplers, twenty-five minutes after hanging the samplers, and after removing all samplers from the chamber. Assuming that the mass of chlorine gas reacting with *o*-dianisidine within the passive samplers linearly increased with time, the sampling rate (R_s , m^3/h) can be calculated as follows:

$$EV = \frac{N_s}{C_{\text{Cl}_2, \text{air}}} = R_s t \quad (1)$$

where EV is the equivalent air volume (m^3), N_s is the mass of chlorine gas reacting with *o*-dianisidine (mol), $C_{\text{Cl}_2, \text{air}}$ is the chlorine gas concentration in the chamber (mol m^{-3}), and t is the deployment time (h). The sampling rate (R_s) of the passive sampler was obtained from the slope of a plot, EV vs t .

2.3 | Panel study

To estimate the personal exposure levels of chlorine gas during household disinfection using bleach, we recruited a panel of ten volunteers (five from Gyeongsan-si, Gyeongsangbuk-do, Republic of Korea, and five from Gimhae, Gyeongsangnam-do, Republic of Korea), who were asked to wear the PPAS patch, while they cleaned bathrooms using disinfectants. This panel study was approved by the institutional review board (IRB) of Korea University (Approval number: KUIRB-2019-0175-03).

2.3.1 | Experimental design

The panel study was conducted in February 2020. The package per participant included two PPAS patches (Figure 1A shows the configuration of a passive sampler patch); two types of household chlorinated disinfectants, that is, a spray-type bleach (Product of LG Household & Health Care, Ltd.) and a liquid-type bleach (Product of Yuhanrox, Inc); and nine glass vials containing 10 mL of isopropyl alcohol, which were delivered to the residence of each panel member. The passive sampler patches for the panel study were prepared meticulously to prevent any oxidation of *o*-dianisidine within the

passive samplers (eg, wrapped with aluminum foil and stored in plastic bags sealed with vacuum packing, using staplers and pins to fix passive samplers). All panel members lived in apartments with areas and volumes of bathrooms being considerably similar (ranging from 3.15 to 3.83 m²), and with 1-2 bathrooms in their units (nine had two bathrooms, while one had one bathroom). All bathrooms possessed air ventilation systems.

The panel experiments were performed over two days: on day one, each panel member cleaned their bathroom(s) using one type of bleach (eg, spray-type); on day two, they cleaned their bathroom(s) similarly but using the other type of bleach (eg, liquid-type) wearing a PPAS patch (Figure 1B). After completing the process, each panel member was asked to record the type of disinfectant used, cleaning time, bathroom area, and whether they turned on the air ventilation systems. Pictures were taken by each panel member after the process to check for color changes of the PPAS; each passive sampler was stored in the glass vial containing 10 mL isopropyl alcohol. All the used bleach products and PPAS containing glass vials were sent back to the laboratory for measuring the amounts of disinfectants used and for an instrumental analysis (which were conducted after methods described in section 2.1.2) of passive sampler extraction, respectively.

2.3.2 | Estimation of exposure levels of air concentrations

To estimate the Cl₂ equivalent exposure, we first calculated the equivalent mass of reacted Cl₂ gas with *o*-dianisidine in the passive samplers (M_{sampled}) that each panel member used, using Equation (2):

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

where C_i and C_f are initial and final *o*-dianisidine concentrations in 10 mL extraction solvents (isopropyl alcohol), respectively (g/L); V_E is the volume of extraction solvent (0.01 L); and M_w is the molecular weight of *o*-dianisidine (244.30 g/mol). A factor of 0.5 was

applied to this equation, since a molar ratio of *o*-dianisidine to Cl₂ was 1:2 in the oxidation reaction shown in Figure 2.

Then, the time-weighted average concentration equivalent to Cl₂ gas (C_v , mol Cl₂ m⁻³) was calculated as

$$C_v = \frac{M_{\text{sampled}}}{R_s t} \quad (3)$$

where R_s is the sampling rate (m³ h⁻¹, obtained from Equation 1), and t is cleaning time of each panel (h). Unit conversion of C_v from mol Cl₂ m⁻³ to ppbv was conducted applying the ideal gas equation.

