Quantitative Analysis of Some Metals in Almond Kernel in Erbil City

Kamal M. Mahmoud* and Roza T. Yasin

Department of Chemistry, College of Science, Salahaddin University- Erbil (SUE),
Iraqi Kurdistan Region, Iraq
*E-mail: kamal.mahmoud@su.edu.krd or kamal_k58@yahoo.com

Abstract

This paper includes determination of moisture (7.2%) and total ash (2.5%) from the sweet and bitter almond kernel fruit of Erbil city. The amounts of elements including: Na, Ca and K as alkaline metals and Cd, Co, Pb, Ni, Cr as heavy metals have been determined by using both atomic emission and absorption spectrometry. The analysis results indicate that amount of potassium was the highest (276.525 µg ml^{-1}) this is an importation, because it is necessary for the function of all living cells, and the sodium was the lowest (64.91 µg ml^{-1}) as an alkaline metals. While, for heavy metals the amount of chromium was the highest (4.577 µg ml^{-1}) which is a suitable biochemical nutritional to promote weight loss, muscle development and to treat the symptoms of type 2 diabetes , and the lead was the lowest (1.598 µg ml^{-1}), which is good because lead is toxic to kidney, brain and bone demineralization.

Keywords: Almond, Alkaline metals, Heavy metals, Atomic emission spectrometry, Atomic absorption spectrometry.

1. INTRODUCTION

Almond (*Prunus dulcis*) is a member of the Rosaceae family (Nurhan, *et al*. 2010). Every year 2,035,489 tons of in-shell almonds are produced in the world from an area of 1,797,927 hectares. Almond kernels are one of the complete sources of energy as well as nutrients. The nuts are rich in mono unsaturated fatty acids that help in lowering LDL and increasing HDL in human body. Almond kernels are rich source of vitamin E, B-complex, protein, and minerals. Besides, it has significant levels of antioxidant activity and scavenging effect on free radicals. Almond kernels can be sweet, slightly bitter (semi bitter) or bitter. Bitter taste of almond and other Prunus species is related to the content of cyanogenic diglucoside amygdalin (Arrazola, *et al*. 2012, and Lee *et al*. 2014).

Atomic absorption spectrometry (AAS) was used to determine calcium, iron, magnesium, zinc, copper and manganese from Indian almond, while flame atomic emission spectrometry (FAES) was used to determine sodium and potassium in the sample. (0.17%) potassium, (0.25%) magnesium, (245.65 µg ml^{-1}) sodium, (845.45 µg ml^{-1}) calcium, (92.12 µg ml^{-1}) zinc, (70.62 µg ml^{-1}) iron and (9.21 µg ml^{-1}) copper were evaluated (Agunbiade and Olanlokun 2006).

Mutalik *et al.* (2011) were determined the potassium content in dry fruits such as (almond, cashewnut, pepper, pistachious, drydates, raisin (black), raisin (common), amla, acrota and apricot) using FAES. Its content in almond was (29.84 µg ml^{-1}), and the (RSD=1.67%). Potassium was found to be the most abundant with a level as high as 1.251 µg ml^{-1} in apricot and as low as 0.2184 µg ml^{-1} in Chinese beans.

The concentrations of some heavy metals (Cu, Cr, Ni, Pb, Co and Cd) in dry fruits such as almond were determined by AAS. The concentration of Cu ranges from (0.522-2.633 µg ml^{-1}), Co (0.01- 1.001 µg ml^{-1}), Cr (0.02- 0.909 µg ml^{-1}), Ni (2.550- 5.990 µg ml^{-1}), Pb (1.001- 10.002 µg ml^{-1}), and Cd (0.722- 8.332 µg ml^{-1}) (Manzoor, *et al.* 2013).

Yapo *et al.* (2014) were investigated on three heavy metals cadmium (Cd), chromium (Cr) and lead (Pb) in samples (almonds, teguments, fresh juice and fermented juices) of cocoa (*cocoa mercedes*). The purified liquid extract was analyzed by AAS with graphite furnace. The results revealed the bioavailability of the three heavy metals with variable concentration in different parts of the cocoa. The lowest concentrations were observed in Cr (min = 4.50 µg l^{-1}, max = 8.90 µg l^{-1}). The study brought up the concentrations (µg kg^{-1}) higher for Pb (min = 454.17 µg l^{-1} and max = 1690.0 µg l^{-1}) and Cd (min = 126. 08 µg $l^{-1}$and max = 644.0 µg l^{-1}). The (R^2) of the linear regression of the curves were superior to 0.99. The LOQ was respectively: (Cd = 0.5 µg l^{-1}), (Pb = 10.0 µg l^{-1}) and (Cr = 5.0 µg l^{-1}).

