Identification and determination of disinfection byproducts in chlorine-containing household cleansing products

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HIGHLIGHTS

- Seven DBPs were identified and detected in chlorine-containing household products.
- Haloacetic acids were identified and characterized for the first time.
- The daily average exposure was calculated based the exposure algorithm.

ARTICLE INFO

ABSTRACT

Seven halogenated volatile organic compounds (HVOCs) and two haloacetic acids were detected and quantified in 15 household products, including sodium hypochlorite, by gas chromatography-mass spectrometry (GC-MS). Chloroform was detected in a range of 0.2–30.2 mg kg^{-1} in all products, and carbon tetrachloride was observed in 13 samples in a range of 0.05–352 mg kg^{-1}. Dichloroacetic acid and trichloroacetic acid were also detected up to 94 and 146 mg kg^{-1} in household products. The estimated human exposures of chloroform, carbon tetrachloride, dichloroacetic acid and trichloroacetic acid were calculated to 0.041, 0.240, 0.913 and 2.39 mg/kg/day by the exposure algorithm from the Japan National Institute of Technology and Evaluation, respectively. According to the calculated result, the total estimated human exposure of chloroform were determined to exceed the tolerable concentration of inhalation exposure presented by the World Health Organization. The DBPs should be controlled to the lowest concentrations in the chlorine-containing household cleansing products.

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1. Introduction

Sodium hypochlorite (NaOCl) is widely used in many household products, such as bleaches, mildew removers, drain cleaners and washing machine cleaners (Odabasi, 2008; Odabasi et al., 2014). Chlorine containing products can irritate the eyes and skin through direct contact, and damage the respiratory tract through inhalation (Helen, 2015). Moreover, NaOCl can generate toxic disinfection by-products (DBPs) through a reaction with organic compounds, such as alcohols, ketones and esters (Chaidou et al., 1999; Chu et al., 2009; Bond et al., 2014a, 2014b; Zhang et al., 2012; Chen et al., 2011; Xu et al., 2011; Li et al., 2009). Because certain DBPs are potentially carcinogenic substances (Barker and Stuckey, 1999), the

formation of DBPs in the chlorine-containing household cleansing products have been interesting for many researchers to determine if the use of household products is safe. In particular, chloroform, carbon tetrachloride, 1,4-dichlorobenzene and bromodichloromethane were classified as probably carcinogenic to humans (group 2B) by the International Agency for Research on Cancer (IARC) (IARC, 2013). Additionally, dichloroacetic acid and trichloroacetic acid were classified by IARC as probably carcinogenic to humans (group 2B) because of their potential carcinogenic toxicity (Richardson et al., 2007, 2010; Martınez et al., 1998).

A few studies reported that chloroform, carbon tetrachloride and chlorobenzene were identified in cleansing products (Odabasi, 2008; Thomas and David, 1992). Chlorophenols were detected in personal hygiene products, including free chlorine and triclosan (Fiss et al., 2007). Consumers could be exposed to DBPs by respiration when using the products. The exposure assessment has also been studied in several nations (Steiling et al., 2014; McNamara

et al., 2007; Kang et al., 2012), especially through the development of the exposure assessment model (Odabasi, 2008; Odabasi et al., 2014; EU, 2007; NITE, 2008; RIVM, 2007). However, only limited DBP compounds and a limited number of household products were used for the human exposure assessment. A wide variety of target DBP compounds and household products should be required to test for exposure assessment.

The purposes of this work were to (1) ascertain which DBPs are present in selected household products available on the market using gas chromatography-mass spectrometry (GC-MS) and (2) calculate the amount of human exposure for each of the DBPs using the exposure algorithm developed by the Japan National Institute of Technology and Evaluation.

2. Experimental

2.1. Materials

All organic solvents used were HPLC grade. Sodium chloride (99%), sodium sulfate (99%), sulfuric acid (95%), copper II sulfate (99%), sodium bicarbonate (99.7%), dichloromethane (99.9%), potassium phosphate monobasic (KH_2PO_4)(99%), methyl *tert*-butyl ether (MTBE)(99.8%), methanol (99.8%) and ascorbic acid (99%) were obtained from Sigma-Aldrich (St. Louis, MO, USA). EPA 502/524 volatile organic calibration mix A (each 2000 μg ml^{-1} in methanol), EPA 552.2 haloacetic acids mix (each 2000 μg ml^{-1} in methyl *tert*-butyl ether), EPA 551B halogenated volatiles mix (each 2000 μg ml^{-1} in methyl *tert*-butyl ether), EPA 502 internal standard mix (each 2000 μg ml^{-1} in methanol), 4-chlorophenol (99%), 2,4-dichlorophenol (99%), 2,4,6-trichlorophenol (98%), pentachlorophenol (97%), 2-chlorophenol-d4 (98%), trifluoroacetic acid (98%), and 4-bromofluorobenzene (98%) were obtained from Sigma-Aldrich (St. Louis, MO, USA).

