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FOOD AND NUTRITION

Monitoring of the Sorbic Acid, Benzoic Acid and Sulfur Dioxide for Commonly Consumed Beverages, Snacks and Instant Ramens in Korea

Xionggao Han, Sun-Il Choi, Seung-Hyun Choi, Bong-Yeon Cho, Wan-Sup Sim, Gill-Woong Jang, Hee-Yeon Kwon, Ye-Eun Choi, Dan-Bi Kim* and †Ok-Hwan Lee**

Graduate Student, Dept. of Food Science and Biotechnology, Kangwon National University, Chuncheon 24341, Korea
[*]Researcher, Food Analysis Center, Korea Food Research Institute, Wanju 55365, Korea
[**]Associate Professor, Dept. of Food Science and Biotechnology, Kangwon National University, Chuncheon 24341, Korea

Abstract

This study was to investigate the sorbic acid, benzoic acid and sulfur dioxide in commonly consumed beverages, snacks and instant ramens in Korea. A total of 150 food samples including 50 beverages, 50 snacks and 50 instant ramens were examined using the Korea Food Code method. Sorbic and benzoic acid were analyzed by the HPLC method, whereas sulfur dioxide was measured by Monnier-Williams method. Our results indicated that benzoic acid was detected in six beverages samples, and its concentration was in the range of 3.08-11.94 mg/kg. The contents of both sorbic and benzoic acid in 50 beverage samples did not exceed the residue allowance standards set by the Ministry of Food and Drug Safety (MFDS). Sulfur dioxide was detected in 12 beverages samples, but its content was lower than the detection limit specified in the method by the Korea Food Code. On the other hand, sorbic acid was not detected all samples. These results provide a basic data regarding sorbic acid, benzoic acid and sulfur dioxide in commonly consumed beverages, snacks and instant ramens in Korea.

Key words: commonly consumed foods, food additives, sorbic acid, benzoic acid, sulfur dioxide

Introduction

Food additives such as sorbic acid, benzoic acid and sulfur dioxide are widely used to food products for the extension of shelf life and enhancing of food quality. In Korea, permitted preservatives include sorbic acid and its salts, sulfites, benzoic acid and its salts, sodium dehydroacetate, *p*-hydroxybenzoic acid ester and propionic acid and its salts. Among them, sulfites should be labeled with their name and usage (bleaching agent, synthetic preservatives, antioxidants) when used in food products (Park et al. 2008; Yun et al. 2017). Sulfur dioxide is generated from sulfites and is used as an acceptance criterion for sulfites (Kang et al. 2001). However, sodium hydrosulfite, calcium benzoate and ethyl *p*-hydroxybenzoate are not allowed to be used as preservatives in the United States of America (USA), while the European Union (EU) does not allow the use of sodium hydrosulfite and sodium dehydroacetate. The Codex Alientarius Commission (CODEX) does not allow the use of sodium hydrosulfite, and Japan does not allow potassium benzoate, calcium benzoate and methyl-*p*-hydroxybenzoate to be used as additives (Table 1). In order to ensure human safety upon consumption of preservatives, Joint FAO/WHO Expert Committee on Preservatives (JECFA) sets the acceptable daily intake (ADI) by carrying out animal toxicity tests (Table 2). The use of preservatives is allowed if their content is within the residue allowance standards, thereby securing human health.

Recent research reported that some food additives have been monitored in various food ingredients (Nagayama et al. 1983; Nagayama et al. 1986). In Korea, Kim et al. (1999) reported the contents of benzoic acid and sorbic acid in 39 plants used as

† Corresponding author: Ok-Hwan Lee, Associate Professor, Dept. of Food Science and Biotechnology, Kangwon National University, Chuncheon 24341, Korea. Tel: +82-33-250-6454, Fax: +82-33-259-5565, E-mail: loh99@kangwon.ac.kr

Table 1. The domestic and international amount used criteria of sorbic acid, benzoic acid, sulfites

Preservative type	Food type	Allowable amount (g/kg)			
		Korea	EU	USA	Japan
Sorbic acid and its salts	Surface treatment of unpeeled fresh citrus fruits	-	0.02	-	-
	Olives and olive-based preparations	-	1	-	-
	Potato dough and pre-fried potato slices	-	2	-	-
	Fermented milk drinks (excluding pasteurized product)	0.05	-	-	0.05
	Syrups, fruit paste for manufacture of confectioneries, fruit juices	2	-	0.1	1
	Cheese	3	1	0.3	3
Benzoic acid and its salts	Olives and olive-based preparations	-	0.50	-	-
	Non-alcoholic beverages, syrups, soy sauce	0.60	-	-	0.60
	Fruits / vegetable drinks, carbonated drinks	0.60	0.20	-	1
Sulfites	Molasses	0.20	-	GMP[1]	0.25
	Fruit juice, concentrated fruit juice	0.15	0.07		0.15
	Sugar	0.02	0.01		0.03
	Sauce	0.30	-		0.03
	Grain products, spices	0.03	-		0.03
	Dried fruits and nuts	1	0.50		2

[1)] GMP: Good manufacturing practices.

