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Measuring and comparing the concentration of heavy metals (arsenic, cobalt, cadmium, lead and mercury) in canned foods (strong acid, acid, low acid) in Ahvaz city

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ABSTRACT

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The presence of heavy metals such as arsenic, cobalt, cadmium, lead and mercury in canned food is of great importance from the point of view of their toxicity and nature, and it covers a wide range of food. The presence of these metals in canned products is sometimes the source of the food, the type of can or the possibility of corrosion of the inner body of the used can is attributed. Therefore, the purpose of this study was to measure and compare the concentration of heavy metals in canned food (strong acid, acid, low acid). In order to analyze the data, descriptive statistics methods were used to compare the mean and difference between the data, the one-way multivariate variance measurement and the Kolmogorov-Smirnov test were used to ensure the normality of the data and if there was a significant difference between the data , then Tukey's test was performed to separate the data. The results of this research showed that the average concentration of heavy metals was in the order of lead > mercury > cobalt > arsenic > cadmium, and among the available metals, lead with a total average of 0.2670 ± 0.019723 mg/ kg had the highest value and cadmium had the lowest value with an average of 0.0028 ± 0.0049 . Compared to international standards and other studies, all metals except lead were lower than the maximum value. Although the concentration of these metals in canned food samples was acceptable but it is necessary to pay attention to the factors that increase the presence of these metals in canned goods in order to control them and achieve a high-quality product.

1. Introduction

Foods of animal origin are known for their valuable nutrients, and the food industry employs various technologies to produce products with extended shelf lives. Canned foods, in particular, offer the advantage of long shelf life without the need for refrigeration or special handling during transportation and distribution. These products, whether enclosed in metal cans, glass containers, or plastic containers, undergo processes like pasteurization and airtight packaging to ensure their extended shelf life by preventing air access and contamination. Some canned foods may also contain chemical preservatives such as sodium nitrate or potassium nitrate. However, despite their taste and nutritional value, canned food products can also potentially contain chemical pollutants. These pollutants can originate from the environment, improper technological processes, or inadequate packaging. While industrial and agricultural laws have been implemented to regulate food production, it is challenging to completely eliminate the presence of chemical pollutants in food due to environmental pollution. Among these pollutants, heavy metals pose a significant threat to human health [1].

While many metals are natural components of ecosystems and play essential roles in the survival of living organisms [2][3], their excessive presence beyond certain limits can endanger the lives of animals and plants. Heavy metals, such as lead, nickel, arsenic, cobalt, cadmium, and mercury, are particularly

concerning as food contaminants due to their toxicity at certain levels. Human activities, such as dyeing industries, metal plating (used for preserving canned foods), and battery manufacturing, contribute to the release of heavy metals into the environment [4][5]. Long-term exposure to heavy metals can lead to a decrease in aquatic animals' reproductive capacity, respiratory and nervous problems, food scarcity, hormonal imbalances, abortions, and more. These contaminants can also be transmitted to subsequent consumers, including humans, causing irreversible complications [6][7].

In industrial societies, it is difficult to escape heavy metals. Every year, thousands of tons of industrial waste containing heavy metals, such as arsenic, zinc, cadmium, and nickel, enter the soil and subsequently the human food chain. These heavy metals have toxic effects and can accumulate in humans and aquatic organisms, leading to various diseases. Nickel exposure, for instance, can cause dermatitis, asthma, bronchitis, skin cancer, and lung cancer. One significant issue with heavy metals is their non-metabolism in the body, resulting in their accumulation in tissues such as fat, bones, muscles, and organs, leading to numerous diseases and complications. Heavy metals are systemic poisons that can cause death through specific effects on the nerves, kidneys, embryos, and carcinogenesis. They also impact human behavior by disrupting the mental and nervous system, interfering with

neurotransmitters, cardiovascular function, and the immune system [8][9].

The symptoms of arsenic poisoning vary depending on the duration of exposure. Acute poisoning may cause vomiting, abdominal pain, encephalopathy, and bloody diarrhea. Long-term exposure to arsenic can result in skin thickening, skin darkening, abdominal pain, diarrhea, heart disease, muscle weakness, and cancer [10]. In a 2014 study, Zhang et al. demonstrated that arsenic exposure increases the risk and incidence of cardiovascular diseases. Prolonged inhalation of this compound can lead to additional skin complications, neurological disorders, an increased risk of lung cancer, and complications in the digestive and urinary systems [11].

Cadmium, a highly toxic metal commonly found in industrial settings, poses a significant risk due to its low allowable limits. Inhalation of cadmium can cause cold-like symptoms such as chills, fever, and muscle aches, while higher levels of exposure can lead to bronchitis, pleurisy, and pulmonary edema [12]. Ingesting small amounts of cadmium over an extended period can result in the formation of insoluble metal salts in the kidneys, leading to kidney damage. Furthermore, long-term exposure to cadmium can cause prostate atrophy, cardiovascular problems, osteoporosis, and various cancers [13].