2.2. Sampling

Four chlorine bleaches, three mildew removers, six drain cleaners and two washing machine cleaners were purchased from five local supermarkets in the Republic of Korea (Table 1). All samples were stored at 4 °C until analysis. Four methods were applied for sample pretreatments of DBPs in household products.

2.3. Sample pretreatment

2.3.1. Extraction procedures of halogenated volatile organic compounds (HVOCs)

The extraction procedure for the HVOCs analysis of samples was a slight modification of US EPA method 8012B. A 5.0 g sample was placed in a 10-mL headspace vial. A 50-μL volume of fluorobenzene and 1,2-dichlorobenzene-d_4 (1.0 mg L^{-1}) were used as the internal standards. Sodium chloride (1.6 g) and ascorbic acid (0.3 g) were added to the solution, and the vial was sealed with a septum lined cap. The sample vial was placed in a heating block of headspace equipment for 30 min at 40 °C.

2.3.2. Extraction and derivatization procedures of haloacetic acids

The extraction and derivatization procedure for the haloacetic acids analysis in samples was a slight modification of US EPA method 522.2. A 5.0 g sample was placed in a 20-mL test tube and adjusted to pH < 0.5 using 0.2 mL of concentrated sulfuric acid. A 50-μL volume of trifluoroacetic acid (1.0 mg L^{-1}) was used as the internal standard. Copper II sulfate (0.25 g), sodium sulfate (2 g) and ascorbic acid (0.3 g) were added to the sample tube, and then 0.5 mL of MTBE was used as the extraction solvent. After the sample tube was mechanically shaken for 30 min, the upper MTBE layer was combined with 1.0 mL of 10% sulfuric acid in methanol. After the derivatization reaction was conducted at 50 °C for 2 h in the heating block, the solution was neutralized with 0.5 mL of a saturated sodium bicarbonate solution. Approximately 0.2 mL of the organic phase was placed into a 2-mL vial and used for the instrumental analysis.

2.3.3. Extraction procedure of haloacetonitriles

The extraction procedure for the haloacetonitrile analysis of samples was a slight modification of US EPA method 551.1. A 5.0 g sample was placed in a 20-mL test tube and 50 μL of 4-bromofluorobenzene (1.0 mg L^{-1}) was used as the internal standard. Sodium chloride (2.0 g), ascorbic acid (0.3 g) and MTBE (0.3 mL) were added to the sample tube. After shaking the sample for 20 min, the organic phase was placed into a 2-mL vial and used for the instrumental analysis.

2.3.4. Extraction procedure of halophenols

The extraction procedure for the halophenol analysis of samples was a slight modification of US EPA method 604. A 5.0 g sample was placed in a 20-mL test tube and adjusted to pH < 4.5 using KH_2PO_4. A 50-μL volume of 2-chlorophenol-d_4 (1.0 mg L^{-1}) was used as the internal standard. Sodium chloride (5 g), ascorbic acid (0.3 g) and methylene chloride (0.3 mL) were added to the 20-mL sample tube. After shaking the sample tube for 20 min, approximately 0.2 mL of the organic phase was placed into a 2-mL vial and used for the instrumental analysis.

2.4. Apparatus

The analytical instruments that were used included an Agilent 7890 A gas chromatograph with a split/splitless injector (Agilent Technologies, Santa Clara, CA, USA) and an Agilent 5975 B mass spectrometer (Agilent Technologies, Santa Clara, CA, USA). A Combipal Autosampler (Agilent Technologies, Santa Clara, CA, USA), which allows automated headspace injections, was also used. The ion source was operated in the electron ionization mode (EI; 70 eV). Full-scan mass spectra (*m/z* 40–400) were recorded for analyte identification. An HP - InnoWax capillary column (60 m × 0.25 mm I.D. × 0.25 μm film thickness) for the HVOCs and HP - 5MS capillary column (60 m × 0.25 mm I.D. × 0.25 μm film thickness) for haloacetic acids, halophenol and haloacetonitrile analyses were used, respectively. Samples were injected in the split mode (10:1). The flow rate of helium as a carrier gas was 1.0 mL min^{-1}.

The same temperature conditions for all compounds were as follows: The injector temperature was set at 250 °C. The oven

Table 1
Type of cleansing products, number and ingredients of purchased cleansing products.

