

Migration of Bisphenol A from Canned Sardines into Food Simulants: Effect of Temperature and Concentration

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ABSTRACT

Epoxy resin coatings containing Bisphenol A (BPA) are widely used in canned food packaging, including sardine cans. They may pose a risk of chemical migration into food products under specific conditions. This study aimed to evaluate BPA migration into food simulants, acetic acid (1%, 3%, and 10%) and ethanol (10%, 20%, and 50%), at three temperatures (60 °C, 100 °C, and 121 °C). Migration levels were quantified using High-Performance Liquid Chromatography (HPLC) with UV-Vis detection. Preliminary analysis of five sardine can brands revealed BPA concentrations ranging from 0.0052 to 0.0487 mg/kg. Results demonstrated a significant increase in BPA migration with both simulant concentration and temperature. In ethanol, migration increased by 437% when the concentration rose from 10% to 50% at 121 °C, while a 92% increase was observed in acetic acid from 1% to 10% under the same conditions. Temperature had a more pronounced effect: BPA migration in 20% ethanol rose by 3,714% between 60 °C and 121 °C. Migration in 3% acetic acid increased from undetectable to 0.1515 mg/kg across the same temperature range. These findings indicate that BPA migration is significantly influenced by simulant type, concentration, and temperature, underscoring the necessity for stringent control over packaging conditions to ensure food safety.

Keywords: Sardine Cans, BPA Migration, Food Simulants, Temperature and Concentration

1. Introduction

Canned packaging is currently one of the most widely used types of packaging for food and beverage products. Its use offers several advantages, including high mechanical strength, excellent barrier properties against contaminants due to its hermetic and light-resistant nature, resistance to extreme conditions, and suitability as a medium for communication and information through labeling, given its ideal surface for such purposes [1]. As a result, canned packaging is commonly adopted by the food and beverage industry for its ability to preserve product quality and extend shelf life.

Packaging is the process of designing and producing containers, wrappers, or enclosures for a product. Packaging encompasses three key elements: the brand, the package itself, and the label [2].

According to Winarno, canned packaging offers several advantages, including high mechanical strength and excellent barrier properties against gases, water

vapor, microorganisms, dust, and dirt, making it suitable for hermetically sealed packaging. Additionally, it has relatively low toxicity, although the potential for migration into the packaged material exists [3].

According to Bakhori, despite its advantages, canned packaging has several drawbacks, particularly its vulnerability to chemical damage such as corrosion. Corrosion is a significant issue in food and beverage packaging, influenced by factors such as the presence of corrosive compounds, product pH, the type and characteristics of the can, and the integrity of the protective coating. External factors such as temperature, pressure, ambient humidity, and the canning method also affect the level of corrosion in metal cans [4].

Most modern metal cans are coated with enamel or lacquer on the inner surface [5]. Bisphenol A (BPA) is an industrial chemical commonly used in the production of polycarbonate plastics and epoxy resins,

including enamel varnishes applied to food-contact surfaces of cans [6], [7]. These coatings may undergo migration from the food-contact material into the packaged food. BPA and epichlorohydrin are resin components frequently used in can linings [8]. BPA-based coatings, such as Bisphenol A Diglycidyl Ether (BADGE), are often the primary material in epoxy resins. However, such coatings are prone to migration into food products [9].

In general, the interaction between food products and packaging involves several aspects: the migration of packaging components into food, gas and water vapor permeability through packaging materials, absorption of organic vapors from food into the packaging, interactive transfer due to light exposure, and flavor scalping (sorption), which refers to the absorption of taste, aroma, or color from food into the packaging material. These interactions occur due to direct contact between the food and packaging, raising concerns about the potential long-term health effects of consuming migrated chemical substances [10].

Migration occurs throughout all stages of the product's lifecycle—from production to consumption. This process is generally categorized into two types: total migration and specific migration. Total migration refers to the overall transfer of all substances from the packaging into the food during contact. In contrast, specific migration refers to the transfer of particular substances that may pose health risks to humans [10].

In the food industry, heating can be done in two ways: either after packaging or before packaging into containers. The canning process, for instance, involves sterilizing the food product within the can using a steam retort, with heating durations typically ranging from 40 to 120 minutes, or even longer, depending on specific requirements [11].

