LEADCONTENTINFRUIT JUICES

A PROJECT REPORT SUBMIITED TO THE

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SUBMITTED BY

HONEY SANJAY DUMRALIA

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Dr. SULEKHA GOTMARE

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Shree Hansraj Pragji Thackersey College of Science

Conducted by: -

S.N.D.T WOMEN'S UNIVERSITY, MUMBAI

CERTIFICATE

This is to certify that **Ms. HONEY DUMRALIA**, a student of M.Sc. Il year has successfully completed the research project in Analytical chemistry on the topic "**LEAD CONTENT IN FRUIT JUICES"** under the guidance of **Dr. SULEKHA GOTMARE** in partial fulfillment for MSc. Analytical chemistry program during the year 2020-2021 This project is absolutely genuine and does not indulge in plagiarism of any kind.

Signature(GUIDE) Signature (HOD)

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The research opportunity l had with **S.H.P.T.College of Science** was a great chance for learning and knowledge enhancement. Therefore, I consider myself as very individual as I was provided to be a part of it. I am also grateful for having chance to research on the topic thoroughly and applying it accordingly.

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INDEX

INTRODUCTION

We have learned in the past few months and years that the food and juice we think is safe has contained some very harmful heavy metals.They may also contain potentially harmful levels of arsenic, cadmium, and lead, according to new tests from Consumer Reports.

The recent Consumer Reports article exposed common juices such as apple, grape, pear, and fruit blends as being high in a variety of different heavy metals. Of the forty-five brands tested, all had some heavy metals and half had levels that were considered dangerous for consumption. Both organic and conventional juices showed these levels, meaning that there wasn't any benefit in choosing organic products to reduce heavy metal load. Most alarmingly, the products tested were typically juices that were marketed to kids, a group that is particularly vulnerable to the negative effects of metal toxicity since it interferes with healthy development and may have cognitive implications. Fruit juices tend have high levels of heavy metals because metals that are released into the environment are absorbed into the soil, water, and air surrounding the fruit crops. As the crops grow, they absorb these metals, integrating the elements into their makeup. Furthermore, the vast majority of apples in the United States are imported from other countries. These countries don't have as strict of laws in regulating exposure to metals as the United States, thus increasing the amount present in the food that they export. Tip: To reduce your exposure to metals in fruit juice, try to significantly limit your consumption. Children should have no more than 4 fl oz of fruit juice, due to the risk of heavy metals and also the blood sugar impact of drinking such a concentrated source of sugar.

The toxicity of these metals has two main aspects:

(a) the fact that they have no known metabolic function,but when present in the body they disrupt normal cellular processes, leading to toxicity in a number of Organs.

(b) the potential, particularly of the so-called heavy metals mercury and lead, to accumulate in biological tissues, a process known as bio-accumulation. This occurs because the metal, once taken up into the body, is stored in particular organs, for example the liver or the kidney, and is excreted at a slow rate compared with its uptake. This process of bio-accumulation of metals occurs in all animals, including food animals such as fish and cattle as well as humans. It is therefore necessary to control the levels of these toxic metals in foodstuffs and juices in order to protect human health.

Components of Fruit Juice

Fruit juice is not a major source of dietary vitamins and minerals, although orange juice is rich in vitamin C. the mineral content of some common fruit juices. The major inorganic ion is potassium.The mineral content may change during fruit juice processing and storage. For example, iron content may be higher in canned juice than fresh juice. The mineral content of reconstituted juice may differ from fresh juice, since the water used for juice reconstitution may add some minerals to the product. The profile of minerals in fruit juice can be used for juice authentication (Fry, 1990). New juice based drinks are appearing on the market which have been fortified with calcium, specifically citrus juices. Also, vitamins, dietary essential fatty acids, phytochemicals, antioxidants, and proteins are added to increase the nutritional functionality of juices. Other ingredients, such as pigments, phenolics, and volatile compounds also contribute to the sensory and nutritional qualities of fruit juices. The level of endogenous antioxidants and bioactive compounds is a current area of interest and much work is being conducted to determine what the profile of juice pigments and antioxidants is and how this may be nutritionally beneficial. The juice making process may or may not result in a loss of phenolic antioxidants. Biological variability between culti vars of fruit, as well as length of time in storage, cultivation conditions, and extraction methods can all affect the level of bio-active components in juice.

	Orange, fresh	**Orange, canned**	**Orange**	**Grapefruit, fresh**	**Apple juice**	**Grape juice**
Na	8	21	8	8	29	33
Ca	113	83	92	92	71	96
Mg	113	113	104	125	29	104
Zn	0.50	0.71	0.50	0.50	0.29	0.54
Mn	0.15	0.15	0.15	0.21	1	4
K	2067	1817	1971	1667	1229	1392
P	175	146	1667	154	71	117
Fe	2	5	1	2	4	2.5

Cu	0.45	0.59	0.46	0.34	0.23	3

Harmful Effects Of Heavy Metals

The harmful effects of heavy metals are Depending on how long children are exposed to these toxins and how much they are exposed to, they may be at risk for lowered IQ, behavioral problems (such as attention deficit hyperactivity disorder), type 2 diabetes, and cancer, among other health issues.Though the risks of heavy metals from any one source may be low, when people are exposed to even small amounts from multiple sources, over time the danger multiplies. And such exposure is common. Previous tests from CR and others have found elevated levels of heavy metals not just in juices but also in infant and toddler foods, rice and rice products, protein powder, some types of fish, and sweet potatoes. The toxins may also be in the environment, including the water, the air, and the soil. “In the course of a lifetime, the average person will come into contact with these metals many times, from many sources,” Heavy metals may be less risky to adults, but exposure can still lead to health problems. Over many years, even modest amounts of heavy metals may raise the risk of bladder, lung, and skin cancer; cognitive and reproductive problems; and type 2 diabetes, among other conditions. And arsenic, cadmium, and lead each pose their own set of potential harms.

The Toxic Effects Of Lead

The toxicity of these metals has two main aspects: (a) the fact that they have no known metabolic function,but when present in the body they disrupt normal cellular processes, leading to toxicity in a number of organs; (b) the potential, particularly of the so-called heavy metals mercury and lead, to accumulate in biological tissues, a process known as bio-accumulation. This occurs because the metal, once taken up into the body, is stored in particular organs, for example the liver or the kidney, and is excreted at a slow rate compared with its uptake. This process of bio-accumulation of metals occurs in all animals, including food animals such as fish and cattle as well as humans. It is therefore necessary to control the levels of these toxic metals in foodstuffs and juices in order to protect human health.

Lead is associated with high blood pressure, heart disease, and fertility problems. exposed to lead in the course of their work. Short-term exposure to high levels of lead can cause brain damage, paralysis (lead palsy), anaemia and gastrointestinal symptoms. Longer-term exposure can cause damage to the kidneys, reproductive and immune systems in addition to effects on the nervous system. The most critical effect of low-level lead exposure is on intellectual development in young children and, like mercury, lead crosses the placental barrier and accumulates in the foetus. Infants and young children are more vulnerable than adults to the toxic effects of lead, and they also absorb lead more readily. Even short-tem, low-level exposures of young children to lead is considered to /have an effect on neurobehavioural development. Consumption of food containing lead is the major source of exposure for the general population

LITERATURE REVIEW

Another knock against fruit juices: Many contain potentially harmful levels of arsenic, cadmium and lead, according to Consumer Reports.

The non-profit consumer research and advocacy group tested 45 fruit juices (apple, grape, pear and fruit blends) sold across the U.S. and found elevated levels of those heavy metals in nearly half of them. Particularly concerning to the researchers was that many of the juices were marketed to children.

Consumer Reports tested 45 drinks and found 21 contained enough of a single heavy metal or a combination of the metals to concern experts who worked with Consumer Reports on the study. Drinking just 4 ounces a day can cause concern, said Consumer Reports chief science officer James Dickerson.

Drinking lots of fruit juice could compound their risk, the researchers say, because children may also encounter elevated levels of heavy metals in baby foods, rice products, and other foods, as well as from water and the environment.

“Exposure to these metals early on can affect their whole life trajectory,” says Jennifer Lowry, a physician and chairperson of the American Academy of Pediatrics’ Council on Environmental Health, in the report. “There is so much development happening in their first years of life.”

The drinks tested were from 24 national, store, and private-label brands including Capri Sun, Gerber, Minute Maid, Mott's and Welch's. Researchers bought three samples of each product from retailers across the country.

The researchers noted that their findings should not lead to "definitive conclusions about specific brands."

Among the findings:

•Each of the 45 products had measurable levels of at least cadmium, inorganic arsenic, lead, or mercury.

•Twenty-one of the juices had concerning levels of cadmium, arsenic, and/or lead.

