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Investigation of heavy metal levels in canned tomato paste, olives, and pickled

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Canned pickled cucumbers, tomato paste, and olives are three commonly consumed products in Iranian households that may be a source of heavy metals for individuals due to the type of packaging. Therefore, in this study, samples of these three types of food were collected from the market and were measured for mineral and heavy metal content. The levels of metals including Cadmium, Copper, Arsenic, Iron, Lead, and Zinc were determined using an AAS- Flame and Graphite furnace. Moreover, the concentrations of Mercury and Tin were determined using the ICP-MS. In canned cucumber samples, only two metals, tin and lead, were detected. The levels of heavy metals in these three products were compared using statistical tests. A significant difference was observed in the amount of cadmium ($p < 0.05$). The average lead content in these three products was above the permissible limit. The levels of copper, arsenic, iron, cadmium, zinc, mercury, and tin in the canned food samples were found to be within the acceptable limits set by national and international regulatory authorities.

Keywords Atomic absorption spectrometry, Canned tomato paste, Heavy metals, Olives, Pickled cucumbers, Toxicity

Minerals and heavy metals are non-biodegradable substances that have the potential to accumulate in the environment and food[1–3]. These components can enter the human body through inhalation, oral ingestion, and skin exposure[4]. Minerals, such as sodium (Na), calcium (Ca), iron (Fe), magnesium (Mg), potassium (K), and phosphorus (P), play a crucial role in promoting human health[5]. On the other hand, heavy metals including mercury (Hg), tin (Sn), lead (Pb), arsenic (As), and cadmium (Cd) can pose significant health risks even at low concentrations[6,7]. These metals have been demonstrated to induce both acute and chronic poisoning in humans[8]. The metals mentioned induce oxidative stress within cells, leading to an increase in oxidative damage. This damage affects lipids, proteins, and DNA molecules, ultimately leading to cancer development[9]. Heavy metals originate from natural sources or as a result of anthropogenic activities[10,11]. Both of these processes contaminate the environment and food. Natural activities such as volcanic eruptions lead to the release of metals into soil and surface water[12]. Recently, there has been a significant increase in human exposure from anthropogenic activities[13,14]. The anthropogenic activities include industrial, mining, transport and agricultural activities, which are major sources of heavy metals[15,16]. One of the most important sources of human exposure to heavy metals is through food[17,18]. Food can become contaminated with heavy metals in several ways. One of the major causes of food contamination with heavy metals comes from the environment[17]. Other factors that cause food contamination with heavy metals include food processing and packaging[19,20]. One of the most common packaging and food technology is canning[21]. Heavy metals in canned food can migrate into the food contents of the cans[22,23]. Canned foods may contain heavy metal residues due to factors such as soldering (Sn, Pb), migration from metal packaging, and contamination during processing[24]. In a study, the levels of heavy metals in a variety of canned food products were measured. Lead levels ranged from 0.002 to 2.84 mg/kg and cadmium levels ranged from 0.03 to 0.65 mg/kg[25]. In another study, lead levels in canned foods were measured in the range of 1.40 to 1.76 mg/kg, above the established limit[26].

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Determining these compounds in foods plays an important role in increasing food safety[27]. The 2013 priority list of hazardous substances from the US Agency for Toxic Substances and Disease Registry (ATSDR) ranked As, Pb, Hg, and Cd as the first, second, third, and seventh most critical elements, respectively[28,29]. Canned tomatoes[30]olives[31]and pickles[32] can be mentioned among the most commonly used canned foods in Iranian households. Therefore, assessing the safety of these products is essential. This study aims to investigate the metals including lead, copper, arsenic, iron, tin, zinc, mercury, and cadmium in these products.

Materials and methods

Materials and sample collection

49 samples of canned tomatoes, olives, and pickled cucumbers from the 5 most popular brands were collected from stores in Tehran. All samples were transported to the chemistry laboratory. According to standard protocols, all samples were stored in a clean and dry place until digestion and analysis[33].

All chemicals used were of analytical reagent grade. Ultrapure water was used with a Milli-Q system (Millpore, Bedford, MA, USA). All plastic and glassware were cleaned by soaking 24 h in 10% (v/v) HNO3. After cleaning, all containers were rinsed three times with ultrapure water. Stock solutions of each metal (1000 mgL^{-1} in 10% HNO_3) were obtained from (Merck, Darmstadt, Germany) to prepare standard solutions for calibration curves and spiked to samples. The necessary working standards were prepared according to the linear range listed in Table 1 by diluting the stock standard with ultrapure water.

