

Leaching of Iron and Zinc into Food Simulant from Tin Can Packaging

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Received: September 2019; Revision: November 2019; Accepted: November 2019; Available online: November 2019

Abstract

Cans are widely used as primary packaging in various food products. Ferrous (Fe) and zinc (Zn) metal as the constituent components in the manufacture of can packaging bodies can experience corrosion and dissolve in food so that it will affect food quality and finally affect to health. This study aimed to determine the content of Fe and Zn metal at different treatments (time) with 3% acetic acid and vegetable oil as food simulators on can packaging using Atomic Absorption Spectrophotometer (AAS). The results of the analysis showed that the range of Fe and Zn metal content in 3% acetic acid food simulants were respectively 0.15-27.46 mg/kg and 0.0006-0.007 mg/kg, while in vegetable oil simulants 3% Fe and metal content Zn were 0.6-2.46 mg/kg and 0.0004-0.0025 mg/kg with 80-100% recovery, respectively. Thus, food from can packaging should not be exposed to oxygen for a long time, especially when it has been opened because it will increase the leaching of Fe and Zn metals from the packaging into food.

Keywords: Can packaging, food simulant, metal analysis.

DOI: [10.15408/jkv.v5i2.12526](https://doi.org/10.15408/jkv.v5i2.12526)

1. INTRODUCTION

Tin cans are commonly used in products that undergo a thermal sterilization process. The advantages of can packaging are easy packaging, sterilization, delivery, transportation and minimized vitamin loss (Parkar J and Rakesh M, 2014). The disadvantage of can packaging is due to its non-inert property to chemicals which reacts with the environment and the contents causing loss of taste (Setyowati 2000).

Food products can experience interactions with cans at the time of storage which causes the transfer of packaging compounds into food products. Transfer of packaging components into food compounds that probably occurs is metal corrosion (Abdel-Rahman, 2015) such as zinc (Zn) and iron (Fe) because both metals are the compilers of can packaging (Syarief RS 1989). Iron (Fe) is used as a basic element in metal packaging while zinc (Zn) is utilized to improve packaging resistance to corrosion (Cardeber et al, 2015). Fe and Zn metals are essential metals needed by the body, but the excessive amount of them will affect the quality of food and be harmful

to health (Wagner, Castle, Oldring, Moschakis and Wedzicha, 2018). Excessive Fe metal will cause swelling in the liver and reduce the ability of the body to absorb copper, while excessive Pb metal will cause brain damage and nerve disorders.

The possibility of moving packaging components into food must be analyzed. Analysis using direct food is sometimes difficult to do because food products are a very complex matrix (McCort-Tipton and Pesseelman 1999). Therefore, to imitate certain food characteristics, a food simulation can be used (POM 2011). In this study, food simulants representing fatty and fatty foods used are 3% acetic acid and vegetable oil. According to Arora's research (2000), acidic foods such as tomatoes and tamarind juice with can packaging occur an increase in Fe metal content. Research by Parkar and Rakesh (2014) shows that Fe content increases in cans of orange juice contents with varied time and temperature. Therefore, research on the metal content in food simulants needs to be done because it deals with the migration of packaging components into food products.

2. MATERIALS AND METHODS

Materials and Instrumentations

The materials used in this study were standard pure analysis, distilled water, Nitric acid (HNO₃) merck KgaA, Hydrogen Peroxide (H₂O₂) 30% merck KgaA, Standard solution Fe 1000 ppm, Standard solution of Zn 1000 ppm (CertiPUR Merck KgaA), Tin cans, Vegetable oil and Acetic acid 30%.

Glass Tools, Flame-AAS type Shimadzu AA 2000, Hollow cathode lamp Fe and Zn, Oven, Desiccator, Analytical balance and Close microwave digestion type MDS 6G SINEO.

Physical Analysis of Can Packaging

The can packaging used in this study was the can packaging for sardines obtained from the market with the same identity (batch number and expiration date). Intact cans were opened and poured its contents into a tub, then the cans were cleaned and dried. Clean cans were measured the dimensions and enamel coating uniformity.

Dimension measurement of fish cans including the inner diameter, outer diameter, depth and thickness of the cans using calipers. The test was carried out on 3 cans. The uniformity of the enamel coating was conducted on 3 cans by cutting the 1.5 cm x 1.5 cm can plate and then immersed in the test solution (distilled water: copper sulfate: HCl with a ratio of 70:20:10) for 2 minutes at room temperature. The plate was washed with clean water and then observed.