•Seven of those 21 juices had levels that could harm children who drink 4 ounces or more daily; nine posed risks to kids at 8 ounces, or 1 cup, or more daily.

•Five of the potentially harmful drinks were juice boxes or pouches containing 4 to 6.75 ounces.

•Grape juice and juice blends had the highest average levels of heavy metal.

•Juice brands marketed to children did not fare better or worse than other juices.

•Organic juices did not have lower levels of heavy metals than conventional ones.

The seven juices that Consumer Reports found could harm children who drink 4 ounces or more daily were: Trader Joe’s Fresh Pressed Apple Juice, 100% Juice; 365 Everyday Value (Whole Foods) Organic 100% Juice, Concord Grape; R.W. Knudsen Organic Just Concord Grape Juice; Welch’s 100% Grape Juice, Concord Grape; Welch’s 100% Grape Juice, With Grape; Great Value (Walmart) 100% Juice, Cranberry Grape; Welch’s 100% Juice with Antioxidant Superberry.

For the full list, including healthier alternatives, go to Consumer Reports' website.

The U.S. Food and Drug Administration has a guideline for lead in juice of 50 parts per billion (ppb), but the CR researchers think that should be lower. That's because more than half of the drinks tested 1 ppb or less. Only Welch’s 100% Juice With Antioxidant Superberry and Welch’s 100% Grape Juice, Concord Grape were found to have an average of more than 5 ppb.

CR asked Welch’s about the "comparatively high lead levels" in those juices and a company spokesperson said, “All Welch’s juice is safe and strictly complies with all applicable legal requirements. Naturally occurring elements such as lead and arsenic are present in the soil, air, and water. Therefore, they are also found in very low, harmless levels in many fruits and vegetables.”

The FDA has not set a guideline on inorganic arsenic, but five years ago proposed limiting it to 10 ppb in apple juice, the equivalent to the standard for drinking water. Only one juice, Trader Joe’s Fresh Pressed Apple Juice, had inorganic arsenic levels above the FDA's proposed guideline – and 58 percent of the juices had levels below CR’s recommended cutoff of 3 ppb.

A Trader Joe’s spokesperson told CR it would "investigate your findings, as [we are] always ready to take whatever action is necessary to ensure the safety and quality of our products.”

The FDA has not proposed a limit on cadmium for juice. However, three juices had cadmium levels above CR's recommendation of 1 ppb higher than that amount.

This is just the latest health flag raided about fruit juice and children. Two years ago, the American Academy of Pediatrics said children should not drink fruit juices in their first year, citing concerns about obesity, tooth decay and other health concerns.

The academy's other recommendations include limiting children ages 1 to 3 years old to 4 ounces of juice daily or less and kids 4 to 6 years old from 4 to 6 ounces each day. Older kids up to age 18 should not drink more than 8 ounces per day.

Many children drink fruit juice. More than 80 percent of parents of children age 3 and younger give their kids fruit juice at least sometimes, a recent Consumer Reports survey of 3,002 parents found. For 74 percent of respondents, kids drink juice at least once a day or more.

The problem is caused, in part, because of the globalization of the food supply and lack of regulation in other countries, says Natalie Sexton, health expert and vice president of marketing at Natalie's Orchid Island Juices in Fort Pierce, Florida. "Only 4 percent of apples produced in the world are from the US," she said. "Most are sourced from China where regulations are not as stringent in terms of what chemicals can be used in the pesticides, insecticides and fertilizers."

Apples and grapes are processed with the skin "co-mingling with the inside of the fruit," which can elevate heavy metal levels, she said.

The researchers note that heavy metals can also be harmful to adults. "Five of the juices we tested pose a risk to adults at 4 or more ounces per day, and five others pose a risk at 8 or more ounces," Dickerson says.

Lifetime exposure to "modest amounts of heavy metals," the researchers say, can increase risk of bladder, lung, and skin cancer; cognitive and reproductive problems, as well as type 2 diabetes. Lead is also linked to high blood pressure, heart disease, and fertility problems, while arsenic is associated with cardiovascular disease. Cadmium can increase the risk of bone damage and kidney disease.

2) There are many products obtained from fruits, including fruit juice, canned, dried, and frozen fruit; pulps; and marmalades. Fruit composition is mainly water (75–90%), which is mainly found in vacuoles, giving turgor (textural rigidity) to the fruit tissue. Juice is the liquid extracted from the cells of mature fruits. Fruit cell wall is made of cellulose, hemicellulose, pectic substances, and proteins (1). Fruit Juices and portable water and also tea are the most widespread beverages in the habitual diet, and they contribute significantly to trace element dietary intake. Fruit juices are a highly appreciated, tasty food and usually have exceptional nutritional qualities. However, they can be a potential source of toxic elements, some of them having an accumulative effect or leading to nutritional problems due to the low concentrations of essential elements, justifying the control of mineral composition in juice (2-4). In Iran just like most of other countries fruit juices are the usual beverages, and used in most of the festivals, ceremonies and celebrations and even in hospitals and schools. Fruit juices found in all retail markets and mostly derived from citrus fruit but some chemicals are added in their formulation.
They are served in dinner or lunch with biscuits, snacks or pastries and occasionally with breads. However, they can be a potential source of toxic elements, some of them having an accumulative effect or leading to nutritional problems due to the low concentrations of essential elements, justifying the control of mineral composition in juice (2-4). Chemicals may be encountered as reactants, solvents, catalysts, inhibitors, as starting materials, finished products, by-products, contaminants, or off-

specification products. They may vary from pure, single substances to complex proprietary formulations. An exposure to a specific chemical in relatively low concentrations over a period may result in chronic effects. At higher concentrations, the effects may be acute. Some chemicals produce local damage at their point of contact with, or entry into, the body; others produce systemic effects, i.e. they are transported within the body to various organs before exerting an adverse effect.

Heavy Metal Removal from Commercially-available Fruit Juice Packaged Products by Citric Acid

The concentration of heavy metals in fruit juice products varies depending on their origin, storage condition and processing technologies Heavy metal contamination has become one of the major issues of public health concern, but still has not received much research attention in many developing countries such as Iran especially in case of fruit juices. The heavy metal and trace element levels of fruit juices may be expected to be influenced by the nature of the fruit, the weather conditions, the mineral composition of the soil from which it originated according to the geographical conditions, the composition of the irrigation water, the agricultural practices such as the types and amounts of fertilizers used, and other factors such as water used in the fruit juices reconstruction in the manufacturing process.

Citrates have been reported to assist in platting of copper , nickel (8), chromium and lead (9) and various heavy metals (10). Citric acid is also an preferred nucleating or blowing agent in polymeric foams for food and beverage use and its esters are used as plasticizers in the preparation of polymer compositions(10). Over half of global consumption of citric acid is used for the beverage industry. The food industry consumes about 15–20%, followed by detergent and soaps (15–17%), pharmaceuticals and cosmetics (7–9%), and industrial uses (6–8%) (11) . Citric acid which was used in carry study is one of the organic acids commonly used as chelating agents and neutralization (12,13), Citric acid form square planer complex with heavy metals through binding to citrate anions with cations. Information on the citric acid content of fruit juices and commercially-available formulations is not widely known. 60 % of citric acid product is mainly used in the food and beverage industry, because of its general recognition as safe having pleasant taste, high water solubility and chelating and buffering properties. Citric acid is used extensively in carbonated beverages to provide taste and complement fruit and berry flavors. It also increases the effectiveness of antimicrobial preservatives. The amount of acid used depends on the flavor of the product. It usually may vary from 1.5 to 5 % Citric acid also inhibits color and flavor deterioration in frozen fruit . Amounts in concentration of 0.005 – 0.02 % citric acid are used as an antioxidant synergism in fats, oils and fat containing foods .According to the last researches by author on food safety and obvious documented findings in presence of heavy metals in vegetables and fruits during last decade and this fact that food can be contaminated with heavy metals by ingestion of contaminated or polluted food and water, achieving the safe solution to remove or reduce these chemical hazards is the main goal of this study. Exposure of people to toxic chemicals such as cadmium and lead could be probably reduced by appropriate method. Due to the first hypothesis of capability of citric acid form square planer complex with heavy metals through binding to citrate anions with heavy metal cations , we decide to comprehend this compound to remove the possible heavy metals being exist in packaged fruit juice.

The objectives of this study were:

- To determine the concentration of heavy metals (Pb, Ni and Cd) in most known fruit juices available commercially in the form of packaged in Tehran market (Iran), using Atomic Absorption Spectrophotoscopy (AAS)
- To compare these results with the maximum admissible limit set in drinking water by different international organizations: United States

Environmental Protection Agency (USEPA) and World Health Organization (WHO) and also national standard.

