

The element contents in chickpeas grown under organic and conventional farming regimes using WDXRF analysis for human nutrition and health

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Abstract

A comparative study on elemental composition of various chickpea (*Cicer arientînum L*) samples was conducted by using wavelength dispersive X-ray fluorescence (WDXRF). 22 elements, Al, Ca, Cu, Fe, Mn, Ni, P, S, Sr, Zn, Br, Cl, K, Mg, Na, Ba, Rb, Si, Au, Cr, La and Sn, were determined in chickpea samples (n = 10) grown under organic and conventional farming regimes. Results obtained from each group were analyzed statistically using the SPSS statistic program. It was observed that the concentration and peak intensity values of Ca, Fe, P, Cl, K, Mg and Na elements were higher in the chickpea samples grown under organic farming regime. Likewise, Al, Ni, Cr and Sn levels were found in higher levels in the samples grown under conventional farming regime. Ba was detected only in organic samples; although Sr, Br, Au, La were detected only in conventional samples. Our findings clearly revealed that organic chickpeas are likely to have higher nutritional mineral content. And the chickpea samples grown under conventional farming regime could contain harmful metals like Al, Ni, Cr and Sn that might damage the various systems and/or organs of humans and animals.

Key Words: Elemental analysis, chickpea, organic farming, conventional farming, WDXRF

1. Introduction

The intensification and expansion of modern agriculture is amongst the greatest current threats to worldwide biodiversity [1]. It is suggested that organic farming usually increases species richness, having on average 30% higher species richness than conventional farming systems. And the efficiency of agricultural subsidy programs for preserving biodiversity and improving the environment has been questioned in recent years. Organic farming operates without pesticides, and inorganic fertilizers, and usually with a more diverse

crop rotation [2]. The prevalence of animal birth defects is increased in the regions that pesticides, fungicides are extensively used [3]. The pesticides used intensively in industrial agriculture are also associated with elevated cancer risks in workers and consumers and are coming under greater scrutiny for their links to endocrine disruption and reproductive dysfunction [4]. Thereby organic farming is considered very important for sustainable agriculture, food quality, and soil and environmental health. It was observed that conventional farming reduces organic soil content and decreases biological activity in soil; on the contrary, organic farming increases microbiological activity in soil [5]. Soil quality investigated chemically and biologically in which longterm conventional and organic farming activities were applied, and consequently, it was established soils in organic farming were observed to have much better nutritional status [6]. On this point, consumers are looking for variety in their diets and are aware of the health benefits of fruits and vegetables. Of special interest are food sources rich in elemental nutrients. In fact, the intakes of these several elements are associated with reduced risk of cardiovascular disease, stroke, and cancers like mouth, pharynx, esophagus, lungs, stomach, and colon [7]. On the contrary, ingestion of metals, especially heavy metals, through fruits, vegetables and legumes can cause accumulation in organisms, producing serious health hazards such as injury to the kidney, symptoms of chronic toxicity, renal failure and liver damage [8].

Chickpeas are reported to be a cool season grain legume of exceptionally high nutritive value and most versatile food in use. The major producers, India, Pakistan and Turkey, contribute 65%, 9.5% and 6.7% respectively, to the world harvest. While it is a cheap source of protein and energy in the developing world, it is also an important food to the affluent populations to alleviate major food-related health problems. However, more research is denominated to be necessary for revealing the food and nutraceutical benefit of this important food legume through breeding [9]. Gil et al. [10] found that chickpea seeds contained 20–30% protein, approximately 40% carbohydrates, and only 3–6% oil. Again it was emphasized that chickpea was a good source of Ca, Mg, K, P, Fe, Zn and Mn [11]. Since it contains more beneficial carotenoids such as β -carotene and not high amounts of isoflavones [12, 13], chickpea is considered a functional food or nutraceutical [14–16].

To the best of our knowledge, there is no comprehensive study in the literature comparing the element content of chickpeas grown under so-called organic conditions to chickpeas grown under conventional farming regimes. In the present study, the 22 element contents (Al, Ca, Cu, Fe, Mn, Ni, P, S, Sr, Zn, Br, Cl, K, Mg, Na, Ba, Rb, Si, Au, Cr, La and Sn) of the samples grown under two different farming regimes were determined by Wavelength-Dispersive X-Ray Fluorescence Spectrometry (WDXRF) method for the first time. The advantages of X-ray fluorescence spectrometry are increasingly relevant in applications to the analysis of clinical and biological materials as demand increases for non-destructive and/or spatially resolved determinations [17–22].

