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Determination of Heavy Metals in Fruit Juices by Flame Atomic Absorption Spectrometry

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In this study, direct determination of Cu, Fe, Cr, Mn, Zn, Pb, Na, Mg, Ca and K in commercially available fruit juices in Turkish markets, which are often consumed in daily nutrition, was carried out by using flame atomic absorption spectrometry (FAAS). It was found that the average values were below the tolerance limits of analytes. The detection limits (3σ values, N = 10) lie between 1.8 and 4.7 μg L^{-1} depending on the element. The results were compared with the average daily intake amounts permitted as well as the values written on the packages.

Key Words: FAAS, Trace Elements, Fruit Juices.

INTRODUCTION

Flame atomic absorption spectrometry (FAAS) is the most widely used technique for elemental determination owing to its simple set up, low running costs and good selectivity[1,2]. The use of FAAS for direct determination of trace elements in food and beverages samples can help to improve frequent difficulties in analytical procedures *i.e.*, quantification of metals at trace levels and time spent in sample preparation. These problems are frequently achieved in quality control of the foods[3].

Organic compounds such as proteins, carbohydrates and oils form the major parts of the food composition. Beside these compounds, there are small amounts inorganic compounds and elements. Although the amount of these elements is not high, their importance in human health is not negligible[4]. Their absence or high dosages may cause different diseases even death. Therefore, the determination of the metals in foods and beverages is important due to their essential or toxic action.

Heavy metals can be classified as vital and non-vital according to their contribution rates to biologic processes. The vital ones should be exist in the organisms up to a certain concentrations and these metals should be taken into the body regularly due to their contribution to biological reactions.

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Zinc, copper, iron, manganese are known to be essential nutrients, but they can be toxic depending on the concentration[4-7]. The determination of chromium and lead is very important due to their high toxic effect. Zinc constituents about 33 mg kg^{-1} of an adult body mass and is essential as a constituents of many enzymes involved in several physiological functions, such as protein synthesis and energy metabolism[8]. It is mainly taken to the body by the meat group foods such as liver, sea foods. An adult human body contains about 100 mg of copper and the amount of daily uptake is declared as 1.0-3.0 mg[4,8]. Copper is essential as a constituent of some metaloenzymes and is required in hemoglobin synthesis and in the catalysis of metabolic oxidation[9]. All kind of foods and their biological materials contain iron. Its daily uptake amount is 1.7-8.7 mg for children and 14.8 mg for adults. Iron complexes provide the transportation of oxygen to the body *via* hemoglobin[3,10]. Manganese is one of the essential elements that its biological function is to activate the enzymes. It is also a necessary mineral for the central nerve system. It presents in all animal and vegetal tissues. Its daily consumption is 4.5 mg per person. Suggested daily amount is 1.4 mg for adults and 16 µg for children[3,10]. The amount of chromium in foods is generally low level. It plays important physiological role on the glucose and insulin. The limit chromium values are 25 µg for adults and 0.1-1.0 µg for children[3,6,10]. Lead exists in the foods as a natural component. But, it should be removed when its level in foods reaches toxic amount for human health.

Dietary sodium is measured in milligrams (mg)[3,6,10]. The most common form of sodium used is table salt, which is 40 % sodium. Sodium is also added to various food products, both for taste and as a preservative. Thus, the more processed the food, the higher the sodium content is likely to be. Foods reconstituted with water (*e.g.*, soups, bouillon cubes, processed meats) also contain salt. Its concentration in fruits varies between 1.4-3.5 mg/100 g. The minimum daily amount for adults is 460 mg.

Potassium is classified as one of the essential elements[4,10]. It arranges the concentrations and diffusions of the liquids out of cells. It is also a component for balancing the pH of bodies and for healthy nervous system and brain function. Generally, all the foods contain high amount of potassium. Its concentration in fruits is between 100-300 mg/100 g. The recommended daily potassium intake is 4.7 g a day.

Magnesium is the fourth most abundant mineral in the body and is essential to good health[11]. Magnesium is needed for more than 300 biochemical reactions in the body. It helps maintain normal muscle and nerve function, keeps heart rhythm steady, supports a healthy immune system and keeps bones strong. Magnesium also helps regulate blood sugar levels, promotes normal blood pressure and is known to be involved in energy metabolism and protein synthesis[12]. The daily value for magnesium is 400 mg.

