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The Level of Some Heavy Metals in Canned Fruit Juices Collected from Some Benghazi City Markets

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Abstract:
Fruit juices becoming an essential part of the modern diet in many communities. Fruit juices contain nutrients as minerals, trace elements, vitamins and phytochemicals antioxidant. Fruit juices are nourishing beverages, in a healthy diet can play a major part because a variety of nutrients found naturally in fruits, also offer good taste in natural concentrations or processed forms. Fruit juices are available in any place in the world are available in bottles, cans, laminated paper packs, pouches, cups and almost every other form of packaging in diet of most people, irrespective of age included significantly thus, it contributes to good health.
This study explored the heavy metals contamination of 15 samples of canned fruit juices collected from Benghazi markets (Libya). The amount of heavy metals was determined by the atomic absorption spectrophotometer (AAS).
Heavy metals such as (Sn, Cd, Fe, Pb, Zn, Cu, Mn and Cr) contents in the collected samples for eight different types (mango, peach, apple, grape, pineapple, orange, banana and strawberry, pineapple with orange and peach) were found at different levels. The Sn was the highest average concentration (0.8 – 3.49 mg/L); followed by Fe (0.709 – 2.307 mg/L), then Cu (0.099 – 0.513 mg/L), Mn, (0.01 – 0.102 mg/L), Pb (0.005 – 0.012 mg/L), Zn (0.003 – 0.064 mg/L) finally, the concentration level of Cd and pb were below detection limit (BDL) which was 0.005 mg/L.The results showed that there was a significant statistical difference in the concentration level of Sn, Fe, Zn, and Cu in the samples compared to Libyan allowed limits for each one (P=0.000 for each). Also, there was a significant statistical difference in the concentration level of Cd, Pb, Mn, and Cr in the samples compared to WHO allowed limits for each one (P=0.000 for each).

Key Word: *Fruit juices; Heavy metals; atomic absorption spectrophotometer; permissible limit; Benghazi.*

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I. Introduction

Heavy metals are potential environmental contaminants with the capability of causing human health problems if present to excess in the food we eat.[1] several cases of human disease, disorders, malfunction and malformation of organs due to metal toxicity have been reported.[2] Heavy metals composition of food is of interest because of their essential or toxic nature. For example, iron, zinc, copper, chromium, cobalt, and manganese are essential, while lead, cadmium, nickel, and mercury are toxic at certain levels.[3] Metals are widely found in our environment, and other elements can be naturally present in food or can enter as a result of human activities such as industrial and agricultural processes. The metals or particular concern in relation to harmful effects on health are mercury, lead, cadmium, tin and arsenic. Canned food is subjected to heavy metal contamination during the canning process. The ingestion of food is an obvious means of exposure to metals, not only because many metals are natural components of food stuffs, but also environmental contamination and contamination during processing. Toxicological and environmental studies have prompted interest in the determination of toxic elements in food.[4] Heavy metals are found naturally in the ground and their quantities vary in different regions, due to the different properties of each mineral and the effect of environmental factors on it. There are many metals in the natural environment, some heavy metals have vital functions in humans but not all metals are necessary because they do not have a defined biochemical role.[5]Heavy metals enter the environment in a natural and anthropogenic way through many sources such as: natural sewage effluent, pest or disease control agents that use it to plants, air pollution fallout, and can enter the human body through food, water, air that is widely distributed in all environmental components. The toxicity of heavy metals has two main aspects: the fact thatthey have no known metabolic function. But when present in the body they disrupt normal cellular processes, leading to toxicity in a number of organs, also the potential, particularly of the so-called heavy metals mercury and lead, to accumulate in biological tissues, a process known as bioaccumulation. This occurs because the metal, once taken up into the body, is stored in particular organs.[6] Fruit and fruit juices are a very important part of the modern diet in every society and have become an important component of the daily diet around the world. It is widely known that fruits are a good source of vitamin C, carotenoids and minerals (especially Mg and K) all of these compounds have a protective effect against diseases.[7] Depending on the water content of the juice, fruit juices can be divided into concentrated fruit juice, fruit powder juice, and fruit nectar.[8] Fruit juices are important for a human diet since they contain different nutrients, vitamins, and especially minerals.[9]Major and minor elements are considered as essential nutrients in food. The routine monitoring of the levels of these elements in fruit juices is a common quality control process.[10, 11] On the other hand, the quality of fruit products is diminishing with increasing concentrations of toxic compounds, environmental pollutants (especially pesticides), polychlorinated bisphenols (PCB's), and heavy metals, especially lead and cadmium. Some of the compounds in the juices have been identified as mutagenic or carcinogenic.[12,13] Taking into account all these cases, as well as the widespread consumption of fruit juices, it is very important to evaluate industrial fruit juices for consumer safety.[14, 15] Toxic heavy metals are the most dangerous form of contaminant when consumed in excess over a long period through food or water.[16] The study was conducted to determine the levels of trace minerals and essential minerals in selected fruit juices (Zn, Cu, Fe, Mn, Na, Cd, Pb, Cr) in Mina, Nigeria, using atomic absorption spectrometry (AAS) and flame torch meter. The trace elements were within the permissible limit recommended by the World Health Organization.[17]Anwar et al.[18] conducted a study on heavy metals in fruit juices in different fillers. The study aims to identify toxic metals such as (Pb, Cd) in various fruit juices and their impact on human health. Conducted by Khan et al.[19] This study is to analyze and detect heavy metals present in fruit juices in the markets of Lahore, Pakistan, using (AAS). The results showed that the levels of copper and cadmium were below the permissible limit and that the concentration of nickel 24% in the samples was above the permissible limit and may lead to adverse effects on humans. Ali et al.[20] conducted a study on lead and cadmium levels in some peach juice samples collected from supermarkets in El-Koums city in Libya., lead levels were below the maximum permissible limits and Cd was higher in 4 samples.