- To evaluate the citric acid efficiency in removal the heavy metal containments in packaged fruit juice products.
- Investigating the role of citric acid as chelating agent in order to remove heavy metals especially nickel, lead and cadmium and find the optimum concentration of citric acid for removing process .

Sampling method

180 varieties of 200 ml packaged fruit juices from 5 recognized manufacturers (Pineapple, Orange, Mango, Tropical, Cherry and Grape) were investigated for the presence of heavy metals and study for removing possible chemical contamination, purchased from recognized market of Tehran from the month of September to December 2014. At least 5 samples of each category were analyzed to overcome sampling bias. pH was determined using digital pH meter (Inolab digital pH meter). .Moisture and ash contents of fruit juices were determined using standard AOAC methods .

Heavy metals: lead, Nickel and cadmium in each sample were determined In order to studying in treating samples as well as determination of heavy metals each samples divided into half (100 ml) after shaking for two steps of experiment. In this survey, 2.5 mL of 69% pure Merck nitric acid and 0.5 mL Hydrochloric acid 36.5% Merck were added to 2.5 mL of fruit juices in a Teflon receptacle tightly closed. The whole system was put in an oven at 180◦ C for 12 hours. A colorless solution resulted, and deionized water was added up to 50 mL. Thus, the fruit juices samples were diluted 1: 20 v/v. For each sample analysis three replicates were measured in order to assure the control quality of our measurements.

Heavy metals were determined using atomic absorption spectrophotometer (AAS) by wet digestion method in Pharmaceutical Sciences Branch, Islamic Azad University Tehran-Iran. Heavy Metals were analyzed using calibration curves made up of at least five standards with the minimum values of determination coefficient (R2) of Pb, Ni and Cd. Different parameters are employed for elemental analysis of heavy metals. The flame fuel used is air-acetylene mixture. The sensitivity of the instrument is 0.001. Appropriate quality assurance procedures and all necessary precautions were taken to avoid any possible contamination of the sample as per the AOAC guidelines precaution were carried out to ensure reliability of the result. Samples were carefully handled to avoid contamination .

Treatment of Fruit Juice Samples with Citric acid

The Fruit Juice samples (100 mL each) were separately measured into clean dried and labeled plastic containers. Citric acid by the different concentrations: 0.005%, 0.01%, 0.015%, 0.02% and 0.05% were introduced into the samples at a concentration of 0.2/100 ml and stirred for 15 minutes. Two controls were also obtained by treating one fruit juice sample with the citric acid solvent used for the removal heavy metals from the juices (0.2ml/100mL) while the second was untreated. The plastic containers were firmly covered and shaken to mix the citric acid and fruit juice. The precipitations were separated and filtered by Quantitative Ash less Filter Paper: Whatman – Grade 41. The treated and control samples were stored under ambient conditions. Initial assessments of the removal levels of the heavy metals from samples were carried out after 15 minutes. Sampling and subsequent analysis were carried out to monitor the changes in parameters associated with the formation of complexes in the stored treated samples.

Statistical Method

State differences on the basis of the states: fruit juice samples and treated samples by citric acid were determined by student t-test. The changes were calculated by one way Anova and for analysis of the role of multiple factors univariate analysis was used by SPSS 18. Probability values of <0.05 were considered significant.

Results

The pH, total carbohydrate and sugar content of these 6 fruit juices are almost the same and pH≤ 3.4. The main sugars present in fruit juices are sucrose, glucose and fructose generally but the content of these three types of sugars is different in fruit juices according to the kind of fruit and brand too.

Pb level in the fruit juices ranged from 0.0285 ± 0.0001 to 1.9621 ± 0.0013 (mg/l ± SD). Concentrations of Pb in mango juice and Ni in pineapple and tropical juice were relatively high. Cd was not detected in the most of selected juices. Additionally, Pb, Cd and Ni were not detected in 90% cherry juice samples from different brands but were present in most of mango and tropical samples. However, the cadmium levels of selected fruit juices were within permissible levels except for mango juice. The range and arithmetic mean concentration of Pb and Cd in different fruit juices are also given in table 2 as average of three replicates of the individual fruit juices. Each code belongs to a special brand.

Fruit Juice	Pb (mg/l)	Pb(mg/l) after	Cd(mg/l)	Cd(mg/l) after	Ni(mg/l)	Ni(mg/l) after
sample		treating by 0.02%		treating by		treating by 0.02%

		Citric acid		0.02%Citric acid		Citric acid
Mango1	1.9621 ±0.0013	0.9401± 0.001	0.157 ± 0.0024	0.0062± 0.0015	0.098 ± 0.0001	0.0043±0.0001
Mango2	0.2268± 0.0018	0.0087 ±0.0004	0.0034± 0.0006	ND	0.040 ± 0.0	0.0007± 0.0001
Mango3	0.127 ± 0.01	0.0048± 0.0002	ND	ND	0.059 ± 0.0002	ND
Mango4	1.950 ±0.0	0.9736±0.004	0.018 ± 0.0001	ND	0.086±0.0012	0.0072 ±0.0002
Mango 5	0.0452±0.002	ND	0.017 ±0.0	ND	0.110 ± 0.0	0.010±0.0001
Mean	0.86222	0.38544	0.03908	0.00124	0.0786	0.00444
Pineapple 1	0. 345±0.0003	0.1667	0.064 ± 0.0	ND	0.1266±0.001	0.0087±0.0004
Pineapple 2	0. 145±0.007	0.0004±0.0	0.0012±0.0	ND	0.2844±0.004	0.0026±0.0001
Pineapple 3	0.043±0.0001	ND	ND	ND	0.0083 ± 0.0002	ND
Pineapple 4	0.1062±0.0004	0.0056±0.0001	0.028 ± 0.0002	ND	1.730 ± 0.0	0.0889± 0.0003
Pineapple 5	0.0427±0.0003	ND	ND	ND	0.0989±0.0001	ND
Mean	0.13638	0.03454	0.01864	ND	0.44964	0.02004
Orange 1	0.2738±0.0005	0.0083±0.0001	0.0852 ± 0.0	0.0138±0.0003	0.118±0.0003	ND
Orange 2	0.1667±0.0002	0.0076±0.0003	0.0178 ±0.0002	ND	0.0444±0.0002	ND
Orange 3	0.1003±0.0001	ND	0.0020 ± 0.0001	ND	0.0222±0.0001	ND
Orange 4	0.0882±0.0004	ND	0.014 ± 0.0001	ND	0.2004±0.0001	ND
Orange 5	0.0285±0.0001	ND	ND	ND	0.1081±0.0001	ND

Mean	0.1320	0.00318	0.0238	0.0276	0.09862	0
Cherry 1	0.2833±0.0002	0.1245 ± 0.0004	0.064 ± 0.0	ND	1.7352	0.0512
Cherry 2	0.0545±0.0001	ND	0.043 ± 0.0002	ND	0.0348	0.0020 ± 0.0
Cherry 3	0.027 ± 0.0	ND	ND	ND	0.0032	ND
Cherry 4	0.0889±0.0002	ND	0.064 ± 0.0	ND	1.890 ± 0.0	0.0556±0.0002
Cherry 5	ND	ND	ND	ND	0.045 ± 0.0001	ND
Mean	0.09094	0.0249	0.0343	ND	0.80428	0.04536
Grape 1	0.1267 ± 0.0005	0.0044	ND	ND	0.058 ± 0.0001	ND
Grape 2	0.096	0.0008±0.0001	0.026	ND	0.082	ND
Grape 3	0.2811±0.0003	0.0044±0.0002	ND	ND	0.0942±0.001	ND
Grape 4	1.5208±0.0015	0.0889±0.0004	0.0342±0.0003	ND	1.4857±0.0012	0.1393±0.0003
Mean	0.50615	0.024625	0.01505	ND	0.429975	0.034825
Tropical 1	3.6572±0.0043	0.8678±0.0009	0.0126±0.0002	0.0012±0.0001	2.423 ± 0.0005	0.886±0.0014
Tropical 2	0.7866±0.0042	0.0044±0.0002	0.008 ± 0.0	0.0018±0.0001	0.1815±0.0002	ND
Tropical 3	0.0086±0.0008	ND	ND	ND	0.667 ± 0.0002	0.0456±0.002
Tropical 4	0.9345±0.0034	0.1876±0.0026	0.0033±0.0001	ND	0.08724±0.0001	ND
Tropical 5	0.0063±0.0003	ND	0.085 ± 0.0	ND	0.1423±0.0002	ND
Mean	1.07864	0.21218	0.02178	0.0006	0.7002	0.18632

Table 2- The concentrations of heavy metals: Ni, Cd and Pb, in analyzed commercial packaged fruit and treated form after adding citric acid

