

METAL FOOD PACKAGING DESIGN BASED ON HAZARD ANALYSIS CRITICAL CONTROL POINT (HACCP) SYSTEM IN CANNED FOOD SAFETY

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Abstract: This study aims to design metal food packaging with hazard analysis critical control point (HACCP). First, theory of HACCP was introduced in detail. Taking empty cans provided by Wuxi Huapeng Food Packaging Company as an example, we studied migration of bisphenol compounds in coating of food can to food stimulant. Moreover, packaging design of luncheon meat can was taken as an example to confirm whether HACCP system could effectively control migration of phenolic substance. Results demonstrated that, coating of such empty were more likely to contain multiple bisphenol compounds such as bisphenol A (BPA), and bisphenol A diglycidyl ether (BADGE) was considered as the leading bisphenol pollutant; food stimulant of different types, storage temperature and time could all impact migration of bisphenol compounds. HACCP system was proved to be effective in controlling hazards of phenolic substance in luncheon meat can and could reduce various phenolic substance indexes to an acceptable range. Therefore, HACCP can control migration of phenolic substance and recontamination of food and thus ensure food safety.

Keywords: HACCP system; Metal food packaging; food safety

INTRODUCTION

Food is essential for mankind. Food quality and the degree of food industry technology reflect the human living standard directly (Carse, 2007). But, with the rapid development of food processing industry, food safety problems occur constantly. To control and reduce the occurrence of food safety affairs, most food processing enterprises adopt HACCP system to control the food safety. World academic institutions, international organizations and governments all devote themselves to the research of HACCP and hope to solve food safety problems (Chen *et al.*, 2012). For the application of HACCP system to food processing enterprise, foreign researchers have

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studied deeply in early time. Wallace et al., (2014) studied the design, implementation, control, management and other safety production factors of HACCP system, and regarded hazard analysis in HACCP theory as the core brace of HACCP plan. Kafetzopoulos et al., (2013) thought that building the proper model could measure the validity of HACCP food security system accurately, that was feasibility. Garayoa et al., (2011) considered that training skilled staff and solving the funding of infrastructure were the important issues that HACCP implementation should settle; Semos and Kontogeor (2007) adopted questionnaire survey to research the 91 food production enterprises in Greece and found that staff training and the investment of new equipment were the most prominent costs in the application process of HACCP system; Bata et al., (2006) thought that the application of HACCP system needed technical support, investment of equipment and capital, the costs of system development, application and maintain were the critical factors that influenced the implementation of HACCP. The HACCP system in domestic mainly studies 3 aspects: (1) the critical factors of HACCP system implementation; (2) HACCP improves the product quality; (3) HACCP system application cost and benefits. However, the study of HACCP application to food processing enterprises mainly concentrates on HACCP build and application of certain product, and its effect and cost analysis, lacks the study of food packaging security monitoring and control, especially the specific packing material, ignores the harm that improper food packaging design does to food hygiene. The study took food packaging design as the object, researched the HACCP system establishment of metal canned food safety.

Metal food cans mainly adopt epoxy resin and organosol resin as inside coating, which can protect the cans from corrosion of content and prevent cans heavy metal migration from migrating to food (Verissimo and Gomes, 2008). Epoxy-bakelite resin and vinyl organosol resin are the most common internal coatings that used in metal food can, which have excellent suppleness, chemical Resistance and adhesive force. The former is mainly composed of the reaction of bisphenol A (BPA) and bisphenol A diglycidyl ether (BADGE) (Munguia-Lopez and Soto-Valdez, 2001); the latter should be added BADGE and bisphenol F diglycidyl ether (BFDGE) to neutralize the hydrochloric acid that comes from curing reaction in productive process, which can prevent the coating from being resolved (Ivana *et al.*, 2003; Jana *et al.*, 2005); BFDGE is consisted of bisphenol F (BPF) and epichlorohydrin. Due to the strict restriction of BPA using, as the succedaneum, bisphenol E (BPE) and bisphenol B (BPB) can be used in producing resin coating (Pozdnyakov *et al.*, 2010). Canned food suffer high temperature sterilization in processing, be exposed under the sun in storage process, be shocked severely, which may cause bisphenol contaminant migrate to food and do

