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Elemental Analysis of Various Cherry Fruits by Wavelength Dispersive X-Ray Fluorescence Spectrometry

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A comperative study on elemental composition of various cherry fruits was conducted by using a sensitive method, wavelength dispersive X-ray fluorescence (WDXRF). Elements such as Na, Mg, Al, Si, Cl, K, Ca, Cr, Fe and Zn were determined in sweet (*Prunus avium* cv. Napolyon), sour (*Prunus cerasus* cv. Kütahya) and native cornelian (*Cornus mas* L.) cherries. Significant differences ($p < 0.05 – p < 0.01$) were observed in the mineral contents of cherry fruits. The concentration of elements in sour, sweet and cornelian cherry fruits was 1.21, 1.98 and 2.31 % of the total mass, respectively. Na was detected only in cornelian cherry fruits and its level was 150 ppm. The amounts of major elements potassium, magnesium, calcium and phosphor in cherry fruits were ranged to 9267-16778, 1012-2113, 510-2438 and 585-1546 ppm, respectively. The results show that the cherries are rich in the mineral elements that are of importance in man's well being. However, another result with this study shows that the main advantage of this method is the non-modification of the original sample, both during sample preparation and in the exciting X-ray beam.

Key Words: Wavelength dispersive X-ray fluorescence, Mineral elements, Sour cherry, Sweet cherry, Cornelian cherry.

INTRODUCTION

Minerals are essential to life and a certain minimum quantity of each is required for health. Although this quantity varies from person to person, needs are defined within certain limits. A perfect diet will supply all of these requirements.

The minerals in human bodies fall into 4 distinct groups seperated by their character and their concentration. One group comprises those metals that are present in high concentration and includes Ca, Mg, Na and K. The second group embraces all those that are present in much lower concentration but whose importance is no less in ensuring health. Cr, Fe, Mn, Mo, Co, Cu and Zn are in this group. The third group are non-metallic elements that are abundant and these high levels are reflected in the quantities of H, C, N, O, P, S and Cl present in the body. Two non-metalic

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elements, I and Se, make up the fourth group. Groups of 2 and 4 together comprise the so-called trace minerals or trace elements[1].

There is a growing interest in the trace elements in the area of medicinal science. It is beleived that the great majority of these elements act as key compenents of essential enzyme systems or other protein, *e.g.*, the hemoprotein hemoglobin, which performs vital biochemical functions[2,3].

All available evidence suggests that a diet rich in vegetables and fruit is benefical to health, in popular for the reduction of risk from heart disease, diabetes and some forms of cancer. Research also provides some clues to the actual substances largerly referred to as phytochemicals or plant chemical that might be responsible for the protective effect of vegetables and fruits. It appears most benefical to eat these substances in the food rather than just alone as a supplement[4-6]. Besides several organic compounds, it is now well established that trace elements play a vital role in general well-being as well as in the cure of disease[7].

Cherries are still under-researched and less utilized among fruits[8]. They are nonclimatic fruits that are usually peak maturity for optimal taste and appearence. Cherries fruits are widely grown in orchards different region of Turkey. However, in Turkey and in other countries sweet cheriries (*Prunus avium* L.) are mainly consumed as fresh fruit whereas sour cherries (*Prunus cerasus* L.) and cornelian cherries (*Cornus mas* L.) are not only consumed fresh but also used to produce jam, sweeted fruit marmalade, syrup and several types of soft drinks[9]. Cherries are characterized by high content of phenolic compounds, which are also responsible for their colour and taste and presumably also their antioxidant properties[10]. Furthermore, fruits are rich in sugar, organic acid, tanins and phenolic compounds, the researchers paid attention to the above-mentioned nutrients only a few previous works, deal with the content of mineral compounds in these fruits, despite the fact that they are rich source of these compounds.