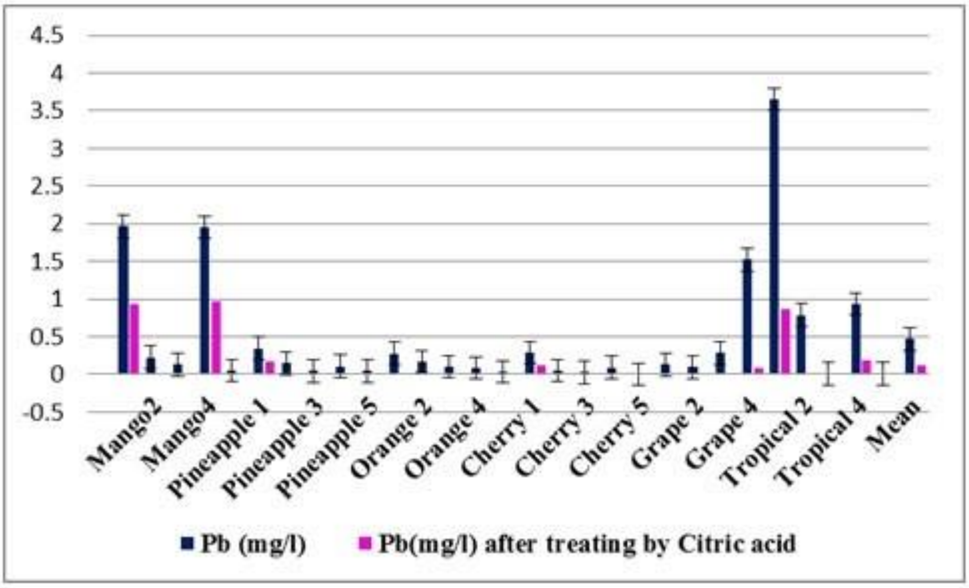


Figure3- Lead content(mg/L) in treated and untreated fruit juice samples

Heavy metal concentrations in treated samples mostly were below the recommended safety limits, untreated within this and some exceeding the threshold limits established by WHO and ISIRI. The maximum permissible limit for Pb is 0.01 ppm set by WHO while it is 1 ppm according to FSSAI and ISIRI safe limit (28, 29). The level of Pb recorded in this study was found to not be within the safety limits set by ISIRI :1 ppm for apple and orange juices and 0.3 ppm for mango juices. The present study shows that in 76% of samples, the Pb content is much above this safe limit .Our study shows that the concentration of lead in fruit juices is much higher than permissible limit for mango and tropical juices but for cherry and orange samples are lower than it.

The different between mean value of Pb in different juice samples and WHO safe limit value is statistically significant. The concentrations of cadmium in our fruit juice sample is far below the permissible limit value after treating while before treating in some samples such as Mango1 and tropical 4 are higher than maximum permissible level . Lead toxicity causes many signs and symptoms such as abdominal pains, anemia, brain damage, anoxia, convulsion and inability to concentrate etc.,(30).

The grape and then pineapple juice samples in our study have the less content of cadmium among other samples and treating by citric acid cause to removal of cadmium significantly ($p \leq 0.003$). Results revealed that The Cherry, grape and pineapple samples after treatment have no detectable cadmium content and for other samples the remained concentrations of cadmium are much lower than safe limit.

The allowed limits in drinking water for Ni are 100μg/L (by USEPA) and 70μg/L (by WHO). Results revealed that 15values of Ni concentrations from investigated fruit juices before treating by citric acid were over these limits. The Ni content is much above this safe limit set by WHO, but after treating by citric acid 0.02% they are all in the safe level. The higher Ni content observed for the untreated samples could arise from contamination either from the processing step in the factory or from an existing contamination in the drinking and pipeline water used in fruit juices processing.

The sources of fruit juices contamination are most probably either the water used in the fruit juices reconstruction or the added sugar or the imported unqualified dried fruits. Cd is highly toxic and responsible for several cases of poisoning through food. Small quantities of Cd cause adverse changes in the arteries of human kidney. It replaces Zn biochemically and causes high blood pressures, kidney damage, and so forth. Because of their high toxicity, As, Pb, and Cd need to be quantified in food and beverages. The analysis of Pb content reveals the fact that three fruit juices samples (Mango 1, Mango 4, Tropical 1 and grape 4) much more exceed the allowable limits for drinking water. Taking into account that lead is less mobile than Cd in the soil-plant system (36), the lead in fruit juice could be related to imported dried fruits in factories.

Due to the poor screening and monitoring system in developing countries like Iran, it is very difficult to evaluate how the consumer can be affected by taking fruit juices. While most juice quality with low price sold in the market, in addition to having the properties of the fruit, is harmful to health risks as well.

Although in last several decades enough knowledge on biochemical mechanisms leading to citric acid overflow have accumulated to generally understand the phenomenon, however many details still remain unexplained. Our Findings proved that obviously the citric acid as chelating agent, act complexion with cations such as lead, cadmium and nickel. In this study with the aim of decreasing the amount of heavy metals by citric acid has proposed recovery of citric acid by precipitation of the complexes of metal-bonded- citrate. An additional advantage of this method is that complex formed by citrate has a definite crystalline structure and can be participate and removed by centrifuge or be filtered easily.This study proved that the chelating and pH adjusting properties of citric acid enable it to optimize the removal heavy metals especially cadmium, nickel and lead from fruit juice products by enhancing the complex formation and probably effecting on enzymes.

Copper and other heavy metals in grapes: a pilot study tracing infuential factors and evaluating potential risks in ChinamXiaomin Li, Shujun Dong & Xiaoou Su

In this study, grapes (Vitis vinifera L.) were systematically sampled across the main grape-producing areas in a nationwide survey of China. Grapes from special regions, such as heavy metal polluted areas (e-waste dismantling area) and pesticide free areas (courtyard) were also collected to make a comparison. Grape skins and pulps were separated to evaluate infuence of accumulation behavior, environmental transport and water cleaning efficiency to heavy metals. **Levels of copper in grape** skins (5.02±3.18μg/g) were higher than in pulps (3.74±1.48μg/g). Only high level of copper in two grape skins (sampled from an e-waste dismantling area) showed obvious decrease during water clean-up procedure, indicating the infuence of air deposition. Statistical analysis showed no signifcant diference in the copper levels of grapes from markets, courtyards and e-waste dismantling areas.

Concentrations and sources of chromium (Cr), manganese (Mn), nickel (Ni), cadmium (Cd), lead (Pb) and arsenic (As) were also analyzed. Higher levels of these heavy metals were observed in grape skins than pulps. Finally, we evaluated the risk of ingesting heavy metal through grapes using the estimated daily intake (EDI). No health risk was found by consuming grapes according to the data from this study.

Grape (*Vitis vinifera L.*) is one of the most widely consumed fruits around the world. It is not only a popular table fruit, but is also the raw material to produce wine worldwide. Recent studies have suggested that the good cardiac health condition of inhabitants around the Mediterranean area was related to rich content of phenolic compounds in grapes from their diet which might further promote grape consumption. As known, viticulture will be abundantly applied with copper-based pesticide, because this kind of plants is vulnerable to fungal diseases (e.g. downy mildew). In order to control downy mildew, about 400–800 kg per hectare of Bordeaux mixture (mixture of quicklime and copper sulfate, the concentration of copper is about 2.55g/L) was sprayed several times during the whole grape growing season. During the process of which, the sprayed copper pesticide can be deposited on the fruit surfaces and might fnd its way into the fruit tissues. Soil in vineyards was also considered to be a seriously copper polluted area due to year by year application of Bordeaux mixture . Te copper could also be able to transport to grapes through root adsorption. To limit copper concentration, the dose of copper in vineyard soil is limited to 8 kg Cu per hectare in vine cultivation.Normally copper is nontoxic to mammals , and copper defciency could even result in inflammation, anemia and other discomforts. However, excessive digestion of copper might cause a series of health problems. Several studies have revealed that too much copper accumulating in human bodies could result in liver cirrhosis, cell hemolysis, anemia, kidney disorders and osteoporosis. As such, grapes and grape products that are susceptible to copper might arouse public health concern due to the universal application of copper-based pesticides in viticulture. Some of these previous studies focused on whether the heavy metal contents exceeded the tolerable daily intake (TDI) and some of them discussed copper distributions in underground and aerial parts of the plant, but few of them discussed the influence of pesticides application or other potential factors (such as environmental pollution) on grapes. In this study, we not only sampled grapes from the main grape-producing areas, but also from e-waste dismantling areas with environmental heavy metal pollution and from home

Institute of Quality Standard and Testing Technology for Agro-Products, The Chinese Academy of Agricultural Sciences (CAAS), Beijing, 100081, China. Correspondence and requests for materials should be addressed to X.S.