Type of cleansing products	Number	Ingredients
Chlorine bleach	4	NaOCl, fragrances, surfactant, potassium hydroxide
Mildew remover	3	NaOCl, fragrances, acid regulation agents, surfactant, potassium hydroxide
Drain cleaner	6	NaOCl, fragrances, surfactant
Washing machine cleaners	2	NaOCl, fragrances, surfactant, potassium hydroxide

Table 2
The selected ion, detection limits, calibration curves, precision, and accuracy of DBPs.

Group	Compound	Selected ion		Detection limit (mg kg^{-1})		Calibration curve		Precision and accuracy (%)			
		Quantification ion	Qualification ions	LOD	LOQ	Conc. range	Linear equation (R^2)	Spiked Conc (mg kg^{-1})	Mean ± SD (mg kg^{-1})	Accuracy	Precision
HVOCs	Chloroform	83	85, 47	0.003	0.009	0.01−50	y = 1.852x − 0.008 (0.999)	0.010	0.010 ± 0.001	95.1	2.5
								0.100	0.113 ± 0.011	113	4.4
	Carbon tetrachloride	119	117, 121	0.005	0.015	0.01−500	y = 2.393x − 0.064 (0.997)	0.010	0.009 ± 0.001	94.4	6.3
								0.100	0.114 ± 0.004	114	5.5
	Chlorobenzene	112	77, 114	0.001	0.003	0.005−1.0	y = 4.511x − 0.046 (0.998)	0.010	0.009 ± 0.001	93.9	3.8
								0.100	0.108 ± 0.006	109	1.1
	2-Chlorotoluene	91	126, 63	0.003	0.009	0.01−1.0	y = 5.714x − 0.072 (0.998)	0.010	0.010 ± 0.001	99.2	4.2
								0.100	0.108 ± 0.006	109	2.4
	4-Chlorotoluene	91	126, 63	0.009	0.027	0.05−1.0	y = 6.504x − 0.157 (0.996)	0.010	0.010 ± 0.001	95.3	4.0
								0.100	0.100 ± 0.007	100	3.4
	1,4-Dichlorobenzene	146	148, 111	0.003	0.009	0.01−1.0	y = 4.374x − 0.042 (0.998)	0.010	0.009 ± 0.001	91.5	3.6
								0.100	0.095 ± 0.005	95.1	1.8
	1,2-Dichlorobenzene	146	148, 111	0.003	0.010	0.01−1.0	y = 3.431x + 0.003 (0.998)	0.010	0.009 ± 0.001	93.4	3.3
								0.100	0.103 ± 0.007	103	4.2
Haloacetic acids	Chloroacetic acid	77	64, 108	0.005	0.015	0.01−200	y = 0.1174x - 0.286 (0.994)	0.020	0.017 ± 0.001	89.6	3.9
								0.100	0.954 ± 0.008	95.4	8.8
	Dichloroacetic acid	83	85, 87	0.0005	0.002	0.005−200	y = 0.7634x - 0.177 (0.998)	0.020	0.019 ± 0.001	89.6	3.9
								0.100	0.964 ± 0.008	95.4	8.8
	Trichloroacetic acid	117	119, 121	0.001	0.003	0.005−200	y = 0.3157x - 0.278 (0.999)	0.020	0.021 ± 0.002	104	7.5
								0.100	0.970 ± 0.006	96.6	6.1
Halophenols	4-Chlorophenol	128	65, 100	0.003	0.010	0.01−1.0	y = 9.904x - 0.001 (0.999)	0.005	0.005 ± 0.001	102	5.5
								0.050	0.051 ± 0.005	104	8.8
	2,4-Dichlorophenol	162	126, 164	0.002	0.006	0.005−1.0	y = 17.82x - 0.003 (0.996)	0.005	0.005 ± 0.001	107	3.5
								0.050	0.05 ± 0.0002	100	4.7
	2,4,6-Trichlorophenol	196	132, 198	0.012	0.038	0.05−1.0	y = 10.50x - 0.003 (0.999)	0.005	0.005 ± 0.001	93.0	11
								0.050	0.048 ± 0.006	96.0	13
	Pentachlorophenol	266	264, 268	0.001	0.004	0.005−1.0	y = 5.189x - 0.003 (0.995)	0.005	0.005 ± 0.004	97.7	8.3
								0.050	0.053 ± 0.001	107	14
Haloacetonitriles	Bromochloroacetonitrile	74	76, 155	0.004	0.010	0.01−1.0	y = 0.7513x − 0.005 (0.998)	0.005	0.051 ± 0.001	96.8	7.8
								0.050	0.054 ± 0.003	107	5.4
	Dichloroacetonitrile	74	82, 84	0.003	0.010	0.01−1.0	y = 0.7198x − 0.002 (0.999)	0.005	0.005 ± 0.001	92.4	9.0
								0.050	0.047 ± 0.002	93.6	5.1
	Trichloroacetonitrile	108	110, 73	0.004	0.010	0.01−1.0	y = 0.4073x − 0.003 (0.999)	0.005	0.067 ± 0.001	92.0	6.3
								0.050	0.046 ± 0.003	92.4	6.7

temperature programs were: initial temperature of 40 °C (held for 5 min) then increased to the final temperature of 250 °C at 8 °C min^{-1}. The ions selected for quantization and conformation are presented in Table 2.