Fruit juices are widely consumed in all ages due to flavour and nutritive value. The concentrations of the above mentioned elements can vary in a wide range. In this study, the direct determination of zinc, copper, iron, chromium, manganese, zinc, lead, sodium, magnesium and calcium in commercially available fruit juices samples sold in Turkish markets was achieved without any preliminary sample preparation except dilution.

EXPERIMENTAL

An Analytik Jena Vario 6 flame atomic absorption spectrometer was used throughout the experiments. The instrumental parameters for all elements determined were set according to the manufacturer recommendations and given in Table-1.

TABLE-1
INSTRUMENTAL CONDITIONS FOR ANALYZED ELEMENTS

Elements	Wavelength (nm)	Slit width (nm)	Flame type
Cu	324.8	1.2	Air/Acetylene
Fe	248.3	0.2	Air/Acetylene
Cr	357.8	0.2	Air/Acetylene
Mn	279.3	0.5	Air/Acetylene
Zn	213.9	0.8	Air/Acetylene
Pb	283.3	1.2	Air/Acetylene
Na	589.0	1.2	Air/Acetylene
Mg	285.2	0.8	Air/Acetylene
Ca	422.7	1.2	N_2O_2/Asetylene
K	776.5	0.2	Air/Acetylene

All solutions were prepared using analytical-reagent grade and deionized water. Standard solutions of all the elements were prepared by diluting the stock solutions containing 1000 mg L^{-1} (Merck) with deionized water. Different brands commercial juices (cherry, apple, orange, peach and apricot) that were bought from local markets were analyzed. For the measurements of sodium, magnesium, calcium and potassium, all sample solutions were diluted to appropriate concentrations with deionized distilled water immediately before use while for other elements samples were given to the flame directly without any dilution.

RESULTS AND DISCUSSION

The figures of merit for the analyzed elements can be seen in Table-3. Calibration curves were obtained with aqueous reference solutions for each analyte.

Linear calibration with aqueous reference solutions was applied. The limit of detection (LOD) was defined as the concentration corresponding to three times the standard deviation of 10 measurements of the blank divided by the slope of analytical curve. Three replicates were measured for each sample. The calibration graphic for each elements analyzed was drawn and slopes values were obtained from these graphics. The concentrations of the elements were calculated by using the linear calibration graphics.

Apple, cherry and orange juices were introduced to the instrument directly. Peach and apricot juices were filtered prior to measurement to prevent accumulation of solid deposits on the burner and flame fluctuations[13]. All elements in the samples were found in the linear range. Different brands of 5 cherry juices, 4 orange juices, 1 apple juice, 2 peach juices and 2 apricot juices of samples were chosen to compare. The results are given in Table-2. The concentrations of Cu, Fe, Mn, Zn, Na, Mg, Ca and K could be determined by directly aspirating the samples into the flame without any treatment while those of Pb, Cr, were below their detection limits. The detection limits (3σ values, N = 10) for Cu, Fe, Mn, Zn, Na, Mg, Ca and K in aqueous solution were 4.7, 3.1, 2.5, 2.5, 1.7, 1.8, 5.1, 3.1 μg L^{1}, respectively. As can be seen from the table, the concentrations of analyzed elements

TABLE-2
CONCENTRATIONS OF THE ANALYZED ELEMENTS IN THE SAMPLES

Sample**	Analyzed elements (mg/L)									
	Cu	Fe	Cr*	Mn	Zn	Pb*	Na	Mg	Ca	K
Cherry A	0.019	2.238	–	0.434	0.136	–	94.9	27.9	34.7	358.0
Cherry B	0.019	1.285	–	0.258	0.097	–	36.8	52.4	60.0	421.5
Cherry C	0.019	0.476	–	0.176	0.214	–	12.8	50.9	118.1	456.0
Cherry D	0.019	0.476	–	0.164	0.166	–	16.5	55.8	100.0	451.0
Cherry E	0.019	1.143	–	0.293	0.175	–	123.8	44.2	37.6	475.5
Orange B	0.112	0.262	–	0.117	0.214	–	29.3	67.0	53.2	779.0
Orange C	0.093	0.500	–	0.270	0.224	–	18.1	18.1	126.9	784.0
Orange D	0.074	0.167	–	0.211	0.214	–	17.6	66.4	112.7	691.0
Orange E	0.093	0.333	–	0.117	0.185	–	123.8	54.0	35.1	755.0
Apple D	0.037	0.952	–	0.668	0.146	–	29.8	63.7	124.0	824.0
Peach A	0.130	0.815	–	0.164	0.314	–	67.7	37.2	36.1	588.0
Peach C	0.112	0.529	–	0.117	0.266	–	9.4	46.2	80.0	735.0
Apricot B	0.130	1.498	–	0.117	0.290	–	4.1	39.6	25.9	931.0
Apricot D	0.074	0.661	–	0.176	0.185	–	9.8	44.0	74.2	882.0