3 | RESULTS AND DISCUSSION

3.1 | Development of PPAS

Among several dyes that change their colors via oxidation-reduction reactions (eg, *N,N'*-diphenyl-1,4-phenylenediamine (DPPD), *N,N'*-diphenyl-benzidine (DPB), and *o*-tolidine),^{26,27} we chose *o*-dianisidine because (a) it changes color rapidly and vividly on exposure to oxidizing gases, (b) it is relatively environmentally friendly as compared to other oxidation dyes as a component in the passive sampler,²⁸ and (c) *o*-dianisidine doping within PDMS is stable over ten days under vacuum. The possible oxidation of *o*-dianisidine with oxidizing gases generated from bleach products (eg, HOCl and Cl₂) was previously suggested by Claiborne and Fridovich (1978),²⁹ shown in Figure 2. On exposure to Cl₂ gas, 2 mol of *o*-dianisidine reacts with 1 mol of Cl₂ gas, forming an intermediate product, dianisidine quinonediimine. Exposure of *o*-dianisidine to an oxidizing environment over a long duration produces bisazobiphenyl. The PDMS is initially transparent on doping with *o*-dianisidine, but on oxidation, changes to green (dianisidine quinonediimine) or brown (bisazobiphenyl) (Figure 2).

To optimize the PPAS, we compared passive samplers using two different PDMS thicknesses (0.22 and 0.55 mm) and varying *o*-dianisidine doping concentrations in toluene ranging from 0.12 to 2.0 g/L. Figure S1 shows that with 0.22 mm thickness, *o*-dianisidine

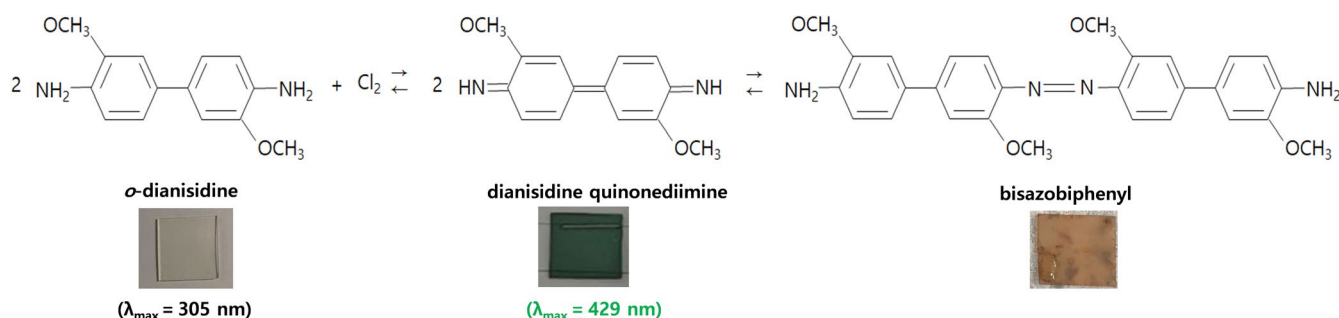


FIGURE 2 The oxidation of *o*-dianisidine. When *o*-dianisidine reacts with oxidizing gases such as Cl₂ or HOCl, dianisidine quinonediimine forms as an intermediate product. Further oxidation produces bisazobiphenyl, a stable product. Figures below the scheme show the color changes of a passive sampler after each product is created, and the maximum absorbance of UV/vis after extracting the passive samplers with isopropyl alcohol

crystallized, showing white spots in the PDMS for all doping concentrations ranging from 0.12 to 0.51 g/L. Crystallization might have limited the reactivity of the passive sampler owing to a decreasing amount of free *o*-dianisidine.²⁶ With a PDMS thickness of 0.55 mm, crystallization did not occur for doping concentrations of 0.09 and 0.50 g/L, while the colorimetric response of the passive samplers on exposure to the headspace of the liquid bleach was highest at a doping concentration of 0.5 g/L. Hence, we chose 0.55 mm as PDMS thickness and 0.50 g/L of *o*-dianisidine as the optimal doping concentration.