Lead and mercury are heavy metals that can enter the body through ingestion, inhalation, and even skin absorption. Lead poisoning

primarily affects the central nervous system, making it the most vulnerable organ in the body. Common symptoms include abdominal pain, constipation, headaches, irritability, memory problems, decreased fertility, and tingling in the hands and feet [14]. Disturbingly, lead poisoning is responsible for nearly 10% of mental disabilities with unknown causes and can lead to behavioral problems and various types of cancer. Moreover, some complications caused by lead poisoning are permanent and irreversible. In severe cases, anemia, convulsions, coma, or even death may occur [15].

Mercury poisoning, on the other hand, presents different symptoms depending on the dose, method of poisoning, and duration of exposure. Weakness, poor muscle coordination, numbness in the hands and feet, skin rashes, memory problems, difficulty speaking, hearing problems, and vision issues are some common symptoms [16]. Long-term exposure to low doses of methylmercury, a form of mercury, is not well understood. However, exposure to high levels of methylmercury can cause Minamata disease. Furthermore, contact with mercury in children can lead to acrodynia (pink disease), characterized by reddening and peeling of the skin [17].

When heavy metals are ingested in amounts exceeding the permissible limit, they accumulate in the body until reaching toxic levels, resulting in various toxic effects. Therefore, it is crucial to consistently evaluate the levels of these compounds in canned foods. Additionally, the amounts of these metals serve

as indicators to assess product quality. Given that Khuzestan province serves as a major hub for all kinds of goods, including canned foods, with easy access to the free trade zone, conducting a study on the impact of toxic metal pollutants on consumer health is necessary. It is noteworthy that no similar study has been conducted in this area thus far, further underscoring the importance of such research.

2- Materials and Methods

2.1. Sample Preparation

A variety of canned foods from three desired groups (strong acid, acid, low acid) were purchased from local grocery stores. Four samples were obtained from each product, resulting in a total of 48 samples. Immediately after purchase, the samples were transported to the laboratory and stored at -18 °C until analysis.

2.2. Sample Digestion

Two grams of each product were placed in specialized containers along with 5 ml of 65% nitric acid (w/w) and 2 ml of 30% hydrogen peroxide (w/w). The containers containing the samples were then subjected to microwave digestion. After digestion, the sample containers were allowed to cool to room temperature. Subsequently, the samples were transferred to 25 ml flasks and diluted to the desired volume with deionized water [18].

2.3. Analysis of Metals

The concentration of arsenic, cobalt, cadmium, and lead in the samples was measured using an atomic absorption device equipped with a GFABS graphite furnace. To ensure accuracy, each sample was injected into the device in triplicate. Mercury measurement was conducted using the direct method of mercury analysis, eliminating the need for sample preparation. The obtained results were compared with standard metal values [18].

2.4. Statistical Analysis

Descriptive statistical methods were initially employed to analyze the data. Statistical analysis was performed using SPSS version 22 software, employing one-way multivariate variance measurement to compare means and differences in the data. The data for each measurement are presented as mean value \pm standard deviation (mean \pm SD). The Kolmogorov-Smirnov test was utilized to assess the normality of the data distribution. Once the normality of the observations' distribution was confirmed, statistical analyses were conducted. In the case of significant differences in the data, Tukey's post-test was applied to separate the data, with a confidence level above 95% ($P < 0.05$) used to determine significance.

3- Results

After normalizing the data, according to this study, the comparison of the average concentration of heavy metals (arsenic, cobalt, cadmium, mercury, lead) in 3 groups of food products (strong acid, acidic, low acid) was

investigated. According to table 1, the average concentration of arsenic metal in strong acidic, acidic and low acid canned products is equal to 0.00851 ± 0.0164 , 0.01272 ± 0.0232 and 0.00876 ± 0.0194 mg/kg, respectively. Also, the highest average concentration of arsenic metal among canned products belonged to acidic products. Examining the average concentration of cobalt metal in strong acidic, acidic and low acid canned products showed 0.01276 ± 0.0239 , 0.01344 ± 0.0255 and 0.01382 ± 0.0273 mg/kg, respectively, and low acid products had the highest amount of cobalt metal. Also, the average concentration of cadmium metal in strong acidic, acidic and low acid canned products was equal to 0.00491 ± 0.0028 , 0.01363 ± 0.0195 and 0.00799 ± 0.0188 , respectively, and the test results indicated the highest amount of this metal in acidic products. The average concentration of lead metal in strong acidic, acidic and low acid canned products was 0.09725 ± 0.0566 , 0.05334 ± 0.2776 and 0.09805 ± 0.4955 mg/kg, respectively, and the low acid products had the highest amount of this metal. The average concentration of mercury metal in strong acid, acid and low acid canned products was equal to 0.01705 ± 0.0342 , 0.01304 ± 0.0251 and 0.01265 ± 0.0204 mg/kg, respectively, and the highest amount of this metal belonged to strong acid products. Available metals, lead with a total average of 0.2670 ± 0.019723 mg/kg and cadmium had the lowest amount with an average of 0.0049 ± 0.0028 .

