تقدير بعض العناصر النادرة في عينات خل مختلفة في السوق الليبية باستخدام مطياف الانبعاث الذري لحث البلازما

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الملخص العربي :

تم جمع عشر عينات من الخل من السوق المحلية الليبية في مدينة طرابلس. العناصر التي تم تعيينها هي: As و Pb و Cu و Zn و Fe. تم معالجة العينات وتجهيزها وفقا للمواصفة الهندية IS 14703-1999 ، ومن ثم تحليل العناصر باستخدام جهاز الحث المزدوج لطيف البلازما (ICP-AES) الموجود بمعهد النفط الليبي. أظهر التحليل أن تركيز الزرنيخ لجميع العينات كانت أقل من 0.02 ملغ / كجم بينما كان تركيز الرصاص أقل من 0.03 ملغ / كجم. تراوح تركيز كل من Cu و Feو Zn عند 0.11-0.59 ملغ\كلغ و 0.72-2.67 ملغ\كلغ و 0.08-0.28 ملغ\كلغ على التوالي. تركيزات العناصر As و Pb و Cu و Fe و Zn تقع ضمن حدود مجموعة متنوعة من المعايير القياسية مثل المواصفة الليبية والمواصفة الهندية والمواصفة الباكستانية.

Determination of Some Trace Elements in Different Vinegar Samples from Libyan Market using Inductively Coupled Plasma Atomic Emission Spectrometer ICP-AES

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Abstract

Ten vinegar samples were collected from the Libyan local market in the city of Tripoli. The elements have been investigated were:

As, Pb, Cu, Fe and Zn. The samples were treated and prepared according to Indian standard IS 14703-1999, and the measurements have been done by using inductively coupled plasm – atomic emission spectroscopy (ICP-AES) available in the Libyan Petroleum Institute. The analysis indicated that the concentration of Arsenic of all the samples was less than 0.02mg/kg whereas, the concentration of lead is less than 0.03mg/kg. The concentration ranges of Cu, Fe and Zn were 0.11-0.59mg/kg, 0.72-2.67mg/kg and 0.08-0.28mg/kg respectively. The concentrations of the elements AS, Pb, Cu, Fe and Zn are within the limits of a variety of standards such as Libyan, Indian and Pakistani ones.

Key words: Trace elements, Vinegar, Libyan market, Inductively Coupled Plasma Atomic Emission Spectroscopy ICP-AES.

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Introduction

Vinegar is a liquid, acceptable for human consumption. It has a habitual use in different house purposes such as kitchen condiment in salad dressings and sauce, health remedies etc. Vinegar is an old fermented product in the world and its invention dates back to around 2000 BC (Morin and Lees, 2013). Vinegar solely produced from products containing starch and/or sugar such as rice, wheat, millet and sorghum (Cruess, 1958). For the production of vinegar a process of double fermentation is used. After producing alcohol by the first step of fermentation, acetic acid solution is obtained in the second step by genus of bacteria, 'Acetobacter' acetic acid is producced. Vinegar is also can be produced by chemical synthetic from natural gas and

Petroleum derivatives in a form of high concentrated acetic acid (Huang et al., 2004).

Vinegars have also been characterized to distinguish different types and fermentation behavior during the production processes (Cirlini et al., 2011). Studies on the metal elements in vinegar are rare and have been done by few workers (i.e. Qin-bao et al., 2012; Mahmood et al., 2013).

Determination of different trace elements in food stuff is interesting because of their nutritional and toxicological characteristics. Critical micronutrients such as copper, zinc and selenium are important in human physiology, but they are not synthesized by human body (Qin-bao, 2012). The elements in vinegar could originate from the raw materials of the vinegar itself, or from production location and environmental conditions, processing method, and packing material (Qin-bao et al., 2012; Mahmood et al., 2013). Different methods of sample preparation and different techniques have been used for the determination of trace elements in vinegar (Qin-bao et al., 2012 and Mahmood et al., 2013). The aim of this study is to examine the concentration of some trace metal (As, Pb, Cu, Fe and Zn) in the vinegar samples available in the Libyan markets in the city of Tripoli Libya.

Experimental work

All chemicals used in this study were analytical grade and deionized water was used for all solutions. Ten different bottled vinegar samples were randomly selected from different supermarkets in Tripoli. Table 1 shows the type and identification of vinegar samples which were investigated.