To select an appropriate extraction solvent for *o*-dianisidine and its oxidized form, we compared two extraction solvents: isopropyl alcohol and acetonitrile with 0.1% (v/v) formic acid. Extracting passive samplers with isopropyl alcohol before exposure to the headspace of the bleach solution indicated UV/vis spectrums with a maximum absorbance at 305 nm (*o*-dianisidine); the spectrum was stable for three days (Figure 3A). Extracting passive samplers after exposure to the headspace of undiluted bleach indicated a UV/vis absorbance with two distinct maximum peaks: 305 nm (*o*-dianisidine) and 429 nm (oxidized *o*-dianisidine). The absorbance spectrum was stable after 4 h (Figure 3B). However, using acetonitrile, passive samplers both before and after exposure to the headspace of the bleach solution indicated only one distinctive peak at 305 nm (Figure S2). Hence, we chose isopropyl alcohol as an extracting solvent and 24–48 h as the extracting time.

3.2 | Sampling rates of the PPAS

The PPAS sampling rate was calibrated using the amount of Cl_2 gas that reacted with *o*-dianisidine in the passive samplers and the ambient Cl_2 gas concentration in the test chamber ($C_{\text{Cl}_2, \text{air}}$) measured by the PTR/SRI-MS. We confirmed that $C_{\text{Cl}_2, \text{air}}$ changed

insignificantly during the experiments. Concentrations of *o*-dianisidine (UV/vis absorbance at 305 nm) in the passive sampler decreased linearly, while its oxidation product (UV/vis absorbance at 429 nm) increased proportionally with time (Figure 4A). This indicated that the concentration of Cl_2 gas reacting with *o*-dianisidine increased with time until 45 min, and the concentrations of Cl_2 reacting with *o*-dianisidine per unit volume of the passive sampler (C_s , mol m^{-3}) were 0.33 ± 0.04 and 0.91 ± 0.03 , at 10 and 45 minutes, respectively (Figure 4B). Figure 4C shows that the PTR/SRI-MS response of Cl_2 signals ($m/z = 70$) inside the 125 L chamber was significantly higher, compared to that outside (background); the raw response of Cl_2 isotope species was determined by calculating differences between the signals inside and outside (background) the chamber. The resultant observed ratio of the Cl_2 isotope was the same as the expected ratio of naturally occurring chlorine isotopes (Figure 4C). Based on the Cl_2 gas calibration curve obtained using Cl_2 standard gas (Figure S3; a coefficient of determination (r^2) of linear regression of the standard curve was 0.9942), the raw response of PTR/SRI-MS was converted to the Cl_2 gas concentration inside the chamber ($C_{\text{Cl}_2, \text{air}}$), which was calculated as 1508 ppbv. Then, the sampling rate of the passive air sampler was determined as $0.00253 \text{ m}^3 \text{ h}^{-1}$ using Equation (1).

3.3 | Passive sampler-derived personalized Cl_2 -equivalent exposure estimates

Since the passive sampler patches were prepared carefully to prevent any oxidation of *o*-dianisidine before use, the concentrations of *o*-dianisidine in the passive samplers were confirmed to not have changed for twelve days (Figure S4).