Additionally, the results of one-way multivariate analysis of variance (Table 2) indicate a significant statistical difference between the groups of food products ($P < 0.05$). Further analysis using the post-Tukey test (Table 3) reveals that the average concentration of arsenic and cobalt metals in the target groups did not show a statistically significant difference. However, the average concentration of cadmium, mercury, and lead metals exhibited a significant difference among the target groups ($P < 0.05$). Specifically, the post-Tukey test results indicate that the amount of mercury in the strongly acidic product group significantly differs from the group of canned products with low acidity ($P < 0.05$). However, there was no statistically significant difference in the concentration of mercury between the strongly acidic and acidic product groups. Furthermore, the average concentration of cadmium metal in the strongly acidic product group was found to be statistically significantly different from the other two groups ($P < 0.05$). The average concentration of lead metal also demonstrated a statistically significant difference across all food groups ($P < 0.05$). Moreover, a general comparison of the average concentration of metals reveals that the amount of mercury increases with the increase in saturation acidity, while the concentrations of cobalt, lead, cadmium, and arsenic metals decrease with the increase in saturation acidity (Fig. 1-5).

Table 1. Descriptive indicators of heavy metal concentration in 3 groups of canned products (High-acidic, Acidic and low-acidic)

Sample		Element(mg/kg)				
		As	Co	Cd	Pb	Hg
High	Mean	0.0164	0.0239	0.0028	0.0566	0.0342
	Std	0.00851	0.01276	0.00491	0.09725	0.01705
	Lower Bound	0.011	0.017	-0.020	0.014	0.027
	Upper Bound	0.022	0.031	0.008	0.099	0.041
Acidic	Mean	0.0232	0.0255	0.0195	0.2776	0.0251
	Std	0.01272	0.01344	0.01363	0.05334	0.01304
	Lower Bound	0.018	0.019	0.015	0.235	0.018
	Upper Bound	0.028	0.032	0.024	0.320	0.032
Low	Mean	0.0194	0.0273	0.0188	0.4955	0.0204
	Std	0.00876	0.01398	0.00799	0.01979	0.01265
	Lower Bound	0.014	0.00	0.014	0.450	0.013
	Upper Bound	0.025	0.05	0.024	0.541	0.028
Total Mean		0.0197±0.01041	0.0255±0.01310	0.0134±0.01226	0.2670±0.19723	0.0268±0.01526

As: Arsenic- Co: cobalt- Cd: cadmium- Pb: Plumbum- Hg: hydrargyrum.

Table 2. Results of one-way multivariate analysis of variance in 3 groups of canned products (acidic, semi-acidic and low-acidic)

Effect		Value	F	Hypothesis df	Error df	Sig.	Partial Eta squared
Intercept	Pillai's Trace	.963	200.367 ^b	5.000	39.000	.000	0.963
	Wilks' Lambda	.037	200.367 ^b	5.000	39.000	.000	0.963
	Hotelling's Trace	25.688	200.367 ^b	5.000	39.000	.000	0.963
	Roy's Largest Root	25.688	200.367 ^b	5.000	39.000	.000	0.963
sample	Pillai's Trace	1.048	8.802	10.000	80.000	.000	0.524

Wilks' Lambda	.126	14.167 ^b	10.000	78.000	.000	0.645
Hotelling's Trace	5.553	21.101	10.000	76.000	.000	0.735
Roy's Largest Root	5.292	42.338 ^c	5.000	40.000	.000	0.841

a. Design: Intercept + sample - b. Exact statistic- c. The statistic is an upper bound on F that yields a lower bound on the significance level.

Table 3. Comparison of the average concentration of heavy metals in 3 groups of canned products (High - acidic, Acidic and low-acidic)

Food Sample	mean± SD(mg/kg)				
	As	Co	Cd	Pb	Hg
High	0.0164±0.00851 ^a	0.0239±0.01276 ^a	0.0028±0.00491 ^a	0.0566±0.09725 ^a	0.0342±0.01705 ^b
Acidic	0.0232±0.01272 ^a	0.0255±0.01344 ^a	0.0195±0.01363 ^b	0.2776±0.05334 ^b	0.0251±0.01304 ^{ab}
Low	0.0194±0.00876 ^a	0.0273±0.01398 ^a	0.0188±0.00799 ^b	0.4955±0.09805 ^c	0.0204±0.01265 ^a

Dissimilar letters indicate significant differences (P<0.05) at columns. As: Arsenic- Co: cobalt- Cd: cadmium- Pb: Plumbum- Hg: hydrargyrum.