Generally, elements in plants are determined by using AAS, ICP-MS, ICP-AES, *etc.*[11]. These techniques imply prior total destruction of the matrix by mineralization, which may lead to problems of contamination by reactants such as HCl and H_2SO_4 or disturbances of the measured concentrations by element losses due to incomplete solubilization. Moreover, the method of matrix destruction used strongly depends on the chemical composition of the sample and on the element to be determined[12].

Wavelength dispersive X-ray fluorescence (WDXRF) method offers several unique advantages over other analytical methods. Both the sample preparation and measurements are usually simple and fast. The sensitivity of this technique is high and compares to that provided by optical-based techniques such as ICP-MS, ICP-AES. The sample preparation does not require any chemical treatment, thus reducing drastically any chance of contamination[13]. The goal of the work was to study how to change the composition and concentration of macro and micro elements in various cherry (sour, sweet and cornelian) fruits by using WDXRF.

EXPERIMENTAL

Collection and preparation of fruit sample: Sweet (*Prunus avium* cv. Napolyon), sour (*Prunus cerasus* cv. Kütahya) and native Cornelian (*Cornus mas* L.) cherries were collected at their optimum commercial maturity from the same same garden orchards in Uzumlu district, Erzincan. All orchards had alluvial soil. The fertilizer program and irrigation scheduling were almost the same for all fruit orchards. Fruit samples were kept in cool bags to transport to the laboratory and washed in distilled water. The seeds were removed manually. For elemental composition measurements, *ca.* 25 g of the fruit was homogenized using a blender. The homogenization was performed on ice and Whatmann filter paper No. 1 was used to filter the sample.

Determination of elemental composition: The measurements were carried out at the Wavelength-dispersive spectrometer (Rigaku ZSX-100e with Rhodium target X-ray controlled by a software ZSX computer). The ZSX 100e, with tube above optics, offers the most flexibility and highest performance of any WDXRF spectrometer which has 4kw 70kv end window X-ray tube; up to 5 primary beam filters, 10 analyzing crystals and 8 limiting area diagrams; optional secondary collimators and automatic sample changer.

WDXRF spectrometry was used for analysis of the semi-qualitative method. The measurements are automatically correcting for all matrix effects, including line overlaps by the semi-quantitative software package, SQX (Rigaku). SQX can also correct for secondary excitation effect by photoelectrons, varying atmospheres, impurities and different sample sizes. Increased accuracy is achieved using Matching Library and Perfect Scan analysis programs.

For the measurement, the cellulose paper discs (2 cm diameter; Rigaku) were impregnated with 100 µL sample and dried at room temperature for 15 h. The samples were placed in a target holder inside the chamber for analysis. The measurements performed in five replicates.

Statistical analysis: To identify significant differences the data were analyzed by analysis of variance using the general linear model that permits the analysis of sample with different number of replicates and bivariate correlation. Statistical analyses were made with the SPSS 13.0. The mean values were separated by Duncan's multiple range test.

RESULTS AND DISCUSSION

The elemental composition and concentration of some cherry fruits were evaluated by wavelength-dispersive X-ray fluorescence (WDXRF) analysis. Elements such as Na, Mg, Al, Si, Cl, K, Ca, Cr, Fe and Zn were determined in fruit samples. The limit of detection and the mean recovery of the elemental concentrations vary with the atomic number. Fig. 1 shows the spectra obtained from measurements. Qualitively, the peak amplitudes are directly related to the elemental concentrations of the elements in samples. The average concentrations found for different elements in fruits are listed in Table-1.