Elemental Analysis

Clean and dry cans were filled with food simulants ± 150 mL (3% acetic acid and vegetable oil) and sealed with polyethylene plastic. Food simulants were stored at 38 °C with a variation of time (0,2,4,6,8,10,12) weeks and measurements of Fe and Zn metal content in food simulations was conducted by using AAS machine.

The destruction process was carried out using the microwave digestion method. The food simulant sample was weighed as much as 0.5 gram using an analytical balance, then the sample was put into a vessel tube. The vessel tube containing the sample was added 7 mL HNO₃ (p) and 1 mL H₂O₂ 30%, then put into the Microwave Digestion. After the

digestion process was complete, the solution was left until it reached room temperature, then the solution was transferred to a 50 mL measuring flask, and fulfilled with double distilled water and homogenized. A blank solution with the addition of reagents was prepared and the same treatment was applied as the example. Microwave digestion settings can be seen in Table 1.

Table 1. Setting digestion with microwave digestion

Stage	Temp (°C)	Time (Minute)	Power (W)
1	130	10	300
2	150	5	600
3	180	15	500

Testing Analytical Methods

Precision and Accuracy

This test was carried out using a sample that was added (spiking) with a standard solution of seven replications. Spiking was done at the beginning of sample preparation before being treated with microwave digestion. Each spiking was done by seven replications. Accuracy was determined by calculating The recovery percentage (recovery).

Precision was determined by comparing the RSD value of the analysis with the RSD Horwitz. Precision was said to be good if it had an RSD analysis value < 2/3 CV Horwitz.

Linearity

Testing the linearity of Fe mineral with concentration of 0-0.5 mg/L while Zn mineral concentration was of 0-1.0 mg/L. Each of the standard solutions was measured by absorbance repeated 3 times. Linearity was considered good if it had a correlation coefficient (r) more than 0.995 or R² more than 0.990.

3. RESULTS AND DISCUSSION

Physical Analysis of Can Packaging

Measurement of can dimension

Tin cans used were round cans. A round can was a type of can that is physically circle or round with its constituent elements in the form of body and end components. The measurement results of can dimension can be seen in Table 2.

Table 2. Measurement results of can dimension

Replication	Inner Diameter (cm)	Outer Diameter (cm)	Depth (cm)	Thickness (cm)
1	4.695	5.270	8.590	0.575
2	4.725	5.225	8.595	0.550
3	4.835	5.260	8.465	0.575

The Uniformity of The Enamel Coating

The enamel coating is a non-metallic coating on cans that coat metal (prevents corrosion) and protects direct contact with the product. Inner enamel serves to prevent metal contact with food, minimize interactions between food and packaging such as sulfide staining reactions while outer enamel serves to prevent corrosion caused by the environment and for decoration. The results of the analysis of the uniformity of the enamel coating can be seen in Table 3. The interaction between food compounds and packaging can cause corrosion resulting in unwanted color and flavor, including the formation of a black color caused by the reaction between iron or lead with sulfide in low-acidic (high protein) food, and red pigment bleaching from vegetables/fruits such as beets or grapes due to reactions with steel, lead or aluminum.

Table 3. Results of analysis of enamel coating uniformity testing

Testing Media	Treatment	Result		
		Black Stain	Reddish	Scratch
Can plate with the size of 1.5x1.5 cm	Aquadest: copper sulfate:HCl	√	x	x

From the results of observations, it was seen that the inner layer that was not given enamel occurred corrosion because the metals contained in the inside of the could react with food, especially food containing acid. On the outer layer, there were black spots (corrosion) on the edges because there was a reaction between iron or tin with Cu. Enamel was used to prevent corrosion on the inside and outside of the can.

Corrosion is a defect in the form of rust (black spots) caused by the chemical reaction process which was corrosive, both water and acid. Generally, the material that is not coated

with enamel is easily exposed to acidic chemicals or humid air, so that it causes oxidation reactions resulting in further rust.

Elemental Analysis

Metal measurement was carried out using the microwave digestion method. This method has several advantages compared to conventional digestion (wet and dry digestion). Some of them are: the reagent used is lesser and it processes in faster time (Altundag and tuzen, 2011; Mustafa *et al.*, 2003; 2004; Korn *et al.*, 2008). A sample with high oil content only requires a small amount of sample, but a sample with high water content requires a higher amount sample (Mindak *et al.*, 2010).

The advantages of can as food and drink packaging are its high mechanical strength, good barrier against gas, steam, water, microorganisms, dust and dirt making it suitable for hermetic packaging. The toxicity is relatively low although there is a possibility of metal elements migration into the packaged material. It is resistant to changes or extreme temperature conditions. In addition, it has an ideal surface for decoration and labeling (Syarif *et al.*, 1989).