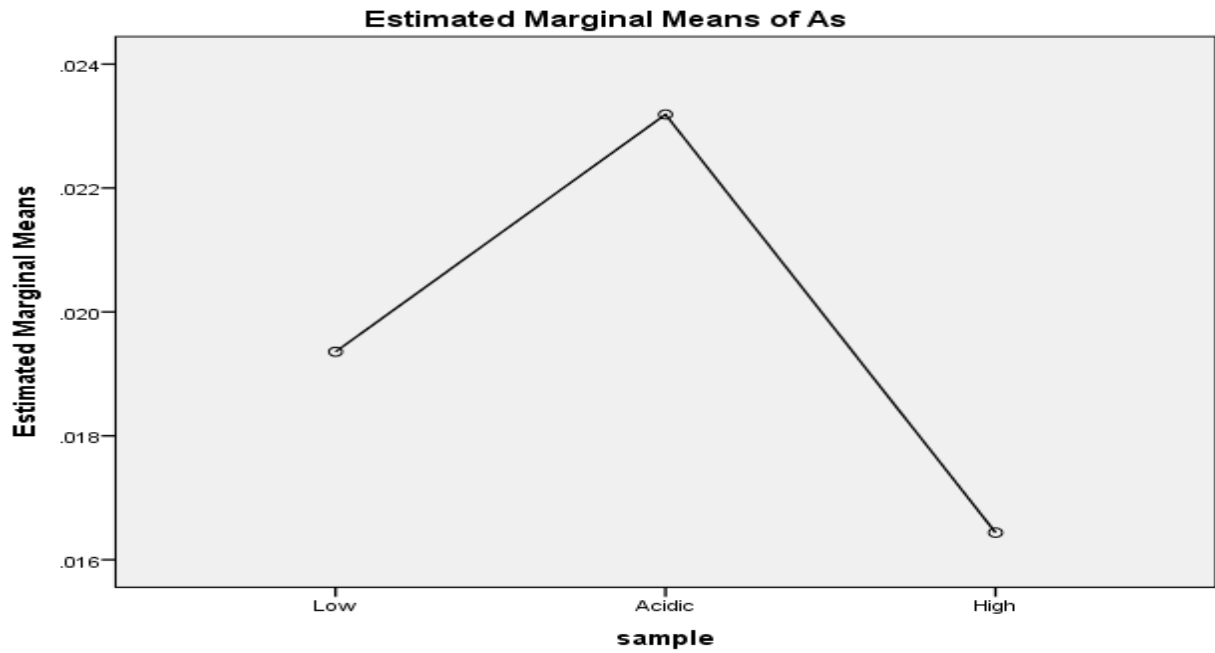


Fig. 1. The average concentration of Arsenic (As) metal in 3 groups of canned products (High -acidic, Acidic and low-acidic)