2.5. Calibration and quantification

The standard spiking samples for calibration curves were prepared by adding 0.01, 0.025, 0.05, 0.1, 0.5, 2.0, 10.0, 50.0, 100.0, 250.0 and 500.0 μg of the analyte standard solutions (1.0–1000.0 mg L^{-1}) and 0.05 μg of the internal standards in 5.0 mL Milli-Q water. The subsequent extraction procedure (and derivatization procedure in case of haloacetic acids) was the same as the sample pretreatments. The corresponding concentrations of the standard were 0.002, 0.005, 0.01, 0.02, 0.1, 0.4, 2.0, 10, 20, 50, 100 mg kg^{-1}. The ratios of the peak area of the standards to the peak area of the internal standard were used to quantify the analytes. The 5.0 mL Milli-Q water was used as blank sample because a real sample without analytes could not be obtained.

2.6. Daily inhalation exposure of DBPs

An exposure assessment was carried out to determine the exposure levels based on the chemical concentrations. The DBP concentrations in the room air (C_{air}) were estimated by the method suggested from National Institute of Technology and Evaluation (NITE) of Japan (NITE, 2008). Daily-used product amount, room volume, room ventilation rate and chemical release time are based on the parameters defined on risk assessment subjects and methodology for risk concerned products from National Institute of Environmental Research (NIER, 2014) and Ministry of Environment of Korea (MOE, 2007).

Exposure scenarios were assumed maximum exposure situations for risk assessment. This study assumed that there was no disappearance effect through adsorption and desorption of emitted compounds on the inner surface of the room and that the all DBPs were released to the room during the use of products. The concentration of the chemical in a room's air space can be calculated by the following equation (NITE, 2008).

$$C_{air} = \frac{\frac{A_o \times W_f}{N \times V} \times \left\{ t - \frac{1}{N} \times [1 - \exp(-Nxt)] \right\}}{t} \qquad (1)$$

where, C_{air} is the concentration of compound in the room air (μg m^{-3}), A_o is the amount of product used (μg), W_f is the weight fraction of the compound in the product, t is release time (h), N is ventilation rate of the room (number of air changes per time) (1 h^{-1}) and V is room volume (m^3). When the values have the wide distributions, their 95th percentiles were used for the safety of consumers (Table 3). The daily inhalation exposure of DBPs by cleaning activities was calculated by the following equation.

Table 3
Exposure factors for concentration of DBPs in air by household products use.

Type of disinfectants	Eq. (1)			
	A_o (mg)	V (m^3)	N (1 h^{-1})	t (h)
Chlorine bleach	282,860	9.3	2.0	0.53
Mildew remover	212,800	9.3	2.0	0.50
Drain cleaner	148,650	24.5	2.5	0.02
Washing machine Cleaners	119,850	9.3	2.0	0.03

$$D_{inh} = C_{air} \times IR \times ET \times 0.001/BW \qquad (2)$$

where D_{inh} = Daily inhalation exposure of DBPs by product use (mg/kg/day), C_{air} = Concentration of exposure in indoor air (μg m$^{3-1}$), IR = intake rate (m^3 h^{-1}), ET = exposure time (h day^{-1}) and BW = body weight (kg).

3. Results and discussion

3.1. Method validation and quantitation of DBPs

3.1.1. Validation of analytical method

The use of a polyethylene glycol stationary phase for the GC separation of HVOCs was determined to be efficient, and a 5% phenyl-methylpolysiloxane stationary phase was used for efficient separation of derivatized haloacetic acids, halophenols and haloacetonitriles.

The analytes showed sharp peaks as shown in Fig. 1, and the ratios of the peak area of the standard to internal standard were used to quantify each DBP's compound.