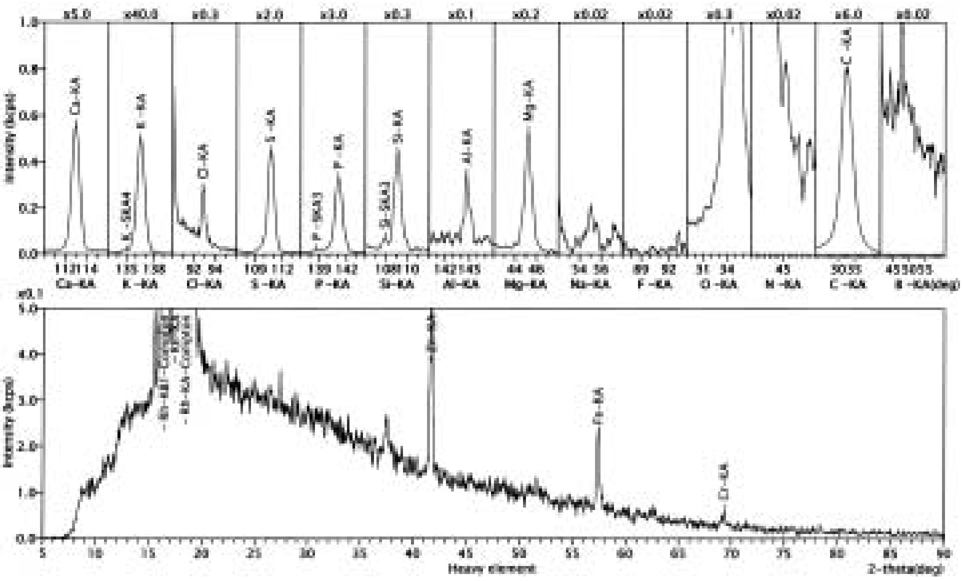

Fig. 1. A typical WDXRF spectrum obtained from Cornelian cherry fruits. The lines showed intensity of Ka-rays of elements *versus* 2-θ function

TABLE-1
MINERAL CONTENT OF FRUITS (ppm)†

Fruit species	Na	Mg	Al	Si
Cornelian cherry	150.8 ± 12.1	2113.5 ± 119a*	94.7 ± 5.3ab	401.7 ± 13.9a
Sour cherry	–	1012.5 ± 30.3b	104.1 ± 8.8a	181.3 ± 11b
Sweet cherry	–	2085.9 ± 99.3a	89.8 ± 10.2b	182.2 ± 9.2b
		$p < 0.05$	$p < 0.05$	$p < 0.01$
	P	S	Cl	K
Cornelian cherry	1059.1 ± 20.2b	402.3 ± 15.7a	181.5 ± 10.2a	16778.7 ± 365.3a
Sour cherry	585.6 ± 18.4c	209.8 ± 7.9c	116.4 ± 7.1c	9267.7 ± 250.2c
Sweet cherry	1546.3 ± 46.3a	315.5 ± 12.5b	144.2 ± 8.9b	14907.3 ± 313b
	$p < 0.01$	$p < 0.01$	$p < 0.01$	$p < 0.01$
	Ca	Cr	Fe	Zn
Cornelian cherry	2439.2 ± 98.1a	1.9 ± 0.2	34.8 ± 8.7b	43.1 ± 6.9
Sour cherry	586.4 ± 20.6b	1.6 ± 0.4	38.7 ± 6.6a	42.7 ± 8.2
Sweet cherry	510.8 ± 19.3c	1.5 ± 0.5	30.5 ± 8.7c	40.5 ± 7.1
	$p < 0.01$	$p > 0.05$	$p < 0.01$	$p > 0.05$

*Within columns, means followed by the same letters are not significantly different.
– Not detected; †The results, in units of per million (ppm).

The mean concentrations of Mg, Al, Si, Cl, K, Ca and Fe were significantly different depending on the species ($p < 0.05$ – $p < 0.01$), except Cr and Zn. The concentration of elements in sour, sweet and cornelian cherry fruits were 1.21, 1.98 and 2.31 % of the total mass, respectively. According to the results shown in Table-1, the amounts of major elements K, Mg, Ca and P were ranged to 9267-16778, 1012-2113, 510-2438 and 585-1546 ppm, respectively. Furthermore, Kolayli *et al.*[14] suggested that the major elements in cherry Laurel fruits were potassium, magnesium and calcium. The results of this study support Kolayli *et al.*[14] findings.