The usage amount, bathroom area, and time for cleaning bathrooms using a spray-type/liquid-type bleach product are summarized

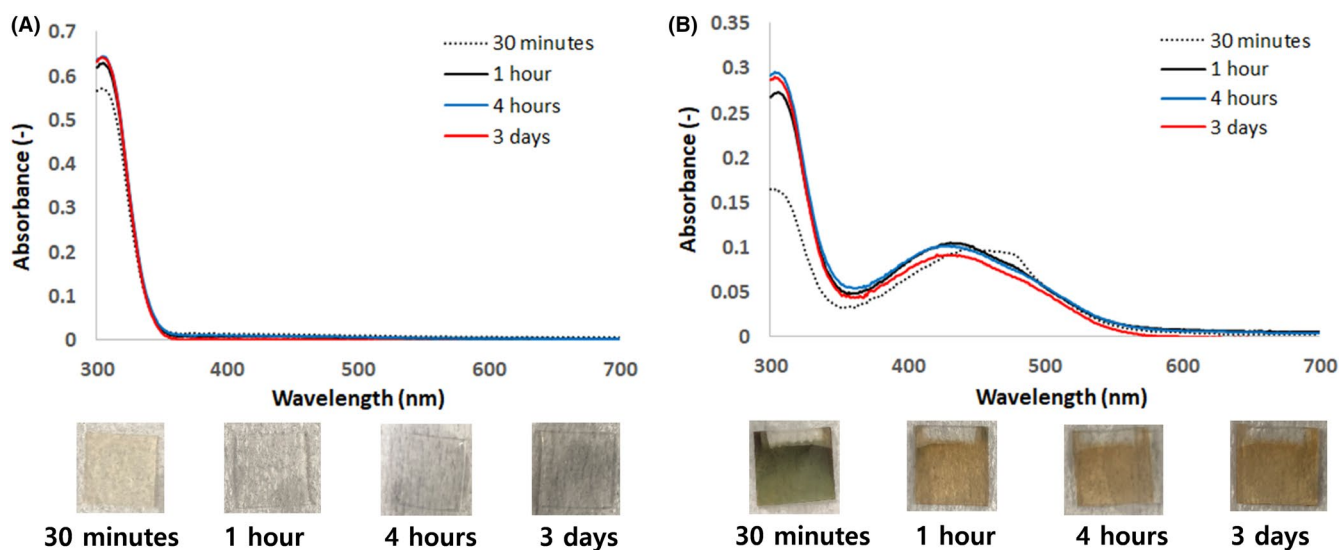


FIGURE 3 UV/vis absorption spectrum of the extraction solvent (isopropyl alcohol) corresponding to extraction of the passive samplers (A) before and (B) after 3 h of exposure to the headspace of undiluted bleach. Figures below the UV/vis adsorption spectrums are passive samplers extracted from the extraction solvent (isopropyl alcohol) after the corresponding times