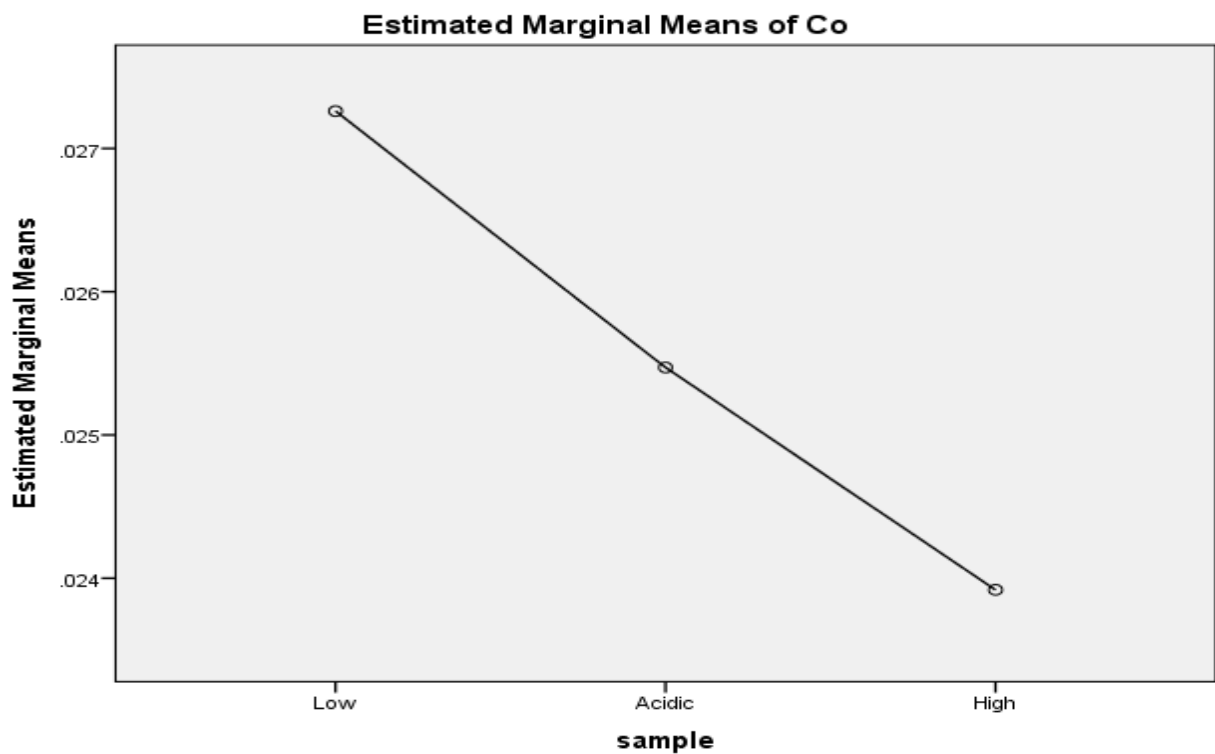


Fig. 2. The average concentration of Cobalt(Co) metal in 3 groups of canned products (High -acidic, Acidic and low-acidic)

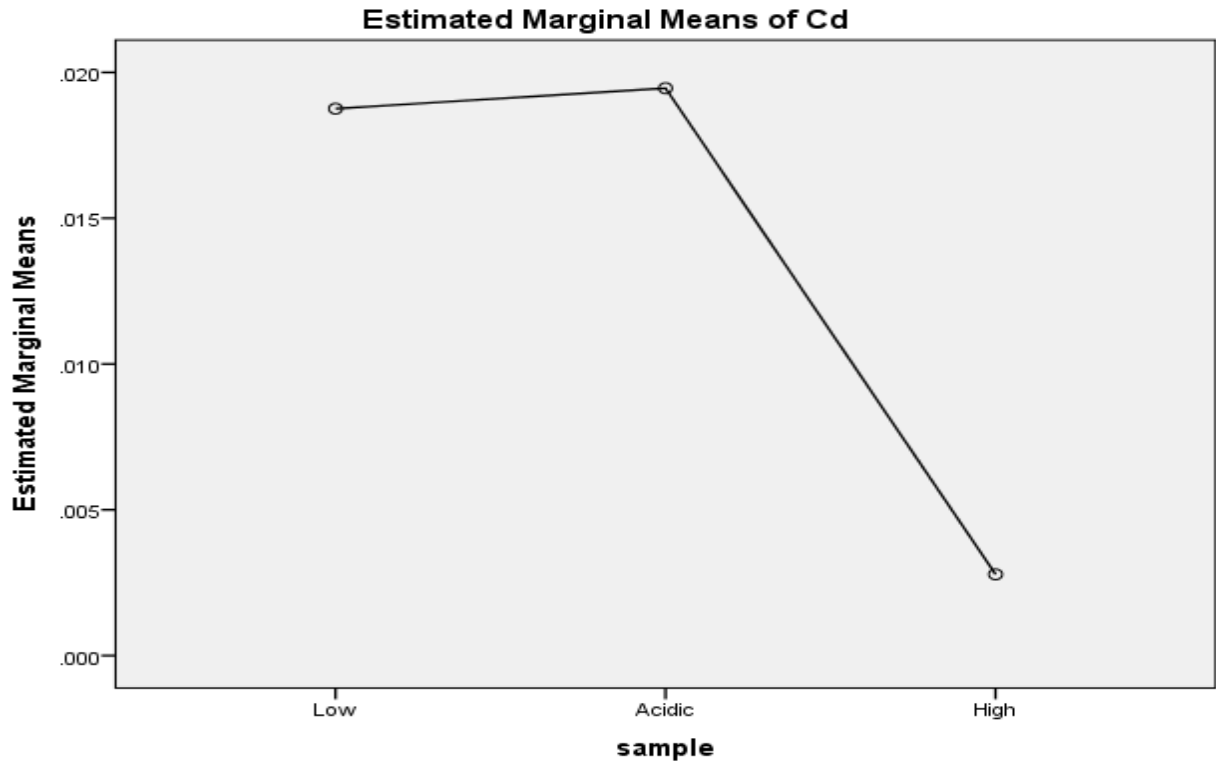


Fig. 3. the average concentration of Cadmium (Cd) metal in 3 groups of canned products (High -acidic, Acidic and low-acidic).