2. Materials and methods

2.1. Instruments

WDXRF system consists of a detector, amplifier, discriminator, counter and printer units. The detector converts the infalling X-rays to measurable pulse. X-ray detector used in the following three spectrometers: proportional, gas flow and scintillation detectors. Discriminator filters pulses that coming from detector, and allows them to pass through of certain height pulses. These pulses are saved in a recorder, from which, if required, the number of pulses can be plotted against the wavelength and the angle of reflection. The Figure 1 diagrams use of the WDXRF system and its units.



Figure 1. The used WDXRF system and its units.

In this study, a digital scale (Ohaus TS 120, USA), a WDXRF spectrometer (ZSX-100e with Rhodium target X-ray controlled by a software ZSX computer), a SPEX, $P_{\text{max}} = 25 \text{ tons/cm}^2$; a mortar agate and an oven were used.

All our samples were prepared under laboratory controlled conditions, including the grinding method, grinding time, pelletized pressure and time. The samples were ground in a mortar agate, then were dried in an oven at 60 °C for 40 minutes. After, ground samples were pressed into uniform pellets of 20 mm diameter using a hydraulic press machine (SPEX, $P_{\rm max} = 25 \text{ tons/cm}^2$) with a standing time of 60 s. Since pellets were easily formed, no additional matter (e.g. cellulose microcrystalline) was used in the sample powders as a binder.

2.2. Sample collection

All chickpea samples were purchased from a local certified company in Aydın, Turkey. They were harvested from nearby regions and during the same harvest period. Only the applied farming regimes were different. For the chickpeas grown under organic farming regime, chemical inputs, synthetic chemical pesticides, growth regulators, synthetically compounded fertilizers, hormones, preservatives, colorings or artificial additives and the farm on which they were grown and processed have has operated under said regime for at least seven years. In contrast, these inputs were used in the production of the chickpeas grown via conventional farming regime.

2.3. Sample preparation

The vacuum condition of the sample chamber of the system was affected by the presence of humidity. Consequently, the samples were dried at 60 $^{\circ}$ C for 40 min, both a low temperature and short time. The amount of dry matter can decrease as a result of removal of moisture. Yet, a serious reduction in the quantity and content was not observed. Sample of 10 organic and 10 conventional samples (each about 2 g) were analyzed on a sequential ZSX 100e WDXRF spectrometer equipped with a Rh X-ray tube. Matrix-correction process is made automatically by this system. The measurement room temperature was on the average 20–21 degrees in a relatively dry environment. The obtained spectra were drawn using Origin 7.0 software. 10 samples from each of the two groups were prepared for good counting statistics.

2.4. Statistics

The obtained results were statistically examined using SPSS statistical software and t-test. By this statistical examination, it was investigated whether the differences observed between the element concentration and peak intensity in each group were statistically significant.



Figure 2. The intensities of some elements versus diffraction angle obtained from the chickpeas sample grown under organic farming regime.

282

Table. Concentrations and peak intensities of 30 elements for chickpea samples. Results of the analysis are given as average of samples (n = 10) from each groups; ND denotes not detected; symbol # indicates the value is statistically different from organic farming regime at the level of 0.05 for same element; X denotes mean value, and Sd denotes standard deviation of values.

