Heavy Metal Contents of Common Fruit Juice Drinks bought in Sulaimani market, Kurdistan region, Iraq.

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Abstract
The use of fruit juice is common in Kurdistan region especially by children and it becomes an important part of the modern diet nowadays. However presence of some heavy metals in these juices are harmful. The aim of the present study was to determine the safety of these fruit juices in the region by comparing the result with World Health Organization (WHO) limit for each of metals. In this study concentration of some heavy metals (Manganese, Lead ,Zinc ,Copper and Mercury) were measured using atomic absorption spectroscopy in 40 samples of different fruits juices. Results showed that Mean concentration of Manganese 1.69 , Lead 0.03 , Zinc 0.4 , Copper 2.71 and Mercury0.05 ppm , and minimum – maximum ranging from (ND-4.6), (ND-0.38), (ND-0.7), (1.30-3.54), (ND-0.25) ppm respectively . Manganese in 60%, Lead in 15%, Copper in 100% and Mercury in 17.5% of samples exceeded the permissible limit set by WHO.This research is of important in view of its being first study of the heavy metal content in fruit juice samples in the region unexpected finding obtain. Therefore, we suggested that ministry of health and quality control in each governorate (KRG) should test those kinds of drinks before passing the products into the market for consumption.

Keyword: Fruit juice, Heavy metal, toxic metal, atomic absorption spectroscopy.

Introduction

The use of fruit juice is common in Kurdistan region especially by children, it becomes an important part of the modern diet nowadays(Abdel- Rahman, and Abdellseid, 2013).Fruit juices that found themselves in the retail markets are mostly derived from citrus fruits. Nevertheless several cases of human disease, disorders, malfunction and malformation of organs due to metal toxicity have been reported(Jarup, 1998). Heavy metals composition of food is 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(Onianwa et al. 1999, Cabrera et al. 1995, AOAC. 2005).Both of Pb and Cd toxicity are well documented and are recognized as a major environmental health risk throughout the world. Lead affects both of humans and animals of all ages, nonetheless, the effects of lead are most serious in young children(Krejpcıo, 2005). Pb has been cited as one of the 3 most toxic heavy metals that has long term negative impact on health causing anemia, encephalopathy, hepatitis, and nephritic syndromes.Mn is an essential metal, at excessive levels in the brain, produces extrapyramidal symptoms similar to those in patients with Parkinson's disease, decreased learning activity in school-aged children, and increased propensity for violence in adults (Finley, 2008). An adult body contains 1.5-2.0 ppm Cu, above which it will be toxic (Kies, 1989). Toxicity due to excessive intake of Copper causes liver cirrhosis, dermatitis and neurological disorders. Deficiency of Cu includes bone demineralization; depressed growth, de-pigmentation, and gastro-intestinal disturbances(Silvestre et al. 2000).Zinc constitute about 33 ppm of an adult body weight and is essential as a constituent of many enzymes involved in several physiological functions, such as protein synthesis and energy metabolism.Zinc deficiency, resulting from poor diet, alcoholism, and malabsorption, causes dwarfism, hypogonadism, and dermatitis, while the toxicity of zinc due to excessive intake may lead to electrolyte imbalance, nausea, anemia, and lethargy (Onıonwa et al. 2001). Intakes of 150 to 450 mg of zinc per day have been associated with low copper status, altered iron function, reduced immune function, and reduced levels of high-density lipoproteins (the good cholesterol). One case report cited severe nausea and vomiting within 30 min after the person ingested four grams of zinc gluconate (570 mg elemental Zinc)(Valko et al. 2005).In recent study, about 40 of more common companies were selected to test their samples of artificial fruits juices andmeasure the concentrations of some heavy metals in the sulaimaniin Kurdistan, Iraqincludes: (Manganese, Lead, Zinc, copper and mercury), in order to comparative the results values with acceptable values were proposed by food administration of American and WHO.

Material and Methods

Sampling

Collection of fruit juice samples was performed from commercially available markets. Forty different fruit juices have bought from the sulaimani market between October and November 2014.The most frequently consumed brands were select.

Chemicals, Stock Solutions

All the chemicals used were Analytical Grade Reagents. The element standard solutions utilized for creating the calibration curves were prepared from 1000 mg/L Merck stock solution of the relevant element.

Sample digestion

The samples were digested using 2 mL sample, 5mL concentratehydrogen peroxide H_2O_2 drop by drop and 10 mL concentrate sulphoric acid H_2SO_4 then heating in heating block of kjeldale for 30 minute at higher degree then turn into half degree for 15 minute and cool in room temperature, diluted into 100mL in volumetric flask with deionized water performed at research laboratory in agricultural technical college of Halabja,Sulaimani polytechnic university. Deionizer water was from Kurdistan foundation for strategy and research,sulaimani, Kurdistan.

