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RESEARCH ARTICLE

Evaluation of a GC–MS method for benzyl chloride content in processed food, meats, and marine products distributed in Korea

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Abstract Benzyl chloride is a harmful chemical that contaminates air, water, and food. A static headspace GC–MS method for determining benzyl chloride in food was developed and validated. Two food matrices (fat/oil and chicken) were used for method validation. Sample preparation involved ultrasonication extraction and purification (syringe filtration). Linearity (R^2) was > 0.99, accuracy ranged from 86.91% to 110%, the limit of detection was 0.04–0.17 mg/kg, and the limit of quantification was 0.13–0.52 mg/kg. Recovery varied from 88.19% to 111.77%, and precision ranged from 0.10% to 1.17% in intraday and interday analyses. Among 102 food items (oils, fats, meat, marine, and egg products) distributed in Korea, benzyl chloride was only detected in six of the marine products. The validated analytical method can be used for routine monitoring of benzyl chloride residues in food and thereby prevent the human health risks associated with the consumption of food contaminated with this chemical.

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Keywords Benzyl chloride · Headspace GC–MS · Validation · Analytical method · Harmful chemical

Introduction

As industrial development progresses, there is growing environmental and public health concern about the potential for the ever-increasing number of hazardous substances, such as environmental pollutants and harmful materials, to transfer through the food chain (Kashtock, 2009; Rasheed et al., 2019). Benzyl chloride, the main substance in this study, is mainly used to produce the chemical intermediate as various industrial purposes in the manufacture of dyes, medicines, perfumes, flavor products and food packaging (U.S. EPA, 1986). Therefore, since benzyl chloride is used in the process of food packaging or manufacturing, there is a high possibility of penetration and contamination into food (Bhunia et al., 2013). According to the FACTS, Failure and Disasters Technical Information System website, there globally have been five cases of benzyl chloride leakage accident in 1980s and 1990s. The leakage pathway of benzyl chloride was usually carried out in the manufacturing (processing), storage, transportation. Benzyl chlorde is exposed to ecosystem such as water, soil, air, through various accidents. Therefore, it is also likely to be contaminated with benzyl chloride, and it can also affect humans and animals who consume it. In addition, it is highly likely to penetrate humans or animals through inhalation, skin contact, or eyes during the manufacturing process using benzyl chloride or in the process of treating residues (Environment Canada, 2009a). Industrial chemical spills have recently continued to occur in Korea (National Institute of Chemical Safety), which leads to the possibility of bringing pollution to foods in the manufacturing process and the process of being thrown residue away. Either intentional or unintentional, food contamination can cause acute or chronic toxicological disease, depending on the amount and duration of the intake (Kashtock, 2009; Rather et al., 2017). Some long-term health effects following exposure to hazardous chemicals include rapid fatigue, persistent headaches, and dystonia of the autonomic nervous system (Choudhury et al., 2008). There are many steps in the food supply chain in which chemicals might contact food, from farm to fork (Gilbert et al., 1994; Kashtock, 2009). Numerous factories deal with harmful industrial substances worldwide, and there are frequent chemical leaks. Consequently, various hazardous substances are present in the air, soil, and water (International Labour Organization [ILO], 2021). Moreover, some hazardous substances are produced as byproducts during manufacturing. In addtion, benzyl chloride (C_6H_5-CH_2Cl), known as chloromethyl(benzene) and α-chlorotoluene (Hong et al., 2020), is also a chemical intermediate in the production of plasticizers (e.g., benzyl butyl phthalate), benzyl alcohol, phenylacetic acid via benzyl cyanide, pesticides, dyes, flavors, cosmetics, perfumes, and disinfectants and is classified as a possible human carcinogen (EPA, 2014; IARC, 1999). This organic compound is a colorless liquid at room temperature with high solubility in non-polar and organic solvents and has a strong, unpleasant odor (Rossberg et al., 2006; Smit, 2010). Benzyl chloride is classified as an accident precaution chemical in the list of hazardous chemicals. Accident precaution chemicals are chemical substances that are highly toxic and explosive, with a high possibility of a chemical accident or that the scale of damage is likely to be significant in a chemical accident (K. Lee et al., 2019). It also refers to a substance that can contaminate food or be transferred to food raw materials through contamination of the agri-food ecosystem directly or indirectly. With the frequent use during the manufacturing process, benzyl chloride may be leaked out intentionally or by accident, causing human exposure at the workplace or environmentally (Hong et al., 2020). Among its many potential human health effects, it causes extreme irritation to eyes, skin, and mucous membranes, upper respiratory tract and lung damage, along with pulmonary edema and other effects ranging from mild gastroenteritis to fatal cases of hepatic, renal, and neurological syndromes. Thus, various foods must be inspected and measured for the presence of this chemical contaminant (Rather et al., 2017). However, no studies have evaluated an analytical method to detect the contents of benzyl chloride in food products. Therefore, this study was conducted to establish and validate an analytical method with for benzyl chloride to detect possible food contamination due to accidents related to the leakage of benzyl chloride. Based on the following definition, method validation was performed. The calibration curves showed suitable linearity ($R^2 > 0.99$) of the method for estimating benzyl chloride in both matrix types (Moosavi and Ghassabian, 2018). LOD and LOQ are two important parameters in quantitative analysis (Şengül, 2016). The LOD is the lowest concentration of analytes that can be detected under explicit experimental conditions but not necessarily quantified (Şengül, 2016), while the LOQ is the minimum concentration of an analyte that can be quantified at acceptable levels of accuracy and precision under specified experimental conditions (Muscarella et al., 2007; Şengül, 2016; Taverniers et al., 2004).