The migration of BPA from food packaging into food products can occur in various packaging types, including metal cans, paper, plastic, glass, and Tetra Pak containers [12]. BPA can enter the human body through ingestion, inhalation, and dermal absorption. As an endocrine-disrupting compound, BPA exhibits estrogenic and anti-androgenic effects that may impair the function of tissues and organs, including the reproductive, immune, and neuroendocrine systems [13].

BPA migration testing using a 20% ethanol simulant showed levels ranging from undetectable to 0.050 mg/kg, whereas testing with a 10% ethanol simulant revealed no detectable BPA in any sample. BPA migration levels were tested using 3% acetic acid and a 10% ethanol–3% acetic acid mixture as food simulants. The results showed BPA migration levels of 0.010 mg/kg in the 3% acetic acid simulant and 0.008–0.010 mg/kg in the ethanol–acetic acid mixture [14].

Further research reported BPA levels in baby-use products below 0.005 mg/kg, and in other products, levels remained below the specific migration limit of 0.050 mg/kg [15]. BPA migration levels ranging from 0.014–0.407 mg/kg in 10% ethanol, 0.012–0.113 mg/kg in 4% acetic acid, and 0.001–0.030 mg/kg in olive oil simulants [16]. Starker demonstrated that BPA migration at 60 °C storage temperature was higher than at 40 °C, with epoxy-coated can concentrations ranging from 4.84–9.40 µg/L at 60 °C and 0.60–0.76 µg/L at 40 °C [17].

BPA is a compound with very low water solubility but is highly soluble in ethanol, ether, benzene, alkalis, and acetic acid [18]. Previous studies have not comprehensively investigated the effects of simulant concentration and temperature on BPA migration. Such investigations are necessary to determine the influence of BPA migration from canned food packaging into food simulants under varying concentrations and temperatures.

BPA is an industrial chemical commonly used in the manufacture of polycarbonate, a hard, transparent plastic widely found in consumer products. BPA is also used in epoxy resins, which serve as protective coatings on the inner surfaces of some metal food and beverage cans. Bisphenol A (BPA) is a chemical compound classified under the phenol group (alkylphenols), first synthesized in 1891. Today, it is widely distributed in the environment and used in the production of various industrial and consumer products, particularly plastics [19].

Therefore, this study was conducted to provide comprehensive information and data on BPA migration from canned food packaging into various food simulants at different concentrations and temperature conditions.

2. Methods

In this study, canned packaging samples were used as the primary research material. The methods employed in this research included: (1) a preliminary test on five sardine can packaging samples of different brands, (2) BPA migration testing on sardine can samples under the influence of varying food simulant concentrations, namely 1% acetic acid, 3% acetic acid, 10% acetic acid, 10% ethanol, 20% ethanol, and 50% ethanol, and (3) BPA migration testing on sardine can samples under the influence of temperature using 3% acetic acid and 20% ethanol simulants at 60 °C, 100 °C, and 121 °C. HPLC-UV-Vis analyzed BPA migration levels.

2.1. Materials and Tools

The equipment used in this study included canned packaging samples, an oven, an analytical balance, 50 mL, 100 mL, and 1000 mL volumetric flasks, a wash bottle, 100 mL and 1000 mL beakers, a 50 mL graduated cylinder, and 200 µL and 1000 µL micropipettes. The materials utilized in the research comprised distilled water (aquabidest), Bisphenol A (BPA) standard, acetic acid (CH_3COOH), ethanol ($\text{CH}_3\text{CH}_2\text{OH}$), and methanol (CH_3OH). The instrument used for the analysis was a High-Performance Liquid Chromatography system with UV-Visible detection (HPLC UV-Vis).

2.2. Preliminary Test

In this study, a preliminary test was conducted on several sardine can package samples from various brands. During this stage, the sardine can samples were cleaned and dried. Each sample was then filled with 20% ethanol simulant and stored at 121 °C for 2 hours. The solution was subsequently analyzed by HPLC-UV-Vis.

2.3. Testing the Effect of Simulant Type and Concentration on BPA Migration

To examine the effects of simulant type and concentration on BPA migration, the canned samples were filled with food simulants containing 1%, 3%, 10%, 10%, 20%, and 50% acetic acid, and 10%, 20%, and 50% ethanol. The samples were then heated in an oven at 121 °C for 2 hours. Afterward, the simulant

solutions were analyzed for BPA migration using HPLC UV-Vis.