II. Materials and Methods

Analytical grade HNO_3 Merck 65% and deionized water were used throughout this research work. Standard stock solutions (1000 ppm) of respective metal ions, which were obtain from Merck. The laboratory glass wares were washed with detergent and rinsed with distilled water dried in oven and stored in a place which was free from dust and fumes. Watman filter paper 40 was used filter digested juice samples.

Sample Collection: Total 15 commercial samples of canned fruit juices (imported from many countries, about 15 companies) including (Mango, Peach, Apple, Grape, Pineapple, Orange, Banana and Strawberry, Pineapple with Orange and Peach) were collected from different market locations in Benghazi city Libya.

Digestion of Sample: The juices were digested by weighing 1 ml of sample into evaporating dish and 10 ml of Conc. nitric acid was added until all volatile or readily combustible matter has been removed, allow it cool and then add 5 ml hydrogen peroxide and heat for 5 minute and transfer the solution to the volumetric flask and then diluted up to the mark with deionized water. Prepare a sample blank solution by following the same procedure as described for the sample. Use the same quantities of reagents including deionized water for both sample and blank. Subject both sample and sample blank to identical treatment (even the length of time kept on heat etc.)

Instrumentation: In this study atomic absorption for the samples was determinedby the used atomic absorption device type (932 Plus - Atomic Absorption Spectrophotometer equipped with a deuterium lamp for background correction). Instrument was calibrated by blank solution and finally analyzed metals content in fruit juice.

Statistical Analyses: Data analyses were performed using Statistical Package for the Social Sciences (SPSS) version 20 values were expressed as mean appropriate test statistics (ANOVA) was done to determine heavy metals content in fruit juices which were pack in different packing.

III. Results and discussion

Fifteen samples of canned fruit juices were evaluated for the assessment of selected eight heavy metals which included Sn, Cd, Fe, Pb, Zn, Cu, Mn, and Cr. The (mean ± standard deviation) concentration of each examined metal for each sample are presented in Table (1) and Table (2). The results showed that the average concentration level of Sn ranged from 0.795 to 3.493 (mg/l) in 15 samples, and the average concentration level of Cd was below the detection limit (BDL) in all samples (BDL for Cd is 0.005 ppm). In all samples, the average concentration level of the Fe ranged from 0.709 to 2.306 mg/l. While the average concentration level of the Pb was below the detection limit (BDL) in most samples (BDL for Pb is 0.005 ppm) however, the average concentration level of the Pb ranged from 0.006 to 0.012 mg/l in the rest of the samples. The average concentration level of the Zn was below the detection limit (BDL) in most samples (BDL for Zn is 0.003 ppm); however, the average concentration level of Zn varied from 0.019 to 0.064 mg/l in the rest of the samples. Whereas, the average of metal concentrations of Cu was 0.099 – 0.513 mg/l in all samples, and the average concentration level of Mn ranged from 0.01 to 0.102 (mg/l) in 15 samples. While the average concentration level of Cr was below the detection limit (BDL) in all samples (BDL for Cr is 0.01 ppm).

