



# 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.

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## 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<sup>-1</sup> in all products, and carbon tetrachloride was observed in 13 samples in a range of 0.05–352 mg kg<sup>-1</sup>. Dichloroacetic acid and trichloroacetic acid were also detected up to 94 and 146 mg kg<sup>-1</sup> 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 byproducts (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; Martinez 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

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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<sub>2</sub>PO<sub>4</sub>)(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<sup>-1</sup> in methanol), EPA 552.2 haloacetic acids mix (each 2000 µg ml<sup>-1</sup> in methyl *tert*-butyl ether), EPA 551B halogenated volatiles mix (each 2000 µg ml<sup>-1</sup> in methyl *tert*-butyl ether), EPA 502 internal standard mix (each 2000 µg ml<sup>-1</sup> in methanol), 4-chlorophenol (99%), 2,4-dichlorophenol (99%), 2,4,6-trichlorophenol (98%), pentachlorophenol (97%), 2-chlorophenol-d<sub>4</sub> (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<sub>4</sub> (1.0 mg L<sup>-1</sup>) 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<sup>-1</sup>) 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 haloacetoneitriles

The extraction procedure for the haloacetoneitrile 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<sup>-1</sup>) 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<sub>2</sub>PO<sub>4</sub>. A 50-µL volume of 2-chlorophenol-d<sub>4</sub> (1.0 mg L<sup>-1</sup>) 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 haloacetoneitrile 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<sup>-1</sup>.

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

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