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Formation of volatile halogenated compounds in fresh-cut cabbage treated with sodium hypochlorite

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Abstract

This study was conducted to investigate factors affecting the formation of disinfection by-products in fresh-cut cabbage during sodium hypochlorite treatment. Fresh cabbage was disinfected with a sodium hypochlorite solution (100 mg/L) for 10 min, with and without organic acids. Volatile organic compound residues in the fresh-cut cabbage were analyzed using headspace GC/MS. Chloroform was detected as the main by-product. Chloroform formation was dependent on contact time, pH, temperature and initial concentration of sodium hypochlorite solution. The use of sodium hypochlorite solution in combination with hydrochloric acid or some organic acids did not affect chloroform formation, except that citric acid reacted with hypochlorite to produce large amount of chloroform. When the citric acid was coupled with sodium hypochlorite solution, the chloroform level in the sample was dependent on the pre-mixing time of the solution, but was independent on the contact time of the mixed solution with the sample. Rinsing with water effectively reduced chloroform contaminants in the fresh-cut cabbage to the levels of chlorinated drinking water.

Keywords : trihalomethanes, chloroform, sodium hypochlorite, cabbage, citric acid

I Introduction

Sodium hypochlorite is used as a disinfectant in the processing of fruits, vegetables, and other fresh foods. Chlorine is also widely used as a disinfectant for drinking water, and it is well known that chlorine reacts with natural organic compounds in water, resulting in the formation of trihalomethanes (THM)^{1, 2)}. THM are a group of chemicals that commonly include chloroform, bromodichloromethane (BDCM), dibromochloromethane (DBCM) and bromoform. The presence of THM in drinking water is a human health concern. The US Environmental Protection Agency (USEPA) has set the maximum contaminant level for total THM at 80 µg/L as the locational running annual average³⁾. The European Union drinking water directive (98/83/EC) has set the maximum standard for total THM at 100 µg/L⁴⁾, while the World Health Organization (WHO) has announced the drinking water guidelines for chloroform (300 µg/L), BDCM (60 µg/L), DBCM (100 µg/L) and bromoform (100 µg/L)⁵⁾.

The Ministry of Health, Labour and Welfare of Japan has set the maximum contaminant level of total THM at 100 µg/L, for chloroform at 60 µg/L, for BDCM at 30 µg/L, for DBCM at 100 µg/L, and bromoform at 90 µg/L⁶⁾.

The U.S. Food and Drug Administration (FDA) has monitored residual chemical contaminants in foodstuffs through the total diet programs for over 40 years. THM and other chlorinated volatile organic compounds (VOC) have been detected in several foodstuffs, including butter, cheese, margarine and soft drinks⁷⁻¹¹⁾. Several studies have reported that treatment with chlorine solution on poultry, milk and fresh-cut vegetables may induce the formation of reaction by-products¹²⁻¹⁶⁾. Huang *et al.* investigated the THM formation potentials of foods and beverages during production with chlorinated drinking water and observed that THM were formed in the preparation and cooking of foods¹⁷⁾. Recently, Klaiver *et al.* and Lopez-Galvez *et al.* investigated effective washing procedures for microbe removal, and residual THM content in fresh foods^{18, 19)}.

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The Joint FAO/WHO Expert Committee met in 2008 to conduct a risk and benefit assessment of chlorine-based disinfectants in food production and food processing²⁰. The chemical hazard risk of disinfection by-products in foods was discussed in the context of microbial control. Referring to several case studies on the use of chlorine-based disinfection in foods, it was concluded that they posed no health concerns. However, there is a lack of quantitative information on the formation and presence of by-products in foods during disinfection. Therefore, the dietary exposure assessment of these by-products is required for food safety. The meeting recommended further scientific study on the formation, identification and quantification of disinfection by-products in foods at the point of consumption.

The antimicrobial efficacy of sodium hypochlorite solutions can be enhanced by acidification, shifting the predominant chlorine species from hypochlorite ion to hypochlorous acid²¹. Therefore, a sodium hypochlorite solution has often been used with hydrochloric acid or organic acids to adjust the pH value between 6.0 and 7.5²². However, it remains unclear whether any significant risks are associated with the use of acidified hypochlorite treatment on foods.

Our research objective was to investigate the factors that affect the formation of disinfection by-products in fresh-cut cabbage. The effects of sodium hypochlorite concentration, contact time, pH, and acids on the formation potential of THM in fresh-cut cabbage were assessed using Headspace-Gas Chromatography/Mass Spectrometry (HS-GC/MS). Moreover, we investigated the effect of a washing procedure on residual chloroform concentrations in fresh-cut vegetables.