As a result, method validation including calibration curve, linearity, LOD, LOQ, accuracy, precision, recovery was successfully performed and the results of validation for each of the two matrices (Fatty liquid, fatty solid) is obtained in this research.

Materials and methods

Chemicals and materials

The standard benzyl chloride (purity ≥ 99%) and the internal standard (IS; benzyl chloride-d_7, purity ≥ 98%) were both of analytical quality and were purchased from Supelco, Inc. (Bellefonte, PA, USA). Dichloromethane (DCM) of HPLC-grade was used as a solvent and purchased from Burdick & Jackson (Muskegon, MI, USA). Syringe filters (30 mm, 0.22 μm) were purchased from Advantec (Toyo Roshi Kaisha, Ltd., Tokyo, Japan). For the static headspace (SHS) analysis, 20-mL headspace vials (23 × 75 mm for CTC PAL) and 20-mm crimp caps (w/3-mm thick PTFE/silicone septa, ultralow bleed, suitable for high temperatures of ≤ 24 °C) were acquired from Advantage Moulding, Inc. (ML Lab Friends, Gyeonggido, Korea).

Preparation of benzyl chloride standard solution

The standard stock solution (10,000 mg/L) of benzyl chloride was prepared by dilution in DCM. This stock solution was used to prepare working solutions of the benzyl chloride standard at six different concentrations (1, 2, 5, 10, 20, and 40 mg/L). The IS stock solution of 2,000 mg/L benzyl chloride-d_7 was prepared by dilution in DCM and further diluted to obtain a working solution of 50 mg/L.

Samples and sample preparation

Samples were purchased from traditional markets and local grocery stores at five places in South Korea: Daejeon;

Gongju, Chungcheongnam-do Province; Iksan, Jeonllabuk-do Province; Seongnam, Gyeonggi-do Province; Seoul, the capital city of South Korea. These five places basically were chosen based on the high possibility of pollution hazards according to the location of companies that produce various kind of products using benzyl chloride and transport. Sample selection was based mainly on the properties of benzyl chloride (a non-polar substance with high lipid solubility). In other words, considering the lipid or physical properties of many foods, meats and marine products, and processed foods with high lipid contents were mainly selected and purchased for analysis in this research.

The products were categorized by matrix into liquid oil/fat (M1) and solid-fatty samples (M2). Eight high-fatty liquid samples were purchased from each of 3 regions (Seoul, Seongnam, Iksan) (24 products in total), and 26 items of meat, marine, and egg products were purchased from each of 5 regions (Daejeon, Gonju, Iksan, Seoul, Seongnam) (78 products in total). To validate the analysis of benzyl chloride, soybean oil and chicken were used as the representative samples of M1 and M2, respectively. After removing the non-edible parts, like bone and entrails, from solid samples (chicken), the samples were ground for homogenization treatment with a blender (Philips viva collection blender) were purchased from Philips (Amsterdam, Netherlands) through fine Labtech (Seocho-gu, Seoul, Korea) and placed in a conical tube. Ten grams of blended sample was placed in a 250-mL amber bottle with 10 mL DCM and ultrasonicated using an ultrasonic bath (60 Hz, 330 W; JAC-2010, Kodo Co., Ltd., Gyeonggi-Do, Korea) for 20 min to extract the benzyl chloride. And 100 μL of DCM was collected and filtered using a syringe filters (pore size 0.22 μm) which were purchased from Advantech (Taipei, Taiwan). After extraction and filtration, the samples were diluted with DCM to 200 μL with the addition of benzyl chloride-d_7 at a concentration of 50 mg/kg. Preparation of the liquid samples followed the same method as the solid samples but without grounding. The samples that sealed with parafilm were stored below 20 °C in a refrigerator and placed in a headspace vial with a cap for subsequent analysis.

Extraction and purification

Fatty liquid samples

Ten-gram aliquots of the fatty liquid samples without homogenization were placed in 10 mL DCM in an amber bottle, followed by the addition of 1 mL of 50 mg/L IS (benzyl chloride-d_7), and extracted by ultrasonication in an ultrasonic bath (60 Hz, 330 W; JAC-2010, Kodo Co., Ltd., Gyeonggi-Do, Korea) for 20 min. The extract was transferred to a separatory funnel and gently shaken for 5 min to separate the DCM layer, which was removed using a 10-mL syringe and filtered through a 0.2-μm syringe filter. Afterward, 200 μg of the sample was placed in a vial for headspace analysis, and gasification and separation were carried out using the headspace analyzer (DANI-HS 86.50 plus, Dani instruments s.p.a, Colongno, Italy).