Generally, DBPs can be generated during sample pretreatment in the presence of NaOCl. Therefore, samples were analyzed by adding ascorbic acid to remove the residual chlorine. The amount of DBPs formed was studied in accordance with the addition amount of ascorbic acid. In the case of chloroform, the concentration of DBPs increased to 0.1 g ascorbic acid in liquid-type and 0.3 g ascorbic acid in solid-type samples, and the concentration was maintained beyond that. The concentrations of DBPs without the addition of ascorbic acid increased to 2.5-fold in liquid samples and to 3000-fold in solid samples than those in the samples after the addition of ascorbic acid as shown in Fig. 2. The addition of ascorbic acid is recommended to be 0.3 g to remove the residual chlorine in samples.

The methods modified above were verified. Blank samples were prepared at a concentration of 1% NaOCl solution, which was similar to NaOCl concentration of products.

Limits of detection (LOD) and limits of quantification (LOQ) were estimated from this study as shown in Table 2. The LOD and LOQ were determined as the concentrations resulting in a minimum signal-to-noise ratio of 3 and 10, respectively, and the standard deviation for replicate determination ($n = 7$) were 15% or less. The concentration ranges of LOD and LOQ were 0.0005–0.012 and 0.002–0.038 mg kg^{-1}, respectively.

Examination of the typical standard curve by computing a regression line of the peak area ratios of analytes on concentration using a least-squares fit demonstrated a linear relationship with determination coefficients above 0.994.

The reproducibility of the assay was very good, as shown in Table 2. For five independent determinations in the two concentrations, the accuracy was in the range of 89.6%–114%, and the precision was less than 14%.

3.1.2. Quantitation and pattern of DBPs in the household products

The validated methods were applied to analyze HVOCs, haloacetic acids, haloacetonitriles and halophenols in 15 household products collected from five local supermarkets in the Republic of Korea. Quantitative analyses were performed in SIM mode.