Potassium, Ca and Mg contents were high in Cornelian cherries and sweet cherries followed it. Sour cherries had lower contents of these elements among the other tested fruit samples, except for Ca. While Ca in sour cherry (586 ppm) was lower than Cornelian cherry (2439 ppm), it was higher than sweet cherry (510 ppm). A remarkable Ca content was observed in cornelian cherry fruits compared to sour and sweet cherry fruits. Moreover, high level of P was detected in samples. P content was high in sweet cherry (1546 ppm); it was followed by cornelian cherry (1059 ppm) and sour cherry (585 ppm). Potassium is one of the principal cations in the body that plays important roles in nerves system and so it is vital to ensure a normal balance of water between body cells and surrounding fluids[15]. The roles of Mg inside cells are numerous. It is an essential cofactor for many intracellular enzymes, including those required the energy production and for DNA replication, which is the basis of life itself[16]. On the other hand, Ca is the most abundant mineral in human body and most of it is associated with phosphorus as phosphate to form the skeleton. Ca and P, in addition to its function in the skeleton are involved in many and varied chemical reactions in body[17].

It is important to remark that the Na element was detected only in cornelian cherry fruits and its level was 150 ppm. Baytop[18] suggested that cherries are virtually free from Na and particularly rich in K, Ca, Mg and Zn. Present data appear to support these facts and, especially, claming of free or low content of Na element. Excessive Na intake was found to cause an increase in blood pressure[19]. Therefore, low contents or free of Na indicate that cherry fruits are one of the most safe foods for human daily diet.

Also, significant levels of Cl, S and Si were observed in cherry fruits ranged from 116 to 402 ppm.The levels of S, Cl and Si in Cornelian cherry fruits measured by WDXRF were remarkably higher than the levels of S, Cl and Si in both sour and sweet cherry fruits. S, is a certain element which is essential to bodily function and when it is presented in the food combined with metals, the body makes use of both. On the other hand, Si, plays an important structural role in body, influencing the production of collagen and bone. It is essential for maintaining the integrity of surface tissues and those that connect the bones, imparting strength and elasticity by chemically binding the structures. Another structural role is in maintaining the elastic structure of blood-vessel and so allowing them to dilate and construct in the maintenance of blood flow and pressure[1].

The concentration of other elements such as Al, Cr, Fe and Zn ranged from 1.5-104 ppm. The trace elements concentrations were found in lower levels than the other elements. Among the trace elements, the lower concentrations were detected for Cr element in all fruit samples. Although minerals play a vital role for human health, high amounts of certain minerals are also toxic for most organisms. There are toxic reactions produced when those minerals that the body requires are taken in excessive amounts. A mineral may produce ill effects when taken in one large dose or there may be an insidious build-up of the mineral when taken over a long period. It can be stated that if the recommended dosages of these mineral supplements available are adhered to there is absolutely no chance of toxic amounts being taken[20]. In this respect, the low levels of trace elements can prove these fruits to be a safe food.

The concentration of the elements in fruits was evaluated considering standard nutrient values for cherry fruits reported by USDA National Database for standard reference[21]. Recommended dietary allowance (RDA) values of macro elements Ca, K, Mg and P are 1200, 4700, 420 and 700 mg daily[21]. Cherries could nutritionally be important as a good source of these elements. The trace elements Fe and Zn have RDA values of 10-15 and 12-15 mg daily. The amount of these elements in present study, although higher compared to that of RDA value, is well below the toxicity level. However, high amounts of certain elements such as Co, Ni and Pb, which are toxic for most organisms were found to be below the detection limits.

The minerals are all in balance with one another so that excess or otherwise of one or more will affect the level of others. So, the relationship between the various minerals in sour, sweet and cornelian cherry fruits was determined with Pearson correlation test. There is a significant positive and negative correlation for some mineral element measurements of all samples (Tables 2-4). According to the results, the significant correlation coefficients of some mineral elements in cornelian, sweet and sour cherry fruits were ranged to r = -0.988-0.977; r = -0.836 - 0.992; r = -0.994 - 0.993, respectively.