Fatty solid samples

Ten-gram aliquots of the fatty solid samples were weighed after grinding with a blender. Then, the homogenization process and subsequent steps were the same as those described above for the liquid samples.

SHS analyzer and GC–MS analysis of benzyl chloride

To detect benzyl chloride in small amounts in the samples, all samples were prepared, as described above, and analyzed by SHS–GC–MS. The same SHS analyzer (DANI-HS 86.50 plus, Dani instruments s.p.a, Colongno, Italy) was used to analyze all food samples in this research. Briefly, 200 μg of the sample was transferred to a 20-mL headspace vial, sealed immediately with a crimp top aluminum cap, and analyzed to determine the composition of the headspace volatiles. For each sample, the analysis was performed in triplicate. The incubation time (30 min) and the shaking intensity (soft) during the SHS analysis were predetermined. The incubation temperature (oven temperature) and the sample loop temperature were both 180 °C, and the transfer line temperature was set at 190 °C. The sample interval time was 70 min, and the vial pressure was 2.50 bar.

The GC–MS system (7820A/5975 MSD, Agilent Technologies, Santa Clara, CA, USA) was equipped with an HP-1 GC column (0.32 mm × 30 m, i.d. 0.25 μm film thickness; J&W Scientific, Folsom, CA, USA). Ultrahigh purity helium was used as the carrier gas at a constant flow rate of 2.4 mL/min. The injection was performed in splitless mode at 240 °C. The oven temperature was held at 60 °C for 1 min, ramped from 60 to 90 °C at a rate of 8 °C/min, then elevated to 240 °C at 15 °C/min and maintained for 8 min. The ion source and ion quadrupole temperatures were 230 and 150 °C, respectively. The mass selective detector (MSD) was used in selective ion monitoring mode (SIM) to improve the sensitivity by limiting the quality of detected ions to one or more specific fragmented ions of known mass rather than screening a wide range of ions, thereby enabling the detection of specific analytes of interest and eliminating most of the noise. In this study, two ions (one target and one qualifier ions) were searched for each compound, and these ions were unique to the target analytes. The qualifier ions (*m/z*) were 91.1 and 126 for benzyl chloride and 98.1 and 133.1 for benzyl chloride-d$_7$ (the target ions are underlined).

Method validation and analytical quality assurance

As mentioned above, the method was validated for two matrices (M1 and M2), represented by soybean oil and chicken, respectively. Calibration curves were constructed by analyzing a series of standard solutions of benzyl chloride at six concentrations (1, 2, 5, 10, 20, and 40 mg/kg). In addition, the standards were mixed with 50 mg/kg IS (benzyl chloride-d$_7$) to determine the recovery values, one of the validation parameters. These concentrations were based on the publication on the dangers of benzyl chloride by Public Health England (PHE) in 2016 regarding the concentration range setting criteria for standard and IS substances with reference to the American Industrial Hygiene Association (AIHA) 2015 Emergency Response Planning Guideline Values, which suggest that if the concentration of benzyl chloride exceeds 50 mg/kg, it could be life-threatening and lead to death (PHE, 2016).

All standard mixtures were injected in triplicate to obtain calibration curves. According to the AOAC Standard Method Performance Requirements, the method was validated for linearity, limit of detection (LOD), limit of quantification (LOQ), recovery (%), accuracy (%), and precision (%), which was expressed as the coefficient of variation (CV) by repeating the analysis three times a day (intraday) for three consecutive days (interday) (Choudhury et al., 2008). The linear relationship between the concentration of benzyl chloride and the IS (benzyl chloride-d$_7$) relative to the chromatographic peak area of the analyte is shown by the square of the correlation coefficient (R^2) of each calibration curve. LOD and LOQ (mg/kg) were calculated based on signal-to-noise ratios of 3:1 and 10:1, respectively.

Statistical analysis

GC–MS data were acquired and analyzed by the HP ChemStation software (Hewlett Packard, Sunnyvale, CA, USA) and a Microsoft Excel spreadsheet (Microsoft Corporation, Redmond, WA, USA). All experiments were performed in triplicate, and the results were presented as mean ± standard deviation.

Results and discussion

SHS–GC–MS chromatograms of benzyl chloride and benzyl chloride-d$_7$

SHS–GC–MS allowed the identification of benzyl chloride in all food samples to be analyzed under the same conditions. As shown in Fig. 1, IS (benzyl chloride-d$_7$) and benzyl chloride had retention times of 3.752 and 3.884 min, respectively. These retention times were used to confirm the linearity between the peak area ratios of benzyl chloride and benzyl chloride-d$_7$ versus the corresponding concentration of benzyl chloride. The identification of each peak was confirmed in the samples spiked with the standard.

