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ARAŞTIRMA MAKALESİ RESEARCH ARTICLE

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Determination of Some Toxic Element (Cr, Cd, Cu and Pb) Levels in Cumin and Cinnamon Aromatic Plants Frequently Used as Foodstuff[A]

Hacer Sibel KARAPINAR[1*], Fevzi KILIÇEL[2]

Abstract: Aromatic plants are repositories of various elements in a wide concentration range with significant negative or positive health effects. It is known that there are more than twenty elements with physiological activity in mammals and humans. Elements like copper, nickel, cobalt and chromium are necessary ingredients of biological structures. Such elements may be toxic at concentrations above the limit values required for their function. In many biochemical reactions, elements such as lead, cadmium and arsenic have toxic effects. In this study, the amounts of some toxic elements in cumin and cinnamon samples were determined. Elemental amounts of Cr, Cd, Cu and Pb in 8 samples were analyzed with flame atomic absorption spectrometry (FAAS) method. According to the results, Cr element was found to be higher in the studied samples. Cu, Pb and Cd elements were found to be normal. In addition, the analytic method was confirmed by detection limits, accuracy, linearity and recovery experiments, sufficient values were obtained in each case.

Keywords: Toxic elements, cumin, cinnamon, flame atomic absorption spectrometry.

[A] Etik kurul izni gerekmediği beyan edilmiştir. It was declared that no ethics committee permission was required.

[*] **Sorumlu yazar/Corresponding Author:** [1]Hacer Sibel KARAPINAR,Karamanoğlu Mehmetbey Üniversitesi, Bilimsel ve Teknolojik Araştırmalar Uygulama ve Araştırma Merkezi, Karaman, Türkiye, sibelkarapinar@kmu.edu.tr, OrcID 0000-0002-0123-3901

[2] Fevzi KILIÇEL, Karamanoğlu Mehmetbey Üniversitesi, Kamil Özdağ Fen Fakültesi, Kimya Bölümü, Karaman, Türkiye, fevzi@kmu.edu.tr,OrcID 0000-0002-5454-5597

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Gıda Maddesi Olarak Sıkça Kullanılan Kimyon ve Tarçın Aromatik Bitkilerindeki Bazı Toksik Element (Cr, Cd, Cu ve Pb) Seviyelerinin Belirlenmesi

Öz: Aromatik bitkiler önemli olumlu veya olumsuz sağlık etkileri olan geniş bir konsantrasyon aralığında çeşitli elementlerin depolarıdır. Yirmiden fazla element insanlarda ve diğer memelilerde bilinen fizyolojik aktivitelere sahiptir. Kobalt, bakır, krom ve nikel gibi elementler biyolojik yapıların temel bileşenleridir, ancak işlevleri için gerekli sınırların üstündeki konsantrasyonlarda toksik olabilmektedirler. Arsenik, kurşun ve kadmiyum gibi diğer elementlerin çeşitli biyokimyasal reaksiyonlarda iyi bilinen toksik rolleri vardır. Eser elementlerin tayini için kullanılan birçok metod bulunmaktadır. Bu çalışmada kimyon ve tarçın örneklerindeki bazı toksik elementlerin miktarları belirlenmiştir. Toplam 8 örnekte Cr, Cd, Cu ve Pb element miktarları alevli atomik absorpsiyon spektrometresi (FAAS) metodu ile belirlenmiştir. Bulunan sonuçlara göre çalışılan örneklerde Cr elementi yapılan çalışmalara göre yüksek bulunmuştur. Cu, Pb ve Cd elementlerinin normal seviyelerde olduğu tespit edilmiştir. Ayrıca analitik yöntem doğrusallık, tespit limitleri, doğruluk ve geri kazanım deneyleri ile doğrulanmış, her durumda tatmin edici değerler elde edilmiştir.

Anahtar Kelimeler: Toksik elementler, kimyon, tarçın, alevli atomik absorpsiyon spektrometresi.

Introduction

Aromatic plants are examined worldwide as medicinal plants due to macro and micro elements (Subramanian et al., 2012). According to the World Health Organization, developing countries use spices in aromatic plants as traditional herbal medicine (Basgel and Erdemoglu, 2006; Zhang and Li, 2018). These aromatic plants contain large amounts of minerals, fats, proteins and carbohydrates that are necessary for humans and animals (Pferschy-Wenzig and Bauer, 2015). Spices are widely used all over the world. Since spices contain various elements in a wide concentration range, they show positive or negative health effects on the human body (Khan et al., 2014). Some of the elements of micro nutrient category which are required to be taken in small amounts by the human body are manganese, chromium, cobalt, vanadium, zinc, copper and selenium etc. (Karadas and Kara, 2012). Elements such as nickel, chromium, copper and cobalt which are the main ingredients of biological structures, can be toxic at concentrations above the required limit values (Fraga, 2005). Cadmium, lead and arsenic have toxic effects on various biochemical reactions (Karadas and Kara, 2012; Fraga, 2005).