Table 2. Daily intake of sorbic acid, benzoic acid and sulfur dioxide

Category		Jecfa
Sorbic acid and its salts	Sorbic acid	ADI: 0~25 mg/kg bw
	Potassium sorbate	
	Calcium sorbate	
Benzoic acid and its salts	Benzoic acid	ADI: 0~5 mg/kg bw
	Sodium benzoate	
	Potassium benzoate	
	Calcium benzoate	
Sulfites	Sodium bisulfite	ADI: 0~7 mg/kg bw
	Sodium sulfite	
	Sodium hydrosulfite	
	Sulfur dioxide	
	Potassium metabisulfite	
	Sodium metabisulfite	

tea and spices. Lee et al. (2001) reported the content of benzoic acid in Korean, Chinese, Australian and Brazilian propolis extracts. High content of benzoic acid is detected in berries, including cranberries, blueberries and aronia, and some spices, including cinnamon, cloves and cardamom (Yun et al. 2017). Additionally, sulfur dioxide has been detected in cereals, fruits, vegetables, fishes and medicinal herbs (Kim et al. 2000; Kang KJ 2001).

New commonly consumed foods are made available due to the changing food habits every year (Kim & Kim 2018; Ko et al. 2019), but there are only limited studies on the analysis of the content of sorbic acid, benzoic acid and sulfur dioxide. Therefore, a thorough monitoring and a vast database is needed to secure food safety. In this study, we prepared a database of the contents of sorbic acid, benzoic acid and sulfur dioxide in the 150 kinds of products which frequently consumed in Korea, and to check whether they were consistent with existing national regulations.

Materials and Methods

1. Reagents and food materials

Standard solution of sorbic acid and benzoic acid mixture was obtained from Sigma-Aldrich (St Louis, MO, USA). All the solvents such as tetrabutylammonium hydroxide and acetonitrile, suitable for high performance liquid chromatography (HPLC), were purchased from J. T. Baker (Phillipsburg, NJ, USA). A total of 150 commonly consumed food samples (50 beverages, 50 snacks and 50 instant ramens) were collected from grocery markets and stored in a refrigerated warehouse (7℃) until analysis.

2. Sample preparation for HPLC analysis

The samples were prepared according to the method of Korea Food Code (KFIA 2016). Distilled water (100 mL) was added to about 30 g of the sample and mixed thoroughly. Then, 10 mL of 15% tartaric acid solution, 80 g of NaCl, distilled water and one drop of silicone resin were added to the resultant mixture to make it up to 200 mL. The mixture was then distilled by connecting to a distilling flask. The distillate was dispensed after immersing the end of the glass tube that receives the distillate in 20 mL of 1% sodium hydroxide solution. The emulsion was distilled at a rate of 10 mL per min up to 250 mL, then filtered through a 0.45 µm syringe filter and used as an analytical sample for HPLC.

3. HPLC-UV analysis

Quantitative analyses of sorbic acid and benzoic acid were performed by HPLC with an ultraviolet (UV) detector. A standard solution of sorbic acid and benzoic acid mixture was dissolved in methanol to prepare a stock solution and then further diluted using methanol to prepare a working solution for calibration curve. The column used for the sample analysis was CAPCELL PAK MF-C8 (Shiseido, SG 804.5 µm, 4.6×150 mm), and the UV detector was set at 217 nm with an injection volume of 10 µL. The flow rate was set 1.0 mL/min, and the column temperature was maintained at 30℃. The mobile phase was composed of A (0.1% tetrabutylammonium hydroxide solution) and B (acetonitrile) with gradient elution as follows: 0-2.5 min, maintained at 75% A; 2.5-7 min, linear from 75 to 65% A; 7-12min, linear from 65 to 60% A; 12-15 min, linear from 60 to 70% A. These methods are validated in terms of selectivity, linearity, limit of detection (LOD) and limit of quantification (LOQ) according to the guidelines of the International Conference on Harmonization (ICH 2005).