Sample analysis

For analysis were performed to determinate the concentrations of some heavy metals such as: Manganese, Lead, zinc, copper and mercury by using Atomic Spectrophotometer (AAS) Alpha4 at central research laboratory in agriculture college, university of Sallahadin.

Results and Discussion

The results, mean,minimum, maximum show in table(1,2)and table (3) show percentage of contaminated selected sample juice.

Table 1: Concentrations of heavy metals in the fruits juices (ppm)

Sample	Mn	Pb	Zn	Cu	Hg
FJ1	2.00	ND	0.47	3.30	0.25
FR2	2.50	ND	0.42	2.90	ND
FJ3	2.60	ND	0.59	3.10	ND
FJ4	3.10	ND	0.48	3.00	ND
FJ5	2.00	ND	0.40	2.60	ND
FJ6	ND	ND	0.35	2.61	ND
FJ7	2.00	ND	0.41	3.54	0.25
FJ8	1.00	ND	0.45	2.40	0.22
FJ9	ND	ND	0.52	3.45	ND
FJ10	ND	ND	0.53	2.60	ND
FJ11	ND	ND	0.50	2.34	ND
FJ12	4.60	0.17	0.29	3.45	0.25
FJ13	3.30	0.38	0.35	2.54	0.16
FJ14	3.20	ND	0.28	2.15	0.14
FJ15	ND	ND	0.47	1.30	ND
FJ16	ND	ND	0.32	1.70	ND
FJ17	ND	ND	0.38	2.60	ND
FJ18	2.00	ND	0.29	3.54	ND
FJ19	1.80	ND	0.25	2.50	ND
FJ20	ND	0.24	0.35	2.59	ND
FJ21	ND	ND	0.40	2.40	ND
FJ22	3.30	ND	0.52	2.54	0.16
FJ23	2.90	ND	0.47	2.31	ND
FJ24	1.50	ND	0.20	1.90	ND
FJ25	3.30	ND	0.35	2.30	ND
FJ26	4.60	ND	0.70	2.30	ND
FJ27	4.50	ND	0.65	3.00	ND
FJ28	3.30	ND	ND	3.10	ND
FJ29	3.20	ND	ND	2.80	ND
FJ30	3.10	ND	ND	2.90	ND
FJ31	1.00	ND	ND	2.60	ND
FJ32	ND	ND	0.59	3.10	ND
FJ33	ND	ND	ND	3.00	ND
FJ34	ND	ND	ND	3.20	ND
FJ35	3.30	ND	0.52	2.54	ND
FJ36	3.40	ND	0.40	2.10	ND
FJ37	ND	ND	0.64	3.10	ND
FJ38	ND	ND	0.53	2.93	ND
FJ39	ND	ND	0.39	3.17	ND
FJ40	ND	ND	0.31	3.07	ND

ND : not detected

Table (2): Mean, Minimum and Maximum of heavy metals (ppm)

Sample	Mn	Pb	Zn	Cu	Hg
Min	0.00	0.00	0.00	1.30	0.00
Max	4.60	0.38	0.70	3.54	0.25
Mean	1.69	0.03	0.40	2.71	0.05
WHO limit	0.05	0.01	5	0,01	0.01

Table (3): percentage of samples with contaminated metals

Heavy metal	percentage of contaminated samples
Mn	60% of samples exceeded the permissible of WHO limit
Pb	15% of samples exceeded the permissible of WHO limit
Zn	0% no simples were exceeded the value of WHO limit
Cu	100% of samples exceeded the permissible limit of WHO
Hg	17.5% of samples exceeded the permissible of WHO limit

Manganese (Mn)

Manganese was detectable in 24 samples among 40 samples (60%) as shown in table 1 and has min- max concentration between (ND – 4.6 ppm), the mean value detected was1.69 ppm which was more than the reported value (0.325 ppm) by (Hayford et al.2013). Obviously all detected values were high compared to maximum permissible limit for manganese which is 0.05ppm set by WHO or compared to other research (0.020-1.770 ppm) by (Haware et al. 2014),and (0.001–0.730 ppm) for canned and (0.001–0.209ppm) for non-canned beverages (Maduabuchi et al. 2004).

