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Fractionation and Speciation of Cu in Different Processing Apricots

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Abstract

An analytical procedure was proposed to study the operational fraction of Cu in ripe-fresh, sun-dried and sulphited-dried apricots harvested from either treated Bordeaux mixture or unexposed trees. Based on the methods that consists pressurized liquid extraction procedure and solid phase extraction to separate diverse Cu fractions on different sorbents such as Dowex 50Wx8-40 and Amberlite XAD-7, and then flame atomic absorption spectrometry (FAAS) and ion selective electrode were used for off-line determination of Cu concentrations in the effluents obtained.

Total copper concentrations in different processing the apricot samples exposed to Bordeaux mixture were 4.58, 4.48 and 4.25 µg/g in ripe fresh, sun-dried, sulphuring-sun drying, respectively. However, Cu concentrations in the organic apricot samples were determined 2.92; 2.97 and 2.25 µg/g. While circa 40-59% of total copper are extractable with water solvent including about 67-68% cationic copper, 25-33% organically bound copper and 26-44% labile in Kabaaşı apricot samples. Besides, while about 27-48% of total copper are extractable with methanol: water solvents containing about 40-23% cationic copper, 60-78% organically bound copper and 56-71% of copper was absorbed in the stomach.

It was applied to analytical procedures for Cu speciation in the apricot samples were verified and validated.

Keywords: Apricot; Copper; Speciation; Bordeaux mixture; Extraction

Introduction

Speciation is vital for life due to bioavailability of elements, possible mechanism of their environmental and metabolic transport, and their adsorption in the course of digestive processes. Data collected by speciation provides significant information about how elements are metabolized as well as their toxicity and bioavailability. Thereby, total element content must be evaluated by considering not only determination of element activity, but also its chemical and physical form, concentration and oxidation steps [1-5].

The chemical forms of the complexes in which the elements are found in food are quite vital for absorption in the body. The organic and inorganic complex metal-containing species in food affect the transport of food and their absorption of the intestines and stomach. Bioavailability depends on the chemical form of metal-containing species in food, the characteristics of the consumed food, the composition of the diet, and the health and nutritional quality of the individual [6-8].

Copper is a trace metal of vital importance for the normal growth of our bodies, the development and protection in our health and of the many organs. Copper, which has critical qualities for our lives, acts as a cofactor for many enzymes including cytochrome c oxidase and ceruloplasmin, tyrosinase, lysyl oxidase, dopaminemonooxygenase. It plays an important role in the structure and formation of many proteins and energy producing enzymes, in the nerve conduction, and in some mechanisms regulating body functions [6,9].

As a result, copper deficiency and excess in the body can seriously damage the quality of life. Because, Cu can accumulate throughout human body life and cause chronic poisoning. Wilson's disease is an autosomal recessive disorder of copper metabolism resulting from the absence or dysfunction of a copper transporting P-type ATPase encoded on chromosome13. Nutrition and physiological factors change the availability of copper, but in general the copper absorption in the human body ranges from 40% to 60%.

The coppers and complexes found in some foods cannot be dissolved by stomach acids or cannot be completely absorbed into the bloodstream from the small intestine [2,4-5].

The Provisional Tolerable Weekly Intake (PTWI) means the maximum amount that a person can be exposed to during a lifetime of no health risk and once a week.

The tolerable intake of all toxic metals as PTWI has been determined by the Food and Agriculture Organization / World Health Organization (FAO/WHO). The Acceptable Daily Intake (ADI) for Cu limit for an adult human weighing 70 kg was determined to be 1.3 mg/day and 0.05 mg/kg for children (WHO, 1996, 2011) [3,6].

Cu sources primarily are; seeds, fungus, cereal, nuts, sesame, kaju, soya, dried fruits, beans, shellfish and liver [5].

The variation in copper content among foods is primarily due to the variety of plants and soil characteristics, although the use of fungicides can also contribute to the copper content present.

The total copper contents in corn flour (0.3–0.7 µg/g), cassava root flour (0.75–1.26 µg/g), and oregano leaves, coriander and cumin (2.1–3.2 µg/g in all three) were also determined using the developed preconcentration procedure. In similar studies, copper concentrations have been detected in rice flour (2.07±0.08 µg/g), black tea (7.11±0.12

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μg/g) [6], cereal (1.5–10.2 mg kg^{-1}) and vegetable (1.6–6.4 mg kg^{-1}) samples [7].

In the speciation of Cu in wine samples, free and complex bound copper were reported to be detected using differential pulse anodic stripping voltammetry and ion selective potentiometer [8,9].

POHL et al. reported that the Cu ion levels of beer and wine were the richest Cu fraction (72-82% of total Cu content), which are polar and noncationic forms of Cu in the analyzed samples. The fraction of hydrophobic species in wines has the highest share in total Cu content, ranging from 27 to 77% [8].

Abollino et al. developed a method to study the distribution of copper and species in the cow milk. For copper analytes, it involves the determination of analytes by inductively coupled plasma atomic emission spectrometry (ICP-AES) after applying solid phase extraction. Copper species were detected from these fractions; cationic, anionic, neutral and casein-bound. The concentrations of Cu ions in milk were founded 9.5 ± 2.1 cationic, 10.4 total soluble, 12.5 ± 2.4 casein-bound and 23.3 ± 4.3 total Cu [9].

The pre-concentration protocol developed in the study has been reported to contribute to the area of increasing water and wastewater analysis. The described procedure, based on the use of the Dowex 50W-x^4 strong cation exchange resin, enables the enrichment of specific metals from water samples. Cu in mineral and mine water samples were found between 2.59-7.90 μg/L, 0.14-3.57 μg/L, respectively [10-13].

The apricot (Prunus armeniaca L or Armeniace vulgaris Lam.) is highly appreciated due to its specific taste, aroma and nutritive values, and its culture mostly depends on the climate conditions and soil compositions [11].

Turkey is at the top of world's fresh apricot production with the total annual production about 500-800 thousand tons of fresh apricot. The apricot trees had great harmony to Anatolia and especially in the Malatya region. Malatya, which is located in East Anatolia Region of Turkey, produces 80% - 85% of the world's dried apricot production and 7% - 10% of the world's fresh apricot production [13-16].