The treatment of analysed samples was done using a modified official method to obtain an ash (Indian standard IS 14703-1999). 25ml of the sample was transferred to a pre-burned, cooled and weighed porcelain crucible. The crucible with its contents was heated first on water bath till dryness; the dry extract was then introduced into a furnace at 540 ± 10˚C (at rate of 10˚C/min) and kept at maximum for 30minutes. The ash layer in the crucible was broken down and some hot distilled water was added. The solution was then filtered through a filter paper and the filter paper was brought to the crucible which burned again at 525 ˚C for 30minutes. After that, the filtrate was added to the crucible and heated again at 525 ˚C for 15minutes. The crucible was cooled down and 2ml of concentrated HNO_3 was added and the mixture was heated on a hotplate to dryness. 10ml of 2N HNO_3 was added while the crucible on the hotplate and the heating continued for 2minutes. The solution was then filtered receiving the filtrate in 100ml volumetric flask. The crucible was washed 3 times with the 2N HNO_3 solution. Finally the filter paper was washed several times with the same dilute nitric acid solution and the flask was filled up to the mark with the acid solution. The flask was well shaken and taken to the ICP-AES (Varian, Vista-Pro) for analysis. The ICP-AES was accompanied with a cross-flow nebulizer, and elements were measured at wavelengths of 193.7nm, 283.3nm, 324.8nm, 259.9nm, and 213.9nm for As, Pb, Cu, Fe and Zn respectively.

Results and Discussion

Table 2 shows the maximum limits of the elements As, Pb, Cu, Fe and Zn according to the Libyan, Indian and Pakistani standard regulations.

Table 1 Identifications of analyzed vinegar samples

No.	Sample name	Sample identity	Ash (m/m)%	Density (g/ml)
1	Al-Asail	Natural vinegar, Local made	0.0340	0.99888
2	Fersan	Apple vinegar, Turkish made, contains sodium metasulfate, sulfur dioxide	0.1230	1.00276
3	Heinz	White natural vinegar, Egyptian made	0.0240	1.00533
4	Cappana	UAE made, contains caramel	0.0710	1.00693
5	Merry	Apple vinegar, Spain made, contains antioxidants, sulfur dioxide	0.2260	1.01277
6	Merry	White vinegar, Spain made	0.0380	1.00668
7	Golden	White vinegar UAE made	0.0090	1.00481
8	Sabrina	White vinegar, Local made	0.0490	1.00276
9	Al-Sumbola	Apple vinegar, Local made	0.0240	0.99988
10	Nare	Grapes vinegar, Turkish made, contains sodium metasulfate	0.1810	1.01168

Table 2 the standards for maximum heavy metal limits in vinegar

Elements	Libyan		Indian		Pakistani
Max (mg/kg)	natural	Artificial	Natural	Artificial	
As	1.0	1.0	---	1.0	0.1
Pb	1.0	1.0	---	Nil	2.0
Cu	---	10 *	---	Nil	10
Fe	10	---	---	10	30
Zn	---	*	---	10	100
Ash (w/w)%	0.5 min	0.5 min	0.18	---	---
* Libyan standards conceder total of Cu and Zn as 10 mg/kg.					

With comparing the results of the samples showing in table 3 with the standard regulations shown in table 2, one can say that all sample found obeying the standards regarding the elements

As, Pb, Cu, Fe and Zn regardless the vinegar whether it is natural or artificial.

Table 3 the results of As, Pb, Cu, Fe ad Zn in mg/kg.

Sample identification	Element concentrations (mg/kg)				
	As	Pb	Cu	Fe	Zn
Al-Aseel	< 0.02	< 0.03	0.589	0.977	0.212
Fersan	< 0.02	< 0.03	0.355	2.668	0.234
Heinz	< 0.02	< 0.03	0.163	1.245	0.199
Cappana	< 0.02	< 0.03	0.226	1.517	0.218
Merry apple	< 0.02	< 0.03	0.454	1.102	0.276
Merry white	< 0.02	< 0.03	0.330	1.176	0.238
Golden	< 0.02	< 0.03	0.334	1.047	0.183
Sabrina	< 0.02	< 0.03	0.455	2.433	0.251
Al-Sombula	< 0.02	< 0.03	0.184	2.360	0.188
Nare	< 0.02	< 0.03	0.111	0.724	0.087

Arsenic can reach the environment either naturally or anthropogenic way. The natural sources are mainly from volcanic activity and low temperature volatilization (biological methylation), and it is much larger than the anthropogenic ones. Arsenic is also found in ground water. Whereas, anthropogenic sources of arsenic originate from the use of pesticides, copper smelters, mining activity, landfill from dumping slag, wastewater from smelters and refineries, which contribute indirectly to land and water contamination (Sánez, 2012). Arsenic is toxic and can cause several health effects in humans, including cancer. Arsenic in water or plants like berries and grapes are more of concern, because they can be absorbed. Arsenic concentration in vinegar analyzed using Hach Test Kit found to be 0.07ppm (Butterfield et al., 2005). In this research arsenic found to be less than 0.02mg/kg. In 1989, both FAO and WHO established a temporary acceptable dietary intake of 0.015 mg inorganic As/kg body weight/week, or 130 µg/day for a 60 kg adult (IPCS, 2001).