Method validation for benzyl chloride analysis

The Analytical Methods Committee recommends analyzing at least six concentration levels to confirm the linearity of the method (Araujo, 2009). Accordingly, 200-µL aliquots of six different concentrations (1, 2, 5, 10, 20, and 40 mg/kg) of benzyl chloride (standard) and 50 mg/kg IS (benzyl chloride-d$_7$) were injected into the GC–MS to establish the calibration curve. The method validation results for each of the two matrices, including calibration equations, linearity (R^2), LOD, LOQ, accuracy, precision, and recovery, are presented in Tables 1, 2 and 3. In this study, the LOD was 0.17 and 0.04 mg/kg in M1 and M2, and the LOQ was 0.52 and 0.13 mg/kg, respectively in Table 2. Compared to previous studies, this value is considered quite high. Sun et al. (2005) determined benzyl chloride and related compounds in wastewater by headspace GC–MS using a novel activated carbon fiber as the extraction fiber in solid-phase microextraction. The LOD in that article was 20 ng/L, and R^2 was 0.999. The LOD is shown to be in the low range (ng/L) because the water samples spiked with the compounds at low concentrations were used in that study. Lehotay and Hromulakova (1997) described a method for the determination of benzyl chloride, chlorobenzene, naphthalene, and biphenyl in tap and surface water by absorption in 2-methoxyethanol and analysis of the solution by HPLC, which permitted a detection limit of 90 ng/L for benzyl chloride (sample volume of 100 mL of water). The accuracy (%) and precision (CV, %) of interday and intraday results for the benzyl chloride standard mixture at the six different concentrations are listed in Table 3. The accuracy and precision ranged from 86.61% to 110.87% and 0.04–1.71% in M1 and from 93.46% to 115.35% and 0.10–3.25% in M2, respectively. Data for recovery are presented in Table 3. The recovery rates of benzyl chloride measured using the peak area of the IS (benzyl chloride-d$_7$) were 88.19–111.77 ± 0.04–1.98% in M1 and 94.84–117.97 ± 0.04–0.64% in M2. As a result, the analytical method satisfied the linearity ($R^2 > 0.99$), recovery range (80–120%), accuracy range (70–120%), and precision (CV < 20%) requirements of the European Commission directive SANTE/11813/2017 (EC, 2017). Furthermore, the AOAC standards for R^2 (> 0.99),

