Bulgarian Journal of Agricultural Science, 16 (No 6) 2010, 769-774
Agricultural Academy

ELEMENTAL ANALYSIS OF DIFFERENT RADISH (*RAPHANUS SATIVUS* L.) CULTIVARS BY USING WAVELENGTH-DISPERSIVE X-RAY FLUORESCENCE SPECTROMETRY (WDXRF)

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Abstract

KAYMAK, H. C., I. GUVENC and A. GUROL, 2010. Elemental analysis of different radish (*Raphanus sativus* L.) Cultivars by using wavelength-dispersive X-ray fluorescence spectrometry (WDXRF). *Bulg. J. Agric. Sci.*, 16: 769-774

The aim of this work is to study the applicability of a quantitative WDXRF (Wavelength-Dispersive X-ray Fluorescence) method, for determination of minerals in radish specimens. In this study, we have quantitatively and semi-quantitatively analysed the four different radish (*Raphanus sativus* L.) cultivars (cvs. 'Siyah', 'Beyaz', 'Antep' and 'Iri-Kirimizi'). We have found that major elements; namely N and K; a few minor elements; Na, Mg, P, S, and Ca, and a lot of trace elements; Mn, Fe, Cu, Zn, Al, Ti, Cr, Br, Rb, Sr, Sn, Ba and La. The obtained trace element concentrations range from 0.01 to 3.24 mg per 100 g. This rapid method has been found to be a reliable technique for analyzing the mineral content in radish. At the end of this work, it was clearly said that Wavelength-dispersive X-ray fluorescence spectrometry (WDXRF) could be used for the analysis of mineral contents of radish and other vegetables.

Key words: Elemental analysis, radish, *Raphanus sativus* L., Wavelength-Dispersive X-Ray Fluorescence Spectrometry

Introduction

Radish, *Raphanus sativus* L., is a member of the Brassicaceae family. They are cool season, fast maturing, easy to grow annual or biennial herbaceous plants grown for their roots (Decateau, 2000). In addition, they are cultivated almost all year round throughout Turkey and often produce roots and radish production is approximately 170.000 tons annually in Turkey (Kaymak et al., 2010). Due to the fact that radish is appetitive they are grown all over the world. Besides, patterns of radish used differ considerably among cultures and countries. Several alternative hypotheses are considered for example radishes provide macro and micro nutrients; they are traditionally used as drug (Decateau, 2000) or appetitive (Günay, 2005).

The human body needs a variety of elements (often called minerals) for almost all aspects of body function. These elements are required in amounts that range from 50 μg to 18 mg per day. There are more than 20 chemical elements necessary for humans. Deficiency

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in such essential nutrients leads to a wide range of symptoms depending on the deficient mineral such as bone abnormalities and metabolic disorders (Al-Bataina et al., 2003). Therefore, such important elements in radish must be identified.

The use of direct and multi-elemental analysis methods of vegetation samples including X-ray fluorescence spectrometry (XRF) has increased over the last few years. Simplicity of sample preparation, minimum need for manipulation, speed and opportunity of analyzing several different elements have promoted XRF as a useful alternative to conventional spectroscopic techniques (Va´zquez et al., 2003; Margui et al., 2005). Also, XRF can be directly applied in dried samples, avoiding sample digestion dissolution by toxic and corrosive acids. Furthermore, the short analysis time required for this method makes it suitable for routine analysis (Noda et al., 2006). In recent years, XRF has been used for various solid food materials, such as spices (Al-Bataina et al., 2003), potato starch (Noda et al., 2006), tea (Salvador et al., 2002), bread improvers (Ekinci et al., 2002), medical plants (Queralt et al, 2005) and milk-based products (Perring and Andrey, 2003).

As far as we know, except for Kaymak et al. (2010), there is no study to determine the elemental composition of radish samples with Wavelength-Dispersive X-Ray Fluorescence (WDXRF) spectrometer. And also, reports about the element content of radish, especially trace elements, are limited (Kaymak et al., 2010). Since radish is used as a food all over the world it's important to determine its elemental composition. For this reason, the major aim of this study is to determine the differences among the radish cultivars (cvs. 'Siyah', 'Beyaz', 'Antep' and 'Iri-Kirimizi') by using WDXRF spectrometer.

Materials and Methods

The first part of study was conducted in field conditions at Atatürk University, College of Agriculture, Erzurum, Turkey, in 2004 and 2005. In this work, four radish (*Raphanus sativus* L.) cultivars (cvs. 'Siyah', 'Beyaz', 'Antep' and 'Iri-Kirimizi') were used as plant material.