harm to people health. Therefore, studying the metal food packaging design has important significance to HACCP system establishment in canned food security. Taking packaging design of luncheon meat can as an example, this study explored the establishment of HACCP system for metal food packaging design, which lays a theoretical and practical basis for more effective application of HACCP in metal food packaging design.

MATERIALS AND METHOD

Overview of HACCP system theory

Characteristics of HACCP system: The HACCP system is a dynamic and constantly perfected quality control system based on GMP and SSOP, which is preventable, professional, universal, integrate, scientific and effective in controlling food safety.

The development history of HACCP system in China: Since 1980s, China has made research of HACCP system (Bai *et al.*, 2007). In the beginning of 1990s, entry and exit inspection and quarantine system had done a lot of generation work of how to apply HACCP to export honey, frozen pork, frozen skinless shrimp and frozen chicken, etc. At the same time, Ministry of Public Health of China turned attention to HACCP plan, and introduced the HACCP theory in process enterprises and catering firstly. In 2008, General Administration of Quality Supervision issued hazard analysis and critical control point system- requirements for food processing enterprises, hazard analysis and critical control point and general requirements for dairy products processing enterprises to guide food processing enterprise to implement HACCP system in entire angular range. At present, nearly all Chinese medium and large dairy products processing enterprises introduce HACCP system to decrease the harm in food production process (Beekhuis-Gibbon *et al.*, 2011).

Relative practice basis of HACCP: (1) Seven theories of HACCP system. HACCP system takes control measures by hazard analysis; it makes critical control point (CCP) aiming at critical harm; it confirms the critical limit (CL) of CCP; it establishes the supervision and control system of CCP; it builds rectification measures; it establishes validation procedures of HACCP plan; it establishes records and custody system of HACCP plan.

(2) The application plan of HACCP plan. Premise plans of establishing and operating HACCP system should include but not limit as followings. It should establish good production standards and sanitation operation standard processes; it need the support of senior managers; it requires food processing enterprises to establish management of product marking and product tracing

procedures and put into practice; it structures the rapid and thorough product recall procedures, formulates non-qualified products recall system and does product recall test irregularly to examine the validity of program implementation; it should formulate processing equipment and facility maintaining procedure that suits the enterprise, and needs to be verified at suitable time; it also should pay attention to personnel quality and training.

(3) Implementation step of HACCP system. Codex Committee on Food Hygiene and American Advisory Committee on Microbiological Criteria recommend to adopt following 12 steps to realize HACCP (Rajneesh *et al.*, 2014): first, set up HACCP system group; second, do product description; third, make sure of the product intended application and consumption object; fourth, formulate food production process flow diagram; fifth, production process flow diagram verification; sixth, hazard analysis and formulate regulatory measure; seventh, make sure of the critical control point; eighth, make sure of the critical limit of critical control point; ninth, establish monitoring system of critical control points; tenth, establish rectification measures; eleventh, establish review procedure; twelfth, set the record and file preserve management system.

BISPHENOL-TYPE CHEMICALS IN FOOD CAN COATING MIGRATE TO FOOD SIMULACRUM

Experimental material: (1) Experimental material.

Empty cans were provided by Wuxi Huapeng food packaging company, the can bodies were coated with epoxy - phenolic resin coating. Both can bottle and can lid were coated with organosol resin. Before using the can, we should clean it up and put it into 40°C oven until dry.

(2) The allocation of food simulacrum.

In order to make migration research be more representative and universal, we selected different types of food simulacrums to represent the specific food, which could also avoid complicated food ingredient to cause influences on the analysis of trace bisphenol. The selection of simulacrum was shown in Table 1.