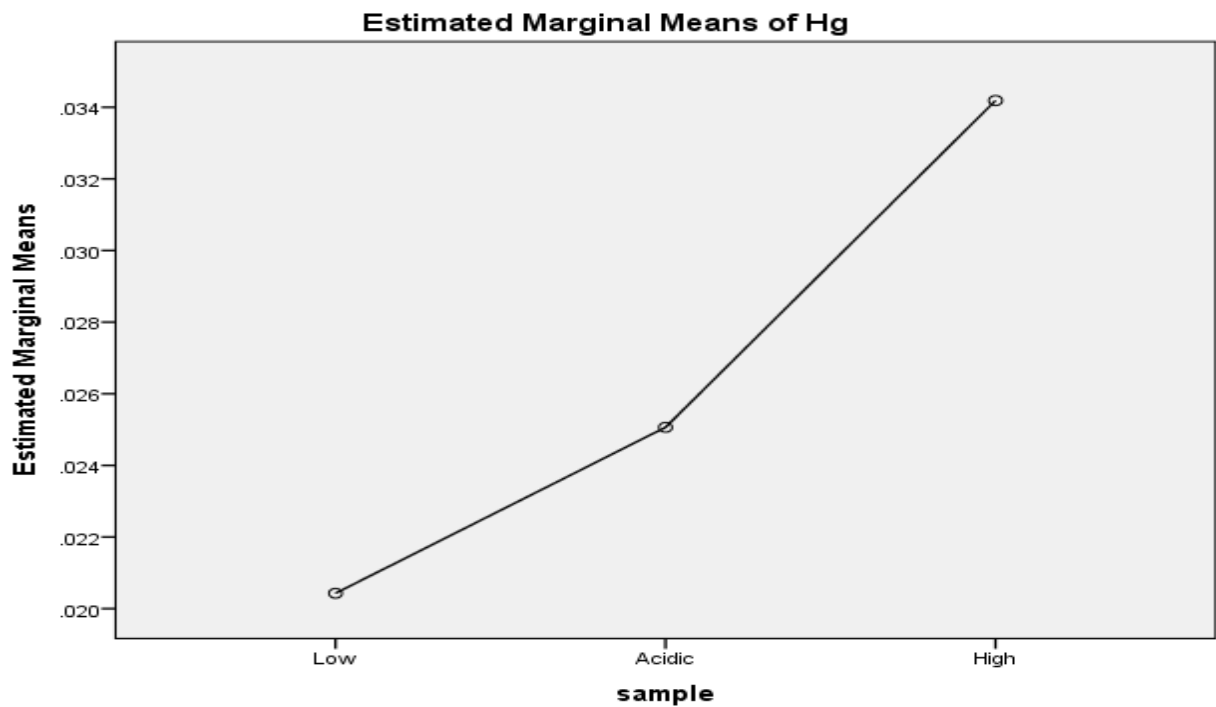


Fig. 4. The average concentration of mercury (Hg) metal in 3 groups of canned products (High -acidic, Acidic and low-acidic).