Seven HVOCs and two haloacetic acids were detected and quantified. The concentration levels of VOCs and haloacetic acids determined in samples are shown in Fig. 3. Chloroform was found in all disinfectant samples in the concentration range of 0.2–30.2 mg kg^{-1}, and carbon tetrachloride was found in the concentration range of 0.05–352 mg kg^{-1} in 13 of the 15 analyzed samples. Chlorobenzene, 2-chlorotoluene, 4-chlorotoluene, 1,2-
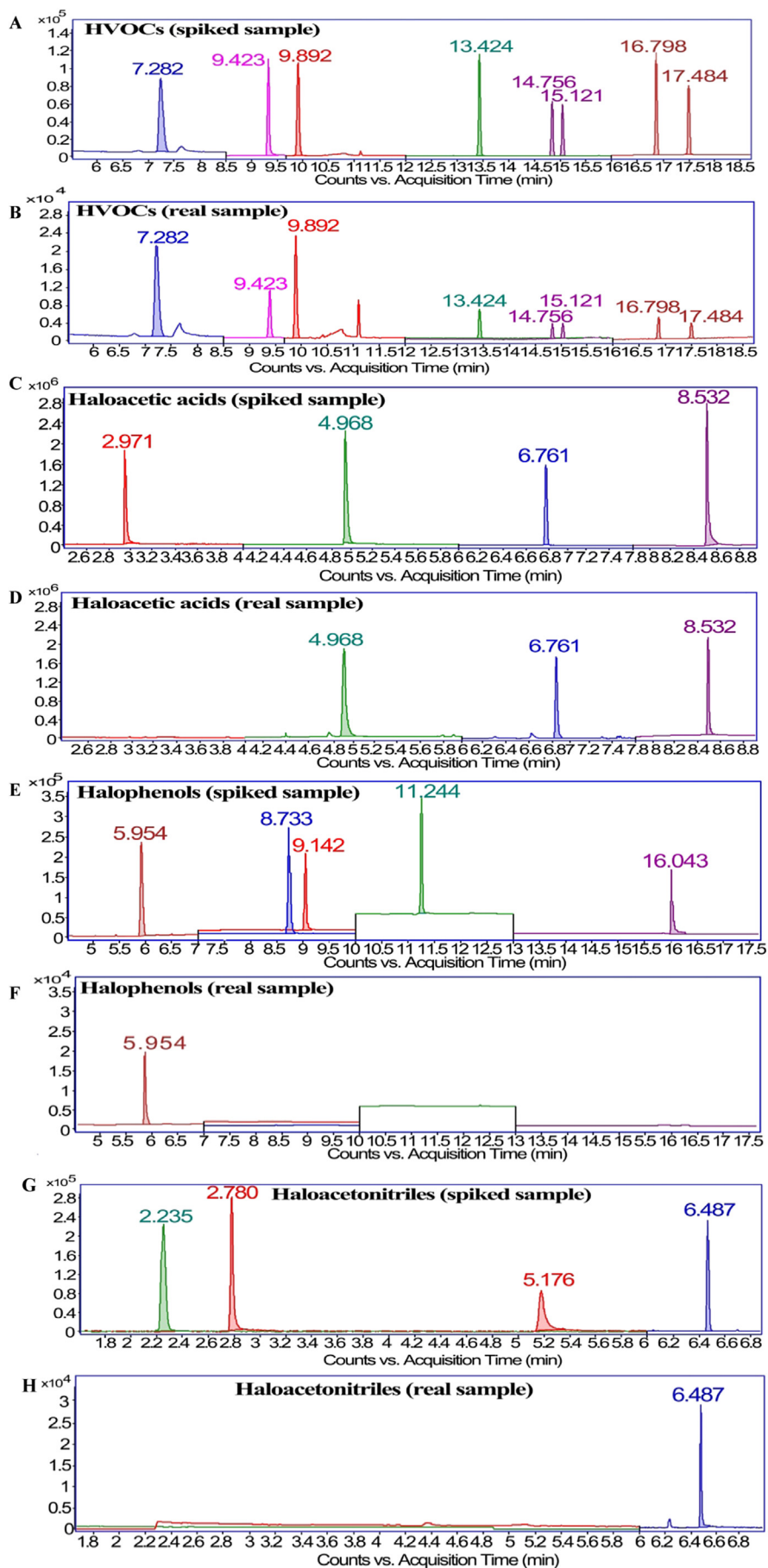
Fig. 1. GC-MS ion chromatogram from spiked samples (A,C,E and G) and real samples (B, D, F and H). (A and B: 7.282 min = carbon tetrachloride, 9.423 min = fluorobenzene, 9.892 min = chloroform, 13.424 min = chlorobenzene, 14.756 min = 2-chlorotoluene, 15.121 min = 4-chlorotoluene, 16.798 min = 1,4-dichlorobenzene, 17.484 min = 1,2-dichlorobenzene, 1,2-dichlorobenzene-d$_4$; C and D: 2.971 min = chloroacetic acid, 4.968 min = dichloroacetic acid, 6.761 min = trichloroacetic acid, 8.532 min = trifluoroacetic acid; E and F: 5.954 min = 2-chlorophenol-d$_4$, 8.733 min = 2,4-dichlorophenol, 9.142 min = 4-chlorophenol, 11.244 min = 2,4,6-trichlorophenol, 16.043 min = pentachlorophenol; G and H: 2.235 min = bromochloroacetonitrile, 2.780 min = dichloroacetonitrile, 5.176 min = trichloroacetonitrile, 6.478 min = 4-bromofluorobenzene).
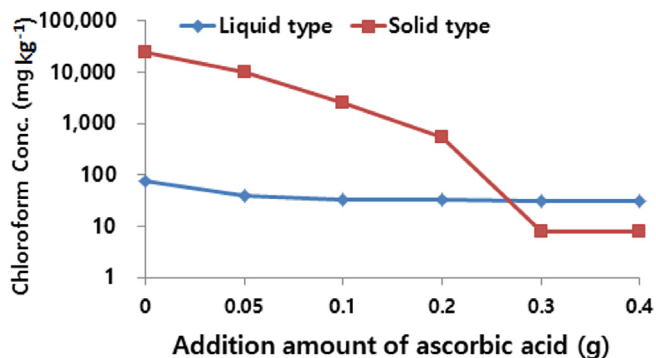
Fig. 2. The change of generated chloroform according to addition amount of ascorbic acid.
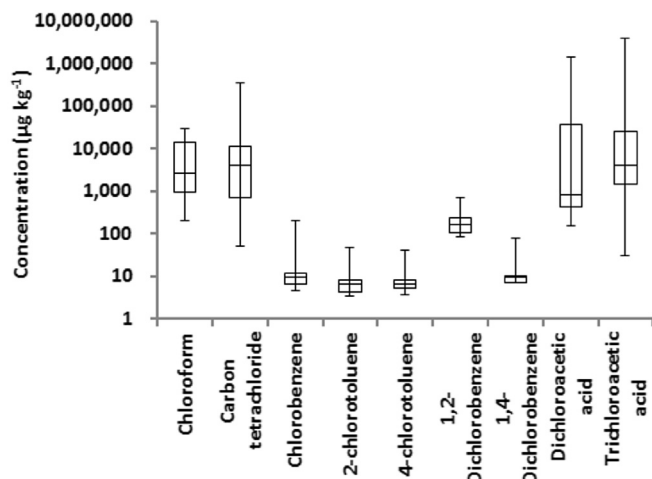

Fig. 3. The box plot of DBPs concentration in the household products.

dichlorobenzene and 1,4-dichlorobenzene were detected in the concentration range of 0.005–0.212 mg kg^{-1}, 0.003–0.046 mg kg^{-1}, 0.004–0.042 mg kg^{-1}, 0.084–0.735 mg kg^{-1} and 0.007–0.077 mg kg^{-1} in all analyzed samples, respectively. Dichloroacetic acid was identified and detected in 11 of the 15 samples in the concentrations range of 0.150–1400 mg kg^{-1}, and trichloroacetic acid was identified and detected in 11 of the 15 analyzed disinfectant samples in the concentrations range of 0.030–3860 mg kg^{-1}.