The aim of this work is the determination of some mineral cations such as (Na, K, Ca, Cd, Cu, Pb, Ni, and Cr) in almond kernel fruit in Erbil city, using (FAES and FAAS) respectively.

2. EXPERIMENTAL

2.1. Chemicals and Reagents:

The chemicals and reagents that were used for the analysis were of analytical grade. Distilled deionized water was used throughout.

2.2. Instruments and Apparatus

Spectral measurements were carried out on flame atomic emission spectrometer (FAES) (Sherwood 420 UK), and flame atomic absorption spectrophotometer (FAAS) (Buck scientific 210 VGP USA).

Oven (Kottermann) < 300 ºC (USA) and muffle furnace Heraeas (7908706 Germany) were used for drying and ignition of the sample.

2.3. Sampling:

The almond kernel food (with both types sweet and bitter) was taken from Kurdistan Region in Hawler market, valley of Balesan, between November and December 2013. The samples were stored in air-tight containers protected from light at room temperature. Dried plant material (almond kernel) was grounded in a beaker to obtain a fine powder.

2.4. Almond analysis:

2.4.1. Determination of Moisture

2.0 g sample was put in a weighing bottle and dried in air oven for 24 h at 100-105 °C, the hot dried sample transferred to a dissector to cool and weighed. The drying was repeated until a constant weight was obtained. The percentage of moisture content was 7.2%.

2.4.2. Determination of Total Ash Content

Ash content was determined by ignition of 2.0 g of the dried sample in a well-cleaned silica crucible and placed in a muffle furnace maintained at 550 °C for 5.0 h (Mutalik *et al.* 2011). The crucible cooled and weighed. Therefore, it could be kept for a longer time without spoilage, while the ash content will be signifies the level of minerals present in the sample.The total ash percentage was determined as 2.5%.

2.4.3. Determination of Alkaline and Heavy Metals

2.4.3.1. Preparation of Solution

The resultant ash was dissolved in 5.0 ml $HNO_3/HCl/H_2O$ (1:2:3), heated gently on a hot plate in a fume cupboard until brown fumes disappeared. To the remaining residue in each crucible, 5.0 ml of distilled deionized water was added and heated till colorless solution was obtained. The mineral solution in a crucible was transferred into 100 ml volumetric flask by filtration through a Whatman filter paper No. 42 and the volume was made up to the mark with distilled deionized water (Mutalik *et al.* 2011).

2.4.3.2. Determination of Na, K and Ca in Almond Using FAES

Elements (Na, K and Ca) were determined according to Mutalik *et al.* (2011) procedure, using flame atomic emission spectrometer with standardization of the instrument with distilled deionized water (blank) and standard solutions (1000 μg ml^{-1}) of Na, K, and Ca were prepared by dissolving 2.5435 g, 1.9130 g, and 1.8845 g of NaCl, KCl, and $CaCl_2$ respectively (these salts were dried previously at 105 °C for 2.0 h) in 50 ml of distilled deionized water, transfer quantitatively to 1.0 L volumetric flask, dilute with distilled deionized water with volume and mixed well.

2.4.3.3. Determination of Pb, Cu, Cd, Ni, and Cr in Almond Using FAAS

The amount of Pb, Cu, Cd, Ni, and Cr were determined according to Mutalik *et al.* (2011) procedure, using FAAS. Suitable hallow-cathode lamps (H.C.L.) were used as a source of radiation and a mixture of acetylene-air with a constant flow (0.8 L min^{-1}) to produced flame for evaporation and atomization of the sample. The instrument was standardized with distilled deionized water (blank) and standard solutions for each element. The stock solution for all metals (Pb, Cu, Cd, Ni, Cr) 1000 μg ml^{-1} were prepared by dissolving 1.0 g of each metal in 2.0% nitric acid and diluted to 1.0 L in a volumetric flask with distilled deionized water.

3. Results and Discussion

3.1. Determination of moisture and total ash contents:

The quality of almond kernel is generally examined with respect to moisture content and total ash. Table (1) shows the result of moisture and ash content for almond kernel.

Table (1): Some quality test results for almond kernel

No.	Qualitative Test	Results (%)	Standard %*
1	Moisture	7.2	7.4
2	Total Ash	2.5	2.81

* Liang and Fang (2006).

The results were acceptable as compared with standard values according to Liang and Fang (2006).