Sample Preparation and digestion

First, the contents of the sample cans were homogenized for more accurate assessment and to facilitate subsequent digestion. The next step was the digestion procedure, to break the matrix, one gram of each sample was weighed and placed into a 150 mL beaker. Slowly and in portions, 50 mL of a freshly prepared mixture of H_2O_2 (30%) and HNO_3 (65%) in a 1:1 ratio (v: v) was added to the beaker. The beakers were covered with watch glasses and heated on a hot plate until the solution became clear. The resulting clear solution was filtered into a flask using a vacuum system with a 0.45 µm pore size filter. To clean up and modify the solution, phosphoric acid (170 µL) was added to each tube and then shaken using a tube-shaker[6,20].

Instrumental analysis

The levels of metals, including Cu, Fe, and Zn were determined using flame atomic absorption spectroscopy and Cd, As, Pb, were determined using graphite furnace atomic absorption spectroscopy (Shimadzu AA-6300). And the concentrations of Hg and Sn were determined using the ICP-MS (The Agilent ICP-MS 7500-Ce).

The hollow cathode lamp of metal was operated at 10 mA with the spectral bandwidth of 1 nm. The selected wavelength in AAS methods was 324.7, 248.3 and 213.9 nm for Cu, Fe and Zn, and 228.8, 193.7 and 217.0 nm for Cd, As and Pb respectively.

Determination of each metal was performed using the calibration curve by the measurement device. The accuracy of the method was checked and confirmed by spiking the standard material to the sample and calculating the related recovery (Table 1). The validation parameters are shown in Table 1. For calculation Limit of detection (LOD) and limit of quantification (LOQ), blank samples are read ten times, and the average and standard deviation (SD) are calculated. LOD for the determination of analyte was calculated based on $C_{LOD}=3S_D/m$ (where C_{LOD}, S_D and m are the limit of detection, standard deviation of the blank, and slope of the calibration graph (, and LOQ based on 10 S_d/m. All analysis was performed in triplicates. The quality control (QC) and quality assurance (QA) analytical approach was conducted by evaluating prepared spiked standard solutions to the blank sample, on a standard protocol. The results for QC/QA analyses were presented in Table 1.

Metal	LOD, µg kg^{-1}	LOQ, µg kg^{-1}	LDR, µg kg^{-1}	R^2	RE	RR%
Cd	0.09	0.3	1.0–100	0.9997	y = 825.82x − 365.6	93.8
As	0.8	3.0	3.0–100	0.9994	y = 490.99x − 290	97.3
Pb	0.7	2.3	2.5–100	0.9981	y = 3396.7x + 1957.2	92.7
Hg	0.5	1.8	2.0–100	0.9999	y = 244.21x − 111.46	95.0
Sn	1.4	4.6	5.0–100	0.9977	y = 165.04x − 320.66	99.2
Metal	**LOD, mg kg^{-1}**	**LOQ, mg kg^{-1}**	**LDR, mg kg^{-1}**	R^2	**RE**	**RR%**
Cu	0.05	0.15	1.0–10	0.9987	y = 0.0314x + 0.0056	94.5
Fe	0.2	0.8	1.0–10	0.9983	y = 0.0166x + 0.0077	98.3
Zn	0.1	0.4	0.5–50	0.9964	y = 0.0088x − 0.0053	96.4

Table 1. The QA/QC results of analytical method for heavy metal concentrations. Note: LOD: limit of detections, R^2: R-squared, LOQ: limit of quantifications, RE: Regression equation, LDR: linear dynamic range, RR: Relative ratio.

Type of metals	Canned pickled cucumbers	Canned tomato paste	Canned olives
Lead	0.22 ± 0.08	0.19 ± 0.07	0.19 ± 0.04
Copper	ND	0.16 ± 0.1	ND
Arsenic	ND	0.0005 ± 0.0004	ND
Iron	ND	0.48 ± 0.4	ND
Tin	0.11 ± 0.05	0.4 ± 0.2	0.32 ± 0.17
Zinc	ND	0.0071 ± 0.007	ND
Mercury	ND	ND	ND
Cadmium	ND	0.008 ± 0.005	0.005 ± 0.001

Table 2. The level of metals in some canned food (mg/kg). ND: none detected.