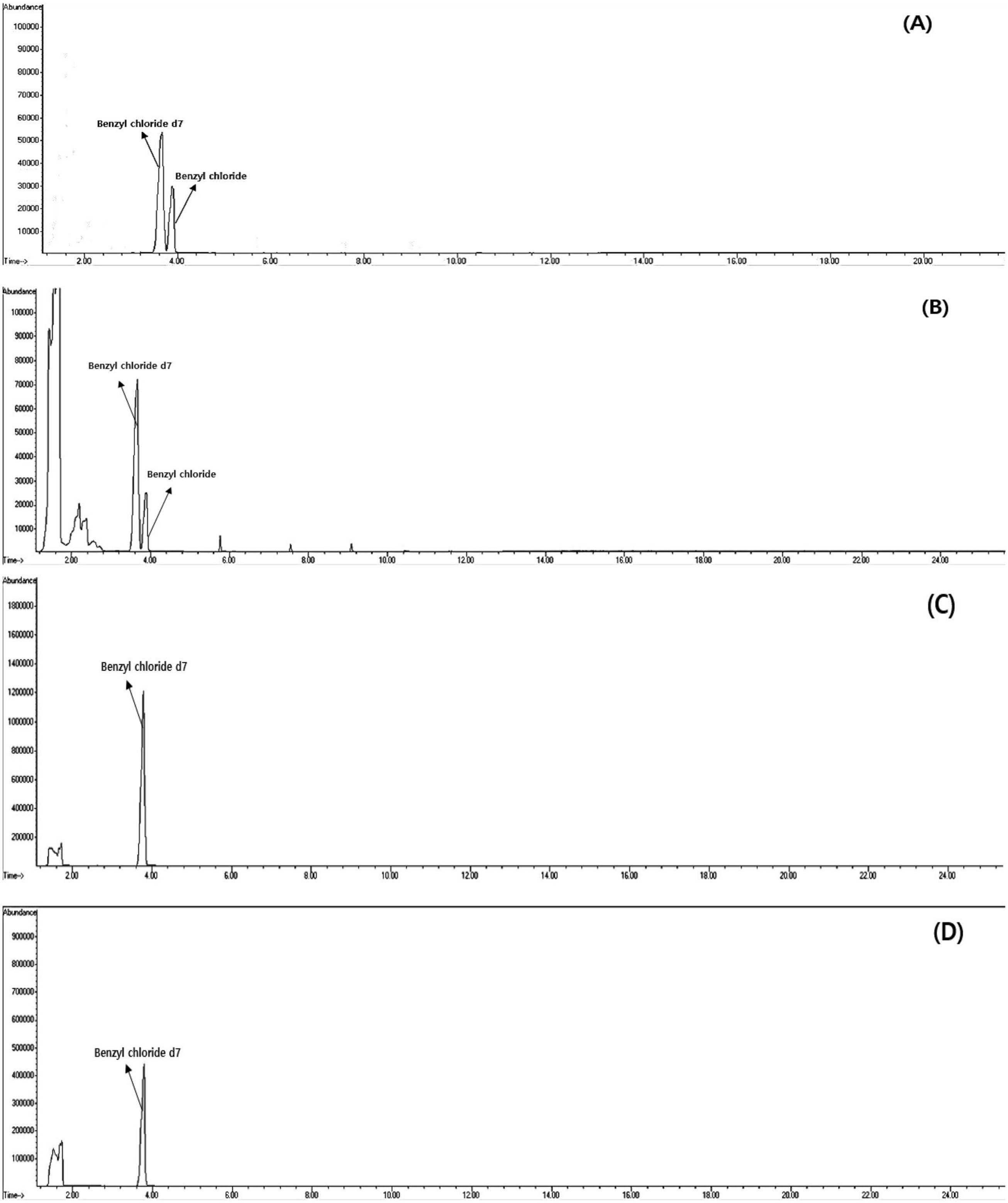

Fig. 1 GC–MS Chromatograms of benzyl chloride standards (**A**); standard spiked sample (**B**); internal standard (IS) with blank in a food sample (**C**); Internal standard (IS) is benzyl chloride-d_7, and chromatograms of benzyl chloride for sample (**D**)

Table 1 Calibration equations, linearity (R^2), limit of detection (LOD), and limit of quantification (LOQ) of benzyl chloride (BC)

Matrix	STD (mg/kg)	Calibration equation	Linearity (R^2)	LOD (mg/kg)[a]	LOQ (mg/kg)[b]
Fatty liquid matrix	Benzyl chloride (1–40)	$y = 0.024x - 0.0022$	0.9996	0.17	0.52
Fatty solid matrix	Benzyl chloride (1–40)	$y = 0.0218x + 0.0051$	0.9995	0.04	0.13

[a] The signal to noise ratio (S/N) of the LOD is 3.3

[b] The signal to noise ratio (S/N) of the LOQ is 10

Table 2 Comparison of accuracy and precision (CV) for benzyl chloride from two matrices (fatty liquid, fatty solid)

	Concentration (mg/kg)	Intra-day (n = 3)		Inter-day (n = 3)	
		Accuracy (%)[a]	Precision (%)[b]	Accuracy (%)[a]	Precision (%)[b]
Fatty liquid matrix	1	86.91	0.47	86.61	0.04
	2	92.87	0.22	93.13	0.34
	5	97.10	0.51	97.14	0.54
	10	110.00	1.63	110.87	0.79
	20	107.00	1.71	105.86	0.51
	40	102.07	1.21	99.83	0.80

	Concentration (mg/kg)	Intra-day (n = 3)		Inter-day (n = 3)	
		Accuracy (%)[a]	Precision (%)[b]	Accuracy (%)[a]	Precision (%)[b]
Fatty solid matrix	1	109.18	0.43	108.98	0.26
	2	115.31	0.33	115.35	0.38
	5	96.91	0.14	97.10	0.44
	10	99.40	0.10	99.66	0.62
	20	95.01	0.22	93.46	3.25
	40	94.48	0.22	94.42	0.12

[a] Accuracy (%) = [1-(mean concentration of measured standard solution-concentration of spiked sample)/ concentration of spiked sample] × 100

[b] Precision (%) = (standard deviation/mean) × 100

Table 3 Comparison of recovery for benzyl chloride from two matrices (fatty solid, fatty liquid)

	Concentration (mg/kg)	Recovery (%)[a]		Concentration (mg/kg)	Recovery (%)[1]
Fatty liquid matrix	1	88.19 ± 0.04	Fatty solid matrix	1	110.02 ± 0.64
	2	93.31 ± 0.28		2	117.97 ± 0.49
	5	97.18 ± 0.70		5	96.93 ± 0.05
	10	111.77 ± 1.98		10	99.36 ± 0.08
	20	108.23 ± 1.95		20	95.36 ± 0.04
	40	101.67 ± 1.37		40	94.84 ± 0.22

[a] Recovery was evaluated with 1, 2, 5, 10, 20, 40 mg/kg spiked concentration and are shown as mean ± relative standard deviation ($n = 3$)

recovery (80–120%), accuracy (< 15%), LOD (< 0.2 mg/kg), LOQ (< 0.6 mg/kg) were also satisfied in this study (AOAC 2012). Cross-validation was conducted with two other laboratories to establish a more accurate analytical method of benzyl chloride. Consequently, the cross-validation deviation for each concentration was within 15%, which means that the method validation can be trusted in this study. The validated analytical method was then applied to analyze and detect benzyl chloride in various food samples.