The distribution of sugars, organic acids, minor and major elements, phenolic compounds and carotenoids, which are the natural components of many fruits and vegetables, plays an important role in determining fruit quality and nutritive value [13]. Therefore, food scientists are interested in changes in the chemical composition and changes in the edible parts of the fruit, which have an impact on the shelf life, technology and nutritive quality of the food product [14].

Within recent years', copper has come to be the most valued agent in combating the ravages of plant diseases as a fungicide particularly. The protective fungicides most widely used against the disease in Malatya are the copper-containing materials and it is known as Bordeaux Mixture (BM) and contains $Ca(OH)^{2+}CuSO_4$. The BM has been systematically applied onto apricot trees since the end of the 20^{th} century. The Apricot trees were sprayed with BM when the blossoms were at pink bud stage in autumn and spring. Where the disease has been severe, two sprays were advised, one at tight cluster stage and one in full bloom. These sprays have been reported that phytotoxic to floral parts of the trees.

After its frequent application, copper may accumulate in the upper layers of soils and on the apricot trees, especially when the application times increase [17,18] Therefore, Cu determination in apricot samples is crucial and very important for better food safety and quality as well as human health.

Many different apricot varieties have been investigated by many researchers in the world and different phytochemical contents have been determined for each apricot variety [17-26].

There have also been extensive researches on the chemical composition of some apricot varieties cultivated in Malatya. As a result of these researches, it is stated that the species grown in Malatya have a rich phytochemical composition [11,13,26-31]. But, there is no any study done on copper speciation in apricot fruits.

Therefore, this study was aimed to determine copper species besides the total copper concentration of apricots from the Malatya region of Turkey. For this, total and fractionable copper contents were determined in the apricot samples which the exposed to BM and unexposed to BM apricot trees

In addition, fruit total and fractionated copper concentrations and effects of sulphur applied on the shelf life of the apricot fruit were investigated.

Materials and Methods

Materials

The selected apricot variety is locally known as Kabaaşı, which has grown approximately 30% among all apricot cultivars in Malatya.

Kabaaşı apricot variety is the most commonly grown variety in Malatya and it is the most preferred variety of dried apricot in the fruit drying technology because of having high soluble solid content (° Brix) which is between 23 and 26.

The ripened apricots were collected from the gardens of the Apricot Research Institute. They were harvested at the optimal commercial maturity stage in June, since it is generally harvested in the last week of June. The apricots were collected from 10 trees of the Kabaaşı variety that were treated with Bordeaux Mixture (**BM)** before harvest and another 10 trees of the same variety that were never treated with **BM** were applied to the selected tree at usual times. After harvesting, some of the samples were processed to obtain ripe fresh, sun-dried and sulfited-dried products, according to the method reported by Asma [12-18,19]. They were carefully selected to ensure that the fruits were free of defects. The samples were then washed quickly and rinsed once with de-ionized water at room temperature to minimize the risk of contamination and then the fruit stones were removed from all apricot samples and finally cut into small pieces with glass knife.

The samples were prepared so that one portion each of samples collected from 10 trees were mixed in the laboratory for three replicate Cu analysis in each of the six different apricot products namely the exposed to BM and unexposed to BM apricot trees before harvest types of the ripe-fresh, sun-dried and sulfited-dried apricots. All apricot samples lyophilized and then, each apricot sample was ground in a stainless steel mixer mill and held in polyethylene containers. These samples were stored in a deep-freeze (-10°C) (Tables 1-4).

Sample preparation

Ripe fresh apricot: They were carefully selected to ensure that the fruits were free of defects. The samples were then washed quickly and rinsed once with de-ionized water at room temperature to minimize the risk of contamination and then the fruit seeds were removed from the ripe-fresh apricot samples and finally cut into small pieces with glass knife.

Sample No	Apricots type exposed to BM
1	Ripe fresh [1]
2	Sun-dried [2]
3	Sulphited-dried [3]
	Apricots type unexposed to BM
4	Ripe fresh [1]
5	Sun-dried [2]
6	Sulphited-dried [3]

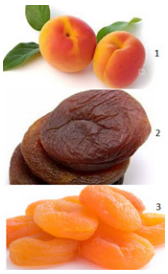


Table 1: Description of the all apricot samples.

Digestion Procedure	Predigestion				Digestion		
Acid mixtures, v	HNO_3 (6 ml)			Cooling in an ice bath	Mixture 1	Mixture 2	Mixture 3
					H_2O_2 (2 ml)	H_2O_2:$HClO_4$ (2:2 ml)	H_2O_2:HCl (2:2 ml)
Step	1	2	3	4	5	6	7
Powers, w	90	180	360	0	600	600	600
Applied time, min	2	2	2	5	1	1	1

Table 2: Microwave assisted wet digestion parameters to total Cu determination in certified reference materials and apricot samples (n=3).

Extraction name	Extraction I	Extraction II
Extraction solvent	Water, v, 100 % include 0.1 g TBHQ	Methanol:Water, v/v, 70:30 % include 0.1 g TBHQ
Temperature, C°	60	60
Pressure, psi	1500	1500
Heat-up time, min	5	5
Extraction time, min	20	20
Flush volume, %	60	60
Number of cycle	3	3
Purge times, min	1	1
Cell volume, ml	11	11
Total extraction time, min[a]	60	60
Total solvent used, ml[a]	23	23

Table 3: Optimized conditions for extraction of Cu from apricot samples (47).

The Number of Sample	Apricots type exposed to BM	Amount of sülfür for sulfuruing (g)	Sulfuring time (h)	SO_2 content[a] ($mgkg^{-1}$, dry weight)	Moisture content (%)
1	Ripe apricot	50,0	24	610.5 ± 12.2	9,6
2	Sun-dried	50,0	24	625 ± 11.8	10,1
3	Sulphited-dried	50,0	24	4321.7 ± 23.4	11,3
	Apricots type unexposed to BM				
4	Ripe apricot	50,0	24	595 ± 16.9	10,1
5	Sun-dried	50,0	24	601 ± 14.0	10,1
6	Sulphited-dried	50,0	24	4396 ± 28.7	11,4

Table 4: Sulfuring parameters, final SO_2 concentration and moisture content of all apricots exposed to BM and unexposed to BM (n=3).

Sun-dried: Approximately 30 kg of fresh fruit was placed on wooden platters in 90 x 180 cm dimensions. These were then exposed to direct sunlight. The drying process was terminated at the end of about 6 days [12].