Table (1): Concentration of some heavy metals (mg/l or ppm) in canned fruit juice samples.

Samples	Sn	Cd	Fe	Pb
1	2.628±0.1	BDL	1.108±0.011	0.009
2	1.396±0.02	BDL	1.351±0.005	BDL
3	2.614±0.004	BDL	0.865±0.051	BDL
4	2.819±0.006	BDL	1.069±0.019	0.010±0.001
5	2.585±0.02	BDL	0.797±0.009	0.008
6	3.077±0.03	BDL	0.857±0.003	BDL
7	3.493±0.01	BDL	1.930±0.004	BDL
8	1.305±0.004	BDL	1.358±0.037	0.006±0.001
9	2.461±0.009	BDL	0.709±0.003	0.012±0.001
10	0.804±0.004	BDL	1.111±0.007	0.008±0.001
11	1.013±0.003	BDL	1.953±0.018	BDL
12	1.886±0.004	BDL	0.963±0.053	BDL
13	0.985±0.02	BDL	2.306±0.006	BDL
14	2.086±0.01	BDL	1.567±0.002	BDL
15	0.795±0.004	BDL	1.028±0.006	BDL

*** (BDL) Below detection limit:** for (Cd) is 0.005 ppm, (Pb) is 0.005ppm, (Zn) is 0.003 ppm and (Cr) is 0.01 ppm.

Table (2): Concentration of some heavy metals (mg/l or ppm) in canned fruit juice samples.

Samples	Zn	Cu	Mn	Cr
1	0.049±0.001	0.333±0.009	0.026±0.001	BDL
2	BDL	0.099±0.001	0.011±0.001	BDL
3	0.024±0.0001	0.321±0.006	0.036±0.003	BDL
4	0.019±0.0001	0.221±0.006	0.062±0.003	BDL
5	BDL	0.424±0.006	0.051±0.003	BDL
6	BDL	0.513±0.004	0.069±0.001	BDL
7	BDL	0.247±0.011	0.102±0.002	BDL
8	BDL	0.227±0.006	0.099±0.001	BDL
9	BDL	0.301±0.006	0.010±0.002	BDL
10	BDL	0.502±0.004	0.081±0.001	BDL

11	0.064±0.002	0.177±0.004	0.057±0.002	BDL
12	BDL	0.163±0.004	0.038±0.002	BDL
13	BDL	0.499±0.008	0.042±0.003	BDL
14	BDL	0.313±0.005	0.024±0.004	BDL
15	BDL	0.493±0.001	0.075±0.004	BDL

(BDL) Below detection limit: for (Cd) is 0.005 ppm, (Pb) is 0.005 ppm ,(Zn) is 0.003 ppm and (Cr) is 0.01 ppm.

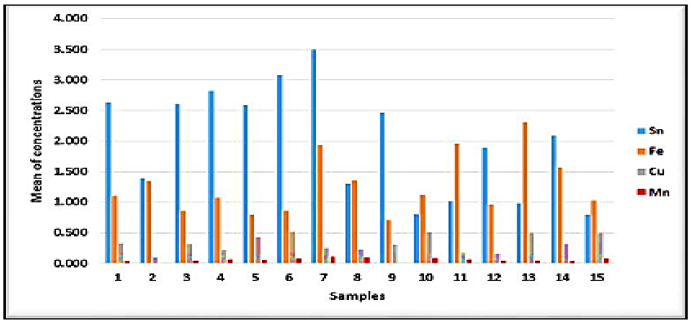

Figure (1): Average concentrations level of Sn, Fe, Cu, and Mn in 15 samples.