2.4. Testing the Effect of Temperature on BPA Migration

To investigate the effect of temperature on BPA migration, the cans were filled with 3% acetic acid and 20% ethanol food simulants, then heated at 60 °C, 100 °C, and 121 °C for 2 hours. The simulant solutions were then analyzed for BPA content using HPLC UV-Vis. The choice of 3% acetic acid and 20% ethanol simulants in this test aims to represent real food product conditions. These simulants are also aligned with the quality standards used in determining both total and specific migration, as outlined by regulatory agencies such as BPOM, FDA, EFSA, and the Indonesian National Standard (SNI 7626-1:2017).

3. Results and Discussion

In the preliminary test, five samples of canned sardine packaging from brands A, B, C, D, and E were tested. The cans were subsequently filled with a 20% ethanol simulant and stored at 121 °C for 2 hours. This procedure was conducted to simulate the heating conditions typically encountered during the production process of canned sardines. It also aligns with the testing conditions stipulated in the Indonesian National Standard (SNI) 7626-1:2017 regarding the migration testing method for bisphenol A (BPA) in polycarbonate plastics.

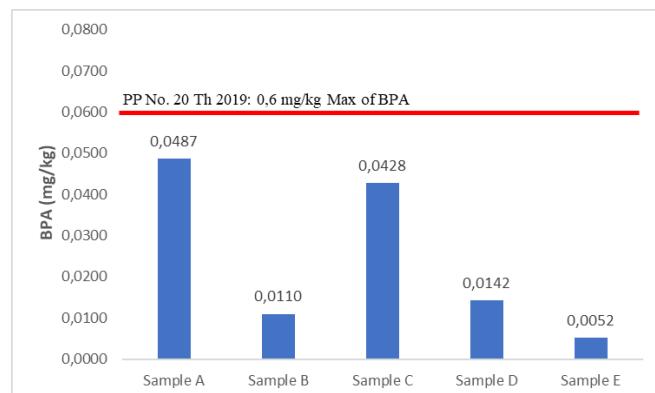


Figure 1. BPA Migration Rate Graph of Various Brands

Based on the preliminary test data concerning BPA migration levels in several canned sardine

packaging samples from different brands, all tested samples yielded positive results. The highest BPA migration level among the five packaging samples was observed in brand A, at 0.0487 mg/kg, while the lowest was in brand E, at 0.0051 mg/kg. The BPA concentrations in all tested canned sardine packaging samples were still below the regulatory limit set by the Indonesian Food and Drug Authority (BPOM), which, according to BPOM Regulation No. 20 of 2019 on food safety requirements for BPA migration from polycarbonate packaging, is 0.6 mg/kg.

In the BPA migration analysis of canned sardine packaging, 60 sardine can samples from the same brand and production code were used. The sardine brand selected for this analysis was Brand A. It was chosen based on preliminary test results showing it had the highest BPA migration level among the tested brands, at 0.0487 mg/kg.

Acetic acid and ethanol were selected as food simulants in this study to represent the characteristics of specific food types. Acetic acid was used to simulate acidic food products, whereas ethanol was used to represent food products containing fats or alcohol. The study employed different concentrations of these simulants: 1%, 3%, and 10% for acetic acid; and 10%, 20%, and 50% for ethanol. The choice of these concentration variations was based on standardized migration testing protocols employed by several regulatory bodies, including the Food and Drug Administration (FDA) and the European Food Safety Authority (EFSA). Additionally, these concentrations reflect the nature of actual packaged food products: 1% of acetic acid represents low-acidity foods, 3% for moderately acidic foods, and 10% for highly acidic foods; ethanol 10% simulates low-fat/alcohol content, ethanol 20% for moderate levels, and ethanol 50% for high-fat/alcohol content. This range of concentrations was selected to encompass both real-life conditions and extreme scenarios, thereby assessing the safety limits of BPA migration in food packaging.

The study also involved testing under different temperature conditions to simulate the thermal environments encountered during sardine can production and distribution. The temperatures of 60 °C were used to simulate storage or warm distribution environments, 100 °C to represent pasteurization

processes, and 121 °C to represent sterilization during sardine canning.