																-		
DETECTION LIMITS (ppm)		Conventional	Sd	0,000000	I	I	I	0,00000,0	0,00000,0	,000341	0,000000	0,000000	0,000000	0,000000	0,000000	0,000000	0,000000	I
	m)		X	0,0002	QN	ND	QN	0,0002	0,0001	0,0003	0,0002	0,0001	0,0002	0,0002	0,0001	0,0001	0,0009	QN
	idd)	Organic	Sd	0,00000,0	I	I	I	0,00000,0	0,00000,0	,000395	0,000562	0,000000	0,000000	0,000000	I	0,000000	0,000000	I
				0,0002	ND	ND	ND	0,0002	0,0001	0,0004	0,0006	0,0001	0,0002	0,0002	ΟN	0,0001	0,000	ND
PEAK INTENSITY (count per second)		onal	Sd	0,012118	I	I	I	0,668399	0,061382	2,290794	0,050964	0,053433	0,657532	0,449137	0,329339	3,018749	0,254235	I
	r second)	Conventi	X	$0,0646^{\#}$	DN	ΟN	QN	$40,3519^{\#}$	1,2051	3,9797#	1,0787	$0,9309^{\#}$	50,2713#	20,8747	2,1528	22,6702	0,7955#	DN
	(count per	Organic	Sd	0,006737	I	I	I	0,938090	0,052898	8,262438	0,473456	0,021843	1,493938	0,479806	I	0,610014	0,046312	I
			x	0,0443	ΟN	ND	ΟN	46,1583	1,2208	18,6101	0,7123	0,7444	58,8294	20,8492	ΟN	20,6823	1,4145	QN
CONCENTRATION (%)		Conventional	Sd	0,000119	I	I	I	0,006314	0,000046	0,000734	0,000138	0,000051	0,003742	0,036576	0,000057	0,000413	0,005601	I
	(2		x	$0,0006^{\#}$	QN	ŊŊ	QN	$0,1060^{\#}$	0,0006	$^{*}0600,0$	0,0024	0,0009#	$0,1644^{\#}$	0,0755	0,0002	0,0088	$0,0168^{\#}$	ŊŊ
	6)	anic	Sd	0,000081	I	I	I	0,002205	0,00000,0	0,019904	0,000673	0,000000	0,002196	0,027150	I	0,001078	0,002243	I
		Org	x	0,0005	ŊŊ	ND	QN	0,1123	0,0007	0,0258	0,0025	0,0006	0,1884	0,0748	ND	0,0088	0,0296	ŊŊ
	ELEMENTS				Bi	As	Cd	Ca	Cu	Fe	Mn	Ni	Р	s	Sr	Zn	CI	Pb

AKBABA, ŞAHİN, TÜRKEZ

DETECTION LIMITS (ppm)	Conventional	Sd	0,000046	0,000000	0,000095	I	0,000046	0,000000	0,000000	l	0,000000	I	I	0,000000	I	I	I
		X	0,0002	0,0006	0,0010	ΟN	0,0000	0,0002	0,0001	1,1382	0,0002	ΟN	0,0010	0,0002	QN	ΟN	QN
	Organic	Sd	0,000053	0,000000	0,000000	0,000000	0,000000	0,000000	I	I	0,000000	I	I	0,000000	I	I	I
			0,0002	0,0006	0,000	0,0008	0,0001	0,0002	QN	ΟN	0,0002	ΟN	ΟN	0,0002	ŊŊ	ΟN	QN
PEAK INTENSITY (count per second)	Conventional	Sd	4,005633	0,008679	0,007765	I	0,362993	0,072199	0,097844	I	0,189061	I	I	2,445378	I	I	I
		X	$278,4709^{\#}$	$0,3129^{\#}$	$0,0153^{\#}$	ND	2,0203	0,3346	1,0577	0,0003	$1,2317^{\#}$	ND	1,4541	6,6703#	ND	ND	ND
	Organic	Sd	7,041088	0,017871	0,089604	0,099864	0,318304	0,007500	I	I	0,026172	I	Ι	0,313544	I	Ι	I
		x	357,0049	0,3270	0,1247	1,4756	3,5368	0,2433	ND	ND	0,2033	ND	ND	2,0737	ND	ND	ND
CONCENTRATION (%)	Conventional	Sd	0,013794	0,002528	0,018341	I	0,00000,0	0,000875	0,00000,0	I	0,000933	I	I	0,001123	I	I	I
		X	0,6675#	$0,0179^{\#}$	0,0021#	ND	0,0003	0,0027	0,0002	0,0009	$0,0044^{\#}$	ND	0,0047	$0,0030^{\#}$	ND	ND	ND
	Organic	Sd	0,014452	0,001211	0,001184	0,000230	0,000046	0,000292	I	I	0,000127	I	I	0,000184	I	I	I
		X	0,8599	0,0201	0,0025	0,0036	0,0004	0,0024	Ŋ	ND	0,0007	ND	ND	0,0009	ND	ND	ŊŊ
ELEMENTS			K	Mg	Na	Ba	Rb	Si	Br	Au	Cr	Ь	La	Sn	Se	Ti	Zr

Table. Conditued.

