Turkish Journal of Engineering

Turkish Journal of Engineering (TUJE)
Vol. 4, Issue 2, pp. 92-96, April 2020
ISSN 2587-1366, Turkey
DOI: 10.31127/tuje.623785
Research Article

ANALYSIS OF THE TRACE ELEMENT CONTENT OF GRAPE MOLASSES PRODUCED BY TRADITIONAL MEANS

Hacer Sibel Karapınar *[1] and Fevzi Kılıçel [2]

[1] Scientific and Technological Research & Application Center, Karamanoğlu Mehmetbey University, Karaman, Turkey
ORCID ID 0000-0002-0123-3901
sibelkarapinar@kmu.edu.tr

[2] Karamanoğlu Mehmetbey University, Kamil Özdağ Science Faculty, Department of Chemistry, Karaman, Turkey
ORCID ID 0000-0002-5454-5597
fevzi@kmu.edu.tr

*Corresponding Author

Received: 24/09/2019 Accepted: 13/12/2019

ABSTRACT

Molasses, sugar and other food additives, such as without adding any substance, concentrated by boiling and shelf life is a long concentrated product. Molasses is an important food for humans in terms of mineral content and high energy content. Grape fruit is considered as a rich food source with strong health effects. Grape fruit generally contains 70-80% water, 15-25% carbohydrate and small amount of minerals, amino acids, phenolic compounds. Heavy metals are highly toxic elements, which can severely influence plants and animals and have been involved in causing a large number of afflictions. Heavy metals in the environment are non-biodegradable and ubiquitous, it can cause serious human health hazards and momentous ecological effects through food chain's bioaccumulation. Inorganic micro-pollutants are of important concern because they are non-biodegradable, highly toxic and have a probable carcinogenic influence. In this study, it was aimed to determine the heavy metal levels in grape molasses collected from the villages of Karaman and to emphasize the importance of nutrition in carob molasses. The samples were prepared to be 2 parallel for each sample and were solutioned by wet burning method. The concentrations of the determined elements were determined by Flame Atomic Absorption Spectrometry (FAAS). Traditional produced grape molasses are determined by comparing metal contents with each other and with standard values.

Keywords: *Molasses, Grape, Trace element, FAAS*

1. INTRODUCTION

Molasses is a traditional sweets prepared in many Mediterranean countries commonly known as 'pekmez' in Turkey. Molasses can be produced from various fruits such as grape, mulberry, apple and carob (Petkova *et al*., 2017). Since molasses contain carbohydrates in the form of monosaccharides such as glucose and fructose, they can easily pass into the blood without being digested. This is especially important for infants, children, athletes and those who need urgent energy (Tosun & Ustun, 2003). It is also a dark viscous liquid containing sugar, amino acids, vitamins and a group of minerals (Zhang *et al*., 2015, Xia *et al*., 2016). Grape has an important place in molasses production. Grape is grown in our country, especially in rural areas and is consumed as molasses after being concentrated and kept in the sun and brought to consistency due to its limited consumption as fresh (Viran *et al*., 2003). There are micro and macro elements in the grape (K, Ca, Mg, Na, Zn, Mn, Fe and Cu). The presence of elements such as As, Cr, Pb and Cd which show toxic properties are caused by anthropogenic activities such as industrial processes, agricultural applications, use of minerals discharge of toxic residues or soil composition (Segura-Muñoz, 2006). Chromium can be considered essential or toxic to living organisms depending on the oxidation state (Quináia & Nóbrega, 1999). The elements Pb and Cd do not have a biological function and are extremely toxic to living organisms. These elements cause various damages to the body (kidney, neurological, hepatic, inter alia cardiovascular) and can also cause various types of cancer such as lung, prostate, and testis. Recently developed analytical methods for the determination of minerals in foodstuffs have features such as high precision, easy to apply, low cost, robustness, selectivity, speed, and environmental friendliness. Analytical techniques that can be used for this purpose are inductively coupled plasma atomic emission spectroscopy (ICP-OES and ICP-MS) (Ohki *et al*., 2016), flame atomic absorption spectrometry (FAAS) (Yıldız *et al*., 2016). In this work, trace element levels of Zn, Pb, Ni, Cu, Cr, Mg, Mn, Ca and Fe in grape molasses produced in 12 different villages of Karaman province were investigated. Samples were prepared according to wet burning method and mineral analysis were performed with FAAS method.

2. MATERIALS AND METHODS

2.1. Study Area

Grape molasses were collected from 12 different places which were produced by traditional. Samples were gathered from Manyan, Burhan, Pınarbaşı, Başkışla, Morcalı, Bozkandak, Aygan, Bostanözü, Bucakışla, Kızılyaka, villages, Ermenek and Karaman center. Fig. 1 shows the sampling locations on the map. In this study, samples of molasses prepared by using freshly harvested grape fruits from 12 different producers without waiting were taken and analyzes were carried out on these samples.