*Under the detection limit of FAAS
**A, B, C, D and E represent different brands. The values were the averages of at least three determination and RSD values were lower than 10 %.

TABLE-3
ANALYTICAL CHARACTERISTICS OF THE ANALYZED ELEMENTS BY FAAS

Parameter	Aqueous									
	Cu	Fe	Cr	Mn	Zn	Pb	Na	Mg	Ca	K
Regression equation y =	0.0454x-0.0003	0.053x-0.002	0.0448x	0.0954x - 0.004	0.1552x+0.0114	0.027x	0.35x + 0.065	0.2556x + 0.0048	1.996x	0.0852x-0.0012
R^2	0.9977	0.9998	0.9995	0.9999	0.9998	0.9975	0.9999	0.9999	0.9998	0.9985
Linear range (mg L^{-1})	Up to 5	Up to 6	Up to 6	Up to 5	Up to 4	Up to 8	Up to 5	Up to 4	Up to 4	Up to 5
LOD (µg L^{-1})	4.7	3.1	**	2.5	2.5	**	1.7	1.8	5.1	3.1
LOQ (µg L^{-1})	15.6	10.3	**	8.3	8.3	**	5.7	6.0	17	10.3

**Under the detection limit of AAS.

TABLE-4
DAILY INTAKES OF ANALYZED ELEMENTS

Element	Cu	Fe	Cr	Mn	Zn	Pb	Na	Mg	Ca	K
Daily intake amount	1-3 mg	8.7-14.8 mg	0.1-1.0 ?g	4.5 mg	9-15 mg	0.024 mg	2-5.9 g	300-500 mg	1.0 g	1.7-6.9 g

TABLE-5
COMPARISON OF WRITTEN AND EXPERIMENTAL VALUES OF SOME ELEMENTS

Sample	Na (mg L^{-1})		K (mg L^{-1})		Mg (mg L^{-1})		Ca (mg L^{-1})	
	Written	Found	Written	Found	Written	Found	Written	Found
Cherry A	84.0	80.0	-	-	-	-	-	-
Cherry C	-	-	1128.0	1000.0	38.0	35.8	76.0	75.0
Cherry D	-	-	1128.0	980.0	38.0	34.5	76.0	72.5
Orange C	-	-	1058.0	925.0	69.0	66.4	57.0	55.0
Orange D	-	-	1058.0	975.0	69.0	71.5	57.0	57.5
Apple D	-	-	1696.0	1560.0	88.0	82.5	86.0	88.0

changed depending on their brands (and thus origin). Variations in element concentrations in the fruit juice samples may be attributed to the composition changes or different botanical structures or chemical treatments producers applied.

The average daily intake amounts of analyzed elements were given in Table-4. The concentration of elements in the fruit juices analyzed are under the range of suggested values and do not damage the human health[4].

The values on packages of some elements (K, Ca, Mg, Na) written by producers were also compared with the experimental results (Table-5). This comparison was made for only the elements given on the packages by the producers. From the data, it can be seen that there is no significant difference between the experimental results and given values on the packages.

Conclusion

In this study, it was shown that copper, iron, manganese, zinc, sodium, magnesium, calcium and potassium in fruit juices could be directly determined. No pretreatment was required thus minimizing the time and reagents consumed in the analysis. The concentration of lead and chromium was under the detection limit of FAAS. This can show that either the fruit juices do not contain these toxic elements or they can be determined by the instruments, which have low detection limit.

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