Table 1 The choose of food simulacrum

Food type	Food simulacrum	Logogram
Water-based food(pH>4.5)	Ultrapure water	Simulacrum A
Acid food (pH≤4.5)	3% acetic acid	Simulacrum B
Alcohol food	10% ethanol	Simulacrum C
Fatty food	Isooctane	Simulacrum D

Experimental method

(1) Infrared spectroscopy identified the ingredient of internal coating in food metal can.

We mixed 2 mg internal coating of untapped empty cans and 100 mg potassium bromide together and made tablettings then. Taking the air as background, we collected the infrared spectrum. Setting scanned area as $400 \sim 4000 \text{ cm}^{-1}$, instrument resolution ratio as 4 cm^{-1} , we scanned 32 times and examined each sample for 5 times repeatedly, all detection should be finished at room temperature.

(2) The Bisphenol substance extraction of internal coating in food metal cans
We added acetonitrile as per the volume of food that put into the metal can and sealed, then took it out after 24 hours reservation in the oven at the temperature of 25. We fetched 100 ml to round-bottom flask, made it to be dry less than 40°C rotary evaporation. We extracted residue by 20 ml acetonitrile in 2 installments and put the mixed solution under 40°C nitrogen to drying it slowly. Then, we used 1 ml acetonitrile to redissolve the solution. The reconstitution fluid was filtrated by $0.45 \mu\text{m}$ Poly Tetra Fluoro Ethylene (PTFE) needle type filter and detected by high performance liquid chromatography-fluorescence detection (HPLC-FD). In order to express the unit area residual quantity of bisphenol contaminant in internal coating, the datum gotten in this chapter used unit $\mu\text{g}/\text{dm}^2$ to represent the $\mu\text{g}/\text{L}$. The contact area of contents and the can is 0.233 dm^2 . And the formula of unit conversion is:

$$C1 = C2 * 0.3 / 0.233 \quad (2-1)$$

In the formula, C1 refers to the concentration of bisphenol in unit area coating ($\mu\text{g}/\text{dm}^2$); C2 refers to concentration of bisphenol in solution ($\mu\text{g}/\text{L}$).

(3) The pretreatment method of enrichment bisphenol in food simulacrum
As to water samples (simulacrum A, B and C), we should filtrate obvious impurities in solution, and then disposed in Solid Phase Extraction (SPE) processing. For simulacrum D, it should be dry under 40°C rotary evaporation, then be redissolved by 100 ml water and adopted SPE method after filtration.

(4) The experiment design of bisphenol contaminant transfer

To cut down experimental time, we usually enhanced experimental temperature to accelerate the transport process, and simulated the physical truth based on foreseeable worst contact conditions and maximum service temperature. If the product experienced two time periods and temperature periods, the tested sample should experience relevant foreseeable worst conditions in proper orders during the simulation process. The experience set hot working condition as $121^{\circ}\text{C}/0.5 \text{ h}$, storage temperature as 5°C , 20°C and

40°C, and the storage cycle was 30 days. The detailed design of migration experiment was shown as follows. We selected 76 cans randomly and divided into 4 groups in average. Each group should be put into one kind food simulacrum, and made heat treatment (121°C/0.5 h) after seal. There was a sample in each group should not be reserved, and the rest samples should be divided into 3 groups and reserved under 5°C, 20°C and 40°C, time for 5d, 10d, 15d, 20d, 25d and 30d. Each can made one parallel. At a certain time point, we opened the can and made contents to finish SPE process according to aforementioned 3, made HPLC-FD examination finally.

HACCP PLAN ESTABLISHMENT AND TEST

The study took the pork luncheon meat can packaging design as the example to make sure whether HACCP system could effectively control the migration of phenolic substances in pork luncheon meat can packaging design. Hazard analysis is presented in Table 2.