3.2. Determination of Alkaline Metals

A series of standard solutions for sodium chloride, potassium chloride, and calcium chloride in the range (50-300) µg ml^{-1} were prepared by taking a specific volume (5.0-30.0) ml from the stock solutions of Na, K, and Ca (1000 µg ml^{-1}) respectively, and transferred into a 100 ml volumetric flask contained 20 ml of distilled deionized water, mixed then diluted to mark with distilled deionized water. The calibration curve was made by plotting emission versus concentration of Na, K and Ca in µg ml^{-1}. Statistical data for calibration curve including; linear calibration range, least square relation, a detection limit, and a correlation coefficient (R^2) are shown in Table (2). The precision and accuracy of Na, K, and Ca by FAES were shown in Table (3).

Table (2): Statistical data for the calibration graph of the determination of alkaline metals by FAES

Metals	Linear range (µg ml^{-1})	least square relation	Detection limit (µg ml^{-1})	Correlation coefficient (R^2)
Sodium (Na)	50-300	$y = 0.1639x - 0.64$	0.000448	0.9941
Potassium (K)	50-300	$y = 0.1024x - 0.32$	0.036100	0.9960
Calcium (Ca)	50-300	$y = 0.1849x - 4.10$	0.026000	0.9902

Table (3): Precision and accuracy of alkaline metals by FAES

Metal	Metal concentration (µg ml^{-1}) (standard solution)	Practical conc. for standard sol. (µg ml^{-1})	S.D	RSD%	E%
Sodium (Na)	150	156	0.158	0.63	-4.0
Potassium (K)	200	198.4	0.158	0.79	0.8
Calcium (Ca)	150	146.5	0.158	0.68	2.33

3.2. Determination of Heavy Metals

3.2.1. Determination of Cadmium

A series of standard solutions for cadmium in the range (0.5-4.0) µg ml^{-1} were prepared by taking a specific volume (0.5-4.0) ml from the working solution of cadmium (100 µg ml^{-1}) and transferred into a 100 ml volumetric flask, then diluted to mark with distilled-deionized water. The calibration curve was made by plotting absorbance versus concentration of cadmium in µg ml^{-1}. Fig. (1) shows this relation. Statistical data for calibration curve including; linear calibration range, a detection limit, and a correlation coefficient (R^2), are shown in Table (4). The precision and accuracy of the method by FAAS was shown in Table (5).

Table (4): Statistical data for the calibration graph of the determination of cadmium by FAAS

Metal	Linear range (µg ml^{-1})	Detection limit (µg ml^{-1})	Correlation coefficient (R^2)
Cadmium (Cd)	0.5-4.0	0.028	0.9969

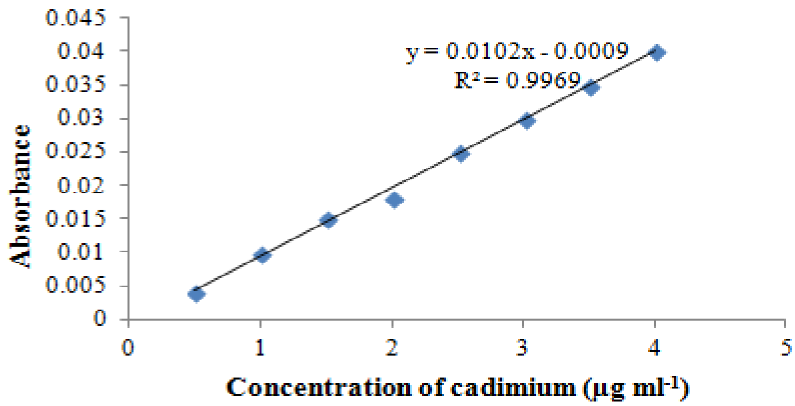

Fig. (1): Calibration graph for determination of cadmium concentration

Table (5): Precision and accuracy of cadmium by FAAS

Metal	Metal concentration (µg ml^{-1}) (standard solution)	Practical conc. for standard sol. (µg ml^{-1})	S.D	RSD%	E%
Cadmium	2.5	2.53	0.000219	2.76	-1.2

3.2.2. Determination of Copper

A series of standard solutions for copper in the range (0.5-14.5) µg ml^{-1} were prepared by taking a specific volume (0.5-14.5) ml from working solution of copper (100 µg ml^{-1}). The calibration curve was made and statistical data for calibration curve including; linear calibration range of (0.5-14.5) µg ml^{-1}, least square relation of ($y=0.0252x + 0.0374$), a correlation coefficient (R^2) of (0.9955) and a detection limit of (0.0074) µg ml^{-1}, are estimated, and Table (6) shows the precision and accuracy of copper by FAAS.