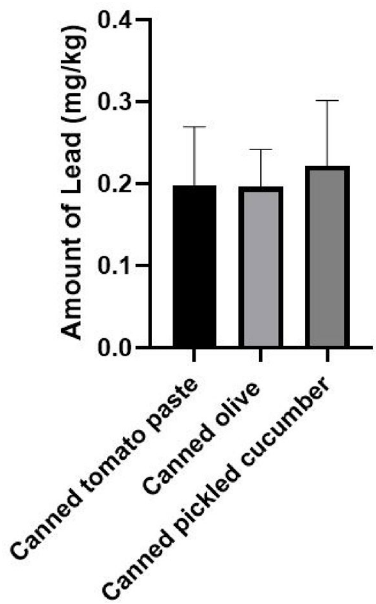

Fig. 1. Lead concentration in tomato, olives, and pickled cucumbers canned.

Results

This study investigated the levels of lead, copper, arsenic, iron, tin, zinc, mercury, and cadmium in canned pickled cucumbers, tomato paste, and olives. Table 2 shows the level of heavy metals and minerals tested. Two metals, tin and lead, were observed in all canned goods. All metals except mercury were detected in canned tomato paste samples. Mercury was not detected in all tomato paste, pickled cucumber, and olive samples. Lead was observed in all samples, with the highest levels observed in canned pickle samples.

Statistical analysis was also performed and significant differences between groups were calculated. Data distribution was checked with the Shapiro-Wilk test, and because the data did not have a normal distribution, Kruskal-Wallis non-parametric tests were used. No significant difference ($P > 0.05$) was observed between the lead amount in the three types of canned food (Fig. 1).

However, a significant difference was observed between the levels of cadmium between canned foods ($P \leq 0.05$). The cadmium in tomato paste was significantly higher than canned olives and pickles (Fig. 2). Furthermore, the Kruskal-Wallis test showed no significant difference between canned pickled cucumbers, tomato paste, and olives regarding other metals levels ($P > 0.05$).

Discussion

The current research investigated the levels of various heavy metals, including Cd, Cu, As, Fe, Pb, Zn, Hg, and Sn, present in commonly consumed canned food products such as pickled cucumbers, tomato paste, and olives. Food contact with packaging materials can be a source of exposure to chemical compounds[34]. The type of these chemical compounds depends on the structure and materials used in the packaging. In present study, all metals except iron and lead were not detected in canned pickle cucumbers samples (Table 2). According to the present study, the average and standard division of lead in canned pickled cucumbers were found to be 0.22 ± 0.08 mg/kg. According to the Codex standard, the permissible limit of lead in canned products is 0.1 mg/kg[35]. Therefore, the results in this study were above the limit established of lead in canned products. In research conducted by Jannat et al. (2021), fifty samples of pickled cucumbers were bought and evaluated by the polarography method. They

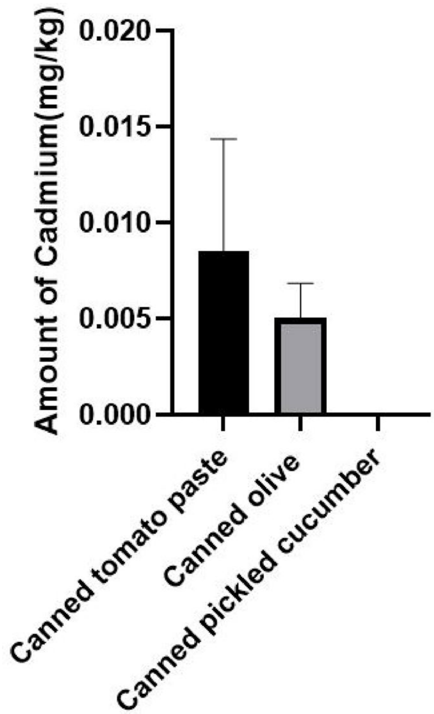

Fig. 2. Cadmium concentration in tomato, olives, and pickled cucumbers canned.

reported the mean level of cadmium and lead was slightly above the limit established by Codex Alimentarius Commission (CAC). The amount of cadmium was higher than in the present study, but the amount of lead in the study of Jannet et al. was lower than in the present study[36]. Furthermore, the previous study conducted by Afrooz et al. (2024), showed that pickled cucumbers had the highest mercury levels among all acidic food products[35]. Unlike the present study, mercury was not detected in canned pickle samples. One of the significant differences between the levels of heavy metals in pickles is the type of water used to irrigate the cucumbers[37]. Experimentally, cucumbers were irrigated with drinking water and wastewater. Copper, cadmium, lead, nickel and chromium were measured in the resulting pickled cucumbers. The levels of these metals were ND in the pickled cucumbers of the first group, but measurable levels were detected in the second group, where the cucumbers used in the pickled cucumbers were irrigated with wastewater[37].