AKBABA, ŞAHİN, TÜRKEZ

3. Results

Concentrations and peak intensities of Al, Ca, Cu, Fe, Mn, Ni, P, S, Sr, Zn, Br, Cl, K, Mg, Na, Ba, Rb, Si, Au, Cr, La and Sn were measured for each sample. The results of the measurements are given in Table. The intensities are plotted as the function of diffraction angle for some elements in the organic samples in Figure 2. Statistical analysis of our findings revealed that Ca, Fe, P, Cl, K, Mg and Na element contents were higher in the chickpea samples grown under organic farming regime. Contents of Al, Ni, Cr and Sn were found at lower concentrations in the chickpea samples grown under organic farming regime. However, the amounts of some elements (Cu, Zn, SN, Zn, Pb and Si) did not show any alterations compared to one other. On the other hand, As, Bi, Cd, Pb, Cr, F, La, Se, Ti and Zr were not detected in any samples. In addition, Ba was detected only in the chickpea samples grown under organic farming regime. Sr, Br, Au and La were detected only in chickpea samples grown under conventional growing conditions.

4. Discussion

Elemental analysis of plant samples is essential to monitoring plants and their development, determining their nutritional value and nutrient insufficiency, and checking for diseases. In the present study we determined the element contents of the chickpea (*Cicer arientinum* L.) samples by WDXRF method since analytical performance of the method previously proposed proved to be effective and robust [23]. There is scarce data on comprehensive elemental analysis in agricultural products. The mineral contents of several products like mulberry [24], radish [25], tea [26], tobacco [27], beans [28] and hazelnuts [29] but not chickpea were examined by using WDXRF. Moreover, the comparisons of chickpea elemental contents grown under organic and conventional farming regimes have not been performed yet.

Statistical analysis of our findings revealed that Ca, Fe, P, Cl, K, Mg and Na elements contents were higher in chickpea samples grown under organic farming. The present results show there exist large differences in the elemental contents of vegetable products, between organic and conventional dairy farming [30–33]. This is consistent with analyses by Worthington [34] who also found that organic crops contained significantly more Fe and P than conventional crops. Gundersen et al. [35] compared the Ca and Mg contents in onions (*Allium cepa*) from conventionally and organically cultivated sites and determined significant content differences between organically and conventionally grown onions. Adotey et al. [36] indicated that the concentration of essential elements in foodstuffs of one region might vary from the other since food supplies are affected by various agricultural practices, type of soil, type of fertilizer and chemicals used type of pesticides and herbicides sprayed. Therefore, the differences of the applied practices could cause the determined increases of major elements (such as Ca, P, Mg, Na and K) and some minor elements or trace elements (such as Fe, Ba) in the chickpea grown under organic farming regime.

The present findings show the contents of Al, Ni, Cr and Sn were found at higher concentrations (but within permitted levels) in the chickpea samples grown via conventional farming. As a matter of fact, food due to the introduction of mechanized farming, ever increasing use of chemicals, sprays, preservatives, food processing, canning etc., are likely to be further contaminated with the toxic elements [37]. Consistent with our findings, Santos et al. [38] reported that chemicals used on both traditional and technological coffee farms might lead to increased toxic metals concentrations in soil and, when taken up by plants, hence lead to increased concentrations in crops and, subsequently, passed on in the food chain. Previous reports indicated that Al was

accepted as toxic to plants, fish, and higher animals [39, 40]. Gjorgieva et al. [41] reported that Ni and Cr were toxic metals to living organisms. Dopp et al. [42] also indicated that Sn could accumulate in the food chain and potential effects on human health were disquieting.

In conclusion, the determined weight percent concentrations of Ca, Fe, P, Cl, K, Na and Mg elements (which are essential for human health) were higher, and the amounts of toxic metals (Al, Ni, Cr and Sn) were lower in the chickpea samples grown under organic farming regime. Thus, we could suggest that this farming regime is crucial for nutritional value of chickpeas. In addition, as seen from the results obtained from present study, the usage of WDXRF analysis is an efficient and useful technique for food science which deserves attention for interdisciplinary studies.

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286

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