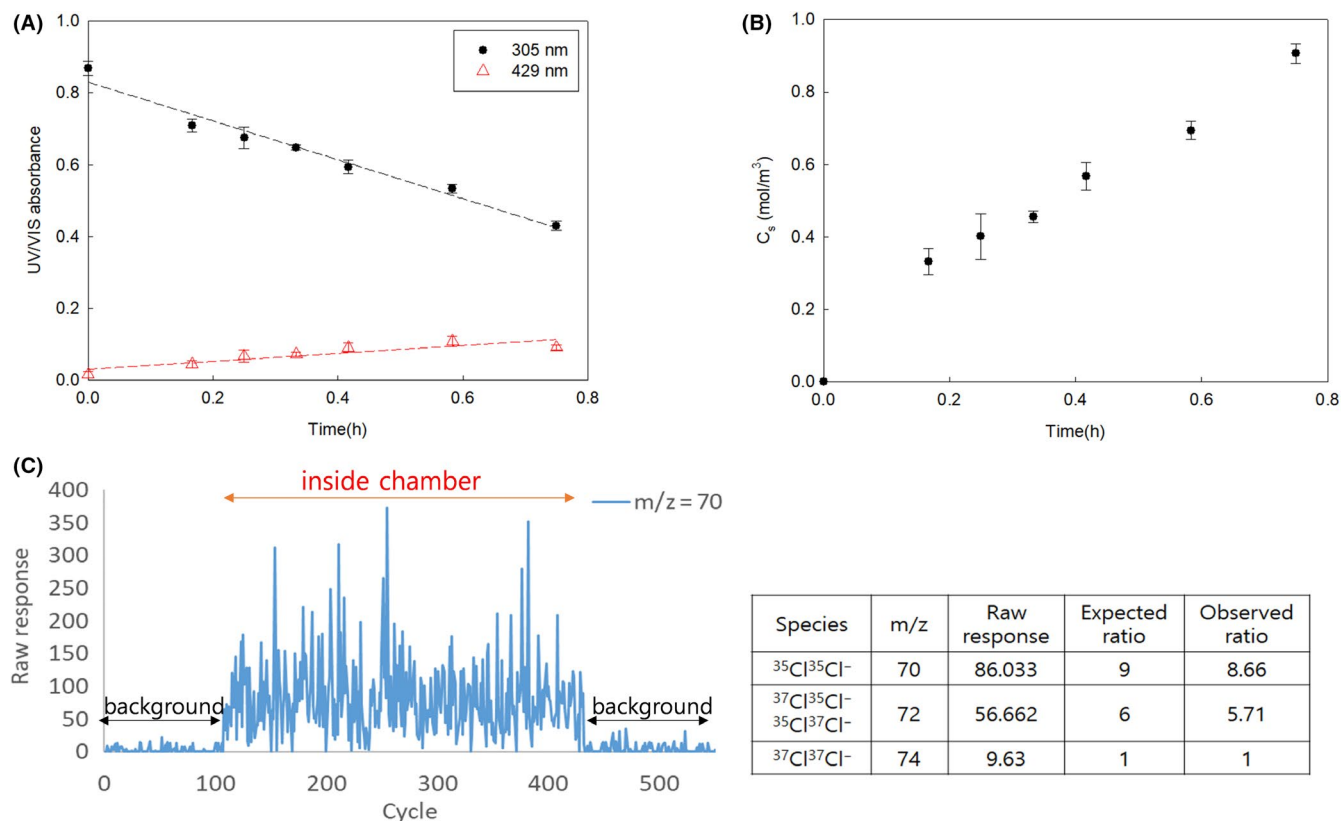


FIGURE 4 Calibration of passive air samplers: (A) UV/vis absorbance of 305 nm (*o*-dianisidine) and 429 nm (dianisidine quinonediimine) after extracting passive samplers that were hung on a 125 L chamber. Liquid-type bleach (30 mL) was spread on the bottom of the chamber; (B) Reaction curve of chlorine gas with *o*-dianisidine in the passive samplers. C_s represents a mole of chlorine gas reacting with *o*-dianisidine per unit volume of a passive sampler. C, Cl₂ gas signals measured by PTR-MS for calibrating the passive samplers. The inserted table shows the raw response by PTR-MS as well as the expected and observed ratios of various ions detected

in Table 1. The disinfectant usage ranges were 39.55–252.85 g and 61.50–593.33 g for spray-type and liquid-type products, respectively. The bathroom areas and usage time of each panel member were considerably similar to each other (Table 1). After usage of the spray-type disinfectants, color changes in the passive samplers of all panels members were detectable by the naked eye (Figure S5A). With the liquid-type disinfectants, seven out of ten passive sampler patches changed colors significantly; it was difficult to detect the color change of three passive sampler patches (#2, #4, and #10) with the naked eye (Figure S5B). The intensity of the color change was not observably dependent on the amount of disinfectants used.

Figure S6 shows the extracted *o*-dianisidine concentrations of each panel member's PPAS. When spray-type bleaches were used, extracted *o*-dianisidine concentrations from panel members #1, #2, #9, and #10 were significantly lower than those of other members (Figure S6A). Conversely, using liquid-type disinfectants, except for panel member #8, there were no significant differences between the extracted concentrations for the various panel members despite using different amounts of bleaches (Figure S6B).

Based on the differences in extracted *o*-dianisidine concentrations between the control (PPAS which stored in vacuum condition) and PPAS of each panel member, the mass of reacted *o*-dianisidine and Cl₂-equivalent exposure gas was calculated as shown in Table 1.