Fig. 1. Map of sampling locations

2.2. Methods

Molasses were produced on the same day without waiting from the harvested grape fruits. In the molasses made by traditional methods, grape molasses are first squeezed in various ways and juice is obtained. The grape juice collected is boiled at 50-60 ° C for 10-15 minutes and molasses soil is added. After resting for 4-5 hours, the substance formed is molasses by removing the sediment from the bottom of the container and boiling again. The samples were brought to the laboratory by placing them in 200 ml bottles of molasses made from newly harvested grapes in 2017. Weighed 2 g each of the samples which were made ready for weighing with precision scales and placed them in 100 ml beakers. 16 ml of HNO_3 (65%, w/w, Merck) was added and allowed to stand for 8-10 hours. Then, 4 ml of $HClO_4$ (70-72%, w/w, Merck) were added and the solutions were heated slowly in the fume hood for 5-6 hours. Heating was stopped near the end of the acids, and after cooling the solutions, 5 ml of H_2O_2 (30%, w/w, Merck) were added. Heating was carried out until clear liquid was obtained. The cooled samples were filtered through blue band filter paper and filled to 20 ml with distilled water and stored in a refrigerator at 4 °C until analysis. Flame atomic absorption spectrometry (FAAS) (Perkin Elmer 900T) was used for elemental analysis of the samples.

2.3. Evaluation of Instrumental and Method Performance

The method and instrumental performance were evaluated by determining the detection limit (LOD) and the quantification limit (LOQ). LOD and LOQ were calculated as 3xSD/b and 10xSD/b, respectively, where SD is the standard deviation of 10 consecutive measures of the analytical blank and b is the slope of the analytical curve (ICH, 1996). Table 1 presents the linear ranges used for calibration and the coefficients of determination (R^2) used to assess the linearity (R^2>0.99). LOD, LOQ and precision are given in Table 2.

3. Results and Discussion

Each molasses sample was prepared for analysis in 2 parallel and 3 replicate measurements were taken from each sample. The concentrations of trace elements in molasses samples are given in Table 3, 4. Pb, Mn, Cr element concentrations of molasses samples taken from 12 different places are shown in Fig. 2, 3, 4. Perkin Elmer 900T series FAAS was used for this work. Instrument operating conditions were given Table 5.

Table 1. Linear range (mgkg^{-1}), regression, correlation coefficient (R^2), for the elements analyzed

Element	Linear Range	Regression	R^2
Cu	0.5 - 5	y=0.020x + 0.002	0.992
Cr	0.5 - 5	y=0.014x - 0.003	0.995
Fe	1 - 10	y=0.042x - 0.023	0.997
Ca	0.1- 10	y=15.20x - 0.111	0.998
Ni	0.1 - 5	y=0.034x - 0.019	0.999
Mg	0.1 - 5	y=2.124x - 0.123	0.999
Mn	0.1 - 5	y=0.054x + 0.005	0.998
Zn	0.1 - 5	y=0.156x + 0.003	0.994
Pb	0.5 - 5	y=0.121x - 0.045	0.998

Table 2. LOD, LOQ and precision (RSD%) for the elemental analyzed

Element	LOD (mgkg^{-1})	LOQ (mgkg^{-1})	Precision (RSD%)
Cu	1.543	5.138	0.565
Cr	2.457	8.181	0.721
Fe	1.451	4.831	0.733
Ca	0.049	0.163	0.119
Ni	2.232	7.432	0.223
Mg	0.124	0.413	0.721
Mn	1.192	3.969	0.869
Zn	0.765	2.547	0.348
Pb	1.487	4.952	0.712

Table 3. Trace element concentrations in molasses samples (mgkg^{-1})

	Average±SD				
	Zn	**Pb**	**Ni**	**Cu**	**Cr**
1	2.887	1.516	1.576	9.985	0.130
	±0.028	±0.042	±0.066	±0.167	±0.038
2	1.466	1.397	0.399	2.102	0.069
	±0.073	±0.167	±0.099	±0.080	±0.047
3	1.417	5.993	0.274	1.580	0.002
	±0.349	±0.131	±0.091	±0.155	
4	1.407	2.151	0.226	2.063	0.009
	±0.021	±0.188	±0.032	±0.172	
5	1.319	2.349	0.050	1.122	0.050
	±0.101	±0.764	±0.034	±0.094	±0.008
6	1.521	1.150	0.112	4.607	0.019
	±0.058	±0.140	±0.090	±0.224	±0.005
7	1.518	1.203	0.145	1.397	0.102
	±0.057	±0.202	±0.064	±0.053	
8	3.390	0.745	0.052	0.769	0.018
	±0.289	±0.184	±0.029	±0.107	
9	1.158	1.072	0.187	2.300	0.067
	±0.060	±0.188	±0.053	±0.111	±0.005
10	1.053	1.120	0.341	1.422	0.093
	±0.074	±0.117	±0.014	±0.084	±0.003
11	1.029	1.274	0.396	1.378	0.014
	±0.021	±0.145	±0.022	±0.049	
12	11.13	1.971	0.274	1.226	0.092
	±0.193	±0.181	±0.055	±0.061	±0.025