II Materials and Methods

1. Sample preparation

Raw shredded cabbage was used as an example of fresh-cut vegetables. Whole-cabbage was purchased from a local market in Tokyo, Japan. The outside leaves and core of the raw cabbage were removed by hand; internal leaves were cut into 1-mm pieces with a peeler to make the shredded cabbage. The shredded cabbage was placed in a bowl filled with distilled water for a few minutes and then removed and dried for approximately 1 h at the room temperature.

2. Reagents

A stock standard solution mixture of 23 VOC and internal standards solution were purchased from Kanto Chemical Co., Inc. (Tokyo, Japan). Methanol and sodium chloride (water quality test grade) were obtained from Wako Pure Chemical Industries, Ltd. (Osaka, Japan). 2, 4-¹³C-Citric acid (99.9% purity) was purchased from ISOTEC, Inc. (Miamisburg,

OH, USA). Food additive grade citric acid, S.C.-malic acid and tartaric acid of food additives grade were used. A food additive-grade sodium hypochlorite solution was purchased from Wako Pure Chemical Industries and analyzed by iodometric titration. The mineral water evian (Évian-les-Bains, France) was used as reagent water, which confirmed the absence of VOC using HS-GC/MS. All other reagents used were of analytical grade.

3. HS-GC/MS analysis

VOC were analyzed using HS-GC/MS according to standard methods for the examination of drinking water in Japan²³. GC/MS analyses were carried out using a HP 5973 Mass Selective Detector (Hewlett-Packard Co., Palo Alto, CA, USA) interface to HP 6890 gas chromatography (Hewlett-Packard) with a HP 7694 automated headspace sampler. Samples were injected splitless, and VOC were separated using a 25% phenyl and 75% dimethyl polysiloxane capillary column (60 m × 0.25 mm diameter with a 1.0 μm film thickness; Aquatic, GL Sciences, Tokyo, Japan). Helium was employed as the carrier gas at a flow rate of 1.0 mL/min. The GC injector temperature was 200°C. The oven temperature was maintained at 40°C for 2 min, then increased at 4°C/min to 200°C. The headspace conditions were as follows: oven, 60°C; sample loop, 130°C; transfer line, 170°C; 25 min thermal equilibration with shaker on; source temperature, 200°C; quadrupole temperature, 150°C. The detected compounds were compared with the NIST/Willey mass spectra library and were further confirmed by comparing with the mass spectra and retention times of standards.

4. Experimental procedure

1) Disinfection protocol for fresh-cut cabbage

Cabbage (2 g) was weighed into a 50 mL screw cap vial. Samples were dipped with a 100 mg/L sodium hypochlorite solution (pH 10) for 10 min at room temperature. At the end of the dipping time, residual chlorine was quenched with adding 3-fold molar excess solution of ascorbic acid to the chlorinated sample mixture. After being quenched, the treated sample was transferred to tea strainer to remove excess solution, and applied to headspace analysis.

2) Headspace sampling procedure

Treated samples were transferred to a 20-ml headspace vial containing 8 ml of water and 3 g of sodium chloride. Following the addition of 20 ng fluoro-benzene and 4-bromofluorobenzene-methanol solution mixture as internal standards, the vials were immediately sealed using crimp top vial caps with a PTFE-lined silicone septum. Quantification of the 23 VOC was performed using HS-GC/MS as described above. All glassware was heated at 105°C for 3 hours prior to

use to remove volatile contaminants.

3) The chloroform formation potential experiments in acidified hypochlorite solution under the different organic acid treatments

An aliquot of sodium hypochlorite solution (10 mL; 100 mg/L) was placed in a 20-mL headspace vial. The solution was mixed with hydrochloric acid or organic acids (citric acid, malic acid, tartaric acid, succinic acid and fumaric acid) and the pH was adjusted to between 6.0 and 7.0. The acidified solution was pre-mixed at room temperature for various time periods (0, 10, 30, 60 min). At the end of the reaction time, residual chlorine was quenched with adding a 3-fold molar excess solution of ascorbic acid to the mixture. Following the addition of internal standards, the vials were immediately sealed using crimp top vial caps with a PTFE-lined silicone septum. The chloroform concentration in samples was determined using HS-GC/MS as described above.