Sulphuring and sun-drying: Commercially produced apricots are usually sulphured to prevent possible enzymatic browning reactions and non-enzymatic browning reactions both during drying and during storage. Approximately 30 kg of fresh fruit was placed in wooden crates in 90 x 180 cm dimensions and the chests were placed in the house of sulphfur at a height of no more than 1 meter on each other. Later, the apricot was made sulfur by burning elemental sulfur. Sulfur was exposed for 2 h. The apricot samples were then placed in this airless room for 1 day. Sulfur doses and exposure times were applied (Table 4). After exposing the apricots to SO_2 gas, the apricots sulphured was removed from the sulphur house and exposed to direct sunlight. The drying process was terminated at the end of about 6 days [13].

Lyophilization of samples: Prior to the lyophilization, all samples were incubated at 40°C for 2 h to maintain the partial removal of the moisture. Dried samples were placed in a tin layered Petri dish and frozen separately in liquid nitrogen and then stored at -50°C with 5 mmHg pressure for 21 h. All of the frozen samples were ground to very fine powder in a Waring Blender, and then placed in polyethylene bottles with cover. The bottles were stored in -10°C until analysis.

Moisture analysis: The moisture composition of all control and BM-exposed apricot samples, sulphited-dried, ripe apricot, sun-dried, was determined by method (Number 934.06) outlined by the AOAC [32] (Table 4).

Sulphur dioxide analysis: Sulphur dioxide (SO_2) was determined in duplicate by the modified Monier Williams distillation method with the minor revision in collecting the SO_2 gas [33,34]. The SO_2 contents of all apricots were expressed as mg/kg (Table 4).

Optimization of microwave-assisted wet digestion procedure for total Cu analysis

The applied microwave digestion procedure was determined by investigating four variables, namely the type of acid mixture, acid volume, digestion time, microwave power input. The time required to complete digestion of the apricot samples was accepted at the time at which no solid residue was observed in the acid digestion solution.

The procedure was applied for all apricot samples. In the procedure, apricot samples were pre-digested with conc. HNO_3, then cooled and then different digestion mixtures (Mixture 1, Mixture 2 and Mixture 3) were added to the digestion vessel (Table 2). The carried programs are given in (Table 2).

After cooling, sample digests were filtered with a microfilter, since microwave digestion left solid residues in the digests; then they were transferred into a 10 ml in volume. The blank digestion procedure was carried out in the same digestion way. The digests and the blanks were analysed by FAAS spectrophotometers [35].

	CRM	Found [a] Cu, mg kg^{-1}	Certified [a] Cu, mg kg^{-1}	Recovery (%)
Mixture 1 (HNO_3:H_2O_2)	**NIST 1547** peach leaves	3.5 ± 0.3	3,70 ± 0,40	94.6
	IAEA-359 cabbage	5.44 ± 0.39	5,67 ± 0,18	95.9
Mixture 2 (HNO_3:H_2O_2:$HClO_4$)	**NIST 1547** peach leaves	2.55 ± 0.45	3,70 ± 0,40	68.9
	IAEA-359 cabbage	3.69 ± 0.15	5,67 ± 0,18	65.08
Mixture 3 (HNO_3:H_2O_2: HCl)	**NIST 1547** peach leaves	2.61 ± 0.23	3,70 ± 0,40	70.54
	IAEA-359 cabbage	4.97 ± 0.27	5,67 ± 0,18	87.65

Table 5: Comparison of Cu recoveries in NIST 1547 (Peach Leaves) and **IAEA-359** (cabbage) for 3 digestion experiments tested.

The method was validated after determination accuracy and precision with certified reference material (peach leaves (NIST 1547) and cabbage (IAEA 359) was analysed each element (Table 5).

Instrumentation

Armfield Model FT-Vacuum Freezer Dryer was used for lyophilization of samples at -50°C. The moisture content of all apricot samples was determined in quadruplicate using a vacuum oven (Heraeus VT 6025, Hanau, Germany). Sulphur dioxide was determined in lyophilizate apricot samples by the Monier Williams distillation method as modified by Reith and Willems (1958). The digestion was carried out for total Cu concentration, in HP-500 CEM MARS 5 (Corp. Mathews, NC, USA) PTFE vessel. To determine the copper concentration in solutions, a Philips PU 9100 X model flame atomic absorption spectrometry (FAAS) interfaced with computers for data collection and copper hallow cathode lamp operated at 10 mA was used with an optimized air-acetylene flame. An Absorption line of Cu at 324.8 nm and a spectral band 0.5 nm were selected for the measurements. Accelerated solvent extraction (ASE) 200 system (Dionex, Sunnyvale, CA, USA) with 11-60 ml stainless steel ASE vessels used for the pressurized liquid extraction was used for the extraction of polyphenol bounded species of Cu from the apricot samples. Shimadzu 2000S Model UV/VIS Spectrophotometer was used for detection of total polyphenol in the apricot samples. An Orion 9429 Model Copper ion selective electrode Metrohm Titroprocessor (Model 686) was used to determine labile copper in extraction solutions. The Cu-ISE was coupled to an Ag/AgCl reference electrode (Orion Model 90-01).

Reagents

All solutions were made using high purity water obtained from Millipore (Bedford, Mass., USA) system. Glassware and other equipment were carefully cleaned starting with 2-4% HNO_3.

All reagents used were of analytical grade. HNO_3, HCl, H_2O_2, n-octanol, ethanol, methanol, $NaNO_3$, acetonitrile, $InCl_3$, tert-butylhydroquinone (tBHQ) were obtained from Merck (Darmstadt, Germany). To determine total Cu concentration in samples optimum conditions for microwave digestion were adjusted with peach leaves (NIST 1547) and cabbage (IAEA 359) as standart reference materials.

A reduction in infection levels in the nursery was achieved by protective sprays of BM at 600 g copper sulphate: 800 g lime: 100 litres water, or 300 g copper sulphate: 400 g lime: 100 litres water.

For total polyphenol analysis, Folin-Ciocalteu and Gallic acid monohydrate were purchased from Sigma (St.Louis, MO, USA). Cu calibration solutions were always prepared by appropriate dilution of stock solution containing 1 mg ml^{-1} Cu and stored in a refrigerator until use.

There were studied Dowex-50X8-200 (Fluka 1320785), a highly acidic cation exchange resin; Amberlite XAD-7 resin (Fluka-1208721) and Amberlite IRA 458 resin (Supelco 10330), a highly anionic exchange resin for Cu fractination in lyophilizate apricot samples.