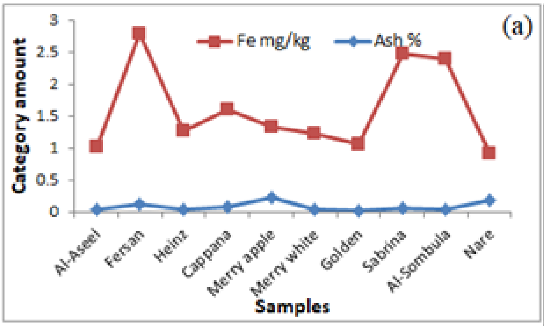
Lead is the most common industrial metal that has become widespread in air, water, soil and food (Mukesh et al., 2008). Lead is very toxic for the nervous system, kidneys and other organs of the body. The safe intake of lead is 15-280 µg/ml for adults and 10-275 µg/ml for children. A range of Lead concentration was found to be 0.20-1.25 µg/ml in variety of vinegar samples (Mukesh et al., 2008). In our case the lead concentration was less than 0.02mg/kg for all the analyzed samples.

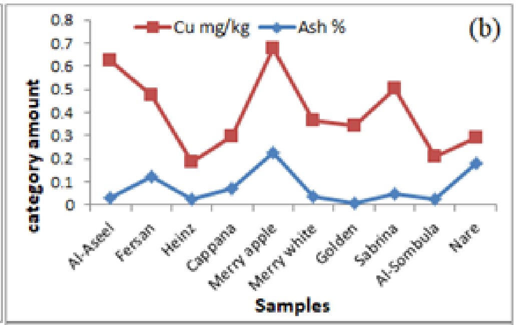
Copper is one of the essential micronutrients required in many life forms. Being a transition metal, copper gets biologically converted between different redox states namely oxidized Cu^{2+} and reduced Cu^{+}. Therefore, copper is then involved in a variety of biological processes, embryonic development, mitochondrial respiration, regulation of hemoglobin levels as well as hepatocyte and neuronal functions (Krupanidhi et al., 2008). A typical recommended daily requirement is 1.2 mg for adults and 0.5-1 mg for children (Rajeswari and Swaminathan, 2014). The copper content in the vinegar investigated in our study ranges from 0.11mg/kg to 0.59mg/kg. The main source of copper in vinegar is apple which contains about 4mg/kg (Downing, 1989).

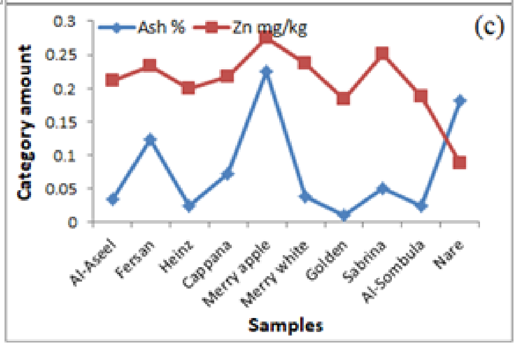
Iron either plays an important role in the metabolic process. The role of iron in the body is clearly associated with hemoglobin and the transfer of oxygen from lungs to tissue cells (Hamilton et al., 2000). The amount of iron in vinegar found by Mahmood et al. (2013) was 3.50µg/ml in cactus vinegar and 0.21µg/mL in Hawthorn vinegar. In this study, the iron concentration was 0.72-2.67mg/kg which is about 0.73-2.64µg/ml.

Zinc is necessary for the growth and multiplication of cells (Seiler, 1994). Zinc is involved in about 100 enzyme activity in the body. There are 2-3 grams of zinc present in the human body and about 1mg/L in plasma (Fraga, 2005). Zinc deficiency causes loss weight, Severe deficiency may lead to acrodermatitis enteropathica (Seiler et al., 1994) and is associated with malnutrition in underdeveloped countries. Mahmood et al (2013) found 4.33 µg/ml of Zinc in Giger vinegar and 0.14 µg/ml in synthetic white vinegar. In our study the zinc concentration is 0.08-0.28µg/ml. zinc recommended intake is 9.6mg based on 50kg adult body weight (WADA, 2004).

From table 1we can see that the ash content of the samples is lower than the limit value of Libyan and Indian standards, except the sample Nare is less than the limit of Libyan standard but it is just within the limit of Indian standard 0.181%(m/m). However, all samples are less than the recommended limit, some samples (i.e. Feras, Cappana, Merry apple and Nare) have about 10 times higher values of ash than the others because these samples contain either antioxidant material such as sodium metasulfate and/or caramel.







Fgure 1 the relation between ash percent and element concentration: Iron (a), Copper (b) and Zinc (c).

However, this large amount of ash does not relate to the concentration of iron (Fig. 1-a). From figure 1-b it is clear that the concentration of copper is following the trend of that for ash content except for the sample Al-Aseel. The concentration of zinc is also in the same trend of the ash content along the samples profile excluding the sample Nare (Fig. 1-c).

Conclusion

Based on the results shown above, we can say that these samples of vinegar are safe to use if the other physical and chemical properties are agree with the standards regulations. Moreover, these samples need to be analyzed for some other important categories such as acetic acid content, Residual alcohol, total solid, soluble solid … etc.

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