Many aromatic plants in Turkey and worldwide has been widely used in our daily diet. To give an example to some of these plants, obesity and sugar regulator (cinnamon), dementia fighting forces (cumin), the fight against cancer (turmeric) are frequently used (Khan et al., 2014). Although much study has been made on the bioactivities and organic ingredients of aromatic spices little care has been paid to trace and minor element contents.

Different techniques are used to detect trace elements in the world. These can be listed as stripping potentiometry (Muñoz and Palmero, 2004), flow injection spectrometric methods (de Araujo Nogueira, 1998), flame atomic absorption spectrometry (Kondyli et al., 2007), inductively coupled plasma mass spectrometry (Llorent-Martínez et al., 2012; Khan et al., 2013), inductively coupled plasma optical emission spectrometry (Kira and Maihara, 2007). Of these techniques, FAAS is easier to use, more cost effective, and analysis is performed in less time (Gondim et al., 2017).

In this study, the amounts of some toxic elements in cumin and cinnamon samples were determined. Elemental amounts of Cr, Cd, Cu and Pb in 8 samples were analyzed with flame atomic absorption spectrometry (FAAS) method. According to the results, Cr element was found to be higher in the studied samples. Cu, Pb and Cd elements were found to be normal. In addition, the analytic method was confirmed by detection limits, accuracy, linearity and recovery experiments, sufficient values were obtained in each case.

Materials and Methods

A total of 24 samples were collected from 6 different locations in Karaman markets during the winter and summer months and brought to the laboratory. Samples were prepared for analysis by a wet burning method. For this purpose, dried samples were extracted and purified from impurities. It was ground by mechanical treatment with a grinder and sieved in suitable sieves. Moisture was removed from the samples by keeping it in a controlled manner in the oven at 105 °C for 50-60 minutes. The samples (1 g) were placed in a solution with 16 ml of HNO_3 (65%, w/w, Merck) for 1 day. Then, 4 ml of $HClO_4$ (70-72%, w/w, Merck) was placed and heated slowly in the heater for 4-5 hours, the acid was removed. After cooling the samples, 5 ml of H_2O_2 (30%, w/w, Merck) was added and the solution was heated until clear. The cooled samples were filtered with filter paper and then filled to 15 ml with distilled water and stored at 4 °C until analysis.

The metal contents were detected using a flame atomic absorption spectrometry (AAnalyst Pinaccle 900T, Perkin Elmer) method. All elements hollow cathode lamps and air-acetylene burner (2.1-2.3 $Lmin^{-1}$) were used. The most precision lamp currents (mA) and wavelengths (nm) used for analysis; Cr (25, 357.9), Cd (..), Cu (15, 324.8) and Pb (440, 217.0). Reference solutions (Cd, Cr, Cu and Pb) were prepared with the appropriate dilutions of stock solutions containing 1000 mgL^{-1} (Merck) of each metal to create analytical calibrations. Validation of FAAS based measurements; linearity of the calibration graph, precision, accuracy, detection (LOD) and quantity limit (LOQ). Linearity was evaluated by correlation coefficients. Quantification (LOQ) and detection (LOD) limits were calculated using Equations (1, 2) (Thomsen et al., 2003).

$$LOD = x + 3S \quad (1)$$

$$LOQ = x + 10S \quad (2)$$

Where; ‘x’is the mean blank and ‘S’ is a standard deviation ofblank responses.

Results and Discussion

Trace elements assessed by the World Health Organization Expert Committee's Elements of Human Nutrition (FAO/WHO, 1996) are reserved into three groups in terms of nutritional importance in humans: (1) potentially toxic elements (Sr, Pb, Al, Sb, Cd, Sn, Li, and Ba); (2) the elements possibly required (Si, Co, Mn, B, V and Ni); and (3) basic elements (Se, Zn, Cu, Fe, Cr and Mo), some have low levels of basic functions.

Concentrations of cumin samples collected in winter and summer months are given in Table 1, Fig. (1, 2). Analytical method validation parameters are listed in Table 2.