Analysis of Mineral and Heavy Metal Content of Some Commercial Fruit Juices by Inductively Coupled Plasma Mass Spectrometry

The presence of potentially toxic elements and compounds in foodstuffs is of intense public interest and thus requires rapid and accurate methods to determine the levels of these contaminants. Inductively coupled plasma mass spectrometry is a powerful tool for the determination of metals and nonmetals in fruit juices. In this study, 21 commercial fruit juices (apple, peach, apricot, orange, kiwi, pear, pineapple, and multifruit) present on Romanian market were investigated from the heavy metals and mineral content point of view by ICP-MS. Our obtained results were compared with those reported in literature and also with the maximum admissible limit in drinking water by USEPA and WHO. For Mn the obtained values exceeded the limits imposed by these international organizations. Co, Cu, Zn, As, and Cd concentrations were below the acceptable limit for drinking water for all samples while the concentrations of Ni and Pb exceeded the limits imposed by USEPA and WHO for some fruit juices. The results obtained in this study are comparable to those found in the literature.

1. Introduction

Fruit juices are a highly appreciated, tasty food and usually have exceptional nutritional qualities. However, they can be a potential source of toxic elements, some of them having an accumulative effect or leading to nutritional problems due to the low concentrations of essential elements, justifying the control of mineral composition in juice.

Trace metals are present in foods in amounts below 50 ppm and have some toxicological or nutritional significance. The elements such as Na, K, Ca, and P are essential for people, while metals like Pb, Cd, Hg, and

As are found to cause deleterious effects even in low levels of 10–50 ppm. However Fe, Cu, and Zn are found to be necessary in certain quantities in foods, but these elements can cause ill effects when are ingested in high amounts. Other non-toxic metals which are not harmful when present in amounts not exceeding 100 ppm include Al, B, Cr, Ni and Sn. The non nutritive toxic metals which are known to have deleterious effects even in small quantities (below 100 ppm) are As, Sb, Cd, F, Pb, Hg, and Se For this reason, the determination of both major and trace levels of metal contents in food is important for both food safety and nutritional considerations The trace element levels of fruit juices may be expected to be influenced by the nature of the fruit, the mineral composition of the soil from which it originated, the composition of the irrigation water, the weather conditions, the agricultural practices such as the types and amounts of fertilizers used,and other factors The aim of this study was the precise determination of mineral and heavy metal content from the most known commercial fruit juices present on Romanian market and to compare these results with the maximum admissible limit set in drinking water by different international organizations:

2. Experimental

21 commercial fruit juices (apple, peach, apricot, orange, kiwi, pear, pineapple, and multifruit) purchased from Romania market were investigated in this study. All determinations were carried out by the Inductively Coupled Plasma Quadrupole Mass Spectrometry. A Perkin Elmer ELAN DRC (e) was used with a Meinhart nebulizer and silica cyclonic spray chamber and continuous nebulization. The operating conditions for Perkin Elmer ELAN DRC (e) were nebulizer Gas flow rates: Nebulizer Gas flow rates: 0.92 L/min; Auxiliary Gas Flow: 1.20 L/min; Plasma Gas Flow: 15 L/min; Lens Voltage: 10.5 V; ICP RF

Power: 1100 W; CeO/Ce = 0.020; Ba++/Ba+ = 0.023. The chosen conditions were a compromise between the highest 103Rh ion signal and the lowest percentage of doubly charge ions (obtained by the intensities ratio Ba++/Ba+, always ≤3%) and of oxide ions (obtained by the intensities ratio CeO/Ce, always ≤3%), precision better than 2% and background <30 cps.The operating conditions were optimized daily, by using an aqueous solution containing 10 g L−1 of Mg, Ba, Ce, Cu, Cd, Rh, In, and Pb, and monitoring the intensities of the isotopes 24Mg, 103Rh, 114In, 208Pb, 138Ba, and 140Ce as well as the intensities at mass 69, 156 and 220 (corresponding to species 138Ba2+ 140Ce16 O+ and background, resp.). The majority of ICP-MS applications involve the analysis of aqueous samples, directly or following sample pretreatment, because of the advantages of working with samples in solution. In this survey, 2.5 mL of ultrapure nitric acid were added to 2.5 mL of fruit juices in a Teflon receptacle, tightly closed. Six such receptacles were inserted in a device made of six stainless steel cylinders mounted between two flanges, to confer pressure resistance. The whole system was put in an oven at 180+C for 12 hours. A colorless solution resulted, and ultrapure water was added up to 50 mL. Thus, the fruit juices samples were diluted 1 : 20 v/v. For each sample analysis three replicates were measured in order to assure the control quality of our measurements.

3. Results and Discussion

The evaluation of commercial fruit juices is a important issue for consumer safety, as they are widely consumed throughout the world Determining cations, such as potassium, sodium, and calcium, in fruit juices is important due to the dietary significance of such cations. For example, recent studies have supported the contention that excess dietary sodium is a contributing factor in heart disease. Ca, though an important dietary component for most, can be an issue for patients with renal insufficiency. K is also essential for good health and is present in significant concentrations in some juices. For these reasons, accurate reporting of cation levels is helpful The obtained concentration of Na, Mg, K, and Ca for 21 commercial fruit juices are presented in

Table 1The SD of measurement samples was: 0.91 for Na, 0.17 for Mg, 3.08 for K, 0.21 for Ca.

Sample	Na	Mg	K	Ca
Apple	36.36	50.42	415.35	72.07
Apple	16.59	45.8	373.32	49.37
Apple	10.39	47.43	368.73	36.71
Apple	32.97	38.18	332.11	26.9
Apple	22.4	47.99	344.63	72.44
Apple	1.12	38.62	391.77	50.34
Peach	129.2	40.33	257.23	26.35
Peach	9.24	20.28	52.52	32.83
Peach	17.56	36.38	265.62	39.48
Apricot	100.03	30.2	301.77	24.76
Apricot	59.52	39.47	377.6	72.67
Orange	15.57	32.79	196.35	43.27
Orange	17.9	28.84	72.91	66.92
Orange	11.08	25.92	75.58	338.35
Orange	81.43	43.61	265.24	35.73

Orange	87.72	55.7	334.92	31.64
Orange	25.12	120.61	642.34	81.02
Kiwi	39.23	23.42	102.74	22.93
Pear	62.19	31.22	170.21	21.54
Multifruit	196.11	13.07	74.91	42.90
Pineapple	119.97	140.42	413.72	103.09

Table 1: The concentrations for minerals (mg/L) of commercial juice samples.

The concentration ranges are the following for the major elements: 1.12–196.11 mg/L for Na, 13.07–140.42 mg/L for Mg, 52.52–642.34 mg/L for K and 21.54–338.35 mg/L for Ca. The higher Ca and K content was founded in orange juices (orange 3 and orange 6), while the bigger amount of Na was detected in the multifruit juices (multifruit) and for the Mg concentration a maximum was observed in pineapple juices (pineapple). Heavy metals composition of foods is of interest because of their essential or toxic nature. For example, Fe, Zn, Cu, Cr, Co, and Mn are essential, while As, Pb, Cd, Ni, and Hg are toxic at certain levels The concentrations of heavy metals, Cr, Mn, Co, Ni, Cu, Zn, As, Cd, and Pb, in analyzed commercial fruit juices samples are presented in Table 2The SD of measurement juice samples was, 0.35, 3.75, 0.05, 0.17, 0.69, 3.38, 0.05,0.03, and 0.10 for Cr, Mn, Co, Ni, Cu,

Zn, As, Cd, and Pb, respectively. The US Environmental Protection Agency (USEPA) has carried out risk assessments dealing with the toxicity by establishing References Doses (RfDs) for a large number of chemicals, including some essential trace elements. The World Health Organization (WHO) has set similar values for toxicity, termed Acceptable Daily Intakes (ADIs) We compared the heavy metals content founded in our investigated fruit juices with international organizations

WHO (2008) USEPA, recommended drinking water standards (Table 3)
Cr is an essential micro nutrient for animals and plants and is considered as a biological and pollution significant The Scientific World Journal 3