Benzyl chloride contents in various food products

The levels of benzyl chloride in 24 samples of oils and fats and 78 samples of meats and marine products purchased from a domestic market and grocery store in Korea are presented in Table 4. All experiments were performed in triplicate. Among the 102 samples, benzyl chloride was not detected in the fat and oils and some processed food products in this study. Consistent with these results, the concentrations in processed foods and beverages are expected to be negligible, based on the uses and physical and chemical properties of the substance. Moreover, the incidental contact of fruits packaged in bins coated with a primer containing residual benzyl chloride has been identified; however, exposure was considered negligible (Environment Canada, 2009; Kashtock, 2009). In addition to the fat/oils, no benzyl chloride was detected in meat and eggs, but it was present in the marine product samples in this study. Benzyl chloride was detected at 0.55 and 0.83 mg/kg in mackerel from Iksan and Gongju, 0.47 and 0.15 mg/kg in cero mackerel from Seongnam and Daejeon, and 0.44 mg/kg in the oyster purchased from Gongju, respectively.

These values exceeded the LOD and LOQ ranges. On the contrary, only the flatfish sample from Seongnam, which presented the level of 0.06 mg/kg, did not exceed the LOQ value in Table 4. It confirmed that the detected concentrations did not exceed 2 mg/kg. In this study, the concentration of benzyl chloride in multiple samples, which contains a high percentage of lipid to their weight, was analyzed. This was because of the physical property of benzyl chloride that is very slightly soluble in water. Therefore, various samples that contain high lipid levels were purchased and collected including the marine products with high fat and protein such as mackerel, oyster, flat fish and cero. With these various collected samples, the analysis was conducted in this research. The marine products samples that detected benzyl chloride were purchased from four different locations (Seongnam, Gongju, Iksan, Daejeon) in South Korea according to geological characteristics and related to a location of manufacturing factories using benzyl chloride.

Iksan and Gonju are the cities located near the west coast and there are huge traditional markets that sell various kind of domestic foods that harvested, produced in the region. Moreover, many factories in manufacturing such as pharmaceutical products or plasticizers are located in Iksan and Gonju. Seongnam was also selected to collect samples because there is one of the largest factories that produces plasticizers and resins using benzyl chloride in South Korea. And also Dajeon was also selected to purchase samples as one of the factories which make germicide and disinfectants. Therefore, the samples for this study that were purchased in Seongnam and Daejeon have been collected nearby the company. In order to measure more accurately about the contamination level of the samples, most of food samples were purchased and collected in the traditional market and local grocery stores which are located close to the factories.

As a result of the experiment, the detected fish's benzyl chloride content was classified by region where the samples were purchased, and benzyl chloride was detected at 0.06 mg/kg in flatfish and 0.47 mg/kg in Cero fish purchased in Seongnam, and 0.44 mg/kg in oyster and 0.83 mg/kg in mackerel that purchased in Gongju. The Benzyl chloride was also detected at 0.15 mg/kg in Cero fish collected in Daejeon and 0.55 mg/kg in mackerel collected in Iksan, as mentioned above. The reasons why the benzyl chloride was detected in the fish could be as follows. Since many factories that produce their products using benzyl chloride were located nearby around the traditional market where samples were collected, benzyl chloride would be accumulated in the fish, as the water that the benzyl chloride polluted drains into an ocean, which causes the water pollution, or the soot and smoke that the factories emit causes the air and ground pollutions. Based on the background of the purchase of the samples, the samples were produced and harvested in the area, they would have been environmentally affected by soil or water, or continued to accumulate in the body due to air pollution during subsequent sales, therefore benzyl chloride was detected in the fish samples. On the other hand, benzyl chloride was not detected in the remaining samples except for marine products. Benzyl chloride has a volatile properties and in the case of processed food samples that remained benzyl chloride, it may volatilize in long-term exposure with high temperature during the manufacturing process of the food. In addition, meat or fish without benzyl chloride detection may have not been continuously exposed to benzyl chloride or have decomposed and volatilized due to very low content of benzyl chloride.

According to the PHE (2016) document on protecting and improving the nation's health, exposure to 10–19 ppm (52–98 mg/m^3) of benzyl chloride causes immediate eye irritation. Therefore, the concentration derived from this study was considered lower than the concentration harmful to the human body. Benzyl chloride is volatile and reacts with water or steam to produce corrosive and toxic fumes (ILO, 2021). Furthermore, experimental and modeled data demonstrate that benzyl chloride has moderate acute toxicity to aquatic organisms (Environment Canada, 2009).

Benzyl chloride was detected in marine products in this study. The reason is probably that more than 50 water pollution accidents occur every year (S. Lee et al., 2019; Smit, 2010). Harmful chemical contaminants cause about 8% of these accidents, and even if the frequency of

Table 4 Concentration of benzyl chloride in fat, oils and meat, marine products, eggs