III Results

1. Development and validation of analytical method

VOC were assessed using HS-GC/MS. All 23 compounds were eluted within 35 min. The isomers *m*- and *p*-xylene co-

elute and have essentially identical mass spectra; therefore, they are quantified as one peak. Benzene also co-eluted with 1,2-dichloroethane. However, the MS detection system could selectively determine these compounds using the specific mass fragments for each compound. The lower limits of quantification (LOQs) were 1 µg/kg for all analyses. The recovery experiments were carried out using fresh-cut cabbage spiked with the compounds at two different analyte concentrations (10 and 100 µg/kg). The mean recovery of spiked standard from samples varied between 72.6 and 109%, and the relative standard deviation ranged from 0.2 to 3.3% (Table 1). These results suggest that all compounds are determined with good accuracy and precision in the samples.

2. Effect of contact time on VOC formation

Figure 1 shows the formation of VOC as a function of contact time during chlorination (at pH 10 and room temperature). Chloroform was detected as the predominant VOC in the chlorinated samples, while BDCM, and tetrachloroethylene (TCE) were observed at lower levels. VOC levels rapidly increased for 20min, and plateaued after 30 min. The other VOC were not detected in the chlorinated samples.

3. Effect of initial sodium hypochlorite concentration on VOC formation

The effect of sodium hypochlorite concentration on VOC

Table 1. Average recoveries (Avg.) and CV resulting from the fortification of the fresh-cut cabbage with 23 volatile organic compounds at 100 µg/kg and 10 µg/kg

No.	Compounds	Amount of added VOCs			
		10 µg/kg		100 µg/kg	
		Avg.* (µg/kg)	CV (%)	Avg. (µg/kg)	CV (%)
1.	1,1-Dichloroethylene	10.0	0.8	101.3	0.7
2.	Dichloromethane	10.7	1.4	106.5	0.6
3.	<i>trans</i> -1,2-Dichloroethylene	10.0	0.9	100.5	0.5
4.	<i>cis</i> -1,2-Dichloroethylene	10.3	0.8	103.4	0.4
5.	Chloroform	10.2	0.9	102.4	0.5
6.	1,1,1-Trichloroethane	9.7	0.6	99.0	0.7
7.	Carbon Tetrachloride	9.4	1.1	97.1	1.7
8.	1,2-Dichloroethane	10.9	1.0	107.6	0.7
9.	Benzene	10.2	0.5	101.4	0.4
10.	Trichloroethylene	9.7	0.5	96.5	0.2
11.	1,2-Dichloropropane	10.6	1.2	104.3	0.5
12.	Bromodichloromethane	10.3	1.1	101.8	0.9
13.	<i>cis</i> -1,3-Dichloropropene	9.7	2.0	95.4	1.5
14.	Toluene	9.6	0.7	94.2	0.3
15.	<i>trans</i> -1,3-Dichloropropene	9.9	1.8	98.8	0.8
16.	1,1,2-Trichloroethane	10.7	2.0	104.5	0.7
17.	Tetrachloroethylene	8.1	2.5	83.5	1.8
18.	Dibromochloromethane	10.1	1.1	99.1	1.7
19+20.	<i>m,p</i> -Xylene	8.2	2.9	77.8	2.0
21.	<i>o</i> -Xylene	8.1	2.9	76.1	1.7
22.	Bromoform	9.5	2.0	95.1	3.3
23.	<i>p</i> -Dichlorobenzene	7.6	1.8	72.6	1.5

* The analyses were replicated five times for each condition.

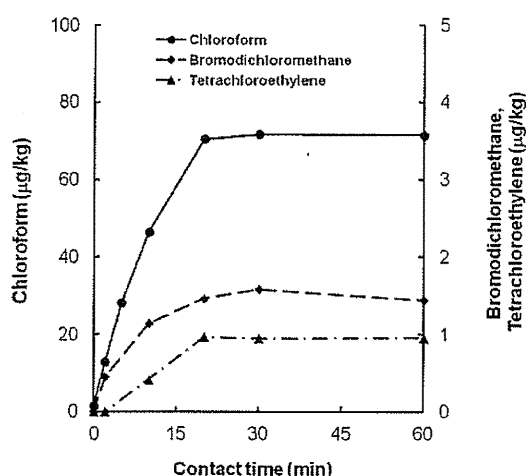


Fig. 1. Effect of contact time on VOC formation in chlorinated fresh-cut cabbage

Samples were disinfected with a 100 mg/L sodium hypochlorite solution at pH 10 and room temperature. VOC concentration in the samples was determined at 0, 5, 10, 20, 30 and 60 min.

formation was investigated (Fig. 2). Samples were disinfected with various sodium hypochlorite concentrations (0, 50, 100, 200 and 500 mg/L as chlorine) and the results indicated that chloroform concentrations increased linearly from 10 to 157.5 µg/kg. BDCM and TCE were detected as minor products above a dose of 50 and 100 mg/L sodium hypochlorite, respectively. The formation of TCE increased with increasing chlorine dose, whereas BDCM formation was not dependent on chlorine dose.