The ranges of mean reacted *o*-dianisidine mass were 2.82–14.00 µg and 5.41–16.67 µg using spray-type and liquid-type disinfectants, respectively. Ranges of estimated Cl₂-equivalent exposure-gas concentrations were 69.1–408 ppbv, and 148–435 ppbv using spray-type and liquid-type disinfectants, respectively. The PPAS-derived exposure level of Cl₂-equivalent gas determined via the panel study was less than that prescribed by Acute Exposure Guideline Levels 1 (AEG1, Endpoint: none to slight changes in pulmonary function in humans), which was reported to be 500 ppbv for 10 minutes–8 hours exposure by the National Research Council (NRC) of the National Academics.³⁰ The Occupational Safety and Health Administration (OSHA) also reported that the time-weighted average for permissible exposure limits of chlorine is 500 ppbv.³¹ However, the various exposure levels of Cl₂-equivalent gases obtained here were higher than the minimal risk levels (MRLs) for humans, which was reported as 60 ppbv for acute-duration inhalation exposure (fourteen days or less),³² and the ambient level of chlorine (34 ppbv) to prevent sensory irritation and ventilator-capacity reduction, provided by the WHO.³³ Thus, prolonged exposure to effective chlorine concentrations estimated by the PPAS might cause health concerns. Boxplots of Cl₂-equivalent exposure-gas concentrations of the ten panel members indicate that the median estimated exposure concentrations using spray-type and liquid-type products were almost similar (Figure 5). However, variations of Cl₂ exposure

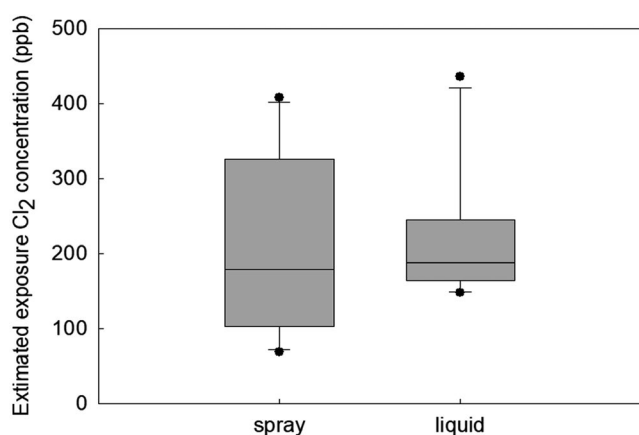
TABLE 1 Summary of the panel study using (A) spray-type and (B) liquid-type chlorinated disinfectant

Panel member	Usage amount (g)	Bathroom area (m ²)	Usage time (min)	PAS color change ^a	Reacted o-dianisidine (μg) ^b	C _v ^c (Cl ₂ -equivalent, ppbv)
(A) Spray-type disinfectant						
1	188.70	3.18	45	O	13.27 ± 1.28 (3)	346.35 ± 33.45
2	109.38	3.68	40	O	13.88 ± 0.84 (3)	407.68 ± 24.61
3	138.76	3.44	45	O	6.82 (1)	178.09
4	165.23	3.68	43	O	4.18 ± 1.59 (3)	114.10 ± 43.41
5	39.55	3.15	40	O	6.09 ± 1.28 (3)	178.72 ± 37.47
6	252.85	3.26	55	O	4.49 ± 1.45 (3)	96.00 ± 30.90
7	252.38	3.52	57	O	5.13 ± 0.42 (3)	105.75 ± 8.64
8	84.93	3.48	48	O	2.82 (1)	69.11
9	234.28	3.08	53	O	14.00 ± 5.15 (3)	310.33 ± 114.11
10	114.94	3.37	42	O	11.38 ± 0.069 (3)	318.18 ± 1.93
(B) Liquid-type disinfectant						
1	201.78	3.18	50	O	7.19 ± 3.45 (3)	168.85 ± 81.02
2	86.10	3.83	40	X	7.88 ± 3.88 (3)	231.29 ± 113.95
3	283.99	3.70	52	O	7.27 ± 1.65 (3)	164.19 ± 37.30
4	221.92	3.68	43	X	6.01 ± 2.57 (3)	164.08 ± 70.25
5	61.50	3.33	40	O	5.85 ± 5.40 (3)	171.72 ± 158.53
6	417.86	3.41	50	O	12.13 ± 0.95 (3)	285.03 ± 22.25
7	593.33	3.22	58	O	10.06 ± 2.11 (3)	203.82 ± 42.71
8	284.26	3.40	45	O	16.67 ± 4.27 (3)	435.07 ± 111.40
9	142.08	3.32	43	O	7.92 ± 2.12 (3)	216.24 ± 57.98
10	158.16	3.37	43	X	5.41 ± 2.76 (3)	147.78 ± 75.36