Average concentrationlevels of Sn, Fe, Cu, and Mn for 15 samples of canned fruit juice samples are shown in Figure (1). The Sn, Fe, Cu, and Mn were the high average concentration levels of heavy metals found in all samples. The Sn was the highest average concentration; followed by Fe, then Cu, finally the Mn. The highest average concentration level of Sn was found in sample 7, while the highest average concentration level of Fe was found in sample 13, and the highest average concentration level of Cu was found in sample 6. The highest average concentration level of Mn was found in sample 7.

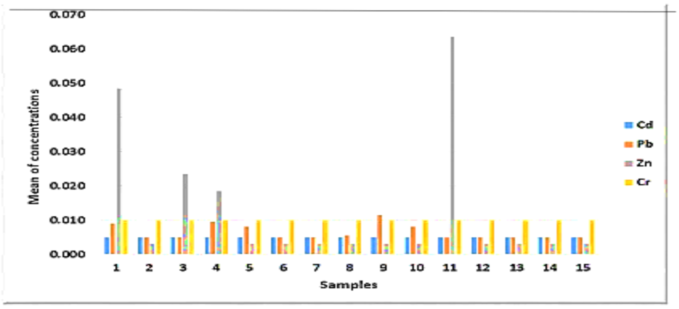

Figure (2): Average concentrations of Cd, Pb, Zn, and Cr in 15 samples.

Average concentrationlevels of Cd, Pb, Zn, and Cr for 15 samples of canned fruit juice samples are shown in Figure (2). The Cd, Pb, Zn, and Cr were the low average concentration levels of heavy metals found in all samples. However, the Zn was the highest average concentration; followed by Cr, then Pb, finally the Cd. The highest average concentration level of Zn was found in sample 11; while all samples had the same average concentration level of Cr, and the highest average concentration level of Pb was found in sample 9. Whereas, all samples had the same average concentration level of Cd.

Table (3): Concentration of some heavy metals (mg/l or ppm) in canned fruit juice.

Some of heavy metals	Mean ± SD	Range (min-max)	P value*
Sn	1.996 ± 0.89	0.8 – 3.49	0.000
Cd	BDL	BDL	0.96
Fe	1.264 ± 0.47	0.709 – 2.307	0.000

Pb	0.006 ± 0.002	0.005 – 0.012	0.01
Zn	0.0124 ± 0.018	0.003 – 0.064	0.023
Cu	0.322 ± 0.13	0.099 – 0.513	0.000
Mn	0.052 ± 0.029	0.01 – 0.102	0.000
Cr	BDL	BDL	0.96

(BDL) Below detection limit: BDL for (Cd) is 0.005 ppm and (Cr) is 0.01 ppm
* P<0.05 is statistically significant

The (mean ± standard deviation) concentration of each examined metal in canned fruit juice samples are presented in Table (3). The results showed that the concentration level of Sn varied from 0.8 – 3.49 with an average value of 1.996 (mg/l); there was a significant statistical difference in concentration among the 15 samples of brands (P= 0.000). The concentration level of Cd was below detection limit (BDL) which was 0.005 ppm; there was not a significant statistical difference in concentration among the 15 samples of brands (P= 0.96). The Fe content ranged from 0.709 – 2.307 with an average value of 1.264 (mg/l); there was a significant statistical difference in concentration among the 15 samples of brands (P= 0.000), and the range of metal concentrations of Pb was 0.005 – 0.012 with the average value of 0.006 (mg/l); there was a significant statistical difference in concentration among the 15 samples of brands (P= 0.01). The concentration level of Zn varied from 0.003 – 0.064 with an average value of 0.0124 (mg/l); there was a significant statistical difference in concentration among the 15 samples of brands (P= 0.023). The range of metal concentrations of Cu was 0.099 – 0.513 with the average value of 0.322 (mg/l); there was a significant statistical difference in concentration among the 15 samples of brands (P= 0.000). The Mn content ranged from 0.01 – 0.102 with an average value of 0.052 (mg/l); there was a significant statistical difference in concentration among the 15 samples of brands (P= 0.000), and the concentration level of Cr was below the detection limit (BDL) which was 0.01 ppm; there was not a significant statistical difference in concentration among the 15 samples of brands (P= 0.96).