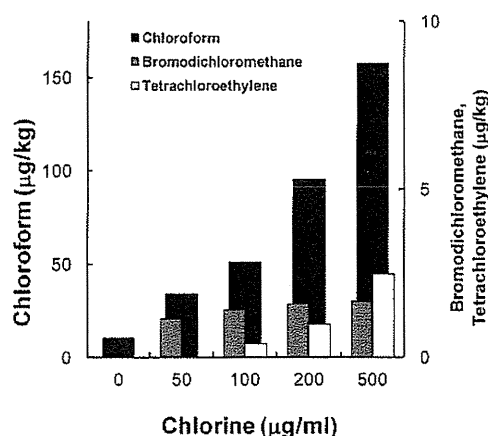


Fig. 2. Effect of sodium hypochlorite concentration on VOC formation in chlorinated fresh-cut cabbage

Samples were disinfected with various sodium hypochlorite concentration (0, 50, 100, 200 and 500 mg/L as chlorine) for 10 min at room temperature.

4. Effect of temperature on chloroform formation

Figure 3 shows the effect of temperature on chloroform formation during disinfection. The samples were disinfected with a 100 mg/L sodium hypochlorite solution at pH 10 at three different temperatures (2, 10 and 21°C). BDCM and TCE were detected at a trace level in chlorinated samples at 21°C. However, it was difficult to constantly monitor these compounds at lower levels. The other VOC were not detected in any of the chlorinated samples. Therefore, we focused on the chloroform formation hereafter. After 10 min of disinfection, the chloroform concentration was increased to 197 and 245%, respectively, when the temperature was raised from 2 to 10 and 21°C. The results suggest that the rate of chloroform formation increases with temperature. At higher temperature (21°C), the chloroform concentration rapidly increased, and plateaued after 30 min. In contrast, chloroform concentration gradually increased with increasing contact time at low temperature (2 and 10°C).

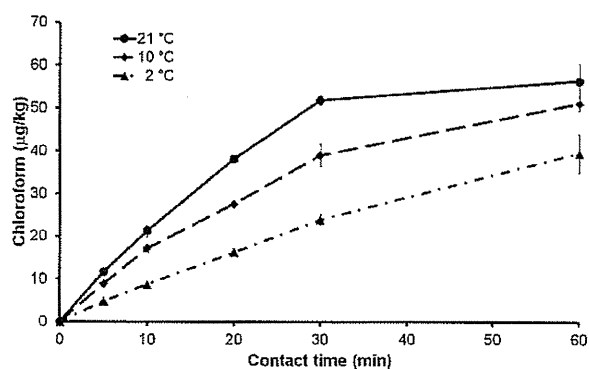


Fig. 3. Effect of temperature on chloroform formation in chlorinated fresh-cut cabbage

Samples were disinfected with a 100 mg/L sodium hypochlorite solution (pH 10) for between 0 and 60 min under various temperature conditions (2, 10, 21°C).

5. Effect of pH on VOC formation

Figure 4 shows the detected VOC concentrations after disinfection with a 100 mg/L sodium hypochlorite solution in fresh-cut cabbage at various pHs (pH 2, 4, 6, 8, 10 and 12). Only chloroform was detected at a high pH. The detected chloroform concentration was 19.7, 33.0, 54.9 and 76.0 µg/kg at pH 6, 8, 10 and 12, respectively. In contrast, there was no significant difference in detected chloroform concentrations at low pH values. In additions, a low-level concentration of carbon tetrachloride was detected only at pH 2.