Table 1. BPA Migration Levels in Sardine Can Packaging under the Influence of Simulant Concentration

| Condition | BPA (mg/kg) |
|-----------|-------------|
| A1 | 0.1351 |
| A2 | 0.1716 |
| A3 | 0.2599 |
| B1 | 0.0784 |
| B2 | 0.1071 |
| B3 | 0.4213 |

Note:

A1: 1% acetic acid at 121 °C

A2: 3% acetic acid at 121 °C

A3: 10% acetic acid at 121 °C

B1: 10% ethanol at 121 °C

B2: 20% ethanol at 121 °C

B3: 50% ethanol at 121 °C

Two testing conditions were established in this study. In the first condition, sardine can package samples were filled with food simulants (acetic acid and ethanol) at varying concentrations. This was conducted to evaluate the effect of food simulant concentration on BPA migration levels. The BPA migration results for acetic acid simulants were: 0.1351 mg/kg for 1% concentration, 0.1716 mg/kg for 3%, and 0.2599 mg/kg for 10%. For ethanol simulants, BPA migration levels were 0.0784 mg/kg for 10%, 0.1071 mg/kg for 20%, and 0.4213 mg/kg for 50%. These findings are consistent with previous studies. For instance, Suyatma reported varying BPA levels in 12 sardine can samples using 10% and 20% ethanol simulants stored at 60 °C for 10 days. The results showed non-detectable BPA levels in the 10% ethanol simulant, whereas the 20% ethanol simulant showed levels ranging from non-detectable to 0.050 mg/kg. Similarly, research by Stojanovic showed higher BPA migration in 50% ethanol (16 µg/kg) than in 10% ethanol (8–10 µg/kg) during storage at 60 °C for 10 days.

In this study, an ANOVA was conducted to determine whether BPA migration differed with increasing food simulant concentration in canned sardine packaging samples. The results of the ANOVA test for the effect of acetic acid and ethanol food

simulant concentrations showed a significance value of 0.000 (< 0.05) for both simulants. This indicates that the concentrations of acetic acid and ethanol food simulants significantly affected BPA migration levels in sardine can packaging samples. The ANOVA was followed by a post hoc Duncan test to determine whether significant differences existed among treatments or simulant concentrations. The Duncan test results confirmed substantial differences among the treatment levels.

Table 2. BPA Migration Levels in Sardine Can Packaging under the Influence of Simulant Temperature

| Condition | BPA (mg/kg) |
|-----------|-------------|
| C1 | 0.0000 |
| C2 | 0.0418 |
| C3 | 0.1515 |
| D1 | 0.0028 |
| D2 | 0.0919 |
| D3 | 0.1068 |

Note:

C1: 3% acetic acid at 60 °C

C2: 3% acetic acid at 100 °C

C3: 3% acetic acid at 121 °C

D1: 20% ethanol at 60 °C

D2: 20% ethanol at 100 °C

D3: 20% ethanol at 121 °C

The second condition tested the effect of different storage temperatures on BPA migration using acetic acid and ethanol simulants. This was aimed at evaluating the influence of simulant temperature on BPA migration in sardine can packaging. For this test, 3% acetic acid and 20% ethanol were used, as these concentrations represent realistic characteristics of canned food and are widely employed in migration testing standards such as those from BPOM, FDA, EFSA, and SNI 7626-1:2017. BPA migration levels for 3% acetic acid were as follows: not detected (ND) at 60 °C, 0.0418 mg/kg at 100 °C, and 0.1515 mg/kg at 121 °C. For 20% ethanol, BPA levels were 0.0028 mg/kg at 60 °C, 0.0919 mg/kg at 100 °C, and 0.1068 mg/kg at 121 °C. These results agree with the study by Starker, which observed differences in BPA migration when 20% ethanol was stored at 40 °C or 60 °C for 10 days. BPA concentrations ranged from 0.60–0.76 µg/L at 40 °C and 4.84–9.40 µg/L at 60 °C. These findings

underscore that simulant temperature significantly influences the extent of BPA migration.

Additionally, an ANOVA was performed to assess the effect of food simulant temperature on BPA migration in sardine can packaging samples. The ANOVA results for 3% acetic acid and 20% ethanol simulants also showed a significance value of 0.000 (< 0.05), indicating that simulant temperature significantly affected BPA migration levels. A follow-up Duncan test was conducted to examine the significance of differences among temperature conditions. The results demonstrated significant differences among the temperature treatments (60 °C, 100 °C, and 121 °C).