The concentrations of sorbic acid and benzoic acid were calculated from the following equation using the measured values obtained from the calibration curve of the standard solution.

$$\text{Additives (g/kg)} = \text{Concentration of STD (mg/L)} \times \frac{PA}{PS} \times \frac{500}{SA} \times \frac{1}{1{,}000}$$

STD: standard solution

PS: Height or area of the peak corresponding to standard solution

PA: Height or area of the peak corresponding to test solution

SA: Weight of the sample

4. Measurement of sulfur dioxide

Sulfur dioxide was quantitatively analyzed according to the Monnier-Williams modified method using a Monnier-Williams distillation apparatus (AOAC 1995). In brief, 400 mL of distilled water, ~50 g of sample and 100 mL of 5% ethanol were placed in the flask and the mixture was heated for 15 min under a nitrogen atmosphere, with a flow rate of 0.2 L / min. Then, 90 mL of 4 N hydrogen chloride was added to the flask and heated for 1 h and 45 min. Later, a glass tube containing 30 mL of 3% hydrogen peroxide solution and methyl red indicator was used to collect sulfur dioxide. Then, sulfur dioxide in the hydrogen peroxide solution titrated with 0.01 N sodium hydroxide solution (KFIA 2016).

The concentration of sulfur dioxide in the sample was calculated from the amount of 0.01 N sodium hydroxide solution consumed, according to the following equation.

$$\text{Sulfur dioxide (mg/kg)} = \frac{320 \times \mathrm{V} \times \mathrm{f}}{\mathrm{S}}$$

V: Consumption of 0.01 N sodium hydroxide solution (mL)

f: Titer of 0.01 N sodium hydroxide solution

S: Weight of sample (g)

(1 mL of 0.01 N sodium hydroxide solution = 320 µg of sulfur dioxide)

Results and Discussion

1. Method validation

Different results can be obtained due to the effect of various factors, such as analyzer, analysis environment and instrument

Table 3. LOD and LOQ of sorbic acid, benzoic acid standard solution

Analyte	Range (µg/mL)	Slope	Intercept	Correlation coefficient (R^2)	LOD (µg/mL)	LOQ (µg/mL)
Sorbic acid	0.47~30	38.68	3.93	0.99	0.07	0.23
Benzoic acid	0.47~30	89.19	8.07	0.99	0.03	0.11

model, even under same conditions. Therefore, in order to confirm whether the difference is resulting from the factors mentioned above, the analytical methods were reproduced using the laboratory equipment. The reproducibility of a method was evaluated by its selectivity, correlation coefficient (R^2), LOD and LOQ.

As shown in Fig. 1, all three kinds of samples and STD were selectively separated from each other without allowing any interference with the other components of sorbic acid and benzoic acid. The correlation coefficients (R^2) of sorbic acid and benzoic acid were 0.99 and 0.99, respectively, which indicate linearity. The LODs of sorbic acid and benzoic acid were 0.07 and 0.03 µg / mL, and the LOQs were 0.23 and 0.11 µg/mL, respectively (Table 4). Therefore, it was judged that the analytical method could be used for monitoring the content of additives.

2. Content of sorbic acid in beverages, snacks, and instant ramens

The content of sorbic acid in beverages, snacks and instant ramens was analyzed (Fig. 1). Sorbic acid was not detected in all samples (Table 4). Also, there were no samples in which sorbic acid was mentioned in the ingredients list. Currently, the research on naturally occurring sorbic acid in foods mainly concentrates on food materials and healthy foods (such as cereals, nuts, fruits, perfumery and plants), as well as the processed