The soil of the experimental area was loamy texture with neutral pH. It had 1.76-1.80 % organic matter, 3.61-3.69 kg ha^{-1} P_2O_5 and 270-278 kg ha^{-1} K_2O in 2004 and 2005, respectively.

Seeds were sown on plots of 6 m^2 in field on 12 July in both 2004 and 2005, in rows 280 cm long, at a separation between rows of 40 cm and between plants of 20 cm (Kaymak and Guvenc, 2007; Kaymak et al., 2010; Kaymak and Guvenc, 2010a, b). The plants were thinned after emergence when they formed 4-5 leaves. The plants were irrigated with furrow irrigation. During the development phases, all of the plant care practices have been applied in each plot irrespectively.

All plots were received 100 kg ha^{-1} N and 80 kg ha^{-1} P_2O_5 as calcium ammonium nitrate and triple super phosphate, respectively (Kaymak and Guvenc, 2007; Kaymak et al., 2010; Kaymak and Guvenc, 2010a, b). All of the P_2O_5 and half of the nitrogen fertilizer were applied uniformly prior to planting onto soil surface by hand and incorporated. The remaining half of the nitrogen was given 20 days after emergence (Srinivas and Naik, 1990).

In the experiment, after the radishes were harvested, their dry weights of their roots were determined firstly. After this process, element contents of roots were obtained in the second part of study. WDXRF Spectrometer (Rigaku ZSX-100e with Rhodium target X-ray tube) was used for the analysis of element contents of roots. This instrument was controlled by a computer using ZSX Software ("Rigaku", Japan). The ZSX-100e WDXRF spectrometer characteristics included; analysis of elements from B to U, 4 kW end-window X-ray tube, micro area mapping down to 0.5 mm, up to five primary beam filters, 7 analyzing crystals, and eight limiting area diaphragms, optional secondary collimators, automatic sample changer, compact design and multi-window, multi-function fundamental parameters software.

Dried root material to determine the dry matter of roots was grinded by using a blender. These grinded materials were used in all XRF analyses. In the XRF Laboratory, 2 g weight, 2.5 mm thickness and 35 mm diameter pellets were produced by applying 15 t of pressure with a spex press (Cat. B25). After the preparation of the pellets, they were incubated at 80^o C for 20 min to remove all moisture and were then used for element determination. LiF, Ge (111), PET (002) and TAP (100) crystals were used to separate the X rays coming from the pellets in WDXRF spectrometer (Kaymak et al., 2010). In addition, all the observations were made on randomly selected 20 roots out of 45 in each replication.

At the end of the WDXRF analysis; the major, minor and trace element contents of radish were determined as mass percentage (wt%) (wt% = element mass x 100 / total mass) (Kaymak et al., 2010). Later, determined elements content as wt% were transformed into mg 100 g^{-1} by using fresh weight of species for getting 100 g dry matter.

The experimental design was a completely randomized block design with 4 replications. ANOVA was applied on the data obtained in this study and the differences between means were compared using Duncan's multiple range test.

Results and Discussion

Dry matter contents of all cultivars used in this study are shown in Table 1. Dry matter contents are varied according to the cultivars and differences between cultivars are statistically significant at 0.01 probability level in both years of the experiment. While the highest dry matter was determined in Siyah (8.2%), the lowest dry matter was obtained in Iri Kirmizi (3.0%) in 2004 and 2005. This is consistent with the results of Alan et al. (1995) which also reported that the highest dry matter content was obtained from Siyah. In similar experiments, it was reported that dry matter contents of radish were varied according to the cultivars (Capecka, 2001; Borisov and TenAEkov, 2004). It was known that the optimal temperature for produce dry matter was 20°C and the dry matter contents of radish were affected by temperature changes (Nieuwhof, 1976). In our study, the temperature was varied from 27.5 to 16.3, and from 28.9 to 9.9 in 2004 and 2005, respectively, during growing period. These temperature variations could affect the dry matter content of radish cultivars. Our findings about dry matter content of radish cultivars in this research were similar with the above studies.

Regardless of the philosophy underlying the use of radish in different countries and cultures, we cannot ignore the fact that radishes have been consumed for centuries all over the world. Accordingly, extensive investigation of different vegetables is very important, especially if one knows that analysis of vegetables has drawn great attention from researchers in recent years. Hence, we have chosen four radish cultivars that are widely used and grown in Turkey to study them for their element composition. The contents of the different elements in the four samples are given in Tables 2 and 3.