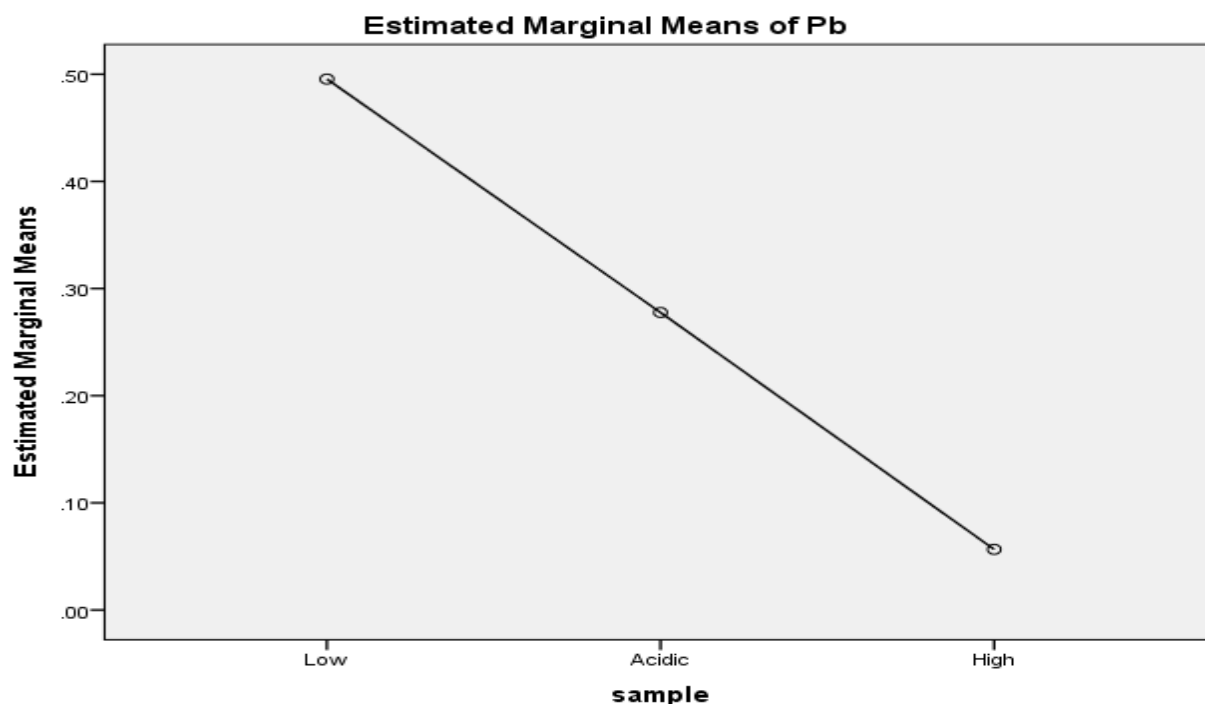


Fig.5. The average concentration of Lead (Pb) metal in 3 groups of canned products (High -acidic, Acidic and low-acidic).

4- Discussion

In this study, we investigated the concentration of heavy metals arsenic, cobalt, cadmium, mercury and lead in 3 groups of canned foods: strongly acidic (pickles and pickled cucumber), acidic (tomato paste, pear, pineapple) and low acid (tuna, corn and beans). The content of the metals investigated in the present study in canned food is in the range of 0.0232 ± 0.01272 - 0.0164 ± 0.00851 for arsenic metal, 0.0273 ± 0.01398 - 0.0255 ± 0.01344 for cobalt metal, 0.0195 ± 0.01363 - 0.0028 ± 0.00491 for cadmium metal, 0.4955 ± 0.09805 - 0.0566 ± 0.09725 for lead metal, 0.0342 ± 0.01705 - 0.0204 ± 0.01265 for mercury metal. Similar to our results that lead and cadmium had the highest and lowest amounts respectively in food samples, in the study of Al-Thagafi et al. (2014), in canned green bean

samples, it was found that the highest concentration of lead was 3.01 mg/kg and the lowest concentration in cadmium was 0.52 mg/kg, which is higher compared to our results [19]. Due to the lack of European Union regulations on limiting the level of arsenic concentration in food, it is difficult to discuss the results. However, due to the high toxicity of that element, many member countries of the European Union introduced a national standard. For example, the maximum permissible levels of arsenic in Poland are as follows: in meat of mammals and poultry it is 0.2 mg/kg, in liver and kidney it is 0.5, and in fish it is 4 mg/kg. The highest amount of arsenic in our research is 0.01272 ± 0.0232 , which is much lower than the international standards and some studies. For example, in a study conducted by Massadeh et al. (2017) on various food items, including canned paste and tomato sauce, the results obtained for canned tomato sauce (ketchup)

samples showed that the concentration of heavy metals (mg/kg) for arsenic, it varied from 4.54 to 1.38 with an average of 3.50 mg/kg [20]. In processed foods, the concentration of cobalt should not be more than 0.05 mg/kg [21], which our results are lower than this value. In a study conducted by Kowalska et al. (2020) on types of canned fish to check the concentration of heavy metals, the results indicated that the average concentration of cobalt metal in these samples was equal to 0.028 mg/kg, which results are similar to results of the present study. In some studies, the content of cobalt in canned fish from the United States of America was from 0.0 to 0.099 mg/kg, which is close to our data (from 0.012 to 0.053 mg/kg). Cobalt content in Iraqi meat products was observed with an average of 0.48 mg/kg in canned corn meat and an average of 0.02 mg/kg in canned chicken samples [1].

Cadmium is another toxic heavy metal that can be harmful to human health if consumed in excess over a long period of time through contaminated food or drink. During a long period of consumption, cadmium accumulates in the human body and may cause causing health problems such as kidney dysfunction, skeletal damage, and reproductive defects. It has been reported that according to the European Commission regulations, the maximum amount of lead for canned products such as canned tuna, beans, and corn is equal to 0.1 mg/kg and for other products it is 0.05 mg/kg. According to our results, the maximum amount of cadmium metal in the examined food samples is 0.01363 ± 0.0195 , which is much

lower than the international standard limit. In the study of Massadeh et al. (2018), cadmium was found from 0.51 to 0.48 with an average of 0.49 mg/kg in samples of canned tomato sauce, which is higher than the results obtained in this study. Also Hadiania et al. (2014) in the study who conducted on acidic products such as canned tomato paste and sausage stated that the content of these heavy metals, including cadmium, in all analyzed samples is lower than the national and international standards. From their investigations, they concluded that the consumption of canned tomato paste and tomato sauce in Tehran during the study period was safe according to Iran and Codex restrictions [20][22]. In this research, the highest concentration of lead was found in low-acid products (corn, tuna, beans), these results are in accordance with the study of Zabadi et al. (2018), in which the highest concentration of lead metal is in canned corn (low acid) [23]. Also, in a study conducted by Russo et al. (2013) on tuna fish, among heavy metals, lead had the highest concentration [24]. Ainerua et al. (2020) in a study they conducted on canned fish, beans and corn observed that the amount of lead metal in these products varied between 0 and 0.1 mg/kg. According to the regulations of the European Commission [25], the maximum amount of lead for low-acid canned products such as canned tuna, beans, and corn is 0.3-0.4 mg/kg, 0.2 mg/kg, and 0.3 mg/kg, respectively. According to these regulations, the maximum lead concentration obtained in our research is higher than the permissible limit [26]. Mercury is a naturally occurring metal element that can be present in food for natural