Another canned food product examined in this study was canned tomato paste. In the present study, the amount of cadmium detected was 0.008 ± 0.005 mg/kg. According to the Codex standard, the permissible limit of cadmium for some plants, including fruiting vegetables, is 0.05 mg/kg. Therefore, the cadmium level was below the permissible limit. A study by Raptopoulou et al. (2012) used electrothermal atomic absorption spectrometry to analyze several heavy metals present in canned tomato paste. The results showed that the concentration of Cd exceeded the maximum permissible level of 0.05 mg/kg[38]. Cadmium metal is a toxic metal that leads to carcinogenesis, increased blood pressure, and kidney damage[39,40]. Also, a study in 2016 reported concentrations of Cd and Fe in tomato samples exceeded the legal limits[41]. Arsenic was detected in canned tomato paste samples. This metal is a toxic and carcinogenic compound[42]. However, trace amounts were detected in canned tomato paste. The study conducted in Ghana analyzed canned tomato paste samples to detect the levels of heavy metals including Fe, Zn, Hg, Cd, and Pb by using flame atomic absorption spectrophotometry. Unlike the current study, cadmium was below the LOD, but mercury was detected in canned tomato samples[43]. The present study showed that the lead content in canned tomato paste was 0.19 ± 0.07 mg/kg that this amount is more than acceptable. Male infertility, damage to the nervous system, decreased learning in children, and anemia are some of the toxic effects of exposure to lead[39]. The result of the lead level was contrary to the findings of the study by Hadiani et al. (2014). They analyzed samples of canned purchased tomato paste. Levels of lead and all metals were below national and international standards[30]. Additionally, another study investigated the concentration of heavy metals in canned tomato paste in Nigeria. The authors of this study reported the lead content in all samples, ND[44].

Reports indicate the presence of tin in various types of canned foods[45]. A thin layer of tin is usually added to cans to prevent corrosion[46]. The acceptable limit of tin in canned foods is 200 mg/kg according to European Union regulations, and 150 to 250 mg/kg according to Codex Alimentarius standards[47]. In our study, the amount of tin in canned tomato paste was 0.41 ± 0.21 mg/kg, which is lower than the standards level. Similar results to this research were observed in many studies. Morte et al. (2012) measured tin levels in canned tomato sauce storage at room temperature (20.0 ± 1.8 °C) for 0 to 150 days. The tin content increased by 43–91% after 150 days, but it remained well below the maximum level allowed of 250 mg/kg[48]. Tin determination in canned foods by flame atomic absorption spectrometry (FAAS) showed the amount of tin in tomato pastes and black olives was non-detectable[49].

The level of metals in the canned olive product was also measured. In our study, we found that the average and standard deviation of lead levels in canned olives was 0.19 ± 0.04 mg/kg. Therefore, the lead content in canned olives was higher than the permissible limit. Similarly, Shariatifar et al. (2022), conducted a study on lead levels in both industrial and traditional canned olive samples from various regions in Iran. They utilized inductively coupled plasma optical emission spectrometry (ICP-OES) for their analysis. The industrial samples showed an average lead concentration of 0.26 mg/kg[50]. Also, in the Karatasli study in Turkey, the lead level in olive samples was measured at 4.55 mg/kg, which was higher than in the present study[51]. Our study showed the level of cadmium in canned olives was 0.005 ± 0.001 mg/kg, which is below the permissible amount set by the EU.

Conclusion

This study was conducted to investigate the presence of minerals and heavy metals including Cd, Cu, As, Fe, Pb, Zn, Hg and Sn in canned pickles cucumbers, tomato paste and canned olives. Only two metals, tin and lead, were detected in canned pickles. The amount of metals in canned tomato paste was higher than other canned products. Mercury was not detected in all samples. All the determined levels except lead were within the limits declared by Codex Alimentarius and the European Union. Therefore, continuous and ongoing monitoring is recommended to determine the amount of heavy metals, especially lead. Furthermore, the origin of heavy metals from packaged materials may be from other components of food ingredients such as salt and spices, which is recommended for future research.

Data availability

The datasets used and/or analysed during the current study available from the corresponding author on reasonable request.

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Author contributions

P.SG. and N.I. wrote the main manuscript text and A.A. and S.M prepared figures and tests. N.Y and P.S reviewed and edited the manuscript.

Declarations

Competing interests

The authors declare no competing interests.

Additional information

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