Separation of different speciation of Cu

Extraction of Cu: Prior to the extraction of Cu from apricot samples, operational parameters of the ASE technique were established (Table 3). For extraction, the parameters were procedure solvent composition, temperature, pressure and static extraction time [11].

A sample of 2.500 ± 0.001 g freeze-dried apricot samples was placed into 11 ml stainless steel extraction cell in the carousel. The sample was then extracted with 45 ml of the solvent. Soda lime glass beads (Q-beads) were used for dispersion of the samples to avoid aggregation and splash, which may alter the extraction efficiency. The solvent was previously degassed to avoid the oxidation of the analytes under the operating conditions.

Extraction procedure was performed under the conditions of 1,500 psi pressure, 60°C temperature and 60 min static extraction time (Table 3) [11]. Each of the analyses was examined with three replicates. Once the extraction finished, the extracts were filtered with 0.25 µm nylon membrane filter and transferred to a 25 ml volumetric flask. Total copper concentrations in all extracts were analysed with FAAS.

Preparation of resins: In this study, the Amberlite XAD^{-7}, a commercial non-ionic macroreticular styrene divinylbenzene copolymer resin, which is with 20-60 mesh size, acrylic ester and 450 m^2/g mean area was used to separate copper that bounds to hydrolyzable polyphenols. The Amberlite XAD^{-7} resin was dried at 110°C and washed twice in ultrasonic bath with methanol, 2M HNO_3 and then water, respectively.

The resin was then placed in the indium solution (In^{3+}) for overnight at pH 5.5 to inactivate the cation adsorbing units. Then, the Amberlite XAD^{-7} resin was transferred into polyethylene columns with a diameter of 1 cm and a length of 10 cm.

Dowex 50W8-40, strongly acidic cation exchanges resin which is with 20-50 mesh size was used for cationic copper (Cu^{2+}) determination. The Dowex 50W8-40 was dried at 110°C and washed twice in ultrasonic bath with 20 M HNO_3 (30 ml) and then water, respectively.

The cation exchange resin (2.00 g) was filled into polyethylene of 25 cm length and 1.0 cm diameter. After the column was filled, it was again washed with 20 ml of purified water.

Amberlite IRA-458, anion exchange resin, which is with 50 mesh sizes, was used for determining anionic copper. Amberlite IRA-458 was filled into polyethylene of 15 cm length and 1.0 cm diameter, after treatment with 0.5 M tartaric acid. The loaded sample volume and flow rates were optimised. Optimized flow rates were determined as 1 ml/min [36-40].

Sequential solid phase extraction for seperation of the organic and inorganic forms of Cu from extraction solutions: 25 ml of apricot extracts were directly pumped at a flow rate of 1 ml/min into polyethylene column filled with Amberlite XAD^{-7} resin (3.0 g).

Then 15 ml of eluent was passed through a column filled 2.0 g of Dowex-50W8-40 and the second part of 10 ml column filled 2.0 g of Amberlite IRA-458 at a flow rate of 1 ml/min respectively.

Copper species retained in the column were eluted with 10 ml of 2 M HNO_3 for Amberlite XAD^{-7} resin and 10 ml 2.0 M HCl for Dowex-50W8-40 and Amberlite IRA-458 sequentially, and then copper was determined by FAAS.

Analytical procedure scheme for the separation of copper species in apricot samples, which can be organics bound to polyphenols, cationic and anionic is presented in (Figure 1).

Determination of total Cu in apricot samples by extracted artifical stomach and intestinal solution:

Synthetic stomach and intestinal solutions respectively were formed to understand how the amount of copper in edible apricot sample was absorbed into our bodies. Extraction was done with 0.1 M pepsin +HCl

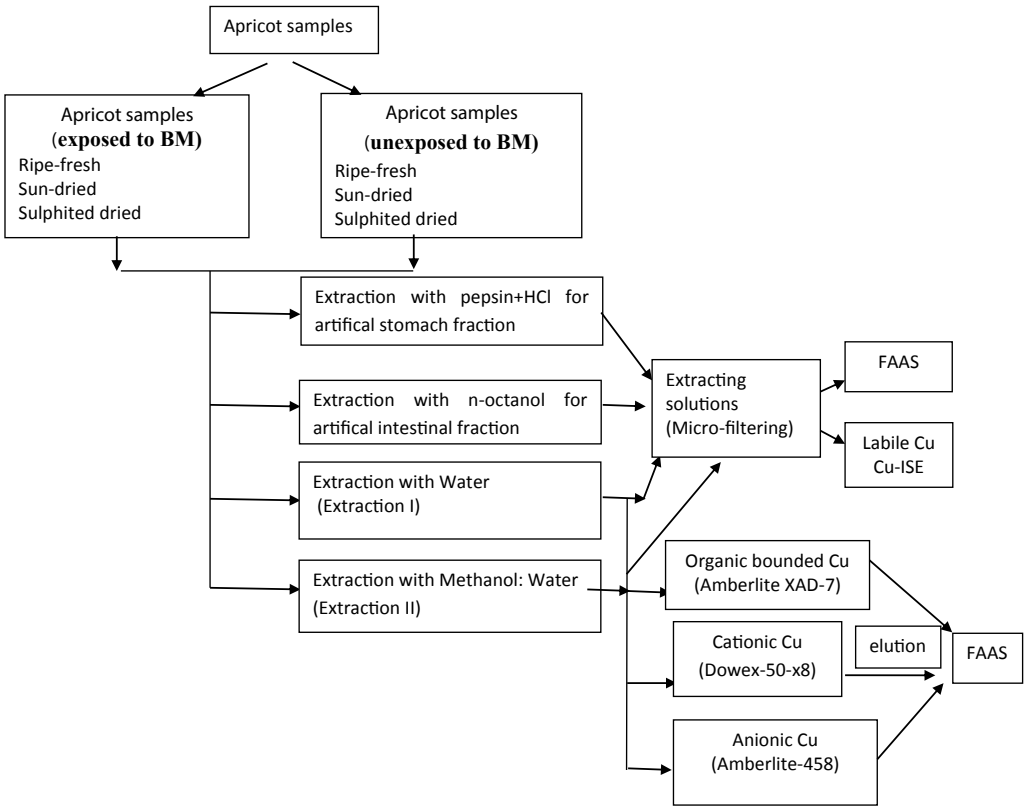


Figure 1: Analytical procedure scheme for Cu speciation in apricot samples.

for synthetic gastric solution and n-octanol solution to detect intestinal absorption. Simulated extraction procedures for some trace elements in some foodstuffs have been previously applied by Hocquellet and L'Hotellier [19]. The extract of apricot was obtained by adding 20 ml of pepsin solution containing of 0.1M HCl to 4.0 g of apricot and shaking it for 4 h at 37°C (pH=1-2). After filtration, it was transferred to a 20 ml volumetric flask. The copper contents of the extracts were determined as total copper concentration by FAAS.