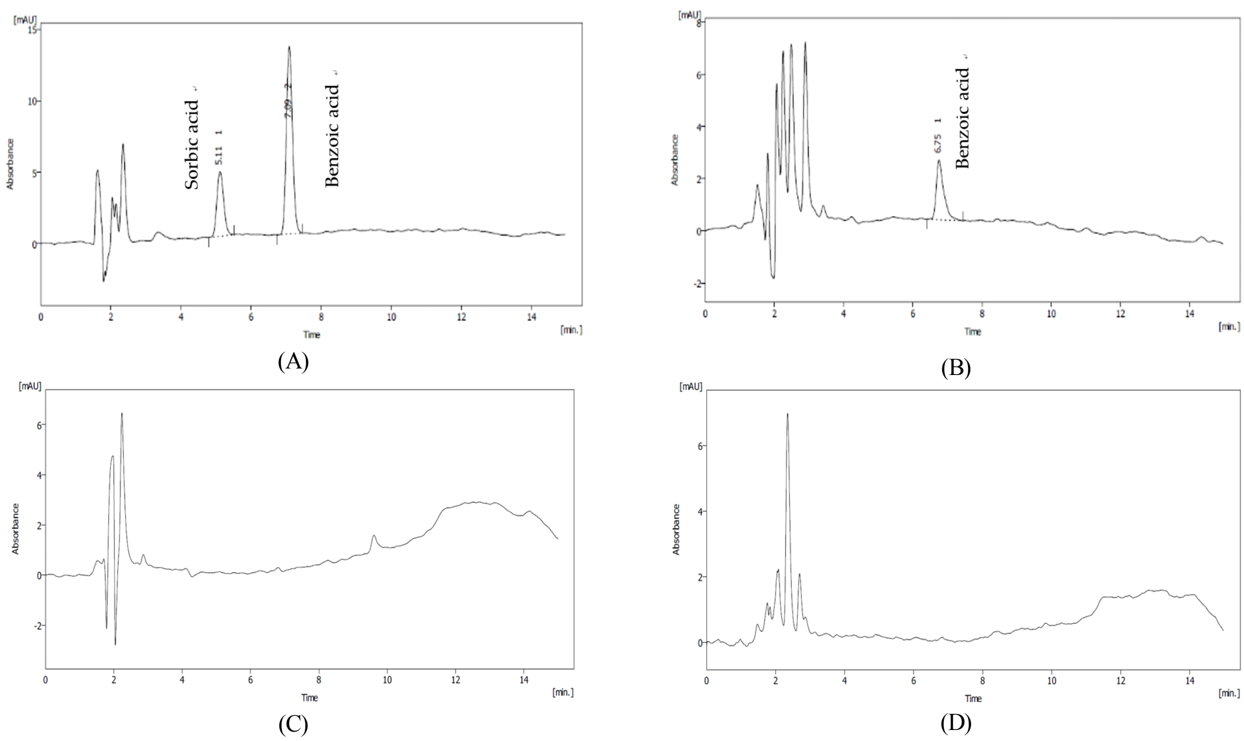

Fig. 1. Chromatograms of sorbic acid and benzoic acid mixture, a standard solution of sorbic acid and benzoic acid mixture (A) the samples of beverages (B) snacks (C) and instant ramens (D).

Table 4. Sorbic acid, benzoic acid and sulfur dioxide levels in in beverages, snacks, and instant ramens

Group	Tested sample	Sorbic acid		Benzoic acid		Sulfur dioxide	
		Detected sample	Level (mg/kg) min~max	Detected sample	Level (mg/kg) min~max	Detected sample	Level (mg/kg) min~max
Processed food	Beverages	ND[1)]	ND	6	3.08~11.94	12	0.25~0.68
	Snacks	ND	ND	ND	ND	ND	ND
	Instant ramens	ND	ND	ND	ND	ND	ND
Total	150	ND		6		12	

1) ND: no detected.

foods such as meat products and fermented foods (Park et al. 2008; Yun et al. 2017). Therefore, our experimental results cannot be compared with those in the other literature. The results of our study indicate that sorbic acid may not occur in commonly consumed foods including beverages, snacks, and instant ramens in Korea.

3. Content of benzoic acid in beverages, snacks, and instant ramens

The content of benzoic acid in different samples of beverages, snacks and instant ramens was analyzed in this study. Benzoic acid was detected in six samples of beverages, with a detection range of 3.08-11.94 mg/kg, while it was not detected in all the tested samples of snacks and instant ramens (Table 4). Benzoic acid was detected in beverages since it was added as an additive during processing, as evident from the presence of its name in the ingredients list. The concentration of detected benzoic acid did not exceed the legally regulated residue allowance standards.

4. Content of sulfur dioxide in beverages, snacks, and instant ramens

The content of sulfur dioxide in different samples of beverages, snacks and instant ramens was then analyzed (Table 4). Sulfur dioxide was detected in 12 samples of beverages and its content ranged from 0.25 – 0.68 mg/kg. No sulfur dioxide was detected in the samples of snacks and instant ramens. The residual amount of sulfur dioxide detected was below 10 mg/kg, which is the detection limit of the Monnier-Williams Modified Method. As per the Korea Food Code, if the detected content of sulfur dioxide is less than 10 mg/kg, it can be treated as undetected (KFIA 2016). Some foods, such as wine and fruit wine, produce sulfur dioxide during the fermentation process. In addition, sulfur dioxide present in the atmosphere can also enter the plant by means of absorption, and a certain amount of it will also be accumulated in animals when they eat such plants; so, there is a certain amount of natural sulfur dioxide present in animal and plant foods (Yin et al. 2009). However, all the 12 samples of beverages in which sulfur dioxide is detected are neither wine nor fruit wine, and only contain a trace plant component. So, these results may have been obtained due to some other mechanism, and further research is needed to determine it.

Conclusions

This study was monitored the contents of the sorbic acid, benzoic acid and sulfur dioxide in 150 commonly consumed food in Korea. Benzoic acid was detected only within the range of 3.08-11.94 mg/kg in the six samples of beverages. Also, benzoic acid was used as an additive in all the samples in which it was detected, as indicated by the presence of its name in the ingredients list of these samples. However, the detected concentration does not exceed the legally regulated residue allowance standards. On the other hand, sorbic acid and sulfur dioxide were not detected in any of the three kinds of tested food samples. Nonetheless, this study has made available the information on the content of the sorbic acid, benzoic acid and sulfur dioxide in commonly consumed foods based on the generated data.

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