Table 2. Hazard analysis

No		1	2	3
(1)	Package design process	The choice of inside coating dye	The choice of metal	Vacuum seal
(2)	Potential hazard	Phenolic substance migrated to food	Chemical hazards	Biohazard caused recontamination of bacteria
(3)	Whether the potential food safety was notable	Yes	Yes	Yes
(4)	Criterion	Experiment results of last chapter	Some metals would cause chemical reaction with contact material	Bacteria isolated the outside world through double seams
(5)	Precautionary measures	Controlled the storage food type, temperature and time	Made the test before choosing the metal package	Controlled the double seams isolated the outside world
(6)	Whether the step was critical control point	Yes	Yes	Yes

The confirmation of seal critical limit: Canned food could keep the good quality for a long time and supply healthful and nutrient food for customers, which mainly depended on seal and sterilization of the product. The sealed container was aimed to guarantee the content from microbial invasion after the content being sterilized and guaranteed commercial sterilization. Therefore, sealed food in sealed container could preserve food from decay for a long time after sterilization and make sure to provide the customers with fresh products. Therefore, seal was the most important part in canned food package design process, and the can seal mainly depended on the integrity of double seams. The cans passed double seam to make content isolate the outside world and prevented bacteria from contaminating the content again. The critical limits were: no fake seal, knock-down flange, sliding closure, seam fragmentation, cut over, jumped seam, pinlip > 0.62 mm, droop > 1.27 mm, leakage and other serious defects; overlap rating (OL) \geq 50%, tightness rating (TR) \geq 50%, juncture rating (JR) \geq 50%.

HACCP verification: (1) CCPZ empty cans and the verification of cover. No fake seal, knock-down flange, sliding closure, seam fragmentation, cut over, jumped seam, pinlip > 0.62 mm, droop > 1.27 mm, leakage and other serious defects; overlap rate \geq 50%, tightness rating \geq 50%, juncture rating \geq 50%.

(2) The verification of seal. No fake seal, knock-down flange, sliding closure, seam fragmentation, cut over, jumped seam, pinlip > 0.62 mm, droop > 1.27 mm, leakage and other serious defects; overlap rate \geq 50%, tightness rating \geq 50%, juncture rating \geq 50%.

RESULTS AND DISCUSSION

(1) Infrared spectroscopy identification results of internal coating composition of can.

We made authenticate for the internal coating material of food can used in simulation experiment by infrared. As shown in the Figure 1, the main characteristic absorption peak of epoxy resin appeared when wave number was 1606, 1508, 1237 and 828 cm^{-1} , which reflected that the material was epoxy resin or organosol resin based on bisphenol A (Sajiki *et al.*, 2007; Goodson *et al.*, 2004). Therefore, the coating might contained many kinds of bisphenol substances, such as BPA, etc.

(2) The optimization for acetonitrile to extract the bisphenol substances of food cans internal coating

The study compared the effects under two extracting conditions: 25°C/24 h and 40°C/4 h. The results were shown in Figure 2, there was no migration of BPE and BPB in this batch of cans but other four bisphenol substances had quite big volume of migration under the condition of 25°C/24 h. Therefore,

we selected 25°C/24 h as the extraction condition of internal coating in bisphenol substances.