As it is shown in Table 2, major and minor elements were varied according to the cultivars and differences between cultivars were statistically significant at 0.01 probability level in both years of experiment. The major elements with contents of e”0.1 wt% in all samples are N and K. The amounts of N ranged from 102 mg 100 g^{-1} (Beyaz) to 257 mg 100 g^{-1} (Siyah) in 2004 and from 69.7 mg 100 g^{-1} (Antep) to 256 mg 100 g^{-1} (Siyah) in 2005. The amounts of K were 185 mg 100 g^{-1}, 209 mg 100 g^{-1}, 216 mg 100 g^{-1} and 217 mg 100 g^{-1} in Beyaz, Antep, Siyah and Iri Kirmizi, respectively, in 2004. K amounts for the 2005 experiments 2005 ranged from 194 mg 100 g^{-1} to 288 mg 100 g^{-1}.

Table 1

Dry matter contents of radish cultivars, %

		Antep	Beyaz	Iri Kirmizi	Siyah
Dry Matter	2004	4.0 b**	3.3 b	3.0 b	6.7 a
	2005	4.7 b**	4.5 b	3.0 b	9.6 a
	Mean	4.4 B**	3.9 BC	3.0 C	8.2 A

** :Differences between cultivars are significant at the 0.01 probability level

Table 2

The amounts of major and minor elements in radish cultivars, mg 100 g^{-1}

		Cultivars			
		'Antep'	'Beyaz'	'Iri Kirmizi'	'Siyah'
		2004			
Major Elements	N	161 b**	102 b	116 b	257 a
	K	209 a**	185 b	217 a	216 a
	Na	10.7 a**	10.7 a	8.79 b	5.78 c
	Mg	10.2 b**	8.15 d	9.81 c	13.3 a
Minor Elements	P	19.8 b**	15.9 c	12.2 d	23.2 a
	S	24.3 b**	20.4 d	22.3 c	43.5 a
	Cl	8.67 c**	9.61 b	10.6 a	10.6 a
	Ca	21.0 c**	18.5 d	23.4 b	31.7 a
2005					
Major Elements	N	69.7 b**	159 ab	124 b	256 a
	K	194 b**	267 a	217 ab	288 a
	Na	10.6 b**	16.5 a	9.66 b	5.10 c
	Mg	13.3 b**	17.8 ab	14.4 b	21.1 a
Minor Elements	P	19.0 c**	29.8 b	20.7 c	37.8 a
	S	28.8 bc**	34.8 b	25.8 c	57.5 a
	Cl	14.1 b*	18.9 a	14. 8 b	19.7 a
	Ca	22.8 b**	31.5 b	28.0 b	46.1 a

*, **: Significant differences among cultivars at 0.05 and 0.01 probability levels, respectively.

Minor elements with content values of less than 0.1 wt% in all samples in both experiment years were: Na, Mg, P, S, C and Ca. For 2004, Na contests were 5.78 mg 100 g^{-1}, 8.79 mg 100 g^{-1}, 10.7 mg 100 g^{-1} and 10.7 mg 100 g^{-1} in Siyah, Iri Kirmizi, Beyaz and Antep, respectively. The contents of Mg were 8.15 mg 100 g^{-1}, 9.81 mg 100 g^{-1}, 10.2 mg 100 g^{-1} and 13.3 mg 100 g^{-1} in Beyaz, Iri Kirmizi, Antep and Siyah, respectively. The contents of P were 12.2 mg 100 g^{-1} in Iri Kirmizi, 15.9 mg 100 g^{-1} in Beyaz, 19.8 mg 100 g^{-1} in Antep and 23.2 mg 100 g^{-1} in Siyah. S contents were 20.4 mg 100 g^{-1} in Beyaz, 22.3 mg 100 g^{-1} in Iri Kirmizi, 24.3 mg 100 g^{-1} in Antep and 43.5 mg 100 g^{-1} in Siyah. The content of Cl was 8.67 mg 100 g^{-1}, 9.61 mg 100 g^{-1}, 10.6 mg 100 g^{-1} and 10. 6 mg 100 g^{-1} in Antep, Beyaz, Iri Kirmizi and Siyah, respectively. Ca values ranged from 18.5 mg 100 g^{-1} (Beyaz) to 31.7 mg 100 g^{-1} (Siyah). The contents of minor elements in 2005 were similar to those of the experiment in 2004. In general, element contents of Siyah (except for Na) were higher than the other cultivars in both 2004 and 2005 (Table 2).

Trace elements were varied according to the cultivars for both experiments. The differences between cultivars were statistically significant at 0.05 and 0.01 probability levels for both years (Table 2). Trace elements among all samples were: Mn, Fe, Cu, Zn, Al, Ti, Cr, Ni, Br, Rb, Sr, Sn, Ba and La. The content of Mn, Fe, Zn, Al and Ti were higher than the others and the contents of Cr, Ni, Br, Rb, Sr, Sn, Ba and La were lower in Siyah than the other cultivars in both 2004 and 2005. Finally, the values of trace elements were ranging between 0.01 mg 100 g^{-1} and 3.24 mg 100 g^{-1} in all samples.