TABLE-2
CORRELATION COEFFICIENTS (r) BETWEEN MINERAL ELEMENTS IN CORNELIAN CHERRY FRUIT SAMPLES

	Na	Mg	Al	Si	P	S	Cl	K	Ca	Cr	Fe
Na	-										
Mg	-.783†										
Al	-.950‡	-.988‡									
Si	.450	.533	-.396								
P	.287	.845‡	-.917‡	-.030							
S	.443	.593	-.462	.977‡	.070						
Cl	.273	.582	-.449	.996‡	.056	.970‡					
K	-.974‡	.976‡	-.931‡	.703†	.670	.753†	.744†				
Ca	-.709†	.489	-.349	.989‡	-.711‡	.992‡	.994‡	.667			
Cr	-.262	.823‡	-.901‡	-.042	.969‡	.031	.017	.681	-.092		
Fe	-.810‡	.986‡	-.982‡	.451	-.891‡	.515	.503	.951‡	.273	.405	
Zn	-.757†	.287	-.136	.964‡	-.941‡	.271	.946‡	.488	.976‡	-.308	.195

†Significant at 0.05; ‡Significant at 0.01.

TABLE-3
CORRELATION COEFFICIENTS (r) BETWEEN MINERAL ELEMENTS IN SWEET CHERRY FRUIT SAMPLES

	Mg	Al	Si	P	S	Cl	K	Ca	Cr	Fe
Mg	-									
Al	-.836‡									
Si	.411	-.091								
P	.702†	-.830‡	-.008							
S	.609	-.201	.933‡	.082						
Cl	.496	-.223	.811‡	.060	.992‡					
K	.769†	-.671	.703†	.713†	.884‡	.833‡				
Ca	.210	-.395	.647	-.522	.941‡	.899‡	.501			
Cr	.802‡	-.754†	.224	.815‡	.275	.269	.447	.165		
Fe	.947‡	-.855‡	.317	-.710†	.394	.378	.880‡	.276	.113	
Zn	.299	-.054	.970‡	-.730†	.598	.951‡	.399	.877‡	-.104	.087

†Significant at 0.05; ‡Significant at 0.01.

TABLE-4
CORRELATION COEFFICIENTS (r) BETWEEN MINERAL ELEMENTS IN SOUR CHERRY FRUIT SAMPLES

	Mg	Al	Si	P	S	Cl	K	Ca	Cr	Fe
Mg	-									
Al	-.902‡									
Si	.211	-.118								
P	.633	-.890‡	.145							
S	.411	.641	.993‡	.093						
Cl	.541	.550	.805‡	.078	.800‡					
K	.817‡	-.719†	.609	.788†	.447	.556				
Ca	.650	-.103	.993‡	-.647	.909‡	.903‡	.515			
Cr	.669	-.994‡	-.076	.888‡	.175	.186	.799†	.123		
Fe	.799‡	-.991‡	.219	-.924‡	.401	.375	.788†	.333	.313	
Zn	.379	.023	.756†	-.817‡	.339	.989‡	.215	.620	-.114	.288

†Significant at 0.05; ‡Significant at 0.01.

Conclusion

In conclusion, the WDXRF technique was used in elemental analysis of some cherry fruits. Concentrations of 10 elements (Na, Mg, Al, Si, Cl, K, Ca, Cr, Fe and Zn) were determined. The results show that the cherries are rich in the mineral elements that are of importance in man's well being. Potassium, Mg, Ca and P present at the highest concentrations, 9267-16778, 1012-2113, 510-2438 and 585-1546 ppm, respectively. Another result obtained in this study shows that the proposed method is accurate and reproducible and presents several advantages for mineral elements analysis in fruit samples. It allows the determination of some elements without any mineralization, which may lead to problems of contamination by reactants. In addition, only a little amount of fruit being needed for preparing the sample and both the sample preparation and measurements are usually simple and fast. The methodology used in this study can easily be used for food and agricultural product quality control.

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