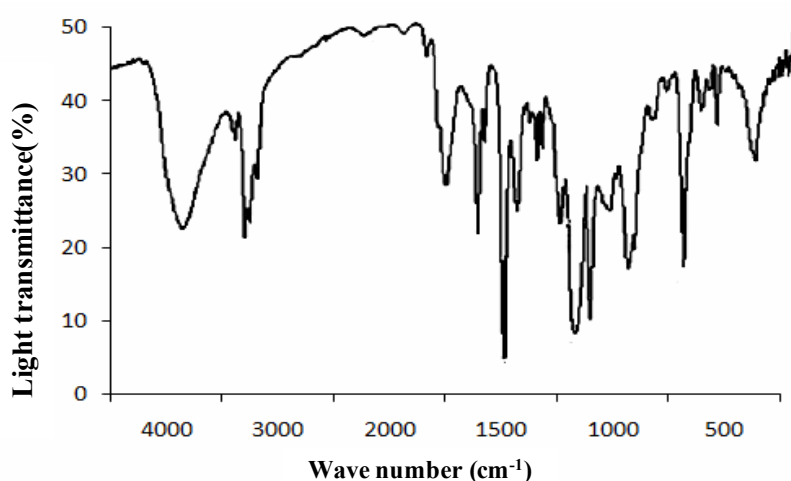


Figure 1. Infrared spectroscopy of food can internal coating composition

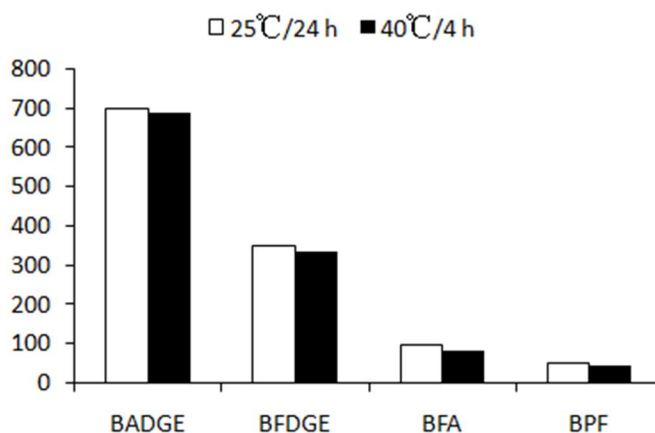


Figure 2. Comparison of the bisphenol extracted from can internal coating by acetonitrile under two conditions

According to the extraction condition 25°C/24 h, we selected 5 cans randomly to do the examination, the migration volume of BADGE, BFDGE, BPA and BPF ranked as 700.43±9.6, 336.12±7.58, 83.84±4.91 and 44.82±2.29 µg/dm², from large to small. The migration volume of BADGE outclassed other substances, which was the leading bisphenol contaminant in this batch of internal coating.

(3)The effect of solid phase extracting the bisphenol substances in enrichment food simulacrum

Since the practical SPE columella could tolerate the extreme PH environment, simulacrum B was not necessary to adjust PH to neutral. But simulacrum D had to be dry and resolved in the water sample or chose the normal phase SPE columella. In order to verify the effects of solid phase extracting the bisphenol substances in enrichment food simulacrum, we chose three concentration levels to make external standard recycle experiment, finished 5 parallels and calculated the average recovery rate and relative standard deviation. The recovery of six bisphenol substances in water simulacrum was 5.95% to 102.21%, relative standard deviation was 1.12% to 4.97%, the degree of accuracy and precision is quite favorable. But the recovery of bisphenol in simulacrum D is 75.92% to 85.85%, relative standard deviation is 3.60% to 6.95%, extraction result is inferior to the result in water simulacrum. The main reason was that simulacrum D should experience more complex treating processes than water simulacrum, which may cause the partial loss of bisphenol substances.

(4)The factor influencing the bisphenol migration

The influence of different types of food simulacrum on bisphenol migration

After the samples experiencing the most violent experiment conditions, the migration of BADGE, BFDGE, BPA and BPF in food simulacrum was shown in Table 3.