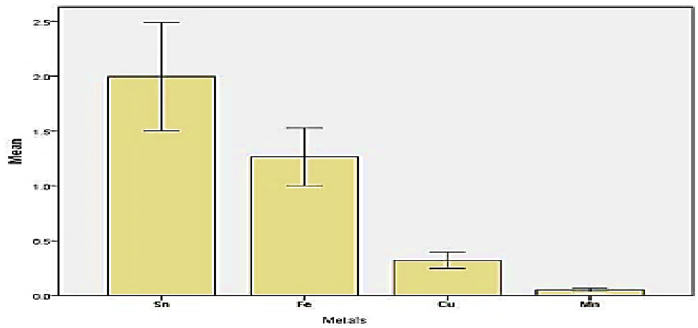

Figure (3): Average concentrations of Sn, Fe, Cu, and Mn in canned fruit juice samples.

Average concentrations of Sn, Fe, Cu, and Mn in canned fruit juice samples are shown in Figure (3). The Sn, Fe, Cu, and Mn were the high concentration levels of heavy metals found in canned fruit juice samples. The Sn was the highest concentration with a mean of 1.996 mg/l; followed by Fe with a mean of 1.264 mg/l, then Cu with a mean of 0.322 mg/l, and Mn with a mean of 0.052 mg/l.

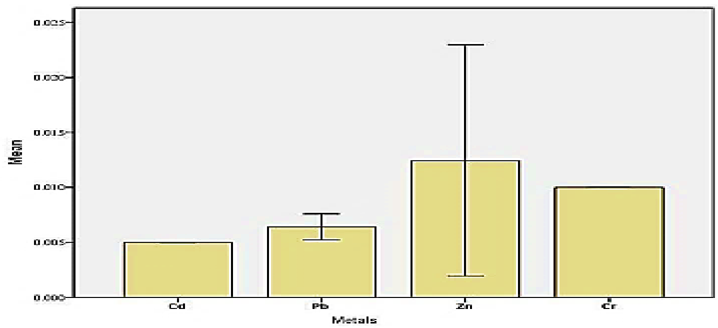

Figure (4): Average concentrations of Cd, Pb, Zn, and Cr in canned fruit juice samples.

Average concentrations of Cd, Pb, Zn, and Cr in canned fruit juice samples are shown in Figure (4). The Cd, Pb, Zn, and Cr were the low concentration levels of heavy metals found in canned fruit juice samples. However, the Zn was the highest concentration with a mean of 0.0124 mg/l; followed by Cr with a mean of 0.01 mg/l, then Pb with a mean of 0.006 mg/l, and Cd with a mean of 0.005 mg/l.

Table (4): Compare the concentration of some heavy metals (mg/l or ppm) in canned fruit juice to Libyan/WHO allowed limits.

Some of heavy metals	Mean (mg/L)	Libyan/WHO allowed limits mg/L	P value*
Sn	1.996	0.1	0.000
Cd	0.005	0.003	0.000
Fe	1.264	0.015	0.000
Pb	0.006	0.01	0.000
Zn	0.0124	0.005	0.000
Cu	0.322	0.005	0.000
Mn	0.052	0.4	0.000
Cr	0.01	0.05	0.000