The occurrence of displacement of packaging components into food is influenced by several factors, including the initial concentration of food contact substances, the time length of the packaging contacts with food, contact temperature, surface area and food properties (acidic, fatty, alcoholic) (BPOM 2009). In this study, the total immersion test method was used due to its simplicity, it was done by making contact between the food simulants and the entire surface of the package. The mechanism for releasing packaging components can be done in 4 ways as shown in Figure 1, namely (a) direct contact with the package, (b) indirect contact from the packaging as a secondary material, (c) from the outside of packaging and (d) from the packaging matrix to the outside environment.

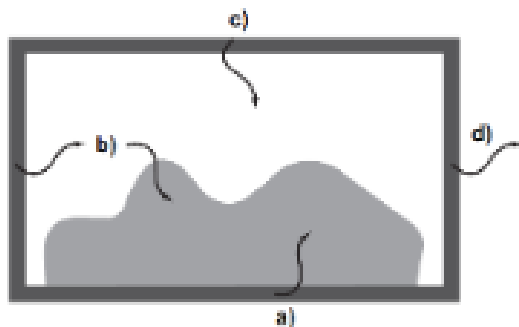


Figure 1. The mechanism of releasing packaged food components (Pocas *et al.*, 2011).

Zinc (Zn) is often used in metal packaging to increase the resistance of lead and steel from corrosion (Mousawi *et al.*, 2018). In this research, 3% acetic acid food simulants were used to represent acidic foods and vegetable oils represent foods with high-at content, with the consideration that cans are widely used for fatty and fatty foods such as acidic drinks, juices and canned fish packaging. The use of food simulants was intended as a substitute for food because food products are a very complex matrix.

The results of the migration of Fe and Zn metal can be seen in Figure 2. From the analysis results, it was obtained that the levels of Fe and Zn metal were increasing, especially in acid food simulants. The results of the analysis were still below the range of the standard specific release limits (SRL) set by the Council of Europe resolution CM/Res (2013) in which the SRL for Fe metal is 40 mg/kg and Zn metal is 5 mg/kg. According to Laroussen and Brown (1997), the longer food is stored, the longer the contact time between

food and container, then the greater the possibility of the metal constituent to be separated and contaminate the packed food.

This shows that the use of tin cans should not interact with oxygen for too long especially if the food sample is acidic because it will result in the migration of Fe metal. Some factors determining the formation of rust on the inside of the can include the nature of food ingredients, especially pH; promoters of rust formation such as nitrates (found in some fruits and vegetables); the amount of oxygen remaining in food, especially in the remaining space; temperature and storage time; as well as several factors derived from packaging materials, such as the weight of the tin layer, the composition of the base steel layer, the effectiveness of the treatment on the surface of the layer, the type of coating, etc. (Julianti and Nurminah, 2006; Laroussen and Brown, 1997). The presence of gas in can is caused by hydrogen production due to corrosion (Dantas, 2016).

Migration of metal packaging will affect the quality (aroma, taste and color) and safety (accumulation of migrant substances). Rust formation occurs because the tin layer is peeled or dissolved into the food simulant so that the metals contained in the inner compartment of the can react and contaminate the food simulant (Itodo and Itodo, 2010). According to FAO/WHO, the maximum limit of iron content in food is 250 ppm. Metal poisoning can be mild or severe poisoning such as nausea, vomiting, dizziness and excessive cold sweating (Syarief *et al.*, 1989).

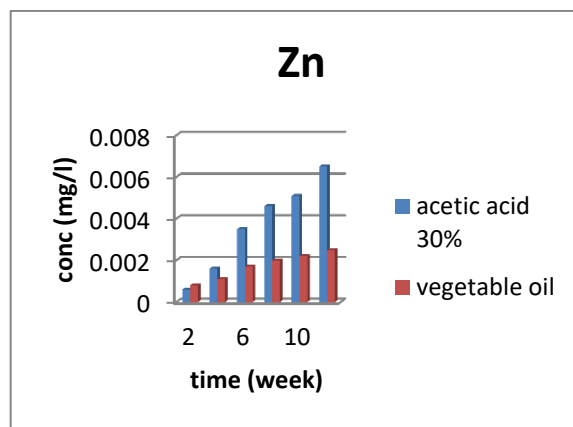
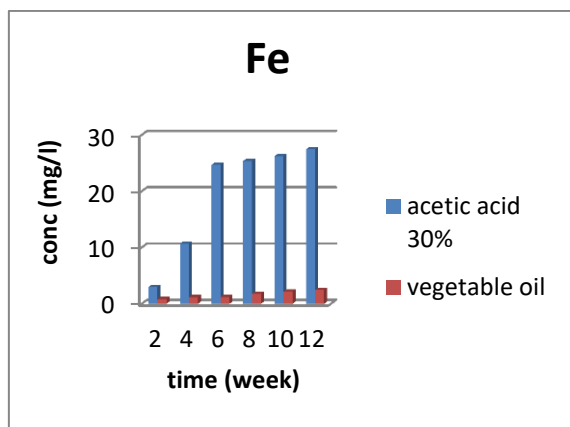