^aPassive air sampler (PAS) color changes after cleaning bathrooms. (O: color changes vividly, X: color does not change, as verified by the naked eye). Figure S5 shows PAS pictures taken by each panel member after cleaning the bathrooms.

^bMass of reacted o-dianisidine in PAS. Average ± standard deviations of triplicate analyses using three PASs in one patch. The number inside the parentheses indicates the number of PAS used.

^cExposure-gas concentration (Cl₂-equivalent) calculated using the PAS sampling rate. Average ± standard deviations of triplicate analyses.

**FIGURE 5** Estimated exposure of chlorine concentrations (ppb) after using spray and liquid-type disinfectants. The mean value of C_v (Cl₂-equivalent concentration) for each panel member listed in Table 1 was used here. Boxplots show the 10th, 25th, median, 75th, and 90th percentiles

between the ten panel members were higher while using spray-type products, rather than liquid-type products, suggesting that when

panel members used spray-type bleaches, gas exposure depended more on personal cleaning habits and bathroom conditions.

3.4 | Comparison of PPAS-derived exposure with ConsExpo model predicted exposure

Even though the usage amounts of both spray-type and liquid-type bleaches varied among the panel members, personal Cl₂-equivalent gas exposure was almost independent of the bleach usage amounts (Figure 6). Hence, other factors such as the gas removal rate via chemical reactions, air ventilation, and drainage during cleaning could be more important than the usage amount. Here, we compared the personal exposure levels of gases (C_v) obtained through the panel study with Cl₂ gas concentrations from the chamber experiment for calibrating a passive sampler (C_{air} = 1508 ppbv) and estimated C_v values using the ConsExpo model (Figure 6). To run ConsExpo, we used an exposure to vapor model and an increasing release-area mode; all other parameters had default values, except that for the amount of solution used (average values of bathroom area and usage times of the ten