Table 1. Average concentrations of heavy metals in cumin and cinnamon (mgkg^{-1}) (SD: Standard Deviation)

	Cr	Cu	Pb	Cd		Cr	Cu	Pb	Cd
WINTER CUMIN	0.715	5.35	0.176	0.219	**WINTER CINNAMON**	1.399	4.58	0.215	0.289
	0.724	5.47	0.170	0.215		1.403	4.53	0.215	0.222
	0.729	5.43	0.168	0.284		1.432	4.09	0.196	0.271
	0.791	5.23	0.195	0.285		1.368	4.52	0.206	0.271
	0.772	4.42	0.189	0.262		1.396	4.87	0.181	0.269
	0.794	4.63	0.199	0.252		1.407	4.65	0.184	0.270
	0.715	4.05	0.189	0.255		1.403	4.98	0.189	0.225
	0.767	4.13	0.196	0.239		1.519	4.67	0.196	0.237
SUMMER CUMIN	0.753	4.23	0.187	0.298	**SUMMER CINNAMON**	1.456	4.65	0.180	0.295
	0.782	4.27	0.172	0.206		1.457	4.86	0.183	0.207
	0.707	4.78	0.182	0.212		1.398	6.87	0.192	0.285
	0.731	4.67	0.184	0.215		1.397	7.11	0.194	0.296
	0.765	4.23	0.195	0.239		1.516	5.59	0.210	0.246
	0.756	4.53	0.199	0.239		1.515	5.71	0.219	0.257
	0.745	4.65	0.195	0.249		1.277	4.77	0.199	0.258
	0.754	4.75	0.195	0.247		1.372	4.97	0.200	0.254
Average ± SD	0.749 ±0.023	4.675 ±0.479	0.187 ±0.011	0.244 ±0.028	**Average ±SD**	1.422 ±0.056	5.086 ±0.861	0.198 ±0.013	0.260 ±0.026

The range concentration of Cd, Cr, Cu, Pb were determined as 0.206 to 0.298, 0.707-0.794, 4.05 to 5.47, 0.168 to 0.199 mgkg^{-1} in cumin samples, and 0.207 to 0.296, 1.277 to 1.519, 4.09 to 7.11, 0.180 to 0.219 mgkg^{-1} in cinnamon samples, respectively.

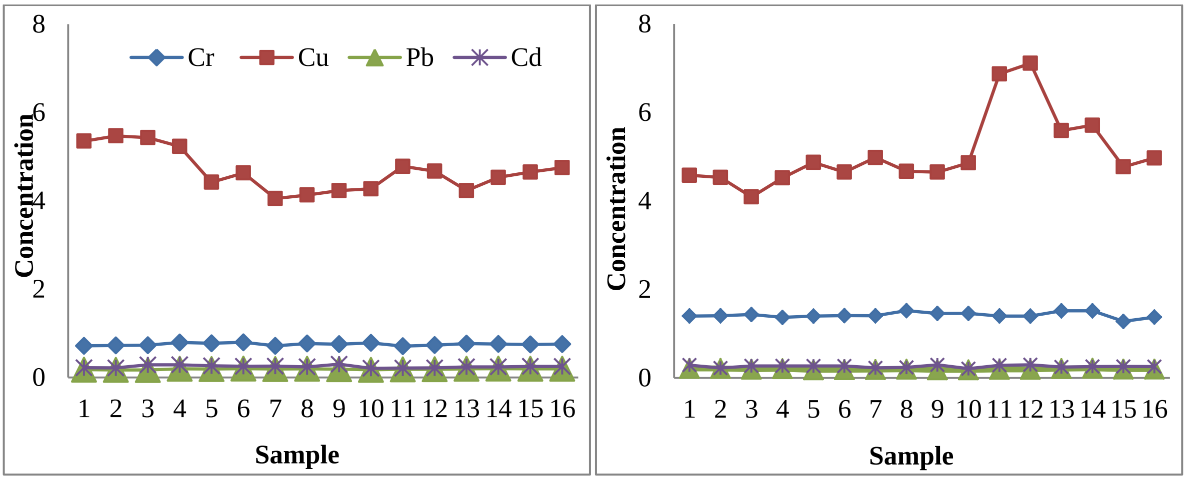

Figure 1. *Concentrations of cumin (a) and cinnamon (b) samples collected in winter and summer months (mgkg^{-1}) (1-8 WINTER; 9-16 SUMMER)*