Table (6): Precision and accuracy of copper by FAAS

Metal	Metal concentration (µg ml^{-1}) (standard solution)	Practical conc. for standard sol. (µg ml^{-1})	S.D	RSD%	E%
Copper	8.5	8.504	0.015	6.32	-0.047

3.2.3. Determination of Lead

A series of standard solutions for lead in range (1.0-15) µg ml^{-1} were prepared by taking a specific volume (1.0-15.0) ml from working solution of lead (100 µg ml^{-1}) into a 100 ml volumetric flask. The calibration curve was made and statistical data for calibration curve including; least square relation as ($y = 0.0026x + 0.0011$), correlation coefficient as (0.9979), linear calibration range of (1.0-15) µg ml^{-1}, and detection limit of (0.0089) µg ml^{-1} are found, the precision and accuracy of the lead are shown in Table (7).

Table (7): Precision and accuracy of lead by FAAS

Metal	Metal concentration (µg ml^{-1}) (standard solution)	Practical conc. for standard sol. (µg ml^{-1})	S.D	RSD%	E%
Lead	9.0	8.8	0.00012	0.57	2.2

3.2.4. Determination of Nickel

A series of standard solutions for nickel in range (2.0-16) µg ml^{-1} were prepared by taking a specific volume (2.0-16.0) ml from working solution of nickel (100 µg ml^{-1}) into a 100 ml volumetric flask. The calibration curve was made and statistical data for calibration curve including; least square relation as ($y = 0.5083x - 0.075$), correlation coefficient as (0.9957), linear calibration range of (2.0-16) µg $ml^{-1}$and a detection limit of (0.000045) µg ml^{-1} are estimated. The precision and accuracy are shown in Table (8).

Table (8): Precision and accuracy of nickel by FAAS

Metal	Metal concentration ($\mu g\ ml^{-1}$) (standard solution)	Practical conc. for standard sol. ($\mu g\ ml^{-1}$)	S.D	RSD%	E%
Nickel	10.0	10.36	0.0150	0.3	-3.6

3.2.5. Determination of Chromium

A series of standard solutions for chromium in range (2.0-16) $\mu g\ ml^{-1}$ were prepared from working solution of chromium (100 $\mu g\ ml^{-1}$) and transferred into a 100 ml volumetric flask. The calibration curve was made and statistical data for calibration curve including; least square relation as ($y = 0.0243x + 0.0039$), correlation coefficient as (0.9953), linear calibration range of (2.0-16) $\mu g\ ml^{-1}$ and a detection limit of (0.0096) $\mu g\ ml^{-1}$ are found. The precision and accuracy of chromium are shown in Table (9). Table (10) show the concentration of alkaline and heavy metals.

Table (9): Precision and accuracy of chromium by FAAS

Metal	Metal concentration ($\mu g\ ml^{-1}$) (standard solution)	Practical conc. for standard sol. ($\mu g\ ml^{-1}$)	S.D	RSD%	E%
Chromium	10.0	10.12	0.0074	2.96	-1.2

Table (10): Results of metals analysis in almond kernel

Metals	**Concentration ($\mu g\ ml^{-1}$)* (n = 5)**
Sodium (Na)	64.91
Potassium (K)	276.525
Calcium (Ca)	265.54
Cadmium (Cd)	2.103
Copper (Co)	2.951
Lead (Pb)	1.598
Nickel (Ni)	3.113
Chromium (Cr)	4.577

3.3. Conclusion

The alkaline metals analysis show that the amount of potassium was found to be high (four times) compared to the amount of sodium, this is an importation, because it is necessary for the function of all living cells and regulates the blood pressure in the body. It helps also to move blood sugar (glucose) from the blood stream into the cells to be used as energy and to turn fats, carbohydrates and proteins into energy. But if high amount were taken it will affects on the stomach and will damage the liver. In addition, calcium amount had seen high level which is useful for the muscles and bones.

In the other hand, for the heavy metals having low concentrations, while the amount of chromium is much more than the amount of other heavy metals (Ni, pb, Cu, and Cd) which are present in almond, chromium is a suitable biochemical nutritional to promote weight loss, muscle development and to treat the symptoms of type 2 diabetes, and the best selling mineral supplements after calcium (Vincent 2007). Nickel contents were also high which is used for increasing iron adsorption, preventing iron-poor blood (anaemia), and treating weak-bonds. It was found that lead has the lowest amount in the almond kernel and this is good because it is toxic to kidney, brain and bone demineralization.

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