In a previous study, chloroform and carbon tetrachloride were detected in a range of 0.08–154 mg kg^{-1} and 0.01–169 mg kg^{-1} in 42 products, respectively (Odabasi, 2008). Additionally, chlorobenzene and 1,2-dichlorobenzene were detected in a range of 0.003–0.007 mg kg^{-1} and 0.003–0.03 mg kg^{-1} in a previous study (Odabasi, 2008). The detected concentration range was not significantly different with our results. However, dichloroacetic acid and trichloroacetic acid have not been published for their detection in the household products; therefore, their identification in this study have not been published previously. Haloacetonitriles and halophenols were not detected in all cleansing products.

DBP type and pattern observed in household products have many differences with those in chlorinated drinking water. Carbon tetrachloride is detected only in household products, and chloroform, carbon tetrachloride, dichloroacetic acid and trichloroacetic acid are major DBPs in household products. Otherwise bromide-substituted DBPs, such as bromodichloromethane and dibromochloromethane, are not detected in household products due to absence of Br$^-$ in the household products. These DBPs have been mainly detected in chlorinated drinking water as following: the concentrations range from 9.6 to 60 μg L^{-1} for chloroform, 2.9–8.2 μg L^{-1} for bromodichloromethane, 0.4–4.1 μg L^{-1} for dibromochloromethane and 0.1–3.0 μg L^{-1} for bromoform (WHO, 2004). The different DBP pattern is thought to stem from the different precursors reacting with chlorine. The precursors of DBPs in drinking water have been known as humic substances, carboxylic acids, amino acids, proteins and carbohydrates (Bond et al., 2011), otherwise, those in household products may be ingredients such as fragrances and surfactants as shown in Table 1. The most characteristic pattern of DBPs detected in household products from our study is that haloacetic acids are found in the highest concentration. This trend is different from the DBPs pattern observed in chlorinated drinking water (Krasner et al., 1989).

3.2. Estimated inhalation exposure associated with cleaning activities

A quantitative exposure assessment of the DBPs from cleaning products has a very great uncertainty due to the large individual variation in the amount of products used and different exposure mechanisms such as skin absorption and inhalation. Although it is not simple to decide whether the detected concentrations are safe or not, toxicity was discussed through the simple calculation of daily inhalation exposure (mg/kg/day) of DBPs.

The DBP concentrations in the room air (C_{air}) by the use of cleansing products were calculated by the equation mentioned in

Table 4
The concentration of DBPs in air, and inhalation exposure by household products use.

Compounds	C_{air} (μg m$^{3-1}$)				D_{inh}				Total D_{inh}
	Chlorine bleach	Mildew remover	Drain cleaner	Washing machine cleaners	Chlorine bleach	Mildew remover	Drain cleaner	Washing machine cleaners	
Chloroform	3.16×10^2	1.30×10^2	2.95×10^2	9.52×10^1	1.55×10^{-2}	6.34×10^{-3}	4.66×10^{-3}	1.45×10^{-2}	4.09×10^{-2}
Carbon tetrachloride	3.69×10^3	9.62×10^2	1.10×10^2	1.45×10^2	1.80×10^{-1}	4.71×10^{-2}	7.12×10^{-3}	5.36×10^{-3}	2.40×10^{-1}
Chlorobenzene	1.30×10^{-1}	8.42×10^{-2}	9.97×10^{-2}	1.23×10^0	6.38×10^{-6}	4.12×10^{-6}	6.01×10^{-6}	4.88×10^{-6}	7.55×10^{-5}
2-Chlorotoluene	7.53×10^{-2}	6.40×10^{-2}	1.36×10^{-1}	2.66×10^{-1}	3.69×10^{-6}	3.13×10^{-6}	1.30×10^{-5}	6.64×10^{-6}	2.65×10^{-5}
4-Chlorotoluene	8.52×10^{-2}	7.66×10^{-2}	1.01×10^{-1}	2.45×10^{-1}	4.17×10^{-6}	3.75×10^{-6}	1.20×10^{-5}	4.93×10^{-6}	2.48×10^{-5}
1,2-Dichlorobenzene	2.54×10^0	1.92×10^0	1.57×10^0	4.25×10^0	1.24×10^{-4}	9.41×10^{-5}	2.08×10^{-4}	7.70×10^{-5}	5.03×10^{-4}
1,4-Dichlorobenzene	1.13×10^{-1}	3.91×10^{-1}	1.42×10^{-1}	4.44×10^{-1}	5.54×10^{-6}	1.91×10^{-5}	2.17×10^{-5}	6.93×10^{-6}	5.33×10^{-5}
Dichloroacetic acid	9.92×10^2	4.79×10^2	1.72×10^4	2.65×10^0	4.86×10^{-2}	2.34×10^{-2}	1.30×10^{-4}	8.41×10^{-1}	9.13×10^{-1}
Trichloroacetic acid	3.50×10^2	1.23×10^3	4.73×10^4	2.55×10^1	1.71×10^{-2}	6.04×10^{-2}	1.25×10^{-3}	2.32×10^0	2.39×10^0