Sample	Cr	Mn	Co	Ni	Cu	Zn	As	Cd	Pb
Apple	4.11	213.72	0.26	18.96	99.12	180.16	3.6	0.14	24.84
Apple	4	127.08	1.24	42.46	57.66	196.96	1.52	0.24	5.86
Apple	55.6	268.22	8.3	58.22	104.78	379.1	<DL	0.84	4.66
Apple	5.69	293.16	DL	36.22	37.58	171.24	0.94	0.26	17.4
Apple	23.58	342.92	4.42	123.6	64.2	103.54	4.36	1.42	75.68
Apple	30.9	207.12	0.74	204.4	153.68	348.76	<DL	0.8	7.82
Peach	39.64	229.8	7.6	26.11	403.88	568.92	1.52	0.52	5.96
Peach	5.61	59.6	<DL	53.12	20.72	236.94	DL	0.64	1.94
Peach	30.44	198.9	6.84	25.42	322.94	1186.06	3.78	1.38	18.58
Apricot	55.45	244.46	7	35.04	139.34	445.74	1.52	0.46	5.36
Apricot	26.98	206.98	1.2	146.6	534.22	516.42	1.52	0.78	3.36
Orange	8.17	64.14	<DL	57	203.72	188.7	<DL	0.12	10.03
Orange	5.69	88.24	<DL	31.24	33.28	199.78	<DL	<DL	1.08
Orange	5.28	71.66	<DL	67.72	37.86	189.56	<DL	0.64	1.02
Orange	17.13	92.42	<DL	40.28	129.74	100.18	1.7	<DL	1.66
Orange	20.71	97.3	2.76	145	88.5	201.04	3.02	0.4	1.96
Orange	28.21	307.88	2.18	134.16	303.9	204.12	1.52	0.26	3.98
Kiwi	8.69	66.7	1.2	46.04	442.38	118.44	<DL	<DL	1.64
Pear	7.56	169.56	6.3	31.52	214.16	123.66	<DL	<DL	0.64
Multifruit	4.46	131.64	<DL	32.2	25.44	277.6	0.38	<DL	1.88
Pineapple	27.05	320.8	6.54	208.96	171.98	498.74	2.84	0.64	1.54

Table 2: The levels of heavy metals in investigated samples (g/L)
DL: detection limit, 0.001g/L.

	Cr	Mn	Co	Ni	Cu	Zn	As	Cd	Pb
US-EPA(2008)	100	50	100	100	1300	5000	10	5	15
WHO(2008)	50	400	aNM	70	2000	NGLb	10	3	10

a NM: not mentioned.

b NGL: no guideline, because it occurs in drinking water at concentrations

Table 3: Drinking water contaminants and maximum admissible limit by different international organizations. Heavy metals (g/L)

well below those at which toxic effects may occur. element. Cr in excess amounts can be toxic especially in the hexavalent form. The data obtained for most samples which were analyzed are smaller than maximum admissible limit set by WHO (2008) (50g/L), excepting two samples: apple 3 and apricot 1. The concentrations of Cr in commercial fruit juices are bellow the USEPA (2008) maximum admissible limit of this element in drinking water (100g/L). In our study, the Mn concentration was above the accept able limit for drinking water, according to USEPA standard, for all samples, but did not exceed the limit allowed by WHO (2008). Co is a necessary co-factor for making the thyroid hormone thyroxin. Co has also been used in anemia treatment as it causes the red blood cells production. The toxicity of Co is quite low compared to that of many other metals.All the samples contained Co present concentrations bellow the maximum admissible limit of USEPA (2008) and WHO (2008). The allowed limits in drinking water for Ni are 100g/L (by USEPA) and 70 g/L (by WHO). It can be noticed that six values of Ni concentrations from investigated fruit juices are over these limits.

Table 4: The metal concentrations of fruit juices in present study compared with the published values.

Type of fruit juices	Concentration ($\mu g/L$) Cr	Zn	Cu	Co	Mn	Ni	Cd	Pb	Reference used method
Orange	5.75	242–480	239–460						[13–15] GFAAS, FAAS
	11.5	842; 511	271; 309	10.3; 20	28.7				[16–19] ICP-MS, AAS
		400	400			20			[17, 20] ASS
	5.57				16–90	19.7–58.7			[17] ASS
		350.2	370.8	3.9	93; 19.6	11.3; 30			[17, 21] ICP-MS, ICP-AES
	2.4	731.5	422.3	2.8	27.5	28.3			[16] ICP-MS
	6.11	921.64; 60	515; 23	8.17; 0.9	21.56; 180	5.90; 20.5		2	[1, 22] GFAAS, ICP-MS
	5.28–28.21	100.18–204.12	33.28–303.90	2.18–2.76	64.14–307.88	31.24–145.00	0.12–0.64	1.02–10.03	Present study ICP-MS (range)
Apple		691	335; 416	30					[10, 19] RIMS
	8; 10	560; 474	535		56	13			[10, 14, 23] GFAAS, spectrofluorimetry
	16; 6.61	544.96	330.50; 73	8.39	24.42; 75	6.46; 3.9		0.2	[1, 16, 22] ICP-MS, GFAAS
	56.04	156.20	315.30	0.75		30.10	0.28–0.43	1.56–3.42	[24] ICP-MS
	4.00–55.60	103.54–379.10	37.58–153.68	0.26–8.30	127.08–342.92	36.22–204.40	0.14–1.42	4.66–75.68	Present study ICP-MS (range)
Pineapple		573.0	160	3.7	1360	43.5	1.1	1.6	[1] ICP-MS
	27.05	498.74	171.98	6.54	320.80	208.96	0.64	1.54	Present study ICP-MS
Pear		370	58		140	15.3	0.3	0.7	[1] ICP-MS
	7.56	123.66	214.16	6.30	169.56	31.52	<DL	1.62	Present study ICP-MS
Peach		400	230		210	21.4	0.6	0.6	[1] ICP-MS
	5.61–30.44	236.94–1186.06	20.72–322.94	6.84–7.60	59.60–229.80	25.42–53.12	0.52–1.38	1.94–18.58	Present study ICP-MS (range)

DL: detection limit, 0.001 $\mu g/L$.

The higher Ni content observed for these samples could arise from contamination either from the processing step or from an existing contamination in the drinking water used in fruit juices processing. Compared with the maximum acceptable limit for Cu concentration in drinking water, cooper's concentrations are lower than their maximum limit values. Zn is one of the important trace elements that play a vital role in the physiological and metabolic process of many organisms. Nevertheless, higher concentrations of Zn can be toxic to the organism. Cd is highly toxic and responsible for several cases of poisoning through food. Small quantities of Cd cause adverse changes in the arteries of human kidney. It replaces Zn biochemically and causes high blood pressures, kidney damage, and so forth .Pb and Cd toxicity are well documented and are recognized as a major environmental health risk throughout the world. Because of their high toxicity, As, Pb, and Cd need to be quantified in food and beverages.In this study, both concentrations of Zn, As and Cd are bellow the limits imposed by USEPA (2008) and WHO (2008). The analysis of Pb content reveals the fact that five fruit juices samples (apple 1, apple 4, apple 5, peach 3, and orange 1) exceed the allowable limits for drinking water. Taking into account that lead is less mobile than Cd in the soil-plant4 .

The sources of fruit juices contamination are most probably either the added sugar or the water used in the fruit juices reconstruction. The concentrations of the metals found in all fruit juices are compared with the values reported in literature for the fruit juices The wide variation range of reported data in literature could be explained both by the variability of used raw materials in the fruit juices production and manufacturing processes employed. Because fruit juices are coming from different countries, the metals content reflects differences in soil composition where the fruits were grown.

4. Conclusions

This study presents data on the concentrations of minerals and heavy metals in commercial fruit juices (apple, peach, apricot, orange, kiwi, pear, pineapple, and multi-fruit) present on Romanian market. The highest content of Ca and K was found in orange juices, whereas Mg concentration had a maximum in pineapple juice. The obtained content of heavy metals and minerals in fruit juices is due to the concentration of these elements in raw materials and also is influenced by the manufacturing process. The metal concentration in raw materials depends on a number of factors, including the soil composition, the external conditions during fruit growing and fruit harvesting

Determination of heavy metal content of grape juice concentrate

Introduction

Grape juice concentrate (GJC)is evaporated, concentrated and shelf-life extended form of grape syrup or the other berries and fruit juices.Since ancient times, evaporated grape syrup has been traditionally produced In most Iranian regions by using varieties of grapes.The color of the GJC changes from dark brown to white depending on the processing conditions, concentration, types of bleaching agents, heat and mixing rate. GJC contains important daily value of nutrition,caloric value and aroma compounds. Since GJC contains high amounts of sugar, minerals and organic acids, it is an important food product in human nutrition. GJC is easily assimilated because it mostly consists of carbohydrate in the form of monosaccharides like glucose and fructose.Furthermore,GJC supplies approximately 1226 kJ/100 g of energy and also contains important organic acids and mineral matters. GJC is a rich source of chemical elements essential to human body, such as copper, zinc and iron. Iron contained in GJC may be useful in the treatment of anemia patients. Clarification ways of GJC are similar to those of clarification of grape juice.In fruit juice industry, clarification is a unified process that comprises the elimination of undesired color and flavor; turbidity; bitterness and gassy.In the process of clarification, clarifiers are utilized which are combined with charged particles of fruit juice such as protein, pectin and phenolic materials and are consequently

separated from the environment.Usual Clarifiers in fruit juice industry are bent on it, gelatin and silicasol, but in traditional production, a certain white soil called GJCS is used as the clarifier material in the production of GJC.In addition to depositing suspending material, the soil neutralizes the acidity of the grape juice.] but this soil might deliver some heavy metals to the final product. So the aim of this study was to determine some heavy metals in GJC samples produced by traditional method.