Matrix	Food categroy	Food products	Area	benzyl chloride (mg/kg)
Fatty liquid (Fat and oils)	Perilla oil	Perilla oil A	Seoul	ND[1]
		Perilla oil B	Seongnam	ND
		Perilla oil C	Seongnam	ND
Fatty liquid (Fat and oils)	Sesame oil	Sesame oil A	Seongnam	ND
		Sesame oil B	Seongnam	ND
		Sesame oil C	Seoul	ND
Fatty liquid (Fat and oils)	Corn oil	Corn oil A	Seongnam	ND
		Corn oil B	Seongnam	ND
		Corn oil C	Seongnam	ND
Fatty liquid (Fat and oils)	Olive oil	Olive oil A	Seongnam	ND
		Olive oil B	Seongnam	ND
		Olive oil C	Seongnam	ND
Fatty liquid (Fat and oils)	Canola oil	Canola oil A	Seongnam	ND
		Canola oil B	Seongnam	ND
		Canola oil C	Seongnam	ND
Fatty liquid (Fat and oils)	Sunflower seed oil	Sunflower seed oil A	Iksan	ND
		Sunflower seed oil B	Iksan	ND
		Sunflower seed oil C	On-line	ND
Fatty liquid (Fat and oils)	Soybean oil	Soybean oil A	Iksan	ND
		Soybean oil B	Seongnam	ND
		Soybean oil C	Seongnam	ND
Fatty liquid (Fat and oils)	Grape seed oil	Grape seed oil A	Seongnam	ND
		Grape seed oil B	Seongnam	ND
		Grape seed oil C	Seongnam	ND
Fatty Solid (Meats)	Chicken	Chicken A	lIksan	ND
		Chicken B	Daejeon	ND
		Chicken C	Gonju	ND
Fatty Solid (Meats)	Beef	Beef A	Daejeon	ND
		Beef B	Gonju	ND
		Beef C	lIksan	ND
Fatty Solid (Meats)	Pork	Pork A	lIksan	ND
		Pork B	Daejeon	ND
		Pork C	Gonju	ND
Fatty Solid (Meats)	Smoked duck	Smoked duck A	Gonju	ND
		Smoked duck B	lIksan	ND
		Smoked duck C	Deajeon	ND
Fatty Solid (Meats)	Chicken gizzard	Chicken gizzard A	Seongnam	ND
		Chicken gizzard B	Gonju	ND
		Chicken gizzard C	lIksan	ND
Fatty Solid (Processed Meat)	Meat balls	Meat balls A	Deajeon	ND
		Meat balls B	lIksan	ND
		Meat balls C	Seongnam	ND
Fatty Solid (Processed Meat)	Smoked chicken breast	Smoked chicken breast A	lIksan	ND
		Smoked chicken breast B	lIksan	ND
		Smoked chicken breast C	Seoul	ND
Fatty Solid (Processed Meat)	Jerky	Jerky A	Seoul	ND
		Jerky B	Seoul	ND
		Jerky C	Seoul	ND

Table 4 continued

Matrix	Food categroy	Food products	Area	benzyl chloride (mg/kg)
Fatty Solid	Ham	Ham A	Seongnam	ND
(Processed Meat)		Ham B	Seongnam	ND
		Ham C	Seongnam	ND
Fatty Solid	Chicken nugget	Chicken nugget A	Seongnam	ND
(Processed Meat)		Chicken nugget B	Seongnam	ND
		Chicken nugget C	Seongnam	ND
Fatty Solid	Fish sausage	Fish sausage A	Seoul	ND
(Processed fish)		Fish sausage B	Seoul	ND
		Fish sausage C	Seongnam	ND
Fatty Solid	Crab meat	Crab meat A	Seongnam	ND
(Processed fish)		Crab meat B	Seongnam	ND
		Crab meat C	Seongnam	ND
Fatty Solid	Boiled quail eggs	Boiled quail eggs A	Seongnam	ND
(Eggs)		Boiled quail eggs B	Seongnam	ND
		Boiled quail eggs C	Seongnam	ND
Fatty Solid	Dried filefish fillet	Dried filefish fillet A	Iksan	ND
(Processed fish)		Dried filefish fillet B	Gonju	ND
		Dried filefish fillet C	Deajeon	ND
Fatty Solid	Half-boiled eggs	Half-boiled eggs A	Seoul	ND
(Eggs)		Half-boiled eggs B	Iksan	ND
		Half-boiled eggs C	Iksan	ND
Fatty Solid	Smoked eggs	Smoked eggs A	Iksan	ND
(Eggs)		Smoked eggs B	Iksan	ND
		Smoked eggs C	Iksan	ND
Fatty Solid	Seafood balls	Seafood balls A	Iksan	ND
(Processed fish)		Seafood balls B	Iksan	ND
		Seafood balls C	Iksan	ND
Fatty Solid	Eggs	Eggs A	Seongnam	ND
(Eggs)		Eggs B	Gonju	ND
		Eggs C	Iksan	ND
Fatty Solid	Flat fish	Flat fish A	Iksan	ND
(Fish)		Flat fish B	Daejeon	ND
		Flat fish C	Seongnam	0.06
Fatty Solid	Octopus	Octopus A	Iksan	ND
(Fish)		Octopus B	Daejeon	ND
		Octopus C	Seongnam	ND
Fatty Solid	Squid	Squid A	Daejeon	ND
(Fish)		Squid B	Gonju	ND
		Squid C	Seongnam	ND
Fatty Solid	Mackerel	Mackerel A	Seongnam	ND
(Fish)		Mackerel B	Iksan	0.55
		Mackerel C	Gonju	0.83
Fatty Solid	Hailtail	Hailtail A	Iksan	ND
(Fish)		Hailtail B	Daejeon	ND
		Hailtail C	Gonju	ND
Fatty Solid	Oyster	Oyster A	Seongnam	ND
(Fish)		Oyster B	Gonju	0.44
		Oyster C	Daejeon	ND