As a result of the WDXRF analyses, it was determined that major, minor and trace elements changed depending on the cultivars and years (Tables 2 and 3). Peirce (1987) notified that radishes had 30 mg

100 g^{-1} Ca, 31 mg 100 g^{-1} P, 1 mg 100 g^{-1} Fe and 322 mg 100 g^{-1} K. Additionally, Decoteau's (2000) results certify Peirce (1987) findings. Similarly, Salerno et al. (2005) reported that radish cultivars had 7.25.10^3 mg kg^{-1} Ca, 8.01.10^4 mg kg^{-1} K, 9.30.10^3 mg kg^{-1} Mg 6.98.10^3 mg kg^{-1} P, 202 mg kg^{-1} Fe, 9 mg kg^{-1} Cu, 31 mg kg^{-1} Mn, 70 mg kg^{-1} Zn and 3.97.10^4 mg kg^{-1} N and nutrient elements varied from cultivars. In a recent study, Kaymak et al. (2010) reported that the values of trace elements (Mn, Fe, Cu, Zn, Al, Ti, Ni, Br, Rb, Sr, Sn, and Ba) were ranging between 0.0003 wt% and 0.026 wt% in all samples. Our present results on elements were obtained from radish cultivars with in accordance of previous studies (Peirce, 1987; Decoteau, 2000; Salerno et al., 2005; Kaymak et al., 2010). Also, differences be-

Table 3

The amounts of trace elements in radish cultivars, mg 100 g^{-1}

Trace Elements	Cultivars			
	'Antep'	'Beyaz'	'Iri Kirmizi'	'Siyah'
		2004		
Mn	0.09 b**	0.06 c	0.08 b	0.14 a
Fe	0.73 b**	0.49 c	0.50 c	2.34 a
Cu	0.07 a*	0.02 d	0.03 c	0.05 b
Zn	0.09 b**	0.08 b	0.08 b	0.14 a
Al	0.95 b**	0.51 c	0.95 b	1.76 a
Ti	0.05 b**	0.04 b	0.04 b	0.13 a
Cr	0.01 c**	0.02 b	0.04 a	0.02 b
Ni	0.07 a**	0.03 b	0.04 b	0.03 b
Br	0.13 b**	0.11 c	0.15 a	0.07 d
Rb	0.14 a**	0.12 a	0.13 a	0.05 b
Sr	0.15 ab**	0.13 bc	0.15 a	0.12 c
Sn	0.03 a**	0.03 a	0.01 c	0.02 b
Ba	0.23 ab*	0.27 a	0.25 ab	0.21 b
La	0.44 a**	0.32 c	0.34 b	0.00 d
		2005		
Mn	0.09 b**	0.10 b	0.10 b	0.19 a
Fe	0.85 b**	1.16 b	0.67 b	3.24 a
Cu	0.02 b**	0.04 b	0.02 b	0.09 a
Zn	0.08 b**	0.11 b	0.08 b	0.24 a
Al	1.11 b**	1.18 b	1.23 b	2.11 a
Ti	0.09 b*	0.12 ab	0.09 b	0.17 a
Cr	0.01 c**	0.05 a	0.05 a	0.03 b
Ni	0.04 ab*	0.05a	0.04 ab	0.03 b
Br	0.13 b**	0.19 a	0.16 ab	0.06 c
Rb	0.10 bc*	0.17 ab	0.20 a	0.07 c
Sr	0.17 ab**	0.24 a	0.27 a	0.13 b
Sn	0.04 a**	0.03 b	0.02 c	0.02 c
Ba	0.27 a**	0.22 b	0.22 bc	0.21 c
La	0.52 a**	0.38 c	0.44 b	0.00 d

*, **: Significant differences among cultivars at 0.05 and 0.01 probability levels, respectively.

tween cultivars may appear from their genetic variability. According to the outcome of this study, all cultivars could be recommended as a source of essential elements.

Conclusions

The analysis time of WDXRF was considerably short (about 1 h sample^{-1}). Thus, WDXRF seems to be a suitable method for rapid prediction of element contents in radish. Also, this rapid method has been found to be a reliable technique for analyzing the element contents. In addition, there was also the opportunity of analyzing some other elements such as sulphur that can hardly be determined by other techniques (Margui et al., 2005), since analysis of sulphur is extremely easy by using WDXRF. As a consequence of this work, it was clearly said that Wavelength-Dispersive X-Ray Fluorescence Spectrometry can be used for detailed analysis of element contents in radish.

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Received December, 2, 2009; accepted for printing August, 23, 2010.