6. Effect of organic acids on chloroform formation

Since sodium hypochlorite is often coupled used with inorganic and organic acids to enhance its anti-microbial

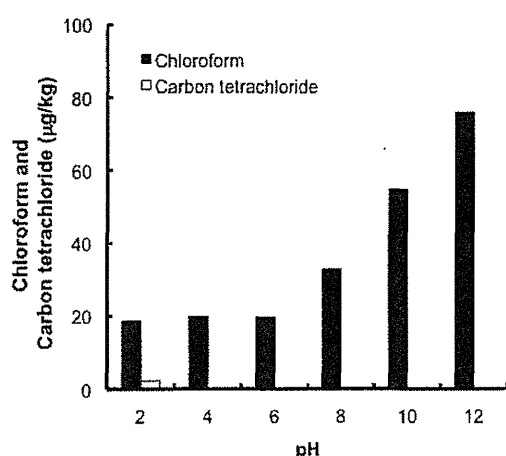


Fig. 4. Effect of pH on VOC formation in chlorinated fresh-cut cabbage

Samples were disinfected with a 100 mg/L sodium hypochlorite solution for 10 min at various pH (pH 2, 4, 6, 8, 10 and 12).

efficacy, effect of organic acids on chloroform formation was assessed (Fig. 5). Sodium hypochlorite solutions (100 mg/L) were mixed with hydrochloric acid or organic acids (citric acid, malic acid, tartaric acid, succinic acid and fumaric acid) and the pH was adjusted to 6.0 - 7.0. The acidified hypochlorite solution was left to stand 0 - 180 min at 10°C. Fresh-cut cabbage were disinfected with a sodium hypochlorite solution for 10 min in the presence and absence of acids. Most organic acids, such as malic acid, tartaric acid, succinic acid and fumaric acid, did not affect chloroform formation. In contrast,

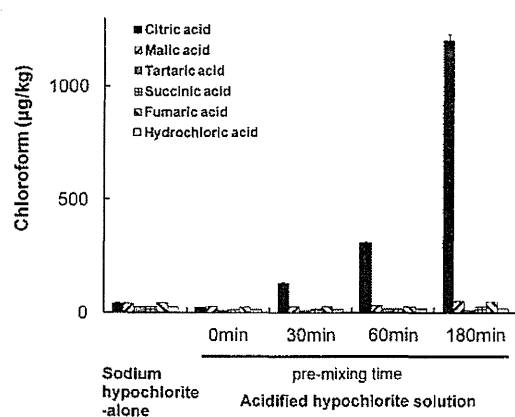


Fig. 5. The combination effect of sodium hypochlorite and organic acids on chloroform formation in chlorinated fresh-cut cabbage

Sodium hypochlorite solution (100 mg/L) was mixed with various acids at 10°C and left to stand 0 - 180 min. Sample were disinfected with the acidified hypochlorite solution or sodium hypochlorite solution-alone for 10 min at pH 6 - 7 at room temperature.

when citric acid was used as a pH buffers, the chloroform levels increased with pre-mixing time. The chloroform levels in fresh-cut cabbage treated with citric acid-activated sodium hypochlorite solution (pre-mixed for 180 min) was 28.7 times greater than with chlorine treatment alone.

7. Effects of pre-mixing time of acidified hypochlorite solution on chloroform formation

The influence of pre-mixing time with citric acid was examined (Fig. 6). A sodium hypochlorite solution was mixed with citric acid and the pH adjusted to 6.8. The mixture was left to stand 0 - 60 min as pre-mixing time at 10°C and was used for the treatment of sample. The concentration of chloroform in the cabbage sample was increased with the contact time, but the initial concentration and the increasing rate of chloroform were different among the pre-mixing time of sodium hypochlorite and citric acid. This fact suggests that citric acid reacts with sodium hypochlorite to form chloroform and the amount of formed chloroform is correlative to the pre-mixing time. On the other hands, the citric acid was found to act suppressively for the formation of chloroform when the pre-mixing time is zero. From these results, we considered that chloroform detected in cabbage is dependent on the pre-mixing time rather than the contact time to disinfectant when the sodium hypochlorite solution is acidified by citric acid.

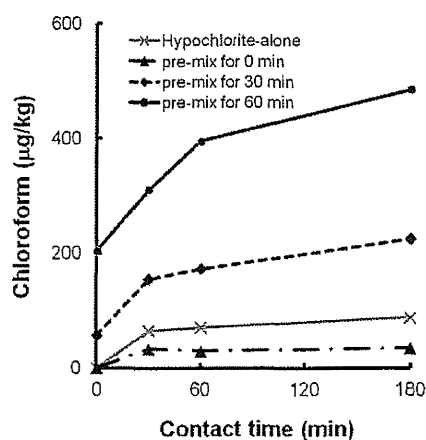


Fig. 6. The combined effect of sodium hypochlorite and citric acid on chloroform formation in chlorinated fresh-cut cabbage

Sodium hypochlorite solution (100 mg/L) was mixed with citric acid adjusted to pH 6.8 and left to stand for 0 - 60 min at 10°C. Sample were disinfected with the acidified hypochlorite solution or sodium hypochlorite solution-alone for 0 - 180 min at room temperature.