Table 4 continued

Matrix	Food categroy	Food products	Area	benzyl chloride (mg/kg)
Fatty Solid	Cod	Cod A	Iksan	ND
(Fish)		Cod B	Daejeon	ND
		Cod C	Gonju	ND
Fatty Solid	Cero	Cero A	Seongnam	0.47
(Fish)		Cero B	Daejeon	0.15
		Cero C	Gonju	ND

[1]ND = not detected, below the limit of detection

discharge of hazardous substances is lower than that of oil spills, the damage to the aquatic ecosystem can be much more serious, and the water environment is at risk of contamination due to accidental or intentional leaks in industrial areas (Ohnishi and Kozo, 1971). In addition, fugacity modeling indicates that if benzyl chloride is released into air, water, or soil, it will remain predominantly in that medium and eventually be degraded through hydrolysis (days or weeks) but may be released continuously or repeatedly (Environment Canada, 2009). Although the substance met the categorization criteria for persistence, it did not meet the criteria for bioaccumulation potential or inherent toxicity to aquatic organisms (ILO, 2021). Benzyl chloride has been detected in stack emissions from waste incineration, and it might also be present in atmospheric emissions from the burning of some fossil fuels (Kashtock, 2009). In considering the use pattern and release information, it is predicted that benzyl chloride would be released in relatively small quantities, mainly into the air, but also to some extent into water (Kashtock, 2009). On this basis, benzyl chloride is readily biodegradable and not bioaccumulating, thus non-persistent in the environment (Environment Canada, 2009).

Short-term studies have shown that exposure to benzyl chloride via inhalation resulted in effects on the respiratory system. In a 4-week inhalation study in male guinea pigs, distended alveoli in the lungs were observed at 180 and 530 mg/m^3 (Monsanto Co., 1983). Neurological effects, consisting of an extension of the duration of the immobility phase in a concentration-dependent manner, were observed in mice exposed to benzyl chloride at 62 mg/m^3 and above for 4 h (De Ceaurriz et al., 1983). However, a lack of dermal studies for repeated-dose and developmental toxicity and a lack of inhalation studies for carcinogenicity and developmental toxicity and no clinical human toxicity studies were identified (Kashtock, 2009).

As mentioned above, no previous studies have analyzed benzyl chloride in various foods. Therefore, an analytical method for measuring benzyl chloride was developed in this study and validated in two different matrices (oil/fat and chicken) to detect the concentration of benzyl chloride in various food samples (fat, oil, meat, marine products, eggs). The benzyl chloride levels in various food products should be compared with other research data, but it could not be proceeded due to a lack of data. Therefore, the concentration of benzyl chloride detected in this study was compared with toxicity levels in several studies. The concentration was also compared to the surveys conducted by the Canadian government (Environment Canada, 2009) and the U.S. Environmental Protection Agency (U.S. EPA, 2013). Benzyl chloride has been reported to cause abnormalities in the thyroid, liver, and blood in vivo based on toxicology data provided by the Integrated Risk Information System (IRIS) of the U.S. EPA (2013) and the National Institute for Occupational Safety and Health, a U.S. federal agency (NIOSH, 1978). It could be concluded that the results of this study were found to be non-hazardous to humans.

The probability of bioaccumulation of benzyl chloride is low, and it could be assumed that it was detected in marine products contaminated by air emissions because, as mentioned above, benzyl chloride is readily biodegradable and not bioaccumulating, thus non-persistent in the environment. When benzyl chloride is released to water or air, it will reside predominantly in the compartment to which it is released, but will fairly quickly be degraded through hydrolysis to benzyl alcohol, which is also readily biodegradable and non-toxic in the environment. It is not considered likely that benzyl chloride pollution has any effects on the global environment (Environment Canada, 2009; Prieto-Blanco et al., 2009). Nonetheless, benzyl chloride has adequate potential toxicity to aquatic organisms because it reacts with water to form benzyl alcohol and hydrochloric acid (Environment Canada, 2009). The half-life for the hydrolysis of benzyl chloride at pH 7 and 25 °C is 15 h, and the rate of hydrolysis is faster at higher temperatures than lower temperatures (Lee and Shin, 2020; Ohnishi and Kozo, 1971).

It should be noted that most of the available experimental data were published several years ago. Another limitation is that there are few research papers or data presenting the actual state of benzyl chloride pollution in Korea. Furthermore, as the industry develops, various and new chemicals are being used more often than in the past. Continuous research is required to determine what harmful effects they have in the human body and the levels at which they are detected. Thus, an accurate quantitative analysis method and the exposure and risk assessment must be established and conducted in Korea. This study provided scientific evidence to support the safety management of hazardous chemical compounds, such as benzyl chloride.

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Declarations

Conflict of interest The authors have no conflicts to declare.

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