SD: Standard Deviation

Table 4. Trace concentrations in molasses samples (mgkg^{-1})

	Average±SD			
	Mg	**Mn**	**Ca**	**Fe**
1	203.1	10.52	231.6	20.72
	±2.447	±0.149	±3.535	±2.581
2	203.4	1.547	163.3	11.62
	±2.688	±0.027	±6.793	±1.540
3	218.0	0.508	190.9	12.27
	±3.102	±0.020	±2.486	±0.383
4	201.2	1.241	232.7	11.58
	±2.413	±0.015	±1.484	±0.756
5	139.3	0.528	214.6	10.21
	±1.532	±0.014	±2.547	±0.560
6	186.5	0.752	221.9	21.73
	±3.758	±0.011	±4.768	±0.627
7	215.5	6.341	152.7	33.89
	±2.819	±0.152	±1.290	±0.442
8	184.7	5.303	233.6	21.68
	±3.366	±0.100	±1.092	±0.460
9	179.8	2.057	214.8	17.78
	±2.375	±0.031	±3.282	±0.417
10	211.8	4.829	228.1	20.83
	±2.972	±0.070	±1.301	±0.203
11	202.4	4.552	229.6	20.90
	±2.598	±0.078	±1.380	±0.706
12	183.3	4.336	197.7	29.59
	±2.709	±0.081	±1.186	±1.126

Table 5. Instrument Operating Conditions

Element	Wavelength (nm)	Current intensity (mA)	Slit width (nm)
Cu	324.8	15	0.7
Cr	357.9	25	0.7
Fe	248.0	30	0.2
Ca	422.7	20	0.7
Ni	232.0	25	0.2
Mg	285.2	20	0.7
Mn	279.5	20	0.2
Zn	213.9	15	0.7
Pb	283.31	440	0.7

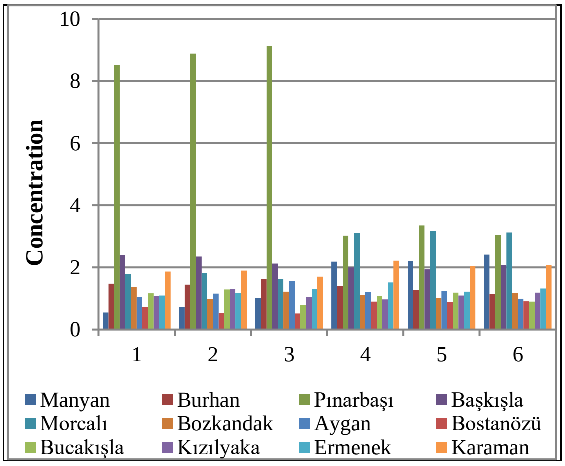

Fig. 2. Pb element concentrations of molasses samples taken from 12 different places (mgkg^{-1})

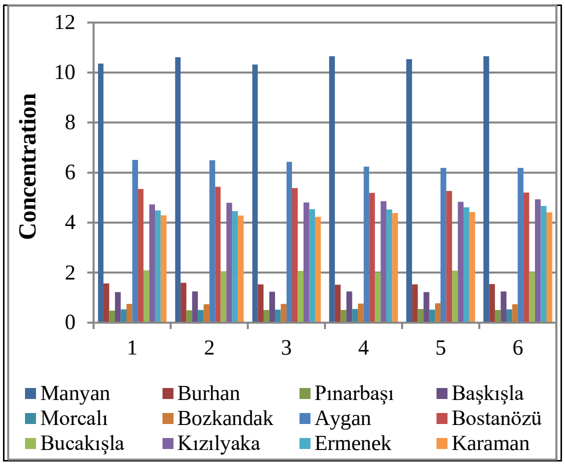

Fig. 3. Mn element concentrations of molasses samples taken from 12 different places (mgkg^{-1})