Extraction with n-octanol solvent was performed by addition of 10.0 ml solvent into 4.0 g apricot and shaking it for 2 h at 37°C (pH=7.5-8.5). The organic phase was decanted and centrifuged because of the viscosity of octanol diluted with ethanol (1:1 dilution, 20 ml) for FAAS. After filtration, total copper concentrations in the extracts were determined by FAAS [9,36,41].

Determination of labile Cu in artifical stomach and intestinal extraction solution: The free metal ion activity can be measured by using an ion selective electrode (ISE). The free Cu concentration that is extractable with artificial stomach and intestinal extraction solutions of apricot samples was measured potentiometrically by using a copper selective electrode (Cu-ISE) after extraction with synthetic stomach and intestinal solvent, respectively.

Cu-ISE characterization was done running the calibration curve for Cu ion. The calibration consisted of recording the ISE potentials for primary ion solutions with different Cu concentrations following the methodology described by Rachou et al. Briefly, 6 standard solutions were used for the daily calibration of the electrode. These solutions were made with 100 ml ranged 100, 10.0, 1.0, 0.10, 0.0150 and 0.01 mg/l.

Total ionic strength adjustment buffer solution (TISAB) used sodium nitrate (4 mol/l) as a total ion intensity adjuster. 600 µl of TISAB solution was added to all extracts and copper standard solutions. After a stable signal was obtained, the measurement of the potential values was recorded (60 s for the stabilization signal). Standard solutions were prepared fresh daily [42,43]. When working with ion-selective electrodes, measured containers were covered with aluminum foil in all measurements of the electrode sensors affected the measurements when exposed to light.

The analytical scheme was developed for stomach and intestinal extraction, fractionation analysis of copper in apricot matrix is shown in Figure 1.

Results and Discussion

As seen in Table 4, 50.0 g sulphur powder was used for all apricot samples (5 kg) in the sulphur process. The amount of elemental sulphur burned for the sulphuring trials of all apricot samples was the same. The SO_2 values of apricots are ranged, in which apricots exposed to BM contained SO_2 from 610.5 to 4321 mg per kg and apricots unexposed to BM (control) contained SO_2 from 595 to 4396 mg per kg.

The moisture values of apricots exposed to BM ranged from 9.6 to 11.3% while they were from 10.1 to 11.4% in control group (Table 4).

To determine total Cu concentration in apricot samples, all solutions for the analytical curve were prepared from the intermediary solution at the following concentrations: 0.02, 0,10, 0,20, 0,50, 2,0, 4,0 and 8,0 µg/l in water. The detection and quantification limit values with FAAS were found for Cu (II) ion. The LOD and LOQ were 0.43 µg/l and

1.44 µg/l, respectively, The relative standard deviation (RSD%, n=10) average was in the ranged from 1 to 2,02% for Cu and the correlation coefficient was 0.9991.

The results of Cu recoveries for certified reference materials are shown (Table 5).

Beside HNO_3/H_2O_2 (6/2 ml), $HNO_3/H_2O_2/HCl$ (6/2/2 ml) and $HNO_3/H_2O_2/HCl_4$ (6/2/2 ml) mixtures were pre-digested by HNO_3. However, $HNO_3/H_2O_2/HCl$ and $HNO_3/H_2O_2/HCl_4$ mixtures gave no more satisfactory results in the digestion of apricot samples for total Cu determination. Concentrations and recoveries of the elements obtained by them, which $HNO_3/H_2O_2/HCl$ and $HNO_3/H_2O_2/HClO_4$ mixtures were lower than those obtained by HNO_3/H_2O_2. According to the results of the obtained CRM copper concentration For the both of the CRM of peach leaves (NIST, SRM 1547) and cabbage (IAEA-359)., it seems that the HNO_3 / H_2O_2 mixture is the most suitable for the digestion of the apricot samples. The approximate time required for microwave digestions was 7 min (Table 5).

The recovery values for total Cu were 94.6% and 95.9% for Mixture I, 65.08% and 65.9% for Mixture II, 70.54% and 87.65% for Mixture III, and both CRM were obtained.

At the optimal digestion conditions, an accurately weighed 0.500 g apricot samples were placed into the digestion vessel, followed by 6 ml of conc. HNO_3, cooled and then were added 2 ml H_2O_2. After the digestion procedure had applied, the vessels were cooled to room temperature in ice bath. Then, the residue was diluted to 10 ml with water and determined the copper concentration in solutions with FAAS.

Amberlite XAD-7 is a suitable sorbent for the separation of organic complexes of metals from different samples. [10,44]. It is stable at all pH values in aqueous solutions [36,37,45].