Bisphenol A (BPA) is a compound with very low polarity in water but highly soluble in solvents such as ethanol, ether, benzene, alkalis, and acetates. BPA contains two hydroxyl (-OH) groups attached to two benzene rings. The hydroxyl groups are polar and can form hydrogen bonds with other molecules, while the benzene rings are hydrophobic. Acetic acid contains a carbonyl (C=O) and a hydroxyl (-OH) group, which can form hydrogen bonds with BPA, thereby influencing its solubility in acetic acid. Similarly, ethanol contains hydroxyl (-OH) groups that can form hydrogen bonds with BPA, thereby enhancing BPA's solubility in ethanol. The hydroxyl groups in BPA thus increase its solubility in polar solvents like acetic acid and ethanol [18].

Increasing the concentration of acetic acid decreases the solution's pH. A lower pH can weaken the chemical bonds between BPA and the packaging matrix. Additionally, the carbonyl and hydroxyl groups in acetic acid can strongly interact with BPA, increasing its migration into the simulant. In highly acidic solutions, the abundance of H⁺ ions can affect the ionization of BPA's hydroxyl groups, significantly influencing its solubility in acidic simulants. These findings are consistent with this study's results, which showed that higher acetic acid concentrations were associated with greater BPA migration. The highest BPA migration in acetic acid was observed in the 10% acetic acid simulant at 121 °C, with a concentration of 0.2599 mg/kg [20].

For ethanol simulants, the highest BPA migration level was recorded under 50% ethanol at

121 °C, reaching 0.4213 mg/kg. These findings indicate that increasing ethanol concentration correlates with higher BPA migration levels. Ethanol is a semi-polar solvent, capable of dissolving both polar and non-polar compounds. Higher ethanol concentrations increase the solvent's affinity for BPA, especially for its non-polar segments (the two benzene rings), which exhibit strong affinity toward ethanol. The hydroxyl groups in ethanol also facilitate BPA release by forming hydrogen bonds with BPA's hydroxyl groups. At higher concentrations, ethanol creates a solvent environment with optimal polarity for dissolving BPA [20].

Migration is a diffusion process governed by kinetic laws and thermodynamic control. Migration can be described as a function of time, temperature, material thickness, the number of migratable substances, and the partition and distribution coefficients. Various factors influence migration, including the type and concentration of chemicals, the nature of the food in contact with the packaging, and the intrinsic properties of the packaging material [21].

Aside from simulant concentration, BPA migration is also influenced by the temperature of the food simulant, as shown in this study. Higher simulant temperatures significantly impacted BPA migration levels in both acetic acid and ethanol. Castle explained that elevated temperatures accelerate the transfer of chemical compounds by increasing molecular activity. Higher temperatures raise the kinetic energy of BPA molecules in the epoxy layer and in the food simulant, enabling BPA to migrate from the epoxy matrix into the simulant more easily [21]. Research by Krivohlavek also showed that BPA release was higher in cans subjected to heating under extreme simulation conditions [15].

Based on the findings of this study, it can be concluded that both the concentration and temperature of food simulants significantly influence BPA migration from canned sardine packaging. BPA can migrate from the can lining into acetic acid and ethanol simulants under various concentration and temperature conditions. The BPA migration levels observed in this study remain below the maximum allowable limit of 0.6 mg/kg for BPA in polycarbonate packaging

materials, as regulated by BPOM Regulation No. 20 of 2019.

4. Conclusion

Based on the results of the study on the migration of Bisphenol A (BPA) compounds from canned sardine food packaging into acetic acid and ethanol food simulants under various temperature and concentration conditions, the following conclusions can be drawn: Bisphenol A (BPA) compounds can migrate from canned packaging into acetic acid and ethanol food simulants. The temperature and concentration of the food simulants influence the migration of Bisphenol A (BPA) from the canned packaging. The higher the temperature of the food simulant, the higher the BPA migration level. Furthermore, increasing the concentration of the food simulant also results in higher levels of BPA migration. The BPA migration levels obtained in this study did not exceed the regulatory limit set by BPOM Regulation No. 20 of 2019, which is 0.6 mg/kg. The highest result obtained in this study was 0.4213 mg/kg under the test condition of 50% ethanol simulant at 121 °C.

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