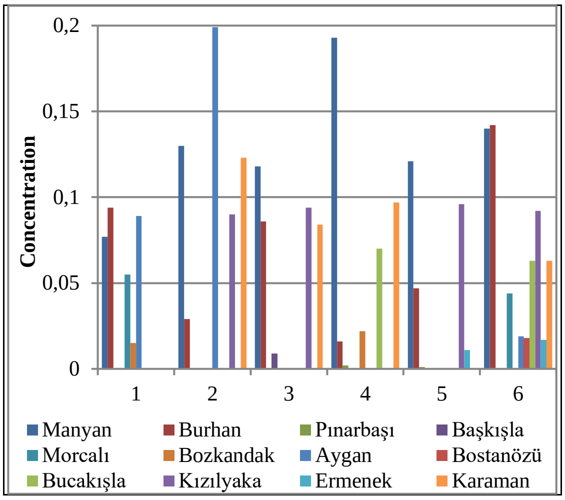

Fig. 4. Cr element concentrations of molasses samples taken from 12 different places (mgkg^{-1})

Food products contaminated with various types of heavy metals threaten human health. Cr and Pb heavy metals are toxic and carcinogenic, especially Pb causes stomach cancers (Zahao *et al*., 2014). Chatterjee (2000), found that Cu is toxic in terms of its negative effects on physiological activities. The concentration of heavy metals and evaluation are given Table 6. In this study, according to the literature values given in Table 6, Ni (0.050-1.576 mgkg^{-1}), Fe (17.78-33.89 mgkg^{-1}), Cu (0.769-9.985 mgkg^{-1}), Mn (0.508-10.52 mgkg^{-1}), Pb (0.745-5.993 mgkg^{-1}), Ca (152.7-231.6 mgkg^{-1}) high amounts; Mg (139.3-218 mgkg^{-1}) at low levels; Cr (0.002-0.130 mgkg^{-1}) and Zn (1.029-3.390 mgkg^{-1}) elements were determined at normal concentrations in molasses samples.

Tosun and Ustun, (2003) found iron content ranging from 26.2 to 163.0 mgkg^{-1} in molasses samples. Artık and Velioğlu, (1993) in their study stated that the iron content in molasses is 100 mgkg^{-1}. According to these studies, iron content remained low in our study. However, it was found to be higher than Table 6. Demirci, (2006) determined that ingredient of calcium in traditional method was 1051.6 mgkg^{-1} in grape molasses.

In this study, Ca content was found to be low levels according to the literature. Copper is found in the structure of some polyphenolase enzymes. Excess copper has a toxic effect on the body. Tosun and Ustun, (2003) studied 11 molasses samples and found that the copper level ranged from 2.9 to 9.4 mgkg^{-1}. Our values are consistent with these values. However, it was observed that it was higher than the literature values given in Table 6. Zinc is found in the composition of certain enzymes and hormones and influence their work. It is also involved in the regeneration of cells and tissues by taking part in DNA and RNA synthesis, but high amounts of zinc have toxic effects on the body (Tarakçı & Küçüköner, 2003). Pb is an element with multiple effects. The absorbed lead passes into the blood and reaches equilibrium in a short time and is distributed to various organs through blood circulation (Assis *et al*., 2008). Zinc values found in our study were consistent with the literature, but lead levels were found to be high.

Table 6. The concentration of heavy metals and evaluation (Demirözü *et al*., 2002; Karababa & Develi, 2005; Akbulut & Özcan, 2008; TFC, 2017)

Element	Founded value (mgkg^{-1})	Accepted value	Evaluation
Cr	0.002-0.130	0.20-45 (µgg^{-1})	Normal
Zn	1.029-3.390	< 5 (µgg^{-1})	Normal
Mn	0.508-10.52	6.2 (µgg^{-1})	High
Mg	139.3-218	730 (µgg^{-1})	Low
Ni	0.050-1.576	0.5 (mgkg^{-1})	High
Fe	17.78-33.89	< 25 (mgkg^{-1})	High
Cu	0.769-9.985	< 5 (mgkg^{-1})	High
Pb	0.745-5.993	< 0.30 (mgkg^{-1})	High
Ca	152.7-231.6	130-144 (mgkg^{-1})	High

4. CONCLUSIONS

Environmental pollutants, food safety and human health are inextricably linked. Sources of heavy metals in food products are changing in developing countries. Heavy metals can be managed by reducing the use of treated waste material or by properly treating sewage before it can be used for irrigation (Cherfi *et al*.. 2015). Optimization of land use improves food safety. Roadside food products tend to accumulate metal on plant leaves and fruit (Nabulo *et al*.. 2006). There may be heavy metal pollution from soil where grapes are grown. In the molasses produced in the traditional way soil is used in the production stage and metal pollution from this can occur in molasses. In addition, Pb, Cd, Cr, Zn and Mn pollution can come from fertilizers used for fruit production (Fan *et al*.. 2017). In order to avoid health risks the available remediation options should focus on reducing the concentration of heavy metals in the soil and food chain. It is necessary to prevent the transfer of metal pollutants to the food chain and formulate appropriate healing strategies.

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