Figure 2. Leaching metal Fe and Zn in food simulant

Testing Method of Analysis

Table 4 . Precision analysis result

	% Recovery Metal Fe											
	Acetic acid 30%						Vegetable oil					
	2	4	6	8	10	12	2	4	6	8	10	12
\bar{x}	84.29	109.88	90.37	81.33	80.32	86.92	100.23	98.81	103.66	82.86	84.69	86.88
		8	7	3	2		1	6		9	8	
	% Recovery Metal Zn											
	Acetic acid 30%						Vegetable oil					
	2	4	6	8	10	12	2	4	6	8	10	12
\bar{x}	82.02	82.14	82.12	80.25	81.87	82.14	79.68	83.94	87.26	90.58	94.38	98.64
	2		2	5	7		4				8	4

Table 5. Accuracy analysis result

	Fe Content (mg/L)													
	Acetic acid 30%							Vegetable oil						
	0	2	4	6	8	10	12	0	2	4	6	8	10	12
Average	0.15	2.97	10.66	24.70	25.37	26.23	27.46	0.60	0.83	1.19	1.20	1.75	2.17	2.46
%RSD	8.65	2.50	0.79	1.30	0.25	0.02	0.37	8.90	8.65	2.65	14.85	6.11	0.83	2.42
2/3 RSDH	14.17	9.06	7.47	6.58	6.56	6.52	6.48	11.51	10.98	10.39	10.38	9.80	9.49	9.32
	Zn Content (mg/L)													
	6	1.6	3.5	4.6	5.1	6.5	7	8	1.1	1.7	2	2.2	2.5	
Average	$\times 10^{-4}$	$\times 10^{-3}$	$\times 10^{-3}$	$\times 10^{-3}$	$\times 10^{-3}$	$\times 10^{-3}$	$\times 10^{-3}$	$\times 10^{-3}$	$\times 10^{-4}$	$\times 10^{-3}$	$\times 10^{-3}$	$\times 10^{-3}$	$\times 10^{-3}$	$\times 10^{-3}$
%RSD	21.65	8.66	7.87	2.99	2.71	2.11	1.97	34.64	17.32	24.74	24.74	27.71	24.74	22.35
2/3 RSDH	32.32	28.16	25.01	23.99	23.64	22.77	22.53	34.69	31.25	29.71	27.95	27.23	26.77	26.36

Linearity

The resulting regression equation for the mineral Fe was $y = 0.084x - 0.0002$ with $R^2 = 0.9970$; mineral Zn was $y = 0.4125x + 0.0086$ with $R^2 = 0.9977$. The linearity curve obtained has an R^2 value of more than 0.990 indicating a direct correlation between the concentration of the standard series and absorbance.

Precision

The results of the precision test can be seen in Table 4. From this table, it can be seen that the precision for the mineral Fe and Zn produces a value of % RSD < 2/3 CV Horwitz. This indicates that the results of the analysis are precise and there are no random errors.

Accuracy

Accuracy aims to see the efficiency of the method based on recovery of standard solutions added to the sample (spiking) (Ajai *et al.*, 2014). The test results for the accuracy of Fe and Zn mineral can be seen in Table 5. The recoveries produced from Fe metal was in the range of 80-102%, these results are still within the acceptability limit of AOAC, which is

around 80-120%. This indicates that the analysis procedure with the modified method for all minerals can be accepted. The accuracy obtained did not differ greatly from the results of the analysis of Ajai *et al.*, (2014) in canned pineapple samples with a recovery of 80%. Accuracy is related to systematic error that can be controlled. Sources of systematic error include the use of glass tools that have not been calibrated.

4. CONCLUSION

The content of Fe and Zn metal in the acetic acid food simulants of 3% is more than the vegetable oil simulations. This is because the acid content is easier to cause corrosion on cans and is accelerated in the presence of oxygen. Therefore, food from tin cans is sought not to be exposed to oxygen for a long time especially when it has been opened.

ACKNOWLEDGMENTS

Bogor AKA Polytechnic as a place to conduct research and as a financial supporter of this research.

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238

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