Materials and Methods

The GJC samples(20) were supplied from local supermarkets of 9 citiesin Khorasan province according to TABLE 1. In this study the GJC samples had been prepared using a certain white soil called grape juice concentrate soil asthe clarifier material. Heavy Metals Including Arsenic(As),Lead(Pb),Mercury(Hg), Cadmium (Cd),Tin (Sn), Calcium (Ca), Magnesium (Mg) and Iron (Fe) were determined byASS method. Preparation of GJC Samples for Atomic Absorption Spectroscopy (AAS) After mixing the samples very well to obtain homogenity, 10g of the samples weighed in a borosilicate glass beaker and the dry ashing method advised by Jorhem (1993) was applie. Later, ash was diluted to 10ml with 10% of nitric acid (Merck). Preparation of standards of trace elements Five standards were set for the calibration of the AAS to determine trace elements. These concentrations were different from metalt another one.The calibration curve of well prepared standard and an accurate Atomic Absorption Spectrophotometer should present as a linear curve. Apparatus AnAnalytik Jena, ContrAA700AAS (Jena, Ger- many) equipped with a GFAAS was used in the ex- periments. Aspect CS Version 1.5.1 software was used. The operating parameters for working This element were set as recommended by the manufacturer. Statistical analysis The data of metals concentrations were analysed by Excel sented

Results and Discussion

Grape contains valuable minerals such as calcium (840ñ866 ppm) and iron (50ñ100 ppm).The high iron content makes it a recommended treat for anemia. So we expect that grape juice concentrate to be rich of these minerals. In the production of GJC, the grape juice is concentrated about 5-6 times and we expect the nutritious metals to be increased in GJC as the same rate, but the resultsinTABLE1 shows that the average content of calcium and iron was 817 and 60 ppm respectively which is equal to the grape samples. However GJC composition deviates due to grape type and production conditions(such as equipments, filter aid,clarifying agent and environmental conditions).We think that in the clarification stage,some elements are also removed in the precipitate.Also the average content of the other metals were as follows:Arsenic 8.2 ppb,Lead 36.6 ppb, Mercury 1.4 ppb, Cadmium 0.37 ppb, Tin 4.9 ppm and Magnesium 1704 ppm. But no limit has been defined for these pollutants in GJC in Iranian standard organization.The national standard no 12968, on fruit juices has limited the heavymetals as described in

Region	No. Of sample	As (ppb)	Pb(ppb)	Hg(ppb)	Cd (ppb)	Sn(ppb)	Ca(ppm)	Mg (ppm)	Fe (ppm
Kashmar	2	0.1	31.9	0.9	0	<0.2	210	1175	5
Torbat-e-heydarie	2	10.1	0	2.1	0	2.7	390	1890	78
Qaaen	2	9.9	0	0.1	0	<0.2	2540	2398	34
Birjand	2	3.1	218	0	1.3	<0.2	740	1292	30
Bojnourd	2	23	0.1	0.9	0	<0.2	630	1058	18
Gonabad	2	20	0	2.2	0	<0.2	500	2250	331
Qouchan	2	0.1	1	1.6	0	<0.2	390	1270	11

Sabzewar	2	0	78	3.3	0	<0.2	1040	1925	28
Average	-	8.2	36.6	1.4	0.37	4.9	817	1704	60
SD	-	8.6	73	1.1	0.75	13.2	698	507	104
Maximum	-	23	218	3.3	2	40	2540	2398	331

TABLE 1: Heavy metals content of GJC samples

TABLE 2.According to this standard, only lead has a limit concentration equal to 0.05 ppm and the Pb content of GJC samples is 36.6 ppb which is lower than

This standard. The other heavymetals, except for tin,are lower than 50 ppb.Tin is a heavymetal which imparts to the food goods Specially when the container or processing vessels are tin coated

.

Heavy metal	**Accepted limit (ppm)**
Arsenic	--
Lead	0.05
Cadmium	--
Mercury	--
Tin	--

TABLE2 :Acceptable dosage for heavy metals in fruit juices according to Iranian national standard

According to the other studies pekmez (local name of GJC in Turkey) contained: Calcium: 51-206 mg/ 100g;Sodium:25-83mg/100g;Manganese: 11-68mg/ 100g; Phosphorus: 81-95mg/100g; Magnesium: 140 mg/100g; Iron: 2.6-16mg/100g;Copper: 0.3-0.9 mg/ 100g and Zinc: 0.2-0.7 mg/100g.

One of the main intervening agents on the qualitative properties of GJC I s the type of clarifying agent used. Clarification is a unified process that comprises the elimination of undesired color, aroma and flavor;turbidity;bitterness and gassy.In the process of clarification, clarifiers are utilized which are combined with charged particles of fruit juice such as protein, pectin and phenolic materials and are consequently separated from the environment.When soil is used as the clarifying agent, in addition to depositing suspending material,the soil neutralizes he acidity of the grape juice

Conclusion

This traditional product is a rich source of chemical elements essential to human body including Iron,Mag- nesiumand Calcium, but some heavymetals also w ere available in concentrations below50 ppb except for tin (4.9ppm). If the clarifying agent could be replaced by non-pollutant agents, this food risk will not be existed anymore.

METHOD

Determination of Lead in Fruit Juices

Procedure

As and Pb standard solutions, 1000 mg/L (SpectrosoL) was obtained from BDH (BDH Chemicals Ltd, Poole, England). HNO3 65%, H2O2 30%, HCl 32%, NaOH, NaBH4, and potassium iodide (KI) were purchased from Merck
Company (Darmstadt, Germany). Deionized water (DI) was used for preparing all solutions. All laboratory glassware and plasticware were soaked in HNO3 solution (20% v/v) for two days. Before using, all of them were rinsed four times with DI water and dried.
Standard working solutions at various concentrations were prepared daily by appropriate dilutions of the stock solution with DI water. A Perkin-Elmer model 3030 atomic absorption spectrometer (PerkinElmer, USA) equipped with graphite furnace, flame, and MHS-10 mercury/hydride system was used for absorbance measurements.

The instrumental parameters were listed in Table 1 and 2. Fifty varieties of commercial fruit juices (grape, apple, orange pomegranate, and multi-fruit) from 5 popular brands (A, B, C, D and E) were purchased from local markets of Mashhad during spring and winter 2016.
The total number of samples was 25 for the winter sampling and 25 for the spring sampling. Five samples of each brand were analyzed for the presence of heavy metals.
To determine the Pb levels in fruit juices by graphite furnace atomic absorption spectroscopy (GFAAS), 5 mL of each sample was transferred into a Teflon digestion vessel with a cover. Then, 6 mL of the acid

mixture (HNO_3/ H_2O_2 2:1) along with 2 mL DI water were added and the mixture left overnight at room temperature.

The following day, some organic contents of the matrix were decomposed by heating the vessel at 100 °C for about 40 min on a hot-plate. After cooling, 2 mL of H_2O_2 was added to the solution and then further decomposed by microwave oven digestion with the following microwave programming: the heating from room temperature to 140 °C for 20 min, holding at 140 °C for 20 min (up to 800 W) and turning off the microwave and waiting for 20 min. When the vessel cooled, the contents were gently heated at 100 °C to evaporate the sample nearly to 4 mL. Next, 3 mL of the acid mixture HNO_3/ H_2O_2 was added again and the above mentioned procedure was repeated. After cooling, the contents of the vessel were transferred to a 25.0-mL volumetric flask by washing the interior surface of the vessel with 0.05 mol/L HNO_3 for three times. Afterward, the solution was diluted to the mark with DI water. Blank solutions were also prepared to document contamination resulting from the analytical process. For determination of As in fruit juice by hydride generation-flame atomic absorption spectroscopy (HG-FAAS), 10 mL of standard or juice sample was transferred into a 15 mL glass tube. Then 3 mL of HCL 32% and 1 mL of KI 10% (w/v) were added and incubated for 60 min at room
temperature thereafter. Finally, a portion of the mixture was injected into the MHS 10 system for the FAAS determination of As III hydrides. Data were statistically analyzed using Student *t*test to determine significant differences in the data of two seasons. Statistical tests were performed using INSTAT software (GraphPad, San Diego, CA). *P*-values less than 0.05 were considered significant. The values are expressed as mean ± standard error of the mean (SEM).