8. Chloroform formation potentials in acidified hypochlorite solution using various organic acid

The chloroform formation potentials of organic acids

were assessed under chlorination (Fig. 7). The organic acid solutions were treated with sodium hypochlorite solution at pH of 6.0 - 7.0 and room temperature. Most organic acids, such as malic acid, tartaric acid, succinic acid and fumaric acid, did not affect chloroform formation. In contrast, only citric acid reacted with sodium hypochlorite to form chloroform. Chloroform formation was correlated with reaction time.

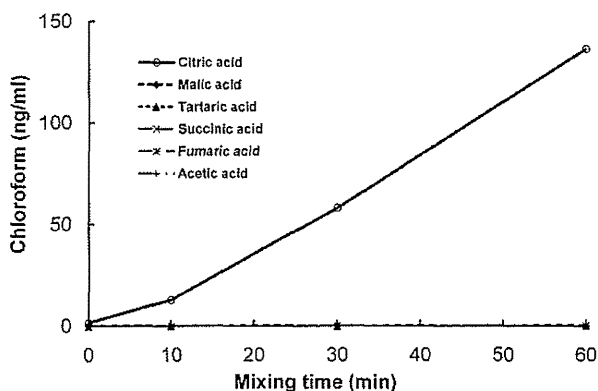


Fig. 7. Chloroform formation potentials in the chlorination of organic acids

A sodium hypochlorite solution (100 mg/L) was mixed with various organic acids at pH 6 - 7 and room temperature.

9. Isotopic study of the mechanism of chloroform formation

To elucidate the reaction pathway of chloroform formation, sodium hypochlorite solution was reacted with 2, 4-¹³C-citric acid or 2, 4-¹²C-citric acid (unlabeled citric acid), and resulting mass spectra of each chloroform were compared using HS-GC/MS (Fig. 8). The mass spectrum of chloroform from 2,

4-¹²C-citric acid has a base ion peak at *m/z* 83. However, the mass spectrum of chloroform from 2, 4-¹³C-citric acid showed a base ion at *m/z* 84. The one mass unit shift from 83 to 84 suggests that the 2 and 4-position carbon atoms in citric acid have been chlorinated with sodium hypochlorite.

10. Effect of water rinse treatment on residual chloroform concentration in fresh-cut cabbage

A sodium hypochlorite solution is used in washing vegetables or in the peeling of fruits and vegetables, and rinsing with potable water to remove the residual chemicals normally follows this treatment. The effect of water rinsing on removal of chloroform was examined (Table 2). The sample were treated with a sodium hypochlorite solution for 10 min with and without citric acid. Chloroform levels were 31.9 µg/kg for the treatment without citric acid and 366 µg/kg for the treatment with citric acid. However, after rinsing with distilled water for 1 min, the levels of chloroform contaminants in the fresh-cut cabbage were effectively decreased to 16.2 µg/

Table 2. The effect of water rinsing on chloroform residue in fresh-cut cabbage

Process* ¹	Sodium hypochlorite solution alone		Acidified hypochlorite solution	
	Avg.* ² (µg/kg)	CV (%)	Avg. (µg/kg)	CV (%)
A. Blank	8.8	0.0	—	—
B. Chlorination	31.9	1.8	366.0	15.8
C. Washing	16.2	0.8	17.9	0.8

*¹ Process A: Control, (no chlorination),
Process B: Chlorinated fresh-cut cabbages,
Process C: Washed fresh-cut cabbages after chlorination.

*² The analyses were replicated three times for each condition.