* $P<0.05$ is statistically significant

Table 4. The results showed that there was a significant statistical difference in the concentration level of Sn, Fe, Zn, and Cu in the samples compared to Libyan allowed limits for each one (P=0.000 for each). Also, there was a significant statistical difference in the concentration level of Cd, Pb, Mn, and Cr in the samples compared to WHO allowed limits for each one (P=0.000 for each). The chemistry of inorganic tin has been reviewed elsewhere [21] but in order to understand the behavior of tin in different food matrices, a basic knowledge of some of its chemical properties is desirable. In addition to the metal, tin can exist in two different chemical oxidation states, namely divalent tin (Sn^{2+}, tin (II) or stannous tin) and tetravalent tin (Sn^{4+}, tin (IV) or stannic tin). Dissolution of metallic tin from the inside of a can body into the food content will result in it being present in the divalent form. The precise chemical nature of the divalent tin in a canned food product is important, as it is likely to have a major influence on its ability to cause an acute toxicological response. However, the exact species present and their distribution will be different in each individual food type, since a number of factors have a role to play. One of the main considerations affecting the species present is pH. Therefore, in food stuff tin may become fixed onto solid particles (fibers) or onto pectins. Tin fixed in this way is not readily released by treatment with hydrochloric acid. [22] Similarly, the attachment between tin and solid food is difficult to break using artificial gastric juices and intestinal enzymes are not involved in the solubilisation of tin adhered to proteins. However, alkaline intestinal juices cause the release of 90% of tin adsorbed onto the solid fraction of food stuffs. [23] It is therefore apparent that the bioavailability and potential toxicity of tin in food will depend not only on the quantity ingested but also on numerous other factors, e.g. pH, valence, extent of complexation or adsorption, solubility etc. All of these factors change as the food moves from the can, to contact saliva, gastric juices or intestinal fluids. The tin concentration levels involved are below that of any laboratory technique for speciation analysis and so experimental confirmation of the exact species present is extremely difficult. The highest average concentration level recorded for iron reflected the normal composition expected for plant derived products. [24] Iron is a vital mineral in the human body. It is necessary in the prevention of anaemia. Iron overload, however, is deadly, as it could be a factor in a range of diseases including diabetes, heart diseases, arthritis, Alzheimer's disease, and cancer and a host of other conditions such as hair loss, hypothyroidism, hyper activebehaviours, and chronic infections. On Turkish canned fruit juices, Williams AB et al.[25] detected and measured cadmium and zinc concentration levels in all 104 samples analyzed and attributed the presence of metals in foods including drinks either as natural components of food products or as a result of human activities such as agriculture, emissions from industries, exhaust fumes from cars, or contamination during the manufacturing process as well as food contamination occurring as a result of the components of raw materials and water used. Cadmium, which is one of the most toxic elements, was determined in all the samples, recording average concentrations of 0.032 mg/L. The highest concentration of cadmium recorded was 0.044 mg/L, about nine times the United States Environmental Protection Agency

Maximum Residue limit of 0.005 mg/L. Akan et al. [26] reported cadmium and zinc levels as 0.004–0.060 mg/L and 0.063–3.39 mg/L in a total of 66 fruit juice samples examined in Poland. Lead is toxic to man and other living organisms. Its toxicity is due its bioaccumulation potential in biologic tissues. Lead also has an effect on the brain and the intellectual development in young children. Long-term exposure in both children and adults can cause damage to the kidneys and reproductive and immune systems in addition to negative effects on the nervous system. The range of lead recorded in the soft drink samples was between 0.024 and 0.304 mg/L, and a mean concentration value of 0.154 mg/L. The respective concentrations of lead in the various fruit bases (i.e., pineapple, apple, and orange) .The results from this study are contrary to a similar research conducted by Tufuor et al.,[27] when they investigated the presence of various heavy metal such as lead, cadmium, iron, manganese, copper, nickel, chromium, zinc in canned fruits juice. Only manganese, zinc and iron had values that were within the statutory safe limits. Every other metals including the highly toxic lead (0.06-1.93ppm) and Cd (0.002-0.49ppm) had levels that were beyond the permissible limits. In another similar investigative analysis where the presence of selected heavy metals were determined in juice and carbonated drinks by Magdas et al,[28] relatively high concentrations were recorded for lead and manganese while those of copper, iron, chromium, zinc, cadmium and cobalt were within the permissible limit. Manganese which ranged 0.00–2.70 ± 0.08 mg/L in this study is essential metal and a potent neurotoxin. Manganese accumulates in mitochondria and acts as a major source of superoxide, which can oxidize Mn^{2+} to the powerful oxidizing agents Mn^{3+}. Oxidation of important cell components by Mn^{3+} has been reported as the cause of toxic effect of manganese. Meanwhile, in present study, trace metals (Pb, Cr, and Mn) was not detected or below detectable limit in all the samples analyzed suggesting that the fruit juices are safe for human consumption indicating that they were within the permissible limit that is non-deleterious to health as recommended by WHO for drinking water.

IV. Conclusion

In this study the concentrations of (Sn, Cd, Fe, Pb, Zn, Cu, Mn and Cr) in 15 samples of canned fruits juices from Benghazi markets were determined by using Atomic Absorption Spectrophotoscopy (AAS) after digestion techniques. Some of these samples were contaminated by Sn, Fe, Cu, Zn and Cd respectively, compared to Libyan and WHO allowed limits for each one and however, the different mean value of Pb, Cr and Mn respectively, Libyan and WHO allowed limits in different juice samples were safe limit value is statistically significant.

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