section 2.5. The room volume and ventilation rate are standardized to 9.3 m^3 and 2.0 L s^{-1} for chlorine bleach, mildew remover and washing machine, and 24.5 m^3 and 2.5 L s^{-1} for drain cleaner by NIER (NIER, 2014). The amount of product used and release time were applied differently according to product type as shown in Table 3 (NIER, 2014). The room air concentrations of nine DBPs were calculated for four different household products. The air concentration levels of DBPs were in the range of 6.40x10^{-2} to 4.73 × 10^4 μg m$^{3-1}$ as shown in Table 4.

To calculate the daily inhalation exposure of DBPs by the use of household products, the following parameters were applied. Korean adult body weight was estimated to 64.2 kg (NIER, 2014), and a breathing rate and the exposure time of 0.65 m^3 h^{-1} and 4.83 h day^{-1} standardized by the MOE were also used as exposure factors (MOE, 2007). The total values of D_{inh} in each product were used because consumers could be simultaneously exposed when the products were used indoors. On this basis, the values of estimated total D_{inh} were from 2.48x10^{-5} to 2.39 mg/kg/day (Table 4). The highest value of the D_{inh} was 2.39 mg/kg/day for trichloroacetic acid, and the second one was 0.913 mg/kg/day for dichloroacetic acid. The exposure of haloacetic acids was mostly from using washing machine cleaners. The daily inhalation exposures for chloroform, carbon tetrachloride, chlorobenzene, 1,2-dichlorobenzene and 1,4-dichlorobenzene were similar with those from the previous study of Odabasi (2008).

Tolerable concentrations of chloroform and carbon tetrachloride by the World Health Organization (WHO) were 0.14 mg m$^{3-1}$ and 11.4 g m$^{3-1}$, respectively (WHO, 2004a, 2004b). When these tolerable concentrations were applied to calculate D_{inh}, the values were 2.74x10^{-2} and 2.23 mg/kg/day for chloroform and carbon tetrachloride, respectively. The total D_{inh} of chloroform exceeded D_{inh} calculated using the tolerable concentration of WHO. In these values, uncertainty exists because scenario, parameters and equations involve imperfect information. Uncertainty level from limitation of realistic release ratio about chemicals of product, lack of reflection of realistic situation and application of basic exposure scenario may be "medium" for calculated D_{inh}.

4. Conclusions

A variety of DBPs was identified and quantified in chlorine-containing household products. Seven HVOCs (chloroform, carbon tetrachloride, chlorobenzene, 2-chlorotoluene, 4-chlorotoluene, 1,2-dichlorobenzene and 1,4-dichlorobenzne) and two haloacetic acids (dichloroacetic acid and trichloroacetic acid) were detected in the products. Especially, dichloroacetic acid and trichloroacetic acid were identified for the first time in this study. When the daily average exposure was calculated based on these concentrations, the exposure of haloacetic acids was mostly severe from using washing machine cleaners. The D_{inh} of trichloroacetic acid was calculated to the highest value of 2.39 mg/kg/day, and that of dichloroacetic acid was the second one of 0.913 mg/kg/day among DBPs. Total D_{inh} of chloroform was 4.09x10^{-2} mg/kg/day and exceeded the tolerable concentration (2.74xE10^{-2} mg/kg/day) defined by WHO. Although all calculated values have great uncertainty, the detected concentrations cannot be overlooked, considering their ubiquity in other sources. The situation is made more serious by the fact that no official controls for DBPs in household exist and this does not make users aware of their health risk. For this reason it is desired that authorities regulate chlorine-containing household products, and the DBPs in the products should be controlled to the lowest possible concentrations. Furthermore, users should further elaborate indoor-air to be well-ventilated after the use of the products.

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