Lead (Pb)

Lead was detectable in 6 samples among 40 samples (15 %) as shown in table 1 and has min - max concentration (ND – 0.38 ppm), the mean value detected was 0.03 ppm. All detected values were high compared to the maximum permissible limit for lead which is 0.01 ppm set by WHO. While the result was not in agreement with the value reported by (Haware et al. 2014) which is (0.063) , the mean value was less than that reported in Accra Ghana fruit juice 1.59 ppm(Hayford et al. 2013). Sources of lead in the diet are from food containers containing lead, e.g. Storage in lead-soldered cans, ceramic vessels with lead glazes and leaded crystal glass. Lead has an effect on brain and intellectual development in young children, while long-term exposure in both children and adults can cause damage to the kidneys, reproductive and immune systems in addition to effects on the nervous system. Lead crosses the placental barrier and accumulates in the fetus. Infants and young children are more vulnerable than adults to the toxic effects of lead and they also absorb lead more readily. Lead toxicity causes many diseases like anemia, anoxia, bone pair, brain damage, convulsion and dizziness (Satarugand Moore, 2004).

Zinc (Zn)

The obtained result of Zinc concentration showed that Zinc was within range of (ND – 0.70 ppm), and it detectable in 37 samples among 40 samples (92.5%) as shown in table 1, these result identical to the results recorded by (Ithar Kamil, 2013).The mean value detected was 0.40 ppm. The maximum contaminant limit for zinc is 5.0 ppm (WHO, 2006). The result was more than that reported (0.301ppm) by (Haware et al., 2014) and less than that reported in Accra Ghana fruit juice (3.33 ppm) by (Hayford et al. 2013). Zinc concentration of all sample fruit juices were below the maximum contaminate level of zinc. Zinc is involved in numerous aspects of cellular metabolism. It isrequired for the catalytic activity of approximately 100 enzymes and it plays a role in immune function, protein synthesis, wound healing, DNA synthesis, and cell division(Institute of Medicine, 2001).The body has no specialized zinc storage system therefor a daily intake of zinc is required to maintain a steady state (Ryan-Harshman, and Aldoori, 2005). The toxicity of zinc due to excessive intake may lead to electrolyte imbalance, nausea, anemia, and lethargy(Onionwa et al. 2001).

Copper(Cu)

The result showed that the copper concentration of fruit juice was ranged (1.30-3.54 ppm)the mean value was (2.71ppm). The results explains that all the recorded values of Copper in juice samples were exceeded the above acceptable values (more than o.o1ppm) of WHO and 0.05ppm of Iraqi standard. Additionally more than that reported (0.072 ppm) by (Haware et al. 2014),and (0.83 ppm) by (Hayford et al. 2013). The deficiency of Copper is manifested by impaired hematopoiesis, bone metabolism, disorders of digestive, cardiovascular and nervous systems (Krizer et al. 1997).

Mercury (Hg)

The result showed that mercury concentration of fruit juice was ranged ND-0.25 ppm the mean value was 0.05 ppm. The maximum contaminant level (MCL) of mercury (Hg) is 0.01mg/L (Masazum and Smith, 1975).The toxicity of Mercury and lead metals is in part due to the fact that they accumulate in biological tissues, a process known as bioaccumulation. This process of bioaccumulation of metals occurs in all living organisms as a result of exposure tometals in food, drinking and the environment. Mercury is associated with a wide spectrum of adverse health effects including damage to the central nervous system (neurotoxicity) and the kidney. Different forms of mercury (i.e. Mercury metal, inorganic mercury salts such as mercuric chloride and organic forms of mercury such as methyl mercury) produce different patterns of toxicity. Organic forms of mercury can cross the placental barrier between the mother and the unborn baby(food safety , 2009). However, the toxic metal ions may be present in concentrations lower than the maximum contaminant level permitted by WHO, they are not easily eliminated from the system and could accumulate over the years affecting diseases like brain damage, liver cancer, skin cancer, lung cancer, memory loss,heart diseases, lymphatic cancer, lung diseases, kidney failure and mental retardation in children(Castro-González and Méndez-Armenta, 2008) .Metals such as mercury, lead enter the environment mainly as a consequence of industrial emissions or through disposal of products containing these metals, including mercury-cadmium or cadmium-nickel batteries, lead-containing ceramics and glass, mercury thermometers.

Conclusion

Obviously the consumption of Fruit juice supplements is broadly spread in Kurdistan region. Outcome of this study indicates that the daily intake of manganese, lead, zinc, copper and mercury through commercial fruits juice may pose a health hazard for consumers because the values were either below the recommended daily intake of these metals in some product or higher in some other, these amounts can be very hazardous if the fruit juices are taken in large quantities especially by children and pregnant women. Monitoring should be performed for toxic metal levels due to their natural geochemical association with these essential metals to provide citizens the safe allowable amounts.

There are many research articles on heavy metals content in water in Kurdistan region. It is of important in view of its being the first study of the heavy metal content in fruit juice samples in the area. In other countries similar studies were previously reported some studies state that analyzed juice samples are safe for drinking, since the level are below maximum permissible level given by WHO, in some other fruit juice were unsafe for drinking**.** The present study provides more data on metal pollution in Kurdistan which may connote to be a potential danger to the health, security and safety of these food items to the unsuspecting consumers. Therefore, we suggested that ministry of health and quality control in each governorate (KRG) should test those kinds of drinks before passing the products into the market for consumption.