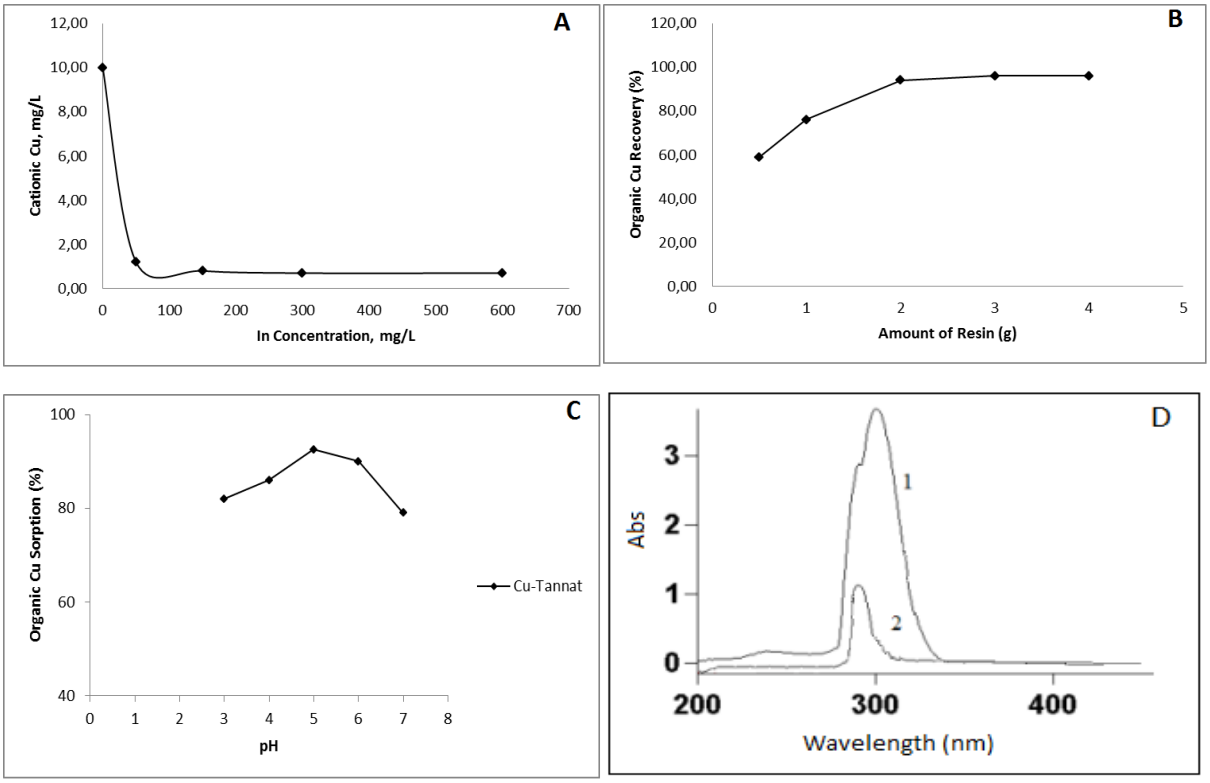
For optimum In^{3+} concentration of the Amberlite XAD-7 surface, the solution contains 10 mg/l (10 ml) Cu $^{2+}$ at pH=5,5. The various concentrations of In^{3+} solution (50-600 mg/l) were passed through the column in which containing Amberlite XAD^{-7} resin.

The concentration of copper in the eluent from the column was then determined by FAAS. The results given in Figure 2A clearly show that the amounts of cationic copper species decrease with increasing In^{3+} concentration.

Only about 8% of the initial Cu $^{2+}$ retained with on resin was treated with 300 mg/l In^{3+} solution (Figure 2A)

We used a model solution containing 10 mg/l Cu and 200 mg/l tannic acid (10 ml) at pH=5 for the optimum amount of resin. The model solution (10 ml) was passed through the column containing various amounts of Amberlite XAD-7 resin (0.5-4.0 g) conditioned with In^{3+} solution. The copper species were eluted with 2N HNO_3 from the resin and total Cu was determined by FAAS.

The recovery values of cationic copper and organic bound copper reaches range 95-98% when 3 g of Amberlite XAD^{-7} and 2 g of Dowex-50x8 sorbent was applied, respectively (Figure 2B-D). Accordingly,



A. Variation of cationic Cu concentration retained on column as a function of In(III) concentration;
B. Variation of hydrolyzable polyphenols bounded Cu recovery as a function of amount of Amberlite XAD-7 resin;
C. The effect of pH on the sorption recovery of Cu-tannat;
D. The UV absorption spectrums ((100 mg /L tannic acid plus 10 mg / L Cu); [1] before introduced, [2] after introduced to the XAD-7 column).

Figure 2: Optimum condition variation for speciation of Cu concentration (n:3).

optimum amounts of the resins in the columns were determined to be 3 g for Amberlite XAD-7 and 2 g for Dowex resin (Figure 2B).

The effect of resin pH on the sorption of organic bounded copper on Amberlite XAD-7 resin was investigated. The pH of the model solution was adjusted the same as the pH (5-5.5) of the original apricot extract.

The solution containing 10 mg/l of Cu^{2+}, 100 mg/l of tannic acid (10 ml) was passed at 2 ml/min flow rate through the column in which containing Amberlite XAD-7 resin (3.0 g) at various pH (3-7) values. Then, organic bounded Cu retained with resin was eluated and determined by FAAS (Figure 2C). Experimental results show that Cu-polyphenol complexes are partially degraded at lower pH values, and at higher pH values, hydroxide complexes of Cu-polyphenol complexes are formed (Figure 2C).

Therefore, when the pH of the resins is different from the original pH of the apricot extracts, the sorption efficiency decreases. The sorption of efficiency of organically bound copper reached 94% at pH 5-5.5. Besides, according to the results of spectrophotometric screening, it was seen that copper was complexed with this polyphenol. It can be seen the UV absorption spectrums ((100 mg/L) tannic acid plus 10 mg/L Cu);

[1]before introduced,

[2]after introduced to the XAD-7 column in Figure 2D.

The accuracy of the method for copper determination in apricot samples was confirmed through spike tests (87-101% recoveries) (Table 6), and analysis of a certified reference materials (94.6-95.9% recoveries) (NIST 1547 Peach Leaves and IAEA-359 Cabbage) (Table 5).

The t-test (95% confidence level) demonstrated that there was no significant difference between the obtained (3.50 ± 0.3 µg/g and 5.44 ± 0.39 µg/g) and the certified value (3.70 ± 0.40 µg/g and 5.67 ± 0.18 µg/g) (Tables 5 and 6).

The ripened apricots were collected from the gardens of the Apricot Research Institute and were prepared for the extraction according to the procedure given in (Figure 1). The amounts of copper in various apricot samples are presented in (Tables 7 and 8).

All copper concentrations were determined on a dry weight basis. The concentrations of investigating element in exposed and unexposed to BM apricot samples were determined on a dry weight basis and given in (Tables 7 and 8) respectively.

Copper concentrations in dried apricot samples were determined 4.58; 4.48 and 4.25 µg/g for ripe fresh, sun-dried, sulphuring and sun drying, exposed to BM. Additionally, apricot samples unexposed to BM were determined 2.92; 2.97 and 2.25 µg/g for ripe fresh, sun-dried, sulphuring and sun drying, respectively.