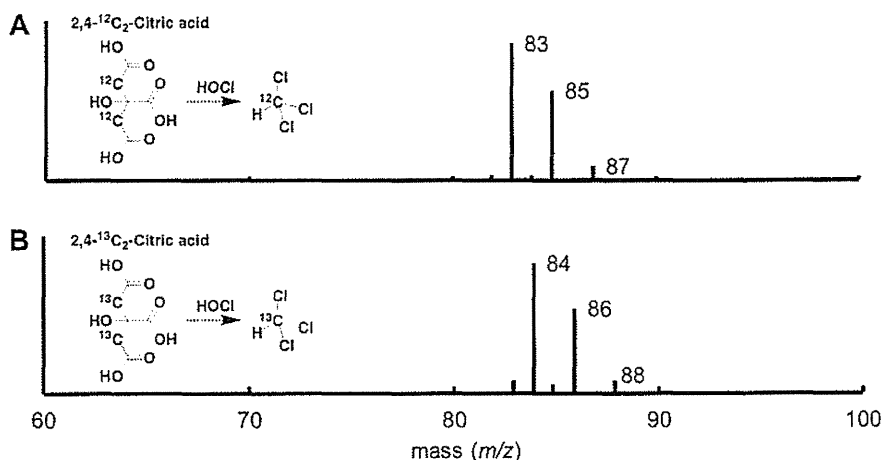


Fig. 8. Mass spectra of chloroform production after the reaction of sodium hypochlorite with 2,4-¹²C-citric acid (A) and 2,4-¹³C-citric acid (B)

A sodium hypochlorite solution (100 mg/L) was reacted with non-isotopically or isotopically labeled citric acid compounds for 10 min at pH 6.8 and room temperature.

kg for the treatment without citric acid and 17.9 $\mu\text{g}/\text{kg}$ for the treatment with citric acid.

IV Discussion

1. Factors affecting VOC formation during chlorination of fresh-cut cabbage

After treatment of fresh-cut cabbage with sodium hypochlorite solution, chloroform was produced as major product. This finding is consistent with the previous studies of Ichikawa et al., in which the formation of chloroform and carbon tetrachloride was observed after the treatment of fresh vegetable homogenates with sodium hypochlorite solution¹⁴. It is well known that THM are formed in water after the reaction of chlorine with humic substances. Typical structures of humic substances are thought to be a mixture of large molecules composed of phenolic and carboxylic substances^{24, 25}. Rook et al. demonstrated the ability of flavonoids to form THM and showed that their *m*-dihydroxybenzene moieties are responsible for THM formation during chlorination²⁶. Since fruits and vegetables contain various flavonoids and other phenolic compounds, they may serve as THM precursors during disinfection.

The chloroform concentration was increased with increase of the contact time, initial chlorine concentration and temperature. These results are in agreement with previous studies in drinking water experiments²⁷⁻²⁹. The contact time, sodium hypochlorite concentration and temperature are considered to be important factors controlling the THM formation. Sodium hypochlorite solution was generally used in the 50 to 200 mg/L concentration in short contact time (5 to 10 min) to sanitize fresh foods at cool temperature. Therefore, in such case, THM concentrations would be controlled at a lower level in fresh foods.

We detected BDCM at lower levels than that of chloroform. The chlorination of water containing inorganic bromide leads to the formation of brominated THM. Bromide is readily oxidized to hypobromite by sodium hypochlorite, and reacts with phenolic compounds to form brominated-THM³⁰. However, disinfectant contains little bromide, and brominated-THM was not detected by the reaction of organic acids with the sodium hypochlorite solution. Therefore, brominated-THM might not be produced from bromide in disinfectant. Since bromide has also been found in foods, this might be the source of BDCM formation. The other VOC were not detected in the chlorinated samples. Some of these compounds, such as *p*-dichlorobenzene, were known as disinfection by-products in drinking water³¹. However, these compounds may not be formed from fresh foods by chlorination.

At basic pH, higher concentrations of THM occurred with

increasing pH values; a number of researchers have reported similar finding in chlorinated drinking waters³²⁻³⁵. The haloform-type reaction mechanism was proposed to be the major pathway for THM formation²¹. This reaction involves a replacement of the three hydrogen atoms with halide on the alpha-carbon of the carbonyl group. The trihalocarbonyl group is then attacked by hydroxide to produce THM and carboxylic acid. Under a basic pH condition, the hydrolysis reaction should be accelerated, thereby increasing the THM concentration.