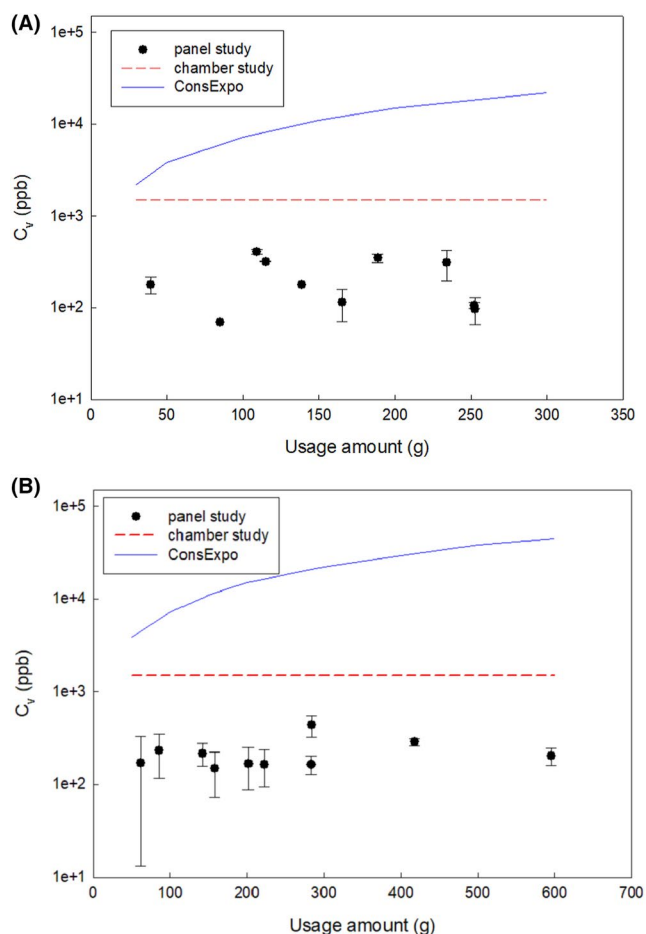


FIGURE 6 Effects of usage amounts of (A) spray-type, and (B) liquid-type chlorinated disinfectants on personal exposure levels of chlorine-equivalent gas (C_v). The black dots represent C_v obtained from the panel study, the redline represents measured chlorine gas concentrations (C_{air}) from the chamber study described in Section 2.2.2, and the blue-line indicates estimated C_v values using ConsExpo. The error bar indicates standard deviations of three replicates

panel members listed in Table 1 were used to derive the room volume and duration of exposure, respectively; a ventilation rate of 10 h^{-1} was used). The exposure-gas concentrations estimated using ConsExpo increased with increasing amounts of bleaches used (Figure 6); the values obtained were approximately 100 times higher than the estimated C_v values obtained using PPAS, even 1.5 to 30 times higher than the C_{air} values obtained from the chamber study. ConsExpo is a higher-tier model for estimating inhalation exposure from consumer products. The reported differences between ConsExpo-derived air concentrations and experimental measurements were within a factor of ten for some consumer products, including transfluthrin³⁴ and silver nanoparticles (AgNP).²⁵ However, this model highly overestimates the exposure level, especially for reactive gas compounds such as chlorine, as various removal mechanisms such as gas-phase reactions and reactive uptake on the surfaces are not considered. In addition, the predicted exposure levels for consumer applications far exceed the NRC standard of 500 ppbv. Thus, the PPAS developed in this study could greatly improve the assessment of exposure conducted by these higher-tier exposure models.

4 | CONCLUSIONS

We developed a cost-effective and user-friendly PPAS for estimating time-weighted personal exposure levels to chlorine gas compounds from the use of household bleaches. After determining the sampling rate of the PPAS, a panel study was conducted to assess Cl_2 -equivalent gas exposure by cleaning residential bathrooms using spray- and liquid-type bleaches. These time-weighted average exposure levels could be compared to the exposure limits of occupational and consumer products, providing more specific and relevant criteria for guidelines for chlorinated gas exposure from bleach use. In addition to estimation of exposure levels, the PPAS changes its color on exposure to chlorinated gases, and the colorimetric responses varied with an increase in exposure concentrations. Thus, this PPAS could find applications as a versatile sensor in preventing accidental inhalation poisoning from bleach usage. Occupational exposure levels to chlorine gases arising from disinfection of public places such as hospitals, schools, and restaurants, which is a priority for preventing infections could also be easily assessed using the PPAS without expensive instruments.

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CONFLICT OF INTEREST

The authors have declared no conflicts of interest for this article.

AUTHOR CONTRIBUTION

Yeonjeong Ha: Conceptualization (equal); Data curation (lead); Investigation (lead); Writing-original draft (lead). **Yoonsub Kim:** Data curation (equal); Investigation (equal). **Eugene Song:** Investigation (equal); Methodology (equal). **HyunJung Yoo:** Funding acquisition (equal); Methodology (equal). **Jung-Hwan Kwon:** Conceptualization (equal); Funding acquisition (lead); Supervision (lead); Writing-review & editing (lead).

PEER REVIEW

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DATA AVAILABILITY STATEMENT

Data available on request from the authors.

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SUPPORTING INFORMATION

Additional supporting information may be found online in the Supporting Information section.

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