According to these results, copper has the highest concentration in ripe fresh apricot samples.

The chemical speciation in some micronutrients and trace elements in food is very important to human health.

Excessive intake of trace elements with nutrition may result in serious health problems like reduction in the immunological defense mechanism.

A number of serious health problems can develop as a result of excessive uptake of dietary trace elements. The consumption of contaminated food can cause a decrease in immunological defenses, too [24]. The evaluation of dried apricot is an important issue for consumer safety.

The FAO/WHO has set a limit for TEs intakes based on body weight. For an average adult (60 kg body weight), the PTDI for copper is 48.3 mg [3,46]. Copper contents in the literature have been reported in the range 0.92-6.49 µg/g the lowest and highest contents of copper ion in different apricot samples from Turkey, respectively [24].

Copper levels in some dried fruit samples consumed in Pakistan were reported in a dry weight range of 3.90 to 25.0 mg/g, and copper levels in fruits sold in the Egyptian public markets were reported to be in the range of 1.22 to 18.3 mg/kg [47,48].

The maximum copper level permission for fruit juices and nectars is determined as 5.0 mg/kg according to Turkish Food Codex [49].

Application of micronutrient fertilizers and copper-based fungicides may sometimes increase it to the alarming levels. Besides, excess levels of copper can cause metabolic disorders and poisoning in the liver because of metal accumulation.

The concentration of copper in apricot fruits treated by BM was determined between 36.2% and 47.06% which is more than untreated ones (Table 7). 48.25% of total copper was extracted via methanol:water mixture from sample 1 apricot of BM treated apricot trees. While 78.28% of this extract was polyphenol-bound copper, 23.98% of that was cationic copper. However, copper content in the extraction applied by only water in the same apricot sample constituted

Experiment	Fraction	Reagent/material	Experimental conditions	Added Cu mg kg^{-1} [a]	Founded Cu mg kg^{-1} [a]	Recovery for Cu %
Microvawe Digestion	Total Cu	HNO_3:H_2O_2 6:2, v/v	90W-600W (9min)	5,67 * 3,7*	5.44 ± 0.39 3.5 ± 0.3	95,9 94,6
Extraction with water	Water soluble Cu	Water, 23 ml, v	Optimum PLE conditions as tabled 3	10,0	9,53 ± 0,37	95,3
Extraction with methanol:water	Methanol:Water soluble Cu	Methanol:Water,v/v 50:50%, 23 ml,	Optimum PLE conditions as tabled 3	10,0	9,89 ± 0,69	98,9
Ion Exchange	Cationic	Dowex-50X8-200	in column	10,0	9,27 ± 0,099	92,7
Ion Exchange	Anionic	Amberlite IRA 458	in column	6,0	5,2 ± 0,091	87
Sorption	Organic- bounded	Amberlite XAD-7	in column	10,0	9,36 ± 0,19	93,6
Extraction with pepsin+HCl	Absorbable Cu in stomach	Pepsin in 0,1 M HCl	2 h at 37 °C	10,0	10,1 ± 0,31	101
Extraction with n-octanol	Absorbable Cu in intestine	n-octanol	2 h at 37 °C	10,0	9,9 ± 0,37	99

Table 6: Results of the recovery % at the optimum operating conditions to the determine total copper and fractionation Cu in samples.

Apricot type exposed to BM		Extraction with methanol:water		Extraction with water	
Apricot samples	**Total Cu**	**Extracted Cu**	**Labile Cu**	**Extracted Cu**	**Labile Cu**
1	4.58 ± 0.50	2,21 ± 0,37	<0,01	2,74 ± 0,21	2,05 ± 0,17
2	4.48 ± 0.46	2,20 ± 0,26	<0,01	2,76 ± 0,12	1,99 ± 0,13
3	4.25 ± 1,23	1,17 ± 0,22	<0,01	1,74 ± 0,15	1,12 ± 0,12
Extraction with artifical stomach		**After Amberlite XAD-7**			
Cu absorbed in stomach	**Labile Cu**	**⬇ Organic bounded Cu**		**⬇ Organic bounded Cu**	
3,16 ± 0,09	2,43 ± 0,11	1,73 ± 0,38		0,71 ± 0,17	
3,16 ± 0,10	2,44 ± 0,12	1,80 ± 0,38		0,75 ± 0,41	
2,62 ± 0,03	1,35 ± 0,03	0,71 ± 0,29		0,58 ± 1,66	
Extraction with artifical intestinal		**After Dowex-50x8**			
Cu absorbed in intestinal	**Labile Cu**	**⬇ Cationic bounded Cu**		**⬇ Cationic bounded Cu**	
*	*	0,53 ± 0,23		1,88 ± 0,43	
*	*	0,56 ± 0,21		1,76 ± 0,29	
*	*	0,47 ± 0,43		1,17 ± 0,29	
		After Amberlite IRA 458			
		⬇ Anionic bounded Cu		**⬇ Anionic bounded Cu**	
		*		*	

a Mean ± standard error, n:3
*undetectable

Table 7: The distribution of total Cu, absorbed in intestinal and organic bounded, cationic and anionic Cu in the water:methanol or water extraction solutions from apricot samples exposed to BM.

59.82% of total copper. 68.61% of water extract was cationic copper as 25.91% of that was polyphenol-bound. It was determined that the labile copper content in water extracts was 44.76% of total copper that could be extracted by water. Copper contents determined in fractions from number 2 apricot samples were similar to number 1 sample. Accordingly, copper in methanol:water extract from number 2 apricot samples formed 49.11% of total copper. It was found that 81.81% of this extract was polyphenol-bound while 25.45% of that was cationic. For the same apricot sample, copper content in only water extract constitutes 61.61% of total copper. In a water extract from number 2 sample, polyphenol-bound copper was 27.17% as cationic copper was 63.76%. It was determined that the labile copper content in water extracts was 44.42% of total copper which was water extractable. Yet, copper content in methanol:water extract from number 3 sample dried by sulphurizing forms 27.53% of total copper content, and 60.68% this extract was polyphenol-bound while 40.17% was cationic. For the number 3 apricot samples, copper content in only water extract constitute 40.94 of total copper. 33.33% of water extract was polyphenol-bound while 67.24% were cationic copper. Labile copper content in water extracts was 26.35% of total copper, which was water extractable. It was seen that the copper content in methanol:water and only water extracts for number 3 apricot sample was lower compared to number 1 and 2 apricot samples. It was observed that copper could not be extracted adequately since extractability of metals from apricot matrix, depending on sulphurizing of apricot samples, was tough (Table 9).