2. The effect of organic acid on chloroform formation during chlorination

When fresh-cut cabbage were disinfected with a combination of sodium hypochlorite solution and citric acid, chloroform levels increased with increasing pre-mixing time of the acidified hypochlorite solution. Larson and Rockwell reported that citric acid acted as a chloroform precursor in chlorinated water under neutral pH conditions³⁶. Streicher and Zimmer further investigated the interaction of aqueous chlorine solutions at various pHs with citric acid and frozen condensed orange juice³⁷. It was found that citric acid reacted with sodium hypochlorite, producing a number of chlorinated compounds. They also proposed the reaction pathway. In the first step, citric acid is oxidatively decarboxylated to form 3-ketoglutaric acid in hypochlorite solution. 3-Ketoglutaric acid is subsequently chlorinated with sodium hypochlorite and decarboxylated to produce polychlorinated propanone, due to the activation of methylene group of 3-ketoglutaric acid by the neighboring carbonyl and carboxyl groups. It is enolized and readily attacked by hypochlorite. Finally, pentachloropropanone is hydrolyzed to form chloroform and dichloroacetic acid. Our stable isotope experiments clearly show that the 2 and 4-position carbon atoms in citric acid have been selectively chlorinated with hypochlorite. The present study proved the hypothetical reaction mechanism previously reported is correct and that citric acid can be the precursor for chloroform formation.

3. The effect of water rinsing on residual chloroform concentrations in fresh-cut cabbage

Chloroform contaminants levels in fresh-cut cabbage were effectively decreased after rinsing with water, falling to those found in drinking water. There was no significant difference in residual chloroform levels after rinsing with water between treatment with sodium hypochlorite alone and the acidified hypochlorite solution. López-Gálvez et al. reported that residual THM were not detected (<5 g/L) in lettuce leaves washed with a 100 mg/L sodium hypochlorite solution. However, when lettuce was treated with a higher concentration (1800 mg/L sodium hypochlorite for 60 min),

and then rinsed with water, large amount of THM remained. Sodium hypochlorite is commonly used in the concentration range of 50 to 200 mg/L, except in special cases, such as with alfalfa seeds intended for sprout production¹⁹⁾. Therefore, in most cases, the washing process could remove the THM contaminants. The levels of THM contaminants could decrease down to as low as those in drinking water. We suggest that the THM levels found in fresh produce are too low to cause adverse health effects.

V Conclusion

We investigated factors that affect the formation of VOC in fresh-cut cabbage. Chloroform was detected as the predominant THM in the chlorinated samples. The formation of THM was dependent on pH, temperature and the initial sodium hypochlorite concentration. Citric acid reacted with hypochlorite to produce large amount of chloroform. When the sodium hypochlorite solution was acidified by citric acid, chloroform level was depending on the pre-mixing time with citric acid rather than the contact time with fresh-cut cabbage. Rinsing with water was useful enough to reduce the residual chloroform in cabbage to the same level as chlorinated drinking water. Since fresh-cut vegetables were usually rinsed with water after disinfection, we consider such vegetables in the market to be safe regarding the health risk of THM.

However, another group of disinfection by-products are formed by the chlorination of drinking water. Wu *et al.* reported that haloacetic acids and haloacetonitriles were formed in instant tea prepared with hot water containing the free residual chlorine (4 mg/L)³⁸⁾. As there is limited information available regarding the occurrence of these compounds on fresh foods, further studies are necessary to investigate their formation. These studies would assist in establishing a risk assessment of chlorine-based disinfectant on foods and contribute to formulating effective sanitizing procedures for fresh foods.

VI Acknowledgments

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論 文

次亜塩素酸ナトリウム処理によるカットキャベツからの揮発性ハロゲン化合物の生成

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概 要

カットキャベツを次亜塩素酸ナトリウムにより殺菌処理したときに生成する消毒副生成物の生成影響因子について検討を行った。カットキャベツは、次亜塩素酸ナトリウム (100 mg/L) 単独あるいは、有機酸と共に 10 分間殺菌処理を行い、カットキャベツに残存する揮発性ハロゲン化合物をヘッドスペースガスクロマトグラフ質量分析装置で測定した。主要な副生成物としてクロロホルムが検出された。クロロホルムは、殺菌時間、pH、温度、初期次亜塩素酸ナトリウム濃度に依存して増加した。次亜塩素酸溶液を種々の無機酸及び有機酸と併用してもトリハロメタンは生成しないが、クエン酸は次亜塩素酸と反応し、クロロホルムを生成した。クロロホルム濃度は、次亜塩素酸・クエン酸混液の混和時間に対応して増加し、カット野菜の殺菌時間には影響しなかった。また、カット野菜に残存したクロロホルムは水洗浄により、水道水中のトリハロメタン濃度レベルまで減少した。