RESULTS

The obtained concentrations of As and Pb for 50 commercial fruit juices were shown in Table 3. The plots of the metal concentrations in these samples were presented in Fig. 1. The contents of Pb were 19.9-43.7 ng/mL in grape, 25.5-52.2 ng/mL in Arsenic and Lead Contaminations in Commercial Iranian Journal of Toxicology 17 http://www.ijt.ir; Volume 12, No 3, May-June 2018.

Apple, 22.9-54.6 ng/mL in orange, 25.4-50.6 ng/mL in pomegranate, and 18.5-54.6 ng/mL in multi-fruit. Orange A and multi-fruit A samples had a higher Pb level than the others, whilst multi-fruit E contained the lowest (Fig. 1a). The Pb levels in fruit juices ranged from18.5 to 54.6 ng/mL, and 83% of these values were above the maximum values stated by the CAC (30 ng/mL). These values for As were 1.52-2.15 ng/mL in grape, 1.82-2.21 ng/mL in apple, 1.68-2.21 ng/mL in orange, 1.62-2.15 ng/mL in pomegranate, and 1.55-2.35 ng/mL in multi-fruit (Fig. 1b). The lowest As content was found in grape B, while the highest was found in multi-fruit C.

The contents of As ranged from 1.52 ng/mL to 2.35 ng/mL and were all

Table 2. HG-FAAS operating condition.

Flame type	Air-acetylene
Wavelength (nm)	193.7
Slit width (nm)	0.7
Lamp current (mA)	6
Ar (purge gas) flow rate (mL/min)	1.5
Pre-reductant solution	KI 10% (w/v)
Reductant concentration (NaBH4)	3% (w/v) of NaBH4 in 1% (w/v) of NaoH

Atomize	2000	1	3	0
Clean	2500	1	2	250

below the maximum value recommended by WHO (10 ng/mL).

Type of Sample	Pb (ng/mL)	Pb(ng/mL)

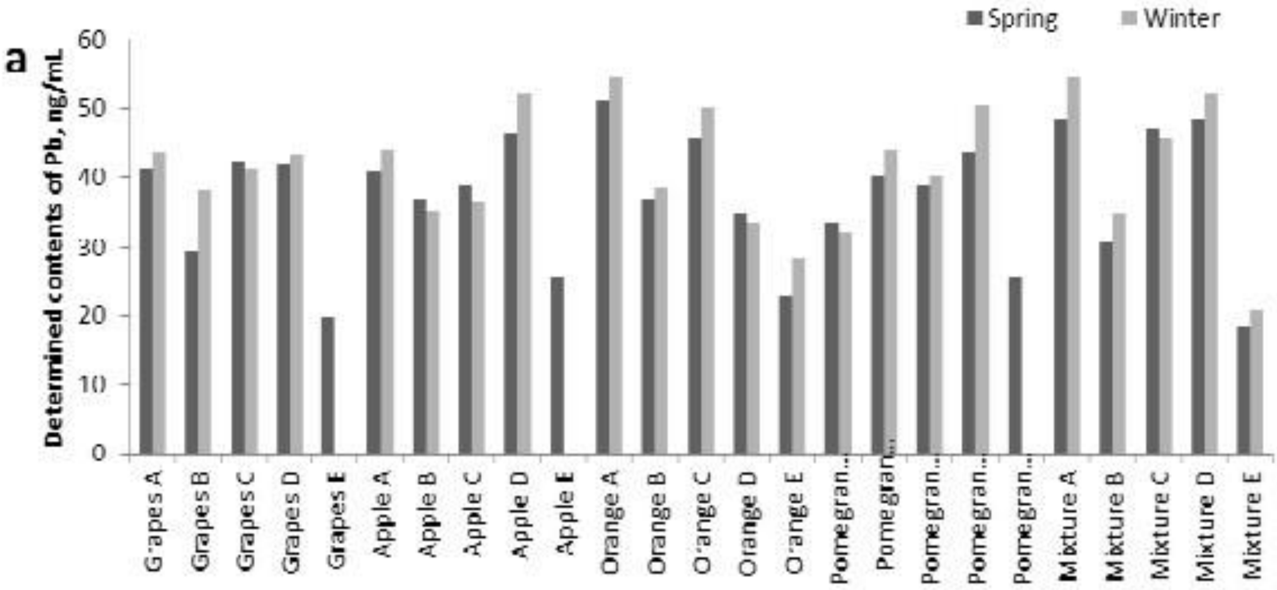
GrapeA	41.5	43.7
GrapeB	29.5	38.1
Grape C	42.5	41.1
GrapeD	42	43.5
GrapeE	19.9	NDa
Mean±SEM	35.1±4.5	41.6±1.31
Minimum	19.9	38.1
Maximum	42.5	43.7
AppleA	40.8	44.2
AppleB	36.8	35.2
AppleC	38.8	36.5
AppleE	25.5	ND
Mean±SEM	37.7±3.43	42.0±3.93
Minimumvalue	25.5	35.2
Maximumvalue	46.4	52.2
OrangeA	51.1	54.6
OrangeB	36.6	38.5
OrangeC	45.6	50.2
OrangeD	34.8	33.5
OrangeE	22.9	28.5
Mean±SEM	38.2±4.84	41.1±4.94

Minimumvalue	22.9	28.5
PomegranateA	1.7	1.88
PomegranateB	40.1	44.2
PomegranateC	38.9	40.1
Pomegranate	43.8	50.6
Mean±SEM	36.3±3.20	41.8±3.83
Minimumvalue	25.4	32.3
Maximumvalue	43.8	50.6

Pb concentrations in commercial packaged-fruit juices collected during spring and winter 2016. On the whole, 50 samples were analyzed (five samples for each brand): spring, 25 samples and winter, 25 samples.

DISCUSSION

The results were compared to those of other published studies (Table 4).



The reported levels of Pb in some of mentioned studies [4,20–22] were higher than those of the present study. Moreover, Pb levels in the rest of mentioned studies were lower than or nearly equal to our results [5,6,23–

26]. The contents of As in the present study were similar or lower than those of all mentioned studies. The contents of selected heavy metals in commercial fruit juice vary in a wide range. The metal variability comes from the raw materials used in the fruit juices production and used processing technologies. The soil composition, ground-water chemistry, the external conditions during fruit growing and fruit harvesting are factors that may influence the concentration and distribution of metal contaminants in raw material. Therefore, the raw materials must be monitored to trace the origin of these contaminants. In addition, processing equipment and procedures performed during the fruit processing can also be considered as a possible source of heavy metals contamination. For example, some of the Pb and As present in juices may be due to contamination of the water used in the fruit juices reconstruction or the added sugar or the imported dried fruits. Hence, in order to reduce the transfer of these heavy metals to juices, processing procedures are carefully checked to reduce the concentration of these contaminants in final products.

CONCLUSION

All samples had As levels that did not exceed the maximum acceptable levels recommended by CAC. However, in 83 percent of those samples, Pb levels were higher than related maximum permissible levels (>30 ng/mL). Therefore, materials that provide significant exposure to heavy metals such as fruit juices must be closely and regularly monitored.

FUTURESCOPE

Fruit juices are a highly appreciated, tasty food and usually have exceptional nutritional qualities.Fruit juices are widely consumed by all age groups in the world .Fruit juices is the easiest way to add fruit goodness in your daily diet and keep you healthy and boost you immunity.

But what is fruit juices make you seek and add toxicity in your body however their intake over the past two decades has rapidly increased because they can reduce the risks of many chronic and degenerative diseases However, heavy metal contaminants might accumulate during fruit growth, transportation, processing, handling, and packaging The concentration of heavy metals in fruit juices depends on many factors such as the nature of the fruit, the mineral composition of the soil and the irrigation water, the climatic conditions, as well as the agricultural practices such as the types and amounts of fertilizers .Heavy metals are natural constituents of the earth's crust and are found throughout the environment in the air, water, and soil. As results of natural processes or human activity, they can be released and accumulate into the food or water . Lead (Pb) and arsenic (As), for instance, are two of major contaminants of the food supply that can accumulate in the body and cause harmful effects The aim of this study was the precise determination of mineral and heavy metal content from the most known commercial fruit juices present compare these results with the maximum admissible limit set in drinking water by different international organizations: United States Environmental Protection Agency (USEPA) and World Health Organization (WHO) and also with the values of different countries available in literature.

Beacuse Of This Covid-19 Pandamic I Coudn’t conduct This Research Personally so I really want to do this research on indian market.

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