reasons. High levels can also occur due to environmental contamination by industrial or other uses of mercury. In a study conducted by Ebadi Fathabad et al. (2018) on canned fruits such as cherries, peaches, oranges, and pineapples to investigate the concentration of heavy metals, the concentration of this metal was much lower compared to the present study. Since most of the fruit and vegetable products are in the acid and strong acid group, and the highest amount of mercury in the samples tested in the present study were among these two categories, therefore, several factors such as exhaust gases, industrial waste and sewage affect the fruits and vegetables and other plants affect the level of heavy metals. One of the polluting elements of roadside factories is probably exhaust gases. Plants growing along roadsides and factories and other industrial environments are likely to be rich in heavy metals. In addition, fruits should not be harvested from contaminated environments, while their mineral composition changes according to their growing environment, water and soil. Depending on the environment of planting agricultural products (i.e. water, soil, air pollution), suitable equipment such as transport containers and storage containers can be used for the production of fruit juice and preserves [27].

5- Conclusion

Cadmium, lead, cobalt, arsenic, and mercury are harmful elements for the human body. Cadmium is toxic even in low concentrations for the human biological system. Heavy metal poisoning is known as one of the environmental

and food safety hazards. Lead affects humans and animals, but the effects of lead in children are very serious. Cadmium is a carcinogenic and toxic metal. According to the results obtained from the present study, the highest average concentration of arsenic and cadmium among canned products belonged to acidic products. The highest average concentration of lead metal was in low acid products. The highest amount of metal mercury belonged to strong acid products. Among the available metals, lead had the highest amount and cadmium had the lowest amount. All metals except lead had a concentration lower than the standard limit or were similar to other studies. Also, there was no significant difference between the concentration of metals in strong acid, acid, and low acid products. It seems that the use of suitable packaging, stainless steel containers, and the use of agricultural products that grow in the environment and soils with minimal heavy metal contamination can play a major role in reducing heavy metals in canned products.

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اندازه گیری و مقایسه ی غلظت فلزات سنگین (آرسنیک، کبالت، کادمیوم، سرب و جیوه) در کنسروهای مواد غذایی (اسیدی قوی، اسیدی، کم اسیدی) در شهر اهواز

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کلمات کلیدی:

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وجود فلزات سنگینی نظیر آرسنیک، کبالت، کادمیوم، سرب و جیوه در مواد غذایی کنسرو شده از نقطه نظر سمیت و ماهیت آنها از اهمیت بالایی برخوردار است و طیف وسیعی از مواد غذایی را پوشش می دهد. وجود این فلزات در فراورده های کنسروی گاهی اوقات به منبع غذا، نوع قوطی یا احتمال خوردگی بدنه داخلی قوطی استفاده شده نسبت داده می شود. لذا هدف ما از این مطالعه بررسی اندازه گیری و مقایسه ی غلظت فلزات سنگین در کنسروهای مواد غذایی (اسیدی قوی، اسیدی، کم اسیدی) بود. جهت تحلیل داده ها، از روش های آمار توصیفی، به منظور مقایسه میانگین و اختلاف بین داده ها از سنجش واریانس چند متغیره یکطرفه و از تست کولموگروف-اسمیرنوف برای اطمینان از نرمال بودن داده ها استفاده گردید و در صورت وجود اختلاف معنی دار بین داده ها، پس آزمون توکی برای تفکیک داده ها انجام گرفت. نتایج حاصل از این پژوهش نشان داد که میانگین غلظت فلزات سنگین به ترتیب سرب < جیوه < کبالت < آرسنیک < کادمیوم بود که از بین فلزات موجود سرب با میانگین کل 0.19723 ± 0.02670 میلی گرم بر کیلوگرم بیشترین مقدار و کادمیوم کمترین مقدار را با میانگین 0.0028 ± 0.0049 داشت. در مقایسه با استانداردهای جهانی و مطالعات دیگر همه فلزات به جز سرب پایینتر از حداکثر مقدار تعیین شده بود. اگرچه غلظت این فلزات در نمونه های غذایی کنسروی در حد قابل قبول بود اما توجه به عوامل افزایش حضور این فلزات در کنسروها جهت کنترل آن ها و رسیدن به یک فراورده باکیفیت امری ضروری می باشد.

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