Table 3. The volume of migration of bisphenol substances in food simulacrum under the most acute experiment condition

Migration condition	Simulacrum	BADGE ($\mu\text{g}/\text{dm}^2$)	BFDGE ($\mu\text{g}/\text{dm}^2$)	BPA ($\mu\text{g}/\text{dm}^2$)	BPF ($\mu\text{g}/\text{dm}^2$)
121°C/0.5h 40°C/30h	Simulacrum A	34.00	25.00	46.01	25.32
	Simulacrum B	0.00	0.00	54.21	34.93
	Simulacrum C	105.30	79.56	71.21	41.54
	Simulacrum D	100.55	72.45	30.96	23.32

The research found that the migration of BADGE and BFDGE in different food simulacrum ranked as $C>D>A>B$, all 4 bisphenol simulacrums appeared maximum migration in simulacrum C at the same time. The simulacrum C contained ethyl alcohol and lowered the polarity of solution. According to the similarity-intermiscibility theory, it was easily to lead the migration of target objects. The polarity of simulacrum D was lower than that of simulacrum C, which was closer than the polarity bisphenol substances and easily to cause the migration of lipophilic BADGE and BFDGE (Bradley *et al.*, 2008). But drastic hot working process was easily to cause the target

object, especially the BPA to make oxidizing reaction with isooctane to generate the other substances and cause the decrease of concentration (Munguia-Lopez *et al.*, 2005). Acid system in simulacrum B also caused the decrease of solution, but the existence of hydron would make hydrolysis of BADGE and BFDGE, degraded as their ramification. Particularly, in the high temperature sterilization process, hydrolysis reaction would be much stronger (Poustkova *et al.*, 2004). In simulacrum A, BADG and BFDGE would also cause the hydrolysis reaction, but it was quite feeble.

The influence of storage temperature on bisphenol substances migration

The study chose 5°C, 20°C and 40°C as storage temperature of cold storage, normal temperature and high temperature. In the 30d storage period, we observed the influence of storage temperature on bisphenol substances migration. The results showed that with the increase of temperature, the migration volume of target object in simulacrum changed much faster: the change included the acceleration of migration increase and migration decrease. The migration was influenced by dynamics between the substance molecules and also should consider the chemical reaction that target object and simulacrum may happen. For example, in simulacrum A, the migration volume of BADGE and BFDGE decreased with the increase of temperature, because the increasing temperature quickened their hydrolysis reaction and hydrolysis rate was much quicker than emigration rate; in simulacrum B, the hydrolysis reaction was much stronger; in simulacrum C, the migration volume of four bisphenol substances under different temperature ranked as 40°C>20°C>5°C, because increasing temperature quicken the molecular movement and increased the diffusion coefficient during the migration process; but in simulacrum D, the migration volume of BPA and BPF under different temperature ranked as 20°C>40°C>5°C, therefore, 40°C could also make certain oxidizing reaction and cause the reduce of target object level.

The influence of storage time on bisphenol substances migration

When analyzing the influence of storage time on bisphenol substances migration, we should consider the type of food simulacrum and function of storage temperature together. The migration volume of BPA and BPF rose with the increase of storage time, the level of BADGE and BFDGE in simulacrum C and simulacrum D also had positive correlation with storage time, but appeared negative correlation in simulacrum A and simulacrum B.

Establishment and verification of HACCP plan: According to the appearance, the metamorphism of content in cans could be divided into 2 conditions: swell and flat cover. There were a lot of reasons causing the can to swell, and phenolic substance was one of them. Therefore, we should pay

attention to the choice of metal inside coating dye in making pork luncheon meat can packaging design and avoid the migration of phenolic substance. In addition, during the working process of packing material, we should operate equipment reliably, calibrate correctly and maintain suitably to ensure the high temperature sterilization maintain in the specified range; food contact surface should be cleaned effectively; sanitary conditions in workshop should be kept well; the staff could control their own health effectively and prevent to contaminate the product directly or indirectly. It could be proved that the HACCP plan could control the harm of phenolic substance in pork luncheon meat can effectively and lower the indexes of phenolic substance to acceptable range.

CONCLUSION

Food package safety is an important part of public security. Food packaging design influences the food safety and social stabilization and development directly. The study made research of Metal food packaging design under HACCP system of canned food safety. The results showed that HACCP could control the migration of phenolic substance and food recontamination during the metal food package design to ensure the food safety.

Conflicts of interest

The authors declare no conflict of interest.

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