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دراسة حول العناصر الثقلية المحتوية فى مشروبات عصير الفواكه المشترية في اسواق السليمانية / اقليم كوردستان العراق

الخلاصة

تم قياس التركيز بعض العناصر الثقيلة ك(مغنسيوم , رصاص , زنك, نحاس و الزئبق) باستخدام جهاز التحليل الطيفى للامتصاص الذري في ٤٠ عينات المختليفة من الاعاصيرالفواكه حيث ان تلك العينات شائعة في كوردستان العراق , الذي يستهلك بنسبة عالية من قبل السكان خاصة الاطفال. الهدف من هذه الدراسة هو تحديد السلامة في هذي الاعاصير الفواكه ومقارنة النتيجة الحددة لكل العنصر مع منظمة الصحة العالمية. النتائج بينت بان المعدل مغنسيوم ١.٦٩, رصاص ٠.٠٠٣, زنك ٠.٤ , نحاس ٢.٧١ و الزئبق ٠.٠٠٥ ملغم/ليتر و تتراوح مدى تركيزه (٠–٤.٦) , (٠ – ٠.٣٨) , (٠ – ٠.٧) , (١.٣ – ٣.٥٤) , (٠ – ٠.٢٥) ملغم/ليتر على التوالي . تقيم العينات عالية بالنسبة ٦٠٪ مغنسيوم , ١٥٪ رصاص , ١٠٠٪ زنك و ١٧.٥٪ الزئبق اذا قارنا الحد الادنى من النسبة المحددة المسموح بها مع المنظمة الصحة العالية. تم اجراء للعناصر الثقيلة المحتوي في العينات العصير الفواكه و ايجاد النتيجة غير المتوقعة. لذلك نحن نقترح لوزارة الصحة والسيطرة النوعية في كل محافظات اقليم كوردستان العراق الذي يجب اختبار تلك الانواع من المشروبات قبل عبورها تلك المنتوجاتالى الاسواق من اجل الاستهلاك.

لێكۆڵینەوە دەربارەی چەند توخمێكی قورس لە شەربەتی كڕاو لە بازارەكانی سلێمانی – هەرێمی كورستان/ عێراق

كورتە :

پەیتی چەند توخمێكی قورس دیاریكرا وەك مەنگەنیز , قورقوشم , زینك , مس و جیوە) بە بەكارهێنانی ئامێری ئەتۆمیك ئەبزۆربشن سپێكترۆسكۆپی بۆ ٤٠ سامپڵی شەربەتی میوە . ئەم سامپلانە زۆر بەربلاْون لە هەرێمی كوردستان- عێراق و بە رێژەیەكی زۆر بەكارئەهێنرێن لەلایەن دانیشتوان و بە تایبەتی منالان.

ئامانج لەم لێكۆڵینەوەیە لە دیاریكردنی سەلامەتی بەكارهێنانی ئەم شەربەتی میوانە و بەراوردكردنی ئەنجامەكان لەگەڵ رێژەی رێگە پێدراو لەلایەن رێكخراوی تەندروستی جیهانی . ئەنجامەكان دەریان خست كە تێكرای مەنگەنیز ١.٦٩ , قورقوشم ٠.٠٠٣ , زینك ٠.٤ , مس ٢.٧١ , جیوە ٠.٠٠٥ ملگرام/لیتر وە بواری پەیتیان بریتیە لە (. – ٤.٦) , (٠ – ٠.٣٨) , (. – ٠.٧) , (١.٣ – ٣.٥٤) , (٠ – ٠.٢٥) ملگرام/لیتر بە دوای یەكدا. ئاستی توخمەكان لە ناو سامپڵەكان بەرزە بە رێژەی ٦٠٪ مەنگەنیز , ١٥٪ قورقوشم , ١٠٠٪ زینك , ١٧.٥٪ جیوە بە بەراوردكردنی لەگەڵ رێژەی رێگە پێدراو لەلایەن رێكخراوی تەندروستی جیهانی . رێژەی چاوەروان نەكراو بەدیكرا لەبەر ئەم هۆكارە پێشنیار دەكەین بۆ وەزارەتی تەندروستی و كوالیتی كۆنترۆڵ لەسەرجەم پارێزگاكانی هەرێمی كوردستان – عێراق پێش ئەوەی ئەم جۆرە شەربەتانە رێگە بدرێت بە تێپەربونیان بۆ بازار پشكنینی پێویستیان بۆ بكرێت .