A crucial part of copper was labile in water extracts while it remained under detection limit in methanol:water extracts of all samples.

It was detected that 74.31% of total copper content in number 4 apricot sample untreated by BM passed to methanol:water extract, and 50.34% of copper in this extract was polyphenol-bound as 27.18% of that was cationic. 40.35% of the total copper in the same apricot sample passed to water extract, and 43.69% of copper in this extract was polyphenol-bound while 48.73% were cationic. Copper contents in methanol:water extract from number 5 sample were parallel with the same extract from number 4 apricot samples. Especially, differences were observed for copper content in number 4 apricot sample. 48.44% of the total copper in methanol:water extraction was extractable, and 43.11% of this extract were polyphenol-bound as cationic copper content was under detection limit. Based on sulphurizing, it was determined that there was a decrease in extractable copper concentrations. 36.44% of the total copper in water extraction from number 6 apricot sample was extracted. 27.11% of this extract was labile copper and both polyphenol-bound and cationic copper contents were under detection limits.

Polyphenol-bound copper contents that were able to pass to water extract in apricot samples untreated by BM were between 60% and 84% more compared to BM-treated samples. 81% of copper passed to methanol:water extract was polyphenol-bound. Altogether, these results show that 44.76% of water extractable copper was free copper and it was difficult to extract it through sulphurizing. However, 56 to 70% of copper is absorbed in the stomach and it was found that 31 to 56% of these coppers were labile (Table 9). It has been thought that rest of the copper is absorbed by the intestines, but this part was not detected as a repeat signal could not be taken. While 40-59% of total copper is extractable with water solvent of which is cationic copper 67-68%, organically bound copper 25-33% and labile 26-44% in apricot samples. Besides, while 27-48% of total copper is extractable with methanol:water solvents of which is cationic copper 40-23%, organically bound copper 60-78%.

Conclusions

The average concentrations of total copper ions in the Kabaaşı cultivar apricot samples ranged from 2.25 to 4.58 µg/g.

The highest amount was found in ripe fresh apricot exposed to BM and the lowest in sulphuring and sun drying unexposed to BM (Table 7).

The results show that 56-71% of copper was absorbed in the stomach of both unexposed to BM and exposed to BM apricot samples and the other percentage of copper was absorbed in the intestine (Table 9). Although the amount of copper that can be absorbed in the intestine is low, it is very important. The fractionation studies for dried apricot

Apricot type unexposed to BM		Extraction with methanol:water		Extraction with water	
Apricot samples	**Total Cu**	**Extracted Cu**	**Labile Cu**	**Extracted Cu**	**Labile Cu**
1	2.92 ± 0.12	2,17 ± 0,36	<0,01	1,19 ± 0,09	0,82 ± 0,19
2	2.97 ± 0.17	2,12 ± 0,17	<0,01	1,16 ± 0,10	0,72 ± 0,18
3	2.25 ± 0.14	1,09 ± 0,36	<0,01	0,82 ± 0,15	0,61 ± 0,11
Extraction with artifical stomach		**After Amberlite XAD-7**			
Cu absorbed in stomach	**Labile Cu**	**⬇ Organic bounded Cu**		**⬇ Organic bounded Cu**	
1,92 ± 0,04	1,63 ± 0,11	1,47 ± 0,025		0,52 ± 0,16	
1,96 ± 0,07	1,62 ± 0,13	1,50 ± 0,067		0,47 ± 0,03	
1,28 ± 0,02	0,94 ± 0,07	0,97 ± 0,047		*	
Extraction with artifical intestinal		**After Dowex-50x8**			
Cu absorbed in intestinal	**Labile Cu**	**⬇ Cationic bounded Cu**		**⬇ Cationic bounded Cu**	
*	*	0,59 ± 0,037		0,58 ± 0,08	
*	*	0,47 ± 0,048		0,56 ± 0,016	
*	*	*		*	
		After Amberlite IRA 458			
		⬇ Anionic bounded Cu		**⬇ Anionic bounded Cu**	
		*		*	

[a] Mean ± standard error, n:3
*undetectable

Table 8: The distribution of total Cu, absorbed in intestinal and organic bounded, cationic and anionic Cu in the water:methanol or water extraction solutions from apricot samples unexposed to BM.

Apricot samples	Extracted Cu,%						Organic bounded Cu, %		Cationic Cu, %	
	Extraction with methanol:water		Extraction with Water		Cu absorbed in stomach		Extraction with methanol:water	Extraction with water	Extraction with methanol:water	Extraction with water
Apricot type exposed to BM	Extracted Cu	Labile Cu	Extracted Cu	Labile Cu	Extracted Cu	Labile Cu	Extracted Cu	Extracted Cu	Extracted Cu	Extracted Cu
1	48,25	<0,01	59,82	44,76	68,99	53,06	78,28	25,91	23,98	68,61
2	49,11	<0,01	61,61	44,42	70,53	54,46	81,81	27,17	25,45	63,76
3	27,53	<0,01	40,94	26,35	61,65	31,76	60,68	33,33	40,17	67,24
Apricot type unexposed to BM										
4	74,31	<0,01	40,75	28,08	65,75	55,82	50,34	43,69	27,18	48,73
5	71,38	<0,01	39,06	24,24	65,99	54,55	50,50	40,51	22,17	48,27
6	48,44	<0,01	36,44	27,11	56,89	41,78	43,11	*	*	*

[a] Mean ± standard error, n:3
*undetectable

Table 9: The distribution of copper organic bounded, cationic and labile in the different extraction solutions.

will be improved in the future. These studies can be considered as a preliminary step for fractionation studies on apricot.

An important analytical scheme for fractionation of copper from apricot samples was improved. Accordingly, there are inorganically bound (water-soluble) copper and organically bound copper in apricot fruit.

The present study demonstrated that estimated daily and weekly intakes of selected metals via consumption of apricot were below PTDI and PTWI values established by FAO/WHO.

The study showed that despite exposed to BM apricot samples; levels of Cu (II) ion in apricots are above the safe limit, according to permissible limit of WHO.

Declarations of Interest

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Conflict of Interest

No conflict of interest was declared by the authors.

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