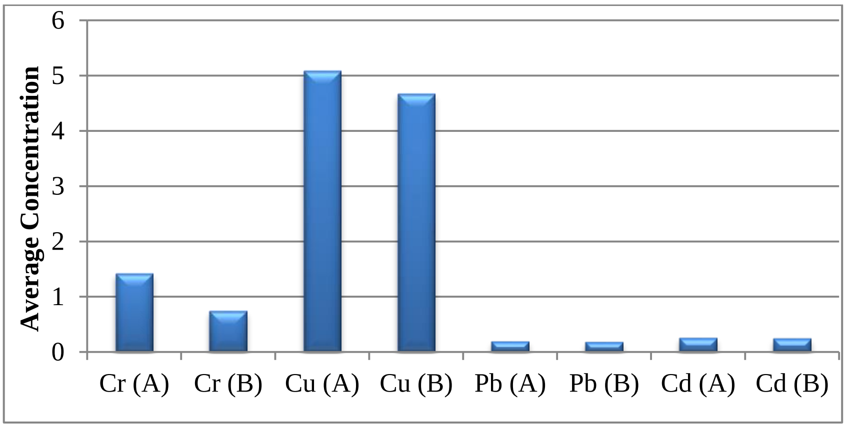

Figure 2. *Average concentration of samples (mgkg^{-1}) (A: Cinnamon. B: Cumin)*

Copper is an indispensable element for plants, animals and humans, but excessive intake is reported to cause health problems. To protect cardiovascular health, the copper deficiency must be prevented although the intake of excess copper to the human body has a potentially detrimental effect (Katz et al., 2011). Daily intake of 2.5 mg Cu can meet the daily need of adults. In general, the copper concentration of plants was determined to be between 4-20 mgkg^{-1} (Mengel and Kirkby, 2004). The copper content determined in this study was found to be compatible with the literature data. The data dedicated in Table 1 indicate that the cadmium concentration in entire samples is under the maximum permissible limit in nutrients (0.3 mgkg^{-1}) (FAO/WHO, 1996). Chromium is an important trace element. The toxicity of trivalent chromium is low and the detrimental effects of over-intake of this species are not readily apparent. There is hexavalent chromium, which shows a much more toxic effect than trivalent chromium. In addition to acute poisoning, chromium toxicity by oral intake is not of great significance to humans (FAO/WHO, 1996). Daily dietary Cr intake of human is advised as 60 µg by WHO

(Krejpcio, 2001). Based on WHO data for chromium, the maximum allowable level in foods is 0.05 $mgkg^{-1}$ (Bilal, et al., 2019). The acceptable daily intake of Pb for adults is 0.21-0.25 mg/day (WHO, 2011). In addition, when the maximum Pb levels (10 $mgkg^{-1}$) recommended by the US Food and Drug Administration were examined, Pb concentrations in all samples were found to be below these values (FDA, 2006).

For this study, calibration graphics were created by injecting 1000 $mgkg^{-1}$ CRM standard in 6 different concentrations and three replicates into the device. The analysis of the lowest concentration of analysis solution used in the calibration line and the certified reference standard substance of the analytical parameter was performed at least 6 times using the relevant analytical technique. Determined on the results, LOD and LOQ values were calculated. Also, at least 6 parallel samples were prepared by adding standard solution recovery samples containing analytes. The prepared samples were given to the device three times and the recovery values were determined from the results obtained (Table 2).

Table 2. Linear range (μgkg^{-1}), correlation coefficient, LOD (μgkg^{-1}), LOQ (μgkg^{-1}), certified reference material ($mgkg^{-1}$) (NIST), recovery, for the element analyzed

Element	Linearrange	R^2	LOD	LOQ	Certified	Found	Recovery (%)	CRM NIST No
Cd	0.1-5.0	0.994	3.2	10.3	-	-	-	-
Cr	0.1-5.0	0.997	10	31.4	2±0.4	1.98±0.01	99.0	3112a
Cu	0.1-5.0	0.996	10	31.4	2±0.4	1.99±0.02	99.5	3114
Pb	0.1-5.0	0.998	33	106	20±4	19.96±0.02	99.8	3128

Conclusion

This is even more important since the contamination of food by toxic metals (especially Cd, Pb) shows toxic effects even at very low concentrations.This is because when heavy metals get into the biological system, they cause great problems for human health and the environment as they do not have any degradation or destruction (Dorak et al., 2019). Heavy metals infect our foods from many sources and threaten our health more and more every day. Therefore the transmission of heavy metals to food is an important problem. In order to prevent heavy metal pollution the sources of contamination should be well defined and these resources should be eliminated and traceability of environmental exposure and hazards should be ensured.

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